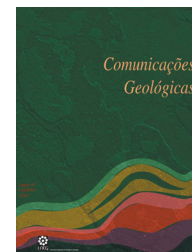


Minero-metallurgical processes for lithium recovery from pegmatitic ores

Processos minero-metalúrgicos para a recuperação de lítio de minérios pegmatíticos

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Abstract: With the expected increase of lithium demand in the forthcoming years, an efficient management of all the available resources is necessary. Rock minerals like pegmatites are important primary sources of lithium that shall be valorized. Minero-metallurgical processes have been developed for lithium recovery from pegmatitic ore deposits, involving physical concentration, thermal treatment, digestion and/or leaching in order to obtain a lithium soluble species adequate to produce lithium carbonate by precipitation. Physical concentration by froth flotation or by optical sorting are the two main alternative operations to produce a Li concentrate. Metallurgical treatment starts by calcination where the silicate structure is transformed to a more reactive solid phase (β -spodumene). Afterwards digestion with sulfuric acid and water leaching allows the dissolution of lithium sulfate. Carbonate pressure leaching is an alternative technology for treating pegmatites and production of lithium carbonate. Energy and chemicals savings is crucial in order to reduce the high costs associated with metallurgical processing of Li rock minerals.

Keywords: Lithium, Minero-metallurgical processes, Pegmatite ores.

Resumo: Com o aumento na procura de lítio nos próximos anos, torna-se necessária uma gestão eficiente de todos os recursos disponíveis. Os minérios pegmatíticos são fontes primárias importantes deste metal que devem ser valorizadas. Neste contexto, têm sido desenvolvidos processos minero-metalúrgicos para a recuperação de lítio, que envolvem a concentração física, o tratamento térmico, a digestão e/ou lixiviação, de forma a obter o lítio em formas solúveis que permitam a posterior produção de carbonato de lítio por precipitação. Na concentração física, as duas principais operações para produzir um concentrado de Li são a flutuação por espumas ou a triagem por processos ópticos. O tratamento metalúrgico começa por uma etapa de calcinação, onde a estrutura original do silicato é transformada numa fase sólida mais reactiva (β -espodumena). Em seguida, a digestão com ácido sulfúrico e lixiviação com água permite a dissolução do sulfato de lítio. A lixiviação sob pressão usando carbonatos é uma tecnologia alternativa para o tratamento de pegmatitos e produção de carbonato de lítio. A gestão eficiente da energia e do consumo de produtos químicos é crucial para reduzir os elevados custos associados ao processamento metalúrgico de minerais de lítio.

Palavras-chave: Lítio, Processos minero-metalúrgicos, Minérios pegmatíticos.

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1. Introduction

The development of the electric vehicle is considered crucial regarding environmental concerns. Nowadays, lithium ion is the preferred battery technology to power these vehicles. Therefore, lithium rapidly became a strategic metal to allow sustainable mobility in the upcoming decades. This will require sufficient supply of lithium. Main reserves of this metal are in brine deposits in South America, but rock Li-bearing minerals are also a potential resource of lithium. Main Li minerals with economic interest are pegmatite silicates like spodumene, lepidolite and petalite. Ambligonite, a Li-Al phosphate, is also a resource to be considered.

With current demand, the economic feasibility of Li recovery from rock minerals is very doubtful (Tahil, 2007), but the situation can change with boosting demand. So, technological solutions for valorization of lithium minerals are necessary, including physical concentration and metallurgical processing, in order to allow the competitive production of lithium commodities, namely lithium carbonate.

For many years, processes for lithium recovery from rock minerals have been developed (Nogueira, 1991) and sometimes applied at relatively low scale, but improvements are necessary in several domains such as energy savings, optimization of materials/chemicals usage and grade enhancement. In this paper, a review of processes for the minero-metallurgical processing of lithium minerals is presented. Several treatment options and operations are described and discussed, illustrated by research results achieved, aiming at contributing to the development of new or optimized routes that allow a more efficient management of lithium primary resources.

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2. Processing options

The main processing options for lithium recovery from pegmatite minerals are presented in figure 1. The Li-bearing minerals are firstly subjected to physical separation operations to produce a concentrate. The further steps are metallurgical, including high temperature

calcination or roasting and digestion or leaching with several reagents, in order to solubilize the lithium salts formed. Finally the lithium commodity Li_2CO_3 is produced from the aqueous liquor by a precipitation operation. The main features of these treatments and operations are hereafter disclosed.

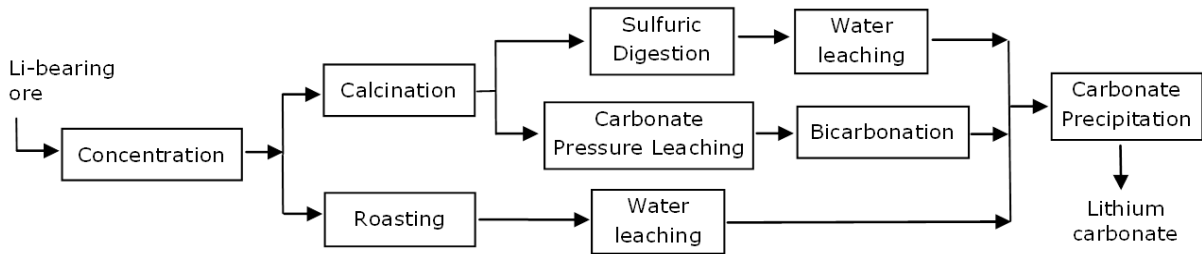


Fig. 1. Overview of main processing options for production of lithium carbonate from rock minerals.

Fig. 1. Visão geral das principais opções de processamento para a produção de carbonato de lítio de minerais rochosos.

3. Physical concentration (Mineral Processing)

The first step of treatment is the physical processing, where the lithium minerals are separated from the gangue minerals using crushing and grinding for mineral liberation and gravity and froth flotation processes for mineral separation (Mular & Bhappu, 1980; Weiss, 1985; Amarante *et al.*, 1999). Since specific gravity of Li minerals is somewhat higher than the bulk of the associated pegmatite minerals (e.g. quartz and feldspar), gravity concentration methods can be successful in some cases. Heavy media separation is practiced in China and Australia, by Galaxy Resources Ltd (Luong *et al.*, 2013). Froth flotation can be, however, applied namely for fine grinding product. Regarding spodumene as an example, under optimized conditions a concentrate with more than 6% of Li_2O can be produced from a run of mine ore with 1-1.5% of Li_2O . In the case of lepidolite, due to the flake/lamellar particle shape, a simple screening operation of the crushed ore allows a preliminary improvement of the Li grade, and froth flotation can be subsequently applied to produce a final enriched concentrate.

Alternative sensing technologies are being developed and applied for Li minerals. For coarser grain sizes, selective fragmentation and liberation of rich mineral fragments followed by optical sorting based on colour/morphology properties has been proved (Brandt & Haus, 2010). This process avoids overgrinding with evident advantages concerning energy savings and fines production. However, the technology is hardly applied to deposits with highly dispersed minerals (with low grain sizes).

4. Thermal treatment by calcination or roasting

The Li-rich fraction produced in the concentrator is sent to a metallurgical plant for further processing. The furnace thermal treatment of pegmatites is an initial mandatory

step to allow the silicate structure to transform into a more reactive form. Without this step, any subsequent chemical treatment would be useless. During the furnace operation at high temperature (typically 800-1100°C), the mineral (α -spodumene, lepidolite or petalite) is transformed to a more reactive species, usually a phase called β -spodumene. The calcination can be simply a decomposition (lost of volatile components) and a structural change, but can be also performed in the presence of additives (reagents like limestone, lime or a sulfate donor) being then described as a roasting operation (Medina & El-Naggar, 1984; Yan *et al.*, 2012). In the latest case, besides the structural change, the silicate simultaneously reacts with the reagents and the lithium is transformed in its oxide or sulfate forms. Chlorination (thermal treatment in the presence of chlorine) is also proposed (Barbosa *et al.*, 2014).

The effect of calcination temperature on the lithium reactivity of a lepidolite is observed in figure 2. The reactivity was assessed by determination of Li dissolution with HCl leaching media. Without calcination the Li leaching is lower than 40% and the recoveries increase substantially when the ore is calcined at 800°C. It is also observed that the particle size influences the yields/recoveries obtained. Li recoveries can reach 98% with the Li leaching of coarse size fractions, while it decreases below 70% for the finer fractions. This behavior is attributed to grain sintering, more relevant when the particle size is finer. This effect is quite marked for higher calcination temperatures such as 950°C, when the yields/recovery drop substantially in all cases, but for the finer particle size ranges the final values attained are even lesser than without calcination.

The high temperature operation is responsible for the high energy consumption and costs associated with Li rock minerals processing. Any attempts for reducing calcination temperature and residence time would be helpful for improving competitiveness.

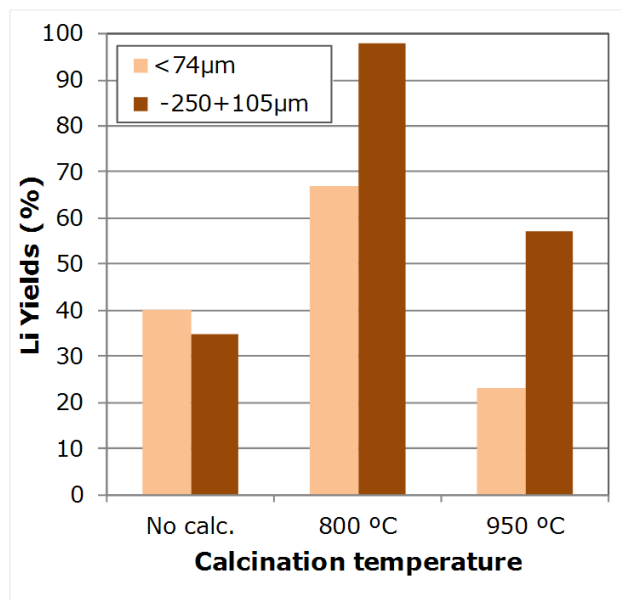


Fig. 2. Effect of calcination temperature on the Li recovery by leaching of a lepidolite ore, for two particle size ranges. Experimental conditions: calcination time = 13 h; leaching with 300 g/L HCl, with liquid/solid=1.5 L/kg, at 90°C and 4 h.

Fig. 2. Efeito da temperatura de calcinação na recuperação de Li por lixiviação de um minério de lepidolite, para duas faixas de tamanho de partículas. Condições experimentais: tempo de calcinação = 13 h; lixiviação com 300 g/L de HCl, com líquido/sólido = 1,5 L/kg, a 90 °C e 4 h.

5. Digestion and leaching

After the calcination or roasting, the following steps are hydrometallurgical, the aim being to solubilize the lithium in an aqueous medium. When roasting is performed, the Li is usually present in the solids as Li_2O or Li_2SO_4 , both easily soluble in water, providing that the Li species are accessible to the leachant (i.e., no occlusion/ passivation of the surface grains occurred during the thermal treatment). In this case, the water leaching allows lithium to pass into the water medium.

When the thermal treatment is a calcination operation, the aqueous medium shall provide the adequate reactants to transform lithium into soluble species. In this way, a well know process is the sulfuric acid digestion (at near 200-250°C) followed by water leaching, producing a lithium sulfate solution (Nogueira, 1991; Amer, 2008; Sitando & Crouse, 2012). This process allows high yields/recoveries of lithium, as figure 3 shows. In a range of digestion temperature of 175-225°C, yields/recoveries over 80% were found. In this alternative, the acid consumption is large concerning the stoichiometric quantity of lithium in the ores (an excess of H_2SO_4 of 3 fold).

The leaching with an aqueous acid solution is an alternative process to dissolve lithium from calcined pegmatites. Sulfuric or hydrochloric acid solutions can be used for such purpose. The Li leaching efficiency from a β -spodumene with several HCl solutions is depicted in figure 4, where is clear that to attain high recoveries it is necessary to use excess of reagent at high concentrations

(in this particular case, for 300 g/L HCl, more than 10 fold the stoichiometric quantity). This suggests that, besides energy consumption, the chemicals managements is also a concern regarding lithium recovery from rock minerals.

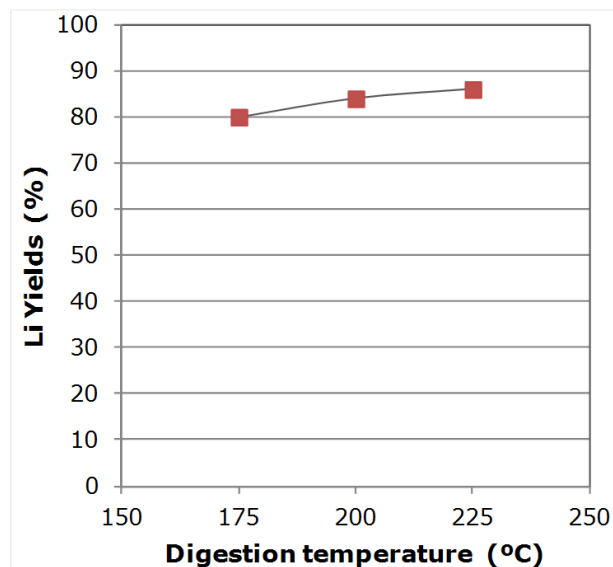


Fig. 3. Lithium recovery from a β -spodumene with H_2SO_4 digestion followed by water leaching: influence of digestion temperature. Conditions: $t = 0.5$ h; 60 g H_2SO_4 /100 g solids; particle size of solids: <250 μm .

Fig. 3. Recuperação de lítio a partir de β -espodumema com digestão com H_2SO_4 seguida de lixiviação por água: influência da temperatura da digestão. Condições: $T = 0,5$ h; 60 g H_2SO_4 /100 g sólidos; tamanho de partículas de sólidos: <250 μm .

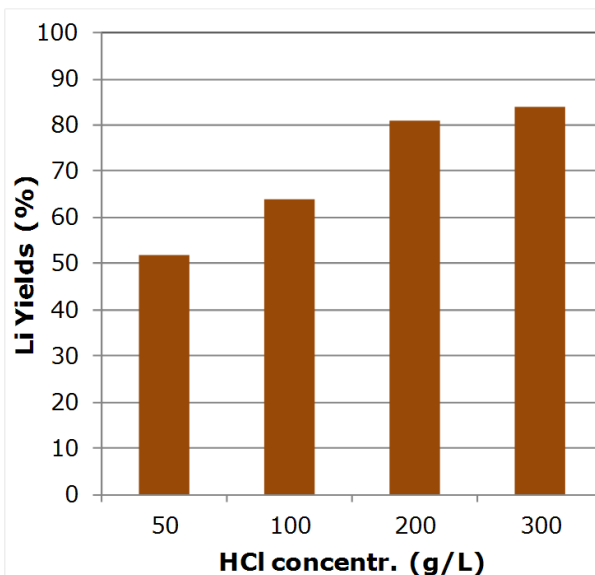


Fig. 4. Lithium recovery from leaching of a β -spodumene with HCl solutions at different concentrations. Leaching conditions: $T=90^\circ\text{C}$; $t=4$ h; liquid/solid=1.5 L/kg; particle size of solids: <250 μm .

Fig. 4. Recuperação de lítio a partir da lixiviação de β -espodumena com soluções de HCl em diferentes concentrações. Condições de lixiviação: $T = 90^\circ\text{C}$, $t = 4$ horas; líquido/sólido = 1,5 L/kg, tamanho de partícula dos sólidos: <250 μm .

An alternative process is the pressure leaching in autoclave, under sodium carbonate medium, where lithium carbonate is formed (Nogueira, 1991; Chen *et al.*, 2011). The leaching is conducted at temperature ranges of 190-235°C. After a bicarbonation step to improve lithium solubility, using CO₂ sparging, the lithium carbonate can be therefore recovered from the solution. The drawback of this process is the high investment and operating costs of the autoclave leaching facility.

6. Lithium recovery

Whatever the previous process steps, a lithium metallurgical plant normally ends with the production of lithium carbonate, the most common lithium commodity in the market, used as raw-material for manufacturing of the succeeding lithium substances and materials for the final applications (e.g. battery electrodes). The recovery of lithium from solutions is carried out by addition of a carbonate donor like Na₂CO₃, producing Li₂CO₃ which has a relatively lower solubility, especially in hot solutions. The purity of the lithium carbonate can be improved by a series of precipitation/re-dissolution and washing steps, in order to minimize contaminants such as sodium.

7. Conclusions

The minero-metallurgical processing of Li-bearing rock pegmatites involves physical concentration, calcination, digestion/leaching and precipitation. Froth flotation and optical sorting are the most usual concentration operations, depending on the mineral liberation size. Calcination or roasting above 800°C transforms the original pegmatites in more reactive species, allowing the accessibility of reactants to lithium inside the solid structure. Further operations are hydrometallurgical, using acid attack (acid digestion plus water leaching, or direct acid leaching) where lithium is solubilized into an aqueous phase. An alternative leaching approach is the carbonate leaching in autoclave. Final solutions containing lithium are treated to precipitate lithium carbonate, the most common lithium commodity in the market.

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References

- Amarante, M.M., de Sousa, A.B., Leite, M.M., 1999. Technical Note Processing a Spodumene Ore to obtain Lithium Concentrates for Addition to Glass and Ceramic Bodies. *Minerals Engineering*, **12(4)**, 433-436.
- Amer, A.M., 2008. The hydrometallurgical Extraction of Lithium from Egyptian Montmorillonite-Type Clay. *JOM*, **60(10)**, 55-57.
- Barbosa, L.I., Valente, G., Orosco, R.P., González, J.A., 2014. Lithium extraction from β -spodumene through chlorination with chlorine gas. *Minerals Engineering*, **56**, 29-34.
- Brandt, F., Haus, R., 2010. New Concepts for Lithium Minerals Processing. *Minerals Engineering*, **23**, 659-661.
- Chen, Y., Tian, Q., Chen, B., Shi, X., Liao, T., 2011. Preparation of lithium carbonate from spodumene by a sodium carbonate autoclave process. *Hydrometallurgy*, **109**, 43-46.
- Luong, V.T., Kang, D.J., An, J.W., Kim, M.J., Tran, T., 2013. Factors affecting the extraction of lithium from lepidolite. *Hydrometallurgy*, **134-135**, 54-61.
- Medina, L.F., El-Naggar, M.M.A.A., 1984. An alternative method for the recovery of lithium from spodumene. *Metallurgical Transactions B*, **15(4)**, 725-726.
- Mular, A.L., Bhappu, R.B., 1980. *Mineral Processing Plant Design*. Society of Mining Engineers, 2nd Edition, 946 p.
- Nogueira, C.A., 1991. *Extracção de lítio de recursos nacionais*. Provas de acesso a Assistente de Investigação (Thesis). LNETI, Lisboa.
- Sitando, O., Crouse, P.L., 2012. Processing of a Zimbabwean petalite to obtain lithium carbonate. *International Journal of Mineral Processing*, **102-103**, 45-50.
- Tahil, W., 2007. *The trouble of lithium: implications of future PHEV production for lithium demand*. Report, Meridian International Research, January, 22 p.
- Weiss, N.L., 1985. *SME Mineral Processing Handbook*. American Institute of Mining, Metallurgical and Petroleum Engineers, Inc.
- Yan, Q., Li, X., Wang, Z., Wu, X., Wang, J., Guo, H., Hu, Q., Peng, W., 2012. Extraction of lithium from lepidolite by sulfation roasting and water leaching. *International Journal of Mineral Processing*, **110-111**, 1-5.