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QUALITATIVE ANALYSIS AND EXTRACTION OF LITHIUM FROM KEFFI SOURCED POLYLITHIONITE ORE BY HYDROMETALLURGICAL PROCESS

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ABSTRACT

This study carried out qualitative analysis and hydrometallurgical extraction of lithium from polylithionite ore obtained from Keffi pegmatite field, Nassarawa state, North-Central, Nigeria. The bulk chemical composition of the lithium rich rock was analysed by both Energy dispersive x-ray fluorescence (EDXRF) and Flame atomic emission spectroscopy (FAES) and was assayed as Li_2O with Li content of 3.25 wt% and was further characterized to have high contents of the oxides: SiO_2 (58.49%)>Al_2O_3 (14.52%) >K_2O(10.68%)> Cs_2O(4.14%)>Na_2O(3.11%)>MnO(1.55%) but very low concentrations of other main components in order Fe_2O_3(0.439%)>Nb_2O_5(0.80%)>ZnO (0.254%)>CuO (0.082%)>MgO(0.01%)>TiO_2(<0.001%). The microstructural phases of the ore sample characterized by X-ray diffraction (XRD) indicated that the ore was primarily polylithionite, having strong sharp diffractograms positioned at 27.8 and 45.5 degrees respectively. Flame atomic emission spectroscopy was used to determine the lithium content in leached solution and leached residue. Thermal roasting with sodium chloride (NaCl) and calcium chloride ($CaCl_2$) salt(s) followed by water leaching were carried out to extract lithium (^{7}Li) from the polylithionite ore. Various operational parameters including roasting temperature, roasting time, mass ratio, fractional mixed mass ratio of the additives ($CaCl_2$ and NaCl), leaching temperature and time, solid to liquid water (S/L) ratio and composition of leaching solution were investigated and optimized accordingly. The optimal Li extraction efficiency of 89.90% was attained with a fractional mix mass ratio of polylithionite ore/NaCl/$CaCl_2$ of 1:0.6:0.4, roasting temperature of 880 °C, roasting time 30 min, solid to liquid water (S/L) ratio 1:2.5, leaching temperature 60 °C and leaching time 30 min respectively. The study therefore showed that the hydrometallurgical extraction of metals of economic potentials is paramount in an era of diversification of Nigerian economy to mineral exploration, since it gave a substantial optimal lithium extraction efficiency of 89.90%.

Key words: Extraction, lithium, polylithionite ore, thermal roasting, water leaching

INTRODUCTION

Nigeria is endowed with several solid minerals. Lithium metal, like tantalum among others is currently experiencing global boom as a result of its broad spectrum applications. Lithium (Li), the lightest metal in nature (^{7}Li), has unique electrochemical properties and the highest specific heat of the solid elements. Li compounds also possess viscosity/temperature ratios [1, 2]. Because of these fascinating properties, Li and its compounds have gained much attention for use in various applications in the battery, glass, lubrication, ceramics and pharmaceutical industries [1, 2]. The journey of Li as the “metal of the future” truly began in the late 1990s when it became greatly popular in portable electronic devices [3]. It is reported that the consumption of lithium and its related products globally has tremendously increased by more than 20% per year in the past several years [4]. This shows great extent of demand for Li.

The main sources of Li are natural brines and minerals. Natural brines refer to salars, lake, oilfield and geothermal brines. Brines are the dominant source for worldwide Li-production due to simpler processes and low cost of production compared to the processes for pegmatitic minerals. Many research studies have been conducted on Li extraction from Li-bearing mineral sources such as lepidolite, spodumene, petalite, zinnwaldite, because of the persistent and tremendous growth in its demand as it is being forecasted that Li-batteries will be used to power both hybrid and fully electric automobiles [4].

The Li-contents of these ores may vary greatly and their grades largely depend on the composition and the degree of fractionation of the host pegmatitic fluid [5]. Among these pegmatite minerals, lepidolite ($K(Li,Al)_3(Si,Al)_4O_{10}(F,OH)_2$) has been characterized by their world wide spread distribution. It is characteristically poor in iron and the additional rare metal content such as cesium (Cs), rubidum (Rb) [6, 7]. The Keffi pegmatite is a rare metal type and lepidolite subtype. In recent time, polylithionite ore has also been identified as one of the mineral subtypes of the Keffi pegmatite [8 -10].

Polylithionite, chemically known as Potassium Lithium Aluminum Silicate Fluoride ($KLi_2AlSi_4O_{10}(F,OH)_2$), is named from the Greek word “POLY”, meaning many or much, and in allusion to its composition with a high Li content. It is found mostly in pegmatites with other rare minerals and in other alkaline rich pegmatitic deposites such as Ilimaussaq alkaline [11].

Polylithionite is certainly not one of the well-known mica minerals. It is a true member of the mica group of minerals closely related to other Li rich micas such as lepidolite, muscovite, tainiolite, celadolite and phlogopite [11].

Various extraction techniques including the most important ones such as lime and sulphuric acid techniques have been developed to extract lithium from the lithium bearing Ores. However, extraction of Li by the lime process ($CaCO_3$) on the one hand, uses too many limestones and high amount of energy are consumed in the process [12, 13]. The sulphuric acid technique on the other hand, involves the use of high concentration acid and complex purification procedure. The use of chloride additives such as hydrogen chloride as roasting agent gives high yield of Li. However, such process is complicated and required highly corrosion resistant equipment [14]. The drawbacks of the above processes therefore limit their further applications.

Hydrometallurgical method of Li extraction using alkali/and or alkaline chloride salt(s) (NaCl, $CaCl_2$) reaction additives is therefore, an emerging alternative technique, which has been proven to be cheaper, less energy consuming and efficient for the extraction. It is also used to refine precious, base and refractory metals like Li [14, 15]. Lithium extraction from ores utilizes thermal roasting followed by leaching. If the leaching agent is water, then, it is called hydrometallurgical process of metal extraction. Hydrometallurgy therefore, is a method of extracting metals from their ores using aqueous Chemistry.

This research work aims at carrying out qualitative analysis and hydrometallurgical extraction of Li from polylithionite ore. The objective of this study is to establish the optimal operational conditions for a new extraction process of Li extraction from polylithionite using water as an environmentally friendly leaching agent. In this study therefore, the effects of roasting temperature, roasting time, mass ratio, leaching temperature/time, solid to liquid ratio in leaching process were studied to optimize the conditions for Li extraction process.

MATERIALS AND METHODS

Materials and Sample Preparation

The lithium rich polylithionite ore was collected from Keffi pegmatite field, Nassarawa State, North central, Nigeria [16]. The polylithionilite was first upgraded by crushing and optical sorting treatment. The crushing was carried out by using jaw crusher with open setting at 100 mm of width and 10 mm of gap. The upgraded polylithionite ore (UP-Ore) was subjected to grinding via a planetary ball mill at 60rmpand screened with a #200 sieve to 100% particle/aperture size of 75µm for a complete pass [16].

Chloride salts, NaCl and $CaCl_2$, were used for roasting for increasing the Li extraction. The leaching agent was water. The whatman filter paper (41) was used for filtration experiments. All chemicals used in the study were of analytical grade.

The bulk chemical composition of the upgraded polylithionite ore (UP-Ore) was analysed by using both Energy dispersive x-ray fluorescence (XRF) (Oxford instrument X-supreme 800, UK) and Flame atomic emission spectrometer (FAES) (280FS, USA).

Roasting was undertaken to produce water soluble cacine for efficient Li leachability [16]. During the chloride salt(s) roasting stage, each stipulated weighed mass ratio of upgraded polytlithionite ore (UP-Ore) was first mixed with stipulated weighed mass ratio(s) of NaCl and / or $CaCl_2$ in the graphite crucible and then heated in an electrically tubular furnaceat the defined temperature [16].

The roasted cacine sample was subsequently leached with water at 60 °C temperature for 0.5 h leaching time, using solid cacine-to-liquid water mass ratios of 1:2.5 to release lithium into solution [16].

The mixture of liquid and solid (residue) phases formed on standing were separated by filtration. The leached residue was dried in an oven at 120 °C for 4h [16].

The dried residue was weighed and dissolved with 70% HF acid in the ratio of 1:2 and heated to near dryness then dissolved with 1% HCl [16].

In all the experiments, FAES was used to determine the content of Li, using standard procedures.

Data Analysis

To acquire more accurate data for Li leachability in all the parameters that were analysed, the content of Li in both leached solution and leached residue after chemical digestion were determined by FAES. The leachability of Li in both leached solution and leached residue expressed in percentage were calculated according to the formulae:

$$L(\%) = \frac{{}_{2}}{{}_{2} + {}_{2}} \; 100 \qquad 1$$

$$R(\%) = \frac{{}_{2}}{{}_{2} + {}_{2}} \; 100 \qquad 2$$

$$V_{Li}\ (\%) = 100 – (L+R) \qquad 3$$

Where:

L = Lithium extraction efficiency by water (filtrate)

R= Residual ratio of lithium in leached residue

M_fLi_2O = Lithium mass concentration in the leached solution (filtrate)

M_rLi_2O = Lithium mass concentration in the leached residue after chemical digestion

V_{Li}= Volatilization ratio of lithium during roasting.

RESULTS AND DISCUSSION

Chemical Analysis of the Ore

Table 1: Result of the bulk chemical composition analysis (%) of the upgraded raw polylithionite ore by XRF and FAES.

Oxide composition	Value (%) w/w
SiO_2	58.49
TiO_2	< 0.001
Al_2O_3	14.52
F	1.78
Fe_2O_3	0.439
CaO	0.06
MgO	0.01
Na_2O	3.11
K_2O	10.68
MnO	1.55
V_2O_5	<0.001
Cr_2O_3	0.045
CuO	0.082
Li_2O	3.25
ZnO	0.254
Cs_2O	4.14
Nb_2O_5	0.80
Ta_2O_5	0.29
L.O.1	0.50

The bulk chemical composition analysis of the upgraded polylithionite ore was determined by using both Flame atomic emission spectroscopy and Energy dispersive x-ray fluorescence respectively, and the relevant compositions are given in Table 1. FAES determined Li, Na and K, because, they are easily ionized elements and required low temperature atomization. XRF determined Si, Al, Ca, Mg, Fe and Ti respectively. The active compositional order of the oxides and fluorine in order of concentration (%) can be expressed thus: $SiO_2 > Al_2O_3 > K_2O > Cs_2O > Li_2O > Na_2O > F > MnO$. The result proved that, the Li content of 3.25% in the ore in question is greater or equal and less or equal the Li content in other Li bearing minerals (lepidolite, spodumene, petellite) and is within the Li content of the global Li bearing minerals (1.55-7.03%w/w). The result of the bulk chemical composition analysis obtained herein is in strong agreement with the findings of Akinola and Co-workers for pegmatitics minerals. According to them, the Li contents of these ores may vary greatly as their grades largely depend on the composition and degree of fractionation of the host pegmatitic fluid [5].

Mineralogical Composition Analysis of the Ore

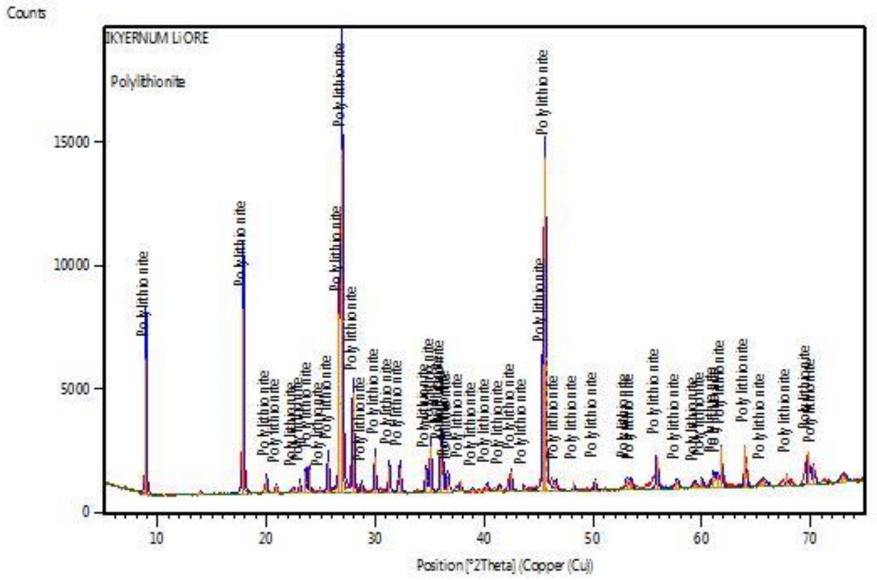

Figure 1: X-ray diffraction (XRD) pattern of the upgraded polylithionite ore

The mineralogical composition analysis of the UP-Ore was determined by X-ray diffraction and the result of the characterization is shown in Figure 1. The result showed that, the ore is mainly polylithionite; $KLi_2 AlSi_4O_{10} (F,OH)_2$. This result on one hand, is not in close agreement with what was obtained by most previous researchers whose XRD patterns of the first upgraded ore gave more than one minerals namely lepidolite, albite, quartz, spodumene [16,17]. This may be attributed to the differences in environmental geological chemistry or setting. On the other hand, the result obtained herein is in strong association with what was obtained by Lucia and co-workers in 2015 whose XRD pattern presented only a single mineral known as spodumene, but not polylithionite in question [18]. This similarity in diffractograms with single mineral may be related to similar environmental geochemistry but different compositions and degrees of fractionation of the host pegmatite.

Effect of Roasting Temperature on Lithium Extraction Efficiency

Table 2: Effect of roasting temperature on Li extraction efficiency based on m (UP-Ore): m($CaCl_2$) = 1:1; 30min roasting time

Roasting Temperature (°C)	L (%)	R (%)	V_{Li} (%)
600	19.87	80.13	0
700	28.47	71.53	0
800	35.33	64.67	0
900	71.41	26.21	2.38
1000	57.98	29.17	12.85

The UP-Ore was mixed with alkaline chloride salt, $CaCl_2$ on a mass ratio of 1:1 and then chloride roasted for 30 min to form the solid cacine soluble state. The effect of roasting temperature from 600°C to 1000°C on Li extraction efficiency (LEE) was then investigated. The related results were shown in Table 2. The result showed that, the Li extraction efficiency increases rapidly from a minimum temperature value at 600 °C to the maximum temperature value at 900 °C due to low volatilization/loss of lithium chloride (LiCl) (2.38%). At very high roasting temperatures beyond 900 – 1000 °C, the volatilization of LiCl increases, thus, resulting to the loss of Li and corresponding decrease in LEE content. This increase in LiCl volatility and loss of Li (12.85%) and decrease in LEE (57.98%) may be attributed to complete breaking of the chemical bonding holding the particulate atoms together due to the absorption of high amount of heat energy at 1000^{O}C roasting temperature [18]. This in turn, results to the increase in vibrational motion between the particulate atoms in question and subsequent bond weakening and breaking thus, favouring LiCl volatilization, Li loss and significant decrease in the LEE (57.98%) at 1000 °C roasting temperature. Considering that, the recovery of Li from leach liquor is more conducive than from gas, the balance of the Li extraction efficiency and the volatilization of Li during chloride roasting are very important. Therefore, it is expected to increase the Li extraction efficiency and decrease the Li volatilization during chloride roasting. Hence, further experiments were carried out at 900 °C as an optimized roasting temperature with high yield of LEE (71.41%) and low Li volatilization (2.38%) during chloride roasting.

Effect of Roasting Time on Lithium Extraction Efficiency

Table 3: Effect of roasting time on Li extraction efficiency based on m(UP-Ore) : m($CaCl_2$): m(NaCl)=1:1:1; 900 °C optimized roasting temperature

Roasting Time (min)	L (%)	R (%)	V_{Li} (%)
5	16.18	83.82	0
15	44.62	55.38	0
30	71.41	26.21	2.38
60	75.32	13.80	10.88
90	76.12	12.74	11.14

A series of experiments were carried out for 5 – 90 min in order to investigate the effect of roasting time on Li extraction efficiency based on the mass ratio of polylithionite ore to NaCl to $CaCl_2$ and optimized roasting temperature 900 °C as the experimental conditions. The results of Li extraction efficiencies (LEEs) are shown in Table 3. The result showed that, the LEEs at 5, 15 and 30 mins were 16.18%, 44.62% and 71.41% respectively. This implies that, the LEEs increased significantly with increase in roasting time from 5-30 min due to low volatilization of LiCl of 2.38% at 30 min roasting time. When the roasting time was increased to 60 min and 90 min, there was no significant increase in the Li extraction efficiency due to the increase in volatilization of LiCl. This slight stepwise increase in the LEEs (75.32% and 76.12%) at these increased roasting times (60 and 90 min) may be attributed to the complete bond breaking among the sample's particulate atoms due to long roasting durations and high resultant heat energy absorption at these roasting times. This high absorption of heat energy increases the rate of atomic vibration and resultant complete bond breaking to let loose the sample's components, hence, favoring high loss of Li by volatilization of LiCl (10.88%, 11.14%) and resultant insignificant increase in LEEs (75.32%, 76.12%) in return [19].

Effect of Mass Ratio of Upgraded Polylithionite Ore to $CaCl_2$ or NaCl on Lithium extraction Efficiency

Table 4: Effect of mass ratio of upgraded polylithionite ore to chloride salt additives on Li extraction efficiency based on m(UP-Ore): m($CaCl_2$)=1:1-2:1; m(UP-Ore): m(NaCl) =1:1-1:2; $900^{O}C$ optimized roasting temperature; 30 min optimized roasting time

Chloride salt additive	Mass ratio of polylithionite ore to chloride salt additive	Lithium extraction efficiency%
$CaCl_2$	2:1	57.51
	1:1	71.41
NaCl	1:1	61.98
	1:2	72.49

A series of roasting experiments were carried out at different mass ratios of upgraded polylithonate ore to $CaCl_2$ or NaCl maintaining the optimized 900 °C and 30 min roasting temperature and time respectively to determine the effect of mass ratio of alkaline/alkali chloride salts on Li extraction efficiency. The results of the LEEs are shown in Table 4. The data obtained showed that, when the polylithionite ore and $CaCl_2$ were in different mass ratios (2:1), the LEE was 57.51%. When the polylithionite ore and $CaCl_2$ were in same mass ratio (1:1), the LEE was 71:41%. Similarly, when the polylithionite ore and NaCl were in same mass ratio (1:1), the LEE was 61.98%. When the polylithionite ore and NaCl were in different mass rations (1:2), the corresponding LEE was 72.49% respectively. The result therefore indicated that, $CaCl_2$ roasting additive is more efficient than NaCl for extraction of Li from polylithonite. This is because, $CaCl_2$ even in equal proportion with NaCl (1:1, UP-Ore: $CaCl_2$ and 1:1, UP-Ore: NaCl) extracts more Li from the ore than NaCl. This may be attributed to the differences in the melting points of $CaCl_2$ and NaCl. $CaCl_2$ additive is a deliquescent salt and has melting point (772 °C) lower than NaCl whose melting point is 801°C and therefore, melts faster than NaCl under same conditions of roasting temperature and time. The earlier melting of $CaCl_2$ into the liquid phase enables its solvent action of dissolution in the chemical bonds among the ore's particulate atoms, setting them loose and converting them to free radicals during the roasting process [20, 21]. These free radicals (between the UP-Ore and $CaCl_2$ solvent) interact and recombined forming a very soluble solid cacine (LiCl) with reasonable LEE than that of the NaCl due to its late melting and solvent functioning [21].

Effect of Fractional Mixed Mass Ratio of NaCl and $CaCl_2$ to Upgraded Polylithionite Ore on Lithium Extraction Efficiency

Table 5: Effect of fractional mixed mass ratio of NaCl and $CaCl_2$ to upgraded polylithionite ore (UP-Ore) on Li extraction efficiency based on optimized $900^{O}C$ roasting temperature; 30min roasting time

m(UP-Ore):m(NaCl):m($CaCl_2$)	Lithium extraction efficiency (%)
1:0.1:0.9	73.82
1:0.2:0.8	75.34
1:0.3:0.7	79.14
1:0.4:0.6	84.21
1:0.5:0.5	86.98
1:0.6:0.4	88.84
1:0.7:0.3	71.72
1:0.8:0.2	63.31

In order to investigate the cost effectiveness of this method, chloride roasting additives (NaCl and $CaCl_2$) were rationed in fractions and termed fractional mixed mass ratio. In this experiment, variable fractional mixed mass ratios of $CaCl_2$ and NaCl were roasted with a fixed mass ratio of UP-Ore (l g) in a series of investigations to optimize the condition of Li extraction under the conditions of $900^{O}C$ and 30 min roasting temperature and time respectively. Table 5 shows the results of LEEs. It can be observed from the results that, the LEE significantly increases with increase in the ratio of NaCl as a partial substitute of $CaCl_2$. When the mixed mass ratio of UP-Ore-to-NaCl-to-$CaCl_2$ was 1:0.4:0.6, the LEE raised to 84.21%. When the fractional mixed mass ratios of UP-Ore-to-NaCl-to-$CaCl_2$ were1:0.4:0.6, 1:0.5:0.5 and 1:0.6:0.4 respectively, the LEE significantlydecreased with further increase in the mass proportion of NaCl. Hence, the mixed mass ratio of 1:0.6:0.4 (UP-re-to-NaCl-to-$CaCl_2$) with an optimum LEE value (88.84%) should be the best proportion combination in terms of economical industrial Li Production.

The stoichiometric reaction for the roasting of polylithionite ore with NaCl and / or $CaCl_2$ for the Li extraction may be proposed thus (M= Li, K):

$$CaCl_{2(s)} + M_2O_{(s)} + Al_2O_{3(s)} + 2SiO_{2(s)} \xrightarrow{heat} 2MCl_{(s)} + CaAl_2Si_2O_{8(s)} \qquad 1$$

$$2NaCl_{(s)} + M_2O_{(s)} + Al_2O_{3(s)} + 6SiO_{2(s)} \xrightarrow{heat} 2MCl_{(s)} + 2NaAlSi_3O_{8(s)} \qquad 2$$

The chemical stoichiometric ratio of Al_2O_3 and Si_2O in above equations (1 and 2) proved that, $CaCl_2$ is more efficient than NaCl in decomposition of the Ore and subsequent Li extraction.

However, roasting the polylithionite ore with a chloride salt mixture (NaCl and $CaCl_2$) gives a better Li extraction yield than either of the single chloride salts. This is because, the melting point of the mixture of NaCl and $CaCl_2$ is lower than either of the chloride salts alone, which increases the fluidity of the chloride melt [22]. This then, allows rapid diffusion of the chloride salt to the surface of the polylithionite, facilitating selective Li extraction and a pure product yield. The result of this study also proved that, this hydrometallurgical method of Li extraction using chloride roasting additives (NaCl, $CaCl_2$) is cost effective since the chloride roasting additives rationed in fractions still gave reasonable LEEs (75.34%, 79.14%, 84.21%, 86.98%) with the optimum LEE value (88.84%) at 1:0.6:0.4 UP-Ore/NaCl/$CaCl_2$ fractional mixed mass ratio. Comparatively, other methods of Li extraction such as sulphuric acid and alkaline ($CaCO_3$) methods, required large amount of acid and limestone thus, making them expensive [22].

Effect of Roasting Time and Temperature on Optimized Fractional Mixed Mass Ratio of $CaCl_2$ and NaCl to Upgraded Polylithionite Ore

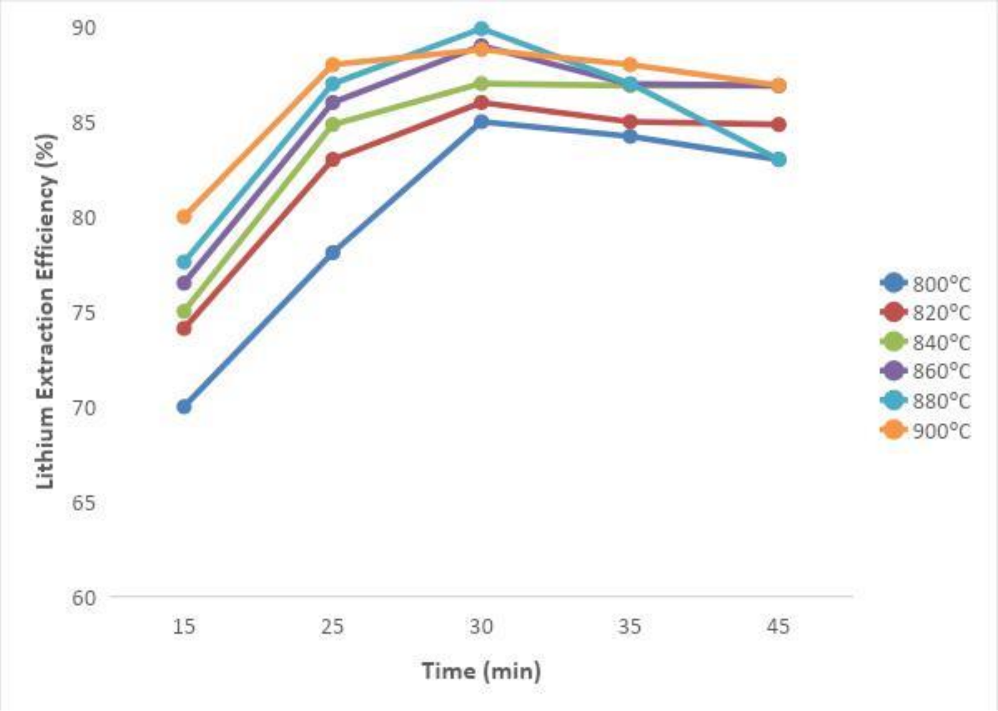

Figure 2: Effect of roasting time and temperature on lithium extraction efficiency based on optimized fractional mixed mass ratio m(UP-Ore):m(NaCl):m($CaCl_2$) =1:0.6:0.4

In order to investigate if there is a downward shift in energy consumption from the optimized 900°C roasting temperature or a downward/upward shift in roasting duration from the optimized 30 mins roasting time now that the chloride roasting additives are expressed in fractional mixed mass ratios, a set of experiments were conducted on conditions of optimized fractional mixed mass ratio 1:0.6:0.4 UP-Ore-to-NaCl-to-$CaCl_2$ so as to optimize the roasting reaction time and temperature conditions for LEE for the fractional mixed mass ratio. The results of LEEs are shown in Figure 2. The result shows a rapid progressive increasing trend in LEE following a significant increase in roasting reaction time from 15-30 min due to the low LiCl volatility. This is because, the chloride roasting additives are now in fractions hence, required less roasting time thus, favouring low melting temperature, less Li volatility and resultant increase in LEE. This therefore, leads to a downward shift in roasting temperature from 900°C to 800°C and no shift in roasting time below or above 30 min with better LEE. Apparently, the LEE however, decreases appreciably on further increase in roasting time to 35 min and 45 min respectively. This may be attributed to the loss of LiCl by volatilization since the longer the sample's roasting duration in the furnace, the more its exposure to heat absorption and the more volatile it becomes due to bond breaking, thus, yielding less LEE in return. On the other hand, roasting temperature also significantly affects the LEE. It can be observed that, LEE increases correspondingly with increase in roasting temperature from 800-880°C with an optimum value of 89.90%. However, LEE drops beyond 880°C roasting temperature. This decrease in LEE value to 89.80% at 900^{O}C and 30 min roasting temperature and time, may be attributed to the high volatility of LiCl since the chloride roasting additives mixture are now in fractional mass ratios (smaller proportions) and therefore, required less roasting temperature for their decomposition unlike when the chloride roasting additives mixture were in whole mass ratios. An optimum value of 89.90% LEE was obtained at 880°C and 30 min roasting temperature and time respectively. Thus, 880°C and 30 min are the optimized roasting temperature and time conditions suitable for the fractional mixed mass ratio 1:0.6:0.4 UP-Ore, NaCl, $CaCl_2$. This outcome proved that, LEE is significantly favored with increase in roasting temperature and time respectively. However, the increase in both roasting reaction temperature and time have a limit of maximum extraction beyond which the LEE has no corresponding increase. The result of this study also demonstrated that, the hydrometallurgical method of Li extraction using chloride roasting additives mixture (NaCl, $CaCl_2$) is not only cost effective but also, less energy consuming since a downwards shift in energy consumption was observed from 900°C to 880°C roasting temperature when the sample's mixture was rationed in fractional mass ratios [23,24].

Effect of Leaching Temperature and Time on Lithium Extraction Efficiency

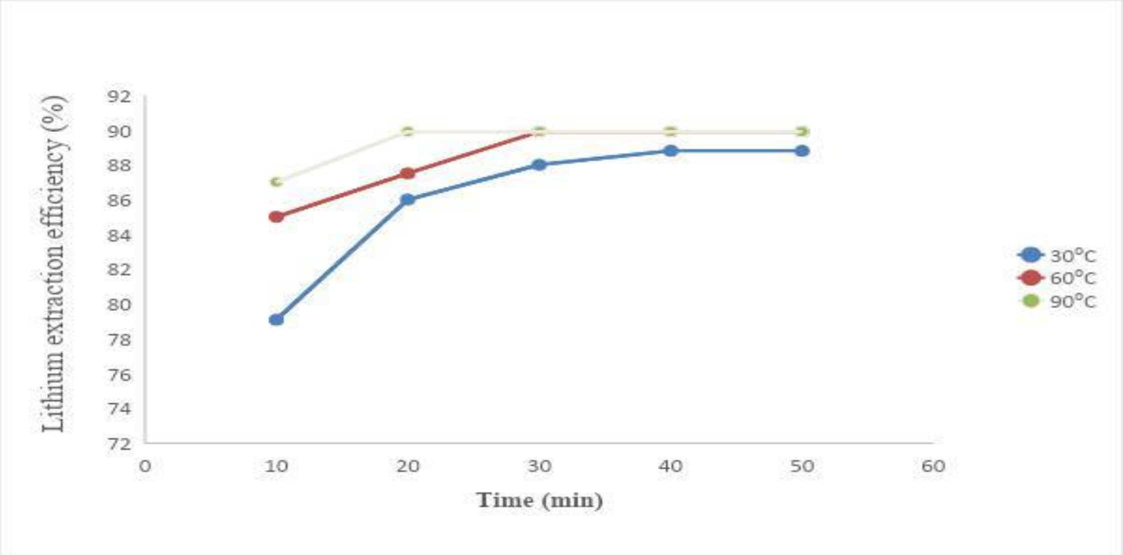

Figure 3: Effect of leaching temperature and time on lithium extraction efficiency based on optimized fractional mixed mass ratio m(UP-Ore):m(NaCl):m($CaCl_2$) =1:0.6:0.4; 880 ^{O}C roasting temperature; 30 min roasting time

To study the effect of leaching reaction temperature and time on LEE so as to determine if there is a downwards or upwards shift in the leaching temperature/time below or above 60 °C and 30 min leaching temperature and time with better LEE now that the NaCl and $CaCl_2$ roasting additives are in fractional mass ratios; experiments were performed on condition of the optimized fractional mixed mass ratio of 1:0.6:0.4 UP-Ore to NaCl to $CaCl_2$, roasting temperature 880 °C, roasting time 30 min, and solid to liquid water ratio 1:2.5 respectively. The result of LEEs is plotted in Figure 3. The data obtained proved that, when the leaching reaction temperature was at 30°C, the LEE increases progressively from 10-50 min leaching time, though, did not reach maximum LEE. When the leaching reaction temperatures were further increased to 60 ^{O}C and 90 ^{O}C, the LEE remarkably increases progressively from 10-30 mins and reaches an optimal value (89.90%) at 30 min. On further increase in leaching reaction time (30-50 min), the LEE almost maintained a steady peak value (89.90%). Although, the LEEs at both 60 °C and 90 °C increased simultaneous and reached the peak value (89.90%) at 30 min leaching time, the LEE at 60 °C leaching temperature increased more progressively further than that at 90 °C before maintaining a steady peak value (89.90%) beyond 30 min leaching time. Therefore, 60 °C and 30 min leaching temperature and time are considered the best convenient optimal leaching temperature and time that favour optimal Li production since the LEEs (79.1%, 86.0%, 88.8%, 88.8%) below 60 °C (that is 30 °C) leaching temperature and below or above 30 min (10 min, 20 min, 40 min, 50 min) leaching time did not reach the optimal LEE value (89.90%) obtained at 60 °C/30 min leaching temperature and time; and LEEs (89.90%, 89.90%) above 60 °C (90 °C) and 30 min (40 min, 50 min) leaching temperature and time also did not show an upwards progressive increase above the optimal LEE value (89.90%) obtained at 60 °C/30 min leaching temperature and time respectively. Thus, the result illustrated that, there is no downwards or upwards shift in leaching temperature/time below or above 60 °C/30 min with better LEE. It is noted from the result that, LEE is a function of leaching temperature and time. As leaching temperature and time increase, LEE raises simultaneous. However, the longer the leaching time, the lower the leaching temperature and thus, the lesser the LEE due to low sample's particulate-leaching water collision and resultant less bond breaking and leaching of Li in the process [25].

Effect of Solid Cacine to Liquid Water (S/L) Ratio in Leaching Process on Lithium Extraction Efficiency

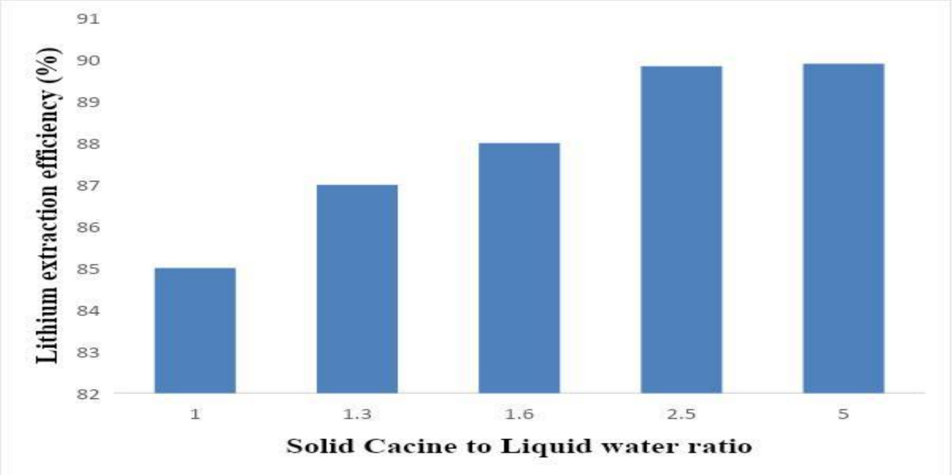

Figure 4: Effect of solid cacine to liquid water (S/L) ratio on leaching process on lithium extraction efficiency based on optimized fractional mixed mass ratio of m(UP-Ore):m(NaCl):m($CaCl_2$) =1:0.6:0.4, 880°C roasting temperature; 30 min roasting time

Solid cacine to liquid water ratio (S/L) effect on LEE was investigated from 1.0-5.0% (w/v) in order to determine if there is a downwards or upwards shift in S/L ratio below or above 1:2.5 S/L ratio now that the NaCl and $CaCl_2$ roasting additives are expressed in fractional mass ratios. The leaching conditions were as follows: Pre-optimized mixed mass ratio 1:0.6:0.4 UP-Ore, NaCl, $CaCl_2$, roasting temperature 880 °C, roasting time 30 min, leaching temperature 60 °C and leaching time 30 min respectively. The results are plotted in Figure 4. It can be observed from the results that, when the S/L mass ratios were 1:1.0, 1:1.3 and 1:1.6 respectively, the LEEs show a slight step-wise increase in values (85.0%, 87.0%, and 88.0%) without attaining the peak. When the S/L mass ratios were 1:2.5 and 1:5.0 respectively, LEEs remarkably increased rapidly and reached the maximum values of 89.84% and 89.90% respectively. Apparently, the S/L mass ratio of 1:2.5 is more unsaturated and efficient in Li extraction (89.84%) than the S/L ratio 1:5.0 which is readily saturated and less efficient in LEE with a slight fractional difference (89.90%). Therefore, the S/L mass ratio 1:2.5 is the most favourable and economical condition for industrial Li production. However, high S/L mass ratio is quite helpful for the accumulation of Li and is more realistic for full scale production since there is no downwards shift in S/L mass ratio of 1:2.5 with better LEEs (85.0%, 87.0%, 88.0%) but a slight increase in LEE (89.90%) above S/L mass ratio (1:2.5) leading to an upwards shift in S/L mass ratio (1:5) [26].

RECOVERY OF Li FROM THE LEACHED SOLUTION

The recovery of Li from the solution can be achieved by addition of NaOH to adjust the pH of the solution between 13 and 14 and then precipitate and remove silicate and aluminum by filtration. Then Na_2CO_3 solution would be added to the resulting filtrate to lower the pH down to 6.5 and the resulting solution would be concentrated by heating to precipitate lithium carbonate, Li_2CO_3 [16].

CONCLUSION

An improved optimization hydrometallurgical process with alkali and alkaline chloride salts (NaCl, $CaCl_2$) roasting followed by water leaching was used to extract lithium from polylithionite ore. The results demonstrated that, roasting temperature, roasting time, leaching temperature and leaching time and mass ratio of chloride salt additives (NaCl and $CaCl_2$) affected the lithium extraction efficiency significantly. The optimum operating process parameters with lithium extraction efficiency of 89.90% were established as follows: fractional mixed mass ratio of upgraded polylithionite ore/NaCl/$CaCl_2$ of 1:0.6:0.4, roasting temperature

880 °C, roasting time 30 min, leaching temperature 60 °C,leaching time 30 min and solid cacine to liquid water (S/L) mass ratio of 1:25 respectively. The study therefore, showed that, the hydrometallurgical extraction of Li using chloride roasting additives (NaCl and $CaCl_2$) is cost effective, less energy consuming and efficient, since the chloride additives rationed in fractions (1:0.6:0.4 ore, NaCl, $CaCl_2$) gave substantial optima lithium extraction efficiency of 89.90% at the optimized conditions.

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