



Integrated process for lithium recovery from zinnwaldite



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ABSTRACT

Process development for production of lithium carbonate (Li_2CO_3) from regionally occurring zinnwaldite concentrate (3.0 wt.-% Li_2O) was conducted. By acid digestion with mineral acids, preferably hydrochloric acid under reflux (approx. 110 °C) and atmospheric pressure, lithium is mobilised up to 94%. In contrast to using sulphuric acid no toxic hydrogen fluoride is released with hydrochloric acid, what is a crucial factor for digestion process design. Separation technologies for recycling of more than 80% of unspent hydrochloric acid, as well as the recovery of associated components, particularly iron hydroxide and potassium/aluminium/fluoride as sodium-potassium-cryolite, are part of the process. After removal of impurities by means of electro dialysis and concentration, technical grade lithium carbonate was obtained by precipitation with soda. Hot water washing furnishes crude-product purities $\geq 98.0\%$ with a total lithium yield of $\sim 70\%$.

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1. Introduction

Lithium is a strategic metal, which most commonly is heard of being indispensable for future technologies such as energy storage, electric mobility and cordless devices. In fact, global lithium production for use in batteries has increased by approx. 20% per annum since 2000, resulting in 35% of the overall lithium consumption in 2015. (Jaskula, 2016; Naumov and Naumova, 2010) However, the use of lithium compounds comprises a far broader spectrum such as glass, enamel and ceramic industry, lubricating greases, pharmaceutical products or aluminium production. (Deberitz, 2006; Ebersperger et al., 2005)

Lithium is almost half as abundant in the upper earth crust as zinc, and according to USGS estimates reserves of more than 13 mill. t Li are available. (Jaskula, 2016) Since no substitution for lithium can be achieved in its most important applications, such as ceramics and glass, (rechargeable) batteries as well as lubricants, the demand for this metal is forecasted to grow by approx. 6–11%/a. (European Commission, 2014; Martin et al., 2016). As a result, Li_2CO_3 price is expected to significantly raise on the short- to mid-term.

In fact, Li_2CO_3 price has experienced an increase by $\sim 15\%$ since November 2015. At present (October 2016) it amounts to ~ 7200 USD/t. (Bundesanstalt für Geowissenschaften und Rohstoffe, 2016) The concerns of some authors, who even see a price jump to 25,500 USD/t not later than 2020 (Grosjean et al., 2012) have to some extent become reality in China, where in March 2016 the spot price was up to 22,900 USD/t $\text{tg-Li}_2\text{CO}_3$ (technical grade, 99.0%). (Asian Metal, 2016)

At present, lithium is predominantly recovered from salt lake brines with Chile as most important producer. (Voigt, 2014) Lithium production from brines considerably profits from lower manufacturing costs combined with less technological effort compared with that for other lithium ores such as spodumene, $\text{LiAlSi}_2\text{O}_6$, petalite, $\text{LiAlSi}_4\text{O}_{10}$, lepidolite, $\text{K}(\text{Li,Al})_3(\text{Al,Si})_4\text{O}_{10}(\text{OH,F})_2$ or zinnwaldite, $\text{KLiFeAl}(\text{AlSi}_3)\text{O}_{10}(\text{OH,F})_2$. (Jandová et al., 2012)

In view of the unequal distribution of global resources (69% of worldwide resources are located in South America and another 18% in China) (Grosjean et al., 2012), the potential supply risks and price uncertainties linked thereto, domestic, yet smaller lithium deposits may become increasingly important with respect to securement of raw material supply. One such deposit is the zinnwaldite deposit covering the Czech/German border at Cinovec/Zinnwald. With $\sim 347,000$ t Li_2O it is the largest known European siliceous lithium deposit. (Bertau, 2013; Röllig, 1990; Starý et al., 2010)

Zinnwaldite with the general formula $\text{KLiFeAl}(\text{AlSi}_3)\text{O}_{10}(\text{OH,F})_2$ is a grey-metallic coloured phyllosilicate mineral which is classified as an iron-rich lepidolite. Belonging to the mica group it is a member of the polyolithionite-trilithionite series. The specimen found in the Zinnwald deposit have the composition $\text{K}(\text{Fe}_{0.6}\text{Li}_{0.3})(\text{Al}_{0.9}\text{Fe}_{0.1})(\text{Li}_{0.2}\text{Fe}_{0.6})(\text{AlSi}_3\text{O}_{10})(\text{OH}_{1.1}\text{F}_{0.9})$, where the Li_2O content ranges between 2.0 and 5.0 wt.-% with the northern mineralisation of the deposit less lithium-rich. (Deberitz, 2006; Jandová et al., 2009)

Lithium recovery from siliceous ores is state of the art (Chagnes and Światowska, 2015; Choubey et al., 2016). The most commonly applied process for Li_2CO_3 recovery from siliceous lithium ores is digestion with sulphuric acid. It is typically used for lithium recovery from spodumene ($\text{LiAlSi}_2\text{O}_6$). Since only meagre amounts can be mobilised from

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naturally occurring α -spodumene the ore is thermally converted at $T \geq 1000$ °C into β -spodumene which readily releases lithium within 2 h at 300 °C (92.5%). Yet, harsh thermal treatment conditions render this process highly energy consuming. In addition, the sulphuric acid used has to be neutralised completely once leaching has been finished, thus consuming significant quantities of cost-intensive sodium hydroxide (NaOH) and producing considerable amounts of sodium sulphate (Na_2SO_4) which is practically unsaleable due to market saturation. On the other hand, neutralisation with NaOH has the majority of impurities precipitated, what allows for facile Li_2CO_3 production through addition of soda (Na_2CO_3). After filtration and drying Li_2CO_3 is obtained in yields up to 90%. (Brödermann et al., 1988; Distin and Phillips, 1982; Rosett et al., 1935; Tan, 2011)

As an alternative to acid digestion a limestone digestion process has been developed, where α -spodumene is converted into β -spodumene, too. The thermal treatment step is conducted in presence of limestone which decomposes to give CaO reacting in situ with the ore to give lithium hydroxide. The latter is obtained through leaching with water. Subsequent precipitation with soda furnishes Li_2CO_3 (Bertau et al., 2013).

Where lithium recovery is to take place from micaceous ores, one typically focuses on lepidolite, $\text{K}(\text{Li},\text{Al})_3(\text{Al},\text{Si})_4\text{O}_{10}(\text{OH},\text{F})_2$, lithium recovery from which is largely similar to that from spodumene. Industrial processes comprise both digestion with sulphuric acid and limestone. In contrast to the spodumene process no highly energy consuming thermal treatment step is involved for activating the mineral. But the mineral's fluoride content mandatorily requires a defluorination step which is commonly conducted at a temperature of 860 °C or higher. (Yan et al., 2012)

It is this context, which prompted Czech scientists to design a lithium recovery process for zinnwaldite. Their gypsum method prevents fluorine from being released through formation of calcium fluoride. For these purposes zinnwaldite concentrate is mixed with gypsum (CaSO_4) and calcium hydroxide and sintered at a temperature from 900 to 975 °C. The sinter is ground and well water soluble. A lithium sulphate containing solution is obtained through leaching with water. After filtration and concentration to ≥ 9 g/L Li, addition of potash (K_2CO_3) furnishes Li_2CO_3 in up to 96% yield. Hitherto, the method has been realised in the lab scale only (Jandová et al., 2009).

In addition, another zinnwaldite digestion with supercritical carbon dioxide in water ($\text{sc-CO}_2/\text{H}_2\text{O}$) had been tested. The underlying idea was to substitute silicate groups by carbonate as this is effectively done with wollastonite (CaSiO_3), for instance. (Daval et al., 2009; Huijgen et al., 2006) In fact, lithium mobilisation by sc-CO_2 treatment is far from being effective, while lattice carbonatisation did not exceed 10%, even by addition of a variety of inorganic additives. (Bohne, 2012; Ebersbach, 2012; Schneider, 2016; Storch, 2010)

In September 2015 Lithium Australia reported on a technology for the recovery of Li_2CO_3 from lepidolite which is claimed to be applicable for zinnwaldite, too. From the published data however, this process appears basically identical with classical Li recovery from lepidolite. At present, there is no indication how to deal both the iron problem and fluorine emissions (Griffin, 2015). A number of further lithium recovery methods has been published or patented, with none of these being suitable for zinnwaldite however (Chen et al., 2011; Cunningham, 1953; Dwyer, 1957).

It is this special situation of iron being present in zinnwaldite in considerable amounts, which hitherto stood against zinnwaldite exploitation on a large scale. In addition, another challenge is the lithium content of zinnwaldite. The lithium content of used zinnwaldite concentrate (3.0 wt.% Li_2O) is significantly below the typical ranges of lepidolite (3.3–4.1 wt.% Li_2O), petalite (3.4–4.5 wt.% Li_2O) and particularly spodumene (4.1–7.1 wt.% Li_2O). (Kogel, 2006)

In fact, viewed from an economic angle, none of the protocols mentioned above is suited for technical lithium recovery from the mineral.

Consequently, a material and energy effective lithium recovery process for zinnwaldite was required the design of which must take into account that

- there exists no protocol for by-element extraction, since upon exploitation of polymetallic mineral deposits there is a clear focus on the primary metal
- current processes are highly energy consuming
- there will be massive release of fluorine, typically in the form of silicon tetrafluoride (SiF_4) in acidic recovery processes of untreated zinnwaldite

Considering the above-mentioned issues led to the strategy to circumvent thermal treatment procedures since energy may turn out to be a prohibitive cost factor on a technical scale, in particular when realised in Germany. It was this unfavourable situation which prompted us to develop an integral process from which not only Li_2CO_3 emerges as target product, but also iron, aluminium, potassium and fluoride in form of tradeable products.

2. Materials and methods

2.1. Materials

Chemicals and solvents were obtained from Sigma-Aldrich Chemie GmbH, Taufkirchen, Germany. Standards were purchased from VWR International GmbH, Dresden, Germany and Carl Roth GmbH & Co. KG, Karlsruhe, Germany. Zinnwaldite was obtained from the lithium deposit in Zinnwald, Germany. Samples were kindly provided by the Mineralogical Collection of Freiberg University of Mining and Technology as well as SolarWorld Solicium GmbH, Freiberg, Germany and UVR-FIA GmbH, Freiberg, Germany. Before use the material was pre-treated by multi-stage crushing to a particle size of < 1 mm followed by dry magnetic separation of zinnwaldite concentrate from gangue (3.0 wt.% Li_2O). The composition of zinnwaldite concentrate is summarised in Table 1.

2.1.1. Equipment

Zinnwaldite concentrate digestions under elevated pressure were carried out in Hastelloy C4 autoclaves, type BR-300 from Berghof Products + Instruments GmbH, Eningen unter Achalm, Germany. Large-scale operations were conducted on a DeDietrich/QVF Optimix™ system equipped with a 16 L double wall vessel and a DN 80 mirrored wall packed column ($l = 1160$ mm, $w = 100$ mm). Particle sizes were analysed by static light scattering measurement conducted on a LS 13320 laser diffraction particle size analyser from Beckman Coulter, Brea, USA. Viscosity measurements were done on a rotational rheometer Rheotest® RN 4.1 from Rheotest Messgeräte Medingen GmbH, Ottendorf-Okrilla, Germany. Electrodialysis equipment was purchased from Deukum GmbH, Frickenhausen, Germany. Monovalent cation exchange membranes (CMS) and standard anion exchange membranes (AMX) were the product of Neosepta® Tokuyama Corporation, Tokyo, Japan. Analyses were conducted using an iCAP 6500 Duo ICP-OES from Thermo Fisher Scientific GmbH, Schwerte, Germany, an ICS-3000 ion chromatograph (IC) from Thermo Fisher Scientific GmbH, Schwerte, Germany and a contrAA 700 continuum source atomic absorption spectroscopy (CS-AAS) from Analytik Jena AG, Jena, Germany. X-ray fluorescence measurements were done on an energy dispersive X-ray fluorescence (ED-XRF) analyser Spectro Xepos from Ametek, Inc.,

Table 1
Composition of zinnwaldite concentrate.

Composition [wt.-%]							
SiO_2	Al_2O_3	Fe_2O_3	K_2O	F	Li_2O	MnO	Rb_2O
50.6	17.3	11.5	8.4	4.1	3.0	1.1	0.6

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