RECOVERING LITHIUM MICA FROM THE WASTE AFTER MINING SN-W ORES THROUGH THE USE OF FLOTATION

ZÍSKÁVÁNÍ LI-SLÍDY Z ODPADŮ PO TĚŽBĚ SN-W RUDY POMOCÍ FLOTACE

Radmila SAMKOVÁ

Ing., Institute of Mining Engineering and Safety, Faculty of Mining and Geology, VSB – Technical University of Ostrava, 17. Listopadu 13, Ostrava-Poruba, tel.(+420) 59 732 5541, e-mail: radmila.samkova@vsb.cz

Abstract

Flotation is one of the possibilities of recovering useful components both at preparation and processing of raw materials, and at recycling and exploitation of a variety of wastes. In the area of Krušné hory occur a number of dumping sites where wastes from treatment of Sn-W ores are deposited, characterized by enhanced content of lithium, rubidium and cesium. These elements are bound to lithium mica – zinwaldite; its recovering is possible through the use of flotation. This paper is devoted to the investigation of factors influencing the flotation process to recover zinwaldite concentrate with enhanced contents of lithium, rubidium and cesium.

Abstrakt

Flotace je jednou z možností získávání užitkové složky jak při úpravě a zpracování nerostných surovin, tak při recyklaci a využívání nejrůznějších druhů odpadů. V oblasti Krušných hor se vyskytuje několik deponií, na nichž jsou uloženy odpady z úpravy Sn - W rud, charakteristické zvýšenými obsahy lithia, rubidia a cesia. Tyto prvky jsou vázány na lithnou slídu - cinvaldit, pro jejíž získání je možno použít metodu flotačního rozdružování. Příspěvek je věnován zkoumání faktorů ovlivňujících průběh flotace pro získání cinvalditového koncentrátu se zvýšenými obsahy Li, Rb a Cs.

Key words: flotation, mica, lithium, Li-mica

1 INTRODUCTION

Lithium is the lightest of the series of alkaline metals. It is a very light and soft metal which quickly reacts with oxygen and water; therefore, it is only found it in the form of compounds in nature. Lithium is present there in a small amount as ingredients of various rocks.. From about a hundred and ten metals containing lithium, spodumen, lepidolite, petalite and amblygonite are the most common. Table 1 below contains a summary of the most significant minerals containing lithium.

Tab. 1 Lithium minerals

Mineral	Chemical formula	Li content (%)	Density (g.cm^{-3})
Lepidolite	$KLi_{1.5}Al_{1.5}(SiAlO_{10})(F,OH)_2$	3.58	2.8 - 2.9
Spodumen	$LiAl(Si_2O_6)$	3.73	3.2
Amblygonite	$LiAl(PO_4)(F,OH)$	3.44	3.0 - 3.15
Petalite	$(Li,Na)(AlSi_4O_{10})$	2.09	2.4 - 2.46
Zinwaldite	$KLiFeAl(Si_3AlO_{10})(F,OH)$	1.59	2.9 - 3.1

According to studies, the world supplies of lithium in the available deposits are estimated at 20 Mt. The world market is dominated by Chile and Australia; both the countries gain lithium in the form of lithium chloride or carbonate from mineral waters. Most of the minerals containing lithium are found in Bolivia; however, available technology for their extraction is still missing there.

Up to now, the need of the Czech Republic is covered by import exclusively, despite the fact that the balance of deposits in the Czech Republic records over 53 Mt of lithium ores with the balance content of Li within the range of 0.208 % to 0.286 %, in some cases even 1.26 % of Li. This is the region of Krušné hory, where zinwaldite is bound to deposits of Sn-W ore [2]. Besides that, Bohemia also has underground mineral waters with lithium concentration exceeding several times the concentration of lithium brines extracted elsewhere. One of the inland raw materials suitable for obtaining lithium is also wastes from tin-tungsten ore extraction, up to now deposited in settling pits of no longer existing preparation plants in Cínovec or Krásno, containing enough raw material, even partly prepared, crushed, enriched for lithium mica.

As a component of Sn-W paragenesis and source of Li, Rb and Cs, zinwaldite is distinctively anomalous within the whole pluton of Krušné hory. After the depletion of pegmatite deposits in the world, zinwaldite greisens of the Krušné hory region may become a reserve source of lithium (rubidium); its acquiring from gravity Li-concentrates has been verified in practice and its industrial application has an upward trend. The preparation plant wastes concentrated in the Cínovec settling pit are a source of by-products of Cínovec ore paragenesis. In 1992, an operational calculation of the settling pit supplies was done; besides the main Sn and W components, even the occurrence of Li and other trace elements was observed. The total settling pit area is 43 500 sqm and the total preparation plant sand amount is 1 025 kt. 50 % of the wste has granularity under 0.25 mm and the following chemical composition: Sn 0.07.%, W 0.011.%, S 0.03.%, Pb 0.01 %, Cu 0.01 %, Zn 0.06 %, Li 0.23 %. Processing these wastes would not only mean coverage of inland lithium consumption but also a significant contribution to the environment improvement in the given areas with view to the large extensiveness of settling pits which are not only a source of dustiness, but also a serious threat to the quality of surface and underground waters. At present, no flotation or magnetic separation is used for Li-mica, the by-product of processing Sn-W ores [3].

2 APPLICATION OF Li, Rb, Cs AND THEIR MOST IMPORTANT COMPOUNDS

From the wide variety of lithium applications, its usage in rechargeable batteries of mobile phones and notebooks should be highlighted. Production boom in these products necessarily initiated demand for lithium as well. Lithium batteries can successfully be used in designing emission-free cars, though their wholesale practical exploitation has been hampered by battery life so far. An increased demand for lithium can be expected in the future especially in the nuclear industry, where it will be used as a source for production of tritium in thermonuclear fusion reactors.(the fusion reactor can be considered an entirely clean power source, with harmless helium as the only waste). Lithium also finds use in the aircraft industry, which requires its light and durable alloys with aluminium. The pure element is used for removing undesirable gases during production of non-ferrous metals. It is further exploited in production of fibreglass or as a substitute for environmentally-harmful elements, such as fluorine.

Industrially, stearate seems to be the most important of lithium compounds, serving as thickener for production of lubricating oils. Lithium carbonate (Li_2CO_3) is employed in ceramics, medicine, as a flux or catalyst. Lithium hydroxide (LiOH) is used in batteries and for the production of lithium salts, oils and soaps. Lithium chloride (LiCl) finds application in air-conditioning units and as a battery filling. Lithium fluoride (LiF) is used in ceramics and optics. Litium bromide (LiBr) is used as adsorbent in cooling units, etc. [1].

Elementary rubidium and cesium are produced by electrolysis of melted rubidium or cesium chloride on an iron cathode. Chlorine gas generates on the graphite anode at that. With view to its exceptional instability and reactivity, metal rubidium and cesium have only minimum practical exploitation. Thanks to their low ionization potential, they can be utilized in photocells used for direct transformation of solar into electric energy. At the same time, they are a prospective medium for ion motors, as spacecraft power units. During production of cathode tubes working with low-pressure inert gas filling, rubidium and cesium are used as getter, which is a substance capturing and removing the last remnants of admixed reactive gases. Rubidium salts are added do mixtures for amusement pyrotechnics, giving a violet shade to the light effects [4].

Besides magnetic separation and gravitation methods of separation, flotation also seems to be a suitable method of separation lithium mica from wastes after the extraction of Sn-W ore. The yield and efficiency of the flotation method, resulting from laboratory tests performed at the department of preparation of mineral raw materials of the Institute of Mining Engineering and Safety HGF, VŠB-Technical University of Ostrava, are comparable with the results of magnetic separation of this raw material. In both cases, efficiency values amount to about 70 % [5].

3 MATERIAL

For the flotation method of waste processing after extraction of Sn-W ores stored at the settling pit of the former mine and plant for processing Sn-W ores at the Cínovec deposit in Krušné hory, samples were taken by surface method in the total amount of 500 kg. Sampling was done by means of dug holes of the depth up to one metre, which covered almost the entire settling pit area. Representative samples were prepared from the mixed sample by quartation and used for further research.

Part of the sample was taken and subject to control grain-size analysis. Tables 2 and 3 indicate the results of granulometric analyses together with results of lithium content chemical analysis. Mineralogical composition of the samples was determined by the RTG diffraction method. The results are stated in Table 4.

Tab. 2 Granulometric analysis of sample No. 1

Grain size (mm)	Yield (%)	Undersize (%)	Li content (%)	Li yield (%)	Rb content (%)	Rb yield (%)
0-0,063	5,76	5,76	0,170	4,67	0,220	5,15
0,063-0,1	9,86	15,62	0,194	9,12	0,236	9,43
0,1-0,315	53,45	69,07	0,211	53,71	0,247	53,28
0,315-0,63	27,79	96,86	0,217	28,73	0,254	28,51
0,63-1,0	2,82	99,69	0,255	3,43	0,290	3,34
+1,0	0,32	100	0,221	0,34	0,189	0,29
Celkem	100,00		0,210	100,00	0,248	100.00

Tab. 3 Granulometric analysis of sample No 2

Grain size (mm)	Yield (%)	Undersize (%)	Li content (%)	Li yield (%)	Rb content (%)	Rb yield (%)
0-0,063	8,12	8,10	0,198	7,35	0,241	8,16
0,063-0,1	11,55	19,67	0,199	10,51	0,233	11,12
0,1-0,315	50,87	70,54	0,219	50,88	0,237	48,96
0,315-0,63	26,60	97,14	0,229	27,82	0,259	28,05
0,63-1,0	2,58	99,72	0,261	3,08	0,290	3,29
+1,0	0,28	100	0,270	0,36	0,201	0,42
Celkem	100.00		0,219	100.00	0,248	100.00

Tab. 4 Mineralogical composition of samples

Mineral	Content [%]	
	Sample No.1	Sample No.2
Orthoclase	X	9.97+-1.86
Calcite	2.00+-0.69	X
Plagioclase Albite	3.34+-1.68	6.89+-2.01
Quartz	68.98+-2.70	61.40+-2.88
Topaz	2.79+-1.11	1.19+-1.17
Zinwaldite 1M	22.89+-2.25	20.56+-2.34

4 FLOTATION LABORATORY TEST

With respect to flotation capacity, silicates differ substantially. Selective division of individual silicates is a difficult process due to their similar flotation properties. Conditions for selectivity of silicates can be created by activation or deactivation of separation minerals in acid or basic medium. Fine fractions should be removed from the material before flotation. Direct as well as reverse flotation is used for minerals containing lithium. Spodumene and amblygonit are well flotable by means of apolar collectors (liquid hydrocarbons, fatty organic acids and their salts); the other Li-silicates can be flotated by cationic collectors. Above all, this applies to primary aliphatic amines, their salts and quaternary ammonium salts [6].

On the basis of specialized literature and consultations with flotation agent manufacturers, flotation collectors of the Aeromine series were used for the flotation of zinwaldite. They are classical cationic collectors on the amine basis, used in acid medium, recommended by the manufacturer for flotation of mica minerals [7,8]. Flotation tests were executed in the laboratory of the Institute of Mining Engineering and Safety, on the VRF laboratory agitator flotation machine with its own air suction and flotation cell volume of 1 litre.

The experiments aimed at verifying the influence of individual factors on the results of lithium mica flotation. Based on statistic planning, a factor plan of the type 2^4 was executed, supplemented with 2 experiments in the zero point. To ensure good reproducibility, all measurements were repeated twice. During the works, the influence of the following factors was monitored: flotation collector dose (Aeromine 3000, 440 - 3080 $g.t^{-1}$), pulp pH (1-7), depressant dose (NaF, 0 – 2000 $g.t^{-1}$) and pulp thickening (100 – 300 $g.dm^{-3}$). Aromatic oil was used as frothing agent (1440$g.t^{-1}$), the flotation time was selected by previous research for 10 minutes. The parameter selected for evaluating flotation experiments was flotation efficiency calculated from yield difference in the products of flotation separation. Evaluation of the results achieved proved that especially the first two factors mentioned, flotation collector dose and pulp pH, as well as their combinations, have a statistically significant influence on the flotation separation course. No significant influence of flotation pulp thickening or variable dose of quartz depressant was proved. The achieved efficiency of the flotation process fell within a very wide range from approx. 1 % to approx. 76 %, depending on the combination of individual parameters of the reagent mode. Table 5 indicates results at these values of individual factors: thickening 100 $g.dm^{-3}$, pH 1, collector 3080 $g.t^{-1}$ and NaF 2000 $g.t^{-1}$. The table data prove the possibility of processing wastes from the Cínovec locality by the flotation method. Although the results presented (efficiency 77 %) are very good, the entire flotation process has to be monitored further, and eventually optimized.

Tab. 5 Flotation test efficiency

Indicator	Mineral	Concentrate	Waste	Inlet
yield [%]		26.2	73.8	100
metal content [%]	1.59	0.6821	0.0148	0.19
metal amount		17.87	1.092	18.96
mineral content [%]	zinwaldite	42.90	0.931	11.927
barren rock content [%]		57.10	99.069	88.073
total		100.00	100.00	100.00
mineral amount	zinwaldite	1123.964	68.694	1192.658
barren rock amount		1496.036	7311.306	8807.342
total				10000
yield [%]	zinwaldite	94.24	5.76	100.00
	barren rock	16.99	83.01	100.00
efficiency [%]		77.25	-77.25	

5 CONCLUSION

The results of laboratory tests executed in the laboratories of VŠB – Technical University of Ostrava give clear evidence that the flotation process using the amine-based cationic collector is suitable for the separation of lithium mica - zinwaldite. This technology may also be employed in case of possible continuation of Sn-W ore extraction in the region of Krušné hory. With respect to the specific mineralogical and chemical composition of Czech Li-micas (zinwaldite), some other processing technologies may be applied besides flotation (with lower operational costs). Zinwaldite features significant magnetic properties; therefore, it can also be gained by magnetic methods.

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