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ADDIS ABABA INSTITUTE OF TECHNOLOGY

CENTER FOR ETHIO-MINES DEVELOPMENT

Master of Engineering in Mineral Processing

The beneficiation of lithium from a brine solution of Afdera lake using Evaporation and chemical treatment method, Afar, North Eastern Ethiopia

By

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A Project submitted to the center of Ethio-mines development, Addis Ababa Institute of technology in the Partial fulfillment of the requirements for the Degree of Master of Engineering in Mineral Processing

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Addis Ababa , Ethiopia

Addis Ababa Institute of Technology
Center for Ethio-Mines Development
Master of Engineering in Mineral Processing

Approval Sheet

This is to certify that the project report prepared by Elias Mamushet entitled “*The beneficiation of lithium from a brine solution of Afdera lake using Evaporation and chemical treatment method, Afar, North Eastern Ethiopia*”, submitted in the partial fulfillment of the requirements for the Degree of Master of Engineering in Mineral Processing, complies with the regulations of the University and meets the accepted standards with respect to originality and quality.

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DECLARATION

I hereby declare that the project “*The beneficiation of lithium from a brine solution of Afdera lake using Evaporation and chemical treatment method, Afar, North Eastern Ethiopia*” has been carried out by me under the supervision of Bogale Tadesse (PhD), Center for Ethio-Mines Development, Addis Ababa University, Institute of technology in the year 2023 as a part of Master program in Mineral Processing. I further declare that this project has not been submitted to any other university or institution anywhere for the award of any degree.

Name: Elias Mamushet Woldeyohanis

Place: Addis Ababa University

Date of submission: _____

Signature: _____

Acknowledgment

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Abstract

Lithium is a crucial metal with a rapidly growing market demand, mostly due to its use in lithium-ion batteries for electric cars and medical devices. Lithium resources connected to pegmatites and rift-bound brine deposits may exist in Ethiopia. The current project work, the beneficiation of lithium was conducted on Afdera brine lake Afar, North Eastern Ethiopia. This project aims beneficiating lithium using Evaporation and chemical treatment method. Totally 20 litter sample were collected from the lake using Purposive and random sampling method in order to analyzed in the laboratory for Atomic Absorption Spectroscopy (AAS) for the Lithium and major cation as well as for beneficiating lithium metal from the brine solution. The AAS result of the Lithium contents in brine water of Afdera lake is 8.7ppm which is relatively higher than other lakes in the main Ethiopian rift. The concentration of Sodium and potassium is extremely higher in the lake which is 82946 ppm and 661.5 ppm respectively while lithium is much lower. Even if the Lithium concentrations is below the cut of grade 200ppm it was processed using evaporation and chemical treatment method and the content of the lithium reached 53.8% in the concentrate. Despite the lake's lithium concentrations being below what can be commercially extracted, it can still be processed as a byproduct during the manufacturing of potash using sun evaporation pans. The current study strongly suggests that additional research is needed merely to assess the lithium resources as a primary product and as a secondary byproduct during the potash mining process in Afdera Lake and the surrounding area.

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Acronyms

AAS: - Atomic Absorption Spectroscopy

ppm:- Parts per million

HCl: - Hydrochloric Acid

HF: - Hydro-florid Acid

HNO₃:- Nitric Acid

MER: - Main Ethiopian Rift

DMS: - Dens Media Separation

LDH:- layered double hydroxide chloride absorbent

CRM:- Certified Reference Material

Ca(OH)₂:- Calcium Hydroxide

Na₂CO₃:- Sodium Bi-carbonate

Li₂CO₃:- Lithium Bi-Carbonate

EMPBFC:- Ethiopian Mineral Petroleum and Bio Fuel Corporation Laboratory

CHAPTER ONE

INTRODUCTION

1.1. Back-ground of the study

Lithium is among the most important metals in use in today's globe, and the demand for it is quickly rising on the global market as more and more power storage systems, portable electronic devices, and electric cars employ energy storage systems with lithium-ion batteries. The market for lithium batteries has significantly expanded in recent years as a result of the quick commercialization of electric vehicles and portable electronics. The quick increase in lithium usage, however, could make the limited availability of lithium resources as a challenge. (<https://clearpath.org/tech-101/supply-chain-for-lithium-and-critical-mineras>).

A rift-bound brine deposit (Afdera brine solutions) and a pegmatite deposit in Ethiopia both have the potential to yield lithium resources. In pegmatite-hosted colombo-tantalite mineral deposits in Kenticha, Ethiopia, lithium minerals (lepidolite, spodumene) are discovered (Tadesse, 2001). Lithium has not yet been economically extracted; instead, the deposit is only being used for surface mining of the minerals niobite and tantalite ore.

According to Muzvondiwa et al. (2015), Ethiopia now has significant potential for potash deposits linked to evaporites in the Danakil depression (Musley area and vicinity of Dallol). Potash has been thoroughly investigated in the evaporite deposit in the Danakil depression. As a result, there have been very few lithium mineral exploration activity in the evaporite rocks of the Danakil depression.

Lithium compounds, such as lithium carbonate, lithium hydroxide, and lithium bromide, are used in the production of aluminum, as catalysts in the pharmaceutical and rubber industries, as well as in air conditioning and dehumidification systems, to improve extreme temperature resistance in glass, ceramics, lubricant, and grease manufacturing (Ebensperger et al., 2005; Peiro et al., 2013). But more recently, lithium minerals have become increasingly in demand due to the use of lithium-ion technology in electric vehicles (Ebensperger et al., 2005; Peiro et al., 2013).

Numerous industries use lithium in a variety of ways. It has been utilized in air purification, glass, ceramics, metallurgy, medicine, and most recently for the batteries in hybrid and electric vehicles. It develops become the best energy source of the twenty-first century (Cui et al., 2016). One embodiment of the effort is the work being done on this project, which is intended to be a beneficiation process for lithium that is found in brine solutions around Dallol area, in the northern Afar Depression, and in some of the lakes in the Main Ethiopian Rift System (MER). It focuses on the extraction of lithium using evaporation and chemical treatment methods. This is to provide fundamental information regarding lithium's presence in the area and its extraction that will aid in future planning for in-depth mineralogical research and processing (beneficiation) of the lithium mineral deposit.

In this project Ethiopia's lithium pegmatite deposit is not included; instead, lithium brine deposits are the main focus.

1.2. General Description of the Project Area

1.2.1. General Location of the study Area

The project area is situated in the MER, which is part of the southern Danakil depression. It is particularly called Lake Afdera that is situated in the southernmost point of the Danakil depression which is a total of 804 km far from Addis Ababa along the main asphalted road and after Semera dry Soil Road to the Kelbet Rasu. The study area is geographically bounded in between 13° 07' 00" to 13° 30' 00" E " Longitude and 40° 50' 00" to 40° 60' 00" N in the Kelbet Rasu, Afar National Regional State.

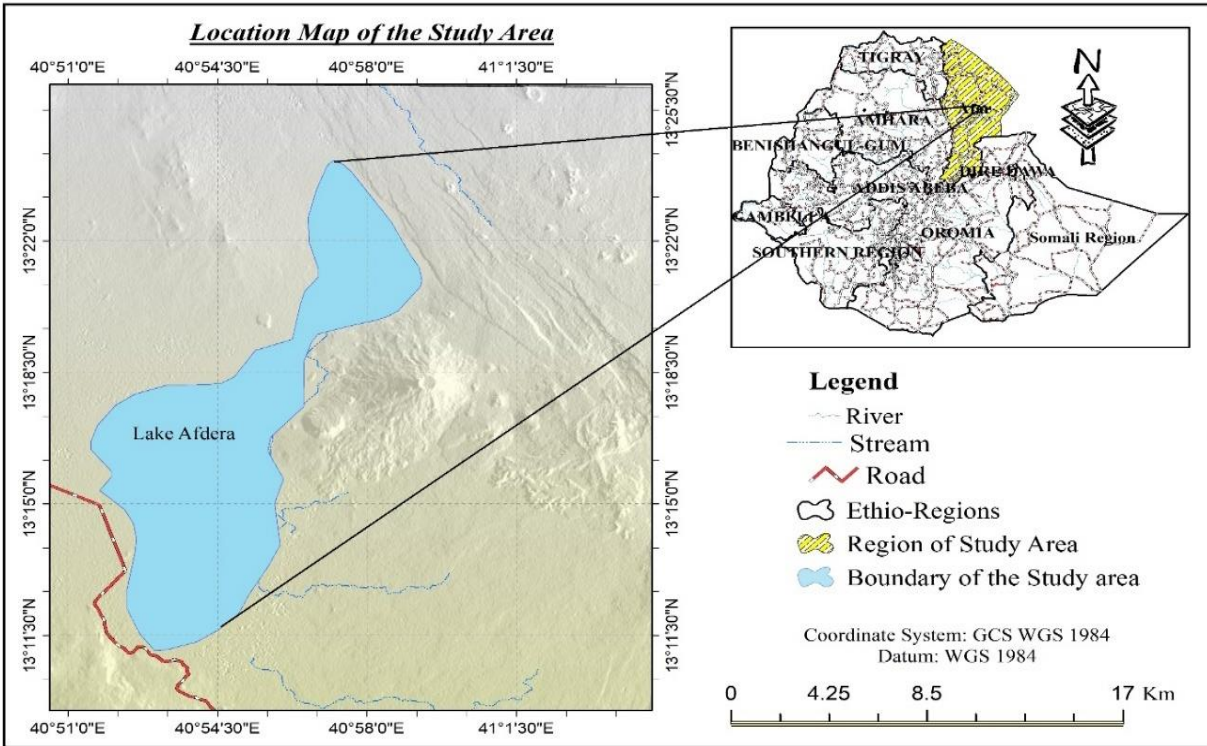


Figure 1: Location Map of the Study area

Garland (1980) claims that the Danakil region is characterized by high average annual temperatures ranging from 25 °C to 45 °C in summer and 45 °C to 47 °C in winter, as well as minimal precipitation (below 200 mm/annul). The lake is situated 102 meters below sea level at its surface.

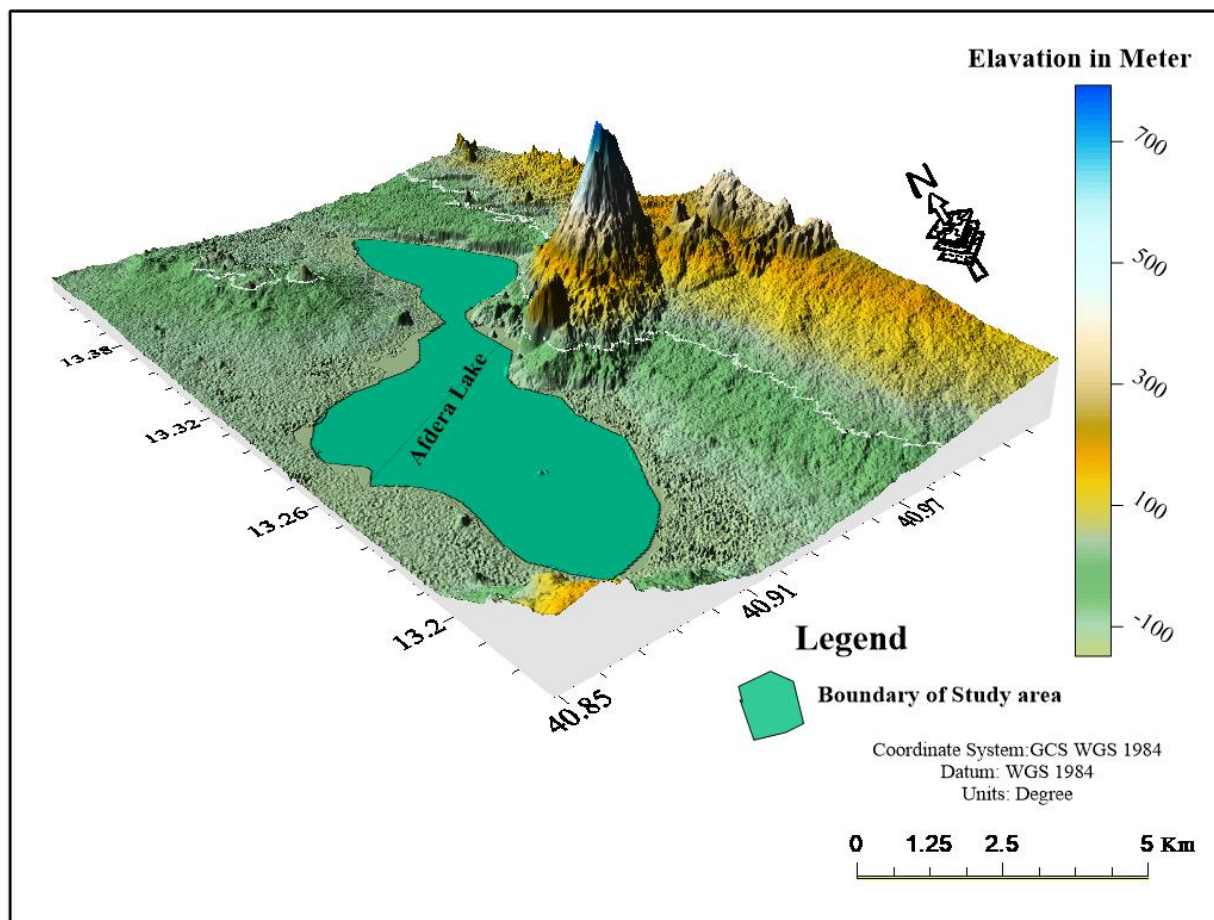


Figure 2: physiography map of lake Afdera

Source: compiled by researcher, 2023

1.3. Statement of the problem

Afdera Lake, the project place, is one of the potential areas because it has a large deposit of evaporite units, hydrothermal hot springs, and surface brines. It is part of the Danakil depression. In the meantime, the evaporite units near Afdera, which are known for their potash deposits, are becoming a promising location for project into lithium deposits that are associated with evaporite and brine solutions. So far there is only a study conducted by [Asnake \(2019\)](#) and [KIGAN and GSE \(2012\)](#).

Determining the mineralogy and beneficiation of lithium from the Afdera brine lake was the goal of the current project. In Afdera and the surrounding area, various researchers conducted their studies over the course of several years. the company Ralph M. Parsons' initial exploration. The first potash exploration in the Dallol area was conducted by the Ralph M. Parsons Company in

1960. Lithium was included in the geochemical analyses of brine and evaporite units, but the results were negative or absent. But they didn't specify the type of analysis they did. Lithium rare metal presence in the Afdera lake has been the subject of a preliminary examination by [KIGAM and GSE \(2012\)](#). Some of the lithium results they discovered from the Afdera lake were relatively enhanced in comparison to the MER lakes' lithium concentration. The exploration study also indicated the necessity for additional research into the geochemistry and beneficiation of the lithium minerals in the lake, as well as the presence of an economically significant amount of lithium mineral in the brine Afdera lake.

This project activity was therefore proposed to close this gap by studying the mineralogy and beneficiation of lithium in the brine solution (Afdera salty lake).

1.4. Objective of the Project

1.4.1. General Objective

The main objective of this project is beneficiating lithium using Evaporation and chemical treatment method.

1.4.2. Specific Objectives

The specific objectives are:

- ✓ To Perform the brine purification to remove contaminants or unwanted elements
- ✓ Observing the filtration process to remove the precipitated solids
- ✓ Knowing the recovery of lithium mineral from the solution
- ✓ Observing the effectiveness of the Treatment methods during the recovery of the lithium mineral

1.5. Significance of the study

This study was expected to provide deeper insights and understanding about a Lithium mineralization potential of the country (Ethiopia) and its extraction and processing techniques from a brine solution (Saline lakes) . In recent time there is a rapid increase in the demand of lithium, so that the study will solve the demand shortage of the lithium metal by improving the beneficiation of the mineral from a solution sample.

The study will also contribute to give the country(Ethiopia) attention to detail in a lithium mineral

resource processing from a brine solution using this paper as an input of information.

This project will also be significant in the following ways:

- ❖ The study will benefit the lithium mineral processing companies by informing techniques of recovering the mineral from a brine solution.
- ❖ The study may help other researchers who may use it as an input for additional research on lithium minerals and to look into the field in a detail and wider scope.

1.6. Scope of the Study

This project work was done on a specific mineral commodity called lithium that was focused on lithium mineral processing from a brine solution obtained from Afdera lake, afar north eastern Ethiopia, using evaporation and chemical treatment method . In general, the project work is scoped in area, commodity type, sample type(solution sample) and methodology. The project work excludes lithium mineral ores, such as spodumene and was only concerned on lithium metal from a salt-brines (saline solutions) source.

1.7. Limitation of the Study

Limitations in terms of time and money, lack of well-organized secondary data that was done so far on the commodity of lithium mineral beneficiation from brine lakes of Ethiopia, instability of the security matter because of the political instability just to get samples from the Afdera lake and inaccessibility of laboratory for Lithium mineral such as inductive coupled plasma (ICP) and network problem just to communicate to advisors. Nevertheless, despite of these limitations, the researcher tried all his best to meet the project's goals.

1.8. Organization of the Study

The project is structured out in a clear and understandable manner to make it easier for readers to comprehend its goals, techniques, and primary inputs and outputs for any potential audience. Five chapters make up this project. The first chapter provides an overview of the study's introduction, which includes a summary of the problem, aims, significance, scope, and limitations. Review of pertinent literature is presented in the second chapter. The project's approach is presented in the third chapter, which includes an overview of the research field, the laboratory method, the research design, the data sources, the sampling procedure and methodologies, and the procedures for

laboratory analysis. The fourth chapter consists the study results and discussion part of the project. And finally, the project's summary, conclusion, and suggestions are offered in the last chapter.

CHAPTER TWO

LITERATURE REVIEW

2.1. General Introduction of Lithium

The atomic weight and number of lithium are 3 and 6.9, respectively, and it has a silvery-white color. Lithium lies at the top of the periodic chart (Krebs, 2006; Warren, 2017). Among the alkali metals, it has the lowest melting point (180 °C), greatest melting point, and highest boiling point (Lide, 2005). Lithium is one of three metals that can float over water, along with sodium and potassium. It has a very low density (0.534 g/cm³) and can float on hydrocarbon oils. Numerous minerals, including spodumene, petilite, lepidolite, and amblygonite, contain lithium. Additionally, potash and lithium are frequently combined in evaporite deposits (salt lakes) in the form of lithium carbonate. The abundance is normally 28–30 ppm in igneous rocks, although it can reach 53–60 ppm in sedimentary rocks (Evans, 2014; Kunasz, 2006). Its crustal abundance or concentration is typically 20 ppm.

2.2. Occurrence and Source of Lithium

Because lithium is extremely reactive, its geochemistry is both complex and fascinating. Lithium-minerals form in magmatic processes and crystallize at the end of the crystallization process. Many lithium-containing minerals are known at the moment, but only a handful of them have high concentrations, and it can also be found in naturally occurring salt solutions as brines in arid Salt Lake settings (Vikstrom, 2013).

Lithium can be obtained from either primary or secondary sources. Lithium is recovered mostly from pegmatites, brines, evaporites, and deep earth water bodies (oil or gas deposits, formation water, and geothermal water). The recycling of lithium-containing items is a secondary source of lithium. The recycling of lithium is minimal, although it has increasingly increased due to the increased consumption of lithium batteries. In British Columbia, Canada, one domestic manufacturer has recycled 28 lithium metal and lithium-ion batteries since 1992 (Jaskula, 2018). In 2015, the newly built company opened the first lithium-ion automobile battery recycling facility in the United States in Lancaster, OH (Jaskula, 2019).

In general, The world's lithium resources are classified into three types: brines and related evaporites, pegmatite, and sedimentary rocks. Brines containing lithium account for 66% of the world's lithium reserve, pegmatite for 26%, and sedimentary rocks for 8% (Gruber et al., 2011). Lithium may be extracted economically from two sources: brines and hard rock ores. More than 60% of global lithium output comes from brines, with lithium ores accounting for the remainder (Ebensperger et al., 2005). Australia, Canada, Zimbabwe, Portugal, and Brazil are the leading producers of lithium concentrate from hard rock ores (US Geological Survey, 2018).

The Danakil depression in Ethiopia is a Tertiary rift basin rich with evaporites comparable to those found in the Dallol Mountains (St. Jhon, 2016). The salt dome fluids and hot springs are thought to be the result of hot mantle fluids interacting with evaporite deposits at unknown depths. According to Darrah et al. (2012), the brine fluids found in the Dallol region are extremely salty, highly acidic, and gas-rich. Lake Afdera is a saline body of water located in the Danakil valley that is fed by hydrothermal springs (Bonatti et al., 2017).

2.3. Demand and Application of lithium

The current demand for lithium is particularly high because lithium turns chemical energy into electrical energy very effectively. According to analysts, the most promising battery type for next-generation energy storage systems is rechargeable lithium-ion (Li-ion). As a result, lithium is in great demand, notably for use in personal electronic devices such as mobile phones, energy storage devices, and (hybrid) electric vehicles. <http://www.polinares.eu/docs/d2> .

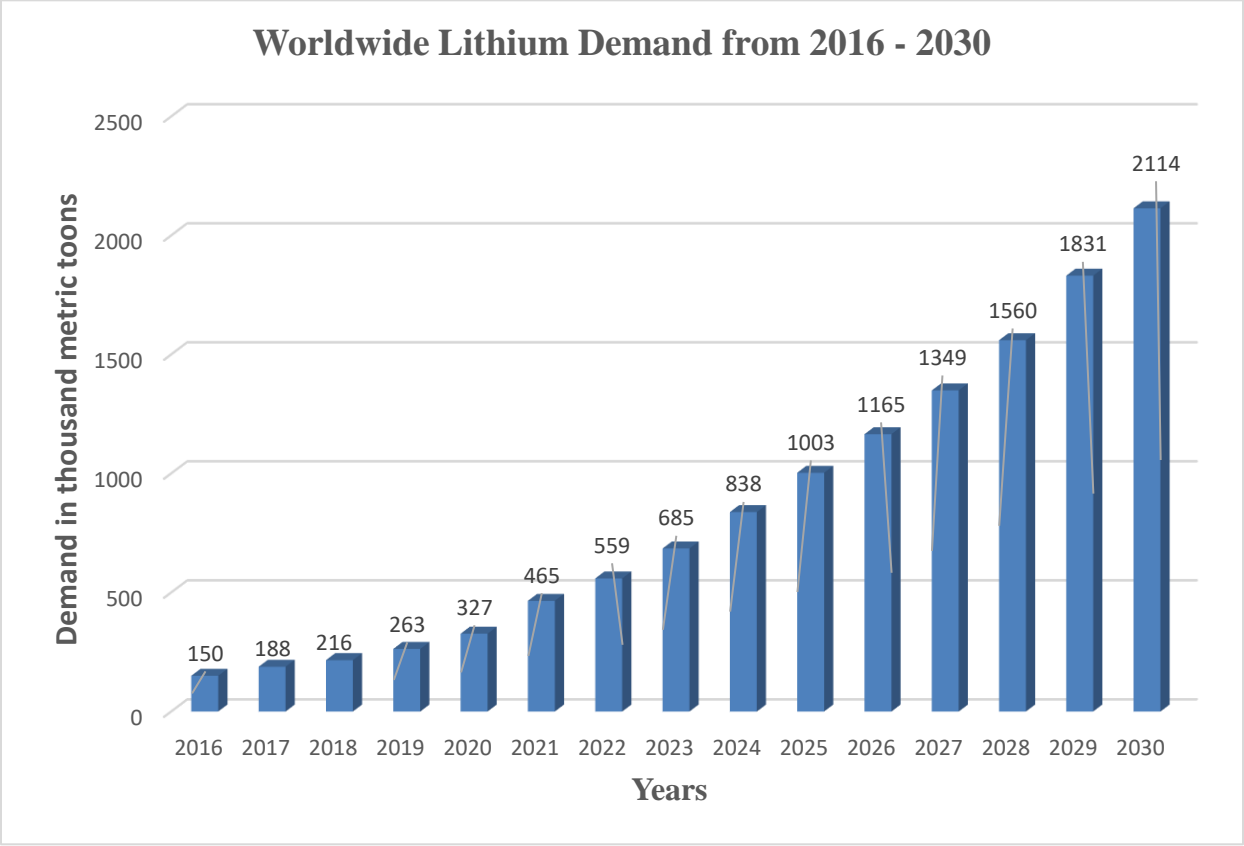


Figure 3: Worldwide Lithium demand from 2016 to 2030, in thousand (1000) metric tons

Source: (Martin, 2022) and [http:// mining.com/lithium-demand](http://mining.com/lithium-demand)

Lithium and its compounds are used in lithium power sources (rechargeable batteries), glass, ceramics, lubricants, oxygen regeneration in autonomous life support systems, polymer materials and chemical technology, metallurgy (Bipolar medicine), pharmaceuticals, medicine, and biological significance, and future applications (hydrogen energetics, electronics, and nonlinear optics, nuclear energy, rocket fuel). (<https://clearpath.org/tech-101/supply-chain-for-lithium-and-critical-mineras>).

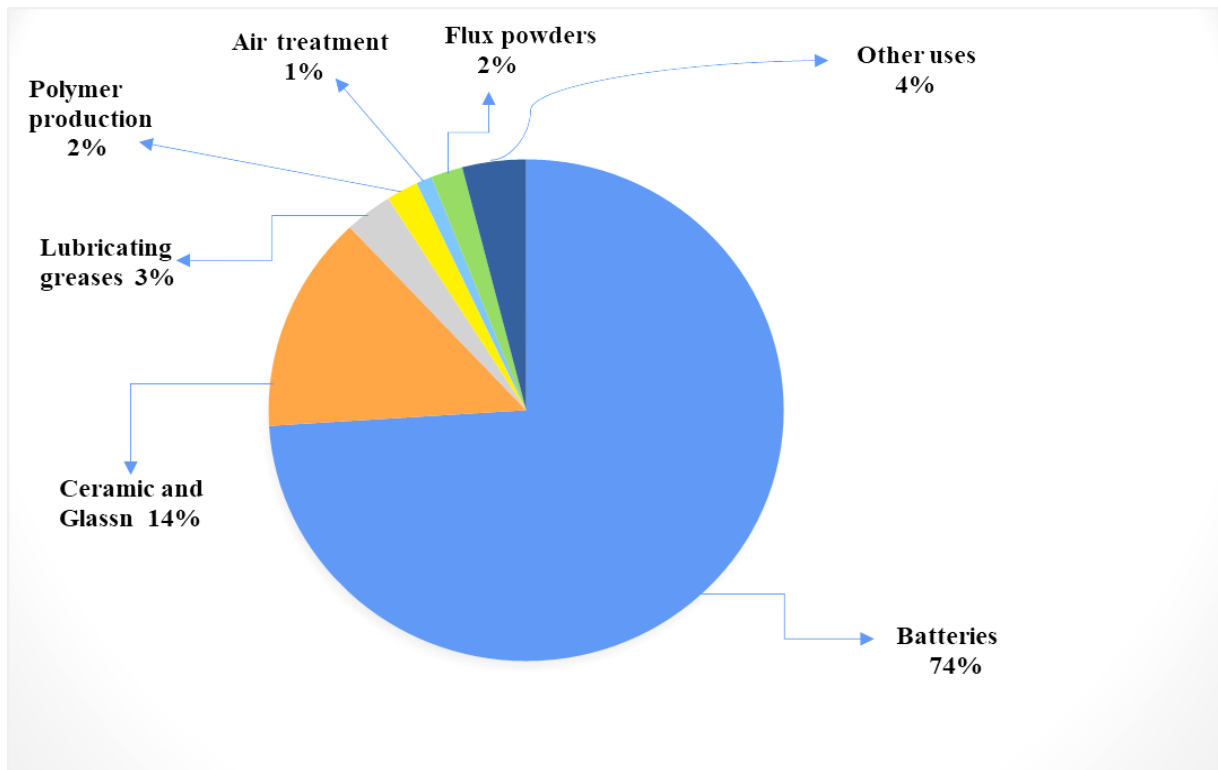


Figure 4: A Pie chart showing the use of Lithium as a percentage of global consumption

Source: U.S geological survey, 2022

2.4. Beneficiation of Lithium

Lithium is a highly reactive alkali metal with strong thermal and electrical conductivity. Pure elemental lithium is not found in nature due to its high reactivity and is instead found as a component of salts or other compounds. <http://www.polinaires.eu/docs/d2>

The majority of commercial lithium comes in the form of lithium carbonate, a very stable molecule that can be easily transformed to other salts or compounds. Lithium extraction is a collection of chemical methods that isolate lithium from a sample and convert it to a saleable form of lithium, typically a stable yet easily convertible compound such as lithium carbonate. The majority of lithium extraction procedures involve mining to reach subsurface deposits of lithium-rich minerals or brines. Depending on the raw material, the methods of lithium extraction and processing differ. (Saxton, 2018).

Traditional brine lithium extraction methods (pretreatment, chemical treatment, evaporation, and filtering), ion exchange, electro dialysis, solvent extraction, and adsorption are among the lithium brine beneficiation processes. (<http://www.samcotech.com/>).

2.4.1. Lithium-Brine Extraction Technologies

Lithium brine resources are found all over the world, but only a small number of them are concentrated enough to be exploitable. The study of [Kesler et al., \(2012\)](#), [Vikstrom et al., \(2013\)](#), and [Kunasz, \(2006\)](#) demonstrates that the current commercially extractable lithium derives from a small high grade lithium brine deposit.

2.4.1.1. Solar Evaporation

Incoming solar energy enables actual evaporation, and the operation should be placed in sunny locations with low annual precipitation rates. The area of the needed ponds is determined by the net evaporation rate. Due to the extended periods necessary for lithium production from brine reserves via sun evaporation, brine deposits might become difficult to adapt to unexpected changes in demand ([Evans, 2008](#)).

Lithium brine beneficiation method is widely employed in today's lithium ore mining ([Kaskey, 2014](#)). Although lithium is abundant in saltwater, economically effective extraction methods have yet to be established ([Martin, 2015](#)). In addition to the conventional sun evaporation techniques, lithium extraction technologies at various scales of production include adsorption, Ion-Exchange, extraction, and membrane separation ([He et al., 2017](#)).

2.4.1.2. Adsorption

One way that researchers are still investigating is the use of sorbents to cling to the lithium for selective removal. This process involves the absorption of lithium ion from brine by a lithium-ion selective sieve, followed by a dilute HCl solution to produce a lithium-rich solution. It is minimal in cost and simple to implement on a wider scale. Adsorbent dissolution reduced adsorbing capability due to ion channel obstruction ([Saxton, 2018](#)). Some sorbents, like a recently tested lithium aluminum layered double hydroxide chloride absorbent (LDH), can recover up to 90% of the lithium present, according to a recent study published in Environmental Science & Technology.

2.4.1.3. Ion exchange

Ion exchange lithium beneficiation systems are used for purification, water softening, and separation in a range of industries. Lithium recovery by ion exchange can change with a simple change in pH, temperature, or stream composition (as do other lithium extraction methods), however researchers believe this process can recover approximately 90% of the lithium present (He et al., 2017).

2.4.1.4. Extraction System

Organic extractants capable of selectively extracting Li from brine are included in the extraction process. However, proper extracting equipment with a small design, low cost, and great efficiency is necessary for this process (Saxton, 2018).

2.4.1.5. Membrane (Electro-dialysis) System

Electro-dialysis is an ion exchange technology that can be used to concentrate and separate lithium. It is a method for concentrating brine that uses positively or negatively charged ions to allow charged particles to flow through a semipermeable membrane. Li and Mg ions are separated in this extraction method due to the different speeds at which monovalent and divalent cations flow through the ion exchange membrane in an electric field (Saxton, 2018). Despite the fact that it is a novel technology with no commercial membrane systems available at the moment, it is simple to control and consumes little energy.

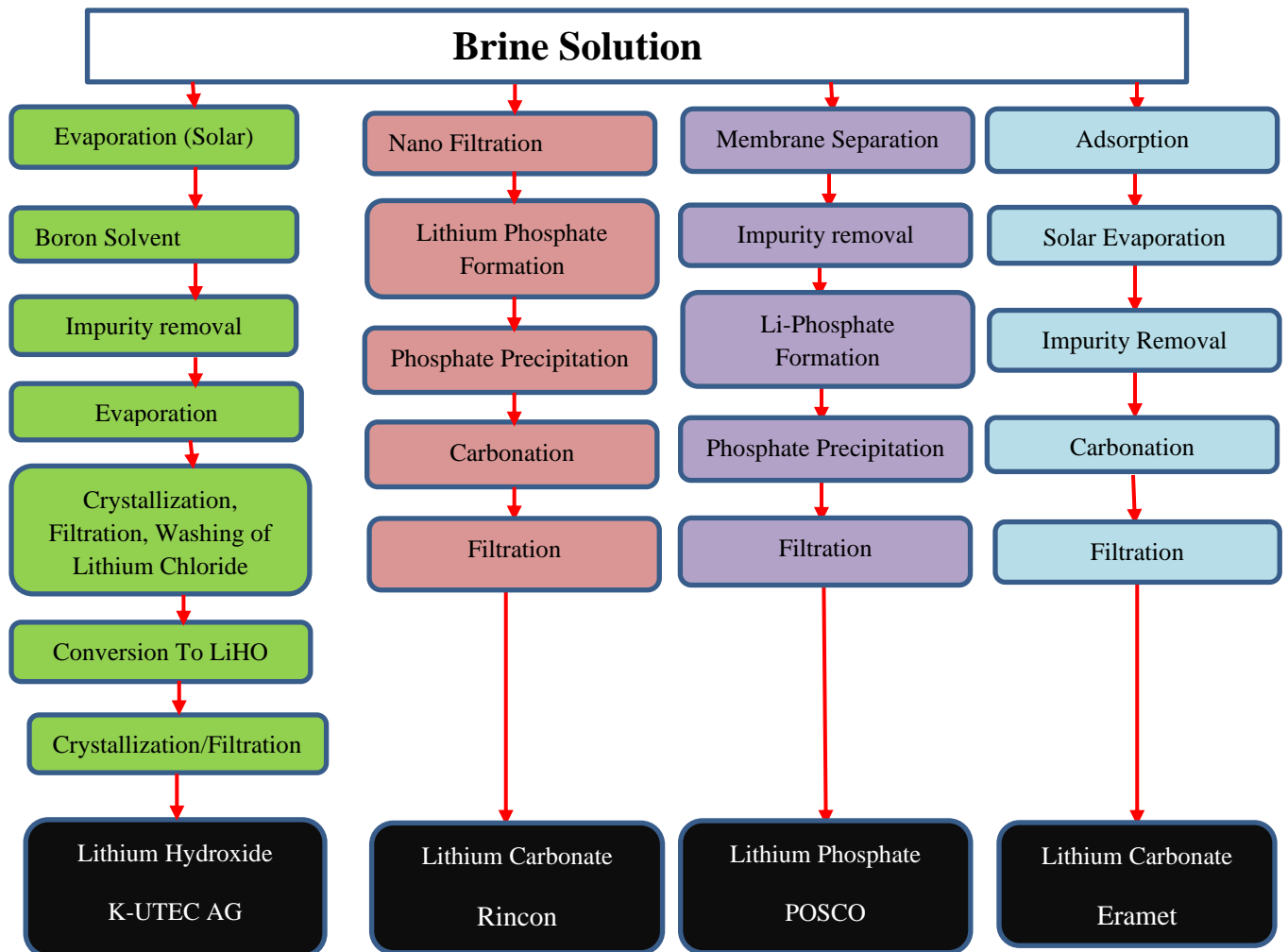


Figure 5: Overview of Emerging Brine Technology (Saxton, 2018)

2.5. Lithium mining impacts

Lithium can be found in salt flat brine. The brine is pushed to the surface through tunnels drilled into the salt flats and left to evaporate in ponds. This facilitates the chemical extraction of lithium carbonate. Lithium mining has significant detrimental effects on the environment and society, primarily due to water poisoning and depletion. Lithium production necessitates the usage of harmful compounds as well. When such chemicals are discharged by leaching, spills, or air emissions, they can damage communities, ecosystems, and food production. Furthermore, lithium extraction inherently damages soil quality and pollutes the air (Democracy Center Special Report, 2010).

CHAPTER THREE

THE PROJECT WORK METHODOLOGY

Several steps and diverse methodologies were used to achieve the aforementioned goals. The research is divided into three phases: office work, field work, and post-field work (laboratory).

3.1. Description of the Study Area

The area's distinguishing features are Neoproterozoic metasedimentary and metavolcanic rocks, gently sloping Quaternary alluvial deposits, evaporites, which include salt deposits (halite and potash), salt and mud deposits on the salt flat, and sulfur deposits, particularly on mount Afdera and its localities (Warren, 2016). The surface of Lake Afdera is characterized by a highly saline solution that is high in sodium cation.

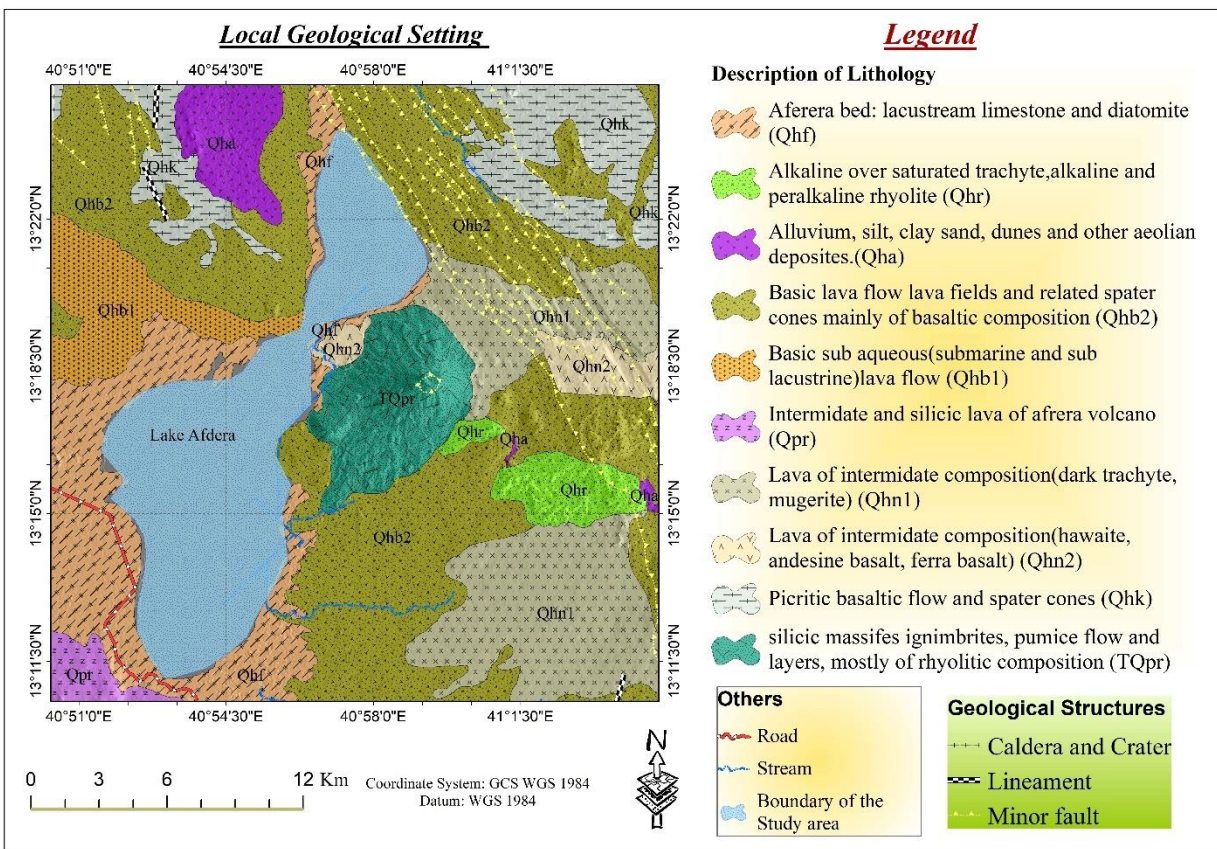


Figure 6: Local geology map of the study area (Compiled by the researcher using Arc GIS, July 2023)

3.2. Research approach

The researcher used experimental project approach together with mixed approach which is a combination of both quantitative and qualitative research techniques. The quantitative approach used to investigate the concentration or quantity of the major ions and the recovery of lithium during beneficiation from Afdera brine lake while the qualitative approach was employed to analyze the grade and purity of lithium concentrate that should be processed from the lake. As a result, the focus of this work was on experimental procedures (where the mineralogy and beneficiated concentrate of lithium were examined after the experiment was completed).

3.3. Sources of Data

Data for this project was acquired from both primary and secondary sources. Because the main focus of the project is the beneficiation of lithium ore from Afdera lake using evaporation and chemical treatment methods, the primary data sources are gathered from laboratory examination of the Afdera lake sample. As a result, primary data are gathered from the laboratory observation of Atomic Absorption Spectroscopy (AAS) and the observation of mineral beneficiation. While secondary data was obtained from various documents such as published and unpublished documents, journals, books, and websites.

3.4. Field work Approach

In the field, a representative brine sample is collected from the main Ethiopian rift lake particularly called Afdera lake. A total of 20 liter sample is taken. During sample selection the following were performed. These are:-

1. A sample container was prepared and then washed by distilled water not to have contamination.
2. Collection of water samples from the lake using purposive and random sampling method
 - ✓ A total of 20 liter sample were taken
3. Field number were recorded and the sample were labeled
4. The sample was packed.
5. The sample were transported to laboratory and processing place.

3.5. Laboratory work

After taking a sample from the field (Afdera Lake) , it is analyzed in the laboratory for the lithium and major cations. The brine solution samples were analyzed by the analytical method of AAS for the Lithium and major cation concentrations. The analytical laboratory work includes:

- ✓ Lithium and major cation content analysis for brine lake samples (Before beneficiation) and
- ✓ The lithium content analysis for the lithium concentrate (After beneficiation)

3.5.1. Analytical Techniques and Procedures

The analytical technique employed for this project is Atomic Absorption Spectroscopy. Since there is no accessibility of Inductive coupled plasma (ICP) machine in Ethiopia only AAS was done in the laboratory. Two different atomic absorption spectroscopy(AAS) was analyzed in the laboratory (for the water brine sample(feed) and for the concentrate).

3.5.1.1. Laboratory procedure of Atomic Absorption Spectroscopy for the feed

To perform AAS the first stage is preparation of analytical sample from the bulk sample.



The procedures of the water sample during AAS analysis are listed below

- i. Water Sample Preparation
 - ✓ Field number is recorded
 - ✓ Laboratory number is given
 - ✓ A minimum of 500mL of a water sample were collected from the laboratory sample
 - ✓ Selecting the analyte sample from the lab sample
- ii. To avoid any chemical changes in the sample, concentrated nitric acid (HNO₃) was added to decrease the pH of the sample to less than 2 (pH stabilization). This will prevent precipitation and microbial activity in the sample.
- iii. Then the sample was transported to the laboratory room.
- iv. Filtration

- ✓ The sample was filtered using a 0.45µm membrane filter to remove any suspended particles.
- v. Acid Digestion
 - ✓ After filtration Add 10mL of concentrated HNO₃ to 100mL of the water sample, and then heat at 150°C for 2 hours. This will perform for digestion of the heavy metals if it is present in the suspended particles.
 - ✓ Perform acid digestion of the filtered sample.
- vi. Cool Down and Volume Adjustment
 - ✓ Allow the sample to cool down after digestion
 - ✓ After cooling, add distilled water to restore the initial volume of the sample
- vii. Storage and AAS Analysis
 - ✓ Storing the samples in appropriate containers until AAS analysis
 - ✓ From 1000ppm Stock solution of lithium 100 stock solution was prepared and from the prepared 100 ppm stock solution 1ppm, 2ppm, 5ppm, 10ppm, 20ppm stock solution was prepared for calibration purpose
 - ✓ Then finally AAS for lithium and major cations was performed.

3.5.1.2. Laboratory procedure of Atomic Absorption Spectroscopy for the Lithium Concentrate

The procedure of the concentrate is different with that of the procedure performed in the feed because the feed is a water sample while the concentrate is a precipitate solid (Evaporite) sample which is obtained from the beneficiation of the water sample in the feed using evaporation and chemical treatment method.

The procedures of the Lithium concentrate during AAS analysis are listed as follows below

A. Analyte Sample Preparation

- ✓ Field number recorded
- ✓ Laboratory number is given
- ✓ Since the sample is not a hard rock crushing using jaw crusher and milling using ball mill is not necessary rather the sample was pulverized using mortar and pestle (Pulverization using mortar and pestle in 200 mesh).

- ✓ The sample was homogenized and then an analyte sample were taken using quarter-four technique (Selection of the analyte sample from the lab sample(a minimum of 0.05 gram)
 - ✓ The sample is putted in the Geochem bag
- B. The analyte sample were gone to the chemical analysis room
- C. Mass balance of the analyte sample was done (feed mass = 0.05 gram) and the balance stability (pressure and temperature) was checked
- D. A 100ml Teflon polymer volumetric flask was prepared
- ✓ The Teflon volumetric flask was washed by distilled water
 - ✓ The laboratory number was written and labeled on the Teflon
- E. 0.05-gram certified reference material for the rock sample of Lithium (Certified reference material(CRM) GBW-07152 was measured which is used for recovery analysis
- ✓ The same quantity of the analyte sample (0.05 gram) was taken in another container
 - ✓ The same quantity of the blank (a standard with no Analyte) (0.05 gram) was added into in another container

Analyte Sample	3ml HF + 6ml HCl was added in each container and wait for one day HF- for silicate digestion purpose HCl- for background correction purpose (to return more accurate results)
CRM	
Blank	
Analyte sample Duplicate	

- ✓ On the next day acid digestion for (Blank, Analyte, CRM and Analyte duplicate) is performed in each container starting at low temperature (110-150⁰C) for 45 minutes.
- F. When droplet was formed 4ml of HCl was added in each container and was heated for 2 minutes.
- G. Then transfer each (Analyte Sample, CRM, Blank and Analyte sample Duplicate) in to the washed and dried 100ml teflon volumetric flask
- ✓ It was labeled up to the mark of the flask by the distilled water
 - ✓ Then it was Shaked for 1-2 minutes
- H. Then it was gone to the AAS rom to perform the AAS

- I. From a 1000ppm Stock solution of lithium 100 ppm stock solution was prepared and then from 100ppm stock solution, 1ppm, 2ppm, 5ppm, 10ppm 20ppm lithium stock solution was prepared for calibration purpose
- J. Then cathode lamp for Lithium and slight width (0.8 best for Li) , photo multiple tube energy gain (280 volt), HCl current=4 in AAS machine was elected. The flame optimization was opened and the absorbance was checked at 1ppm, 2ppm, 5ppm, 10ppm and 20ppm.

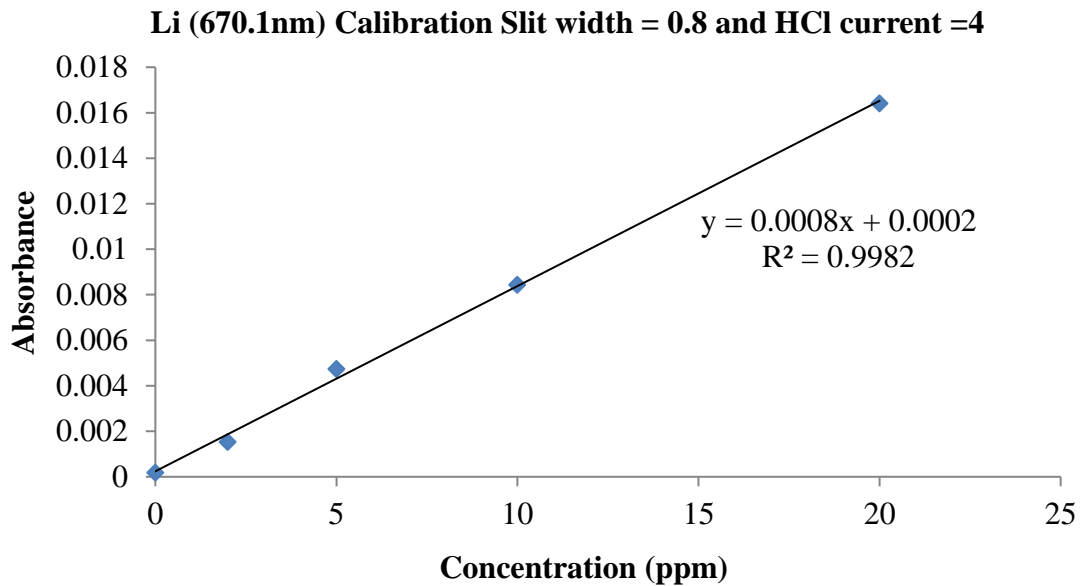


Figure 7: the absorbance curve of calibration analysis

- ✓ Since the absorbance has linearity shown on Figure 8 which tell us the calibration is performed very well.
- K. After ending Calibration
- ✓ It was red for Blank, Analyte, CRM, Blank, Analyte duplicate with its respective order
- L. Finally, the reading was changed to concentration

$$\text{Concentration(ppm)} = \text{meter reading} * \text{dilution factor}$$

$$\text{Concentration (\%)} = \frac{\text{meter reading} * \text{dilution factor}}{10,000}$$

$$\text{Dilution factor} = \frac{\text{total volume}}{\text{Sample weight}} = \frac{100\text{ml}}{0.05\text{g}} = 2000\text{ml/g}$$

3.5.2. Lithium beneficiation procedures

Following an analysis of the lithium concentration in the sample, the following steps were taken only to extract the target mineral (lithium) from the solution.

Step-1:- The water was evaporated in a controlled temperature and pressure setting until a variety of salts precipitated out, leaving brine with a relatively increasing concentration of lithium. It took 13 days to finalize evaporation of 19 liter water sample.

Step-2:- During the evaporation process, hydrated lime (Ca(OH)_2) was added to the brine to precipitate out undesired components, primarily magnesium and boron (as magnesium hydroxide and calcium boron salts). When the lithium concentration reaches a particular level, the brine is piped to a recovery facility for extraction of the metal. The following steps are given below.

Step-3:- Brine purification is used to eliminate pollutants or undesirable materials.

Step-4:- Precipitation of useful products and byproducts via chemical treatment.

Step-5:- Filtration with Whatman filtration paper to remove the precipitated solids.

Step-6:- To precipitate lithium carbonate (Li_2CO_3), the sample was treated with soda ash (Na_2CO_3).

Step-7:- Finally, the completed lithium carbonate product is washed and dried.

3.6. Method of Data Analysis

This project employs both descriptive and experimental analysis. The descriptive analysis is performed to determine the significance of the data presented through the use of experimental results and summaries. The experimental data are presented in the form of tables, graphs, and charts.

CHAPTR FOUR

RESULT DISCUSION, ANALYSIS AND INTERPRETATION

4.1. Geochemical laboratory Result of the Afdera brine lake

Out of 20 litter brine sample taken from Afdera lake, 1 litter sample were analyzed in the laboratory for its lithium content and major cations concentrations. The rest 19 litter water sample were beneficiated and lithium metal were extracted in the form of lithium carbonate. In addition, the duplicate of the brine samples was also analyzed again for its lithium content in Ethiopian Mineral petroleum and Bio fuel corporation laboratory (EMPBFC).

Table 1: Geochemical AAS result of the brine sample of Afdera lake

		Major Cations				
AAS (mg/L or ppm)						
Field No	Lab No	Ca+	Mg+	Na+	K+	Li+
em-12	660	22.13	12.56	82867	625	8.98
	660-d	25.45	13.56	83025	698	8.42
Average Concentration		23.79	13.06	82946	661.5	8.7

Source: Researcher which is done in EMPBFC laboratory (July, 2023)

The AAS results of the brine water of Afdera lake as shown on Table-1 shows that the average lithium concentration in the lake is 8.7mg/L or (8.7ppm). As shown on the table Sodium (82946ppm) and potassium (661.5) are more dominant in the lake Compared to other major cations such as Calcium (23.79 ppm), Magnesium (13.06 ppm) and Lithium. The lake is reach in sodium and potassium. Relatively lithium has the lowest concentration in the lake compared to all other major cations. The table 1 shows the concentration of the major cations and lithium content of Afdera lake before beneficiation.

Table 2 shows that, when compared to the lakes of the major Ethiopian rift and surface brines, the lithium content of the Dallol hot spring and Danakil surface brines was relatively higher than that of the main Ethiopian rift lakes. The lithium content of the Dallol hot spring is 17.2 ppm, and the lithium content of the Danakil surface brines is 9.8 ppm (table 2).

When we compare the secondary geochemical data of different lakes obtained from (KIGAM and GSE, 2012) table 4 and (Asnake, 2019) table 3 with the result done by the researcher on Afdera lake table 1, lake Afdera has higher concentration of lithium compared to Abijata lake, Shala brine lake, Langano lake, Fentale lake, Beseka lake, Asale brine lake, Abijata lake, Shala Lake, Langano lake, and chew-bahir that is recorded as 8.7ppm (table 1).

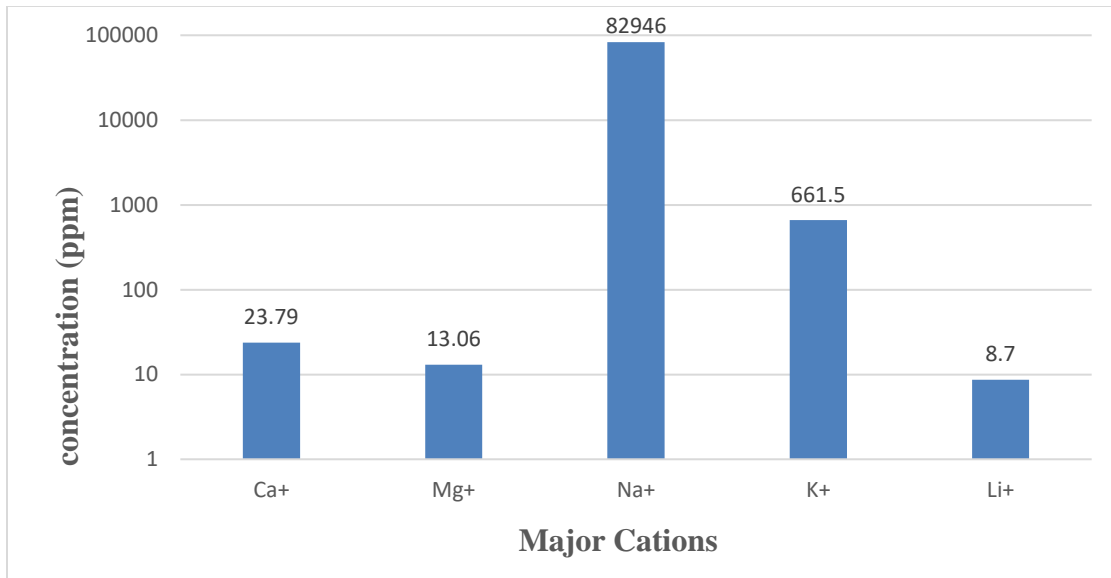


Figure 8: Bar graph log scale plot of the concentration of major cations of Afdera lake

As shown on the bar graph sodium is extremely dominant which is followed by potassium and calcium while Lithium has the lowest concentration relative to all the other cations in the lake.

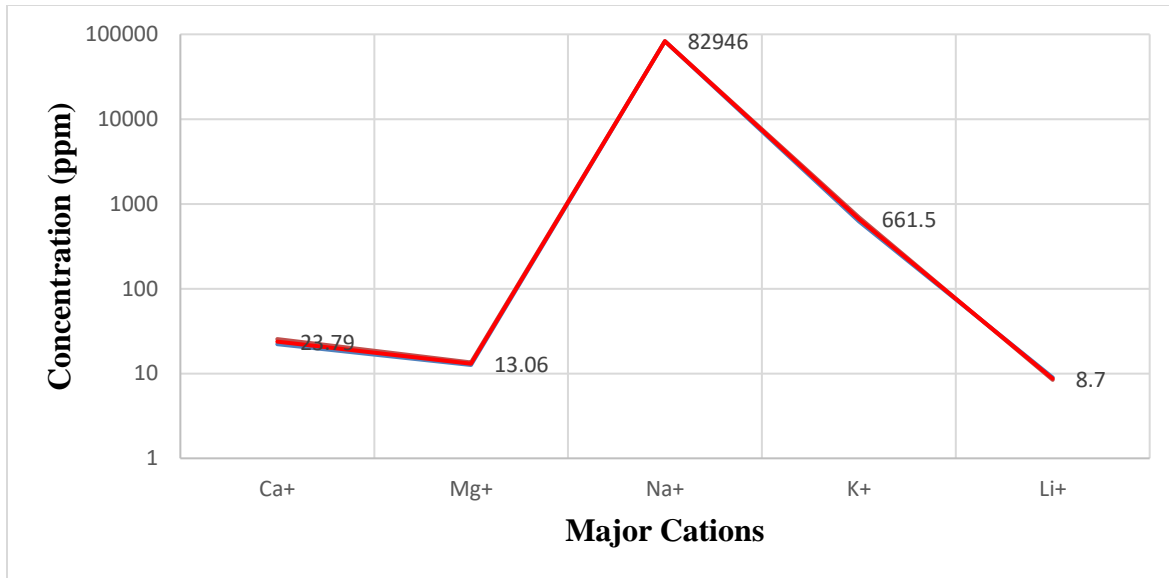


Figure 9: log scale Major cation plot of Afdera brine lake

As shown on figure 9, the content of sodium and potassium are extremely higher compared to other major cations. From all the other cations lithium has the lowest concentration in the lake as labeled on the plot above ($\text{Li}^+ = 8.7$ ppm). This shows lithium is found in a very small quantity in the lake while sodium is the most dominant one.

4.2. Geochemical laboratory Result of the different lakes, hot-springs and surface lakes of Ethiopia by other researchers

Table 2: AAS results from Dallol surface brines, Dallol hot springs, and Lake Chew Bahir (EMPBC lab, Addis Ababa, Ethiopia).

Samples Field ID	YD 1A	YD2A	DL 1A	DL 2A	DL3 A	DH1	DH2	CB 01A	CB02A
Sample Type	Brine					Hot spring		Lake water	
Location	Surface brine from the surrounding of Dallol					Dallol		Chew Bahir	
AAS (ppm)									
Na ⁺	111498	104269	14301	28125	11800	82963	81459	98.9	85.0
K ⁺	3849	3098	987	4698	1100	19896	15269	16.2	5.2
Ca ²⁺	9756	1298 7	9876	11259	9670	1203	2799	10.1	5.7
Mg ²⁺	4180	4987	894	8123	1450	5611	4910	11.3	2.6
Li ⁺	1.9	2.1	4.2	9.8	8.5	17.2	16.1	<0.04	<0.04

Source: (Asnake, 2019) and the sample values described as less than sign () and ND indicate that they are below the detection limit and so not detected by AAS.

Table 3: Geochemical analysis of brine samples from Chew-Bahir, Lake Chamo, Lake Abaya, Weyto River, Lake Shala, and Lake-Abijata .

Samples Field ID	CB 03A	CM 01A	AB 01A	WT 01A	SH-1	AB-Pr	AB-Har	AB-Cr
Sample Type	Lake water			River	Lake	Preconcentration to crystallization pond		
Location	Chamo	Chew Bahir	Abaya	Weyto	Shala	Abijata		
AAS (ppm)								
Na ⁺	252.0	102.0	39.0	50.3	11002	7985	26050	105296
K ⁺	5.6	10	2.3	2.3	238	382.45	714	2620
Ca ²⁺	4.6	5.3	3.2	5.2	0.33	0.10	0.09	0.09
Mg ²⁺	2.3	2.1	2.3	4.3	0.11	0.25	0.23	0.05
Li ⁺	<0.05	<0.05	<0.04	<0.04	0.04	0.05	0.08	0.09

Source: (Asnake,2019).

Table 4: Geochemical data of Lithium and other related elements for the MER lakes

Lab Results	Sample ID	Name	K	Na	Ca	Mg	Li
KIGAM GSE	AB01	L- Abijata	476	11,240	2.45	0.32	0.1
			19.3	12,155	2.6	2 0	
KIGAM GSE	SH02	L-Shala (Brine)	198	5,750	5.29	0.85	0.14
			234	7,058	4.8	4 3	
KIGAM GSE	LA01	L- Langano	44.2	854	2.95	0.34	0.32
			38.5	741	2.9	0.3	
KIGAM GSE	FA01	L- Fentale (hot spring)	19.5	390	2.3	2.31	0.01
			18.1	373	1.9	1.8	
KIGAM GSE	BE01	L- Beseka	45.7	2,174	3.19	0.57	0.040
			49.5	1,420	8.9	0.2	
KIGAM GSE	AF02	L- Afdera (Brine)	2,494	38,628	14,138	1,028	6.2
			281.8	42,760	14.2	980	
KIGAM GSE	AS01	L-Asale	8,025	77,826	33,829	6,167	4.62
			96.5	95,550	34,585	71.3	

(Source: KIGAN and GSE, 2012) and the letter L stands to represent lake

Table 4 shows that the concentration of lithium and potassium in the Danakil lakes (lakes Afdera and Asale) is higher than in the MER's other hot springs and lakes. The lithium content (Table 4) observed from Lake Afdera and Asale, both of which are part of the Danakil depression, is 6.2 and 4.62 ppm, respectively, indicating relatively high values when compared to other MER locales (KIGAM and GSE, 2012). The lithium concentration in Lake Afdera and its adjacent hot springs (Table 4) ranged from 0.1 to 6.2 ppm (Asnake, 2019). The content of lithium recorded by this paper researcher and reorded by (Asnake, 2019) from the same area is a little bit different which is 8.7 ppm and 6.2 ppm.

4.3. Lithium Beneficiation in the Afdera Lake

4.3.1. Geochemical laboratory Result of the Afdera lake Brine Concentrate

Table 5: AAS result of lithium concentrate (Lab observation, July-2023)

Code No	Lab No	SiO ₂	CaO	Li	Na ₂ O	K ₂ O	MgO
em-21	670	0.12	<0.01	53.8	0.13	0.01	4.98
	670-d	0.14	<0.01	52.5	0.2	0.03	4.94

After beneficiation (evaporation and chemical treatment) of the lake sample a dry solid precipitate (evaporite) were AAS was analyzed in the laboratory. Table 5 shows the concentration of the lithium and major oxides of the concentrate in which the content of lithium recorded in the concentrate is 53.8% .

According to the results of this study, the average lithium concentration in the Afdera lakes is 8.7 ppm, and the beneficiated concentrate percentage of lithium is 53.8%. According to prior research by [KIGAM and GES \(2012\)](#), the lithium level of the Afdera lake is 6.2 ppm. However, the concentration of lithium in the Afdera lake remains below the current brine cutoff grade value of 200 ppm ([Bradley et al., 2013](#)) for commercial lithium extraction.

The lithium concentration in Afdera Lake is relatively high when compared to the main Ethiopian rift lakes and the majority of hot springs. The maximum lithium level of the lake brines and hot springs from the Danakil depression is 17.2 ppm. The lithium content of the Dallol hot spring was higher than that of the Afdera brine lake and other brine lakes in the country. However, the entire brine lake is below the cut of grade for economic extraction. Even though the concentration was below the cut-off, the researcher attempted to beneficiate the Afdera lake brine solution and produced 53.8% lithium at the concentrate.

The beneficiation methods of evaporation and chemical treatment were effective since the concentration of the target mineral (Lithium) in the concentrate after beneficiation reached 53.8% from 8.7 ppm in the feed. During the beneficiation process, lithium is consumed. This level of lithium concentration 8.7 ppm is not economical in present technology, and it is 23 times less than the current exploitable lithium brine deposit cutoff grade value (200 ppm), as indicated by [Bradley et al. \(2013\)](#). As a result, while lithium extraction from Afdera Lake is not commercially feasible, it can be used as a byproduct by salt processing industries.

CHAPTER FIVE

CONCLUSION AND RECOMMENDATION

5.1. Conclusion

The results of the atomic absorption spectroscopy investigation provide a novel perspective on the presence and absence of probable lithium brine and associated major cations. The geochemical analysis of the brines from the Afdera lakes has a lithium level of 8.7 ppm. In comparison to the main Ethiopian brine lakes, the study area Afdera lake has a higher lithium concentration than the MER lakes, although dallol hot spring has a larger lithium content than Afdera brine lake. Even if the concentration of lithium was small in Afdera brine lake it was beneficiated by evaporation and chemical treatment method and the concentration of lithium after processing reached 53.8%. Since lithium is extremely soluble it was stored in a carbonate form in the concentrate after processing. From the beneficiation result obtained we can conclude that the solar evaporation and chemical treatment method is effective but there may be other techniques such as ion exchange method that can recover up to 90%.

Generally, the following conclusions are derived based on the results of the lithium analysis in the feed and concentrate. Despite the fact that the lithium content in the Brine Afdera lake is (8.7 ppm), the beneficiation can have commercial implications when combined with Potash and lithium extraction. As a byproduct of potash processing, lithium can be treated. In another manner, lithium production may not necessitate the construction of further processing plants, lowering costs by requiring simply solar evaporation of end brines and separation of lithium from other elements. So that we can concluded that the technique the researcher used to process lithium which is called evaporation and chemical treatment method can be cost effective even if the content is below the cut-off grade because processing using solar evaporation do not need high cost.

5.2. Recommendations

The following recommendations are derived from the project outcome.

- ❖ The lithium concentration in the Afdera brine Lake is low, but it is higher than some other brine lakes and hot springs of the main Ethiopian rift. Even though there is some information regarding the lithium concentration in Afdera Lake and its surroundings, more detailed sampling and inquiry are required for a better understanding of the lithium

distribution in the study area and its surroundings.

- ❖ Because the demand for lithium is quickly increasing, a cost-effective processing technology should be created specifically to treat a brine lake with a substantially lower lithium content than the cut of grade.
- ❖ To gain a better understanding of lithium carrying brines and their beneficiation procedures, thorough investigations of the brines employing various analytical methodologies and processing technologies are necessary. As a result, the aspiring (oncoming) researcher should make every effort to achieve this.
- ❖ Because lithium concentrations may vary depending on the position and depth of the lake, a detailed mineralogical investigation from different depth and position of the Afdera lake and nearby lakes is recommended.
- ❖ Beneficiation of lithium from Afdera lake and nearby brine lakes is currently not economically possible, however potash processing industries are advised to take the end brine after potash production and then employ lithium extraction procedures to utilise the lithium as a byproduct.

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Appendix

Photos taken in the Atomic Absorption Spectroscopy laboratory room



Figure 10: photo taken at the time of AAS result reading of the brine sample in the lab(May, 2023)



Figure 11: Photo taken during AAS reading in Lab, 2023

Photo taken in AAiT laboratory during Beneficiation



Figure 12: Image taken during beneficiation, July 2023



Figure 13: Photo taken during Filtering the precipitated concentrate, 2023

Ethiopian mineral petroleum and bio fuel corporation
Laboratory service center

Form G0004
ADDIS ABABA

E-mail: emindyt@telecom.net.et
water Analysis Report Format
FILE ID: 660-23
Sample type: WATER
Preparation: No
NUMBER OF SAMPLES: 1
Analytical Method: AAS
Analytical Results in: (mg/L)

011-6-613355
box 2543
Originator :- Elias Mamushet Woldeyohannis
Date submitted: 03-06-23
Element to be determined: Li & major cations

Field No	Lab No	Ca+(mg/l)	Mg+(mg/l)	Na+mg/l	K+(mg/l)	Li(mg/l)
em-12	660	22.13	12.56	82867	625	8.98
	660-d	25.45	13.56	83025	698	8.42

Analyst: _____ Checked By: _____ approved by: _____ DATE REPORTED: _____
jun-16-2023




Figure 14: Image of one of the brine samples AAS result, 2023