Extraction of Lithium from Saltpond Pegmatites using Seawater – a Preliminary Study

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Abstract

Due to the increasing use of portable electrical and electronic gadgets as well as hybrid electric vehicles, there is a high demand for materials that can be utilized in producing high energy density and low self-discharge batteries. Thus, lithium is in high demand as it meets these requirements. Spodumene is the core lithium-bearing mineral and it is generally associated with pegmatites, which are currently being explored due to the high lithium content. In Ghana, pegmatites that contain spodoumene occur in several places including Saltpond. Extraction of lithium from minerals and clays can be expensive and energy-intensive. Thus, to meet the rising demand for the metal, it is imperative to develop processes that are cheap and environmentally friendly. This study considered the extraction of lithium from Saltpond pegmatites using seawater as a lixiviant. Lixiviation studies were carried out for 6 hours at a chloride concentration of 10.9 ppm, pulp densities between 20% and 50% and grind size from 80% passing 75 µm to 212 µm. Lithium could be leached from pegmatite using seawater and recoveries increased with decreasing grind size and at higher pulp density. Maximum lithium recovery (75.31%) was achieved after 6 hours of leaching, P_{80} of 75 µm and pulp density of 50%.

Keywords: Pegmatites, Spodumene, Leaching, Seawater, Pulp density.

1 Introduction

Lithium is very reactive and flammable (Karrech *et al.,* 2020). Lithium ion batteries are an essential and vital part of modern technology as they power smart phones, portable computers/tablets, electric/hybrid cars, traders' equipment, and some energy storage facilities. Lithium is also utilised in the ceramic/glass industry, which is the second largest user, to improve mechanical performance, density, and energy consumption of its products throughout production and maintenance (Alvani *et al.,* 2001; Tsuchiya *et al.,* 2006; Vikström *et al.,* 2013). In order to realize the global energy transition, questions of resource availability have drawn more attention (Marscheider-Weidemann, *et al.,* 2016), although it is generally accepted that one element, lithium, on which the world is currently focused, will not be a limiting restriction in this century (Greim *et al.,* 2020). The cost of enriched lithium is also equivalent to the cost of gold. Thus, lithium from solid breeding material waste therefore needs to be recovered and recycled.

Due to lithium's rising importance in a wide range of industries, numerous studies have been done on how to extract the metal from various sources. The estimated global lithium reserves are 14 million

tonnes, of which 70–80 % is found in salt lake brine, geothermal water, and solid lithium in lithium ore. 2600 billion tonnes of saltwater containing lithium, or around 15,000 times greater than solid lithium ores, are the focus of many academics' attention (Ji *et al.,* 2012; Meshram *et al.,* 2014; Martin *et al.,* 2017).

Current lithium resources are thought to be 62 Mt in lithium carbonate equivalent (LCE), according to the United States Geological Survey (USGS). Lithium can be extracted from clays, pegmatites, sedimentary rocks, clays, brines (continental, geothermal, or associated with oil fields), and pegmatites, which are igneous rocks that form at depth and show interlocking crystals. The estimated 14 Mt of lithium deposits in the globe are split 98 % among four countries: China, Argentina, Australia, and Chile (Jaskula 2017; Swain 2017; Greim *et al.,* 2020).

To extract lithium minerals from pegmatite, comminution and physical separation techniques like gravity concentration, froth flotation, and magnetic separation are used (Bale and May, 1989; Amarante *et al.,* 1999). It has been demonstrated that the unique comminution method's utilisation of high voltage pulses enhances the release of spodumene (Brandt and Haus, 2010). It is commonly roasted after producing a lithium mineral concentrate and then leached with acid or water. Meshram *et al.* (2014), and Karrech *et al.* (2020) all define the acid process as heating alpha spodumene to transform it into beta spodumene, which is easier to extract. Alkali processes also exist where lithium bearing minerals are processed using limestone (Kuang *et al.* (2018); and Meng *et al.* (2021). These processes are expensive (Meshram *et al.,* 2014; Karrech *et al.,* 2020).

Recently, brines and bitterns have attracted a lot of attention as a means of supplying the rising demand for lithium. The most popular technique for extracting lithium from brines is the lime soda evaporation process, which involves steps including concentration by evaporation, impurity removal, and carbonation precipitation. Li extraction from brine is frequently 30–50% cheaper than that from hard rock (Tran and Luong 2015). Due to the gradual nature of the evaporation process in ponds, it is accelerated in climates with minimal rainfall and humidity, strong winds, and ample sun exposure (Peiró *et al.,* 2013). The quality of the lithium relative to contaminants like Na, K, and Mg is another important consideration (Rodinia Lithium, Inc. 2011; King *et al.,* 2012; Harrison 2014; Choubey *et al.,* 2017; Blanco 2019)..

Ghana has conventionally concentrated on the mining of gold, diamonds, manganese and bauxite at the large scale level though other minerals are present. In recent times, there is growing interest in lithium deposits and commercial quantities of lithium worth about US$150 billion have been discovered in the Volta, Western, and Ashanti regions. The Ewoyaa Lithium Project predicts that Ghana will become West Africa's first lithium producer (Anon, 2022). These deposits must be exploited, and viable ways of extracting lithium from pegmatites must be developed.

Though lithium is recovered from seawater, there is scanty information in the literature on the use of seawater in leaching solid lithium from hardrock ores. This research aims to use seawater as a lixiviant for lithium in pegmatites. After initial mineralogical and chemical studies, the impacts of residence time and particle size were determined. This paper sheds light on seawater-based lithium extraction from pegmatite, which is expected to be both economical and ecofriendly.

2 Materials, Methods Used

2.1 Materials and Sample Preparation

Pegmatite rock samples were obtained from Saltpond in the Central Region of Ghana. Sea water was also obtained from the Atlantic Ocean at Takoradi in the Western Region of Ghana.

A total sample of 20 kg was crushed sequentially using the Metso Jaw crusher, Metso Cone crusher and a Denver Roll crusher, split using riffles and bagged.

2.2 Grindability Test of Crushed Samples

One (1) kg sample was used for grindability analysis on the samples to determine the optimum time required to mill to 80% passing 212 µm. From the roll-crushed sample, 100 g from the 1 kg sample was screened using 212 µm screen to determine the percentage passing at time zero of milling. The sample was milled for 10 minutes and screened using 212 µm to determine the percentage passing at that time. The procedure was repeated after 20 minutes of milling. The percentages passing 212 µm were plotted against the grinding times, and the optimum time required to achieve 80% passing 212 µm was estimated from the straight line. The same procedures above were repeated to establish the optimum grind time for 106 µm and 75 µm.

2.3 Chloride Testing

The seawater sample was placed in the 100 ml vial after it had been thoroughly cleaned. The cap was adjusted to its proper size and tightened. After that, the vial was inserted in the sample chamber with the arrow marks on the instrument and the vial aligned. One HT13 Chloride T1 tablet was dropped directly into the water sample from the foil. A clean stirring rod was used to crush the tablet until no large fragments were visible. One HT14 Chloride T2 tablet was added to the same water sample directly from the foil and crushed until no large bits were visible. The vial was then tightly closed with the cap and swirled several times to dissolve the tablet.

The vial was inserted into the sample chamber with the marks on the instrument and the vial aligned. On the photometer, the start key was pressed. After waiting two minutes for the reaction to finish, the measurement began, and the findings were displayed in mg/l chloride.

2.4 Bottle Roll Test

After conditioning, the pulp was bottle-rolled for 6 hours at different solid densities of 20%, 40%, and 50%, with particle sizes of 80 % passing 212 µm, 106 µm, and 75 µm. After 0.5, 1, 2, 4, and 6 hours, samples were taken. These samples were filtered, and 10 mL was sent for lithium testing by Shimadzu AA7000 Atomic Absorption Spectrometer.

## 2.5 Acid Digestion of Tailings Samples

A 50-g sample was taken from each of the dried tailings via Jones riffle sampler into a beaker. Hydrochloric acid (75 ml) and nitric acid (25 ml) were added respectively to the samples in the beaker, after which they were heated for 10 minutes and then allowed to cool. On cooling, samples were filtered and the concentration of lithium in tailings determined by Shimadzu AA7000 Atomic Absorption Spectrometer.

3   Results and Discussions

The goal of this research was to extract lithium from Saltpond Pegmatite using seawater as a lixiviant. The leaching test was carried out for 6 hours at a chloride concentration of 10.9 ppm, with varied solid densities of 20%, 40%, and 50%, and particle sizes of 80% passing 212 µm, 106 µm, and 75 µm. Samples were taken at pre-determined intervals, filtered, and 10 mL analysed for lithium using the Shimadzu AA7000 Atomic Absorption Spectrometer. The experiments were duplicated, and the graph depicts the average results.

3.1 Chemical Analysis

The chemical analysis (full suit) conducted on the ore sample is shown in Fig. 1. Observing Fig. 1, the chemical analysis showed that there is a quite an amount of lithium in the ore sample and it is about 96.2 mg/kg. Sodium and potassium were also present in higher concentrations.
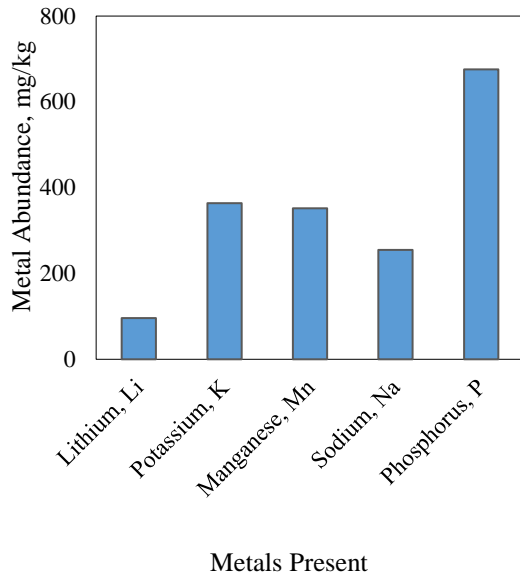
Fig. 1 Partial Chemical Analysis of Ore Sample

Table 1, shows the partial chemical analysis conducted on the seawater. From the table, it can be observed that there were minimal amount of lithium in the seawater (0.2 mg/L). Magnesium, sodium, calcium, potassium and sulfur were present in higher concentrations.

Table 1. Partial Chemical Analysis of Seawater

Minerals Present	Minerals Abundance, mg/L
Boron	5.2
Calcium	518
Lithium	0.2
Magnesium	1500
Potassium	467
Sodium	9784
Sulfur	966

3.2 Mineralogical Studies

Fig. 2 depicts the mineralogical analysis that was conducted on the ore sample using XRD to quantify the various minerals that were present. The XRD results showed that the Saltpond Pegmatite was mainly composed of the following minerals:

- ✓ Quartz-30.4%;
- ✓ Albite low-46.5%;
- ✓ Calcium Carbonate-0.6%;
- ✓ Microline, ordered-5.2%; and
- ✓ Spodumene-17.3%.

According to literature, spodumene is a lithium-bearing mineral, which is generally associated with pegmatites, as confirmed by XRD analysis.
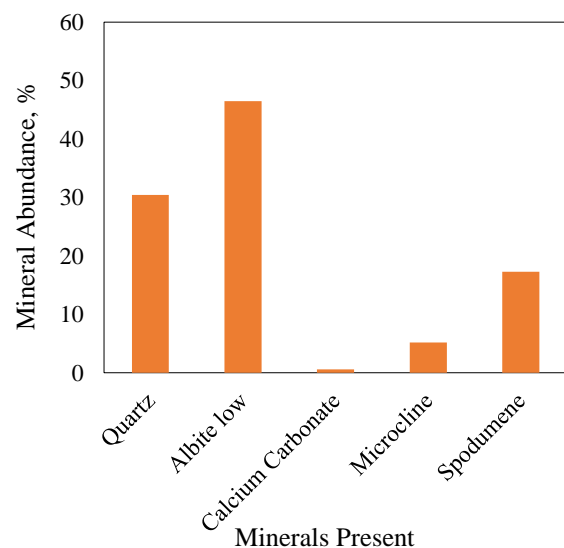

Fig. 2 XRD Analysis of Ore Samples

3.3 Optimization Parameters for Seawater Leaching

For the recovery of lithium from pegmatite, three parameters were investigated: particle size, pulp density, and time, with the concentration of chloride maintained constant. The chloride content of the seawater utilized is 10.9 ppm. These variables were shown to have a significant impact on the extraction of lithium from pegmatite.

3.4 Effect of Leaching time and Grind size on Lithium Recovery

Fig. 3 exhibits the effect of leaching time and grind size on lithium recovery. Initial test works conducted were to determine the leaching kinetics so as to determine a suitable residence time. Leaching was done for 6 hours and also conducted at different grind size to have a fare idea how the ore will respond to leaching. At the end of the 6-hour period, it was established that lithium recovery increased with time. It was also observed that, the ore is fast leaching because at 0.5 hours Li recoveries attained ranged from 44.9% to 55.1%.
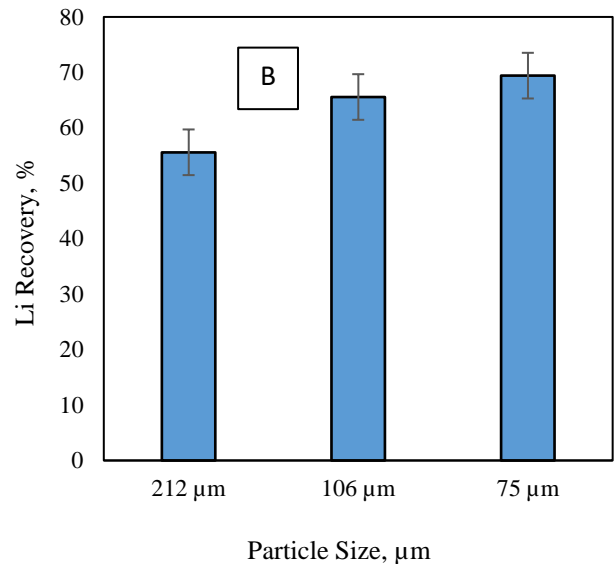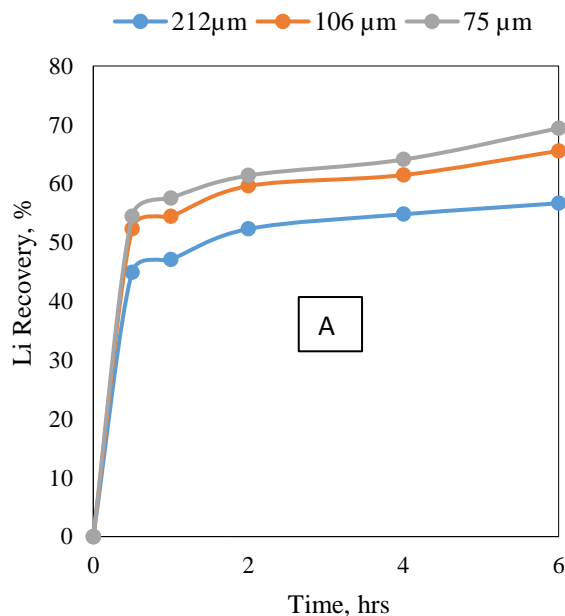
**Fig. 3 Effects of (A) Leaching Time and (B) Particle Size (P80) on Lithium Recovery**

Also from Fig. 3, it is quite obvious that grind size had an influence on Li recovery as recoveries of 55.9%, 65.6% and 69.4% were respectively recorded for 212 µm, 106 µm and 75 µm at 40% solid density.

3.5 Effects of Pulp Density on Lithium Recovery

Fig. 4 illustrates the effects of pulp density on lithium recovery for varying particle size (80% passing 75 µm to 212 µm). From the operating parameters established in Fig. 3, further tests were done to ascertain the influence of pulp density on Li recovery. Indeed from the graphs it could be said that pulp density has a marked effect on Li recovery. For 212 µm, Li recoveries attained for the various pulp densities (20%, 40% and 50%) were 49.4%, 55.9% and 58.1% respectively. The low Li recoveries can be attributed to size of the particles. Liberation was not effective and such contributed to the poor recoveries obtained which were <60%.

In graph B, 106 µm also confirmed the influence of pulp density on Li recovery. 50% pulp density had

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the highest recovery of 69.3%, followed by 40% and 20% with 65.6% and 61.2% correspondingly.

In graph C, it can be seen clearly the influence of pulp density on Li recovery and it can also be said that Li recovery increased as the grind became finer. Recoveries achieved were 64.7%, 69.4% and 75.3% respectively for 20%, 40% and 50%. The highest recovery attained can be attributed to the fact that, the ore was well liberated and as such the lixiviant was able to attack the Li metal due to the exposed and large surface area of the mineral.
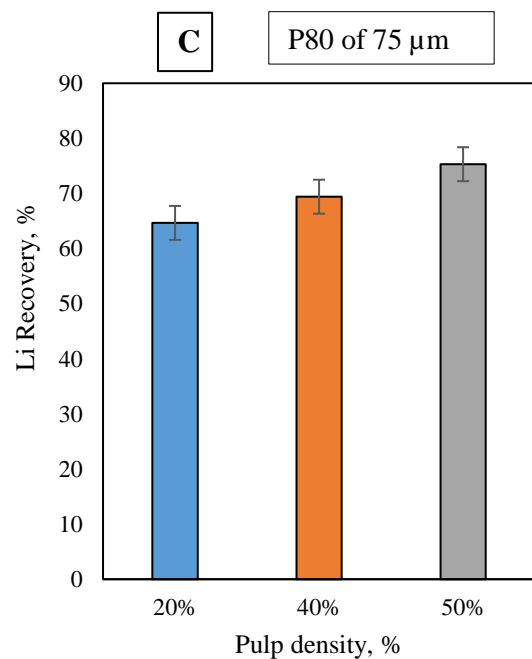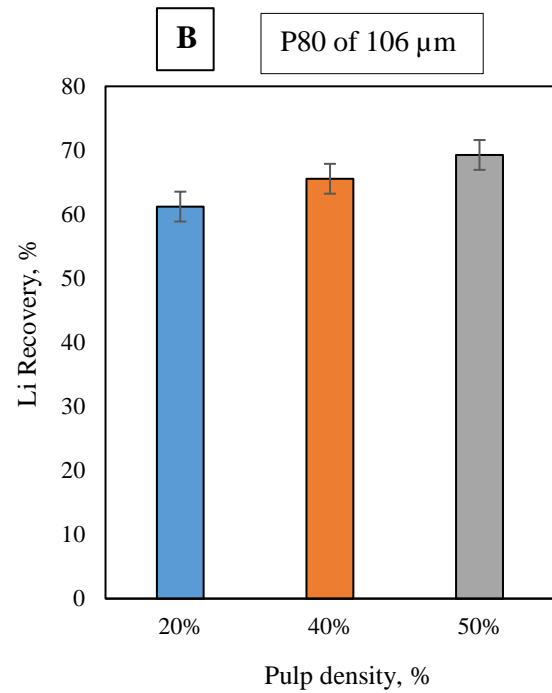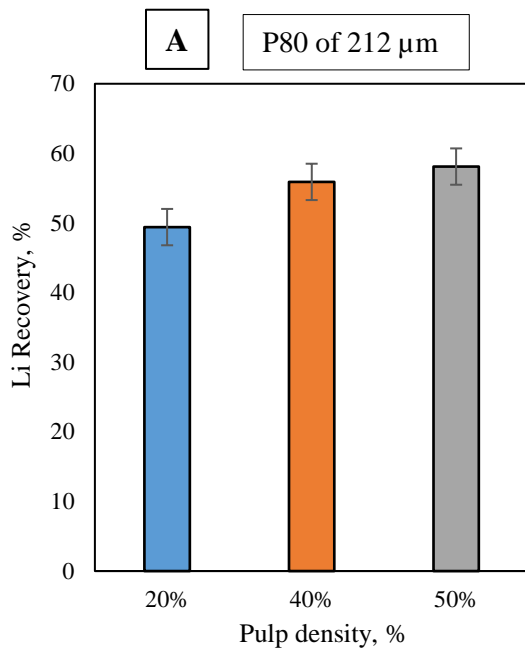
Fig. 4 Effect of Pulp Density on Lithium Recovery

4 Conclusions

The goal of this study was to extract lithium from Saltpond Pegmatite using seawater as a lixiviant. The following conclusions were drawn based on the findings and discussion: the chemical and mineralogical studies proved that, the Saltpond Pegmatites contain 17.3% of the lithium-bearing mineral, spodumene. It was also established that particle size, pulp density and time had marked effect on lithium recovery. Lithium recovery increased at finer grind and high pulp density. Recoveries attained at varying pulp densities (20%, 40% and 50%) for 212 µm were 49.4%, 55.9% and 58.1; for 106 µm, recoveries recorded were 61.2%, 65.6% and 69.3% and 64.7%, 69.4% and 75.3% for 75 µm correspondingly. After 6 hours of leaching period, particle size of 75 µm and a solid density of 50% had the highest recovery of 75.3%.

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