

**DEVELOPMENT OF SAMPLING METHODS AND ANALYSIS
OF BERYLLIUM IN FUME DUST USING FILTERS**

BY

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DHAHRAN, SAUDI ARABIA

In Partial Fulfillment of the
Requirements for the Degree of

MASTER OF SCIENCE

In

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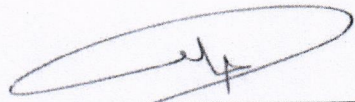
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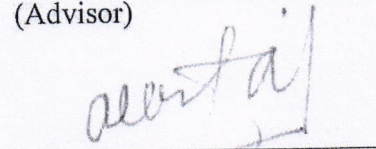


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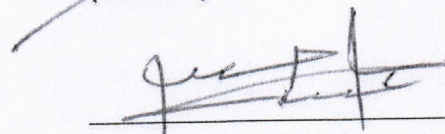
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I would like to dedicate my dissertation work to my parents, wife, thesis committee members, and the chemistry department at King Fahad University of Petroleum and Minerals. Also. Ma'aden Aluminum company management for their support and cooperation |

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LIST OF ABBREVIATIONS

XRD	:	X-ray diffraction
IARC	:	International Agency for Research on Cancer
STEL	:	Short-term exposure limit
EBC	:	Exhaled breath condensate
CBD	:	Chronic Beryllium Disease
QEA	:	Quantitative Exposure Assessment
MSDS	:	Materials Safety Data Sheet
pH	:	Negative logarithm, base 10, of hydrogen ion concentration
OSHA	:	Occupational Safety and Health Administration
NEBOSH	:	National Examination Board in Occupational Safety and health
OEL	:	Occupational exposure limits
PVC	:	Polyvinylchloride
SEM	:	Scanning Electron Microscopy
MBAC	:	Ma'aden Bauxite and Alumina Company
GTC	:	Gas Treatment Center
BTP	:	Bath treatment plant
FTIR	:	Treatment of Aluminum in Crucible

ICP MS	:	Inductively coupled plasma mass spectrometry
MCE	:	Mixed Cellulose Ester
MDL	:	Method Detection Limits
ASTERR Radiometer	:	Advanced Spaceborne Thermal Emission and Reflection
SPL	:	Spent Pot Relining
SEG	:	Similar Exposure Group

|

ABSTRACT

Full Name : [SALAH JABER ALMUTAIRI]

Thesis Title : [Development of Sampling Methods and Analysis of Beryllium in Fume Dust using Filters]

Major Field : [CHEMISTRY SCIENCE]

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Beryllium is a highly toxic element that may cause health issues among workers in the Aluminum industry at a high level. This Thesis research aims to investigate various sampling methods and microwave acid digestion toward precise analysis of fume dust filters and several aluminum raw materials. The process for extracting inorganic beryllium species from emissions particulate matter and working locations has been performed. The speciation process was modified to collect beryllium from airborne particles in a closed-face cassette with a Polyvinylchloride (PVC) filter sampler for individual quantification. Exposure to beryllium through filters and sample cassette with pump has been performed in different locations in the aluminum pot room at Aluminum Industry. This Thesis research has been performed with samples from Ma'aden Aluminum Company. After the beryllium fume dust is collected on the filters, it has been digested through microwave acid digestion to be ready for chemical analysis. The determination of beryllium concentration in the samples has been performed by inductively coupled plasma optical emission spectroscopy (ICP –OES). Multiple measurements of the spiked samples have been used to determine the procedure's reliability.

These species were spiked on cassettes were tested for Beryllium concentration and found insignificant concentrations lower than the exposure limit. Beryllium concentration in PVC is 0.0904 $\mu\text{g}/\text{m}^3$ which is less than the exposure limit is 0.2 as OEL-TWA.

There is a trace level of beryllium in all potential resources of Beryllium in pot room baths such as bauxite, Fresh alumina, Fluorinated alumina, Petroleum coke, tar pitch, Anode cover, and aluminum dross. The chemical digestion of the raw materials has been performed through Microwave acid digestion and then analyzed in Inductively coupled plasma optical emission spectrometry ICP-OES for beryllium concentrations analysis.

Alumina obtained from Ma'aden Bauxite and Alumina Company (MBAC) in Saudi Arabia contains very low trace beryllium (0.3 ppm), which is considered ideal alumina and one of the perfect alumina in the World. The specification limit of beryllium in Alumina should be less than 0.7 ppm.

The exposure assessment results revealed “Insignificant” exposure to Beryllium which means workers at M'aaden Aluminum are not exposed to Beryllium and the exposure level is below the Occupational exposure limits (OEL) which are mainly intended to eliminate workers from inhaling chemicals such as vapors, mists, or dust above the maximum limit. All the data obtained for this research has been validated by an external certified laboratory in the United States of America.

ملخص الرسالة

الاسم الكامل: صلاح جبر مطلق المطيري

عنوان الرسالة: تطوير طرق أخذ العينات وتحليل البريليوم المنبعث باستخدام المرشحات

التخصص: كيمياء

تاريخ الدرجة العلمية: مارس 2022

نظرا لان البريليوم عنصر شديد السمية قد يسبب مشاكل صحية بين العاملين في صناعة الألمنيوم على مستوى عالٍ. يهدف بحث الأطروحة هذا إلى التحقق من طرق أخذ العينات المختلفة وهضم الميكروويف من أجل تحليل دقيق لمرشحات غبار الدخان والعديد من مواد الألمنيوم الخام. تم إجراء عملية استخراج أنواع البريليوم غير العضوية من الجسيمات المنبعثة ومواقع العمل. تم تعديل عملية الانتزاع لتجميع البريليوم من الجسيمات المحمولة في الهواء.

في كاسيت مغلق الوجه بأخذ عينات من مرشح البولي فينيل كلوريد (PVC) للتقدير الكمي الفردي تم إجراء التعرض للبريليوم من خلال المرشحات وعينات الكاسيت بالمضخة في مواقع مختلفة في غرفة وعاء الألمنيوم في صناعة الألمنيوم. بعد جمع غبار دخان البريليوم على المرشحات، يتم هضمه من خلال هضم حمض الميكروويف ليكون جاهزاً للتحليل الكيميائي. تم إجراء تحديد تركيز البريليوم في العينات عن طريق مطيافية الانبعاث الضوئي للبلازما المقترنة بالحث (ICP – OES) تم استخدام قياسات متعددة للعينات المسننة لتحديد موثوقية الإجراء.

تم وضع هذه الأنواع على شرائط كاسيت حيث تم اختبارها لتركيز البريليوم ووجدت تركيزاً ضئيلاً أقل من حد التعرض.

تركيز البريليوم في PVC هو 0.0904 ميكروغرام / متر مكعب وهو أقل من حد التعرض وهو 0.2 مثل-OEL

TWA.

يوجد مستوى ضئيل من البريليوم في جميع الموارد المحتملة للبريليوم في غرفة الأواني مثل البوكسيت، والألومينا، والألومينا المفلورة، وفحم الكوك، وزفت القطران، وغطاء الأنود، وخبث الألومنيوم. تم إجراء الهضم الكيميائي للمواد الخام من خلال هضم حمض الميكروويف ثم تم تحليله في مطياف الانبعاث البصري للبلازما المقترن بالحث-ICP-OES لتحليل تركيزات البريليوم.

يحتوي الألومينا الذي تم تحليله على نسبة منخفضة جداً من البريليوم (0.3 جزء في المليون)، والتي تعتبر الألومينا المثالية وواحدة من الألومينا المثالية في العالم. يجب أن يكون حد مواصفات البريليوم في الألومينا أقل من 0.7 جزء في المليون.

أظهرت نتائج تقييم التعرض تعرضاً "غير ملحوظ" للبريليوم مما يعني أن العاملين في المجال غير معرضين للبريليوم ومستوى التعرض أقل من حدود التعرض المهني (OEL) والتي تهدف بشكل أساسي إلى منع العمال من استنشاق المواد الكيميائية كأبخرة، ضباب أو غبار فوق الحد الأقصى.

تم التحقق من صحة جميع البيانات التي تم الحصول عليها لهذا البحث مع مختبر خارجي معتمد في الولايات المتحدة الأمريكية.

CHAPTER 1

INTRODUCTION

In recent years, beryllium concentrations in aluminum reduction pot room which are concentrated in Cryolite baths used in the Aluminum industry have become a worldwide concern because of its associated hazard. Beryllium is a highly radioactive element that must be treated with great caution to protect workers' health in the aluminum industry. Chronic Beryllium Disease, a pulmonary disease followed by sensitization to the Beryllium, and lung cancer may also be caused by Beryllium exposure. According to NIOSH, (2011), "workers exposed to particles, fumes, mists, and solutions from beryllium-containing materials may develop beryllium sensitization or chronic beryllium disease, a potentially disabling or even fatal respiratory disease. "The International Agency for Research on Cancer [5] classifies beryllium as a Group one carcinogen, and the European Union classifies it as a Category 1B (known or presumed) carcinogen.

Beryllium is considered one of the most toxic elements for living organisms. Toxicologically relevant exposures to beryllium and its compounds are almost exclusively limited to the workplace. Before the introduction of improved emission control and hygiene measures. Several neighboring cases of chronic beryllium disease were reported in 4,444. Several hundred cases of acute beryllium disease occurred in the 1930s and 1940s, particularly among workers at beryllium extraction plants in many countries (Vaessen and

Szteke 2000). Beryllium is also a known Cancer-causing substance. It is classified as a Group 1 - Carcinogenic to humans by the International Agency for Research on Cancer (IARC), and as an A1 - Confirmed human carcinogen by the American Conference of Governmental Industrial Hygienists (ACGIH). In March 2017, OSHA published its final rule Occupational Exposure to Beryllium and Beryllium Compounds in the Federal Register.

The new 8-hour time-weighted average (TWA) permissible exposure limit

(PEL) for beryllium is 0.2 µg/m³ and the new short-term exposure limit (STEL) over a 15-minute sampling period is 2.0 µg/m³. AL: 0.1 µg/m³.

Berylliosis is a form of Beryllium metal poisoning induced by inhaling beryllium dusts, vapors, or compounds, or by skin implantation of the chemical. Occupational exposure to beryllium is the most common cause of harmful consequences.

Beryllium can be found in the earth's crust, coal combustion emissions, surface water, and soil, as well as household dust, drinking water, and cigarette smoke (U.S. EPA, 1987a). Workers in the beryllium production, Aluminum industry, fabrication, or reclamation industries, on the other hand, are at the greatest risk of exposure (ATSDR, 1988). Workers are exposed to a variety of beryllium compounds in the form of dust and fumes; the current occupational standard for beryllium exposure is 2 g/m³ during an 8-hour workshift (OSHA, 1989). Inhaled beryllium is slowly absorbed and concentrates mostly in the lungs, bone, liver, and kidneys.

Because of its chemical characteristics, significant absorption of beryllium or its derivatives via intact skin is improbable (U.S. EPA, 1987b). Beryllium is not biotransformed per se, however, soluble ions in the lungs can be changed to less soluble molecules (U.S. EPA, 1987b). The majority of orally supplied beryllium passes through the gastrointestinal system unabsorbed and is eliminated in the feces (Reeves, 1965), whereas water-soluble beryllium salts breathed are primarily excreted via the kidneys (Zorn). Inhaled beryllium, on the other hand, has well-documented toxicity. Acute berylliosis can be caused by inhaling "large" quantities of beryllium compounds (such as the water-soluble sulfate, fluoride, chloride, and oxide) (Constantinidis, 1978). Based on available evidence, the ATSDR (1988) predicted that the disease might develop at levels ranging from around 2-1000 g Be/m³. Rhinitis, pharyngitis, and/or tracheobronchitis are common symptoms that appear immediately after exposure and can progress to severe lung symptoms. The severity of acute beryllium toxicity is related to exposure levels, and the disease is now uncommon in the United States due to improved environmental controls.

Beryllium is a grey metal that is both stronger and lighter than steel and aluminum. Its high strength-to-weight ratio, high melting point, outstanding thermal stability and conductivity, reflectivity, and X-ray transparency make it an indispensable material in the aerospace, telecommunications, information technology, defense, medical, and nuclear industries.

Beryllium is utilized in the industry in three different forms: as a pure metal, as beryllium oxide, and most commonly, as a copper, aluminum, magnesium, or nickel alloy. Beryllium oxide (also known as beryllium) has a high heat capacity and is used in a variety of sensitive electronic devices

The Materials Safety Data Sheet (MSDS) for Beryllium explains the potential hazard of Beryllium in terms of inhalation, Ingestion, and Chronic long-term health effects.

Exposure to the beryllium through inhalation, ingestion, and skin contact can occur when melting, pouring, slag handling, heat treatment, abrasive cutting, welding, heated scraping the surface of that material in a manner that produces particles.

Exposure can also occur during repair or maintenance work on contaminated equipment such as furnace Remodeling, maintenance or repair of air purification equipment, structural renovation, welding, etc.

Deposits of particles on hands, gloves, and clothing can be transferred to breathing and inhalation of normal movements of the hand to the face, such as rubbing the nose or eyes, sneezing, and coughing.

Inhaling beryllium-containing particles can cause a serious chronic lung condition called Chronic Beryllium Disease (CBD) in some people. Lung disease can be fatal over time. Chronic beryllium disease is an allergic or hypersensitivity condition that causes the tissue in the lungs to become inflamed. This inflammation, sometimes accompanied by fibrosis (scarring), can reduce oxygen exchange between the lungs and the bloodstream.



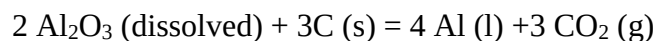
Figure 1 MSDS explained the Hazard of exposure to Beryllium Dust

1.1 Aluminum Production

Aluminum is primarily in the 3+ oxidation state and is a common component of several minerals, especially silicates. It shows amphoteric properties and therefore can react with both alkaline and acidic compounds.

The most common Aluminum minerals are bauxites, which mainly include Aluminum minerals such as gibbsite, boehmite, and diaspora, which very often occur in a mixture with two Fe oxides (goethite and hematite). Due to the versatile properties of Aluminum, it is used in various industrial sectors such as metallurgy, construction, electricity, chemistry as well as transportation, and packaging (especially food).

The Hall Heroult process is the most design applied in the Aluminum smelter process. Aluminum cannot be manufactured by an aqueous electrolytic process because hydrogen is electrochemically much nobler than aluminum. Thus, liquid aluminum is produced by the electrolytic reduction of aluminum oxide (Al_2O_3) which dissolves in an electrolyte (bath) containing mainly cryolite (Na_3AlF_6). The general chemical reaction in the aluminum reduction can be written as:



The pot line section mainly consists of alumina handling and conveying system, Alumina reduction in the aluminum smelting pots using electrolysis, and the Gas Treatment Centre (GTC) to clean the gases emitted from the electrolysis process before venting into the atmosphere. The alumina handling and conveying system starts from the Alumina silos which receive fresh alumina from the alumina refinery plant adjacent to the smelter facility.

The received alumina is first transported to the GTC wherein the fresh alumina is used for dry scrubbing the smelter exhaust gas. This dry scrubbing process captures the fluorine and other harmful gases from the reduction of exhaust gases and the cleaned exhaust is then vented to the atmosphere using the GTC Fans. The resultant fluorinated Alumina is then sent into the aluminum smelter pots for the reduction process.

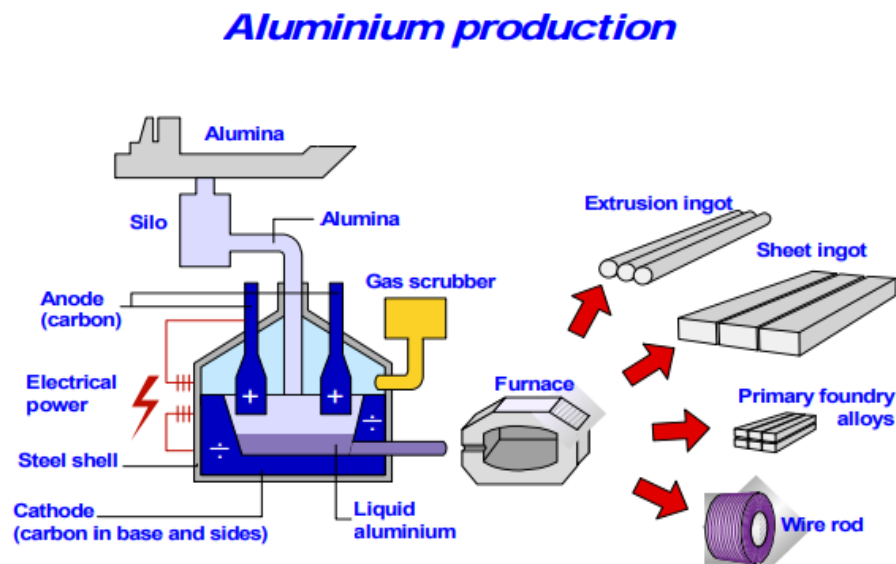


Figure 2 The Hall Heroult process in the Aluminum production process

Aluminum forms at around 900 ° C, but after the formation has a melting point of only 660 ° C. In some foundries, this excess heat is used to melt the recycled metal, which is then mixed with the new metal.

Recycled metal only requires 5 % of the energy it takes to make new metal. Mixing recycled metal with new metal allows for significant energy savings as well as efficient use of the additional available heat. In terms of quality, there is no difference between the primary and recycled metal.

The smelting process required to make aluminum from aluminum oxide is continuous, the pot line typically being in production 24 hours a day throughout the year. A melt can't just stop and start over. If production is interrupted by a power outage of more than four hours, the metal in the pot solidifies and often requires costly modifications.

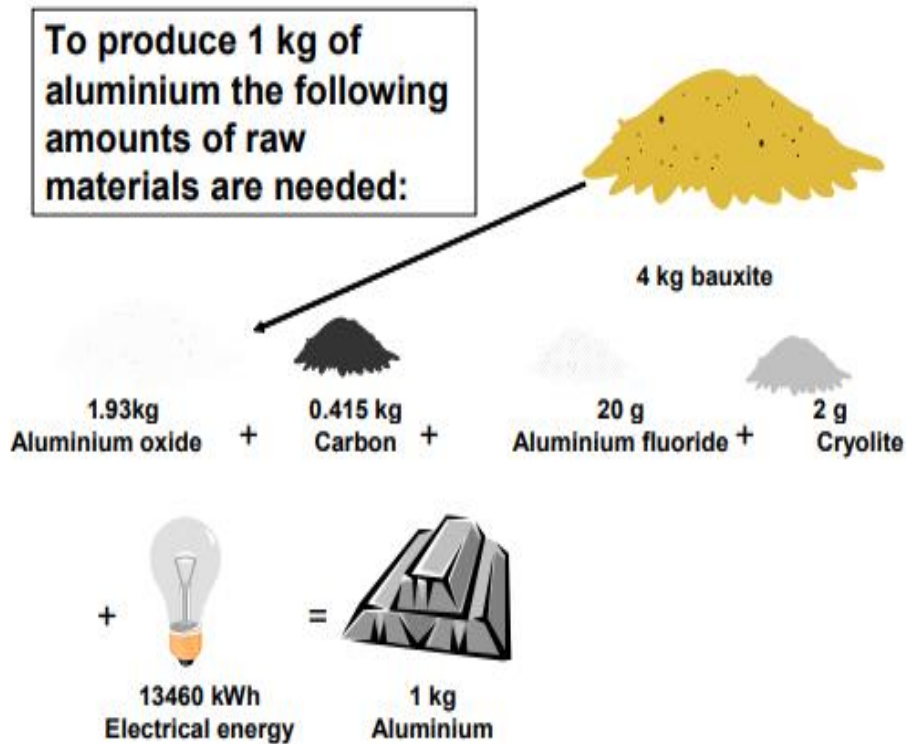


Figure 3 Basic explain to produce 1 Kg of Aluminum

1.2 Description of Raw Materials used in Aluminum Production

1.2.1 Bauxite

It is the most important aluminum-containing mineral for the production of alumina.

The bauxite is found near the surface in streaks from one meter to nine meters, which form as small reddish pebbles (pisolitas). Bauxite contains 40 to 60% mass of aluminum oxide combined with smaller amounts of silicon dioxide, titanium oxide, and iron oxide. Alumina is obtained primarily from bauxite using the Bayer process where it dissolves the aluminum compound of bauxite ore in a sodium hydroxide (caustic soda); caustic soda support removing the impurities from the solution.



Figure 4 Bauxite from the ore of Aluminum oxide to pure Aluminum

A Bayer Process plant is basically a device for heating and cooling a large recirculating stream of caustic soda. Bauxite is added at the high-temperature point, the red mud is deposited at an intermediate temperature, and the aluminum oxide is precipitated in the cycle at the low-temperature point.

The formula of beryllium in bauxite is not known as beryllium and is probably a combination of minerals like beryl, bertrandite, chrysoberyl, etc.

The chemical reaction of bauxite digestion

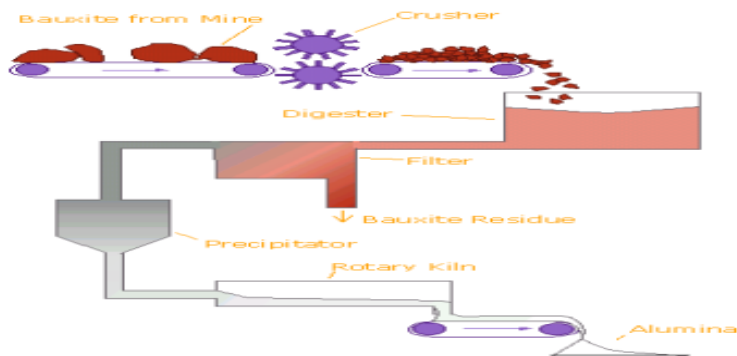
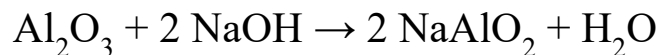
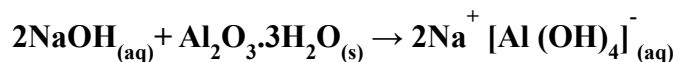


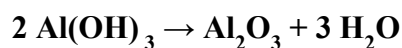
Figure 5 Bayer process plant

The reaction of caustic chemically combined with alumina hydrate



Alumina Tri-hydrate (Gibbsite) sodium aluminate

The final reaction will be Alumina Calciner as the following



1.2.2 Carbon Anodes

In electrolytic aluminum production, carbon consumption ranks second after quantitative aluminum oxide consumption. 415 kg of carbon is consumed per metric tons (MT) of Aluminum production. Carbon quality is of great concern to the pot line room, not only because it is an expensive resource, but also because of the impact poor quality can have on potting operations. The anodes are made of carbon with the least amount of impurities possible. Calcined petroleum coke, butts, and pitch as a binder are used as raw materials to make the backed anode

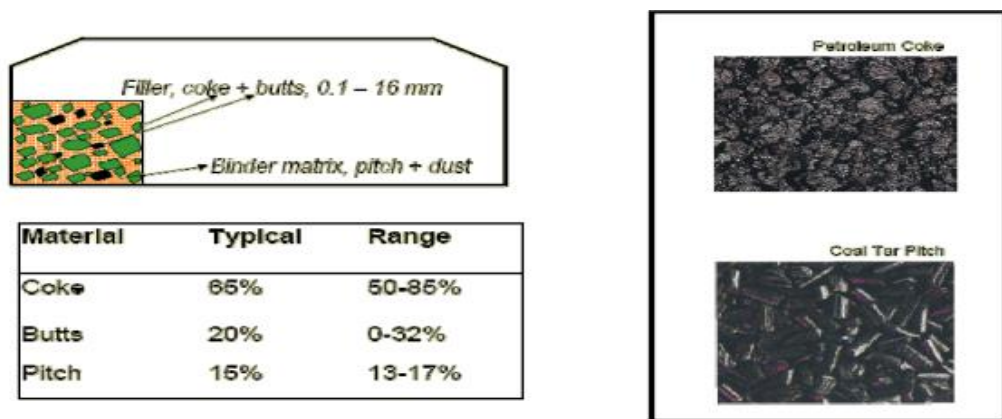


Figure 6 Carbon Anode composition

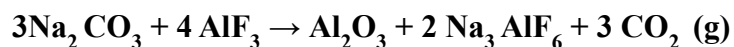
1.2.3 Cryolite Bath

Cryolite is the main component of the electrolyte used in the electrolysis of alumina. From a chemical point of view, it is Na_3AlF_6 , a double fluoride made from sodium and aluminum. It is a white granular powder. Certain impurities can cause a gray or pink discoloration. The freezing point of cryolite is 1009°C . Synthetic cryolite is made from fluorspar (CaF_2), which occurs as a natural mineral. Fluorspar is treated with sulfuric acid to produce HF hydrofluoric acid.



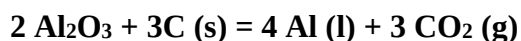
Next, HF is reacted with sodium oxide Na_2O and aluminum oxide to produce cryolite

The chemical reaction of adding aluminum fluoride to generate Cryolite bath will be as the following



1.3 Beryllium in Aluminum Production

Beryllium can accumulate in an Aluminum pot room bath because beryllium is a Group two metal that is found near lithium, sodium, magnesium, and calcium in the Periodic Table. Beryllium is an alkaline earth metal with several poisonous compounds. The electrolytic reduction of alumina (Al_2O_3) dissolved in an electrolyte (bath) primarily having Cryolite produces liquid aluminum (Na_3AlF_6). The following is a representation of the overall chemical reaction:



During the smelting process, beryllium is concentrated in the molten cryolite bath. The primary source of the electrolyte used in Aluminum Reduction of alumina electrolysis is cryolite. The Aluminum smelter workers diagnosed with Beryllium Sulfide either directly operated the pot lines or performed maintenance work on the Aluminum pots, all tasks with high potential for exposure to the cryolite bath. These elements combine to form compounds like beryllium fluoride (also known as beryllium difluoride, BeF_2) and sodium fluoroberyllate (Na_2BeF_4). Fresh alumina and pot room bath from another smelting location are the most popular sources of beryllium. The trace concentration of beryllium is found in some bauxite, it is the ore of alumina that occurs naturally, and the source of beryllium in alumina. Though not always, traces of beryllium and lithium can be found together in bauxite deposits in trace quantity. Aluminum smelting is an electrolytic reduction process during which aluminum oxide is dissolved in molten cryolite bath (sodium aluminum fluoride) contained in a large carbon- or graphite-lined steel container, known as a pot. During the smelting process, beryllium is concentrated in the molten cryolite

bath. During reduction, the pot emits Sulphur dioxide, hydrogen fluoride, particulate fluoride, alumina, and coal tar pitch volatiles. Control of these emissions relies on ventilation systems for collection at the source and respiratory protection during the performance of certain tasks such as opening the hoods on the pots. The aluminum smelter workers diagnosed with BeS either directly operated the pot lines or performed maintenance work on the aluminum pots, all tasks with high potential for exposure to the cryolite bath.

The Beryllium concentrated in Cryolite Bath and can be carried over into aluminum dross, and a trace amount will be found in the aluminum final metal casting.

Aluminum dross containing a proximally of 50 % aluminum oxide will be a part of this study in thesis research, it is a byproduct of the aluminum smelting casting. It can be recycled through the casting furnaces to distinguish the residual aluminum metal casting from the aluminum oxide. Beryllium can be in concentrate in a zone of the spent lining bath.

The following figure will explain where Beryllium can be found to accommodate Aluminum Production.

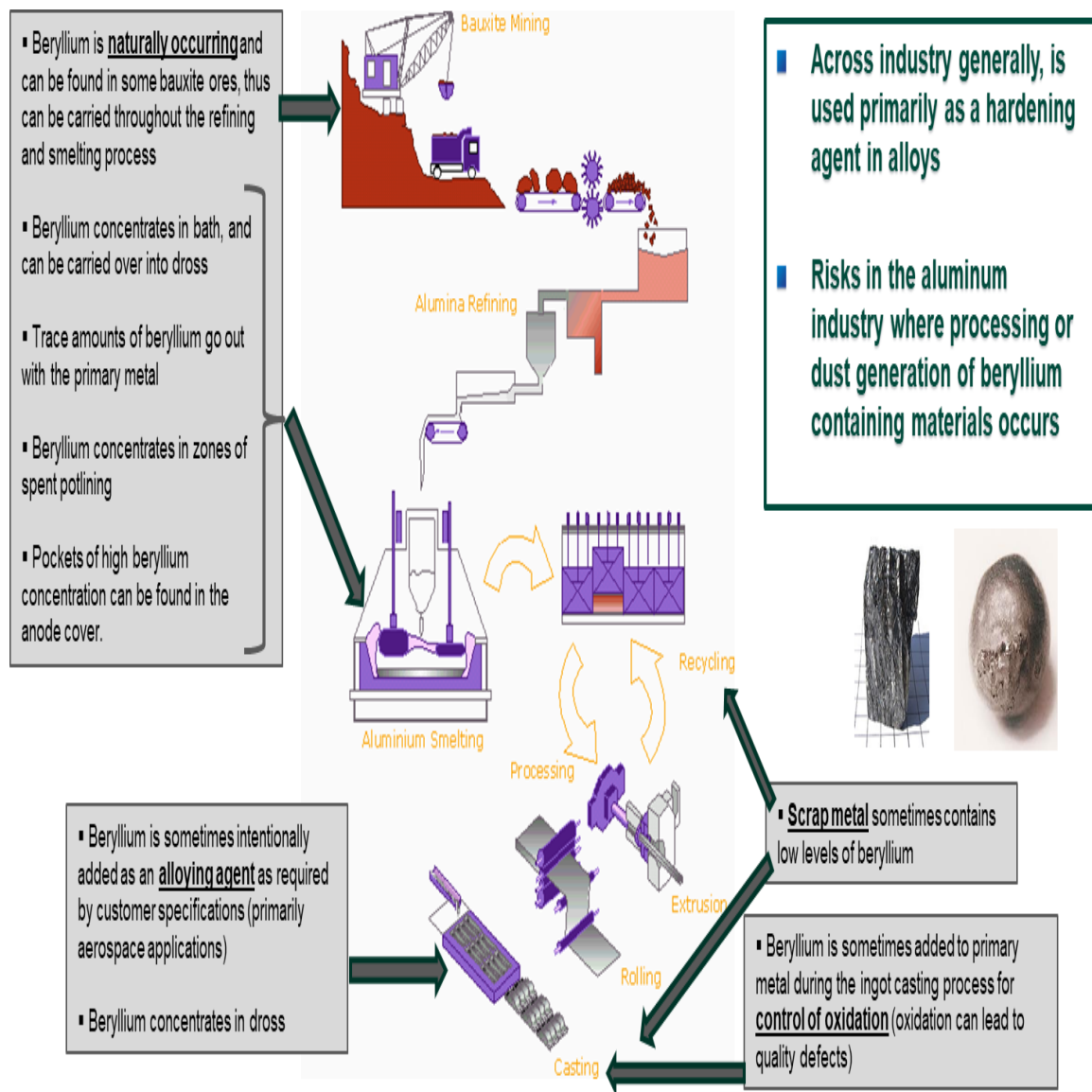


Figure 7 Beryllium in the manufacturing process

Beryllium can be found in some bauxite (Al_2O_3). Adding as an alloying agent in some applications (Aerospace application) Beryllium concentrated in Cryolite bath (Na_3AlF_6) Cryolite bath (Na_3AlF_6) recycled with the spent anode in Pot room bath recycle store (PBRs) having concentrated Beryllium affecting the worker. Area of study for personal exposure to Beryllium

1.4 Bath Chemistry

Bath chemistry is a general term, covering a wide area of topics, not only bath or electrolyte, even though it is the core in aluminum smelting. Cryolite, the magic compound used in aluminum smelting, is the dominant component (~80%) in the electrolyte composition:

1- Part of molten fluoride system which is electrochemically stable or inert

2- Unique capability as a solvent for oxide alumina

3- A unique set of physical-chemical properties to allow passing electricity and yet with a certain resistance for heat generation for self-heating for electrolysis to occur, high productivity and efficiency, easy product (Al and CO_2) separation, highly corrosive and yet easy to contain. The most common chemistry is about 10 to 12 % XS AlF_3 or 1.09 to 1.13 ratio with an operating temperature of 955 to 965 °C.

The Cryolite bath with Aluminum fluoride, sodium fluoride, and alumina is involved in the process of Aluminum smelting where they are remaining in a solid state at ambient temperatures. Then, it will be in a molten state where the solid will be changed to liquid at a specific melting point. From solid-state to molten state, there will be visible changes such as color change and physical change

Behind the states change from solid states to molten metal liquid states by applying an operating temperature of 965 °C, the physical change, and chemical structure can be explained by the following figure

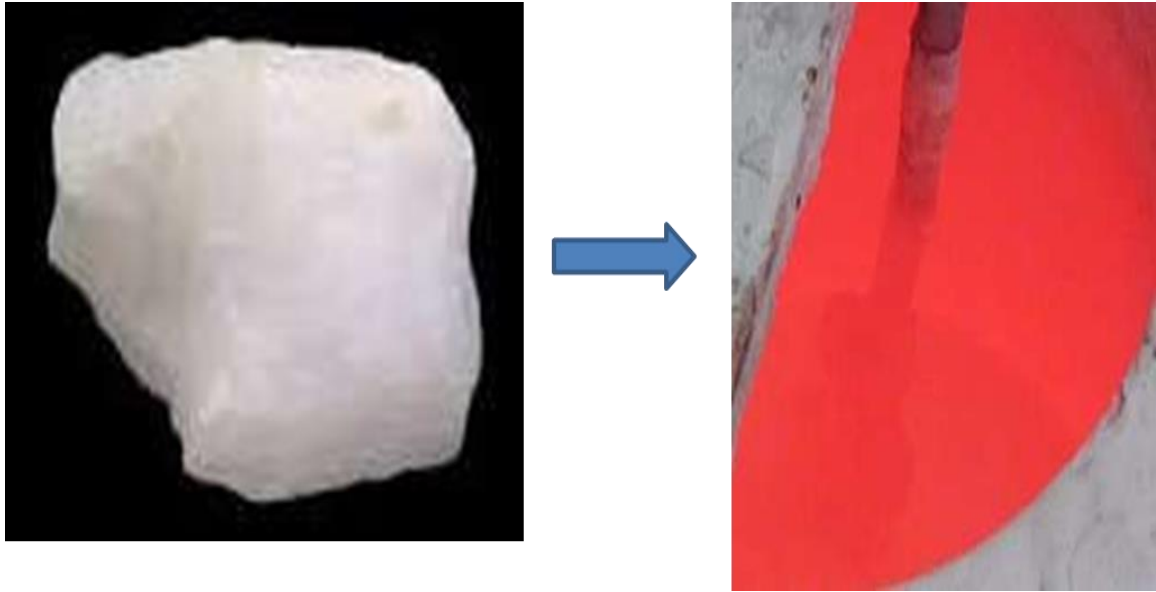


Figure 8 Physical properties of Cryolite bath change from the solid phase to molten metal

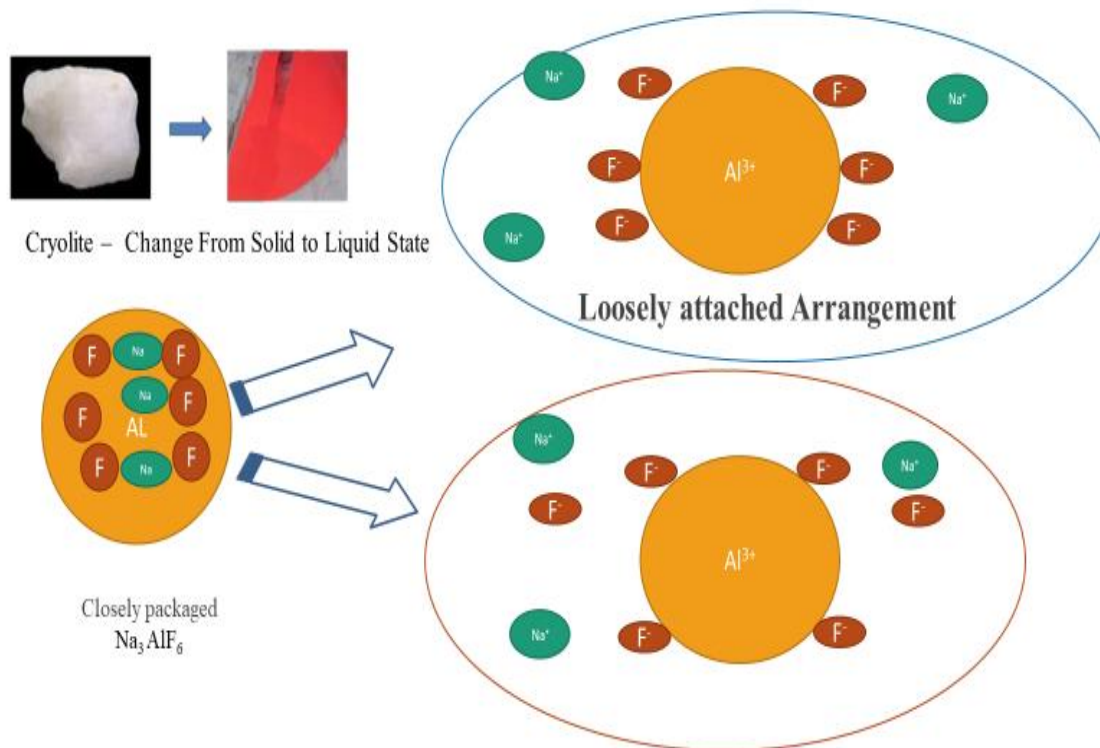


Figure 9 chemical reaction of Cryolite bath before AlF_3 is melted with liquid cryolite

The structural species of cryolite bath is processed once simple and complex ions form. If a cryolite bath is put under a magnetic field, there will be Negatively charged ions, AlF_3^- anions, moving toward to positively charged electrode.

There will be Positively charged ions, Na^+ cations move toward the negatively charged electrode

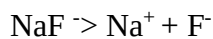
When a current passes through the ionic liquid:

- Electrons (themselves) no longer “available” carrying current through
- Electrons are attached to atoms/molecules as ions (positive/negative charges) to carry the current
- Some ions move faster and carry more amount of electricity than others

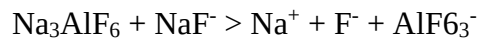


Na_3AlF_6 is compound in the $\text{NaF}^- \text{AlF}_3$ system at $X_{\text{NaF}}=3/4=0.75$ and $X_{\text{AlF}_3}=1/4=0.25$.

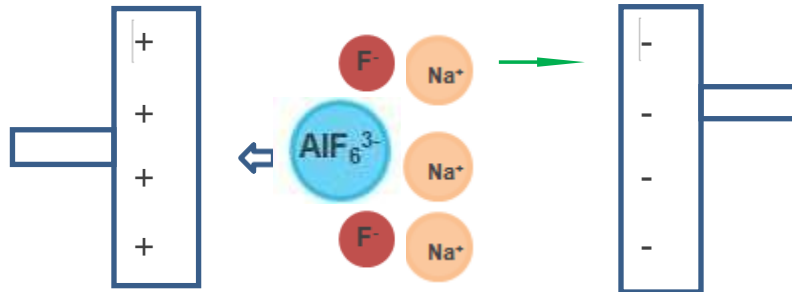
For NaF , Na and F form as monovalent ions, Na^+ and F^- :



If NaF is added in molten cryolite, the following reaction will be formed ;



There are just added ions of Na^+ and F^- , these ions are a lot lot of mobile ions – F^- and Na^+ than AlF_6^{3-}



Cryolite is a solvent for alumina or for alumina to be dissolved in the electrolyte and the only way the oxide can dissolve in cryolite melt – is because Al-O forms complexes with AlF_6^{3-}

When alumina is dissolved in the melt, there can be three complexes:



Cryolite is solvent for alumina and that's why it is accompanied by an Al-O bond. The alumina is dissolved in Cryolite because of the following chemical and physical properties;

- 1- Mobility of ions – change the way how electricity is being carried through an electrical conductivity with the influence of pot voltage ->KWH/kg.
- 2- The Complexes and spacing change of cryolite on how it separates the Al from the electrolyte due to its density of the melt and metal/bath separation ->CE.
- 3- Changes the way in which species escape from the melt due to vapor pressure – fluoride emissions
- 4- Changes the way how species interact with Al or solid materials.
- 5- Changes how much energy to apply to convert oxide to metal due to Electrochemistry and metal purity, energy efficiency and product quality
- 6- Liquids temperature at which the bath starts to freeze
- 7- Electrical conductivity where the ability of a bath to conduct electricity (the opposite of resistivity).
- 8- Alumina Solubility for Max % Alumina (ore) that can remain in the melt without making a muck
- 9- Density is the weight of the bath per volume. Important the bath is lighter than metal
- 10- Viscosity—Thickness of the bath. Important for alumina dissolution and current efficiency

11- Metal Solubility where the Max % of Aluminum metal that can dissolve in the bath.

Metal Solubility is Important for current efficiency in electrochemistry reduction of Aluminum

Bath conductivity or resistivity is probably the most important property, which directly relates to cell voltage (thermal balance), cell cathode-anode distance (stability), current efficiency and energy efficiency

Molten cryolitic bath is an inert and stable electrolyte medium for aluminum smelting, but also a complex fluoride system with varying amounts of the complex. it is species that offers a set of unique physicochemical properties

Phase Diagram Determines if a substance is solid, liquid or gas with composition and temperature. A Ratio/%XS AlF_3 necessary to operate at 950 to 960 °C range (example: if a bath ratio of 1.12 or 10.75% XS with 3% alumina, 6% CaF_2 , is solid or liquid at 940, 950, 960 °C). Side ledge and molten cryolitic bath interactions. Muck Temp-(Pseudo-eutectic) the temperature at which everything freezes

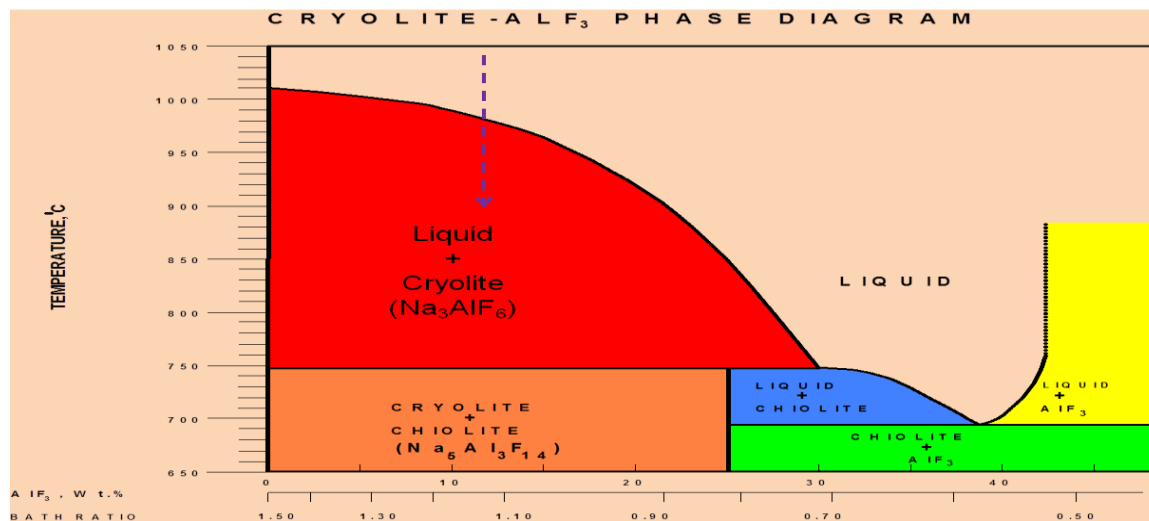


Figure 20 Cryolitic Bath Phase Diagram ($\text{Na}_3\text{AlF}_6 - \text{AlF}_3$)

1.5 Electrochemistry in Aluminum Reduction

Electrochemistry deals with reactions with electron transfers: anodic and cathodic reactions only. Anode Reactions where electrons are given away:



cathodic Reactions where electrons are obtained:



Metal contains electrons that do not occur automatically, force or energy has to be applied which is called anode or cathode voltage. Similarly, energy also has to be applied across anode and cathode to let ions migrate from anode to cathode or from cathode to anode region which is called electrolyte voltage drop.

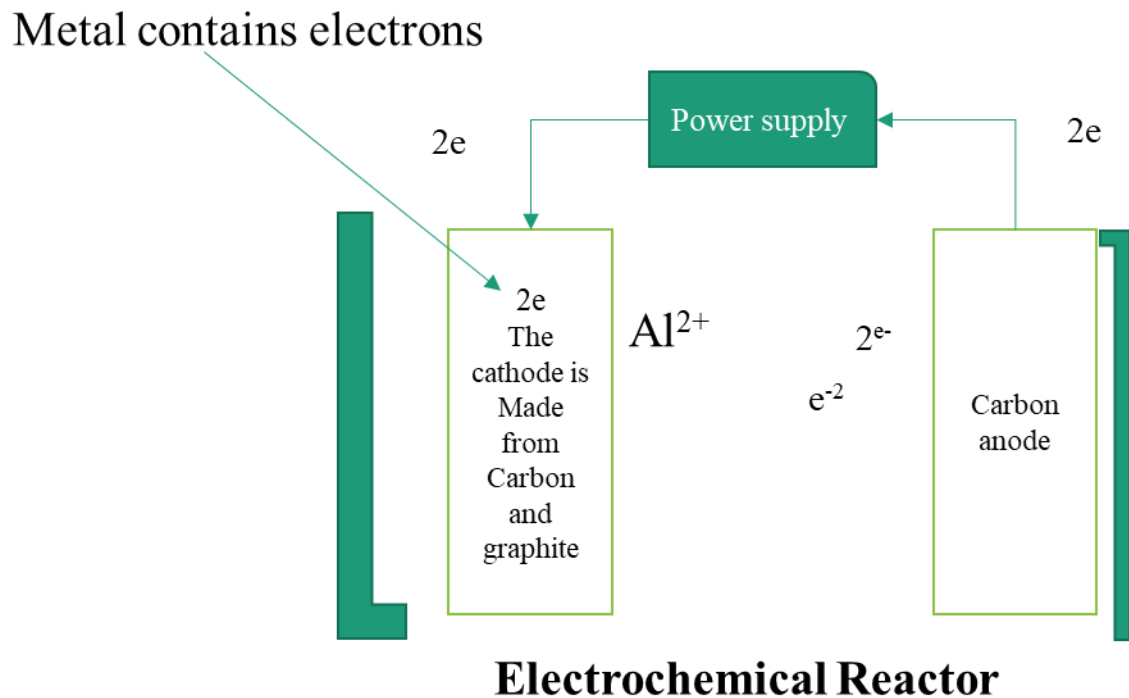


Figure 11 Electrochemical Reactor in aluminum

The Electrochemistry process in Aluminum production is called Hall-Heroult Electrolysis where the aluminum oxide (alumina) is dissolved in molten cryolite and electrolyzed in the molten salt bath, often in a purpose-built cell, which is derived most often from bauxite, aluminum's principal resource, using the Bayer process. At 940–980 °C, the Hall–Hérault method generates 99.5–99.8 percent pure aluminum on an industrial scale.

Because recycled aluminum does not require electrolysis, it is not used in this procedure. [1] The electrolytic reaction emits carbon dioxide, which contributes to climate change, and the process consumes a huge amount of electrical energy.

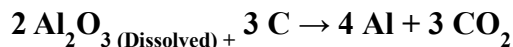
The anode Reaction in Aluminum smelting Electrochemistry is consisting of a Bath with an Anode interface as the following reaction;



On the other hand, the Cathode Reaction in Aluminum smelting Electrochemistry is consisting of a Bath with a metal interface as the following reaction



The general chemical reaction in the aluminum Electrolysis



Aluminum metal is made at bath/metal interface



Al^{3+} is an oxidizing agent

In the aluminum electrochemistry smelting process, there are chemical elements impurities in the molten metal which are brought from alumina, anode, chemicals, and lining materials. These elements are sodium (Na), potassium (K) , Beryllium (Be) , Magnesium (Mg), Calcium (Ca) , Titanium (Ti) , Vanadium (V) , Iron (Fe) , Nickel (In) , Copper (Cu) , Silicon (Si) , Phosphorus (P) , Sulfur (S)

The following elemental impurities in the Aluminum Molten metal Sodium (Na), Potassium (K), Beryllium (Be), Calcium (Ca) are sourced from the bath

1.6 Statement of problem

If the worker in the aluminum industry exposure to a trace amount of beryllium about $0.2 \mu\text{g}/\text{m}^3$, it can cause pulmonary granulomatosis, also known as berylliosis. It is more important to assess the internal dose of beryllium received by the lungs of all workers for occupational health monitoring than it is to assess the external dose of beryllium received by the lungs. Exhaled breath condensate (EBC) is a non-invasive matrix derived from the fluid that lines the airway. In a primal study, EBC beryllium (Be) levels were assessed as a marker of occupational exposure. Even though most of the Aluminum industry is usually performed a Quantitative Exposure Assessment to measure the Beryllium exposure level for the workers, no more studies research has been done to investigate the resource of Beryllium in aluminum production.

In addition, there is no standardized developed analytical laboratory analysis to digest most of the resources raw materials used in the Aluminum industry such as bauxite, Alumina (Al_2O_3), Cryolite bath, carbon materials, Aluminum Dross for Beryllium concentration; this thesis research is aimed to develop the new laboratory techniques for those materials.

There is some Literature review that has been discussing the sampling techniques using the polyvinyl chloride (PVC) sample media filter and their phase structural and crystallinity

As Saudi Arabia is recently starting the Mining industry of Aluminum, there is not much study has been for the ore of Aluminum in Saudi Arabia Bauxite which is located near Qassim in Al Ba'itha Mine.

There are not many certified laboratories in the world from the American Board of Industrial Hygiene that applied OSHA and NIOSH approved Laboratory methods for Beryllium concentration in PVC sample media containing Beryllium that include chemical digestion using a hot plate or microwave digestion, where the samples are then evaluated to determine the airborne concentration of various metals by Inductively Coupled Plasma Spectroscopy (ICP). Clark Testing Laboratories based in US (AIHA-LAP) has been testing those samples and all the results for PVC filter and raw materials obtained in this Thesis have been validated with the same Laboratory.

In addition, most laboratory in the Aluminum industry does not have the ability to do the raw materials testing for beryllium concentration that is required to digest most of the resources raw materials used in the Aluminum industry such as bauxite, Alumina (Al_2O_3), carbon materials, and Aluminum Dross. The only Laboratory that is accepted to do this chemical digestion is Clark Testing Laboratories based in US (AIHA-LAP).

1.7 Objectives

There are many objectives that have been targeted in this Thesis research. This research aims to investigate the resources of an increasing trend of Beryllium Concentration in Aluminum pot room cryolite bath. Therefore, all potential resources of Beryllium in pot room baths such as bauxite, Fresh alumina, Fluorinated alumina, Petroleum coke, tar pitch, and Anode cover, aluminum dross which are in solid phase form materials have been understudy to be digested through Microwave acid digestion and then analyzed in Inductively coupled plasma optical emission spectrometry ICP-OES for beryllium concentrations analysis. All these raw materials in the solid phase need chemical digestion to analyze the Beryllium concentration ICP-OES. The research work has covered all potential resources of Beryllium in pot room. Each raw material has been chemically digested through either microwave or manual develop digestion method with different method setup based on materials chemical composition. Beryllium tends to concentrate in the electrolyte bath around 60 times its concentration in bauxite and alumina. Beryllium can be generated in the aluminum pot room bath from many prospect sources such as Alumina, petroleum coke, tar pitch, cryolite, bath, Anode cover mix, cathode materials, and aluminum dross.

The main objective is to develop a laboratory analyzing the study of Polyvinylchloride (PVC) sample media containing Beryllium used to detect personal exposure to beryllium through FPVC-PW2P - Polyvinylchloride (PVC) filter, 37mm, 2-piece, pre-weighed sample Cassette with pump. The PVC media will

chemically have digested through microwave digestion with a new setup method of control pressure and temperature, then it has been analyzed through Inductively coupled plasma optical emission spectrometry (ICP-OES) for beryllium concentration, and finally, the calculation based on dilution factor and air volume and reading from ICP instruments. The phase structure and crystallinity of bauxite from Saudi Arabia are the main raw materials of Aluminum characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM) to understand the structure and understand the characteristics, and its compositions to check the elemental analysis and if there are any radioactive materials. The sampling techniques of Air sample containing Beryllium through Polyvinylchloride (PVC) sample media with cassette and pump has been performed in this Thesis and make sure it has been done in the correct way which can be tested through recovery after digestion.

One of the objectives of this Thesis is to study how to minimize wherever possible, we will substitute beryllium with safer materials in Aluminum Industry. In addition, another objective of trying to limit the number of beryllium-exposed workers and the frequency of exposure to the greatest extent possible.

Outlining exposure assessment and medical surveillance of workers potentially exposed to beryllium. |

2 | CHAPTER 2 |

LITERATURE REVIEW

2.1 Beryllium solubility in occupational airborne particles:

Sequential extraction procedure and workplace application

One of the main aims of this Theses research is to capture the Beryllium associated hazard and the laboratory analysis techniques to determine the Beryllium concentration among Aluminum workers in the smelting process with the different kinds of materials. This Literature review is a study of the process for extracting inorganic beryllium species from emissions and working areas particulate matter. To accommodate for wall deposits, the speciation process was modified to perform beryllium extraction in a closed-face cassette sampler. This material is used to quantify individuals. The solubility of beryllium species in air samples can be used to determine toxicity, which could be connected to the different chemical forms of beryllium. Beryllium salts are a kind of beryllium (BeF_2 , BeSO_4) Individually, and later in mixes, beryllium oxide (BeO) was examined which is like the Aluminum reduction case which the beryllium will accommodate in the same forms.

Exposure to beryllium is a major bother for all aluminum smelter industries since it can cause beryllium sensitivity in workers who are exposed to Beryllium. This could progress to granulomatous lung disease, also known as chronic beryllium disease (CBD), a cell-mediated immune response. Worker

exposure to beryllium can be measured by sampling a known volume of air through a filter in a sample instrument and capturing airborne particles.

The particles are digested in an acid solution, and the quantities of beryllium are determined by spectrometry techniques Inductively coupled plasma optical emission spectrometry (ICP-OES), or (electrothermal atomic absorption spectrometry, inductively coupled plasma atomic emission spectrometry.

The Literature review is discussing other techniques for sampling to detect beryllium concentration based on the solubility of airborne beryllium compounds. A strategy for determining beryllium concentration based on the solubility of airborne beryllium compounds was validated in this study. This method is based on a four-step sequential extraction approach that separates soluble salts, metallic beryllium, oxides, and residual beryllium-containing silicates using different extraction solutions. [29] Some material may be lost during transfer or owing to adherence to residual inner wall deposits in the sample device because this technique requires the filter to be withdrawn from the sampling device.

The Literature review is discussing the sampling techniques for the detection of beryllium concentration based on the solubility of airborne beryllium compounds similar to the sampling techniques that will be done in this research. Therefore, a strategy for determining beryllium concentration based on the solubility of airborne beryllium compounds was validated in this Literature review study. The sampling method is based on a four-step sequential extraction

approach that separates soluble salts, metallic beryllium, oxides, and residual beryllium-containing silicates using different extraction solutions. [29] Some material may be lost during transfer or owing to adherence to residual inner wall deposits in the sample device because this technique requires the filter to be withdrawn from the sampling device.

The Literature review is discussing the laboratory experiments were used in closed-face four-piece cassettes (Millipore) with a 0.8 μ m pore size mixed cellulose ester (MCE) membrane and a 37-mm diameter (Millipore) which is similar to sampling cassettes, but different in chemical filter media in these research which used Polyvinyl chloride filter, 5.0- μ m pore size, 37-mm diameter; in 2-piece cassette filter, which supports us to compare between two filters Polyvinyl chloride filter and mixed cellulose ester (MCE).

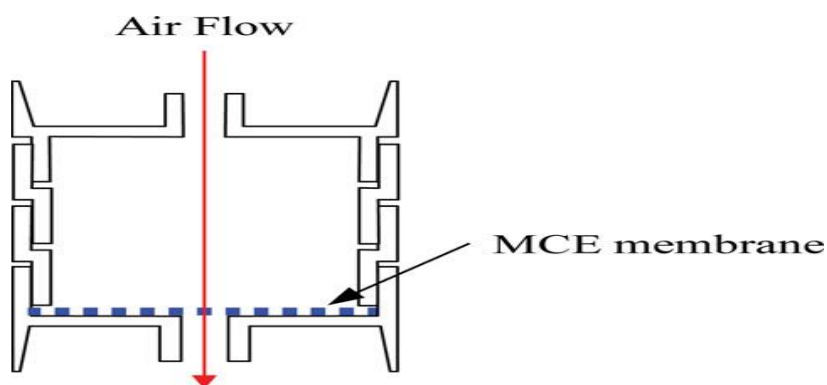


Figure 32 Illustration of the closed-face four-piece cassette with MCE Membrane

The Literature review is highlighting the recovery of beryllium content in MCE membrane which has been done in this Thesis using polyvinyl chloride (PVC) filter.

BeS for beryllium eluted during Step 1 (solubility of beryllium salts), BeM during Step 2 (solubility of metallic beryllium), and BeO during Step 3 (solubility of beryllium oxides).

The levels of BeF₂ and Bemet spikes had a significant influence ($p < 0.05$) on recovery in the two first phases, according to statistical analysis. Moreover, the overall amount of beryllium used was conservative ($\text{BeF}_2 + \text{Bemet} = \text{BeS} + \text{BeM}$), with more beryllium being used.

BeS had less beryllium than expected, and BeM had less beryllium than expected. Bemet solubility increases when BeF₂ is present.

The Literature review is discussing Aluminum smelter as an example of Beryllium solubility in occupational airborne particles. Beryllium in the Aluminum industry can be found as an impurity in primary ore (bauxite) at trace concentrations of less than a few milligrams per kilogram. Cryolite is used to concentrate beryllium during aluminum manufacturing. It forms mostly BeF₂ when it reacts with fluorides and Na₂BeF₄. As the temperature at which BeF₂ vaporizes (800 °C) is lower than the molten cryolite's temperature. Fumes of beryllium fluorides could be produced at (960 °C). Released into the workplace from the electrolytic bath.

The Literature review is discussing the method of analyzing Beryllium content in the MCE membrane which was by inductively coupled plasma mass spectrometry ICP MS with matrix-paired calibration solutions. The standard was freshly prepared prior to each analytical sequence.

After filtering, the samples were diluted 10-fold with HNO_3 Prior to analysis. In ICPMS analysis, it is common that samples need to be diluted as it accepts the low total amount of dissolved solids accepted by the analytical method. Two analysis modes were used: one under normal conditions and a second using Collision Reaction Interface (CRI) gas (H_2 only). The two modes have been optimized to achieve maximum intensity. The method detection limits (MDL) were calculated as 3 times the standard deviation of 10 laboratory blanks subjected to the same analytical procedure as samples.

In the Thesis research, we will use a PVC filter and analyzed it through inductively coupled plasma Optical Emission Spectroscopy. The Literature review is highlighting the point that in Aluminum production, Beryllium fluoride vapors could be released from the electrolyte bath into the workplace atmosphere, where they could form airborne particles through vapor condensation with other fluorides. As a result of this phenomenon, the anode lining crust has been shown to contain up to 900 ppm beryllium. [49] Bursting bubbles on the surface of the electrolyte bath can also create airborne fluoride particles. In the case of Beryllium emissions, Italian law has set a tolerable value of 0.1 mg m^{-3} for total beryllium and its compounds (as Be) for a mass flow of 0.5 g h^{-1} , ignoring the need for speciation [5]. It is proposed that the legislation will set more specific limits for each toxic metal's chemical species. The review discusses the solubility of airborne beryllium compounds which was used to validate a method for determining beryllium concentration. This method is based on a four-step sequential extraction procedure that employs various

extraction solutions. Since this technique necessitates removing the filter from the sampling system, some material may be lost during transfer or due to adhesion to the residual. However, this will result in a beryllium content underestimation. To avoid this problem, the review has set a procedure to modify to allow speciation directly within the CFC, based on the solubility of inorganic beryllium collected on mixed cellulose ester (MCE) membranes. This technique was then extended to air samples obtained from a variety of work environments

This Literature review provides a useful discussion to study the solubility of beryllium in the workplace and could help improve our understanding of beryllium toxicity based on paper findings

2.2 Beryllium in Pot Room Bath

One of the objectives of this thesis research is to study the sources behind the increasing trend of Beryllium in one Aluminum Smelter Company. This Literature review is highlighting the possible sources that can be accomplish the beryllium concentration. Beryllium can enter the Aluminum pot room bath from many. Potential sources. Alumina, coke, pitch, Aluminum fluoride, anode cover mix baths, cathode materials, and others can cause beryllium to come into contact with the bath in the pot room, where it dissolves to form Be ions. These combine to form compounds like beryllium fluoride, also known as beryllium difluoride, BeF_2 , and sodium fluoroborate, Na_2BeF_4 , a material that is not much different from ammonite (its aluminum analog). The most common sources of Be are fresh alumina and a pot bath that comes from another smelter location.

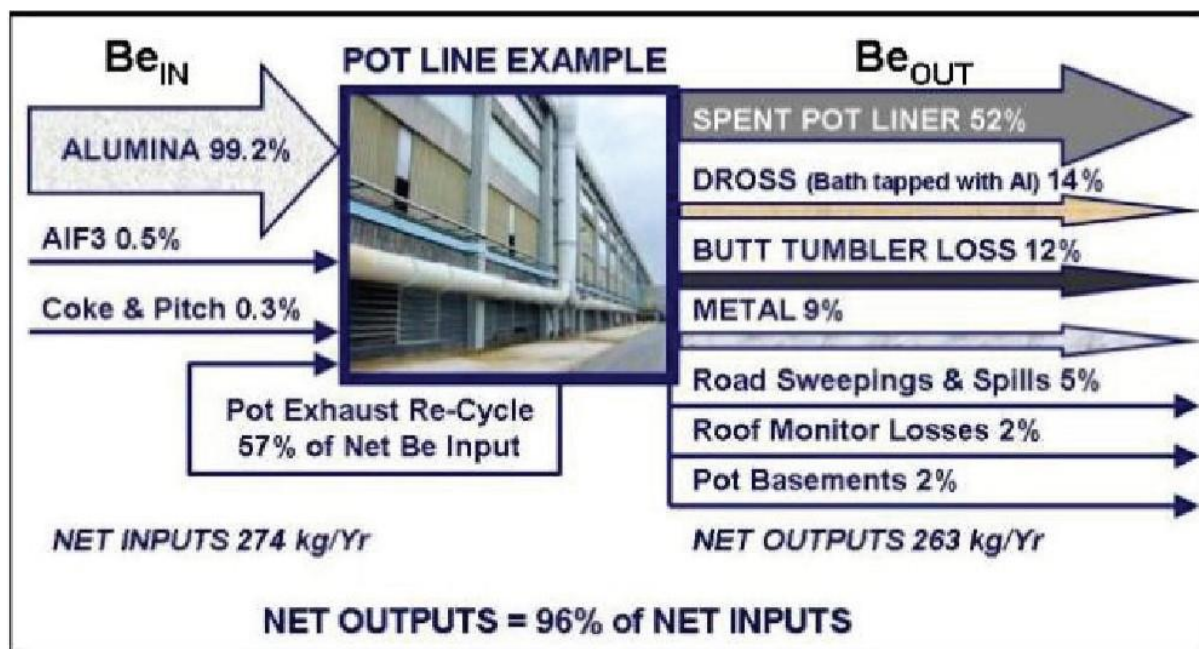


Figure 43 Actual Beryllium Mass Balance Example

Beryllium in the alumina feed from all sources typically produces an equilibrium concentration of less than 10 ppm in the pot bath. In cases where the main source of beryllium is aluminum oxide, the total amount of AlF_3 , coke, pitch, and cathodes typically contribute less than 1% of the total Beryllium input to the melt, as shown in Figure 11. The other common source of beryllium for foundries is a pot bath that was purchased or transferred from a foundry using a source of feedstock containing beryllium. Since Beryllium is concentrated in the pot bath, the transfer of many tons can involve a significant amount of Be, which is generally in the form of beryllium fluorides. In some cases, this transfer mechanism is known to increase the average Be concentration in the liquid bath to 70 ppm.

This Literature review provides an approximate value of beryllium which is concentrated to approximately sixty times the concentration of fresh alumina in liquid baths, limited data indicate that it does not concentrate in all forms of the bath. The anode shell bath, also known as a scab bath, has concentrations of beryllium that range from the proportion of the bath mixed with aluminum oxide to half or an order of magnitude higher than the concentration of beryllium in the liquid bath. This research aims to investigate the resources of an increasing trend of Beryllium concentration in Aluminum pot room cryolite bath. Therefore, all potential resources of Beryllium in pot room bath such as bauxite, Fresh alumina, Fluorinated alumina, petroleum coke, tar pitch, and Anode cover which are in solid form materials are under study in this Thesis research.

2.3 Using reflectance spectroscopy and Advanced Spaceborne Thermal

Emission and Reflection Radiometer data to identify bauxite deposits In vicinity of Az Zabirah, northern Saudi Arabia.

The literature review discusses the Bauxite (ore of Aluminium metal) in Saudi Arabia which will be under study in this Thesis research for a Scanning electron microscope to study the composition and hardness of the ore. The literature review has done a study of Bauxite samples from deposits in northern Saudi Arabia that were identified in the laboratory using X-ray diffraction (XRD) and Spectral Reflectance Measurements (0.3-2.5 μm).

XRD results show that bauxite deposits are composed primarily of 4,444 goethite, gibbsite, and boehmite, with small amounts of kaolinite, hematite, and quartz. The bauxite spectrum showed the presence of significant iron oxides (0.5 and 0.87 μm) with water (1.4 and 1.9 μm) and aluminum hydroxide (2.2 μm). The folded spectrum of the Advanced Spaceborne Thermal Emission and Reflection Radiometer (ASTER) of bauxite sample was characterized by the characteristics of aluminum hydroxide in ASTER band 6 (2.2 μm). The results show that the analytical tape PC2 with the most important component is the best component for bauxite deposit demarcation. The partial bauxite frequency was derived using the matching filtering method.

This study presents reflection spectroscopy and ASTER data to provide spectral information to distinguish economically important minerals from visible and

near infrared and shortwave infrared spectra in dry and semi-arid environments such as Saudi Arabia.

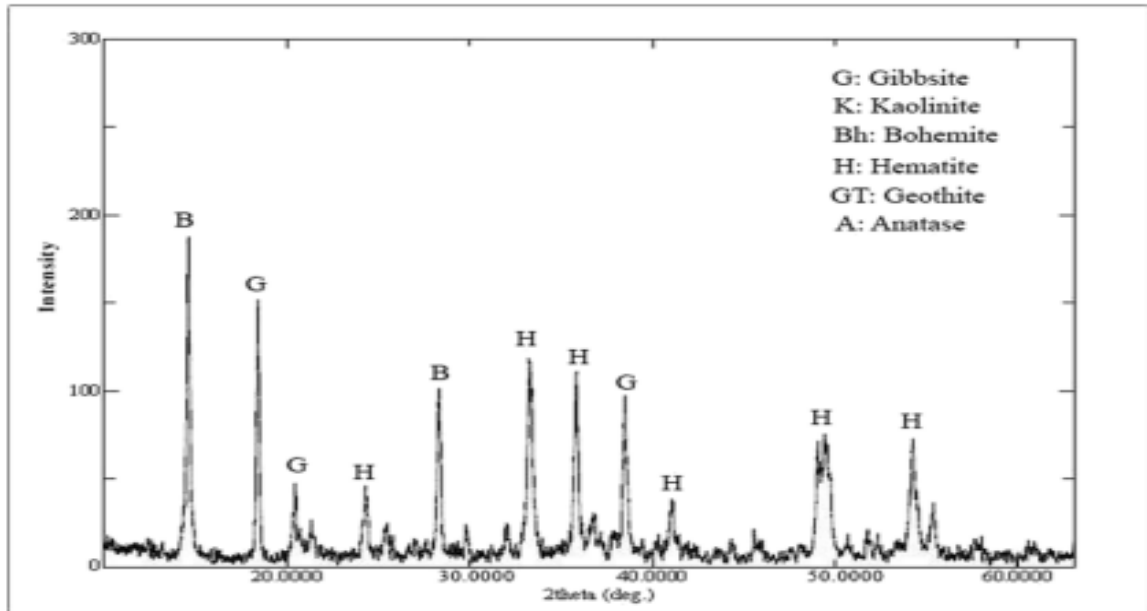


Figure 54 X-ray diffraction (XRD) patterns of collected bauxite samples

Samples are composed of goethite, gibbsite, boehmite, kaolinite, hematite, and quart.

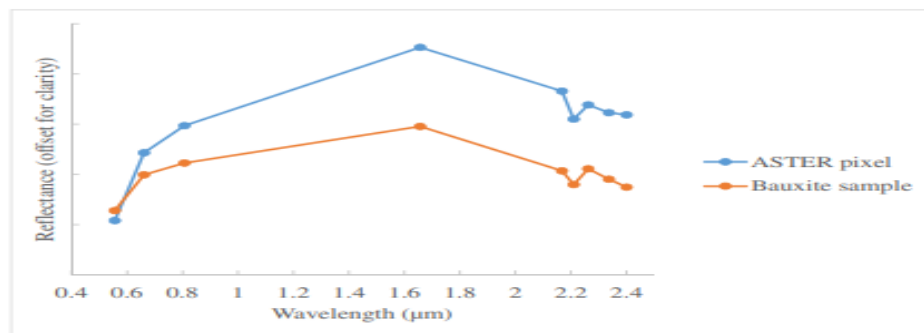


Figure 6 Comparison of laboratory-derived bauxite spectrum with corresponding Advanced Space borne

2.4 Dissolved Metals in Cryolitic Melts

One of the main objectives of this thesis research is to study the chemistry of cryolitic baths. In this Literature review, a tin extraction-stripping approach was used in a laboratory investigation to determine dissolved metals (including aluminum, sodium, and lithium) in cryolitic melts.

The results show that the dissolved metal is not only aluminum, but a mixture of aluminum, sodium, and lithium, whose concentrations are affected by cryolitic composition and temperature. The outcomes are proven to be logical and self-contained. Variations in experimental methodologies can be blamed for differences in total metallic solubility reported earlier in the literature. The solubility of metallic aluminum increased with rising bath temperature and decreased with increasing bath temperature.

Metallic sodium solubility increased as CR and bath temperature increased but declined when LiF concentration increased. Solubility of lithium in metals increased as CR, LiF concentration, and bath temperature increased. However, the temperature was an order of magnitude lower than the other species made of metal. Metallic compounds were formed when the molar CR was larger than 2.5. In terms of total solubility, sodium was the most important component.

The following procedure was used to conduct each experimental test for determining metal solubility's: In compartment A, approximately 6 grams of high-purity aluminum were added and covered by approximately 22 grams of perfused cryolitic material. Ten to eleven grams of tin metal were placed into

compartment B at the same time. Before the BN lid covered the crucible, a marking for the compartment placements was made on the crucible's exterior wall. After that, the crucible was placed in the graphite crucible holder with its cover on. After that, the crucible system was carefully loaded in a specified direction into the temperature-stabilized furnace. The furnace was tilted after around 3 to 4 hours of equilibration. The furnace was tilted 65 to 75 degrees for one to two minutes after 3 to 4 hours of equilibration to allow the transfer of part of the metal soaked. The cryolite bath sample and the tin alloy have been cautiously removed, accrued, and weighed on analytical stability. Light metal contents inside the tin section have been analyzed on an Inductively coupled plasma optical emission spectrometry ICP-OES after digesting the alloy samples. The cryolitic pattern left in compartment A becomes additionally accrued for mass stability take a look at the dissolved metal species. At least checks have been carried out for every experimental situation. An experimental situation is one cryolitic soften composition on the temperature of interest.

Experimental assessments for the metallic solubility were performed following the equation of the light metals distribution among the tin and cryolitic melting phases. Individual solubilities of the metals withinside the cryolitic melts are calculated in step with the subsequent equations:

The outcomes and dialogue display that the dissolved metals inside the cryolitic bath include metals such as aluminum, sodium, and lithium. The magnitudes of those metallic solubilities are depending on the cryolitic electrolyte composition and temperature. Metallic sodium dominates all the species dissolved inside the cryolitic bath. Decreasing

cryolite ratio (growing extra AlF_3) and temperature and growing additive LiF attention can lower the metallic. The theoretical importance of those consequences lies in the right know-how of the thermodynamics of the cryolite dissolved metals system.

Increasing Alumina Al_2O_3 will depress the solubilities of metal sodium and lithium, however, will increase the solubility of aluminum metal. The addition of LiF depresses the solubilities of aluminum and sodium, however, will increase the solubility of metal lithium.

Metallic lithium dissolves with inside the cryolitic melts even whilst the melts comprise as little as 1. zero wt.% LiF. However, lithium's solubility is a minor aspect of the total solubility even if the LiF attention is increased up to Ten wt.%.

2.5 Mineralogical control and characteristics of rare earth elements

Occurrence in Carboniferous bauxites from western Henan Province, north China: A XRD, SEM-EDS and LA-ICP-MS analysis

One of the goals of this Thesis research is to study the Bauxite deposits in the Saudi Arabia which it is under study. This Literature review has studied Bauxite from different location in China. Songqi area of Henan Province, North China, have high amounts of rare earth elements (REE). However, no research of the presence of REE in these bauxite ores has been done. Using petrographic observation, X-ray diffraction (XRD), scanning electron microscope with energy dispersive spectroscopy (SEM-EDS), and LA-ICP-MS techniques, the investigation of the REE occurrence and probable enrichment process in the Songqi bauxite deposits has been studied. Other coexisting minerals in the Songqi bauxite deposits include clay mineral aggregates, with low amounts of hematite, pyrite, anatase, and zircon REE and other essential metals are abundant in bauxite ores (Li, Zr, Nb, and Ga). The majority of REE are adsorbed on the surface of clayminerals and diaspore as ions, and some heavy rare earth elements (HREE) occur as xenotime. Except for the probable co-adsorption of P and REE in the clays and diaspore, the SEM-EDS and LA-ICP-MS investigations demonstrate that REE is closely related to the concentration of P. As a result, various dispersed and modest P-bearing rare earth minerals may occur in the bauxite deposits. Optical Microscopy, Xray Diffraction XRD analysis and SEM microscopic analysis are shown below for different Bauxite from different location in China.

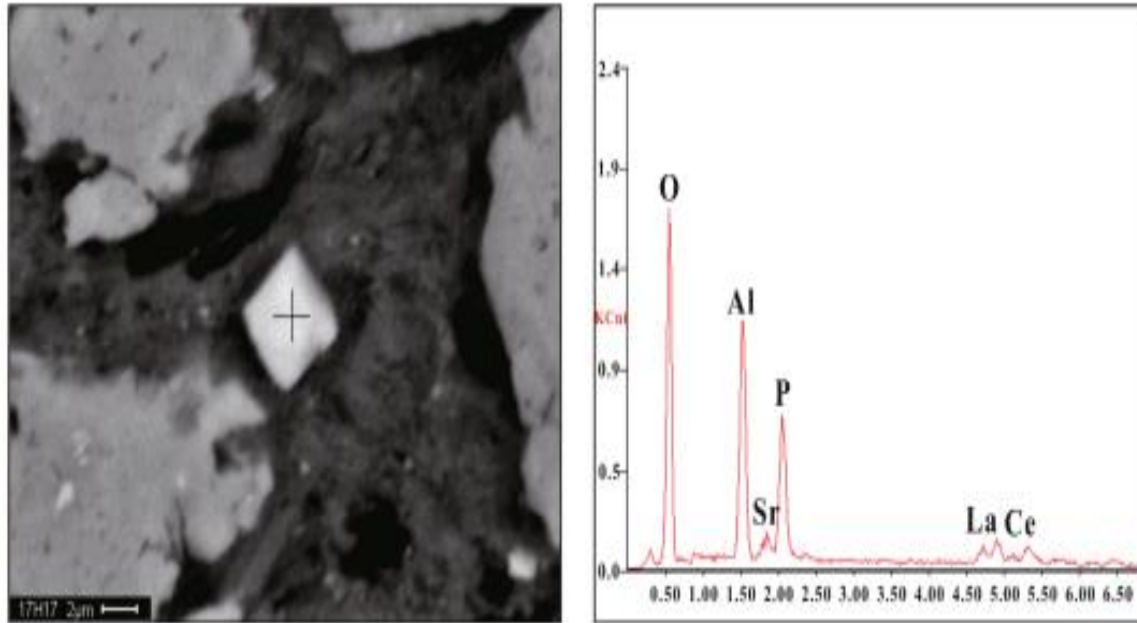


Figure 75 SEM image and energy spectrum diagram in bauxite.

In conclusion in this part of the study, Bauxite in the Song qi region is predominantly rich in the light rare earth element.

The lateralization process causes the accumulation of rare earth elements in bauxite.

The REE grade differs from the vertical profile because bauxite has undergone weathering and Leaching.

2.6 The Aluminum Smelting Process and Innovative Alternative Technologies

This Literature review has described the aluminum manufacturing process and uses of the electrolysis cell technology, the raw materials being used, and addressed the health and safety related to the process.

It is considered for each 1 kg of aluminum production; three-fourth moles of CO₂ per mole of aluminum as a side effect will be produced. Theoretically, half of mol of aluminum oxide should react with 0.33 kg of carbon, producing 1 kg of aluminum and 1.22 kg of CO₂. However, other reactions of carbon with both oxygen and CO₂ actually consume 0.40 to 0.45 kg of carbon per kilogram of aluminum. This is known as net anode consumption, which produces about 1.5 kg of CO₂ per kg of aluminum.

One of the main objectives of this Thesis research bauxite. Bauxite typically contains 40-60 wt.% aluminum oxide, a small amount of iron, silicon, titanium compounds, and many other trace impurities. One of these impurities is beryllium, the concentration varies from less than one part. One to one million to 4,444 million parts in various bauxite mines. Some concerns have been raised as beryllium is toxic to people and is partially found in the atmosphere of pot spaces (typically less than 100 ng / m³). Nonetheless, studies at various aluminum plants have shown that beryllium sensitization levels for pot workers are very low.

2.7 Review of Workplace Based Aerosol Sampler Comparison Studies, 2004–2020

The Literature review has reviewed some research that has been done for beryllium dust sampling. In an aluminum smelter, sampling for aluminum beryllium dust using a Respicon sampler (flow rates of 2.66, 0.33, and 0.11 L min⁻¹ through the ports), 25 mm CFC, and a IOM Inhalable Sampler, Compared to 3.1 L min⁻¹ and 2.0 L min⁻¹ sampler flow rates, the Respicon sampler has both aerosol mass and water-soluble fluoride (fluoride in collected air mass) compared to the IOM sampler for the subsampled inhalable fraction.

Respicon was also subsampled if the concentration was greater than 1.35 mg / m. The beryllium concentration indices from the sample heads decreased in the following order when the sample heads were in a fixed station: IOM Sampler (inhalable) (1.00)> Sierra Cascade Impactor that works for beryllium in air (0.69) classified> 37 mm CFC (total dust) (0.64) > MOUDI impactor to evaluate its behavior against beryllium in air suspension (0.54)> Aluminum cyclone SKC (inhalable) (0.19).

Sampling—Guidance on Procedures for Inclusion of Material Adhering to Internal Sampler Surfaces.

The literature review discusses the sample techniques based on NIOSH CFC method for detecting the beryllium fume dust from air samples which is one of the main points of this Thesis research. The literature review states that Research shows that.

Substances deposited on the inner surface of air sampling cartridges often make up a significant proportion of the aerosol entering the sampler. The following table Shows three NIOSH CFC methods using gravimetric analysis.

When performing CFC sampling, aerosol measurement gravimetric methods include internal capsules such as polyvinyl chloride (PVC) AccuCap (SKC Inc., Eighty-Four, PA), Wood check (MSA, Pittsburgh, PA). Must be used.) Or equivalent.

Which weighs the filter alone, is generally inadequate because it does not consider the material collected on the inner wall of the sampler and the inside of the cap.

Weigh the entire CFC Sampler and can contaminate the outer -cassette.

The surface has a significant effect on sampling distortion, especially in dusty work environments. Also, the absolute mass of the is much higher, which reduces accuracy.) Breathable sampling and gravimetric analysis using the Cyclone /cassette assembly detects internal debris on the outside of the filter, but it is more difficult to explain.

Therefore, it is necessary to minimize the aerosol deposits by collecting them in a Pre-weighed filter using a Cartridge made of conductive materials.

Table 1 Reported results and correction factors for sampler comparison publications

Plant	Aerosol Fraction Assessed/ Compared	Samplers	Dust Assessed	Summary of Results
Aluminum smelters	Total, inhalable and respirable	IOM inhalable sampler (inhalable) SKC Aluminum cyclone (respirable), 37-mm CFC ('total')	Beryllium	The median of median dust concentration ratios computed from the sampling heads at the fixed station decreased as follows: IOM (1.00) > Sierra (0.76) > 37-mm cassette (0.61) > MOUDI (0.48) > respirable (0.12). The median of median ratios of dust were: IOM (1.00) > Sierra (0.56) > 37-mm cassette (0.35) > respirable (0.06)) and Be (IOM (1.00) > Sierra (0.66) > 37-mm cassette (0.48) > respirable (0.11)
	Total and inhalable	25-mm CFC ('total') IOM sampler (inhalable)		The Respicon under-sampled the aerosol mass for the inhalable fraction compared to the IOM sampler at concentrations higher than 1.35 mg/m³ and oversamples at lower concentrations. The overall ratio between aerosol mass collected with IOM and CFC was 4.19 (95% CI = 3.79–4.64)

The Literature review is discussing the Environmental hazard associated with Aluminum pot rooms and focuses on the tasks which support the Thesis research on location and tasks we can consider in the Beryllium sampling process. Atmospheric concentrations of chemical contaminants vary in Aluminum pot rooms and generally depend on the technology used in the smelter pot room and the age of the manufacture.

Typically, in many jobs and tasks, the worker can be exposed to all of these dust and fumes at the same time. However, it depends on the stage of the melting process and the task how the concentrations of the various tasks in aluminum production with the highest exposure potential include anode changes, metal threading, bathing, and potting, although maintenance workers and crane operators may also be exposed to significant exposure to dust and vapor.

Hazard control in a modern pot room has been designed to have more measure controls in the workplace which is based on engineering controls, and design. The Personal protective equipment PPE, and work practices apparatus is another way of the second control. With the possibility of high fluoride and other gas exposure and fume such as Beryllium in Aluminum pot rooms, this becomes a very important step to control the hazard.

2.8 Method for Quality Control of Bauxites: Case Study of Brazilian Bauxites Using PLSR on Transmission XRD Data

The major characteristics of bauxite controlled in the beneficiation process, available alumina ($Av\ Al_2O_3$) and reactive silica ($Rx\ SiO_2$), are usually determined by arduous, expensive, and time-consuming wet chemical procedures. Alternative approaches based on XRD analysis are being investigated in order to offer a valid estimation of these parameters as well as useful ore mineralogical information. The Partial Least Square Regression (PLSR) statistical technique was used to estimate $Av\ Al_2O_3$ and $Rx\ SiO_2$ from Brazilian bauxites using X-ray diffraction data in transmission mode.

The suggested method entails a routine of sample classification using Principal Component Analysis (PCA) and K-means, calibration of the PLSR model for each group of samples, clustering new bauxite samples according to the generated clustering model, and subsequent estimation of the parameters $Av\ Al_2O_3$ and $Rx\ SiO_2$ using the PLSR models for these samples. The results demonstrated that the models created for samples of the primary ore lithology were accurate and precise. This method necessitates the quality and pre-processing of XRD data, which is addressed. The findings showed that this technology has the potential to be used in industry for bauxite quality checking as a quick method.

The below XRD graphs show that Transmission Mode X-ray diffractograms of all the bauxite samples utilized in this study. It should be noted that the four

lithology's' bauxites share the same mineralogical makeup. Gibbsite ($d_{002}=4.85$ and $d_{110}=4.37$) is the primary phase. Kaolinite ($d_{001}=7.14$ and $d_{002}=3.58$) is the only SiO_2 mineral that has been identified. Quartz ($d_{101}=3.34$) is found in some samples, but only in trace amounts. The predominant iron mineral is hematite ($d_{104}=2.69$), with intensity varying greatly among the lithologies, while Al-goethite (d_{110} ranging from 4.18 to 4.14) is also seen, usually as a broad peak due to changes in the isomorphous substitution of Aluminum structure (12,34). Anatase is equal to ($d_{101}=3.52 \text{ \AA}$) and is also present in all samples.

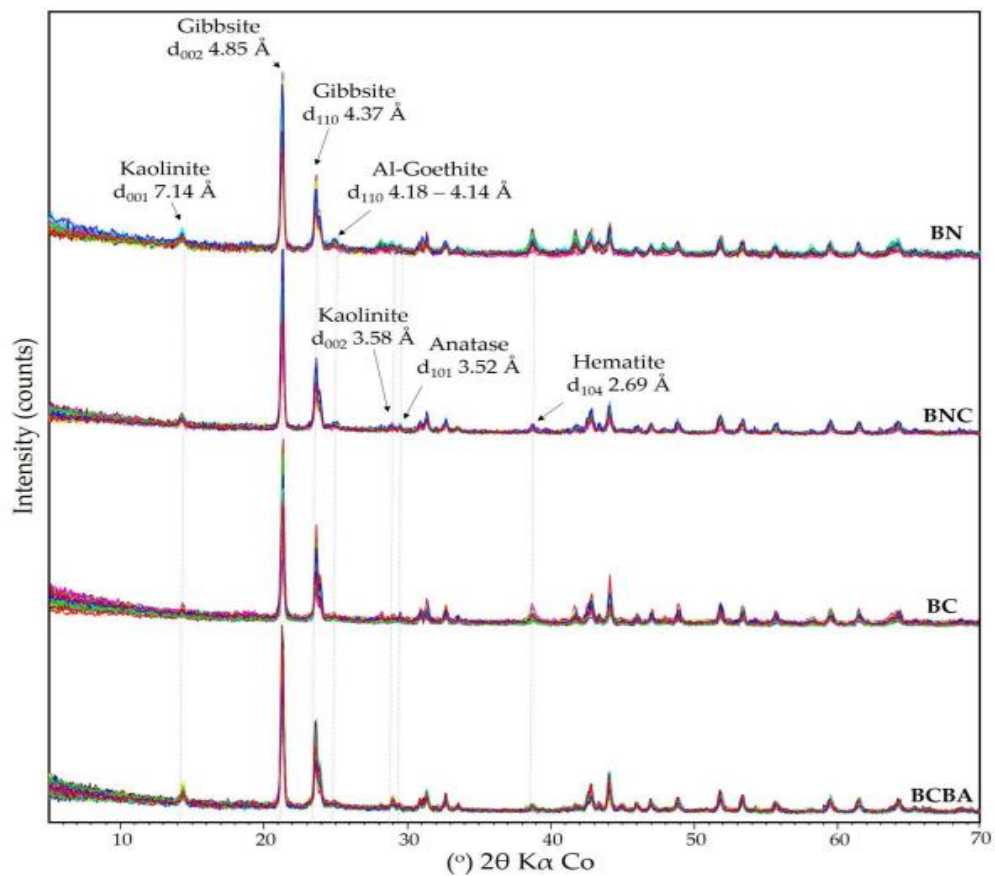


Figure 16 XRD patterns of the bauxite samples from BN, BNC, BC and BCBA lithologies

2.9 Metal and Metalloid Particulates in Workplace Atmospheres (ICP

ANALYSIS)

The literature review illustrates the collection and subsequent analysis of aerial metals and metalloid particles by inductively coupled argon plasma where It gives a rapid simultaneous analysis and data reduction of various elements, eliminating the need for individual analysis with traditional atomic absorption techniques.

The literature review has provided analysis for 13 elements (Be, Co, Cd, Cr, Ni, Fe, Mn, Cu, Mo, Sb, Pb, Zn, and V) in air samples using the filter. The ability to extend the analysis to other elements depends primarily on the experimental equipment based on the stability of the elements to be digested in the acid matrix.

The literature review discussed the use of 37-mm diameter cassettes with filters, 25-mm sampling assemblies, and pre-weighed PVC filters for sampling. The calculation of total fume exposure can be expressed as follows;

Recommended Sampling Times	
<u>Sample Type</u>	<u>Time</u>
Time Weighted Average Samples	240 min
Short-Term Exposure Limit Samples	15 min*
Ceiling Samples	15 min

Table 2 Air Contaminants - OSHA Permissible Exposure Limits

Element	Substance Exposed to	PEL (mg/m ³)	
		TWA	Ceiling
Ag**	Metal and soluble compounds (as Ag)	0.01	
As**	Inorganic compounds (as As) see 29 CFR 1910.1018		
Be#	Beryllium and compounds (as Be)	0.002	0.005##
Ca**	Calcium oxide	5	
Cd	Fume	0.1	0.3
	Dust	0.2	0.6
	(See 29 CFR 1910.1027)		
Co	Metal, dust and fume (as Co)	0.1	
Cr	Metal and insoluble salts (as Cr)	1	
Cu	Fumes (as Cu)	0.1	
	Dusts and mists (as Cu)	1	
Fe	Dicyclopentadienyl iron total dust	15	
	Iron oxide fume (as Fe ₂ O ₃)	10	
Fe, V	Ferrovandium	1	
Mg**	Magnesium oxide fume total particulate	15	
Mn	Mn compounds (as Mn)		5
	Mn fume (as Mn)		5
Mo	Insoluble compounds (as Mo) total dust	15	
Ni	Metal and insoluble compounds (as Ni)	1	
	Soluble compounds (as Ni)	1	

2.10 Synthesis, characterization, and applications of poly (vinyl chloride) nanocomposites loaded with metal oxide nanoparticles

In the case of Beryllium emissions, Italian law has set a tolerable value of 0.1 mg m³ for total beryllium and its compounds (as Be) for a mass flow of 0.5 g h⁻¹, ignoring the need for speciation [5]. It is proposed that the legislation will set more specific limits for each toxic metal's chemical species. The review discusses the solubility of airborne beryllium compounds which was used to validate a method for determining beryllium concentration.

This method is based on a four-step sequential extraction procedure that employs various extraction solutions. Since this technique necessitates removing the filter from the sampling system, some material may be lost during transfer or due to adhesion to residual. However, this will result in a beryllium content underestimation.

To avoid this problem, the review has set a procedure to modify to allow speciation directly within the CFC, based on the solubility of inorganic beryllium collected on mixed cellulose ester (MCE) membranes. This technique was then extended to air samples obtained from a variety of work environments.

3 CHAPTER 3

Experimental and Methods

3.1 Materials and Digestion Laboratory Methods

This Thesis Research comprises developed chemical Digestion methods in the solid phase to wet phase in order to be analyzed in Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES); those materials are raw materials samples used in aluminum products such as Bauxite, alumina, anode cover mix, Pot Room Cryolite bath, pure bath, Dross aluminum oxide from different sample points, petroleum coke, and pitch. In addition, we have developed a method to digest PVC filters containing beryllium collected from air samples. In addition, developing laboratory

3.1.1 Characterization of Bauxite

Bauxite is the most significant alumina ore that contains (40-60%) alumina, along with smaller quantities of silica, and iron oxide. Bauxite is located on earth in the solid phase. Bauxite from Saudi Arabia will be tested for the scanning electron microscope, X-ray diffraction, and Fourier-transform infrared spectroscopy (FTIR). In addition, Bauxite has been chemically digested with microwave-assisted digestion in order to analyze for Beryllium concentration through Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES)

The digestion of Bauxite will be performed in Microwave acid digestion with two steps, First 0.25 g of the sample will be placed into the digestion vessel. Then, 6.5 mL of H_3PO_4 and 3.5 mL of H_2SO_4 will be added to the vessel and mixed. The reaction will be done on a vessel at a control pressure and temperature of 240 °C.

After the first step has been done, 1 ml of HNO_3 , 1 ml of HCl , and 1 mL of HF will be added to the same vessel and waited for 15 minutes before closing the vessel. The reaction will be done on a vessel at a control pressure 800 psi and a temperature of 200 °C. Since Hydrofluoric acid is used in this technique of digestion, a second complexation step with boric acid has been utilized if it is essential to complex the leftover hydrofluoric acid or redissolve insoluble fluorides produced.

The sample will be filtered and diluted to 100 ml to be ready to analyze in Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) for trace elemental analysis including Lithium, beryllium, and Magnesium.



Figure 87 Digestion vessels with pressure and temperature controller

3.1.2 Chemical Digestion Method for Alumina Powder (Aluminum Bauxite)

Alumina will be digested through microwave-assisted digestion where 0.25 g of the sample will be placed into the digestion vessel; 6.5 mL of H_3PO_4 and 3.5 mL of H_2SO_4 will be added to the vessel and mixed, filtered, and diluted the sample to 100 mL. The reaction will be done on a vessel at a control pressure and temperature of 240 °C. The prepared solution is ready to be analyzed in Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) for trace elemental analysis including Lithium, beryllium, and Magnesium.

3.1.3 Pot Room Cryolite Bath through Microwave Digestion

Cryolite bath is used in alumina electrolysis as the main component of the electrolyte. From a chemical point of view, it is Na_3AlF_6 , a double fluoride made

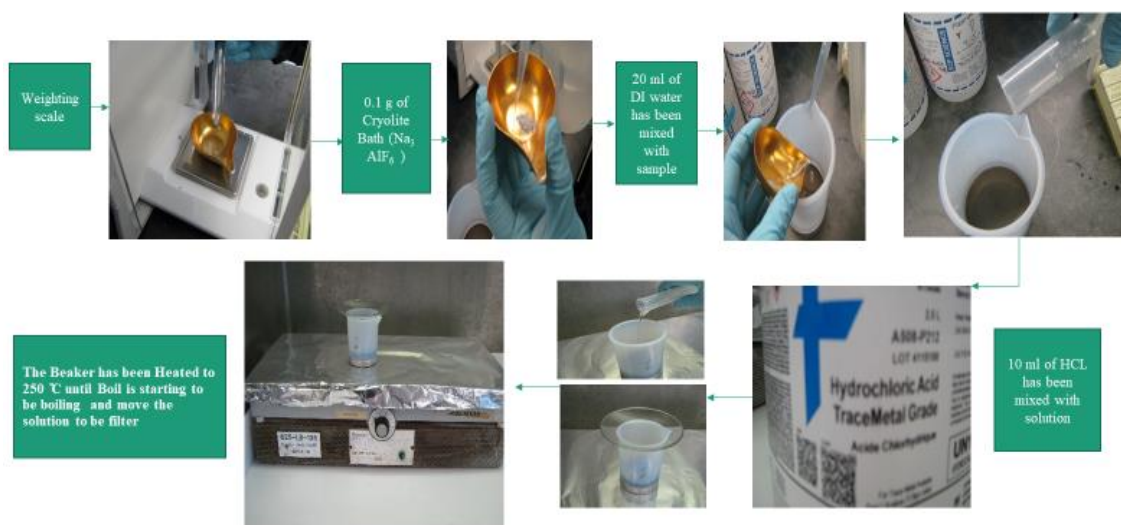
from sodium and aluminum. It is a white granular powder, based on the chemical composition, Cryolite bath has been digested through Microwave digestion with acid digestion where .1 g of the sample has been measured and then two ml of HNO_3 and 6 HCL has been added to the digestion vessel. The reaction will be done on a vessel at a control pressure and temperature of 180 °C. The prepared solution is ready to be analyzed in Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) for trace elemental analysis including Lithium, beryllium, and Magnesium.

The microwave digestion method has been compared with the below developed manual method and a confidence interval of 95 % will be calculated.

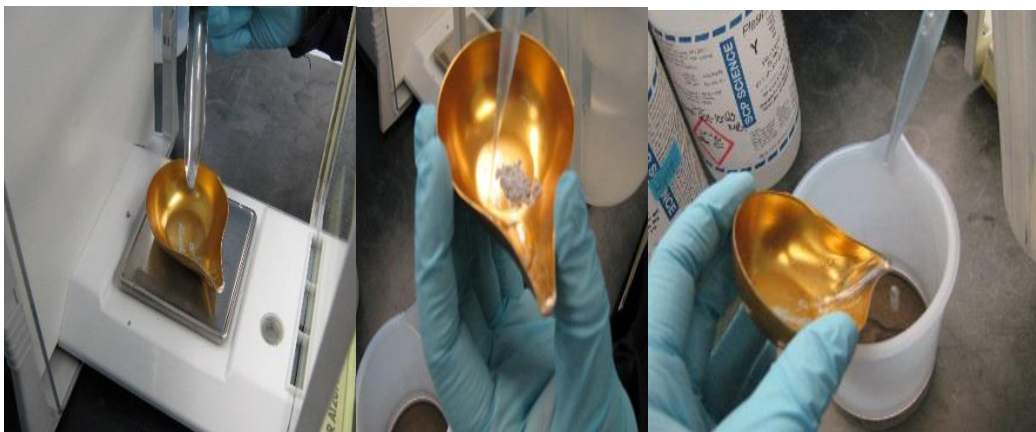
3.1.4 Develop Manual Digestion Method for Pot Room Cryolite Bath

Another digestion method for Pot Room Cryolite Bath is developed using hot plate temperature and acid digestion. The development procedure has been modified as the following;

Figure 98 Manual Digestion method



- 1- 0.1 ± 0.01 g of bath has been weighed in a weighing dish and carefully transferred to a Teflon beaker using a wash bottle filled with ultra-pure water.
- 2- After that 20 mL of ultra-pure water has been added to the beaker containing pot line bath



- 3- Then, 10ml of HCl has been added to the Teflon beaker and placed the beaker on a hot plate. Cover with a watch glass to capture all the fume that contain Beryllium.
- 4- Then, 10ml of HCl has been added to the Teflon beaker and placed the beaker on a hot plate. Cover with a watch glass to capture all the fume that contain Beryllium.



- 5- The Beaker has been Heated to 250 C until Boil is starting to be boiling which means beryllium fume or vapor starting to be formed and materials have been dissolved, and then remove the beaker from the hot plate and let it cool down.



- 6- Then, the prepared solution with the contents of the beaker has been diluted with 100 mL of ultra-pure water into a volumetric flask using a funnel, and then rinsed the watch glass over the beaker with ultra-pure water.



- 7- The prepared solution is ready to be analyzed in Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) for trace elemental analysis including Lithium, beryllium, and Magnesium.

3.1.5 Petroleum coke and Pitch Digestion method

The carbon Petroleum coke and Pitch are used as a binder agent to produce Carbon Anode.

The digestion of those carbon materials has been done by digestion Microwave acid digestion takes care of all the safety precautions with two steps;

0.1 g of the sample has been weighted and placed into the digestion vessel, then 10 mL of H_2SO_4 has been added to the vessel in the first step and closed the vessel. The reaction will be done on a vessel at a control pressure and temperature of 260 °C. After the reaction has been completed, the vessel will go to the second digestion step to add 10 mL of HNO_3 . Both steps will be done with controlled pressure and temperature of 260 °C.

The prepared digestion solution was clear, colorless, and particle-free upon dilution to 100 mL with ultra-water.

The prepared solution is ready to be analyzed in Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) for trace elemental analysis including Lithium, beryllium and Magnesium

3.1.6 Aluminum Dross

Aluminium oxide as dross from three different plants slab, billet, and ingot will be digested through microwave-assisted digestion where 0.25 g of the sample will be placed into the digestion vessel; 6.5 mL of H_3PO_4 and 3.5 mL of H_2SO_4 will be added to the vessel and mixed, filtered, and diluted the sample to 100 ml. The reaction will be done on a vessel at a control pressure and temperature of 240 °C. The prepared solution is ready to be analyzed in (ICP-OES) for trace elemental analysis including Lithium, beryllium, and Magnesium.

3.1.7 Polyvinyl chloride (PVC) used as Beryllium dust collector

The scope of this method varies from element to element. This method is used to analyze metallic and non-metallic dust collected on PVC filters and is also used for gravimetric analysis. This is a simultaneous elemental analysis using a microwave decomposition approach.

Molecular weight within defined polymerization protocol and then study the enclave of molecular weight variance with absorption ability and infinity to beryllium metal.

Polyvinylchloride (PVC) filter containing beryllium has been tested in two different scenarios to check the efficiency of the filter to absorb Beryllium

First, commercially polyvinyl chloride (PVC) sampling media among of FPVC-PW2P - Polyvinylchloride (PVC) filter, 37mm, 2-piece, pre-weighed sample Cassette with pump will be used to detect personal exposure to beryllium.

The cassette filter holders have been opened and the inner cassette surfaces with a 37 mm PVC have been wiped with 2 ml of deionized water.

The PVC media containing Beryllium has been digested through Microwave acid digestion the PVC sample has been added into the digestion vessel, and then 10 mL of HNO_3 has been added. The vessel has been gently swirled with the mixture.

The reaction will be done on a vessel at a control pressure 800 psi and a temperature of 215 °C. The solution obtained from the reaction was clear, colorless, with free particles upon digestion

REAGENTS	Equipment/materials	Sampling requirements
Nitric acid, conc., trace metal grade*	Polyvinyl chloride filter, 5.0- μ m pore size, 37-mm diameter; in the 2-piece cassette filter holder	Calibrate each personal sampling pump with a representative sampler connected to the pump (in line.)
Calibration standard 1000 ppm for Beryllium (Be), Lithium, and Magnesium (Mg)	Personal sampling pump, 1 to 4 L/min, with flexible connecting tubing	Sample at an accurately known flow rate between 1 and 4 L/min
10 mL of HNO ₃ used for digestion	Microwave Acid Digestion	Digestion vessels are applicable for higher temperatures and pressures required for the digestion of rigid samples.
De-ionized Water	Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES)	A filter loading should not be exceeded by approximately 2 mg of total dust

The solution will be filtered and diluted to 100 ml to be ready to analyze in Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) for trace elemental analysis including Lithium, beryllium, and Magnesium.

Measurement

- Calibrate the spectrometer in Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) for Beryllium (Be), Lithium, and Magnesium (Mg), a blank containing 2 ml of a nitric acid and 98 ml ultra-water has been used for a single or multi-element working standard calibration. For each standard, 2 ml of nitric acid, standard content and filled with water to 100 ml as per below concentration

Standard preparation for 5 ppm = 5 ppm / 1000 * 100 ml dilution factor = 0.5 ml

Standard preparation for 10 ppm = 10 ppm / 1000 * 100 ml dilution factor = 1 ml

Standard preparation for 15 ppm = 15 ppm / 1000 * 100 ml dilution factor = 1.5 ml

Standard preparation for 20 ppm = 20 ppm / 1000 * 100 ml dilution factor = 2 ml

- The standards have been analyzed at applicable wavelengths for each element.

To calculate the beryllium concentration as below formula;

$$C = \frac{(C_s V_s) - (C_b V_b)}{V}, \text{ mg/m}^3$$

Where C_s is the concentration of the sample, V_s is the volume of sample being digested, C_b is the concentration of blank, V_b is the volume of blank being digested, and V is air volume for sampling

- $0.2 \mu\text{g/m}^3$ as an Eight Hour Time Weighted Average (TWA)

Table 3 PROPERTIES AND SAMPLING VOLUMES

Element (Symbol)	Properties [13] Atomic Weight	MP, °C	Air Volume, L @ OSHA PEL [4] Min	Air Volume, L @ OSHA PEL [4] Max
Beryllium (Be)	9.01	1278	1250	2000
Lithium (Li)	6.94	179	100	2000
Magnesium (Mg)	24.31	651	5	67

Note;

(1) PEL, REL, or STEL data not found [1,14].

(2) In the presence of chloride from the C filter, these metals, as well as tin and antimony, form a precipitate in nitric acid.

Table 4 EXPOSURE LIMITS

Element (Symbol)	Exposure Limits, mg/m ³ (C = ceiling limit) OSHA	NIOSH
Beryllium (Be)	0.002, C 0.005	C 0.0005
Magnesium (Mg)	15 (dust) as oxide	-

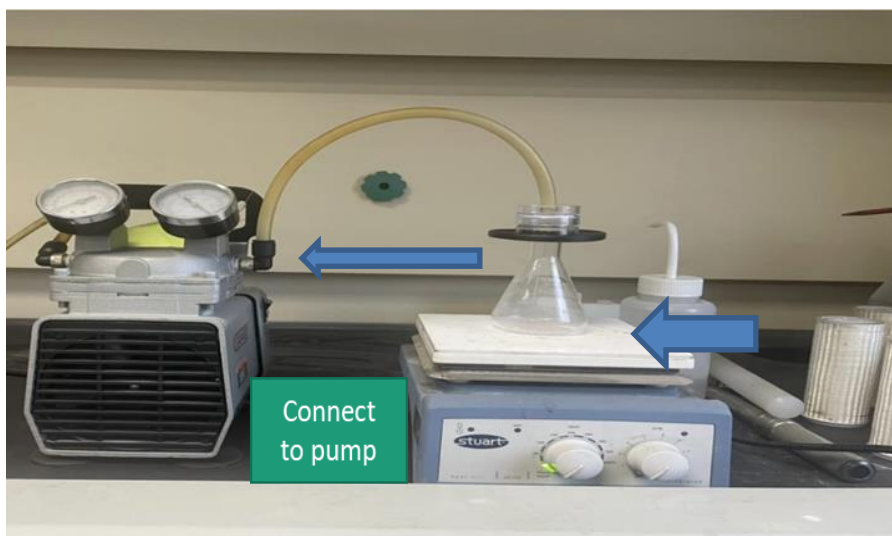
Table 5 MEASUREMENT WAVELENGTHS AND RECOVERY DATA

Element	Wavelength (nm)	LOD (µg) Sample	Lower Limit				Higher Level			
			Sample µg	N =	% Recovery	Precision	Sample µg	N =	% Recovery	Precision
Beryllium (Be)	313.04	0.008	0.15	6	102.3	0.08	15.2	6	107.71	107.71
Lithium (Li)	670.78	0.06	1.50	5	97.51	0.0253	150	6	81.96	0.0378
Magnesium (Mg)	279.08	0.9	15.0	5	105.25	0.0088	1500	6	97.47	0.0077

3.2 Sampling Techniques of Air Samples Containing Beryllium

3.2.1 Sampling Methods Laboratory setup

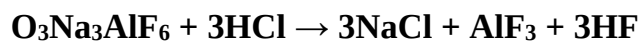
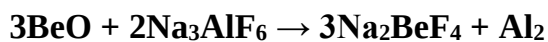
Laboratory sampling experience using pot room sample, pump, PVC filter, and set up method as shown below figures;



Laboratory sampling setup with using hot plate, pump and sample collected cassette Polyvinylchloride (PVC) filter, 37mm, 2-piece, pre-weighed

0.1 g of Cryolite Bath (Na_3AlF_6) containing Beryllium to be digested with 10ml of HCl

Reaction Cryolite Bath (Na_3AlF_6) containing Beryllium will be reacted with HCl



As the Beryllium is found in pot room in form of dust or fume, the PVC has been used for sample collection through cassette Polyvinyl Chloride (PVC) filter, 37mm, 2-piece, pre-weighed.



Then PVC is being collected and digested through microwave, Solution has been filtered and ready for (ICP-OES) analysis

3.2.2 Sampling Methods and Equipment Used

Table 6 Sampling Techniques

Environment Agents	Analytical Method ID	Sample Collection Medium
Beryllium	A-I86-155 - Alcoa - ICP/OES for metals	FPVC-PW2P - Polyvinylchloride (PVC) filter, 37mm, 2-piece, pre-weighed
Total Dust	N-0500m02-010	FTEF-PW2P - Teflon filter, 37mm, 2- piece, cellulose BUP, pre-weighed

Recommended Sampling Times

Time weighted Average (TWA) samples	240 min
Short- Term Exposure limit (STEM) samples	15 min
Ceiling samples	15 min

3.3.2 Sampling Equipment and Cassettes



Figure 19 Air Sampling Pump Sampling Media (Cassettes) sampler at Work

- Personal air samples will be collected to measure exposures in the worker's breathing zone. Full shift samples will be collected at 2.5 to 3.0 liters per minute with a minimum air volume of 1250 liters. Short-term samples will be collected with a minimum air volume of 45 liters. Filter cassettes are positioned behind face shields (if utilized) to avoid collecting metal fragments associated with metal cutting and grinding operations, and to reflect accurate breathing zone concentrations
- Air samples will be analyzed at an American Industrial Hygiene Association accredited (Clark Laboratory) as well as the laboratory analysis that has been in this Thesis research with follow International Guideline for the Analysis of Industrial Hygiene Samples with OSHA and NIOSH approved methods. Both laboratory results will be compared for validation. The laboratory's analysis through Inductively Coupled Plasma-

Optical Emission Spectrometry (ICP-OES) determines a lower limit of detection for beryllium provides enough sensitivity to measure exposure levels below 50%, and preferably below 30% of the TWA and STEL OELs. The analysis will include microwave digestion of PVC filter that absorbs Beryllium from Air samples to ensure that all beryllium is measured.

- In addition, surface dust samples have been collected to measure housekeeping within beryllium work subject to beryllium contamination. Surface contamination samples are a measure of housekeeping and are not a measure of exposure or health risk.
- Surface contamination samples have been collected during non-operational periods. It is useful to collect samples on worker contact surfaces. The specific sampling locations should be marked or photographed to facilitate data interpretation and re-sampling
- The surface contamination samples will be collected in accordance with NIOSH Method 9100. A pre-moistened towel is used to sample a 10 cm x 10 cm area (100 cm²). Disposable gloves are used to prevent skin contact and cross-contamination of samples. The area is wiped several times in different directions. The exposed sampling media is then placed in a zip-seal plastic bag with labels.

The samples have been analyzed and reported in this Thesis research.



Worker at site



Cassette



pump

3.4 Laboratory Instrumental

3.4.1 Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES)

Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) with the axial view, and wavelength of 234.861 is used in this research to determine all target sample materials after the liquid is digested. For the sample introduction method, a seaspray nebulizer with a cyclonic chamber is used. Beryllium concentration in this study is expected to be at trace levels, so it will be evaluated axially for maximum sensitivity. Certified Beryllium Calibration standard is used using $1000 \text{ mg}\cdot\text{L}^{-1}$ standard solutions and diluted for different concentrations to build the calibration curve. A linear dynamic range (LDR) and method detection limit (MDL) study is performed on this research.

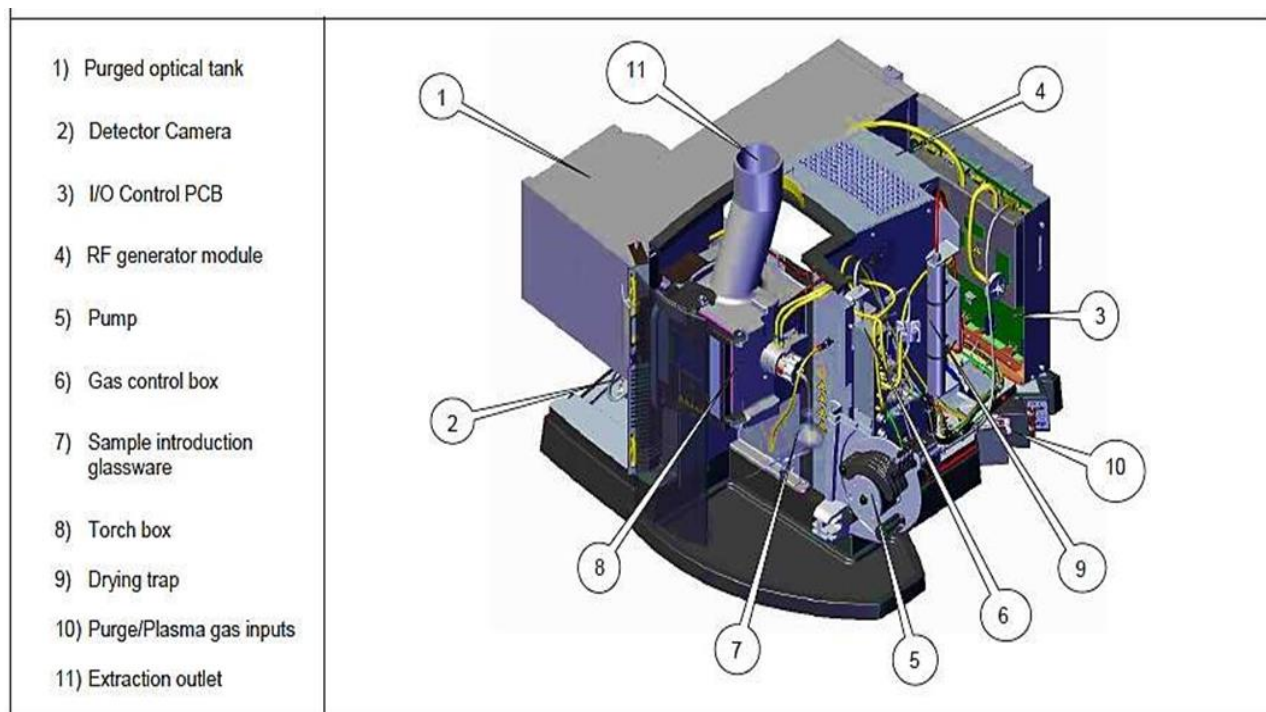


Figure 20 Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) layout

The Functional parts of Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) are as the following;

- a- Sample introduction parts where it contains Pump, Nebulizer, Spray chamber, Centre tube, and Plasma torch.
- b- Gas control as the spectrometer is required argon at 90 psi that it is Used for operation and optical path purge.
- c- Radio frequency power generator
- d- Optical system; Polychromator for Wavelength Range and selection with the optimum line for a given element. The actual line that is selected is dependent on a number of factors containing the presence of the interfering elements, and the desired sensitivity range.
- e- CID detector with thermoelectric cooling.

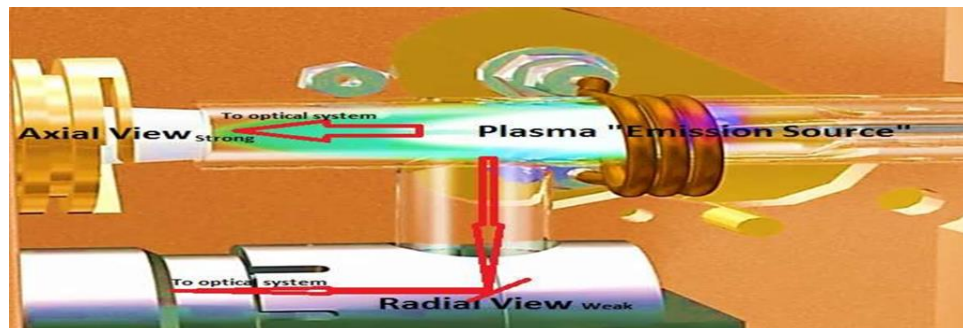


Figure 21 Dual-view with Axial, Optical system, and plasma

Dual-view with Axial, Optical system, and plasma are direct to each other “direct view”. Radial, optical systems, and plasma are indirect views of each other.

The standard Calibration in Inductively Coupled Plasma-Optical Emission Spectrometry ICP -OES determines the relationship between the analytical echo (signal) and the analytic concentration. Accurate calibration and standardization are very important parts to be performed in Inductively Coupled Plasma-Optical Emission Spectrometry ICP -OES and it is followed in all analytical procedures.

The calibration is usually determined using certified chemical standards.

Optical emission in ICP spectrometry is a comparative technique that used signals from solutions of known certified standards and then used to create a calibration curve compared to the signals of unknown samples to generate results.

In this thesis research, we are targeting Beryllium concentration in solid various samples.

Various lines are emitted for Each element based on wavelength selection. The analyst can select the optimum line for a given analysis.

The existing line that is chosen is dependent on several factors such as the presence of the interference elements, and the desired sensitivity and selectivity range.

In this Thesis study, the Beryllium, Lithium, and Magnesium concentration have been calibrated and tested in the prepared Raw Materials used in this study.

The calibration curve has been done by certified Beryllium, Lithium, and Magnesium 1000 mg/l for 5 ppm, 10 ppm, and 15 ppm based on analytical detection limits.



Figure 22 Certified calibration standards for Beryllium, Lithium, and Magnesium

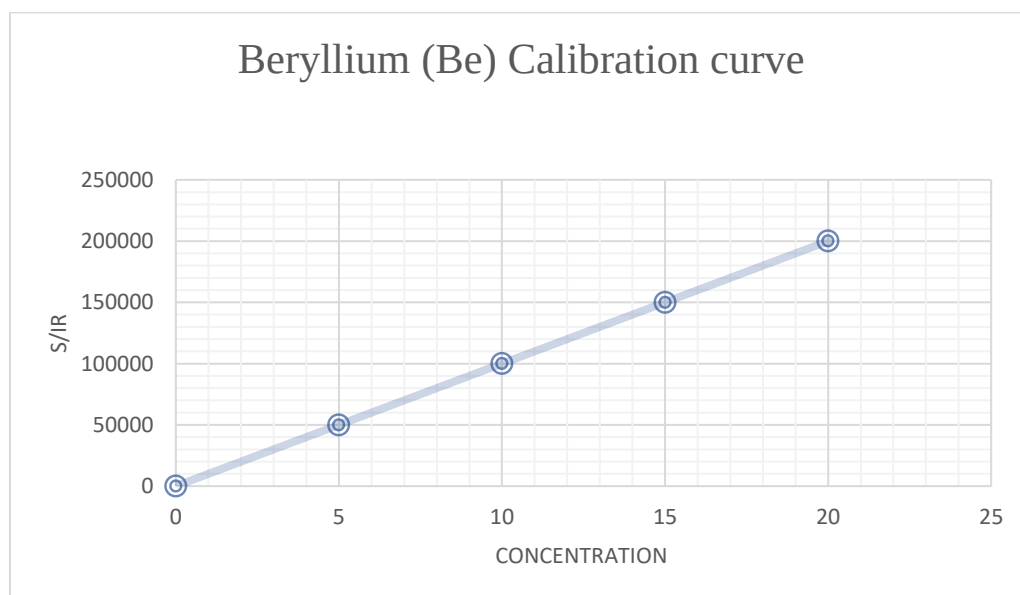


Figure 23 Calibration curve of Beryllium

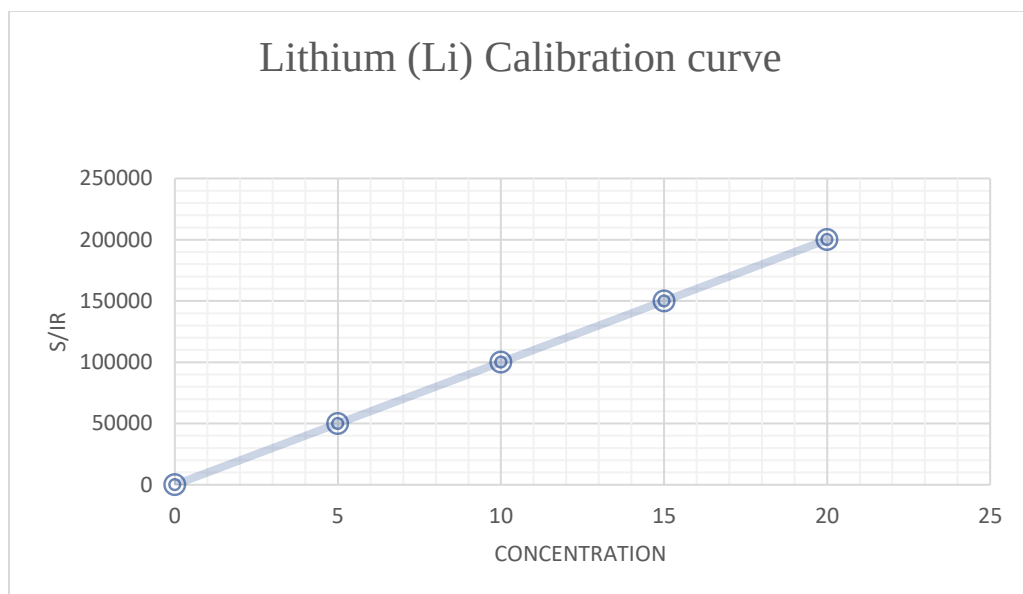


Figure 24 **Calibration curve of Lithium**

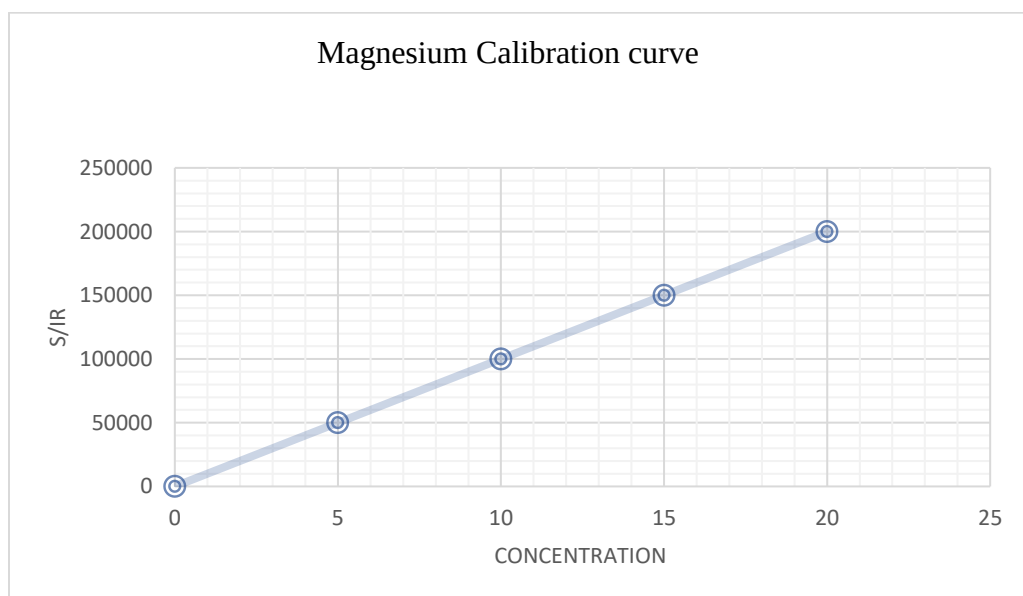


Figure 25 **Calibration curve of Magnesium**

The samples used in this research thesis study have been chemically digested and diluted to 100ml, so the **dilution factor** calculation is shown in the following

Table 7 Dilution Factor Calculation

Volumetric flask (ml)	100 ml
Sample weight (gm)	Based on the sample test method with the required grams to be digested
Lithium (ppm) reading from ICP-OES	-
Beryllium (ppm) reading from ICP-OES	-
Magnesium (ppm) reading from ICP-OES	-
Lithium fluoride (%)	Digestion volume * Lithium (ppm) reading from ICP-OES/ Sample weight (gm) 10000)/ 0.2676
Beryllium (ppm)	Digestion volume * Beryllium (ppm) reading from ICP-OES/ Sample weight (gm)
Magnesium oxide %	Digestion volume * Magnesium (ppm) reading from ICP-OES / Sample weight (gm) (10000)/ 0.603

- Lithium concentration = Dilution (100 ml) * ICP reading for Lithium/ Weight of sample collecting that being Digested.
- Beryllium concentration = Dilution (100 ml) * ICP reading for beryllium / Weight of sample collecting that being Digested.
- Magnesium Concentration= Dilution (100 ml) * ICP reading for Magnesium / Weight of sample collecting that being Digested.

3.4.2 Microwave acid Digestion

Microwave acid Digestion is a technique for dissolving the metal in a liquid that is bound with the same sample matrix. This is carried out by exposing a sample to a strong acid in a closed vessel and then using microwave irradiation to raise the temperature and pressure. The rate of thermal decomposition of the sample is accelerated, as is the solubility of heavy metals in the solution. Once these heavy metals have been mounted, a closed vessel microwave digestion system will be used to digest all the target sample materials for sample decomposition.

The Microwave acid digestion is able to contactless in-situ temperature analysis using temperature sensors and vessel



Figure 26 **The Microwave acid digestion that is being used in this Thesis**

3.4.3 Scanning Electron Microscope

Scanning electron microscopy (SEM) uses a focused beam of high-energy electrons to generate a variety of signals on the surface of a solid sample.

The signals obtained from the interaction of electronic samples provide information about the sample, such as its external morphology (texture), chemical composition, crystal structure, and orientation of the materials that make up the sample.

In most applications, the data is collected in a selected area of the sample surface to produce a two-dimensional image showing the spatial changes in these properties.

Areas about 1 cm to 5 micrometers wide can be imaged in scan mode using traditional SEM technology (magnifications in the range of 20x to about 30000x, spatial resolution of 50-100 nm).

The SEM can also perform an analysis of selected point locations on the sample. This approach is especially useful for qualitative or semi-quantitative determination of chemical composition (using EDS), crystal structure, and crystal orientation (using EBSD).

The structure and function of SEM are very similar to EPMA, and there is considerable overlap in function between the two devices.

In this research thesis study, we will examine the Bauxite the ore of aluminum with a Scanning electron microscope (SEM) as there is no probably other Laboratory instrument that is better than SEM in terms of checking the solid material characterization such as Bauxite comparable to SEM.

Although this post is primarily related to geological applications, it is important to note that these applications are a very small subset of the scientific and industrial applications that exist on this instrument.

Most SEMs are relatively easy to use and have a user-friendly "intuitive" interface. Many applications require minimal sample preprocessing. Data acquisition is fast for many applications (less than 5 minutes/image for SEI, BSE, and spot ED's analysis).

The reason to include SEM analysis in this Thesis research on Bauxite is that SEMs are also widely used to identify phases based on qualitative chemical analysis and crystal structure.

Even very small structures and objects up to 50 nm in size can be accurately measured by SEM.

Backscattered electron imaging (BSE) allows you to quickly distinguish the phases of a polyphase sample.

SEMs with Diffraction Backscatter Electron Detectors (EBSD) can be used to study the microstructure and crystallographic orientation of many materials.

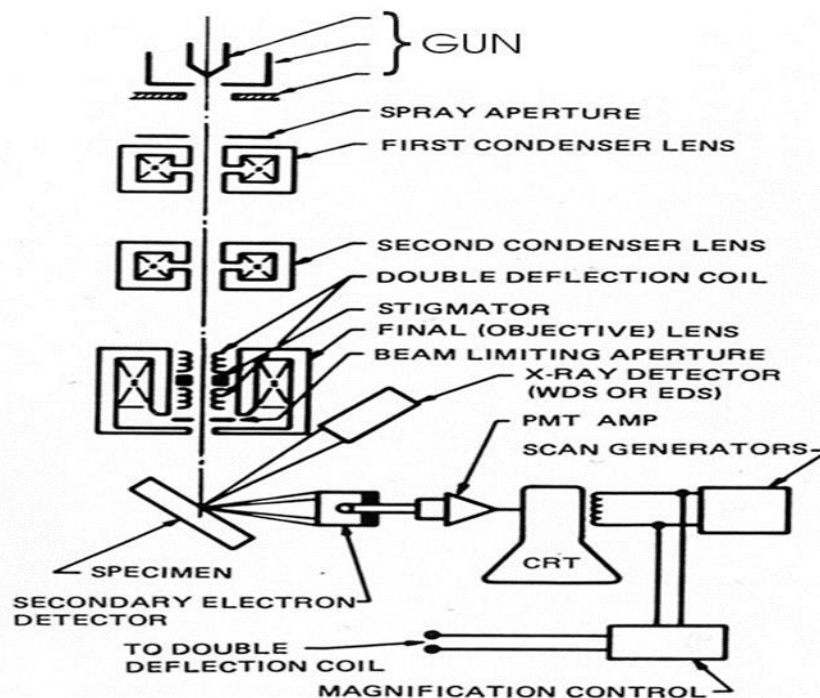


Figure 10 SEM Layout

3.4.4 X-Ray diffractometers (XRD)

XRD with the brand of D2 PHASER X Flash detector has been used in this Thesis to check the solid identification and crystallite of Bauxite (ore of Aluminum oxide)

The eminent vitality determination of the Flash permits for great filtration of undesirable $K\beta$, white radiation as well as test fluorescence for most elevated quality powder patterns with the best crest to foundation proportion. Whereas for standard powder XRD the $K\alpha_{1,2}$ doublets are utilized, the X Flash locator can furthermore be exchanged to a subjective wavelength inside the X-ray range. Regularly, this would be $K\beta$ in arrange to get monochromatic powder designs with tall escalated, maintaining a strategic distance from crest cover characteristic to the commonly utilized $K\alpha$ radiation ($K\alpha_{1,2}$ doublets).

3.4.5 Fourier-transform infrared spectroscopy (FTIR)

FTIR has been used in this Thesis as a technique for obtaining an infrared spectrum of Bauxite (an ore of aluminum) where the FTIR spectrometer simultaneously collects high-resolution spectral data over a wide spectral range.

The Aim of FTIR analysis of Bauxite is to use Infrared spectroscopy to support X-Ray diffractometers' (XRD) results to clarify the structure and identify different phases of bauxite ore.

The range used to obtain the IR spectrum was in the range $4000\text{--}400\text{ cm}^{-1}$ while the interesting area to be detected is from $2000\text{--}400\text{ cm}^{-1}$.

CHAPTER 4

ANALYSIS AND CONCLUSION

3.3 Characterization of Bauxite

The Reason for discussing the Phase Content of Bauxite. It is main compounds in bauxite consist of hydrous aluminum oxides, iron and titanium oxides, quartz, and other silicate species. The identify “bauxite” is in many instances used for hydrous clay rocks of assorted compositions and geological origins. Bauxite is the primary source of industrial aluminum production. The below results are obtained by Xray Diffraction (XRD) with the brand of D2 PHASER X Flash detector of Bauxite ore of aluminum in Saudi Arabia. The intensity 2θ ° was started from 5.00 to 90 °.

X-rays (XRD) can be also utilized to perform quick and accurate cluster analysis, phase identification, and mineral quantification in iron ore. Hematite, goethite, and magnetite, as well as the gangue minerals gibbsite $\text{Al}(\text{OH})_3$, kaolinite $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$, and quartz SiO_2 , are all found in the ore. Based on the analysis of Bauxite from Saudi Arabia, in total, 11 phases were used in the research. The scale factors and cell characteristics for all of the minerals studied were revised, and the comparative intensities of the Bragg reflections were calculated from the crystal structures. The fundamental parameters technique was used to describe the instrument contribution to the peak form of all phases, whereas a single crystallite-size parameter per phase was used to model the individual contributions from each phase.

Phase Analysis of Bauxite from Al Baitha Mine, Saudi Arabia

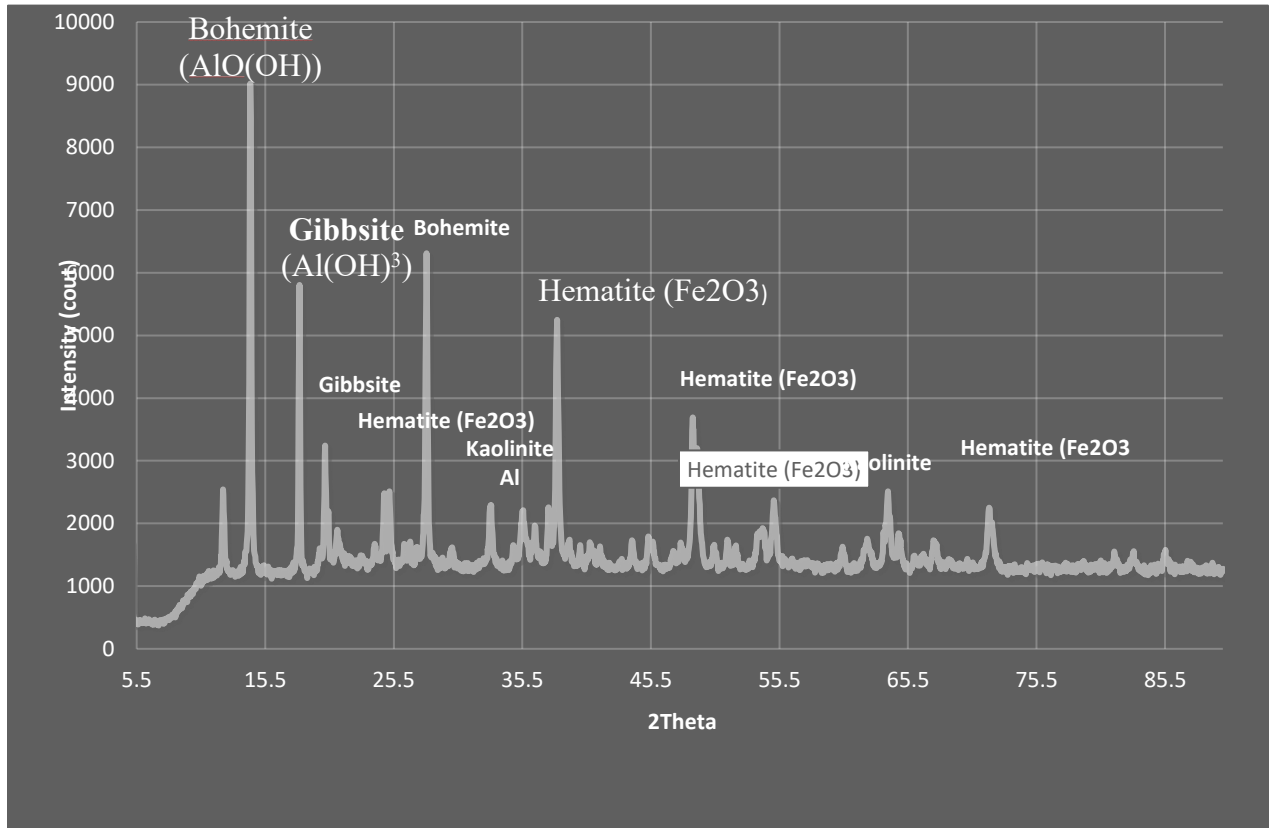
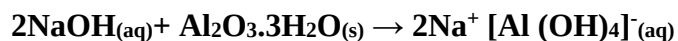


Figure 28 Quantitative phase analysis of bauxite using D2 PHASER X Flash detector

As per the data collected above, the Bauxite from Al Baitha Mine, Saudi Arabia is considered high Bauxite grade to be extracted as Alumina and used in Aluminum smelting process. It has an ideal chemical composition of Alumina Tri-hydrate (Gibbsite) $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}_{(s)}$ which is reacted with the alumina for Bauxite digestion as per the following reaction



Alumina Tri-hydrate (Gibbsite) sodium aluminate

Moreover, the other mine in Saudi is The Az Zabirah which is considered as low-grade Bauxite grade as the silicon chemical composition is higher than the limit which it is required more of the chemical digestion with caustic as per the following chemical reaction

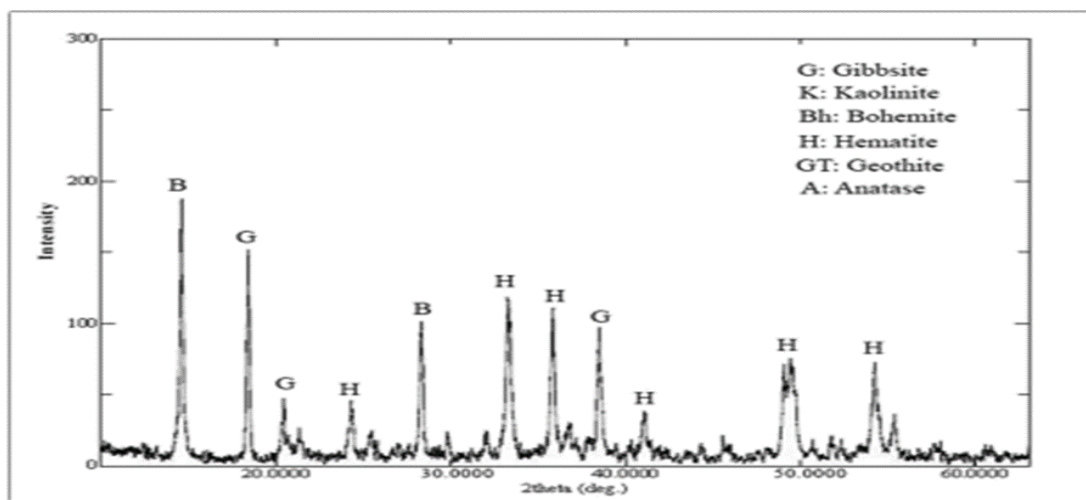
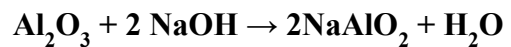


Figure 29 Quantitative phase analysis of bauxite using D2 PHASER X Flash detector

4.1.2 SEM for Bauxite

Two samples of Bauxite from Saudi Arabia have been tested for the Scanning Electron microscope to Investigate the morphological and compositional characteristics of raw bauxite. Typical secondary electron SEM images of raw bauxite polished and etched surfaces; the pictures obtained from SEM are shown below;

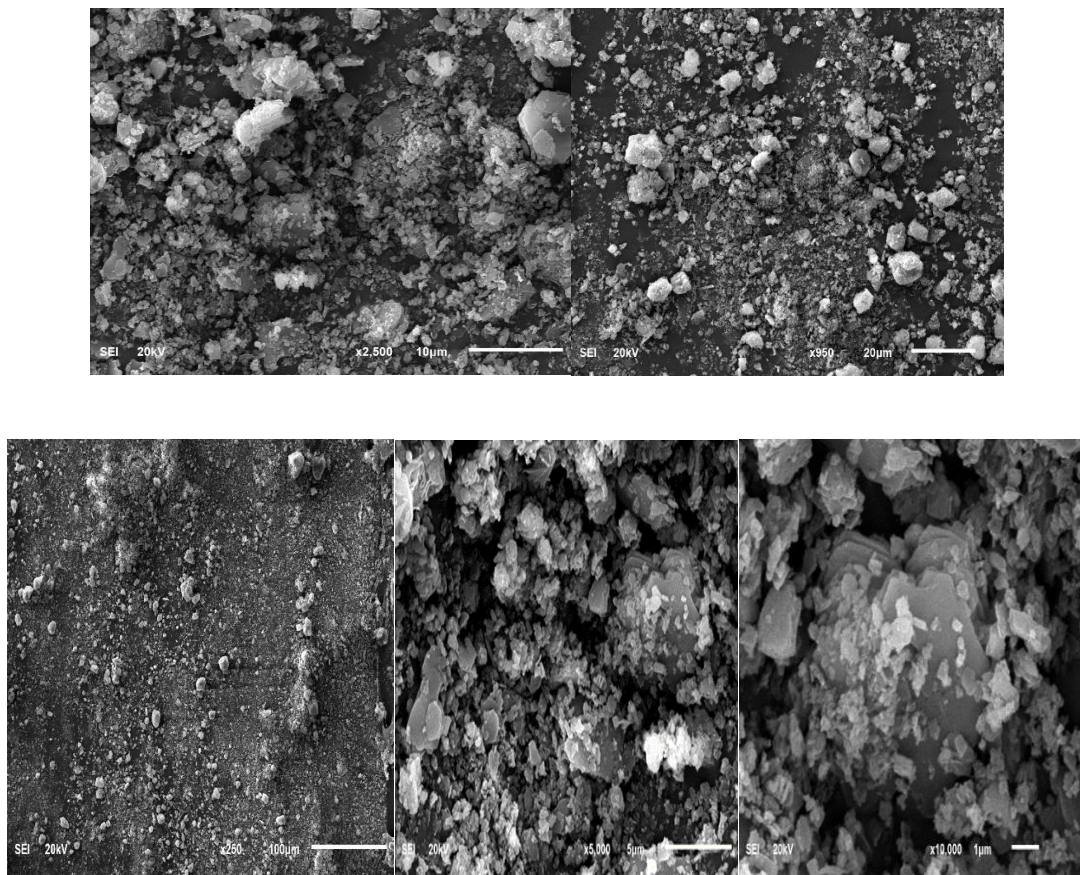
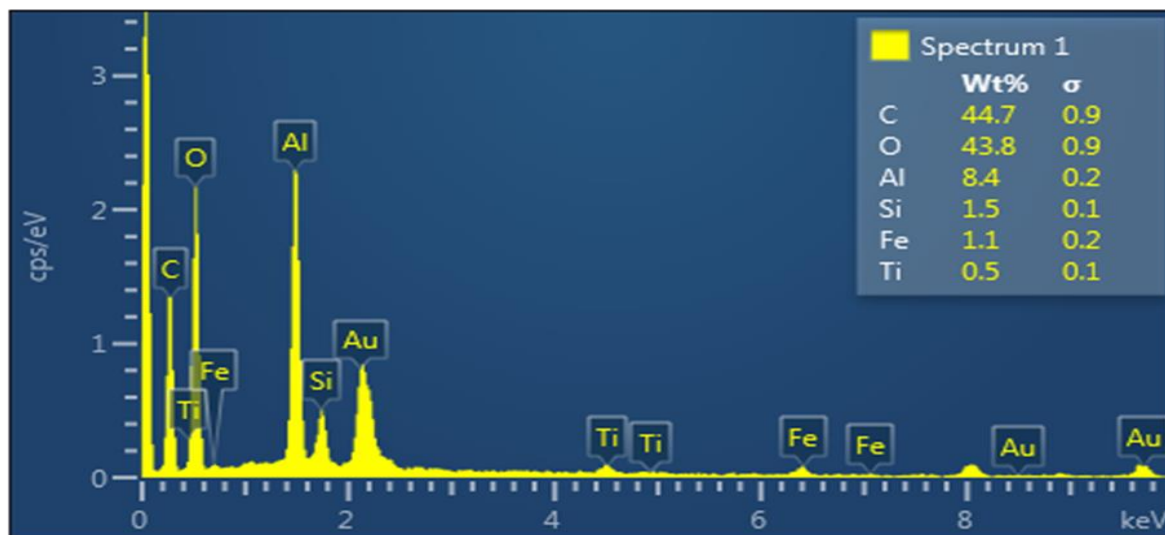
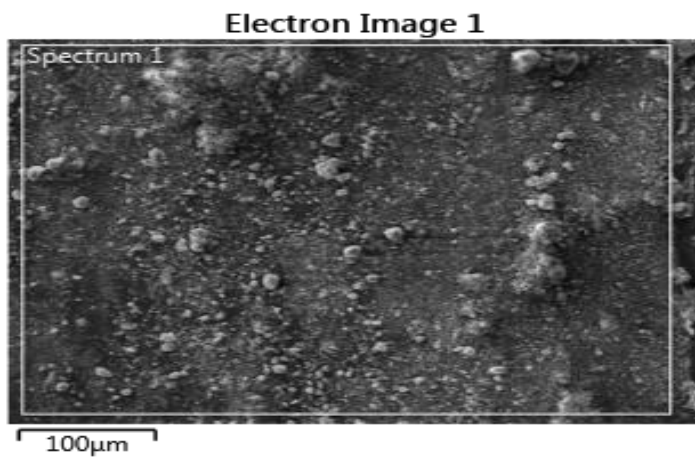


Figure 30 SEM for Bauxite from Saudi Arabia

The results of the Frist Bauxite Sample are shown in the following graphs



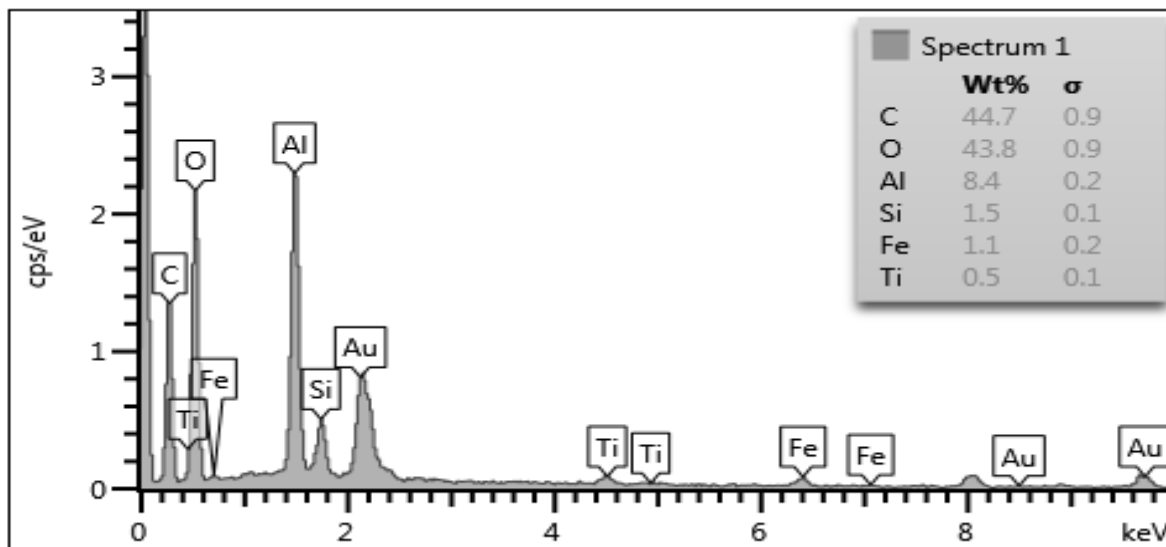


Table 8 SEM summary report for Bauxite

Element	Line Type	Apparent Concentration	k Ratio	Wt%	Wt% Sigma	Standard Label	Factory Standard
C	K series	16.41	0.16409	44.73	0.94	C Vit	Yes
O	K series	36.42	0.12254	43.81	0.90	SiO ₂	Yes
Al	K series	13.37	0.09602	8.40	0.24	Al ₂ O ₃	Yes
Si	K series	2.33	0.01845	1.49	0.11	SiO ₂	Yes
Ti	K series	0.78	0.00780	0.51	0.10	Ti	Yes
Fe	K series	1.64	0.01645	1.07	0.15	Fe	Yes
Total:				100.00			

The presence of higher silica content can be confirmed with cristobalite phases detected by XRD

No Beryllium has been found in the ore samples

4.1.3 FTIR for Bauxite

The Infrared spectroscopy of Bauxite from Saudi Arabia has been shown as the following:

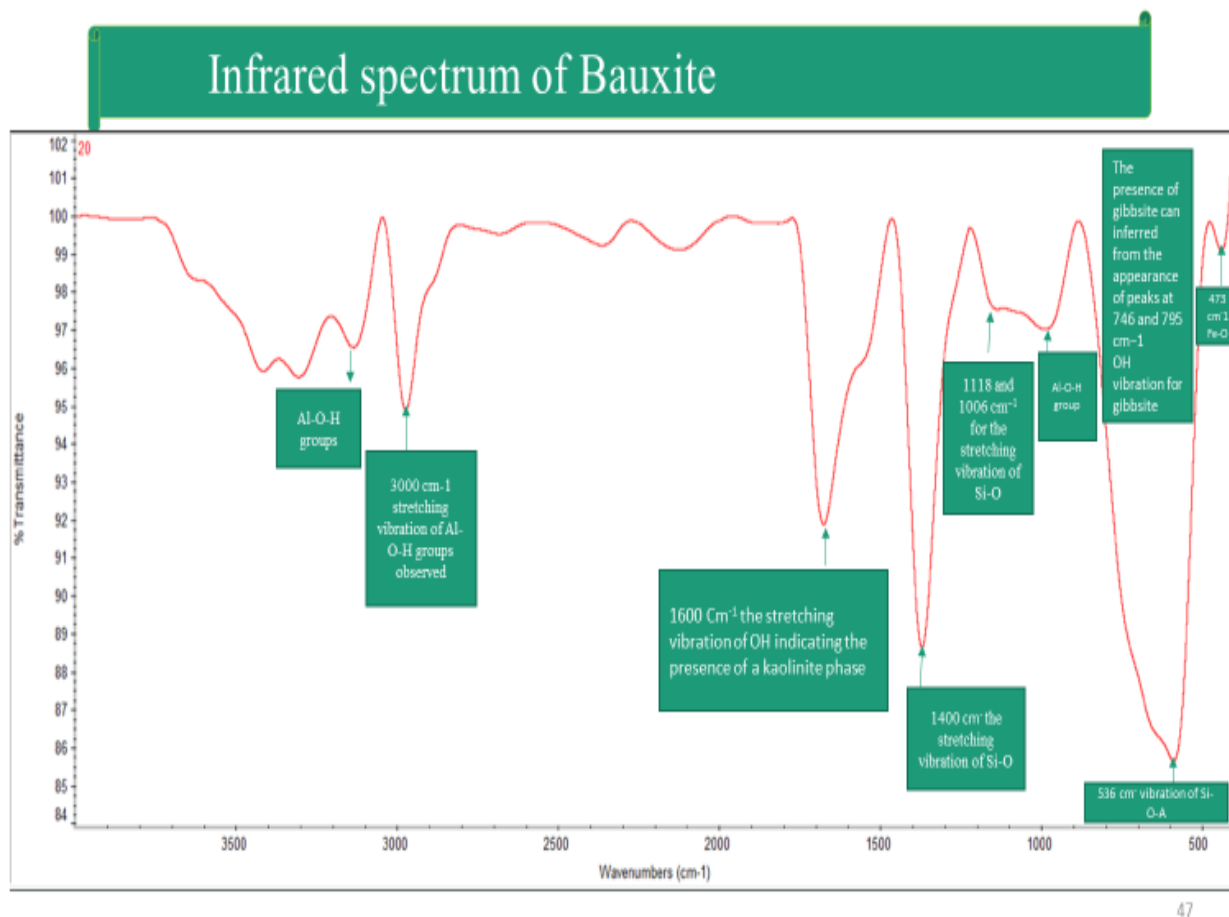


Figure 31 FTIR analysis of Bauxite sample from Saudi Arabia

As shown in the above FTIR spectrum of Bauxite, the IR spectrum range was in the range 4000-400 cm⁻¹ while the interesting area to be detected is from 2000-400 cm⁻¹.

The inset shows the bands associated with the stretch oscillations of the Al-OH groups observed at about 3620 cm⁻¹ associated with gibbsite and kaolinite

minerals. The 3695 cm^{-1} band is assigned to the stretch vibration of OH, and the 1118 and 1006 cm^{-1} are assigned to the stretch vibration of Si-O bond, which indicates the presence of the kaolinite phase [27–29]. The band observed at 914 cm^{-1} is due to the deformation oscillation of the Al-OH group [30]. The presence of the gibbsite can also be inferred from the appearance of 746 and 795 cm^{-1} peaks of OH oscillations at the gibbsite.

4.1.4 Analysis of Beryllium in Bauxite

The Bauxite from Saudi Arabia is almost considered free of trace Beryllium and the amount is very traced and can hardly be detectable in Inductively Coupled Plasma-Optical Emission Spectrometry ICP –OES as shown in the below figure.

Beryllium Concentration= Dilution (100 ml) * ICP average reading for beryllium /

Weight of sample collecting that being Digested

$$C = 100\text{ml} * 0.0001 / 0.2541 \text{ g} = 0.039 \text{ ppm}$$

The alumina used in this Thesis research is being extracted and refineries from Bauxite of Saudi Arabia which is considered ideal alumina in regard to Beryllium concentration based on this study. The ideal Alumina should contain a max of 0.3 ppm of Beryllium. The amount of Beryllium is 0.3 ppm which was detected by Inductively Coupled Plasma-Optical Emission Spectrometry ICP – OES and the results were compared with the external lab in the US.

Beryllium Concentration= Dilution (100 ml) * ICP average reading for beryllium / Weight of sample collecting that being Digested

$$\text{C sample one} = 100\text{ml} * 0.0008 / 0.2600 \text{ g} = 0.30 \text{ ppm}$$

$$\text{C sample two} = 100 \text{ ml} * 0.0007 / 0.2600 \text{ g} = 0.269 \text{ ppm}$$

Analysis of Beryllium in Bauxite							
Sample Number	1	2	3	4	5	6	7
Dilution volume (ml)	100 $\pm$ 1	100	100	100	100	100	100
Sample Weight (gm)	0.25 $\pm$ 0.2	0.25 $\pm$ 0.022	0.25 $\pm$ 0.2	0.25 $\pm$	0.25 $\pm$ 0.2	0.25 $\pm$ 0.2	0.25 $\pm$ 0.2
ICP Reading (Be)	0.0001	0.0002	0.0002	0.0003	0.0004	0.0004	0.0001
Be (ppm)	0.04	0.08	0.08	0.12	0.04	0.04	0.04
Average	0.068						
Standard Deviation	0.030						

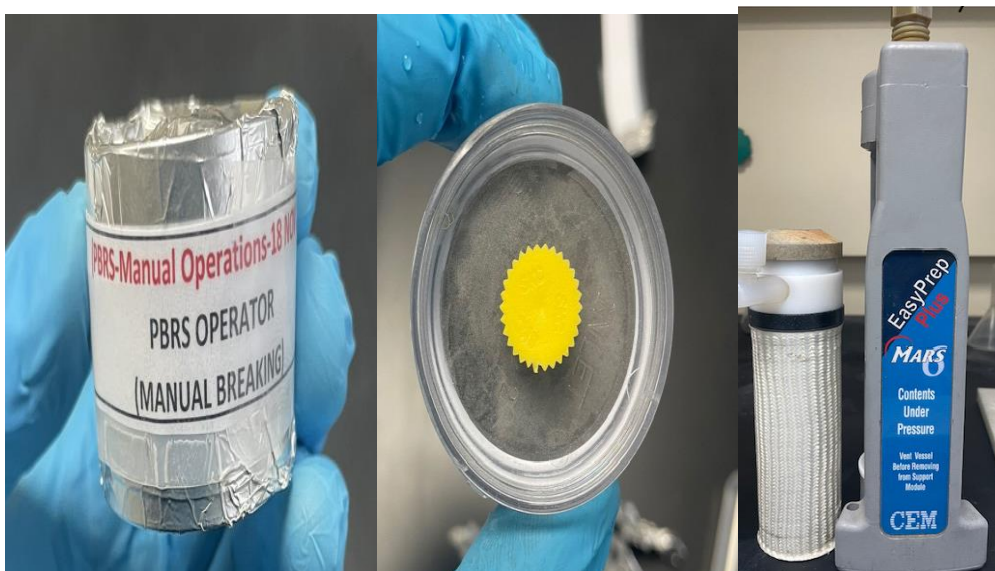
Figure 11 Beryllium concentration of Bauxite

The Bauxite from Saudi Arabia is almost considered free of trace Beryllium and ideal raw materials for Aluminum.

Can hardly be detectable in Inductively Coupled Plasma-Optical Emission Spectrometry ICP –OES for low detection limit concentration.

3.4 Analysis of Beryllium in PVC Filter

The PVC media containing Beryllium has been digested through Microwave acid digestion the PVC sample has been added into the digestion vessel, and then 10 mL of HNO_3 has been added. The vessel has been gently swirled with the mixture.



The reaction will be done on a vessel at a control pressure 800 psi and a temperature of 215 °C. The solution will be filtered and diluted to 100 ml to be ready to analyze in Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) for trace elemental analysis including Lithium, beryllium, and Magnesium

The calibration curve has been done by certified Beryllium, Lithium, and Magnesium 1000 mg/l for 5 ppm, 10 ppm, and 15 ppm based on analytic detection limits.

Standard preparation for 5 ppm = 5 ppm /1000 *100 ml dilution factor = 0.5 ml

Standard preparation for 10 ppm =10 ppm /1000 *100 ml dilution factor = 1 ml

Standard preparation for 15 ppm =15 ppm /1000 *100 ml dilution factor = 1.5 ml

To calculate the beryllium concentration as below formula;

$$C = \frac{(C_s V_s) - (C_b V_b)}{V}, \text{ mg/m}^3$$

Where C_s is the concentration of the sample, V_s is the volume of sample being digested, C_b is the concentration of blank, V_b is the volume of blank being digested, and V is air volume for sampling.

Analysis of Beryllium in PVC Filter

Analysis of Beryllium in personal exposure in PVC Filter								
sample #	Concentration of sample $\mu\text{g/m}^3$ (ICP reading)	Volume of dilution sample	Concentration of blank (ICP reading)	Volume of blank	Air volume mg/m^3	concentration	Limit $\mu\text{g/m}^3$	Decision
1	0.069	50 ml	0.007	100 ml	2.1	0.12	0.2	Statistically Insignificant
2	0.07	50 ml	0.007	100 ml	2.1	0.17	0.2	Statistically Insignificant
3	0.068	50 ml	0.007	100 ml	2.1	0.07	0.2	Statistically Insignificant
4	0.067	50 ml	0.007	100 ml	2.1	0.02	0.2	Statistically Insignificant
5	0.07	50 ml	0.007	100 ml	2.1	0.17	0.2	Statistically Insignificant
6	0.07	50 ml	0.007	100 ml	2.1	0.17	0.2	Statistically Insignificant
7	0.068	50 ml	0.007	100 ml	2.1	0.07	0.2	Statistically Insignificant
8	0.067	50 ml	0.007	100 ml	2.1	0.02	0.2	Statistically Insignificant
9	0.068	50 ml	0.007	100 ml	2.1	0.07	0.2	Statistically Insignificant
10	0.07	50 ml	0.007	100 ml	2.1	0.17	0.2	Statistically Insignificant
Mean						0.10		
Standard Deviation						0.070		

33

TABLE 9 analysis of Be in PVC filter

3.5 Analysis of trace metals in Pot room sample by developed manual method and compared with microwave Digested method

The developed manual digestion method for Bath analysis used in the aluminum industry has been compared with the Microwave acid digestion method for beryllium, lithium, and magnesium concentration through Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) for trace elemental analysis including Lithium, beryllium, and Magnesium. Six Samples of the bath are being analyzed in both methods as comparison and method validation

The following table are showing the compression between two methods of concentration with Manual and microwave methods by checking Lithium fluoride in present concentration, beryllium in part per million (ppm) concentration, and Magnesium fluoride in present concentration.

Developed Manual digestion method and then analyzing Lithium, Beryllium, Magnesium
By ICP-OES

Microwave Digested method then analyzing Lithium, Beryllium, Magnesium By ICP-
OES By ICP-OES

Table 9 Comparison between two methods Manual and microwave methods

Seq.	Sample#	Manual Method Average reading			Microwave method average reading		
		Li (%)	Be (ppm)	Mg (%)	Li (%)	Be (ppm)	Mg (%)
1	D-091	3.05	57	0.75	3.00	53	0.63
2	D-091 R	3.04	55	0.75	2.97	53	0.64
3	D-092	3.09	55	0.78	2.03	56	0.74
4	D-092 R	3.02	55	0.80	3.06	56	0.76
5	D-093	2.93	53	0.71	2.94	54	0.66
6	D-094	2.95	51	0.75	2.83	48	0.68

Based on the above Standard Deviation calculation, the variation between the two methods is acceptable and within the acceptable limit. It is confirmed that the tests for both methods are successful and can.

When applying the 95.0% Confidence Level between the two methods for all the readings of six POT line bath samples, the following tables are summarized the calculation

Table 10 95.0% Confidence Level

Beryllium			
Mean	54.92		
Standard Error	0.315805848	Mean	54.92
Median	55	Confidence Level (95.0%)	0.651791234
Mode	55		
Standard Deviation	1.579029238		
Sample Variance	2.493333333	Higher	lower
Range	6	55.57179123	54.26820877
Minimum	51		
Maximum	57		
Sum	1373		
Count	25		
Confidence Level (95.0%)	0.651791234		

The analysis method for Beryllium in bath (Na_3AlF_6) is very essential to be monitored in the aluminum industry and no developed method has been certified

Beryllium concentration between two methods

	Manual Method	Microwave Method
Average	54.33	53.33
Variance	8.67	4.267
Standard Deviation	2.07	2.94
Comments	Lower SD	Higher SD
	Better precision	

Comparison between the Two Methods

Benefits

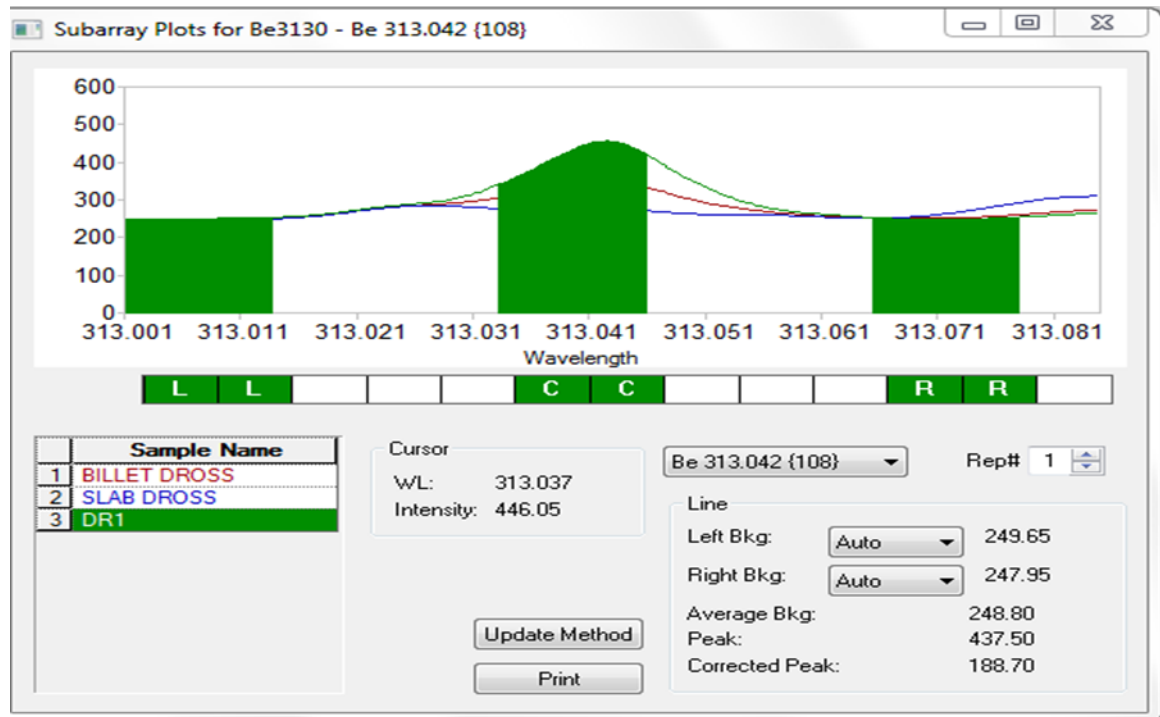
Manual	Microwave
• Less analysis time 10 min	• Easier, less human error
• Cheaper to be used for daily operation	• Less Exposure to chemicals fume

Limitation

Manual	Microwave
• Analysis precision may be affected -Human error	Analysis precision may be affected - Human error
• Exposure to chemicals fume while analysis	Exposure to chemicals fume while analysis

3.6 Analysis of Beryllium in various resources in Aluminum Industry

Three samples from three different area Slab, Billet, and ingot has been tested for beryllium concentration through ICP -OES after acid digestion



Beryllium Concentration in Ingot sample= Dilution (100 ml) * ICP average reading for beryllium / Weight of sample collecting that being Digested

Ingot sample = 100ml *.0075/0.2580 g = 2.9 ppm trace concentration

Billet Sample = 100ml *.0060/0.2590 g= 2.3 ppm consider trace concentration

SLAB sample = 100ml *.0055/0.2581 g = 2.1 ppm trace concentration

The three samples are having acceptable limit of Beryllium as per smelter plant's design for the three products

Table 11 Analysis of Beryllium concentration in various materials used in Aluminum Smelting

Sample	Laboratory Method	Beryllium Results (ppm)		Standard Deviation
		Laboratory	Certified Lab in the US	Limit >5
Coke A	Digestion Carbon Anode by Microwave digestion and analysed by ICP-OES	0.01	NA	NA
Coke B		0.01	NA	NA
Pitch		0.01	NA	NA
Fresh GTC-1	Chemical Digestion Method for Alumina Powder (Aluminum Oxide)	0.25	0.30	0.035355
Fresh GTC-2		0.25	0.30	0.035355
Fresh GTC-3		0.24	0.29	0.035355
Fresh GTC-4		0.23	0.30	0.049497
Fluorinated GTC-1		0.45	0.56	0.077782
Fluorinated GTC-2		0.45	0.59	0.098995
Fluorinated GTC-3		0.44	0.56	0.084853
Fluorinated GTC-4		0.45	0.59	0.098995
Cover Mix GTC-1	Microwave Digested method for Pot room bath sample	45	45.99	0.700036
Cover Mix GTC-2		50	50.21	0.148492
Cover Mix GTC-4		45	42	2.12132

3.7 Conclusion

Since This Thesis research is aimed to develop various acid digestion techniques to be used to investigate the resources of an increasing trend of Beryllium Concentration in Aluminum pot room cryolite bath. Based on the study, all Potential resources of Beryllium in pot room baths such as bauxite, Fresh alumina, Fluorinated alumina, petroleum coke, tar pitch, Aluminum Dross, and Anode cover are having acceptable limits and are below the concentration limit.

Based on the results obtained in this Thesis for Beryllium concentration in pot room using alumina (0.3 ppm), the beryllium should be about 18 ppm only as of the Beryllium is tends to concentrate in the electrolyte bath around 60 times its concentration in bauxite and alumina.

The analysis of the concentration of personal exposure to beryllium through FPVC-PW2P - Polyvinylchloride (PVC) filter containing Beryllium, 37mm, 2-piece, pre-weighed sample Cassette with pump has been found to be insignificant with the low the exposure limit. Beryllium concentration in PVC is $0.0904 \mu\text{g}/\text{m}^3$ which is less than the exposure limit is 0.2 as OEL-TWA.

This thesis is very important as there is only one certified laboratory approved to do the Beryllium test in the air exposure (Clark Lab), The analysis of the concentration of personal exposure to beryllium has been found to be Statistically Insignificant

The phase structural, elemental analysis, and crystallinity of Bauxite (ore of Aluminum) has been characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy FTIR, and scanning electron microscopy (SEM) which shows bauxite from Saudi Arabia is ideal bauxite and there are any radioactive materials. The studied Bauxite has trace beryllium concentration only. The presence of higher silica content can be confirmed with cristobalite phases detected by XRD; low silica is low cost for the digestion process using NaOH.

The calcined Alumina used in this study has only trace beryllium concentration with a range of 0.3 ppm (Ideally below 0.7 ppm). This means the generated Cryolite Bath should have only 18 ppm.

Developing a method of Manual acid Digestion of Cryolite Bath has been Validated with the microwave method successfully. Manual acid Digestion is better precision than the microwave method

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