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Technical note

Study of the relationship between zinnwaldite chemical composition and magnetic susceptibility

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ABSTRACT

This study investigates the relationship between chemical analyses and magnetic susceptibility of zinnwaldite through magnetic separation of various size fractions. Statistical analyses were used to increase information about magnetic properties of this mineral as a future source of lithium. Statistical modeling indicated that magnetic susceptibility (as a main factor of magnetic separation) accurately can be predicted based on cations content of zinnwaldite. However the size of particles had a significant effect on magnetic susceptibility. The small difference between the estimated and measured values for the non-linear relationship of this prediction (less than 1 (10^{-8} m^3/kg)) shows that these accurate theoretical techniques can be also applied to estimate magnetic properties of zinnwaldite in other resources, and in-situ analysis.

1. Introduction

Lithium as the lightest metal in nature with its unique electrochemical properties makes it ideal for use in batteries (lithium battery production represents 70% of the total rechargeable battery market (USGS, 2010; Siame and Pascoe, 2011). It is also used in the production of aluminium refining, preparation of greases, rubbers, alloys, glass and ceramics production, and pharmaceuticals (Garret, 2004; Harben, 2002).

Some estimation indicated that the demand for lithium till 2016 is expected to increase by ~60% (Jandová et al., 2010; Thompson, 2011).

A wide variety of lithium containing natural minerals is known and just a few of these have been commercially extracted (Aluminosilicates; spodumene, petalite, lepidolite) (Wietelmann and Bauer, 2003). Zinnwaldite ($(Li, K, Al, Fe)_3(Al, Si)_4O_{10}(F, OH)_2$ (Li_2O: 3.30–7.74%)) is a silicate mineral in the mica group that can be exploited as a source of lithium in the near future (Jandová and Vu, 2008; Jandová et al., 2010; Siame and Pascoe, 2011). The recommended processing for zinnwaldite to prepare a pre-concentration mostly involves comminution and after that physical separation techniques such as gravity concentration, or magnetic separation The high iron content in this mineral makes it suitable for magnetic separation techniques (Hawkes et al., 1987; Bale and May, 1989; Amarante et al., 1999; Kondás and Jandová, 2006; Jandová et al., 2010; Siame and Pascoe, 2011).

In magnetic separation, the difference in behaviour of particles in magnetic fields is based on the magnetic susceptibility (MS – χ). The MS of minerals is a valuable parameter to evaluate the potential of magnetic separation. All minerals have a MS value which is measurable by sensitive techniques (McAndrew, 1957). The variation in mineral composition and grain-size has an important influence on MS (Vernon, 1961; Stacey and Banerjee, 1974; Dunlop, 1990; Dahlin and Rule, 1993; Hunt et al., 1995). It has long been known that the MS of a single mineral can be determined by its cations content (Vernon, 1961; Dahlin and Rule, 1993; Li et al., 2014). Therefore it is possible to calculate approximate susceptibilities from the chemical analyses to determine if magnetic separation is a viable processing option (Vernon, 1961; Silberberg, 1998).

In this study, statistical methods (Pearson correlation, linear and non-linear multivariable regressions) were used to study the possible relationship between chemical analyses and magnetic susceptibility of zinnwaldite (ZIN) (as a source of lithium) through magnetic separation. Various size fractions were analysed to better understand the possible relationship. To our knowledge, this is the first study that explains the statistical relationship between zinnwaldite and magnetic susceptibility as a factor of magnetic separation.

2. Experimental method

For the mineralogical investigation, samples were collected from an old underground mine (Zinnwald/Cinovec deposit) located

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in the Ore Mountains on the German/Czech boarder. The ore comprises of 67 wt.% quartz, 20 wt.% zinnwaldite, 8 wt.% topaz, 3 wt.% muscovite and 2 wt.% other minor minerals (Leißner et al., 2012). To prepare the ZIN concentrate to 100% passing 1.0 mm, the bulk sample was crushed and milled in a jaw crusher, gyratory crusher, cone crusher and then pin mill. The pin mill product was to achieve the following sized fractions −0.1, +0.1–0.2, + 0.2–0.315, +0.315–0.5 and +0.5–0.8 mm. Each size fractions was then progressively separated into different magnetic susceptibility classes using an isodynamic magnetic separator. The isodynamic magnetic separator was built in the 1960s in the former German Democratic Republic, a principle copy of the Frantz-type separator (because of Germany sanction). The magnetic separation for each size fraction was started with 1.05 A to split the majority of liberated gangue phases, and then the product was subjected to the next step of separation. The current strength of the magnetic separator was varied in steps of 0.05 ampere from 1.05 to 0.8 A. The procedure was stopped at a current of 0.8 A to have the minimum mass needed for chemical analysis and susceptibility measurements. Since magnetic separations were performed in currents over 0.8 A, MS was not calculated based on Frantz isodynamic separator equation ($\chi = (20\ \sin\alpha)/I\text{\^{}}2 \cdot 4\pi$; applies only to electromagnet currents of less than 0.8 A (McAndrew, 1957)). The magnetic susceptibility was measured by the Johnson Matthey magnetic susceptibility balance MSB MK II auto. The chemical analysis of product for each size fraction was done by ICP–OES with a Thermo scientific iCAPTM 6300 Duo (Table 1).

3. Results and discussion

The first determination of the bulk magnetic susceptibility of micas was reported in 1960s (Syono, 1960; Hood and Custer, 1967). Rochette (1987) studied the relationship between the cations content of micas with MS, which led to empirical and theoretical formulas that correlate the magnetic cation content with the bulk MS (Rochette, 1987).

Pearson correlation (inter-correlation) is a measure of linear association between two variables. Pearson values range from −1 to 1. The sign of the correlation indicates the direction of the relationship, and its absolute value indicates the strength, with larger absolute values indicating stronger relationships. A negative value for the correlation implies a negative or inverse association, where a positive value means a positive association. Table 2 shows inter-correlation between variables (cations and current) with MS of ZIN. Results indicate there was a strong relationship between Fe and Li with MS, and a strong negative inter-correlation with the current (−0.86). These results were in good agreement with other investigations which indicated that the MS of minerals increases with increasing Fe content, and decreases with increasing the current strength (Fraas, 1964; Dahlin and Rule, 1993; Cavanough et al., 2006).

In addition, the linear and non-linear enter-remove regression methods show that the MS of ZIN is predictable based on cations content and the current for each size classification (Table 3). As evident in Table 3, there is a cubic relationship between the current strength and MS for each size class, and a linear (multivariable) relation between cations and MS. Variations in the measured MS for each constant current (0.8–1.05 A) demonstrated that the current strength is not a suitable MS predictor. The higher correlation

Table 2
Inter-correlation (Pearson correlation) between zinnwaldite cations content, the strength current and magnetic susceptibility.

Variables	Fe	Li	K	Al	Current
Susceptibility	0.76	0.58	0.49	0.23	−0.86

Table 1
Chemical analyses of zinnwaldite, with different magnetic susceptibility for the various size fractions.

Size class (mm)	Current (A)	%Li	%Fe	%K	%Al	χ (10^{-8} m^3/kg)
−0.1	0.8	1.33	8.49	8.19	11.77	28.11
	0.85	1.26	8.06	7.98	11.64	27.30
	0.9	1.14	7.35	7.40	10.70	27.06
	0.95	1.05	6.95	7.29	11.23	26.39
	1.0	0.93	6.20	6.79	10.80	25.59
	1.05	0.60	4.42	5.33	9.86	20.73
+0.1–0.2	0.8	1.47	8.51	8.03	11.07	26.74
	0.85	1.39	8.14	8.05	11.42	25.36
	0.9	1.27	7.50	7.89	11.81	24.23
	0.95	1.03	6.28	7.08	11.01	22.87
	1.0	0.87	5.54	6.53	10.64	21.63
	1.05	0.42	3.29	4.52	9.26	17.17
+0.2–0.315	0.8	1.48	8.34	7.68	10.58	26.83
	0.85	1.44	8.08	7.74	10.78	25.71
	0.9	1.32	7.55	7.59	11.06	24.27
	0.95	1.14	6.66	7.15	10.87	23.04
	1.0	0.91	5.46	6.18	9.81	21.03
	1.05	0.54	3.66	4.41	8.65	17.05
+0.315–0.5	0.8	1.44	8.44	7.48	10.01	26.97
	0.85	1.41	8.33	7.50	9.99	25.73
	0.9	1.37	8.14	7.48	10.16	25.48
	0.95	1.26	7.43	7.20	9.66	23.57
	1.0	1.08	6.52	6.45	8.51	22.06
	1.05	0.77	4.91	5.06	8.44	17.29
+0.5–0.8	0.8	1.43	7.93	7.69	9.88	26.04
	0.85	1.39	7.61	7.73	9.90	24.98
	0.9	1.36	7.50	7.72	10.29	23.41
	0.95	1.18	6.65	6.89	9.52	22.02
	1.0	1.13	6.40	6.83	9.75	20.86
	1.05	0.74	4.51	4.99	8.16	15.27