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Research Article

Hydrometallurgical Treatment of Pegmatite Ore for the Recovery of Battery-grade Lithium Chloride (LiCl) Precursor Compound

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ABSTRACT

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This study presents a hydrometallurgical process for the recovery of battery-grade precursor compound from pegmatite ore, adopting calcium chloride-assisted roasting and aqueous leaching technique were employed. Pegmatite ore of Nigerian Origin were subjected to thermal treatment in the presence of CaCl_2 at varying temperatures (500–750 °C) to enhance the solubility of target metal species of lithium. This was subsequently followed by aqueous leaching under controlled conditions of 85 °C temperature, 10 g/L solid-to-liquid ratio, 120 minutes to optimize lithium recovery. The influence of parameters of CaCl_2 dosage on leachability was systematically investigated. Study reveals that a temperature of 700 °C and 1: 3 ore / CaCl_2 gave maximum lithium extraction of 91.1 %. Analytical techniques including XRD, ICP-OES, and SEM-EDS were employed to characterize the roasted solids and leachates, confirming the transformation of phases into soluble intermediates. The process achieved selective recovery of high-purity precursor chloride compound of high-grade value.

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INTRODUCTION

Pegmatite ores are coarse-grained igneous rocks enriched in alkali and alkaline earth metals, commonly hosting minerals such as montebrasite, amblygonite, albite, quartz, and muscovite. Pegmatite holds vast abundant lithium metals and their aluminosilicate matrix presents significant challenges to direct hydrometallurgical extraction due to its crystallinity nature. Conventional acid leaching methods are often inefficient or environmentally unfriendly when applied to untreated pegmatite except when aided. Therefore, a pre-treatment step is essential to solubilize the metal content and improve extraction (Abaka-Wood *et al.*, 2022).

The global demand for high-purity lithium precursor compounds has driven the search for alternative raw material sources beyond the conventional brine lithium sources. Over the years, brine-based extraction has dominated industrial production of lithium compounds due to its simplicity and low operational cost (An *et al.*, 2012; Butt *et al.*, 2022). However, limitations, including low metal concentrations, long evaporation cycles, limited accessibility, and significant environmental concerns remain a critical challenge in the hydrometallurgical treatments of brine sources. Grageda *et al.*, 2020, studied the analysis of a process for producing battery-grade lithium hydroxide from brine sources, with major emphasis on process high cost due to several purification stage requirements and high waste generation. These challenges, amidst others, have prompted interest in hard rock lithium sources, particularly pegmatite ores, which offer higher concentrations of lithium metals and present a more viable pathways for the recovery of battery-grade lithium compound as a battery grade precursor (Bishimbayeva *et al.*, 2018; Choubey *et al.*, 2016).

Hydrometallurgical chloride-assisted roasting using salts of NaCl, KCl, or CaCl₂ promotes the breakdown of aluminosilicate or phosphate pegmatite structures and the formation of water-soluble metal chlorides, enabling efficient extraction under mild leaching conditions (Karrech *et al.*, 2020). This, approach offers a cleaner and more selective alternative to aggressive acid digestion or high-pressure processes. Several authors have adopted aqueous chlorination extraction process adopting digestion process by hydrochloric acid or hydrogen chloride gas at 935°C for the production of lithium chloride from

lepidolite (Barbosa *et al.*, 2014). However, this process has little adaptation compared to the sulfuric acid processing. Authors stressed the use of HCl for digestion is sometimes regarded undesirable due to the corrosive nature, also it is considered to be non-specific towards lithium as it dissolves most of the other components along, making purification more complex (Margarido *et al.*, 2014; Karrech *et al.*, 2020). Recently, Martin *et al.*, (2017) experimented a novel method to recover lithium from zinnwaldite using HCl. Zinnwaldite ore was first digested by 29 % HCl under reflux and atmospheric pressure for 7 hours, reaching efficiency of 94%. Significantly, authors noted that by-products formed during HCl digestion, has advantages over the conventional H₂SO₄ digestion process. In a related study, Ni *et al.*, (2024) investigated thermochemically driven crystal phase transformation through mechanical activation-assisted chlorination roasting for the selective extraction of lithium from spodumene. The researchers utilized Chinese spodumene ore, subjecting it to a 3-hour activation process that enabled complete chlorination using a CaCl₂/spodumene ratio of 1:1 at an activation temperature of 900 °C. Subsequent leaching was conducted at 50 °C for 30 minutes, resulting in a 91.34% lithium extraction and the conversion of spodumene into water-soluble LiCl. Similarly, Braga *et al.* (2025) explored the chlorination treatment of Brazilian spodumene ore using calcium chloride (CaCl₂) and magnesium chloride (MgCl₂). The process involved thermal treatment with spodumene/chloride at a ratio of 1:6, and chlorides combined at a 2:1 CaCl₂/MgCl₂ ratio, heated to 1150 °C for 30–120 minutes. This was followed by water leaching at 95 °C for 240 minutes, yielding approximately 95% lithium extraction and producing a pregnant leach solution of LiCl.

The extraction of Li, K and Rb was also carried out by Kristianova *et al.*, (2023). Optimum extraction of 77 % Li, 90 % K and 90 % Rb, were reported at four times stoichiometric amount of CaCl₂ at 1000 °C roasting temperature at 20 minutes at the heating rate of 10 °C/min

Although chlorination-assisted roasting has been widely applied for lithium liberation from ores, concerns persist regarding its environmental impact and operational cost, particularly due to high energy consumption and reagent dosage requirements. Despite these advances, limited studies have focused on CaCl₂-assisted roasting of

Nigerian pegmatite ores, which remain under-explored despite their potential. Prior works largely emphasize spodumene or lepidolite, leaving a gap in understanding the behavior of Nigerian pegmatite under chloride roasting conditions. Moreover, CaCl_2 has shown superior chlorination efficiency and thermal stability compared to NaCl and KCl , particularly in breaking down aluminosilicate matrices (Ni et al., 2024), yet its target application to Nigerian pegmatite has not been systematically evaluated.

Thus, this study adopts a chloride-roasting and aqueous leaching technique using CaCl_2 to improve lithium recovery while reducing environmental impact and operational cost. It contributes to sustainable extraction technologies by optimizing temperature, ore-to-salt ratio, particle size, and time duration for lithium recovery from Nigerian pegmatite using a low-thermal chlorination approach.

2.0 MATERIALS AND METHODS

Materials

The experimental raw material comprises pegmatite ore concentrates (LiAlPO_4F) from Iwore-Ile Oyo-State, Nigeria. The raw ore underwent crushing, ball milling, drying and sizing to obtain experimental samples of varying particle sizes. Its chemical composition was primarily determined through analysis as ICP-OES and XRF respectively (Baba et al., 2018; Ni et al., 2024). For the ICP-OES analysis, samples were digested using aqua regia ($\text{HCl} : \text{HNO}_3$ in a 3:1 ratio) to ensure complete dissolution of metal constituents. Calibration was performed using certified multi-element standard solutions, and detection limits for lithium and associated elements were maintained within the range of 0.01 – 0.05 mg/L to ensure analytical accuracy.

Procedure

Mechanical activation of the pegmatite ore (LiAlPO_4F) and the calcium chloride (CaCl_2) salt was conducted in a ball-mill machine with rotating speed of 300 rpm. The activated mixture was then charged into the muffle furnace until the desired temperature is reached, to form the roasting process. This is then allowed to cool and followed through to leaching procedure. The setup is mounted on a digitally controlled hot plate to maintain temperature and stirring speed. The experiments were conducted at a set condition of 10 g/L, 85 °C, and a leaching duration of 120 minutes. Thereafter, the residue obtained was dried and the leaching rate calculated from equation 1.

$$\Lambda = (c \times V) / (m \times w) \times 100\% \quad (1)$$

(Λ) denotes the leaching efficiency in (%), (c) represents ion concentration in (g/L), (V) denotes the volume of filtrate in (L), (m) represent weight of ore in (w) denotes the Li content in the original ore sample in (%) (Peng et al., 2012; Ni et al., 2024).

RESULTS AND DISCUSSION

Chemical composition of pegmatite ore

The chemical composition of the digested concentrate was thoroughly examined using ICP-OES and XRF instruments. The major compositions include Al (11.55%), P (0.682%), Li (2.2%), Mg (0.009%), Na (1.88%), Fe (3.7%), Zn (3.3%) and Ca (3.5%) among others, as represented in table 1. The surface morphological structure reflects the concentrate exhibited a non-porous small to medium grain packed structure as depicted in figure 1a. The EDS image as depicted in figure 1b also supported the ICP-OES analysis with presence of peaks correspondence to the analysed metals.

Table 1: Elemental composition of pegmatite ore - LiAlPO_4F (wt%)

Elements	Al	P	Li	Mg	Na	Fe	Zn	Ca	Cr	Mn
Composition	11.55	0.682	2.2	0.009	1.88	3.7	3.3	3.5	1.1	1.6

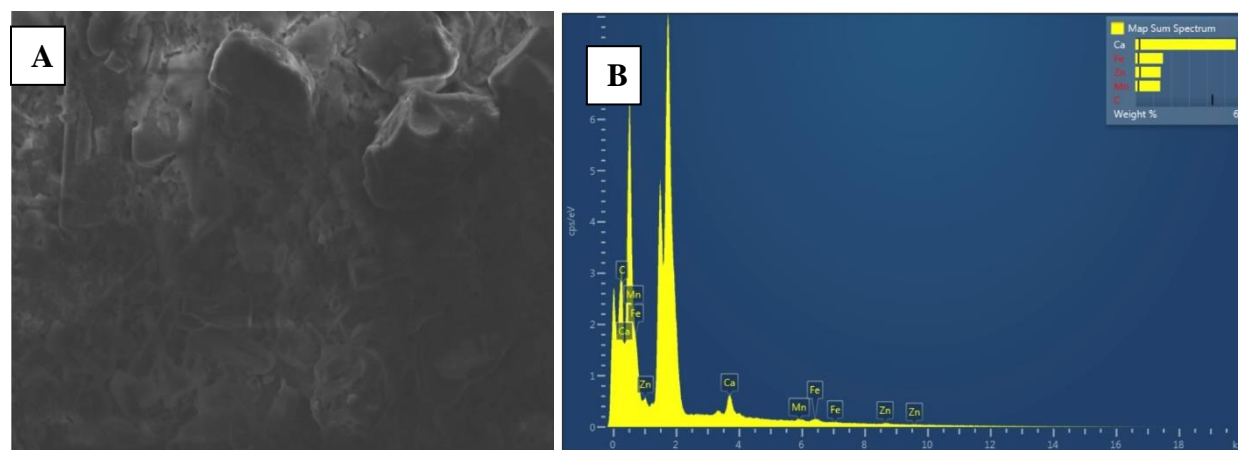


Figure 1a-b: SEM image of raw pegmatite ore & EDS image displaying elemental composition of raw ore

Effect of Pegmatite Ore: CaCl_2 (w/w)

Figure 2 shows the extraction efficiency as a function mass ratio of amblygonite to calcium chloride salt. The roasting product was leached at the conditions of 45 μm ore size, 300 rpm rotating speed, 10 g/L solid/liquid ratio, 85 $^\circ\text{C}$ temperature within 120 minutes using water as the leachant. During the experiment, mass ratios of ore : salt were varied as 0.5:1, 1:1, 1:2 and 1:3 respectfully.

The extraction efficiency of lithium increases as CaCl_2 mass increased. This suggests that the addition of CaCl_2 is significant on the extraction of lithium as represented as equation 2. At the mass ratio of 1:4 at 600 $^\circ\text{C}$ dissolution increased to a maximum of 88.5% before decreasing. However, the mass ratio over 1:4 was not considered to minimize the usage of salt or to prevent over-roasting.

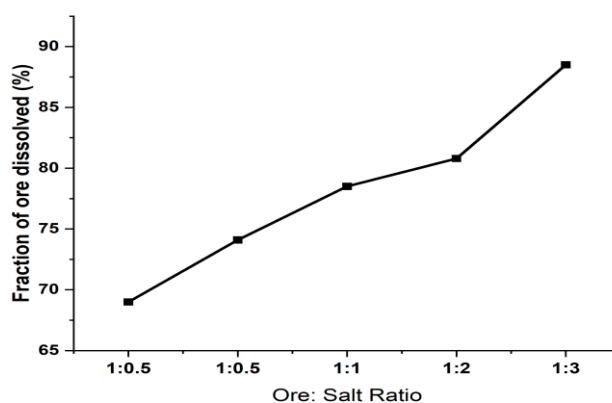
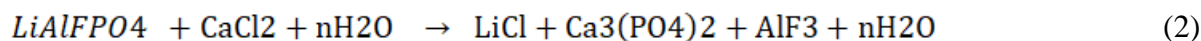


Figure 2: Effect of pegmatite ore and calcium chloride salt ratio

Effect of Roasting Temperature ($^\circ\text{C}$)

To optimize the temperature effect of CaCl_2 cum pegmatite ore roasting, the effects of the parameter were investigated from 500 to 750 $^\circ\text{C}$ (Figure 3).

In these experiments, a constant ore and CaCl_2 ratio of 1:3 was maintained at the varying set temperature for 60 minutes, the relationship between the efficiency of lithium and the roasting

temperature as demonstrated reveals, the extraction efficiency increases and then reached maximum values of 91.1%, as the roasting temperature was increased from 500 to 700 °C. However, the extraction efficiency of lithium decreases when the roasting temperature is high at around 750 °C, at this temperature, roasted samples indicates adhesion to crucible which is as a result that one or more reaction byproducts during chlorination process exist in a molten state and consequently

resulted into the fusion causing efficiency decrease. This finding is similar to the observation of Ni *et al.*, 2024, with reports of decrease in efficiency at over 900 °C during the roasting process of spodumene ore in CaCl_2 roasting agent, authors reported similar adhesion to crucible and molten form to causing efficiency decrease, and with indication that the phenomenon was less pronounced at reduced temperature

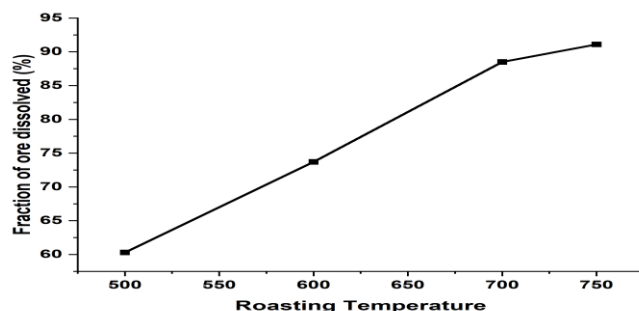


Figure 3: Effect of Temperature on pegmatite ore

Effect of roasting time (minutes)

Roasting time is another parameter that affects the thermal process of calcium chloride and pegmatite mineral. Ore: salt ratio was kept at 1:3, and the

mixture was heated at 700 °C and maintained at this temperature for 30-120 minutes. The extraction efficiency and roasting time profile is presented in figure 4.

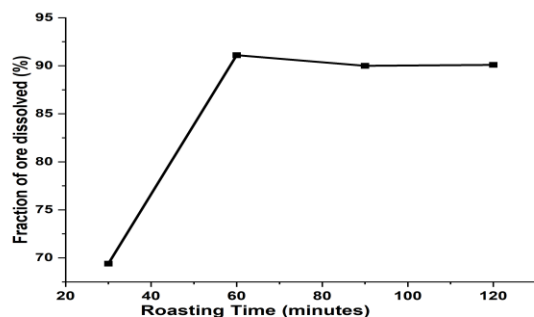


Figure 4: Effect of Time on pegmatite ore

The extraction efficiency of lithium gradually increases from 69.4% to 91.1%, when roasting time increases from 30-60 minutes. However, further prolonging of the roasting time to 90 minutes, causes the leaching rate to slightly decrease from 91.1- 90.0 %. Effective roasting time at 60 minutes observed in this study is quite favorable with respect to cost effectiveness when compared to chlorination roasting of spodumene achieved at 120 minutes by Braga *et al.*, (2025) and Barbosa *et al.*, (2015) during the CaCl_2

roasting treatments of β -spodumene ore to liberate lithium.

Purification and production of compounds

At the optimum dissolution conditions of leaching, the residue obtained when subjected to characterization by SEM-EDS analysis reflect major components in the raw ore, re-occurring in the residual product. This infer the selective ability effect of calcium chloride on the ore to selectively extract the element Li. Consequently, the leachate solution was chemically analysed and revealed

dominating impurity concentrations of Fe and Al. The purification is then proceeded, which infer to as the neutralization and the precipitation of metal hydroxides using slaked lime. The precipitation of Al and Fe as the corresponding hydroxides is then followed by addition of stoichiometry CaCl_2 to remove the excess lime (Viaceli *et al.*, 2017, Liu *et al.*, 2023, Yan *et al.*, 2012).



At the end of theses procedure, the obtained crystal was dried and analysed. Prior to crystallization, the obtained leach liquor was analysed by ICP-OES instrumentation, the chemical composition is

The initial solution occurring at a pH of 0.6 was neutralized up until pH of 3.5, with the occurrence of a cloudish white precipitate dignifying the formation of aluminium hydroxide as equation 3, the solution was filtered to obtain a clear solution. At pH near 4.5, a brownish precipitate indicating Fe^{2+} was observed, which was then oxidized in air to Fe^{3+} as equation 4.

represented in table 2 and the major composition of Li, while the Al and Fe mass balance is based on the total content of Al and Fe present in the ore.

Table 2: Elemental composition of purified leach solution (g/L)

Elements	Al	P	Li	Mg	Na	Fe	Zn
Composition	2.214	0.682	4.52	0.002	0.040	1.167	0.03

Consequently, the filtrate obtained was evaporated and concentrated, during this process the solution is heated at 90°C for an hour to allow the precipitation of lithium as LiCl . Consequently, the lithium chloride powder obtained was subjected to purity tests to ascertain the purity level through melting point analysis. Typically, the melting point range of 1 – 2 °C indicates its relative high purity. In this study, the melting point for the obtained LiCl powder was 608 °C, and a 1°C variation from the established 608 °C melting point was observed.

CONCLUSION

This study demonstrates a hydrometallurgical route for recovering lithium chloride (LiCl) from Nigerian pegmatite ore using calcium chloride-assisted roasting and aqueous leaching. Optimal conditions of 700 °C roasting temperature, 1:3 ore-to- CaCl_2 ratio, and 60-minute roasting time—yielded a maximum lithium extraction efficiency of 91.1%. Analytical techniques (XRD, ICP-OES, SEM-EDS) confirmed the transformation of lithium-bearing phases into soluble intermediates. The purification process, involving neutralization and selective precipitation of Al and Fe hydroxides, effectively enhanced lithium purity in the leachate. Final crystallization yielded high-purity LiCl , validated by a melting point of 608 °C with minimal deviation. This process offers a cost-effective and scalable method for producing battery-grade lithium precursors from indigenous mineral resources. The findings contribute to

sustainable lithium sourcing and support Nigeria's potential role in the global energy materials supply chain compounds. Future research should explore the integration of the recovered precursor compound into lithium-ion cathode fabrication, optimizing its compatibility and performance within battery systems.

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