The use of ultrasonic assisted extraction of lithium from Zimbabwean spodumene ore

L.T. Hlerema, H.M. Muchada, and E.K. Chiwandika

Harare Institute of Technology, Zimbabwe

Zimbabwe holds vast lithium reserves but currently exports raw ore without beneficiation. Lithium-ion batteries are crucial for modern technology, but extracting lithium from ores like spodumene is challenging and inefficient. This paper proposes using ultrasonic technology to improve lithium recovery. Conventional methods like sulphuric acid roasting have been reported to have extraction yields ranging from 85 to 90%, while ultrasonic technology offers a promising solution for efficient extraction. Atomic absorption spectroscopy revealed the lithium oxide expressed in the ore concentrate was around 3.41 wt%. The spodumene was initially pre-heated at 1000°C then roasted with concentrated sulfuric acid at 250°C. This stage facilitated the liberation of lithium from its bound state within the ore's crystal structure. Subsequent water and ultrasonic-assisted leaching steps efficiently dissolved the resulting lithium sulfate (Li_2SO_4). Ultrasonic treatment was employed at 60 kHz, and 70°C to enhance the dissolution rate by promoting cavitation effects and inter-particle collisions within the solution. Future research efforts could focus on refining the purification process, exploring alternative precipitation methods, and potentially introducing additional leaching stages to remove stubborn impurities and achieve the desired high-purity Li_2CO_3 suitable for battery production. By delving deeper into the process parameters and exploring alternative techniques, this research lays the groundwork for establishing an efficient route for extracting lithium from the abundant spodumene resources in Zimbabwe. This could contribute to the global lithium supply chain and also empower the local economy by creating valuable jobs and fostering technological advancements in the region.

Keywords: Spodumene ore, Roasting, Sonication, Lithium carbonate. Ultrasonic Assisted Extraction, UAE, calcinate.

INTRODUCTION

Lithium (Li) is one of the critical elements with widespread applications in next-generation technologies. A steady annual demand increase of 8–11% is anticipated for Li due to its unique applications, according to Shihua Han and Mohammad Rezaee (Han and Rezaee, 2021). The major source of high purity lithium is the spodumene mineral, containing over 1% to 8% Li_2O. Naturally, spodumene exists in a compact and low reactive α-phase that cannot be directly leached for Li extraction. It is modified to a porous, reactive, and leachable β-phase by heating at 1000°C (Gao 2023), a common industrial practice. This heating process is energy-intensive and often the rate-determining step in the economic extraction of lithium from spodumene. Additionally, it contributes significantly to CO_2 emissions, estimated at around 9 tonnes of CO_2 per tonne of lithium carbonate produced (Lithium Harvest, 2024).

Zimbabwe has the largest reserves of lithium in Africa and this has attracted investors from Australia, Canada, China and United Kingdom (Minerals Marketing Cooperation of Zimbabwe, 2023). Bikita resources alone have over 11 million metric tonnes of lithium reserves (Minerals Marketing Cooperation of Zimbabwe, 2023). In Zimbabwe, lithium mining primarily involves traditional extraction methods such as open-pit mining, complemented by significant beneficiation efforts to enhance the value of the lithium ore before export. The country has banned the export of raw lithium to develop local processing capabilities. Major lithium mining projects include the Arcadia Lithium and Bikita Lithium mine focus on producing lithium concentrate, which is then processed into lithium carbonate or lithium hydroxide, essential components for battery manufacturing (Zimbabwe Geological Survey, 2019); (Mining Weekly, 2024).

Sulphuric acid roasting has been reported to be suitable for even low grade spodumene ores with extraction yield ranging from 85 to 90 % from ultrafine ores, and at an industrial scale spudumene ore with particle size of less than 74 µm is mixed with 30% to 40% excess sulphuric acid (93 w/w) then baked for 10 to 60 minutes at 250°C (Salakjani *et al.,* 2019). The excess sulphuric acid is then neutralised in the water leaching stage and leaching can be enhanced by stirring. Microwave assisted acid roasting showed improved yield of up to 96% for β spodumene after 20 minutes of microwave pretreatment. This method decreased the power consumption by decreasing the amount of roasting time (Salakjani *et al.,* 2019). The current inefficiencies and costs associated with lithium recovery hinder the advancement of sustainable energy technologies that rely on lithium-ion batteries (Marcinov *et al.,* 2023). There is a need to provide methods with better efficiency that will make the extraction process of lithium from its ores more economical. This is the basis of this paper to investigate the possible use of ultrasonic assisted extraction of lithium from the Zimbabwean spodumene ore. This might improve extraction efficiency and may provide a basis for investigating the use of other environmentally-friendly acids in lithium leaching from ores.

Studies of ultrasonic-assisted leaching from spent Lithium batteries has shown increased efficiency and yield since more than 95% of all valuable metals were obtained in a short time at a relatively low temperature in the extraction of valuable metals from spent hydro-processing catalysts (Jiang *et al*., 2018). Kinetic analysis indicated that the ultrasound-assisted leaching of cobalt and lithium from spent lithium-ion batteries was controlled by diffusion and the fast diffusion using ultrasound promoted the leaching rate, and improved the leaching efficiency (Jiang *et al*., 2018). The improved efficiency in ultrasonic-assisted leaching of metals might be due to the improved mass transfer and may allow for the use of environment-friendly organic acids in the recovery of the Lithium (Xiao *et al.,* 2021).

In this investigation, ultrasonic-assisted extraction was done to a sample that had been heated to a temperature of 1000°C for two hours to allow for phase change in the ore. This is expected to increase the leaching efficiency, allowing for low amounts of acid to be used since the extraction kinetics are expected to be improved.

EXPERIMENTAL

The spodumene ore sample collected from Bikita deposits was crushed using primary and secondary jaw crushers and milled into fine powder using a ring and puck mill (pulverised) to increase the surface area. The pulverised sample was split using a riffle splitter to obtain a representative sample for particle size analysis. A sample of 200 g was used for the dry sieve analysis. Sieve sizes used were 300, 212, 150, 106 and 75 µm and were arranged in such a way that they have decreasing opening sizes from top to bottom through the stack. The sieve stack was placed on a sieving shaking machine with shaking done for an hour. The ore particles retained from each sieve were removed and weighed using an analytical balance. The sieves were carefully inverted, and the bottom of the sieve was gently brushed to remove any particles caught on the screen.

About 0.25 g of spodumene ore was weighed using an analytical balance and then fused with 3 g of sodium peroxide. The ore was then digested using hydrochloric acid until complete dissolution was achieved. The resulting solution was analyzed using an atomic adsorption spectrometer. The chemical composition of the ore is shown in Table I.

Table I. Chemical composition of the ore

Analyte	SiO_2	Al_2O_3	K_2O	Li_2O	MgO	CaO	Fe_2O_3
wt.%	61.83	20.76	10.51	3.41	0.13	0.12	0.30

Ore pre-treatment by calcination

The pulverized spodumene sample of particle size below 75 µm was first heated at 1000°C for two hours in a muffle furnace. Heating spodumene ore to high temperatures results in an irreversible phase change from α spodumene to a β-spodumene-SiO_2 solid solution which is more reactive to acid and base attack (Marcinov *et al.*, 2023).

Acid baking

About 200 g of the beta spodumene ore was weighed into 15 glass beakers and a specific amount of sulphuric acid was added to the ore in the beaker. The exact ratio was varied and a ratio of 1: 3.5 (ore to 25% concentrated sulphuric acid) was first used as a baseline. About 400 ml of concentration H_2SO_4 was added. The mixture was heated to 250°C for 30 minutes and distilled water was added to extract the lithium salt from the roasted ore. The beaker was transferred to the ultrasonic extractor and ultrasonic energy was applied for a set period to enhance leaching. The leaching temperature, time, roasting temperature, pressure, concentration and particle size were varied during ultrasonic extraction to determine the optimal conditions. The experimental variables used in the acid baking and ultrasonic assisted leaching are shown in Table II. Impurities were removed by the addition of Na_2CO_3 together with pH control.

Table II. Experimental variables used in the acid baking and leaching experiment

Leaching parameters	Varied range
Solid-liquid ratio	0.4, 0.33, 0.25, 0.2
Baking temperature(°C)	100,150,200,250,300
Baking time (minutes)	30, 60, 90, 120
Leaching temperature (°C)	50, 60, 70, 80, 90
Leaching time (minutes)	30, 60, 90, 120, 150
Ultrasound frequencies (kHz)	20,30,40,50,60,70
Acid concentration (wt. %)	10,20, 30, 40, 50, 60, 70,

Experimental setup

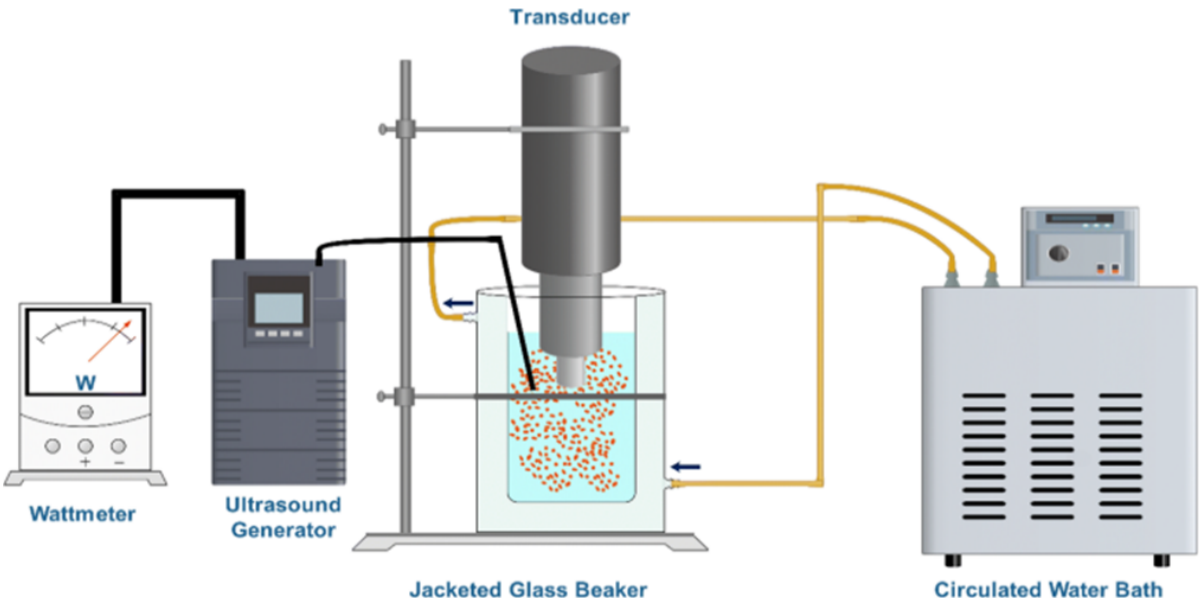

Diagram 1. Experimental setup of ultrasonic assisted extraction.

Chemical reactions taking place

Calcination

$\mathrm{LiAlSi_2O_6 + heat\ (1000°C) = LiAlSiO_4 + SiO_2 + H_2O(water\ vapour)}$ Eqn [1]

Acid baking

$\mathrm{LiAlSiO_4 + H_2SO_4 = LiSO_4 + Al_2(SO_4)_3 + SiO_2\ (250°C)}$ Eqn [2]

Ultrasonic leaching

$\mathrm{Li_2SO_4 + H_2O = Li_2SO_4 + H_2O}$ Eqn [3]

Impurity removal to Li_2CO_3 powder

at $\mathrm{pH} = 4$ to 6

$\mathrm{Li_2SO_4 + NaOH = LiOH + Na_2SO_4}$ Eqn [4]

$\mathrm{2Al + 6H_2O = 2Al(OH)_3 + 3H_2}$ Eqn [5]

$\mathrm{Fe + Na_2CO_3 + H_2O = F(OH)_2 + H_2 + Na_2CO_3}$ Eqn [6]

at $\mathrm{pH} = 7$ to 10

$\mathrm{2LiOH + H_2SO_4 = Li_2SO_4 + 2H_2O}$ Eqn [7]

$\mathrm{2LiOH + Na_2CO_3 = 2NaOH + Li_2CO_3}$ Eqn [8]

RESULTS AND DISCUSSION

Spodumene ore phase transformation analysis

The change in phase of the spodumene ore from alpha to beta was investigated using Fourier-transform infrared spectroscopy (FITR) and the results are shown in Figures 1 and 2.

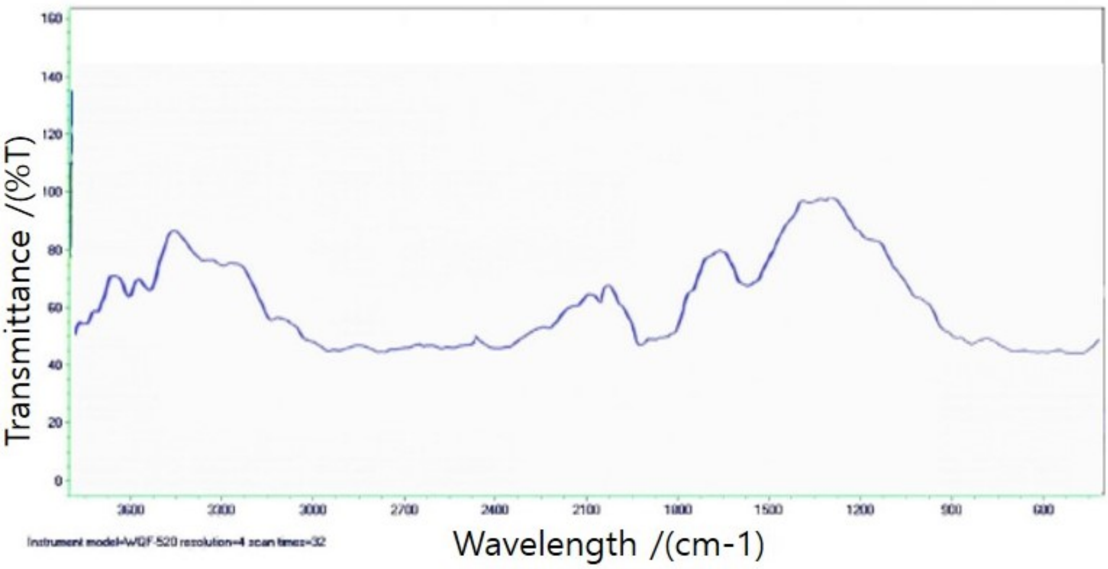

Figure 1. FTIR analyses of spodumene ore before calcination.

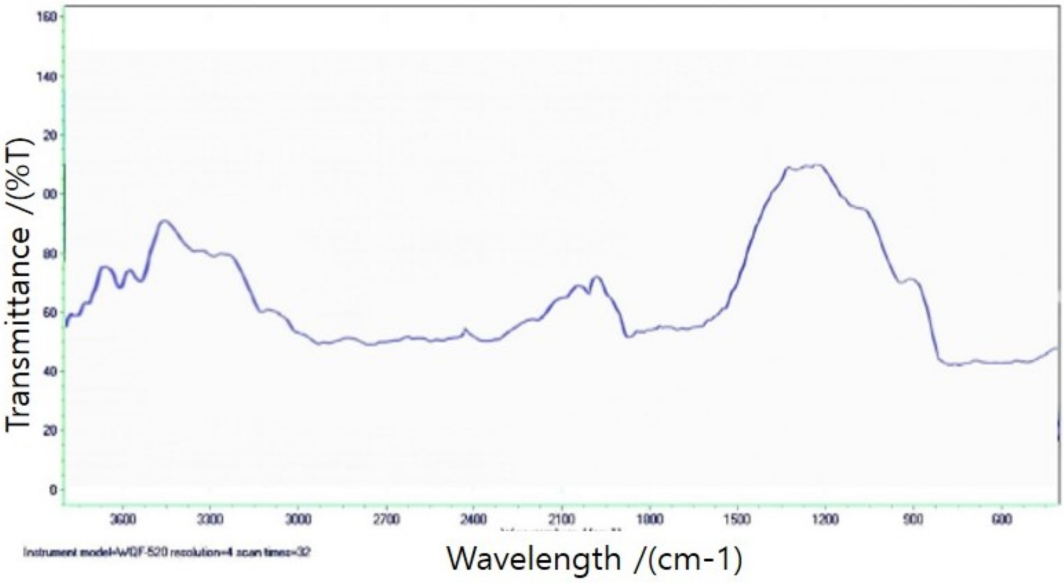

Figure 2. FTIR analysis on spodumene ore after calcination.

The provided infrared (IR) spectroscopy graph shows transmittance (%) versus wavenumber (cm^{-1}), indicating key features before and after heating a sample to 1000°C. Strong peaks at 3400 cm^{-1} and 1200 cm^{-1}became well-defined after heating. A notable peak at 1900 cm^{-1} observed before heating disappeared post-heating. These changes might suggest a phase change in the sample. These spectral changes help identify functional groups and elucidate the molecular structure of the sample. The IR spectrum was obtained using a WQF-520 instrument with a resolution of 4 and 32 scan times.

Effect of solid liquid ratio on lithium extraction efficiency

The effect of solid/liquid (g/mL) ratio on the dissolution of lithium was also examined. A ratio of 1: 3.5 (ore to 25% concentrated sulphuric acid) was used as a baseline. About 400 ml of concentrated H_2SO_4 was added. The mixture was heated to 250°C for 30 minutes and distilled water added to leach out the lithium salt from the roasted ore using 60kHz ultrasonic frequency. The results of different solid to liquid ratios are illustrated in Figure 3.

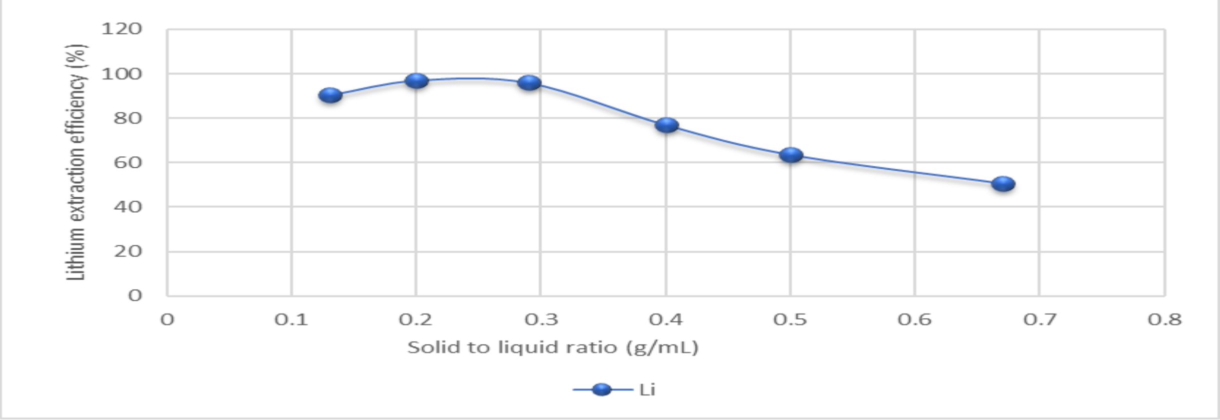

Figure 3. Effect of solid liquid ratio on lithium extraction after two minutes holding time at 60 kHz.

The graph shows that lithium extraction efficiency is highest (close to 100%) at low solid to liquid ratios (0.1 to 0.2 g/mL), indicating effective extraction at these lower solid concentrations. The efficiency remains high and stable between 0.2 and 0.3 g/mL, marking the optimal range. However, beyond 0.3 g/mL, the efficiency declines, and it drops significantly at higher ratios (0.5 to 0.7 g/mL), demonstrating that increasing the solid to liquid ratio decreases extraction effectiveness.

Effect of acid baking temperature on the extraction efficiency of lithium

The effect of acid baking temperature on the extraction efficiency of lithium was investigated, varying the acid baking temperature from 100 to 300°C at 120 minutes holding time. The acid baking temperature was varied with the leaching temperature held at 80°C at a solid-liquid ratio of 1:3.5 g/mL, leaching time at 120 minutes and ultrasound frequency of 60 kHz.

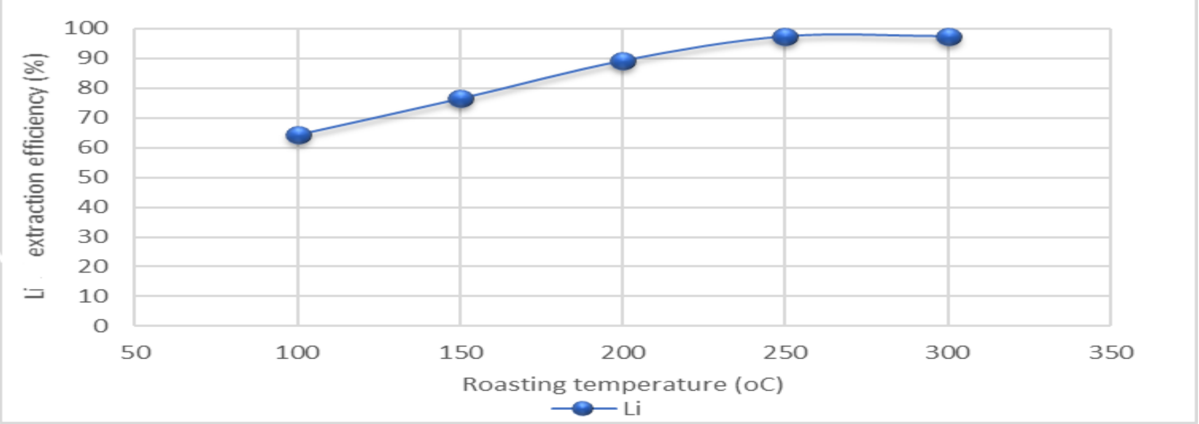

Figure 4, Effect of acid baking temperature on lithium extraction efficiency.

From the results in Figure 4, it can be concluded that the extraction efficiency of lithium increased with the acid baking temperature from 100 to 250°C and then decreased when the temperature was increased to 300°C. The highest extraction efficiency of lithium was 97.34% at 250°C.

Effect of acid baking time on the extraction efficiency of lithium

The effect of acid baking time on the extraction efficiency of lithium was investigated, with varying time from 30 minutes to 120 minutes. The other parameters were kept constant during all experiments with the acid baking temperature at 250°C, leaching temperature at 80°C, solid-liquid ratio at (1:3.5 g/mL), leaching time at 120 minutes and an ultrasound frequency of 60 kHz.

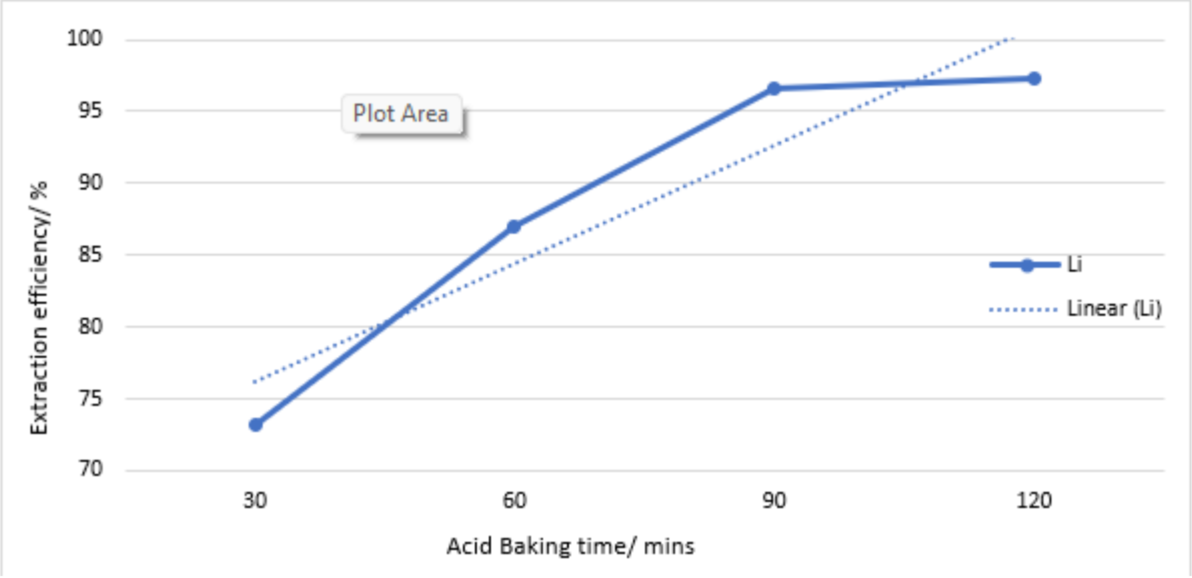

Figure 5. Effect of acid baking time on the extraction efficiency of lithium ore.

Generally, there was an increase in extraction efficiency as shown by the trendline. From Figure 6 the extraction rate from 30 minutes to 90 minutes was about 0.39 %/min. It was noted that there was a significant decrease in rate from 90 minutes onwards to 0.023 %/min. Therefore, increasing the contact time between the acid and spodumene ore resulted in higher extraction efficiency. Hence about 97.34% extraction efficiency was obtained at 90 minutes acid baking time.

Effect of leaching time during sonication on the extraction efficiency of lithium

Effect of leaching time on the dissolution of lithium was investigated by keeping the acid baking temperature at 250°C , acid baking time at 90 minutes, leaching temperature at 80°C , solid-liquid ratio at (1:3.5 g/mL), and frequency at 60 kHz. The results in Figure 6 show that the leaching time has a significant effect on the dissolution of lithium.

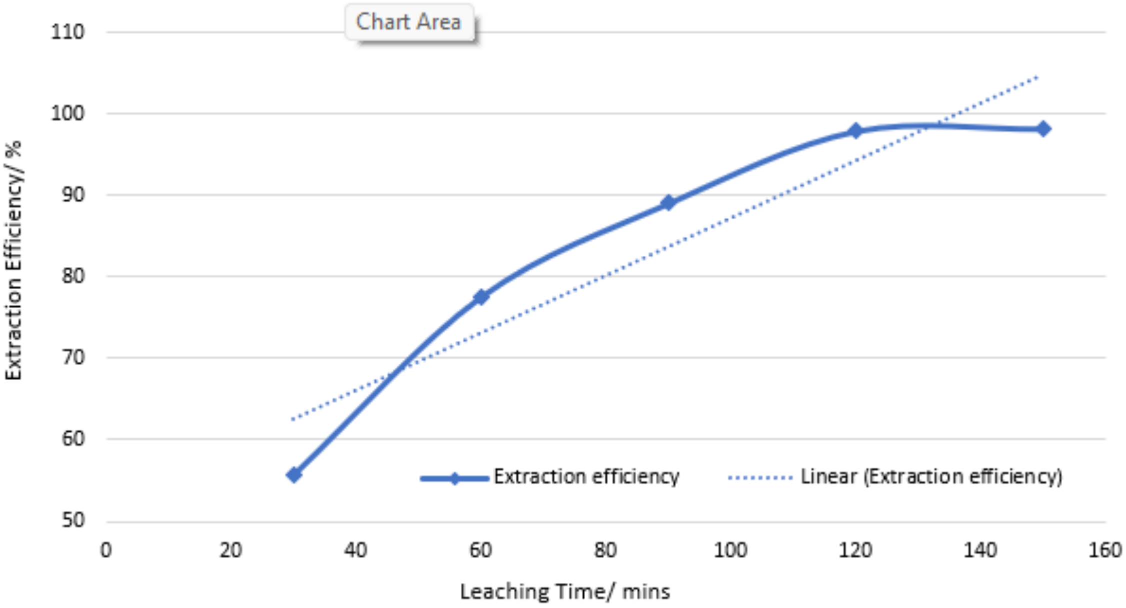

Figure 6. Effect of time during leaching of lithium with ultrasonic radiation.

Generally, there was an increase in extraction efficiency against leaching time as shown by the trendline in Figure 6. The rate of extraction from 30 minutes to 120 minutes was about 0.47 /min. However, there was a significant decrease in the rate of extraction from 120 minutes onwards to 0.01%/min. Therefore, the maximum extraction efficiency of about 98.2% was obtained after 120 minutes of leaching time.

Effect of ultrasound frequency on the extraction efficiency of lithium

Figure 6 shows that ultrasonic-assisted extraction rapidly increases lithium extraction efficiency, achieving high yields within 120 minutes. The effect of ultrasonic frequenct was therefore investigated by keeping the acid baking parameters constant at 250°C with 90 minutes holding time in all experiments with the leaching temperature at 80°C , solid-liquid ratio at (1:3.5 g/mL), leaching time at 120 minutes and frequency was varied from 20 kHz to 70 kHz.

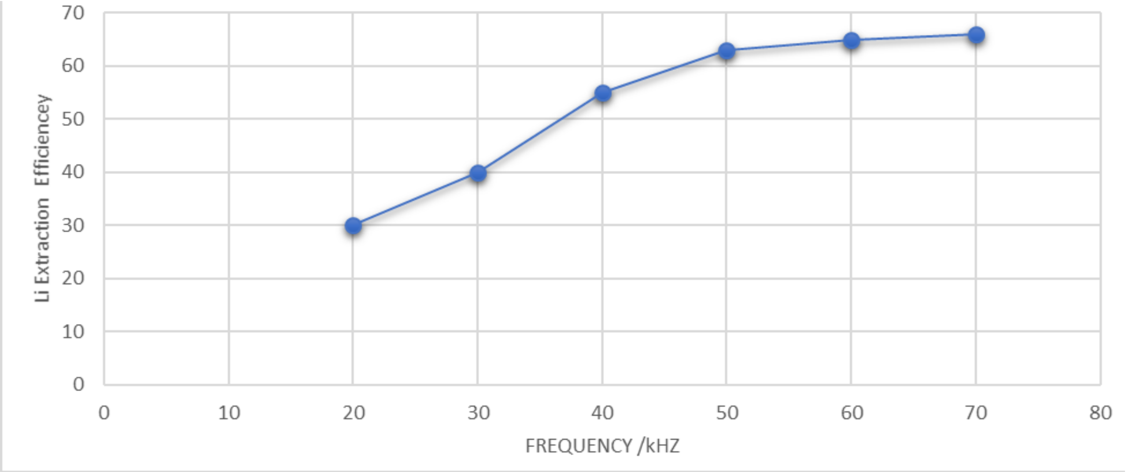

Figure 7. Effect of ultrasonic frequency on the extraction efficiency of lithium.

Figure 7 indicates that lithium extraction efficiency increases significantly up to 50 kHz, reaching around 60%, and then plateaus from 50 kHz to 70 kHz. Choosing 60 kHz as the optimum frequency showed high extraction efficiency. Beyond 60 kHz, the efficiency gains are less, suggesting that higher frequencies would result in unnecessary additional energy consumption without substantial improvements in extraction efficiency. Therefore, 60 kHz is optimal for maximising efficiency.

Effect of leaching temperature on the extraction efficiency of lithium

This was done by keeping the acid baking parameters constant at 250°C with 90 minutes holding time in all experiments with the leaching temperature varied at 30 to 80°C, solid-liquid ratio at (1:3.5 g/mL), leaching time at 120 minutes, frequency of 60 kHz while the leaching temperature was 120 minutes.

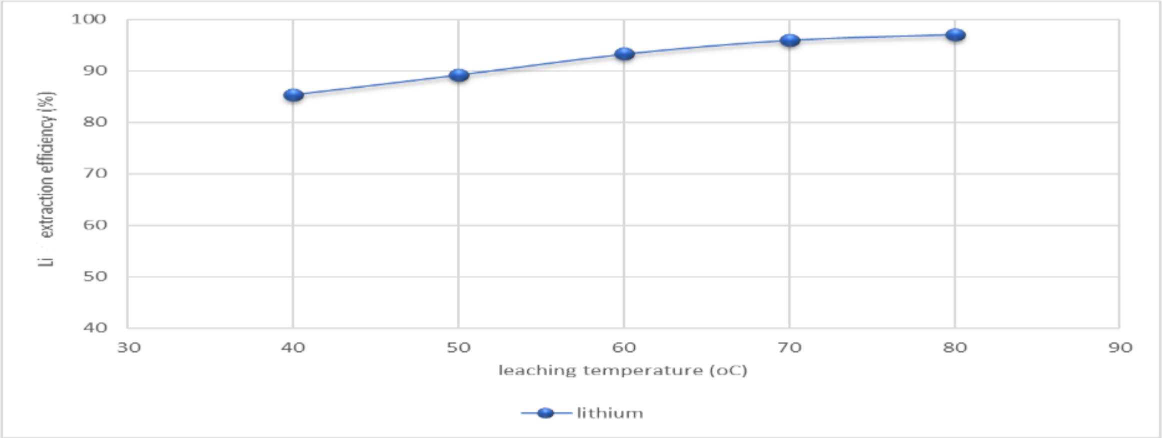

Figure 8. Effect of leaching temperature on lithium extraction efficiency.

It was concluded that temperature has an effect on the extraction of lithium during leaching. The increase in temperature resulted in a slight increase in extraction efficiency because an increase in temperature in the reaction system within a certain range will enhance the collision probability of molecules, which is conducive to the full reactions of material, therefore improving the leaching of lithium. The highest extraction of around 97.10 of lithium was achieved after 120 minutes at 80°C and the optimum temperature was taken as 70°C .

Effect of H_2SO_4 acid concentration on extraction efficiency

The effect of H_2SO_4 concentration during acid baking on the extraction efficiency of lithium was investigated, varying the acid concentration from 15 to 98% w/v. The acid baking temperature was 250 °C with 90 minutes holding time in all experiments at a leaching temperature of 80°C, solid-liquid ratio of (1:3.5 g/mL), leaching time at 120 minutes, frequency of 60 kHz, leaching temperature 70°C and frequency at 60 kHz.

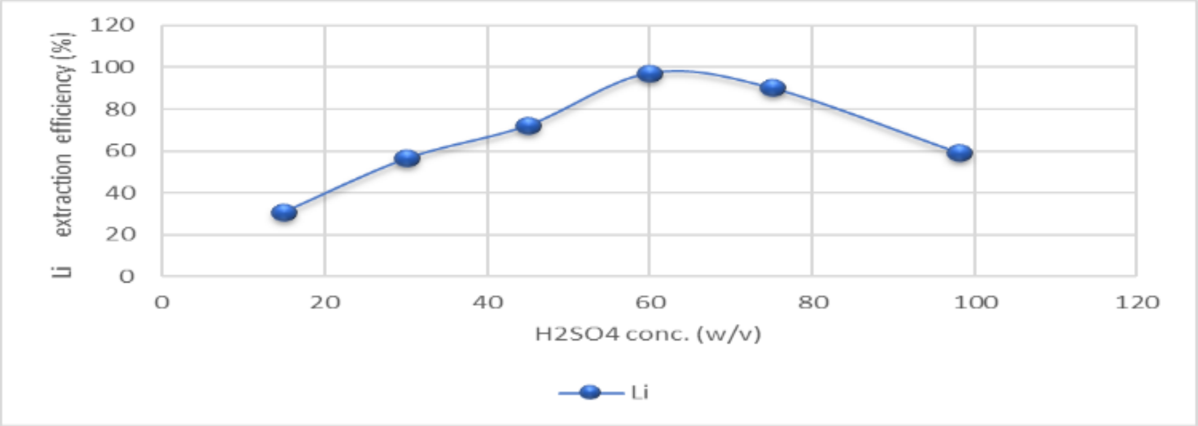

Figure 9. Effect of acid concentration on lithium extraction efficiency.

From the results in Figure 9, it can be concluded that the acid concentration has a significant effect on the dissolution of lithium. The extraction efficiency of lithium increased with an increase in the acid concentration from 15 to 60% w/v and the extraction yield of lithium decreased sharply from 97 to 59 % with increasing acid concentration above 60% w/v. The optimal acid concentration can be taken as 60% w/v. The achieved metal yield of around 97% is considerably higher than that achieved using 93 w/w sulphuric acid in the conventional acid leaching process with yields of around 85 to 90% (Salakjani *et al.*, 2019).

CONCLUSION

The optimal leaching conditions which were determined are summarised as shown in Table III.

Table III. Optimal leaching conditions

Parameters	Optimum conditions
Solid to liquid ratio	(1:3.5) g/ml
Acid baking temperature	250°C
Acid baking time	90 mins
Leaching time	120 mins
Leaching frequency	60kHz
Leaching temperature	70°C
Acid concentration	60 w/v

In summary, ultrasonic-assisted extraction offers more efficient lithium extraction from its ores, with potential benefits in terms of yield, and has potential of increasing metal yield shown at the optimal acid concentration of 60w/v sulphuric acid that achieved 97% yields compared to yields of around 85 to 90% achieved by using the 93 w/w sulphuric acid used in the conventional acid leaching (Salakjani *et al.*, 2019).

REFERENCES

Gao T, Fann N, Chen W and Daia T, (2023). Lithium extraction from hard rock lithium ores (spodumene, lepidolite, zinnwaldite, petalite): Technology, resources, environment and cost, China Geology, 6, 137-153.

Han S and Rezaee M, (2021) Lithium critical element for next generation technology, Royal Society of Chemistry, 45-47.

Jiang F, Chen Y, Ju S, Zhu Q, Zhang L, Peng J, Wang X and Miller J. D, (2018) Utrasonic assisted leaching of cobalt and lithium from spent lithium ion batteries, Ultrasonics – Sonochemistry, 48, 88-95

Lithium Harvest, (2024) Environmental impacts of lithium mining and extraction. Retrieved from: https://lithiumharvest.com/knowledge/lithium-extraction/environmental-impacts-of-lithium-mining-and-extraction/

Marcinov, V, Klimko, J , Takáˇcová, Z, Pirošková, J, Miškufová, A, Sommerfeld, M, Dertmann, C, Friedrich, B and Dušan Orá, D, (2023). Lithium production and recovery methods: Overview of lithium losses, Metals, 13, 1213. https://doi.org/10.3390/ met13071213

Minerals Marketing Cooperation of Zimbabwe, (2023). Zimbabwe's lithium reserves and the interest from international investors. Retrieved from: https://mmcz.co.zw/wp-content/uploads/2024/07/MMCZ-Strategic-Plan-2021-2025-Reviewed-2023-planning-horizon-2024.pdf

Mining weekly, (2024): Zimbabwe leading the sub-Saharan African lithium mining boom. Retrieved from: https://www.miningweekly.com/article/zimbabwe-leading-the-sub-saharan-african-lithium-mining-boom-2024-05-13

Salakjani N,K, Singh P and Nikoloski A,N, (2019) Production of lithium –A literature review. Part 2. Extraction from spodumene, Mineral processing and extractive metallurgy review, https://doi.org/10.1080/08827508.2019.1700984

Xiao X, Hoogendoorn B, W, Ma Y, Ashoka S, Gardener M. J. Forsberg K and Olsson R, T, (2021) Ultrasound- assisted extraction of metals from lithium ion batteries using natural organic acids, Green Chem, 23, 8519.

Zimbabwe Geological Survey. (2019). Lithium exploration and development potential in Zimbabwe. Retrieved from: https://www.geologicalsociety.org.zw/sites/default/files/documents/GSZ%20NL%20Feb%202019.pdf

L.T. Hlerema

Student
Harare Institute of Technology