



Recovery of indium from sphalerite ore and flotation tailings by bioleaching and subsequent precipitation processes



Mirko Martin*, Eberhard Janneck, René Kermer, Anke Patzig, Susan Reichel

G.E.O.S. Ingenieurgesellschaft mbH, Schwarze Kiefern 2, 09633 Halsbrücke, Germany

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ABSTRACT

Flotation tailings dump material of the former lead–zinc mine near Freiberg (Germany) consists of fine grained quartz, feldspar, mica as well as the sulphide minerals pyrite, galena and sphalerite not recovered by flotation. Sphalerite contains, aside from iron, copper and cadmium, significant amounts of indium (up to 0.38% (w/w)) leading to indium contents up to 70 mg/kg in the mine tailings. Preliminary thermodynamic assessment showed a comparatively small Eh–pH-range where bioleaching is possible and indium is not hydrolytically precipitated. Shake flask bioleaching of original polymetallic sphalerite ore from the Freiberg mining district (400 mg/kg indium) showed maximum zinc and indium recovery rates of almost 100% or 80%, respectively. First bioleaching tests on tailings material achieved zinc and indium yields of up to 80%. A stepwise precipitation process is being developed for indium recovery from the PLS (pregnant leaching solution) consisting of combined iron/indium precipitation and subsequent processing of the indium pre-precipitate.

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1. Introduction

In the Freiberg mining field in the lower Erzgebirge mountains in Germany mining has been carried out from the end of the 12th century until the last third of the 20th century. In this area a polymetallic Ag–Pb–Zn vein deposit was mined until closure in 1969 mainly for silver, lead and zinc (Baumann, 1958; Seifert and Sandmann, 2006). As a legacy numerous waste rock dumps evolved. Two flotation tailings ponds (“David Schacht” and “Hammerberg”) were in operation in the central Freiberg mining field during the last mining period 1937–1969 when the ore was beneficiated by flotation processes (Table 1).

During the last two decades the dumps were under investigation for environmental reasons, because seepage water leaching especially zinc and cadmium caused heavy metal contaminations in the groundwater plume and the receiving surface water (Kluge et al., 1995; Graupner et al., 2007).

Growing industrial demand for critical elements led to various F&E projects for re-assessment of mining residues as potential source of such raw materials. Consequently, the aforementioned tailings materials with their content of residual sphalerite containing a relatively high indium concentration were addressed as subject for study.

The dumps consist of fine grained flotation tailings with quartz, feldspar and phyllosilicates as major and the sulphides pyrite, arsenopyrite, sphalerite and galena as minor components (Graupner et al., 2007). The flotation plants achieved metal yields of 60–80%. Thus the tailings contain significant amounts of sulphides not recovered in the flotation process resulting in metal contents of about 0.5–1.5% zinc and 0.3–1.0% lead as well as arsenic and cadmium. Because of the indium content of up to 3800 ppm in the sphalerite of the Freiberg deposit, the tailings contain about 5–70 ppm of indium. The indium is present in sphalerite as solid solution. An assessment of the indium amount within the two ponds resulted in 31 t or 9 t, respectively (Table 1).

Within a R&D project sponsored by the Federal Ministry of Education and Research (Grant no. 033R095B) the tailings dams are currently investigated with regard to recovery of strategically important raw materials accompanied by reducing environmental problems. In 2013 a drilling campaign was carried out and amongst others a 30 m deep borehole drilled in the tailings dam “David Schacht” near Freiberg. The recovered material was investigated for the potential exploitation of residual valuable metals e. g. zinc or indium by using alternative technologies like bioleaching.

Indium extraction from sphalerite concentrates was previously investigated regarding chemical, especially acid pressure leaching by Li et al. (2006, 2010), whereas investigations on bioleaching of such materials are scarce.

Preliminary thermodynamic assessment showed a comparatively small Eh–pH-range where bioleaching is feasible and indium

* Corresponding author. Tel.: +49 3731 369 296; fax: +49 3731 369 200.

E-mail address: m.martin@geosfreiberg.de (M. Martin).

is not hydrolytically precipitated. For this reason, at first bioleaching of indium from sphalerite was examined. Subsequently the optimised technology was applied to the leaching of material from the flotation tailings dams.

2. Materials and methods

2.1. Minerals and media

For preliminary bioleaching tests in shake flasks and the up-scaling in columns 1 kg sphalerite from the Freiberg mine was obtained from the mineralogical collection in Freiberg, Germany. The sphalerite was milled using a vibratory disc mill (Retsch, Germany). During a drilling campaign in 2013 additional samples of tailings material from the “David Schacht” tailings dam were taken. Analysis of the resulting grain fractions from sphalerite and analysis of the tailings material revealed the composition displayed in Table 2. Due to intensive milling prior to flotation the tailings material is very fine grained (70% dry matter <0.05 mm). Drill cores showed a finely stratified structure.

As inoculum for the bioleaching experiments and the column bioleaching a culture obtained from a leachate sample (pH 2.3) of the Mauriliden zinc–lead mine (Sweden, BOLIDEN Group) was used. The inoculum contained uncultured acidophilic ferrous iron-oxidising and sulphur-oxidising species and was enriched in modified basal salts medium (Wakemen et al., 2008) with a ferrous iron concentration of 200 mM and 7.5 mg l⁻¹ cycloheximide to inhibit fungal growth. The medium without FeSO₄ was autoclaved and FeSO₄ was added separately from a filter sterilized (0.2 µm cellulose nitrate filter) stock solution. To adapt the culture to the Freiberg sphalerite ore the milled mineral (<63 µm, fraction 3) was added to the medium at a concentration of 4% (w/v). After cell

growth was observed the culture was inoculated into fresh basal salts medium with 4% (w/v) sphalerite.

For indium precipitation tests a 1 mol l⁻¹ In₂(SO₄)₃ stock solution was prepared from indium metal (>99.97% In) and diluted as required. The As was added as 1 mol l⁻¹ Na₂HAsO₄ stock solution.

2.2. Experimental procedures

2.2.1. Flask tests

Various pre-tests were run with different sphalerite grain size fractions resulting in an optimum of 63–200 µm. The bioleaching tests in shake flasks were carried out in 500 ml Erlenmeyer flasks with 150 ml of the aforementioned basal salts medium and a solid concentration of 4% (w/v) sphalerite milled to a grain size of 63–200 µm (fraction 2). Three parallel approaches were done at each pH value (1.6, 1.8 and 2.0). A sterile control was run to determine the influence of chemical leaching of the sphalerite. Sterilization was achieved by the addition of 0.1% (w/v) sodium azide to the medium. After adjusting the pH of the medium with 7 M sulphuric acid the shake flasks were inoculated with the adapted leaching culture resulting in an initial cell concentration of 10⁷ ml⁻¹. To compensate the evaporation loss sterilized distilled water was added. The pH value was adjusted periodically with 7 M sulphuric acid. The shake flasks experiments were carried out at 30 °C and 130 rpm.

2.2.2. Column tests

For the column bioleaching glass columns with a diameter of 3.5 cm and a filling level of 12 cm were filled with about 230 g milled sphalerite of a grain size of 0.2–2 mm (fraction 1) and about 9 cm³ gravel bed at the bottom of the column. The experiments were carried out at room temperature and a pH value of 1.8 using basal salts medium with 200 mM ferrous iron. Prior to the start of the experiments the feed medium and the column were inoculated with the aforementioned adapted Mauriliden culture, resulting in an initial cell concentration in the medium of approximately 10⁷ ml⁻¹. The leaching-solution was re-circulated with a flow rate of 100 ml d⁻¹, and pH was adjusted manually on a daily basis with 7 M sulphuric acid to 1.8. For appropriate aeration the medium was permanently stirred. The experiment duration was 225 days. When the ferrous iron concentration in the medium was depleted and the progress of the leaching receded due to inhibition by the high metal concentrations the medium was replaced.

During all experiments redox potential, pH and cell concentration were measured every two days. Periodically and adapted to the leaching course samples for the measurement of Fe²⁺, total Fe, Zn and In concentration were taken from the leaching solution, filtered (0.45 µm cellulose nitrate filter) and stabilized with nitric acid prior to measurement. Additional samples of the leaching solution were taken immediately after inoculation and at the end of the experiments for the analysis of Fe, Cu, Zn, In, Cd, As, Pb and Mn.

2.2.3. Reactor experiments

Bioleaching experiments in reactor-scale were accomplished in a 2 L glass vessel (bioreactor Fermac 200, Electrolab Biotech Ltd., UK) with 1.5 L modified basal salts medium (100 mM ferrous iron) and by using tailings material (David Schacht flotation tailings dam) at a solid concentration of 10% (w/v). After addition of the tailings material and pH adjustment (pH 1.8) with 3.7 M sulphuric acid the bioleaching approach was inoculated with the above mentioned adapted Mauriliden culture resulting in an initial cell concentration of 9.4 × 10⁶ ml⁻¹. The reactor approach was accomplished at 30 °C, 150 rpm and pH 1.8 with automatic pH adjustment (3.7 M sulphuric acid, 2.5 M sodium hydroxide). Aeration

Table 1

Characteristics of the flotation tailing dams “David Schacht” and “Hammerberg” in the central Freiberg mining field (Jobst et al., 1993).

	Surface area (m ²)	Volume (m ³)	Element content (% w/w)
Flotation tailings dam “David Schacht”	63,000	745,000	0.2–0.5 Pb 0.6–1.2 Zn
Flotation tailings dam “Hammerberg”	50,000	195,000	0.2–0.5 Pb 0.6–1.2 Zn

Table 2

Chemical composition of the sphalerite samples and the tailings material “David Schacht”.

Element	Sphalerite fraction 1 0.2–2 mm	Sphalerite fraction 2 63–200 µm	Sphalerite fraction 3 <63 µm	Tailings material “David Schacht”
(mg kg ⁻¹ dm ^a)				
Zn	175,000	203,000	220,000	10,000
Fe	181,000	167,000	160,000	159,000
Cd	2290	2990	3180	92
As	101,000	82,700	46,900	8450
Cu	14,500	15,600	20,800	1000
Mn	3930	4070	4750	4400
Ni	20	16	15	20
Pb	60,600	31,200	33,300	4680
In	315	410	450	14
Ga	2	2	2	n.a.
Ge	11	3	4	n.a.
Se	26	<1	<1	n.a.

n.a. – not analysed.

^a dm – dry matter.

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