Lithium and rubidium extraction from zinnwaldite by alkali digestion process: Sintering mechanism and leaching kinetics

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ABSTRACT

Lithium and rubidium were extracted from zinnwaldite $[KLiFe^{2+}Al(AlSi_3)O_{10}(F,OH)_2]$ by (1) its sintering with and $CaCO_3$ powders and (2) water leaching the obtained sinters—the alkali digestion process. The experimental results showed that sintering proceeded in three partly overlapping stages: (1) decomposition of zinnwaldite at temperature up to 800 °C, (2) formation of new phases in the temperature range between 750 and 835 °C, and (3) formation of amorphous glassy phase at temperature above 835 °C. Densification of the reaction mixture occurred via a liquid phase sintering at temperatures above 750 °C and diffusion of calcium, potassium, silicon and rubidium resulted in the formation of the new phases. The decomposition of zinnwaldite and the formation of the new phases increased extraction of lithium and rubidium. The formation of glassy phase probably hindered extraction of lithium but did not affect that of rubidium because of its outward diffusion to sinter's surface. The optimal extraction efficiencies of 84% of lithium and 91% of rubidium were achieved at sintering temperature of 825 °C and leaching temperature of 95 °C. The good fit of the hyperbolic and uniform reaction models to the leaching data indicated that dissolution of lithium and rubidium proceeded through two stages. Application of the shrinking core model showed that dissolution of lithium was controlled by diffusion. The formation of a layer of $Ca(OH)_2$ on surface of sinters apparently slowed and then terminated dissolution of lithium and rubidium in the later stage of leaching.

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1. Introduction

As the lightest metal in nature with the unique electrochemical properties, lithium is becoming the key material in manufacturing of primary and secondary batteries used in various portable devices and hybrid/electric vehicles (Garret, 2004; Harben, 2002; Thompson, 2011). The annual global demand, measured as lithium carbonate equivalent, is expected to increase from current 100,000 to 160,000 Mt in 2015, with batteries representing about 40,000 Mt of the perceived growth (Hykawy, 2010). Other main applications of lithium include aluminum refining; glass and ceramics production; synthesis of rubber, plastics, pharmaceuticals and organic compounds; and manufacture of specialty greases and desiccants. Rubidium has been available commercially as a by-product of lithium production from minerals (Thompson, 2011). The main use of rubidium is in atomic clocks for global positioning

satellites, magneto-optic modulators, solid-state lasers, phosphors, and glass manufacturing. Rubidium-based chemicals are also used as catalysts or to activate catalysts of various types. Total world demand for rubidium was estimated at about 2 to 4 tones per year but increases in lithium exploration may create new supplies leading to expanded commercial applications (Thompson, 2011; Wagner, 2006).

The main commercially viable sources of lithium are natural brines with a high lithium chloride content and the pegmatitic minerals such as spodumene, amblygonite, petalite and lepidolite (Garret, 2004; Ebensperger et al., 2005; Wietelmann and Bauer, 2008). Given the mining, processing and energy requirements, lithium ores contribute only 15% of current lithium production (Roskill Information Services (2009)). As world lithium demand, driven primarily by increased production of batteries, is expected to grow about two fold in the next 10 years and may exceed supply by 2017, minerals get more attention as an alternative source of lithium to offset the deficit (Chen et al., 2011; Dundeen Securities, 2009; McNulty and Khaykin, 2009; Sitando and Crouse, 2012; Yan et al., 2012). Zinnwaldite $[KLiFe^{2+}Al(AlSi_3)O_{10}(F,OH)_2]$, a variety of lepidolite with high iron content, is one of the minerals of interest that can be exploited to obtain both lithium

and rubidium (Jandova et al., 2010; Jandova and Vu, 2008; Siame and Pascoe, 2011).

Lithium is extracted from minerals by high-temperature digestion with acid or alkali, or by ion-exchange processes using salt, followed by acid or water leaching. Rubidium is obtained from a solution containing mixed alkali metal carbonates, a by-product of the production of lithium from lepidolite, by precipitation followed by pyrolysis or thermal oxidation (Habashi, 1997; Kamienski et al., 2005; Wietelmann and Bauer, 2008). The alkali digestion process, originally developed for spodumene and pentalite, was investigated to process zinnwaldite in recent research studies. Our works have shown that about 90% of lithium and rubidium was extracted by sintering a zinnwaldite concentrate with calcium carbonate (weight ratio 1:5) at 825 °C for 60 min and water-leaching the pulverized sinter (liquid to solid ratio 10:1) at 90 °C for 30 min (Jandova and Vu, 2008; Jandova et al., 2009, 2010). The concentrate was obtained by magnetic classification of lithium-rich sand, a by-product of Sn–W ores processing at Cinovec, Czech Republic. In the contrary, Siame and Pascoe (2011) reported that under the same conditions less than 1% of lithium was recovered from a zinnwaldite concentrate obtained from micas-rich sand, a by-product from china clay production in South–West England. Siame and Pascoe (2011) suggested that formation of eucryptite [LiAlSiO$_4$] and its increased crystallinity with rising sintering temperature might cause the decrease in lithium extraction. But according to Habashi (1997) the formation of an amorphous glassy clinker at high temperature severely hinders extraction of lithium from minerals by the alkali digestion method. In the above mentioned works the mechanism of sintering zinnwaldite with calcium carbonate still remains unclear and the leaching behavior of lithium and rubidium from sinters was not fully studied. The present study was designed to provide an insight into the sintering process and to investigate the leaching kinetics using mathematical models.

2. Experimental

A zinnwaldite concentrate containing 1.29% of Li and 0.94% of Rb was prepared by dry magnetic separation of the lithium-rich sand, the by-product after Sn–W ore mining in the Czech Republic. According to the results of XRD analysis, the concentrate consisted of two main phases: dominant zinnwaldite KLiFe^{2+}Al(AlSi$_3$)O$_{10}$(F,OH)$_2$ and minor quartz SiO$_2$. The concentrate was pulverized in a ball mill for 2 min and mixed with CaCO$_3$ of technical grade at a weight ratio of 1:5. The results of the particle size analysis showed that the size of the pulverized zinnwaldite concentrate varies between 1 and 100 μm with a mean diameter of 30 μm. The mixture was sintered in a muffle furnace at different temperatures for 60 min. The sinter was milled in the ball mill for 1 min and subjected to water leaching. The leaching tests were performed at temperatures ranging from 26 to 95 °C, liquid to solid ratio (l:s) 10:1, stirrer speed of 400 rpm, and leaching time of up to 240 min. The influence of sintering temperature on extraction of lithium and rubidium was determined by leaching sinters at 95 °C for 60 min. After leaching tests finished, the leach residues were separated by filtration, water-washed and dried at laboratory temperature. The lithium and rubidium extraction efficiencies were calculated from the total amount of Li or Rb released into leaching liquor and washing water.

The leaching programme was followed by sampling of the solution at a chosen time interval and measuring Li and Rb concentrations by a GBC atomic absorption spectrophotometer (model GBC 932 plus). Mineralogical analysis was carried out by X-ray diffractometer PANalytical's X'Pert PRO. SEM-EDX analysis was carried out using Hitachi S4700 Scanning Electron Microscope or Vega 3 Tescan Scanning Electron Microscope. Differential thermal analysis (DTA) was performed by TA Setaram, model Setsys Evolution in a flowing in argon atmosphere at a heating rate of 10 °C/min. The thermobalance was connected to a mass spectrometer Pfeiffer Vakuum, model OmniStar. The infrared spectra of zinnwaldite and sinters were recorded on FTIR spectrometer

Nicolet 6700 (Thermo Fisher Scientific, USA). The KBr pressed-disc technique was used for routine scanning of the spectra.

3. Results and discussion

3.1. Sintering process

A similar sharp increase in extraction of both lithium and rubidium was found when sintering temperatures increased from 750 °C to 800 °C, indicating a rapid decomposition of zinnwaldite in this temperature interval (Fig. 1). Lithium extraction efficiency remained almost constant in the temperature interval from 810 °C to 835 °C, with the maximum of 84% at about 825 °C, and decreased rapidly at temperature above 835 °C. In contrast, extraction efficiency of rubidium increased slightly with increased temperature and leveled off at 95% from 850 °C. Different courses of extraction of lithium and rubidium indicated their different behavior during sintering.

X-ray powder pattern analysis of sinters shows a decrease in crystallinity of zinnwaldite with increasing sintering temperatures and a shift of diffraction peaks of zinnwaldite [KLiFe^{2+}Al(AlSi$_3$)O$_{10}$(F,OH)$_2$] toward those of polylithionite [KLi$_2$AlSi$_4$O$_{10}$(F,OH)$_2$] at temperatures higher than 750 °C (Fig. 2a–b). At 800 °C, diffraction peaks of zinnwaldite and polylithionite disappeared, indicating their complete decomposition; the presence of hematite Fe$_2$O$_3$ was detected; and the formation of mainly calcium carbonate-bearing minerals was observed. Most diffraction peaks, except those of lime—CaO and spurrite—Ca$_5$(SiO$_4$)$_2$CO$_3$, decreased in intensity with further increase in temperature and disappeared at temperature higher than 835 °C, suggesting the formation of amorphous glassy phase (Fig. 2b–c). Lithium and rubidium-bearing phases were not observed in diffraction patterns, probably because their content in the sinters (~0.2%) is below the detection limit of XRD technique. Rubidium may have substituted potassium in KCaCO$_3$F because of their similarities in chemical and physical properties.

The TG-DTA curves of zinnwaldite show two peaks: an exotherm in the temperature range 450–825 °C, followed by a sharp and narrow endotherm with the maximum around 910 °C (Fig. 3). The MS pattern shows that the H$_2$O evolution took place in two minor steps at the temperature ranges of 210 – 300 °C and 400 – 700 °C, and followed a larger step around 930 °C. These three steps of H$_2$O evolution were characterized by a weight loss of about 0.20, 0.25 and 0.75 wt%. The exothermic peak can be contributed to the formation of Fe$_2$O$_3$ by oxidation of divalent iron with oxygen released from dehydroxylation according to the following reaction: $-OH^- + -OH^- = H_2O + O^{2-}$ (Gallagher, 2003).
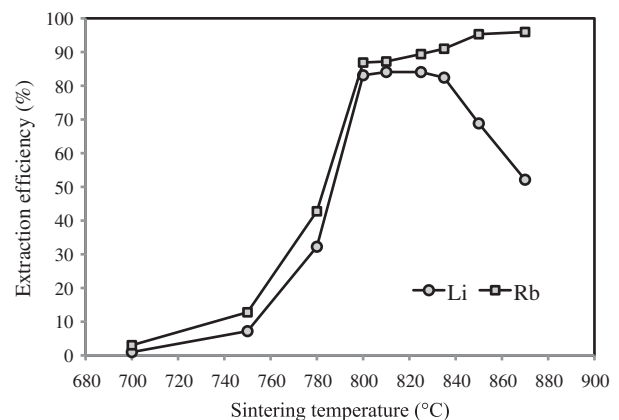

Fig. 1. Influence of sintering temperature on extraction efficiencies of Li and Rb: zinnwaldite: CaCO$_3$ = 1:5, sintering time 60 min, l:s = 10:1, leaching temperature 95 °C, leaching time 60 min.