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Comparison of Processes for Lithium Recovery from Lepidolite by H₂SO₄ Digestion or HCl Leaching

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Abstract – Lithium is becoming a strategic metal due to its important applications in secondary battery electrodes used in electronic appliances and also in electric traction vehicles. Lithium primary resources are brines and rock minerals, the former being nowadays almost exclusively used in the production of lithium commodities. With the expected increase in lithium demand, the development of competitive technologies for recovery lithium from ores like pegmatites is getting imperative. The high energy and reagents consumption in processing minerals is an issue that should be considered. This paper presents some results on the comparison of two acid treatment routes for lepidolite, the H₂SO₄ digestion and HCl leaching.

Before both chemical treatments, lepidolite was calcined at 800°C and was transformed in a more reactive species, β-spodumene. The H₂SO₄ digestion at 175°C (followed by water leaching) allowed 88% Li recovery into the solution in 30 min. By the contrary, the HCl leaching process carried out at 90°C also achieved similar yields but only after 4 h of reaction. In both cases, an acid excess was used, but clearly higher for the essays with HCl. The H₂SO₄ digestion process was also advantageous in what concerns to selectivity over other contained metals. Al, Mn and Fe concentrations in solutions were substantially higher in the hydrochloric acid leaching. These results showed that the digestion with sulphuric acid can be a more efficient and competitive process.

Keywords: Lithium recovery, Pegmatites, Lepidolite, HCl Leaching, H₂SO₄ Digestion.

1. Introduction

Lithium use in rechargeable battery electrodes for electronic devices (essentially portable computers and cell phones) has been continuously increasing in the last years. The widespread utilization of hybrid and electric vehicles with Li-ion batteries, expected for the forthcoming years, will boost lithium demand (Shukla et al, 2013). Without a known and reliable substitute of lithium in battery applications, this light metal is becoming a strategic element (Tahil, 2007). So, the search for lithium primary and secondary resources, as well as the development of technological and economical solutions for its extraction, are nowadays getting growing attention.

Primary sources of lithium are ores and brine deposits (Ziemann et al., 2012). The second one, being easily available and with substantial lower operating costs, have replaced the ore extraction in the last decades. Nowadays, most of the lithium commodities in the market are coming from the exploitation of brines, mainly in South America. Therefore most of the Li-bearing minerals, like spodumene, lepidolite and petalite, are currently extracted together with other silicates, without major beneficiation, for ceramic applications. With the increasing interest in lithium, these sources are again taken into consideration for producing lithium compounds with high purity.

Li-bearing silicates are very refractory to chemical attack. Thus the metallurgical processes always include a first step of calcination to promote reactivity. Afterwards, the hydrometallurgical steps using acid digestion and/or leaching allow the formation of soluble lithium compounds. A well known process for spodumene and also applied to other Li silicates is the acid digestion (Amer, 2008, Sitando and Crouse, 2012), where lithium is cured with concentrated sulphuric acid at near 200°C with formation of lithium sulphate, which is subsequently leached with water. The digestion with other mineral acids (HCl, HNO₃) is however not achievable due to their relative volatility. Alternatively, these acids can be used as leachants in aqueous solutions (up to about 100°C) in order to promote the lithium dissolution from the calcined silicate.

A research of routes for treating Li-bearing minerals is being carried out, aiming at optimizing technologies and operations or developing new approaches. This paper deals with some laboratory results on the comparison between the sulphuric acid digestion and hydrochloric acid leaching for lithium recovery from lepidolite. Aspects such as efficiency, selectivity and reagents consumption are assessed and discussed.

2. Experimental

The sample used in the experimental work was a lepidolite rich ore collected in the Alvarrões mine, Guarda, Portugal. Besides the Li mineral, the sample also contained the major minerals quartz and feldspar (mainly, albite). The run-of-mine ore was grinded in a ball mill for a few minutes. The particle size distribution of the ground material obtained by the sieving technique showed that all material was reduced to minus 250 µm. The ore was calcined in a muffle furnace at 800°C for 14 h being the transformation assessed by X-ray diffraction (XRD).

The sulphuric acid digestion was carried out in a glass beaker provided with a temperature controller. The solid and the concentrated acid were mixed and the resulting paste was cured at 175°C for the time necessary for the test. Afterwards the digested paste was leached with a preset volume of water (liquid-solid ratio of 1.87 L/kg) for 30 min at room temperature. The final pulp was filtered and the solution sent to analysis.

For the hydrochloric acid leaching, the aqueous solution containing the required HCl concentration was previously prepared and heated in a glass stirred reactor until the temperature of the test (90°C) was reached. The solid was then added (at a liquid/solid ratio of 1.5 L/kg) and the reaction time was monitored. At the end of the test, the solution was filtered and analysed. In both tested processes, the leaching yields were assessed from the analysis of the dissolved metals, using atomic spectrometry methods, in relation to the respective initial content in the solids.

3. Results and Discussion

The grinding of the ore produced a sample with a granulometric size less than 250 µm. The particle size distribution showed a median characteristic diameter of $d_{50}=110$ µm, and extreme diameters of $d_{10}=35$ µm and $d_{90}=200$ µm. The XRD peaks of the calcined material corresponded to β-spodumene, the phase usually resulting from calcination of several lithium pegmatites, including lepidolite. The elemental composition of the calcined sample was 1.1% Li, 11.6% Al, 0.07% Fe and 0.2% Mn, besides other elements not evaluated for this specific work.

The digestion with sulphuric acid was tested for two H₂SO₄ additions (92 and 123 g H₂SO₄/100 g solid). Li recovery yields as a function of time are presented in figure 1(a). The yields attained were about 82% after 30 min of digestion and slightly increased to near 88% after 2 hours. Therefore it seems that the process is fast and efficient, and do not depend substantially on the acid added, within the range tested. It is also evident that, under the present conditions, yields above 90% do not seem feasible to achieve, probably due to occlusion of some of the particles by sintering phenomena occurring during calcination.

Regarding hydrochloric acid leaching, two solution concentrations, 100 and 300 g/L HCl, were also tried. In this process, the behaviour was quite different. Although similar yields can be achieved for the higher HCl concentration (near 83%) the reaction is noticeably slower and such result is only obtained

after 4 hours. The yields increased slowly during the residence time and for the lower HCl concentration, the final leaching efficacy was substantially lower (about 67% after 4 hours).

The results show that the sulphuric acid digestion process is more efficient than hydrochloric acid leaching concerning Li recovery from the calcined ore, essentially in what concerns the reaction time. However the digestion is carried out at a higher temperature (near 200°C) than the HCl leaching (below 100°C). This aspect can be pertinent in terms of energy savings, but the reaction time also affects energy consumption, and so a carefully analysis using additional data shall be made to be conclusive.

Table 1 shows the solution compositions obtained, and the selectivity of Li extraction against other metals considered as potential contaminants in the final Li products, namely Al, Fe and Mn. The selectivity factor used was the ratio between the solution concentrations of Li and the other metals. The lithium concentrations obtained in the two processes were quite similar (5-6 g/L) but concerning the other metals the differences found were very relevant, the solution contamination being markedly higher for the HCl leaching. In this case the aluminium concentrations attained were really pronounced (up to 30 g/L when compared to near 3 g/L for the H₂SO₄ digestion process). The selectivity factors were therefore much more favorable for the case of H₂SO₄ digestion, demonstrating the higher selectivity of this option and anticipating technical and economic advantages concerning the subsequent purification and Li recovery operations.

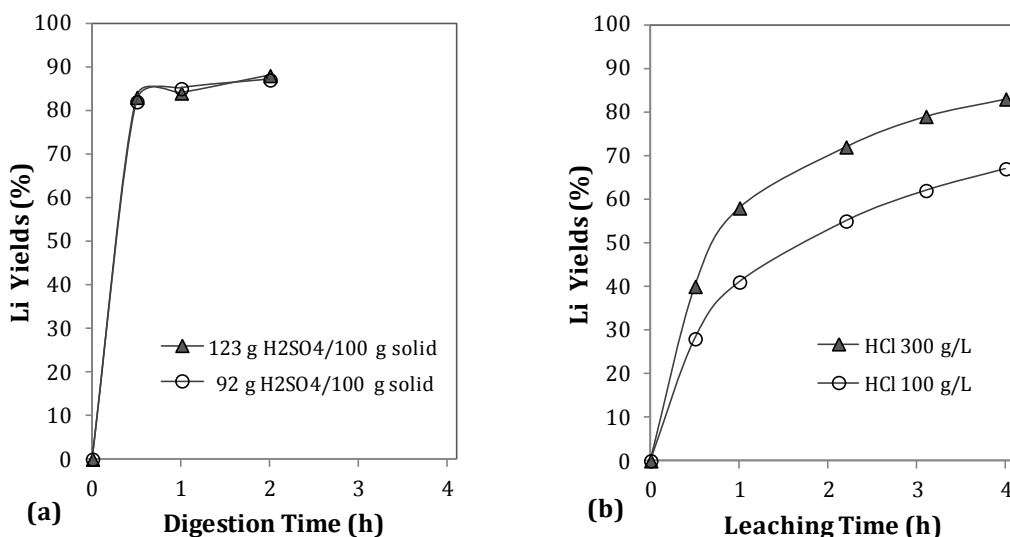


Fig. 1. Lithium yields as a function of time for both processes in analysis: (a) H₂SO₄ digestion at 175°C; (b) HCl leaching at 90°C.

Table. 1. Comparison of processes in terms of final solution compositions, yields, selectivity and reagent excess.

Process and conditions	Solution composition (g/L)				Li yields (%)	Selectivity Li/(Al+Fe+Mn)	Reagent excess ratio (to Li)
	Li	Al	Fe	Mn			
H₂SO₄ Digestion							
92 g H ₂ SO ₄ /100 g	5.1	3.1	0.08	0.17	87	1.53	3.0
123 g H ₂ SO ₄ /100 g	5.2	2.8	0.09	0.17	88	1.69	4.0
HCl Leaching							
100 g/L HCl	4.9	19	0.40	1.17	67	0.24	2.5
300 g/L HCl	6.1	30	0.37	1.19	83	0.19	7.6

Table 1 also reveals an important feature of these processes, the reagents consumption. The values presented correspond to the quantity of acid used related to the stoichiometric acid quantity for Li content

in the initial solid. In both processes, a relatively large excess of acids is required. However, to attain similar Li yields, the HCl leaching process involves the use of more than 7 fold the stoichiometry while the H₂SO₄ digestion process only requires 3-4 fold. So, in terms of chemicals consumption, the digestion also appears favorable when compared to the HCl leaching.

4. Conclusion

The comparison of two processes for Li recovery from lepidolite, by H₂SO₄ digestion or by HCl leaching, was carried out. Factors such as Li yields, selectivity, energy and reagents consumption, were assessed. In both processes, the higher Li recoveries achieved were in the ranges 83-88% with leaching solution compositions in the range 5-6 g/L Li, but the H₂SO₄ digestion reaction was much more fast. The HCl leaching also revealed to be less selective regarding the dissolution of the accompanying metals present in the silicate ore; aluminium contents in the liquors can be so high as 30 g/L Al, being substantially lower (about 3 g/L Al) when applying the H₂SO₄ digestion. Consumption of acid was also found higher for HCl than for H₂SO₄. The digestion is carried out at higher temperature, meaning that this process can eventually be less effective regarding energy consumption, but the residence time also affects energy balances and so further precise analysis in this domain is advisable. From the results so far achieved in this investigation, the H₂SO₄ digestion process seems more appropriate for Li recovery from this type of pegmatite ore.

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