THE INFLUENCE OF MAGNETIC SEPARATION ON SELECTED MECHANICAL - PHYSICAL PROPERTIES OF LITHIUM MICA

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Abstract

Lithium is a commodity undergoing through significant expansion recently. At present, lithium accumulators and batteries rank among very promising means for long-term accumulation of electricity. The main objective of this study was to obtain this metallic element from the feedstock from the locality Cínovec in the Ore Mountains. From the feedstock, we also managed to obtain rubidium and cesium. For materials obtained, detailed mechanical and physical characteristics was carried out, which includes e.g. friction parameters, material compressibility. In the procedural part, magnetic separation was applied to obtain a good quality concentrate with the content of Li, Rb, and Cs. Subsequently, it was compared how mechanical and physical characteristics of the resulting products changed compared to each other and to the original material. It is clear from the first results that the choice of the process of magnetic separation to obtain a high-quality concentrate was very successful. The concentrates contained up to 1.4 wt.% of Li, 0.9 wt.% of Rb, and 0.02 wt.% of Cs. Moreover, after separation, the angle of external friction of the resulting concentrate was reduced to a value of approximately around 18° in all samples. The compression index of the concentrate was twice as high as in the other measured samples, which corresponds to an average susceptibility of the material to compression.

Keywords: Lithium, magnetic separation, angle of external friction, compressibility

1. INTRODUCTION

Lithium belongs among the lightest metals from the alkaline metals series. Its clark content is estimated at 32 ppm and it belongs among 25 most plentiful elements within the earth crust [1]. At present, it is mostly used for ionic lithic charging batteries (LIBs). Such usage is caused by its very high density of energy depending on its weight and electrochemical potential (3.045 V). Consumption of lithium for production of LIBs ranges around 22 % from the overall obtained lithium. In 2020, the anticipated increase of lithium usage for LIBs production should reach around 40 %. Today, apart from batteries, lithium is also used for production of glass and ceramics, oils, then in metallurgical industry or in chemical and pharmaceutical area. It is also obvious that the demand for lithium continues to grow due to its application in nuclear and strategical areas [2]. In metallurgy, the lithium is used as a clear element for removing of undesirable gases within the production of non-ferrous metals [3]. Salt ponds, clays or minerals are the main sources of lithium. The greatest amount of lithium in minerals can be found in pegmatite, spodumen or petalite. Furthermore it occurs in lepidolite, amblygonite, zinnwaldite, eventually in eucryptite. A theoretical content of lithium within these minerals ranges around 3 - 5.5 wt.%. Most of mineral material deposits, in which lithic minerals occur, contain 0.5 - 2 wt.% Li. In general, clay minerals contain 0.3 - 0.6 wt.% Li. Zinnwaldite is an unclear form of lepidolite with a higher content of iron and fluor. A chemical formula of this mineral is as follows: $KLiFeAl_2Si_3O_{10}F_2$. Among supporting elements contained in zinnwaldite belong rubidium, cesium but also beryllium, tin or tantalum [2]. Rubidium and cesium also belong among alkali metals. Their clark content in earth crust is 1.5 $.10^{-4}$ wt.% (Rb) and 3.7 $.10^{-6}$ wt.% (Cs). The main usage of rubidium is in atomic clock for global navigation systems, semiconductor lasers and luminophores. Rubidium-based chemical substances are also used as catalyzers. Cesium has its practical importance in electrotechnics. As the only metal it radiates electrons within illumination by light of all colours and therefore it is suitable for a construction of valves and photocells. Cesium-based salts are used in chemistry (catalyzers, petroleum desulphurization), metallurgy (gases absorption) and also within medicine (treatment by radioisotope ^{137}Cs) [1, 4].

2. EXPERIMENTS AND METHODS

2.1. Materials

The material came from the locality Cínovec in the Ore Mountains in the Czech Republic. A part of the material came from the structural well CS-1 and from the tailings pond originating in the ore adjustment in the past. All together 66 samples were picked within the well. They were picked from individual intervals that were consolidated according to the determinated petrographical types and thus they also represent technological types. Types and their labelling were detached as AGV (alternated granites of the outter cupola) and GR (greisens and greisens granites). Selected AGV samples were characterized by SEM photos (SE detector). The materials from the tailings pond were taken manually from digged sondes 1 m deep. The sondes were irregularly distributed over the tailings pond area. Individual partial samples were mixed and an average sample was obtained by means of quartation. A limit for a technological test sample was a content of Li above 700 ppm, which was reached by 50 samples.

2.2. Magnetic separation

Magnetic separation is used for the concentration of magnetic materials and for the removal of magnetizable particles from fluid streams. The separation is achieved by passing the suspensions or the mixtures of particles through a non-homogeneous magnetic field. This process leads to preferential retention or deflection of the magnetizable particles. The same objective is often achieved in a very different fashion, the common features being a competition between a wide spectrum of forces of various magnitudes and ranges. In magnetic separation the separating (differentiating) external force is the magnetic force. The separation of one material from another or the removal of magnetizable particles from streams depends upon their motion in response to the magnetic force and to other competing external forces, namely gravitational, inertial, hydrodynamic and centrifugal forces. [5]

2.3. Wall friction angle and compressibility

The wall friction and compressibility of the finer powders were measured on an FT4 Powder Rheometer and coarser samples were tested by a ring shear tester Schulze (R01, Dietmar Schulze, Germany).

The FT4 Powder Rheometer rotary shear module for measuring friction parameters consists of a vessel containing the sample powder and a head with a disk to cause normal and shear stress [6]. The blades of the stainless steel head sink into the mass powder and the front face of the head starts to apply normal stress to the surface of the powder bed. The stainless head moves downwards until sufficient and stable pressure is applied between the contact material and the powder bed. Then the head starts to rotate slowly and thus cause shear stress within the bulk mass. The shear plane is formed just below the end of the blades. Since the powder bed prevents rotation of the stainless steel head, shear stress in the measuring plane increases until a slippage occurs. Then, the maximum value of transferred shear stress is recorded. The wall friction angle is then an angle enclosed by a horizontal axis and a join of the onset with a point within a limiting curve of surpassing the shear stress. Value of the wall friction angle is influenced by surface roughness of the contact material (original material, abrasion, corrosion), temperature, humidity and time of rest contact. The principle of the wall friction angle measurement by the ring shear tester Schulze is similar to the FT4 Powder Rheometer, however, there are some slight constructive differences within the device.

Compressibility is measured as the change in volume or density, respectively, depending on a normal load. The data obtained are quantified by expressing the percentage compressibility for a normal load of 15 kPa applied by the module, which is a part of the FT4 Powder Rheometer [5]. Changes in volume are evaluated by the compression index (C). The compression index (%) is calculated as a ratio of compressive density (at 15 kPa) and density (unloaded).

3. RESULTS AND DISCUSSION

3.1. Magnetic separation

The laboratory experiment was carried out with an inductive magnetic separator with permanent magnets with magnetic induction of 0.84 T. The experiment was done in a dry environment and the speed of supply material feed was 100 g in a minute. Conditions for magnetic separation were identical for all experiments. **Table 1** shows individual returns of extract and magnetic separation waste. **Tables 2**, **3** and **4** show individual yields of useful components or waste into concentrate and effectivity of the process.

Table 1 Experiment results - magnetic separation of materials *AGV, GR, Tailings pond* (wt.%)

Product	*AGV*				*GR*				*Tailings pond*			
	A	Li	Rb	Cs	A	Li	Rb	Cs	A	Li	Rb	Cs
Concentrate	10.99	**1.289**	0.893	0.031	25.20	**1.459**	**0.973**	**0.035**	22.18	0.695	0.242	0.011
Waste	89.01	0.056	0.092	0.001	74.80	0.063	0.057	0.001	77.82	0.041	0.069	0.001
Feed	100.0	0.192	0.181	0.004	100.0	0.415	0.288	0.009	100.0	0.187	0.107	0.005
Note: A - return (%)												

Table 2 Experiment results - magnetic separation of materials *AGV*

Sample *AGV*	Return	Li			Rb			Cs		
	(%)	B	C	D	B	C	D	B	C	D
Concentrate	10.99	**73.84**	10.87	62.97	**54.47**	10.91	43.56	79.28	10.99	**68.29**
Waste	89.01	26.16	89.13	-62.97	45.53	89.09	-43.56	20.72	89.01	-68.29
Feed	100.0	100.0	100.0	0.00	100.0	100.0	0.00	100.0	100.0	0.00
Note: B - yield metal into concentrate (%); C - yield waste into concentrate (%); D - efficiency (%)										

Table 3 Experiment results - magnetic separation of materials *GR*

Sample *GR*	Return	Li			Rb			Cs		
	(%)	B	C	D	B	C	D	B	C	D
Concentrate	25.20	**88.67**	24.94	63.73	**85.12**	25.03	60.09	**92.18**	25.20	66.98
Waste	74.80	11.32	75.06	-63.73	14.88	74.87	-60.09	7.82	74.80	-66.98
Feed	100.0	100.0	100.0	0.00	100.0	100.0	0.00	100.0	100.0	0.00
Note: B - yield metal into concentrate (%); C - yield waste into concentrate (%); D - efficiency (%)										

Table 4 Results of experiment - magnetic separation of materials *Tailings pond*

Sample *GR*	Return (%)	Li			Rb			Cs		
		B	C	D	B	C	D	B	C	D
Concentrate	22.18	**82.85**	22.06	60.78	49.99	55.15	27.84	75.82	22.18	53.64
Waste	77.82	17.15	77.94	-60.78	50.01	77.85	-27.84	24.18	77.82	-53.64
Feed	100.0	100.0	100.0	0.00	100.0	100.0	0.00	100.0	100.0	0.00
Note: B - yield metal into concentrate (%); C - yield waste into concentrate (%); D - efficiency (%)										

From the reached results shown in the tables it is obvious that the magnetic separation of the monitored materials proceeds successfully. The reached yields of Li into concentrate vary from 73 to 89 % with the content of Li in the concentrate around 1.4 %. The best results were recorded for a sample with GR mark. As far as Rb is concerned, the results are rather worse. The reached yields of Rb into concentrate have wide dispersion. Again, the best results were reached within the sample *GR*. The greatest problems with Cs are low contents of metal in modification concentrate. It is already caused by a low value of metal in the supply material. Repeatedly, the best results were reached within the *GR* sample. The reached yields of separation mostly range between 60 and 68 % which is not very satisfying from the technological point of view. The low yields of the experiments are caused by a high content of reactive additions in the concentrate. An introduction of a refined and subsequent control magnetic separation would help to increase the yield. Due to these steps it would be possible to reach clearance of the concentrate from the reactive components. Furthermore, the escaped utility metals would be retained.

3.2. Wall friction angle and compressibility

The measured results of chosen measured mechanical physical quantities from samples in particular phases of the modification were recorded in **Table 5** which depicts results of wall friction angles as well as powder density of these minerals.

Table 5 Bulk properties for all powder samples

Material	Processing level	Wall friction angle (°)	Powder density (g.cm^{-3})
Tailings pond	**Original sample**	21.40	1.49
	Feed	20.45	1.39
	Concentrate	18.85	1.55
	Waste	24.35	1.38
GR	**Original sample**	16.75	1.68
	Feed	20.15	1.38
	Concentrate	18.35	1.43
	Waste	26.30	1.88
AGV	**Original sample**	18.50	1.68
	Feed	20.60	1.38
	Concentrate	18.70	1.56
	Waste	26.25	2.12

The process of the magnetic separation led to decrease of the wall friction angle by 9 % in comparison with feed-concentrate samples. On the contrary, during the comparison of feed-waste samples, the wall friction value rapidly increased up to 30 %. A comparison of the result values of the final samples, i.e. result concentrates, show that samples (AGV, GR, Tailings pond) have similar features in connection with the wall friction angle and the powder density which can significantly facilitate transport, respectively allow technologically carefree transport of various kinds of concentrates within same transport facilities. The magnetic separation is thus a suitable technological modification for the particular material. Differences in wall friction ratio (calculated as $f = \mathrm{tg}(\varphi)$, where φ is wall friction angle) of individual concentrate samples vary by 0.01 at maximum, which is an insignificant value during projection of traffic facilities.

The decrease of wall friction angle within concentrates and, conversely, its increase within waste samples is also given by the structure of the tested samples morphology before and after the modification by the magnetic separation. At the Feed sample (**Figure 1**) we can see a representation of silica, mica, potassium feldspar and sodium feldspar. In the concentrate with a lower wall friction angle we can see a larger representation of lithic mica that is distinguished by its bedded structure, cleavage plane and scales (up to 40 %). The waste contains mostly sharp silica (63 %) which can also have ingrown parts of lithic silica that are not separated by the magnetic separation (**Figure 1**).

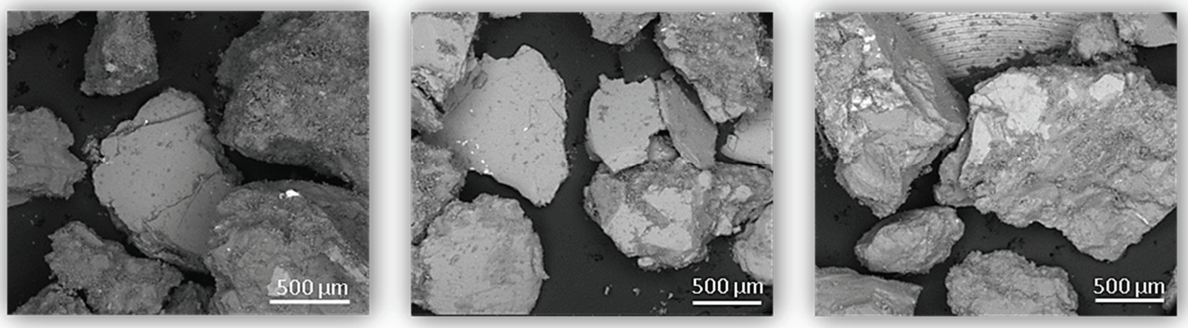

Figure 1 SEM a photograph of AGV sample. (Left - feed, middle - concentrate, right - waste)

Another monitored parameter influenced by the process of magnetic separation is compressibility.

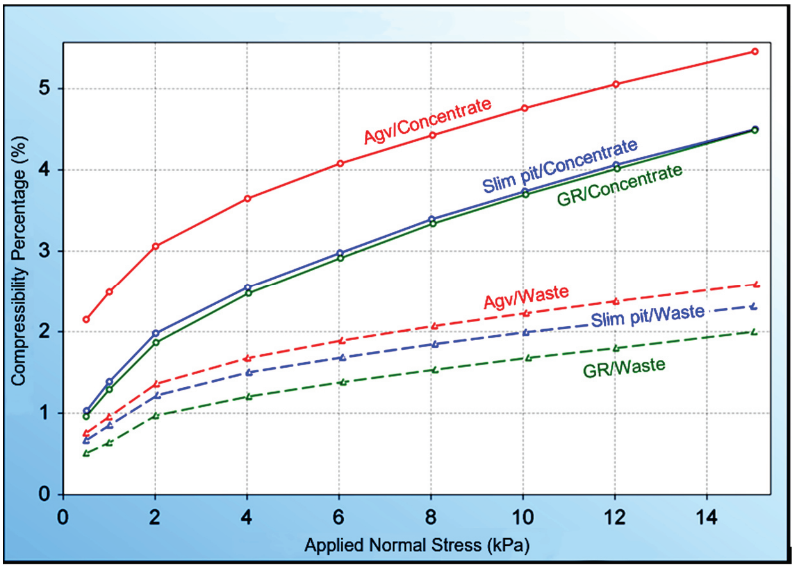

Figure 2 Compressibility tests for samples after magnetic separation

As far as powders are concerned, this feature is influenced by many factors such as distribution and a shape of elements, cohesion and other parameters. Compressibility influences action of the material in its following processing, e.g. in transport, storage in chambers or within disinfecting processes. The results from the course of compressibility measurement show a change of this material parameter due to magnetic separation (**Figure 2**). All samples containing magnetic elements, i. e. a concentrate, show middle sensitivity to compressibility unlike waste samples that have lower compressibility. Such conclusion is proved by such quantified values of C compression index that is approximately twice as high in case of concentrate samples. Their middle compressibility corresponds with an average predisposition to compression.

4. CONCLUSION

The article represents possibilities of obtaining *cinvaldite* mineral as a source of lithium, rubidium and cesium from the locality based in the Ore Mountains, the village of Cínovec. In particular it is a primary deposit (a well: CS-1) and a tailings pond that was growing during the mining in the last century. High quality concentrates with high content of utility metals were obtained by means of magnetic separation. The works were carried out in a dry mode of magnetic separation with a middle efficiency (65 % on average). The best results were reached within the material marked as *GR*, AGV. Within samples from the tailings pond the results were very variable. Within the *GR* sample there was an excellent yield of the utility component (over 85 %). Furthermore, the influence of magnetic separation process on mechanical physical quantities of such processed materials was also investigated. The measured data imply improvement of studied features for concentrates. On contrary, there is a significant aggravation as far as waste is concerned. The wall friction angle was lower after magnetic separation for concentrates. It will enable transport of various concentrates in a singular conveying device without any processional problems. A future plan includes enlargement of magnetic separation process to an aqueous route, eventually further application of a flotation regime in order to conform to contemporary operational conditions in practise.

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REFERENCES

[1] JIRÁSEK, J., SIVEK, M., LÁZNIČKA, P. *Ložiska nerostů*. Ostrava: Anagram, 2010. ISBN 978-80-7342-206-6.

[2] MESHRAM, P., PANDEY, B. D., MANKHAND, T. R. Extraction of lithium from primary and secondary sources by pre-treatment, leaching and separation: A comprehensive review. *Hydrometallurgy*, 2014, vol. 150, pp. 192-208. DOI: 10.1016/j.hydromet.2014.10.012. http://linkinghub.elsevier.com/retrieve/pii/S0304386X14002278.

[3] SAMKOVÁ, R. Recovering lithium mica from the waste after mining Sn-W ores through the use of flotation. *GeoScience Engineering,* 2009, no. 1, pp. 33-37.

[4] VU, H., J. BERNARDI, J. JANDOVÁ, L. VACULÍKOVÁ, GOLIÁŠ, V. Lithium and rubidium extraction from zinnwaldite by alkali digestion process: Sintering mechanism and leaching kinetics. *International Journal of Mineral Processing*, 2013, vol. 123, pp. 9-17. DOI: 10.1016/j.minpro.2013.04.014. ISSN 0301-7516, http://linkinghub.elsevier.com/retrieve/pii/S0301751613001087

[5] ZEGZULKA, J., BOTULA, J., JEZERSKÁ, L., KRATOCHVÍL, M., HLOSTA, J., NEČAS, J. Possibilities to improve the mechanical and physical properties of slag for its secondary utilization. In *METAL 2015: 24th International Conference on Metallurgy and Materials*, Ostrava: TANGER, 2015, ISBN: 978-80-87294-58-1.

[6] FREEMAN R., Measuring the flow properties of consolidated, conditioned and aerated powders - A comparative study using a powder rheometer and a rotational shear cell. *Powder Technology,* 2006, vol. 174, pp. 25-33.