

OBTAINING Li_2CO_3 FROM ZINNWALDITE WASTES

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A zinnwaldite concentrate with 1.40% Li processed in this study was prepared from zinnwaldite wastes (0.21% Li) using dry magnetic and grain size separations. Zinnwaldite wastes originated from dressing Sn–W ores, which were mined in the past in the Czech Republic in Činovec area. The extraction process of lithium, so-called gypsum method consisted of sintering the concentrate with CaSO_4 and $\text{Ca}(\text{OH})_2$, subsequent leaching of the sinters obtained in H_2O , solution purification and precipitation of Li_2CO_3 . It was observed that almost 96% lithium extraction was achieved if sinters prepared at 950°C were leached at 90°C , liquid-to-solid ratio = 10:1, reaction time of 10 min. The weight ratio of the concentrate to CaSO_4 to $\text{Ca}(\text{OH})_2$ was 6 : 4.2 : 2. Lithium carbonate product containing almost 99% Li_2CO_3 was separated from the condensed leach liquor, from which calcium was removed by carbonate precipitation.

INTRODUCTION

The world lithium consumption has been permanently growing in the last 10 years and it is possible to forecast its further gradual growth. The main area of lithium consumption is in production of lightweight alloys and primary or secondary lithium batteries. Another significant use of lithium is in lithium compounds, namely Li_2CO_3 . Lithium carbonate is the starting material for the industrial production of all other lithium compounds including lithium chloride, a raw material for lithium metal production. Lithium carbonate itself finds extensive application in many industrial branches. It is used as an additive in glass, enamels and ceramics. Its function is generally based on reduction of melting point (particularly important for enamels); lowering the viscosity of molten glass; increased surface tension (giving improved reflectivity to enamels and glazes), and improving chemical resistance of glass. The addition of Li_2CO_3 to cement or concrete leads to quicker setting. Lithium carbonate is also used as an additive to molten salt baths for the electrolytic production of aluminium. It reacts with aluminium trifluoride in the melt to form lithium fluoride. Specially prepared high-purity lithium carbonate is used increasingly for the treatment of manic-depressive diseases [1].

In the present time most lithium and lithium compounds are produced from lithium-bearing brines containing 0.06–0.15% Li or from lithium bearing aluminosilicates containing about 1.6–3.6 % Li. The most important lithium minerals are spodumene $\text{LiAlSi}_2\text{O}_6$

(6.0–7.5% Li_2O), petalite $\text{LiAlSi}_4\text{O}_{10}$ (3.5–4.5% Li_2O), lepidolite $(\text{Li}\cdot\text{Al})_3(\text{Al}\cdot\text{Si})_4\text{O}_{10}(\text{F}\cdot\text{OH})_2$ (3.30–7.74% Li_2O), so called lithium mica usually containing 3–5% Rb_2O and zinnwaldite $\text{K}(\text{Li}\cdot\text{Al}\cdot\text{Fe})_3(\text{Al}\cdot\text{Si})_4\text{O}_{10}(\text{F}\cdot\text{OH})_2$ (2–5% Li_2O), which is regarded as a variety of lepidolite with a high iron content [2].

Processing of lithium bearing aluminosilicates is based on breaking down the lithium minerals during their heating with chemicals followed by acid or water leaching of the products obtained. Li_2CO_3 or $\text{LiOH}\cdot\text{H}_2\text{O}$ are then separated from the refined leach liquors. A number of processes have been reported for lithium recovery from spodumene, petalite and lepidolite [2, 3], but only a few from zinnwaldite [4]. Zinnwaldite concentrate (1.40% Li, 0.98% Rb) processed in this study was prepared from zinnwaldite bearing wastes (0.21% Li, 0.20% Rb) originating from gravity dressing of Sn–W ores mined in the past in the Czech Republic at Krušné Hory in Činovec area.

Zinnwaldite concentrate was processed by gypsum method, which is based on heat treatment (sintering) of zinnwaldite with a mixture of CaSO_4 and $\text{Ca}(\text{OH})_2$. During sintering, most lithium is transferred from sparingly soluble zinnwaldite to water soluble compound. Lithium carbonate was precipitated from condensed purified leach liquors using K_2CO_3 as a precipitation agent. Purification of leach liquor and lithium carbonate product was based on the different solubility of Li_2CO_3 and carbonates or sulphates of the impurities present. Conditions of lithium carbonate precipitation was chosen according to its solubility in H_2O [2].

The aim of this study was:

- to determine influence of sintering conditions on the lithium conversion from zinnwaldite to a soluble compound;
- to establish effect of leaching conditions on lithium extraction to water solution;
- to examine the course of Li_2CO_3 precipitation from leach liquors with regards to its yield and purity.

This paper does not deal with rubidium extraction from the zinnwaldite concentrate prepared. In our previous work [5] it was found that processing of zinnwaldite concentrates by gypsum method provided sufficient yield of lithium whilst rubidium extraction did not exceed 25%.

EXPERIMENTAL

Material

Zinnwaldite concentrate containing on average 1.40% Li and 0.98% Rb was prepared from a representative sample of approximately 200 kg zinnwaldite waste, which was mined from the landfill in Cínovec area. The waste was subjected to dry magnetic separation followed by the separation of the fraction >0.1 mm from the magnetic product obtained. Typical content of main elements present in the concentrate was 29.14% Si, 13.80% Al, 6.62% K, 6.08% Fe, 0.49% Ca, 0.22% Na and $<0.1\%$ Cs. The lithium content in the zinnwaldite concentrate is limited because maximum lithium content in zinnwaldite mica, which occurs in Cínovec is about 1.6% Li [6]. XRD analysis, Figure 1, showed that the zinnwaldite concentrate consisted only of three phases: the dominant quartz SiO_2 , zinnwaldite

$\text{KAl(Fe,Li)·(Si}_3\text{Al)O}_{10}\text{F}_2$ and a small amount of polyolithionite $\text{KAl(Fe,Li)·(Si}_3\text{Al)O}_{10}(\text{OH})\text{F}$, a variety of zinnwaldite. The waste fraction <0.1 mm involved two dominant phases, anorthite $\text{Ca(Al}_2\text{Si}_2\text{O}_8)$ and orthoclase $\text{K(Al,Fe)Si}_3\text{O}_8$ as well as an insignificant amount of polyolithionite.

Procedure

The zinnwaldite concentrate was ground to grain size <0.1 mm, mixed with a determined amount of calcium salts and sintered in a laboratory muffle furnace at temperatures ranging from 900 to 975°C for a reaction time moving from 15 to 60 min. The weight ratio of the concentrate to CaSO_4 to Ca(OH)_2 was 6 : 4.2 : 2. Both the composition of the sintered mixtures and sintering conditions were chosen in agreement with the results of our previous studies [5, 7]. Laboratory reagents such as $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and Ca(OH)_2 were used in the process.

The pulverized sinters were water leached in a thermostated, stirred glass reaction vessel with a water cooler at the temperature range from 20 to 90°C and liquid-to-solid ratio (l:s) moving from 3:1 to 15:1. Most of leaching experiments were conducted at 90°C and l:s = 10:1. During leaching, samples were withdrawn at selected time intervals to establish the dissolution kinetics of lithium. Samples of sinters were subjected to chemical and structural analyses.

Lithium was precipitated as Li_2CO_3 at 90°C from a condensed leach liquor using K_2CO_3 as a precipitation agent. Before the condensation the most of calcium was precipitated as CaCO_3 at laboratory temperature using stoichiometric amount of K_2CO_3 . The residual calcium was practically removed during the condensation of leach liquor processed.

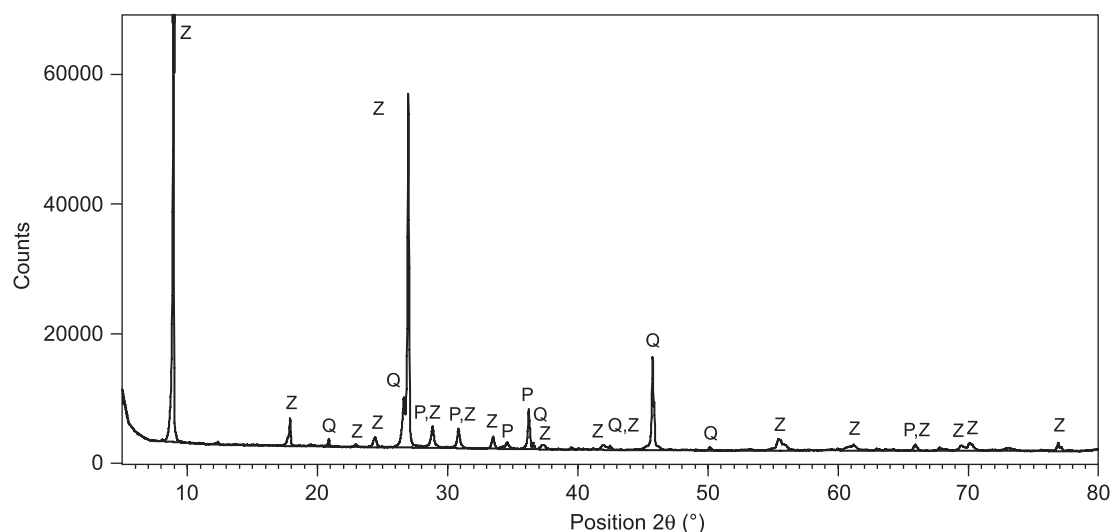


Figure 1. XRD pattern of zinnwaldite concentrate: P = Poly-lithionite, Q = Quartz, Z = Zinnwaldite.

Analysis and equipment

Solid samples were characterized by XRD analyses (diffractometer PANalytical X'Pert PRO) and XRF analyses (spectrometer ARL 9400 XP). For chemical analysis, samples were decomposed by evaporating with $\text{HF-H}_2\text{SO}_4$ to expel SiO_2 followed by dissolution of the residue in HCl . The chemical composition was then obtained using the AAS method (atomic absorption spectrometer GBC AVANTA 932 plus). Silicon was determined by a common gravimetric analysis. Concentrations of elements in leach solutions were determined by the AAS method.

RESULTS AND DISCUSSION

Influence of sintering conditions on zinnwaldite decomposition

The stage of zinnwaldite breaking down during its sintering with a mixture of CaSO_4 and Ca(OH)_2 was determined as lithium steady-state extraction in water solution. Sinters were leached in distilled water at 90°C for 30 min, $l:s$ was 10:1. The obtained dependencies are summarized in Figure 2 and 3. It is evident that almost 96% lithium extraction was achieved if sintering was performed at temperatures in the vicinity of 950°C for 60 min. Further increasing of sintering temperature and/or extending of sintering time did not result in increasing lithium extraction.

Sinters contained on average 0.65% Li and 0.50% Rb. XRD analysis indicated that during the sintering the zinnwaldite concentrate with calcium salts following new phases were formed: leachable LiKSO_4 , andradite $\text{Ca}_3\text{Fe}_2(\text{SiO}_4)_3$, anorthite $\text{Ca(Al}_2\text{Si}_2\text{O}_8)$, cuspidine $\text{Ca}_4\text{Si}_2\text{O}_7\text{F}_2$ and traces of fluorite CaF_2 . All sinters contained residual anhydrite CaSO_4 . XRD of the sinter formed at 950°C within 60 min is shown in Figure 4.

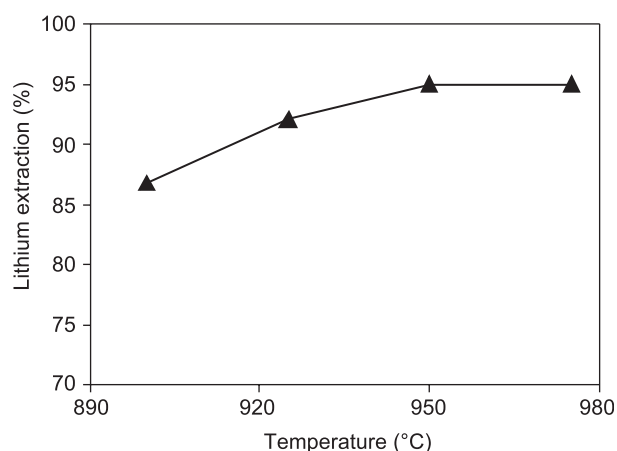


Figure 2. Effect of sintering temperature on steady-state extraction of lithium, sintering time 60 min; leaching at 90°C , $l:s = 10:1$, 30 min.

Effect of leaching conditions on lithium extraction

Effect of leaching conditions on lithium extraction was studied on sinters prepared at 950°C for 60 min. Typical time and temperature dependencies of lithium extraction established at leaching temperatures moving from 20 to 90°C and $l:s = 10:1$ is given in Figure 5. It is obvious that lithium dissolution runs very fast and it is completed practically within 10 min of commencement of leaching independent on the leaching temperature. Decreasing of leaching temperature from 90 to 20°C resulted in lowering of lithium yield about 5%. Effect of $l:s$ on lithium extraction was negligible as it is demonstrated in Figure 6.

The leach liquors which contained depending on $l:s$ from 0.60 to 2.22 g/l Li were contaminated predominantly with potassium and others impurities such as Ca, Rb, Na and traces of Al and Si.

Recovery of Li_2CO_3 from sulphate leach liquors

Lithium was recovered as lithium carbonate from sulphate leach liquor originating from leaching the sinters at 90° , $l:s = 10:1$ for 30 min. The flow sheet of this procedure is illustrated in Figure 7. Purification of leach liquor was based on the different solubility of Li_2SO_4 , CaSO_4 and CaCO_3 . Approximately 80% of Ca was removed from the original leach liquors by carbonate precipitation using stoichiometric amount of K_2CO_3 at laboratory temperature. After filtration of calcium carbonate precipitate the solution was heated to 90°C to increase the lithium concentration by evaporation of H_2O and to remove the residual Ca. Increasing of lithium concentration in solution before Li_2CO_3 precipitation at least to 9 g Li/l is necessary to achieve acceptable precipitation efficiency. After the completion of evaporation the precipitated crystals of

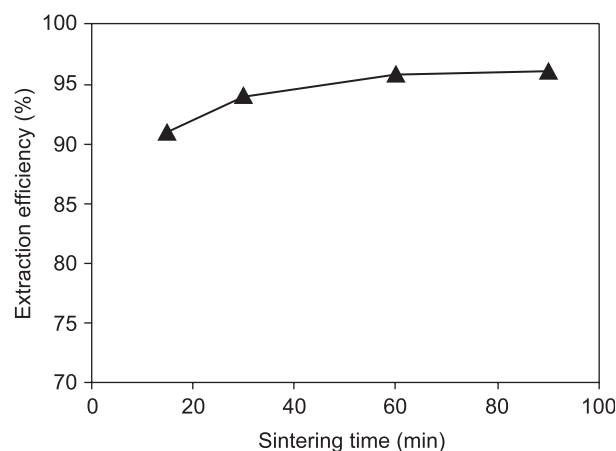


Figure 3. Effect of sintering time on steady-state extraction of lithium, sintering temperature 950°C ; leaching at 90°C , $l:s = 10:1$, 30 min.

mixed calcium and potassium sulphates were filtered off. Lithium carbonate was precipitated by addition of the stoichiometric amount of K_2CO_3 from the condensed solution at 90°C because its solubility increases with decreasing temperature, Table 1 [2]. Lithium carbonate precipitate was filtered off, water-washed and dried.

Changes of lithium and impurity concentration during processing leach liquor are described in Table 2. The total efficiency of lithium carbonate precipitation was about 73%. From the experiments performed with model solutions we found that using stoichiometric excess of K_2CO_3 during Li_2CO_3 precipitation did not result in increasing precipitation efficiency. This is probably caused by an increased solubility of Li_2CO_3 in sulphate solutions. In the continuation of this study we will focus on the recovery of lithium from mother liquors after the Li_2CO_3 precipitation.

According to XRD analysis lithium carbonate precipitate consists of zabuyelite (Li_2CO_3). Purity of precipitated and water-washed lithium carbonate products are described in Table 3. Water-washed lithium carbonate

Table 1. Solubility of Li_2CO_3 (g/100g H_2O).

Temperature ($^\circ\text{C}$)	0	20	40	60	80	100
Li_2CO_3	1.54	1.33	1.17	1.01	0.85	0.72

Table 2. Composition of processed solution

Solution	Elemental concentration (mg/l)				
	Li	Rb	K	Ca	Na
Original leach liquors	690	140	2154	201	43
Condensed leach liquors	8958	1380	32600	26	700
Mother liquor	3221	1460	55600	4	982

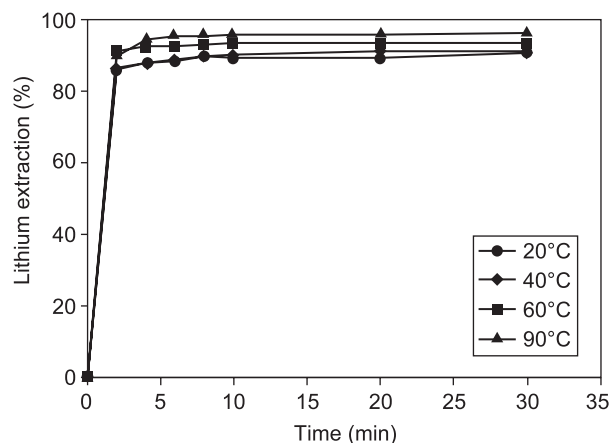


Figure 5. Leaching kinetics of lithium depending on temperature, l:s = 10:1; sintering at 950°C , 60 min.

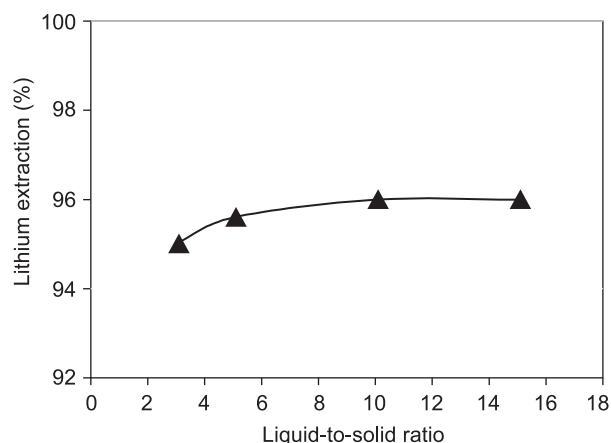


Figure 6. Effect of liquid-to-solid ratio on steady-state extraction of lithium at 90°C , k:p = 10:1, 30 min; sintering at 950°C , 60 min

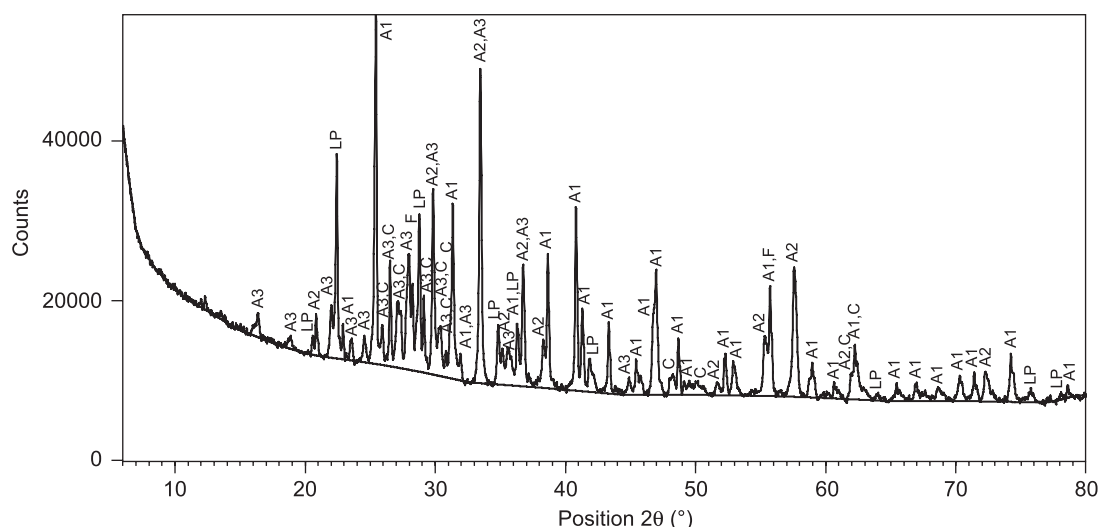


Figure 4. XRD pattern of sinter (950°C , 60 min): A1 = anhydrite, A2 = andradite, A3 = anorthite, C = cuspidine, F = fluorite, LP = lithium-potassium sulphate.

precipitate containing almost 99% Li_2CO_3 was insignificantly contaminated with K, Ca, Na and SO_4^{2-} ions. Lithium carbonate with 99% purity, which was achieved without any recrystallization is sufficient for its direct utilization for example in glass, ceramic and metallurgical industries and it is a suitable intermediate for the production of high-purity Li_2CO_3 and other lithium compounds.

CONCLUSIONS

From the results obtained it is obvious that gypsum method appears to be a promising method for separation of Li_2CO_3 from zinnwaldite wastes originated from dressing Sn–W ores. The experimental studies carried out with the zinnwaldite concentrate containing 1.40 % Li and 0.98% Rb prepared from zinnwaldite

wastes have shown that it is possible to extract almost 96% Li if zinnwaldite concentrate was processed under following conditions: sintering zinnwaldite concentrate with CaSO_4 and $\text{Ca}(\text{OH})_2$ at 950°C for 60 min followed by leaching the sinters in H_2O at 90°C, leaching time of 10 min. The ratio of concentrate to CaSO_4 to $\text{Ca}(\text{OH})_2$ was 6 : 4.2 : 2. Decreasing of the liquid-to-solid-ratio from 15:1 to 3:1 does not practically influence the lithium extraction whilst decreasing of the leaching temperature from 90°C to 20°C resulted in ca. 5% lowering of lithium extraction.

Composition of leach sulphate liquors obtained by gypsum method enables their simple and efficient purification and precipitation of relatively pure Li_2CO_3 , from which it is possible to remove most contaminants only by water-washing. That is given by a low solubility of Li_2CO_3 especially at high temperatures compared with that of alkali metal sulphates or even carbonates and precipitation of sparingly soluble CaCO_3 during the refining precipitation and condensation of leach liquors. Water-washed lithium carbonate salt with Li_2CO_3 content almost 99% was obtained from condensed leach liquors without applying any recrystallization stages. Such Li_2CO_3 is suitable for direct utilization in industry and for production of lithium compounds including high-purity Li_2CO_3 .

Table 3. Average content of impurities in Li_2CO_3 .

Li_2CO_3	Purity	Elemental concentration (mg/l)				
		K	Ca	Na	Rb	SO_4^{2-}
Precipitated	96 %	1.10	0.06	0.06	<0.1	1.86
Water washed	99 %	0.32	0.05	<0.01	<0.01	0.45

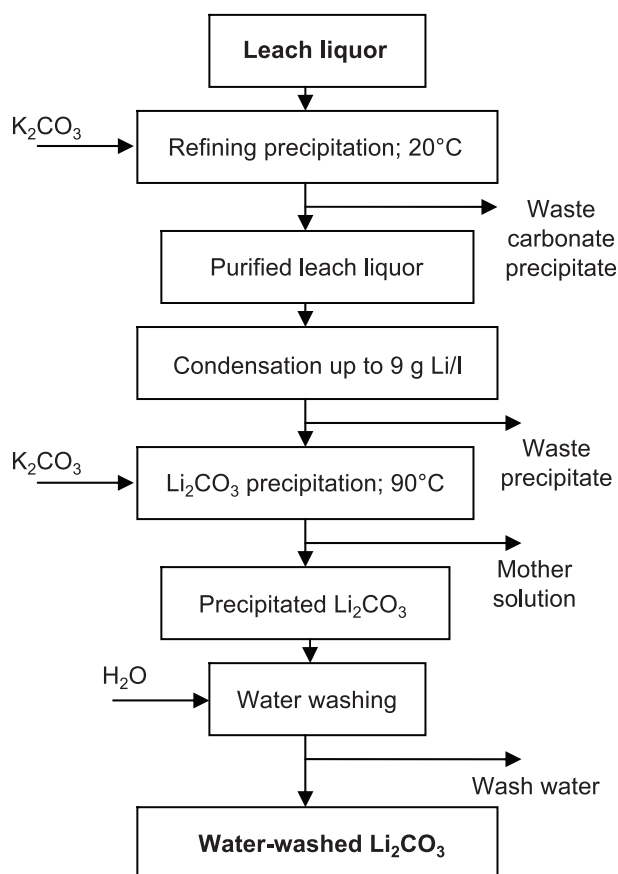


Figure 7. Flowsheet of leach liquors processing.

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