

# Lithium recovery from lithium-containing micas using sulfur oxidizing microorganisms



S. Reichel\*, T. Aubel, A. Patzig, E. Janneck, M. Martin

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

## ARTICLE INFO

### Article history:

Received 27 July 2016

Revised 20 February 2017

Accepted 25 February 2017

Available online 3 March 2017

### Keywords:

Non-ferrous metallic ores

Lithium

Mica

Silicate bioleaching

Sulfur oxidizing bacteria

Membrane filtration

## ABSTRACT

There is about 60,000 t of lithium mica in the German part of the deposit in the Erzgebirge mountains. Lithium can be recovered by high pressure-high temperature leaching with sulfuric acid and further hydrometallurgical processing. Another idea, developed in the EU-project FAME, was to use sulfur oxidizing microbes to produce sulfuric acid and to extract lithium at moderate temperature and pressure conditions. Experiments were carried out in 2 L and 4 L batch reactors at 30 °C. After microbial transformation of elemental sulfur to sulfuric acid, the milled (<45 μm) lithium mica was added at a pulp density of 5%. Up to 26% of lithium was extracted biologically compared to 16% by chemical leaching. The bioleaching solution contained about 1 g/L aluminium, 0.8 g/L iron and 0.2 g/L lithium and could be further processed hydrometallurgically.

© 2017 Published by Elsevier Ltd.

## 1. Introduction

Lithium has been recognized as a potentially critical raw material during recent years because of its wide-ranging uses in a number of applications, including batteries, glasses and ceramics, light alloys and as additive for greases (USGS, 2016, Table 1).

Lithium consumption for batteries has increased significantly in recent years because rechargeable lithium batteries are used extensively for portable electronic devices and in electric tools, electric vehicles, and grid storage applications. Thus, rechargeable batteries are considered the largest potential growth area for lithium (USGS, 2016).

Lithium for chemical and battery applications is recovered mainly from brines in Chile, Argentina and China. Lithium minerals, with focus on spodumene and petalite, are recovered predominantly in Australia for industrial mineral uses, e.g. in ceramics and glasses (Kesler et al., 2012). The growing demand for lithium may lead to a more diverse structure of the lithium industry and a shift to lithium recovery from smaller mineral deposits. This may be accompanied by the recovery of valuable by-products, such as tin, tungsten, niobium or tantalum.

Zinnwaldite, the lithium mineral in the Zinnwald-Cinovec deposit at the German/Czech border, can be easily concentrated from the greisen ore by crushing, milling, sieving and magnetic

separation, potentially complemented by froth flotation for the fine grained fractions (Kondas and Jandova, 2006; Jandova et al., 2009; Samkova, 2009). Lithium can be separated from the concentrate as  $\text{Li}_2\text{CO}_3$  by roasting with sulfates and subsequent leaching and precipitation (Siame, 2011). Alternatively zinnwaldite can be dissolved directly by acid, such as sulfuric acid, to produce  $\text{Li}_2\text{SO}_4$ . The reaction is carried out at 120 °C, consumes large amounts of acid, and produces a leachate with a high concentration of ferrous iron, aluminium, potassium, and lithium.

We investigated the leaching of zinnwaldite using sulfuric acid produced from acidophiles via oxidation of elemental sulfur. This idea to enhance the metal recovery by adding elemental sulfur or sulfur compounds to low grade acid consuming ores is not new (de Oliveira et al., 2014; Bouffard et al., 2009; Salo-Zieman et al., 2005; West-Sells et al., 2007). The use of biologically-produced sulfuric acid from elemental sulfur has also been reported for leaching of vanadium from spent refinery catalysts and leaching of only 11% of the lithium from secondary batteries (Mishra et al., 2007, 2008).

## 2. Materials and methods

### 2.1. Minerals

To produce a zinnwaldite concentrate, samples from a coarse-grained lithium-containing greisen ore were taken from the Cinovec deposit, Czech Republic, and crushed to an appropriate size. From the crushed material, mica was selected by handpicking

\* Corresponding author.

E-mail address: [s.reichel@geosfreiberg.de](mailto:s.reichel@geosfreiberg.de) (S. Reichel).

**Table 1**  
Lithium end-use applications, USGS (2016).

Application	Share
Batteries	35%
Ceramics and glass	32%
Lubricating greases	9%
Air treatment	5%
Continuous casting mold flux powders	5%
Polymer production	4%
Other uses	10%

and milled with an oscillating disk mill using zirconia. The zinnwaldite concentrate size was less than 45  $\mu\text{m}$  fine and contained 52%  $\text{SiO}_2$ , 24%  $\text{Al}_2\text{O}_3$ , 11%  $\text{Fe}_2\text{O}_3$ , 9.5%  $\text{K}_2\text{O}$  and 13,350 ppm Li. Other elements were below 1% (9510 ppm Ru and 110 ppm Gallium).

## 2.2. Experimental procedures

Shake flasks and two batch reactors were used. An uncharacterized and adapted mixed culture of mesophilic sulfur oxidizing bacteria (GEOS culture collection), originally obtained from leaching of sulfide tailings, was used as inoculum. The inoculum was suspended in 100-mL basal salts medium (DSMZ 71) in flasks. 5 g/L of elemental sulfur was added; the pH was adjusted to 5. After the pH dropped to about 2 due to production of sulfuric acid, the zinnwaldite concentrate was added in a concentration of 3% w/v. Experiments were carried out in duplicate. A control with the same mineral medium but without microorganisms was set up. All cultures and the control were incubated at 30 °C for 14 d. The pH of the control was not adjusted; pH and cell number were determined periodically. After 14 d, the supernatant was filtered and analyzed for Al, Fe, and Li.

A 2- and a 4-L bioreactor were filled with the aforementioned medium and sulfur. When the pH dropped to 1.7, the zinnwaldite concentrate was added in a concentration of 5% w/v. For investigation of biofilm formation, pieces of crystalline lithium mica and crystalline sulfur were also fixed in the 2 L reactor. Experiments were carried out at 30 °C and 130 rpm with continuous monitoring of pH and periodic monitoring of cell number. Evaporation loss was compensated daily by adding distilled sterile water. A control without microbes was used to monitor the chemical leaching of zinnwaldite. The pH of the control was adjusted with a 2.5 M  $\text{H}_2\text{SO}_4$  solution to match the pH of the biological tests at regular intervals. The concentrate was added at pH 1.7. Samples of the leaching solution were taken immediately and after 6, 20, 43 and 54 d and analyzed for metals.  $\text{Fe}^{2+}$  concentration was determined by titration with potassium permanganate.

## 2.3. Microscopic investigations

After the tests, samples of crystalline sulfur and mica were removed from the 2-L bioreactor, rinsed, and fixed with 4% paraformaldehyde solution for 4 h. Samples were sent to the University Duisburg Essen for microscopic analyses by epifluorescence microscopy using an Axiovert100MBP microscope (Zeiss®, Germany). Combined atomic force microscopy (AFM) and epifluorescence microscopy was carried out using the BioMaterial™ Workstation to investigate cell distribution on mineral surfaces.

## 2.4. Membrane filtration

The final slurry was centrifuged. The supernatant was titrated with 15 M NaOH to pH 5 and again centrifuged to separate precipitates. 1.5 L of the supernatant was crossflow-filtered using a GE DL nanofiltration membrane with an active membrane surface of

200  $\text{cm}^2$ . Transmembrane pressure was constant at 10 bar. Membrane was held at 18 °C. A sulfate antiscalant was dosed at 5 ppm in the feed solution. Cross-flow velocity was 0.5 m/s (2.9 L/min). Concentrate and permeate were recycled to the feed tank to maintain a sufficient feed volume during the long run experiments.

## 3. Results and discussion

### 3.1. Bioleaching

Leaching of zinnwaldite in shake flasks using a mixed bacterial culture of sulfur oxidizing bacteria was dependent on pH. After 14 d, the final pH in the shake flasks ranged from 1.6 to 2.6. Leaching of lithium, iron and aluminium decreased with increasing pH (Fig. 1). At pH 1.6, 11% Li, 13% Fe and 19% Al was dissolved. The control at pH 5.4 leached 4% Li, 0% Fe and 0% Al.

When zinnwaldite was added to the 4-L reactor, the pH increased from 1.7 to 2.1, but due to continuous sulfuric acid production, the pH decreased and cell growth seemed not to be affected (Fig. 2).

Leaching of lithium in bioreactors was slightly higher (26 and 21%) compared to chemical leaching (16%) (Fig. 3). For iron, 25 and 20% vs. 15%. For gallium, 24 and 20% vs. 11%.

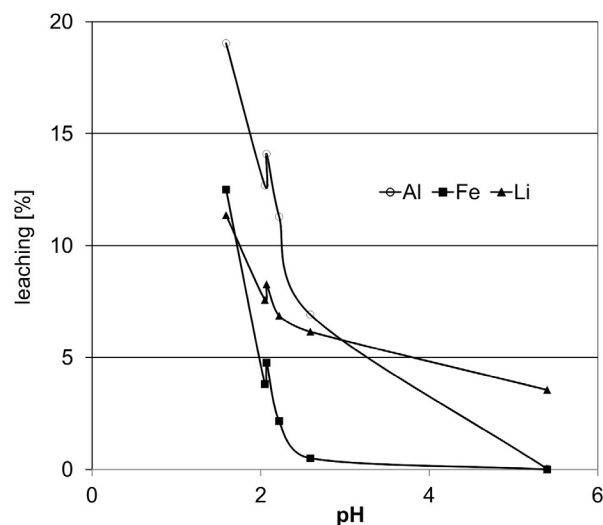
The leaching solution contained 150 mg/L of lithium which was double that of the control. The control had no cell growth.

Only half of the soluble iron (410–920 mg/L) was ferrous iron. Since the culture used was a mixed culture of acidophiles originally enriched from sulfidic tailings, it was expected that abundant iron-oxidizing *Acidithiobacilli* would oxidize ferrous to ferric iron. However, an increase in fluoride concentration in the bioleaching solution could have inhibited ferrous iron oxidation (Brierley and Kuhn, 2010; Andersen and Lundgren, 1969; Dopson, 2008).

### 3.2. Microscopic investigation of biofilm formation

Biofilm formation was investigated to prove whether the acidophilic microorganisms attached on the mica surface and/or accelerated lithium leaching.

Mica blades had a slightly higher microbial colonisation in comparison to the control which had no colonization (Fig. 4) However, no dense biofilm was visible on mica surfaces.



**Fig. 1.** Leaching of aluminium, iron and lithium from zinnwaldite as a function of pH.

Download English Version:

<https://daneshyari.com/en/article/6477812>

Download Persian Version:

<https://daneshyari.com/article/6477812>

[Daneshyari.com](https://daneshyari.com)