ProMine – Nano-particle products from new mineral resources in Europe

Schwertmannite – Raw material and valuable resource from mine water treatment processes

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ProMine bezieht sich auf das Anliegen der Europäischen Kommission, das jährliche Handelsdefizit von ca. 11 Milliarden Euro, entstehend durch Metall- und Rohstoffimporte, zu verringern. Diese Situation könnte verbessert werden durch eine zunehmende Fokusierung auf hochwertige und mehrwertige Produkte auf dem europäischen Markt. Einen entscheidenden Beitrag kann dabei auch die Rückgewinnung von Wertstoffen leisten. Daher ist die Entwicklung verschiedener neuer Nanopartikel-Produkte aus bisherigen Lagerstättenrückständen eines der Hauptziele im Projekt ProMine. In diesem Zusammenhang beschäftigt sich die G.E.O.S. Ingenieurgesellschaft mbH als einer von 27 Projektpartnern aus 11 europäischen Ländern mit der Verwertung des Sekundärminerals Schwertmannit. Die Produktion des Rohstoffes Schwertmannit aus Bergbauwässern im Lausitzer Braunkohletagebau Nochten ist ein wichtiger Schritt zur Aufkonzentration und Gewinnung des Eisens aus dem Wasser. Aus den dabei gebildeten Eisenhydroxysulfaten sollen innerhalb des Projektes ProMine Eisenoxidpigmente entwickelt werden.

ProMine addresses the concerns of the European commission over the annual 11 billion Euro trade deficit in metal and mineral imports. Higher quality and added value products on the European market as well as the recovery of valuable resources from supposed waste materials could efficiently improve this situation. The development of various nano-particle materials from waste products or mining residues is one of the main objectives in ProMine.
In this context the G.E.O.S. Ingenieurgesellschaft mbH as one of the 27 project partners from 11 European countries is dealing with the utilisation of the mineral schwertmannite. The production of the raw material schwertmannite during the water treatment of acid mine water in the Lusatian brown coal mining area is a crucial step to recover and concentrate iron from mine water. One of the main targets of G.E.O.S. in ProMine is to develop iron oxide pigments from schwertmannite.

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1 Schwertmannite a secondary mineral and raw material for pigment production

1.1 Modelsite for pigment production from schwertmannite

The opencast mine Nochten is located in the Lusatian mining area in eastern Germany, Saxony, in the administrative district Görlitz (Figure 1). The exploration of the area started in the 1950s and resulted in an appreciated lignite resource of 1,400 Mio t. Preparatory measures prior to coal production started in 1958 (waterlift: 1960), the subsidiary development in 1968 and coal production at productive stage in 1976. Nowadays the Vattenfall Europe Mining AG operates the mine (VATTENFALL, 2008)

Due to the Lignite mining activity in Nochten about 120 Mio m³ mine water per year are pumped to the subsurface to lower the groundwater level. Dependent on iron concentration and contamination the mine water of Nochten is partially treated using lime milk for precipitation of ferric hydroxide in the treatment plants Tzschelln and Schwarze Pumpe.

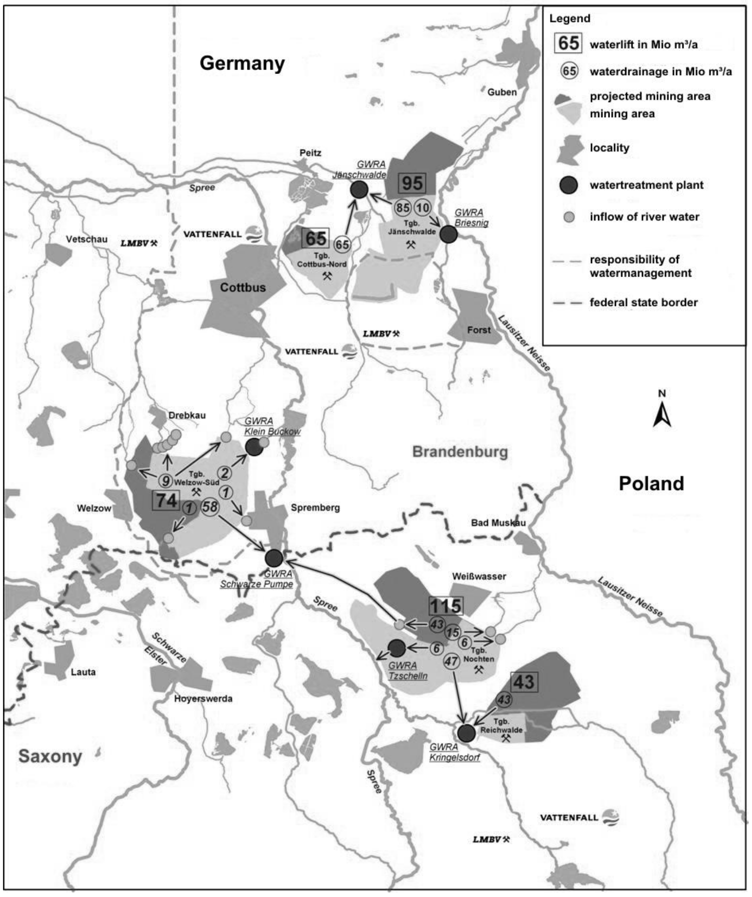

Figure 1: Location of the opencast mine Nochten and the watertreatment plants in the Lusatian mining area

The G.E.O.S. Ingenieurgesellschaft mbH has developed a pilot-scale technology in Nochten (opencast mine) where schwertmannite is formed during microbial treatment of acid mine water. This could become an efficient technology to partially replace the usual lime milk treatment by a microbial pre-treatment of the mine water saving huge amounts of lime.

1.2 Characteristics of schwertmannite

The ferrous iron contained in the pumped mine water of the Lusatian mining area is microbially oxidized to ferric iron. No nutrients have to be provided for the autotrophic iron oxidizing bacteria that use dissolved carbondioxide as sole carbon source. The oxidation rate in the pilot plant is influenced by oxygen supply (aeration), pH, sludge circulation, growth carrier and the composition of the inflowing mine water. The generated mineral Schwertmannite, an ironhydroxysulphate, precipitates at a pH between 2.8 and 4.5 (see equation 1, 2; BIGHAM et al. 1996a) and exhibits a molar ratio of Fe : SO_4^{2-} of 8.00 : 1 or 4.57 : 1, respectively.

$$Fe^{2+} + MO + O_2 + CO_2 \xrightarrow{pH2.5..4.5} Fe^{3+} + biomass \quad (1)$$

$$16Fe^{3+} + 3.5SO_4^{\;2-} + 25H_2O \rightarrow Fe_{16}O_{16}(OH)_9(SO_4)_{3.5} + 41H^+ \quad (2)$$

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 detailed characterisation of the mineral was carried out by Bigham and Schwertmann at the beginning of the 1990s (BIGHAM et al. 1990, BIGHAM et al. 1994, SCHWERTMANN & FOJT, 1996).

The schwertmannite generated microbiologically in the pilot plant is a very pure mineral containing almost no contaminants and with a high specific surface (Table 1). The Schwertmannite sludge exhibits better dewatering characteristics in comparison to the iron hydroxides. Dewatering by gravity yields a dry matter content of 35-45%.

Table 1: Chemical analysis data of several schwertmannite samples generated in the pilot plant Tzschelln

Parameter		Formation conditions				
		pH 2.9-3.0	pH 3.0	pH 2.7	pH 3.3	Mean
		Drying at 30-35 °C				
Analysis-water (106°C)	% by wt	9.1	9.1	10.2	10.8	9.8
Fe	% by wt DM[a]	48.2	47.8	49.0	50.1	48.8
SO_4^{2-} (acid-soluble)	% by wt DM	15.5	16.8	17.1	16.8	16.6
Aluminium	% by wt DM	0.2	0.1	0.1	0.1	0.1
Silicium	% by wt DM	0.6	1.0	0.3	0.2	0.5
NH_4^+ ($CaCI_2$-extract)	mg/kg DM	20	2.22	2.6	1.39	6.6
Potassium	mg/kg DM	206	98	79	88	118
Sodium	mg/kg DM	45	45	49	45	46
Calcium	mg/kg DM	572	485	483	483	506
Magnesium	mg/kg DM	242	167	161	148	180
Arsenic	mg/kg DM	100	103	122	100	106
Nickel	mg/kg DM	<2	<2	<2	<2	<2
Zinc	mg/kg DM	7	12	9	15	11
Manganese	mg/kg DM	12	10	9	9	10
Phosphorous	mg/kg DM	216	219	250	227	228

[a] DM: dry matter

The schwertmannite aggregates precipitating at the carrier material and the basin walls form centimeter-thick encrustations (Figure 1). They have a porous structure incorporating water in its pores and interstices.

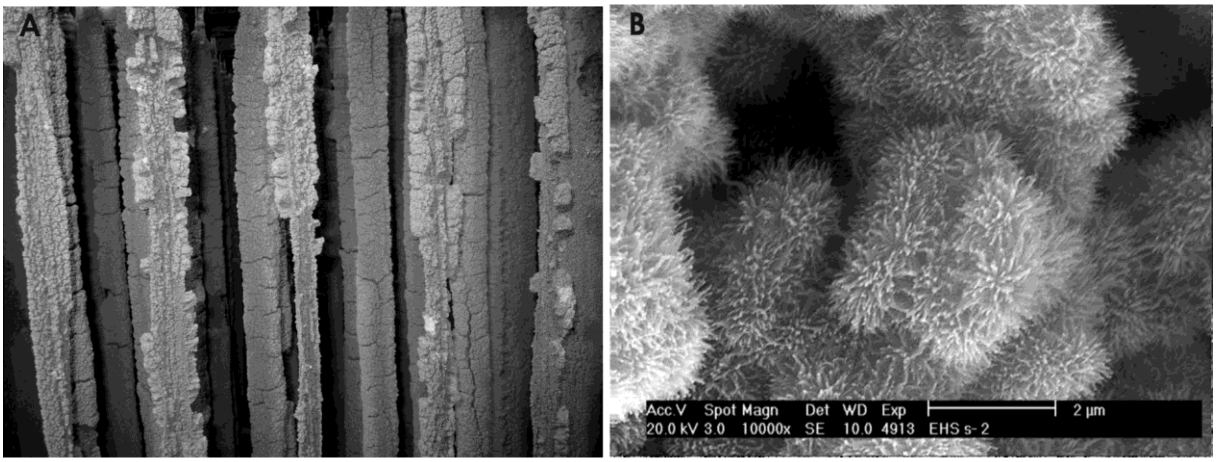

Figure 2: Schwertmannite produced in the pilot plant by microbial treatment of Lusatian minewater, A) encrustatians on the growth carrier material, B) SEM picture of the formed mineral schwertmannite

However, as well as the ferric hydroxide from lime milk treatment, Schwertmannite is a supposed waste product in mine water treatment. But due to its high iron content and other outstanding properties, the mineral has got a high potential for the production of valuable nano-particle products as focused in the ProMine project. The production of marketable iron oxide pigments from schwertmannite appropriate for various applications like colour and coatings or engobes in ceramics is the target of the Ingenieurgesellschaft G.E.O.S. and the project partner WOLA in ProMine.

2 Iron oxide pigments

The global production of iron oxide pigments in 2004 accounted for 85,000 metric tons valued at $77 million (POTTER, 2004). Iron oxide pigments have got a wide range of applications e. g. for construction materials, for colour and coatings, as ferrites in ceramics or as polishing agents for metals. Usually the iron oxide pigments are produced from iron salt solutions of the chemical industry or other ferruginous residues. The Price of iron oxide pigments during the last few years ranged from $1.2 to $2.3 per kilogram (CHEMICAL MARKET REPORTER, 2004) depending on type and pigment quality

The processing of schwertmannite to iron oxide pigments is a new and innovative idea. It is achieved by washing, filtration, drying, annealing and grinding of the raw material (Figure 3).

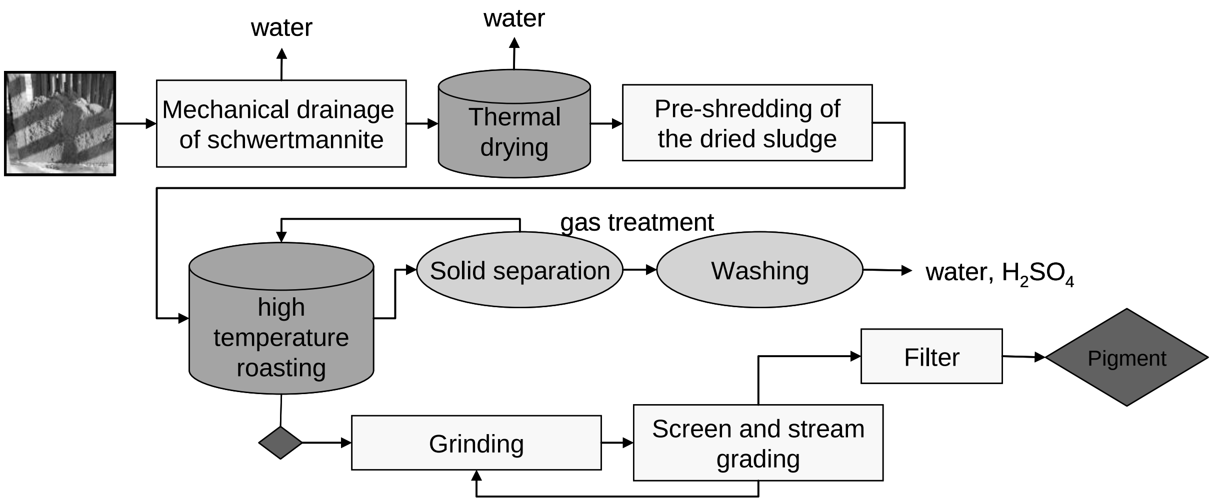

Figure 3: Production of iron oxide pigments from schwertmannite

Finally the obtained iron oxide pigments are evaluated according to general European standards. DIN EN ISO 1248:2008-06 classifies iron oxide pigments with regard to colour, iron oxide content, water-soluble compounds especially watersoluble chlorides and sulfates, Fineness and origin (Table 2, Table 3, Table 4). Thus, iron oxide pigments (Fe_2O_3) should have a Fe_2O_3-content between 10 and 95%. Other constituents are SiO_2 and Al_2O_3.

Table 2: Classification of iron oxide pigments according DIN EN ISO 1248:2008-06

Group	Category	Minimum content of Fe_2O_3 (% by wt)	Colour Index No.
Red pigments	A	95	Pigment red 101 77491
	B	70	Pigment red 102
	C	50	77491
	D	10	
Yellow pigments	A	83	Pigment yellow 42 77492
	B	70	Pigment yellow 43
	C	50	77492
	D	10	
Brown pigments	A	87	Pigment brown 6 77491m 77492 oder 77499
	B	70	Pigment brown 7
	C	30	77491m 77492 oder 77499
Black pigments	A	95	Pigment black 11 77499
	B	70	

Table 3: Types of iron oxide pigments differentiated by total water soluble content and and total content of watersoluble chlorides and sulfates according to DIN EN ISO 1248:2008-06

Parameter	Type I[a] Red and brown pigments	Type II Red and brown pigments	Type II Yellow and black pigments	Type III All pigments	Test procedure
Water-soluble fraction (% by wt determined after drying at 105°C)	≤ 0.3	>0.3 and ≤ 1	≤ 1	>1 and ≤ 5	EN ISO 787-3
Water-soluble chloride and sulfate (% by wt)	≤ 1				EN ISO 787-13

[a] used for corrosion protective coatings

Table 4: Iron oxide pigments classified after fineness according to DIN EN ISO 1248:2008-06

Parameter	Grade 1	Grade 2	Grade 3	Test procedure
	Red, yellow, brown and black pigments			
Sieve residue 45 µm (% by wt)	≤ 0.01	>0.01 and ≤ 0.1	> 0.1 and ≤ 1	EN ISO 787-7

For use in **ceramics** and **concrete** a lower pigment quality is necessary in comparison to the application in **colour and coatings**. DIN EN 12878:2005 summarizes the quality parameters and methods for determination for the colouring of building materials based on cement and/or lime. Parameters that have to be determined are:

- the composition of the pigment,
- water soluble components (EN ISO 787-3)
- water soluble chloride (EN ISO 787-13)
- total chloride content (EN ISO 1158)
- loss of ignition (DIN EN 12878:2005)
- emission of radioactivity (DIN EN 12878:2005)
- release of dangerous substances (DIN EN 12878:2005)
- relative tinctorial strength (DIN EN 12878:2005)
- sieve residue (90 µm), (EN ISO 787-7)
- pH value (EN ISO 787-9)
- solidification time (EN 196-3)
- compressive strength (EN 196-1)

With reference to DIN EN 12878:2005 and the manufacturer guidelines the iron oxide pigments should be lightfast, unsoluble in the mixing water, resistent against the alkaline cement paste, heat, weather and climate conditions.

The iron oxide pigments to be produced from schwertmannite are synthetic red iron oxide pigments (class A) of category A, Type II, grade 3. Initial laboratory pigment production from schwertmannite during the work in ProMine showed that the pigments already met most of the specifications defined by the listed guidelines. But there is still a high need for improving parameters to attain qualities for special applications. This should be done during the further work in ProMine.

However, schwertmannite is not only a valuable resource for iron oxide pigments but exhibits excellent characteristics for the use as water treatment material. Adding biosynthesized schwertmannite to contaminated waters, its transformation to ferric hydroxides and the associated large sorption capacity are suitable to remove heavy metal anions like AsO_4^{3-} by adsorption processes from mine water. Therefore G.E.O.S. currently proves the development of sorption materials for water treatment from schwertmannite.

3 References

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