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Subject/Topic:

HYDROMETALLURGICAL TREATMENT OF LEAD CONCENTRATES FOR THE RECOVERY OF VALUABLE METALS

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DEDICATION

I dedicate this work to my beloved father, Mr. David G.B. Mulbah. You are my first teacher, my most discerning critic, and my most enthusiastic supporter. You have instilled in me the true meaning of hard work and discipline, and those lessons are the foundation of my success today. Your unwavering belief in me has been my greatest source of strength.

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With my warmest appreciation,
Forkpayea Mulbah

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ABSTRACT

Metals play a critical role in electricity, industrialization, and medicine, but their effective recovery from ores while removing impurities remains a challenge. This thesis, titled ’Hydrometallurgical Treatment of Lead Concentrates for the Recovery and Separation of Valuable Metals, tends to focus on the selective leaching of PbS concentrate to recover valuable metals and associated metals. Two different sets of experiments were performed under different conditions of temperature, acid concentration. The first experiment utilized a pressured autoclave system, and different concentrations of oxygen were employed during this experiment. The second set of experiments was performed using a glass reactor to investigate the dissolution behavior of PbS-rich solid residues under various nitric acid conditions. The effects of temperature, leaching time, and reagent concentration on leaching efficiency were assessed. We used ICP-OES and XRD to analyze the leachates and solid residue collected as samples, respectively. From the results of the experiments conducted in the autoclave, metals such as Iron (Fe) and Calcium (Ca) showed the best leaching efficiencies, reaching up to 85% for Iron and 62% for Calcium. Bismuth showed moderate leaching efficiency between 35% and over 70% while lead (Pb) did not dissolve as its leaching efficiency was <0.05%. The results from the glass reactor show better leaching efficiencies for Pb (39%), Bi(73%), and Ag(88%). XRD analysis confirmed the transformation of PbS into $PbSO_4$. These results demonstrate the potential of hydrometallurgical processes in recovering valuable metals, especially under appropriate temperature and oxidant conditions.

Keywords: Hydrometallurgical Treatment; Lead Concentrate; Autoclave Leaching; Glass Reactor Leaching; Metals Recovery

Résumé

Les métaux jouent un rôle essentiel dans l'électricité, l'industrialisation et la médecine, mais leur récupération efficace à partir des minerais tout en éliminant les impuretés reste un défi. Cette thèse, intitulée « Traitement hydrométallurgique des concentrés de plomb pour la récupération et la séparation des métaux précieux », se concentre sur la lixiviation sélective de concentrés de PbS afin de récupérer les métaux précieux et les métaux associés. Deux séries d'expériences ont été réalisées dans différentes conditions de température et de concentration d'acide. La première expérience a utilisé un autoclave sous pression, avec différentes concentrations d'oxygène. La seconde série d'expériences a été réalisée dans un réacteur en verre afin d'étudier le comportement de dissolution de résidus solides riches en PbS dans diverses conditions d'acide nitrique. Les effets de la température, du temps de lixiviation et de la concentration en réactifs sur l'efficacité de la lixiviation ont été évalués. Nous avons utilisé l'ICP-OES et la DRX pour analyser respectivement les lixiviats et les résidus solides prélevés comme échantillons. D'après les résultats des expériences menées en autoclave, les métaux tels que le fer (Fe) et le calcium (Ca) ont montré les meilleurs rendements de lixiviation, atteignant jusqu'à 85 % pour le fer et 62 % pour le calcium. Le bismuth a montré un rendement de lixiviation modéré, compris entre 35 % et plus de 70 %, tandis que le plomb (Pb) ne s'est pas dissous, son rendement de lixiviation étant inférieur à 0,05 %. Les résultats du réacteur en verre montrent de meilleurs rendements de lixiviation pour le Pb (39 %), le Bi (73 %) et l'Ag (88 %). L'analyse DRX a confirmé la transformation du PbS en 〖PbSO〗_4. Ces résultats démontrent le potentiel des procédés hydrométallurgiques pour la récupération de métaux précieux, notamment dans des conditions de température et d'oxydation appropriées.

Mots-clés : Traitement hydrométallurgique ; Concentré de plomb ; Lixiviation en autoclave ; Lixiviation en réacteur en verre ; Récupération des métau

ACRONYMS AND ABBREVIATIONS

ADB	: African Development Bank
BLS	: Boiler and Level System
BMBF	: German Federal Ministry of Education and Research
CAGR	: Compound Annual Growth
CRM	: Critical Raw Materials
EDTA	: Ethylenediaminetetraacetic acid
EOL	: End of Life
EU	: European Union
GSP	: Graduate Studies Program
ICP-OES	: Inductively Coupled Plasma Optical Emission Spectroscopy
IME	: Institute of Process Metallurgy and Metal Recycling
LBE	: Lead-bismuth eutectic
LRF	: Lead-cooled fast reactors
PPE	: Personal Protective Equipment
PGMs	: Platinum Group of Metals
RWTH	: Rhenish Westphalia Technical Institute
SLM	: Supported Liquid Membrane
SEM-EDS	: Scanning Electron Microscopy-Energy Dispersive X-ray Spectroscopy
USGS	: United States Geological Survey
WASCAL	: West African Science Service Center on Climate Change and Adapted Land Use
XRD	: X-ray Diffraction
XRF	: X-ray Fluorescence

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GENERAL INTRODUCTION

RESEARCH MOTIVATION AND OBJECTIVES

Metals play a crucial role in today’s rapidly evolving technological world. From electronics to construction and industries, their recovery and purification are key to optimal performance. They make up 80% of the elements on the periodic table; hence, it is difficult to do without them. For example, Silver (Ag) and Copper (Cu) are good electrical conductors used in electronics and power systems; Lead (Pb) is a key component in lead-acid batteries used for vehicles as a backup for power generation. Metals also play a key role in the human body. Calcium, which is very abundant in the human organism, is used for bones, while Iron is used for transporting oxygen to cells. Most of these metals can be found in ores as concentrates, like Pb-concentrates, and the efficient extraction and recovery of these metals from these concentrates is of vital importance.

Most pure metals are naturally found in ores within the Earth’s crust in many regions of the world. The estimated value of metal production in 2024 increased slightly to $33.5 billion from a revised total of $33 billion in 2023(USGS Survey & Minerals, 2023), while the global metal manufacturing market stood at USD 190.5 billion in 2024 and is expected to achieve USD 290.6 billion by 2033, at a 4.7% from 2026 to 2033 (Verified Market Report, 2024 C.E.).

When it comes to the share of critical minerals, including metals, Africa possesses 30% of the world’s critical minerals, which are useful for clean energy and other technologies. South Africa, for instance, possesses 80% of the world's platinum group (PGMs) metals reserves, while Zambia is the home of the metal-rich Copperbelt region. It produces about 4% of the world's copper (Energy, 2023).

In addition, Africa has a huge potential for a lot of untapped metals. According to the African Development Bank report in 2012, the continent holds 30% of the world’s total mineral reserves(AFDB,2023), thus making it one of the world’s richest continents. Liberia, for instance, has a huge mineral potential, including metals like Gold, Iron Ore, and lead that remain hugely untapped (Gunn et al., 2018). Indeed, Africa does not possess a huge metal production, but it also has a significant share of the world's total mineral reserves.

The essence of processing primary metals is to extract and purify metals that are locked up in the Earth’s crust. Hence, the recovery of metals after they have been used in the economy comes from secondary metals, which provide an alternative for metal extraction from ores. To use metals effectively, the metals must be of high-quality grades and absence from specific impurities.

In most cases, the production or recovery of a single metal is connected or dependent on the generation or recovery of another. For instance, the effect of impurities in lead concentrate ores impacts the matrix of the other metals found in the concentrate. To holistically deal with the issue of impurities in metals and the increasing environmental problems, lots of research has been done to integrate copper production with other metals like lead, zinc, silver, bismuth, and platinum group of metals (PGM) (Verhoef et al., 2004). To recover these metals from the interconnected metal, most of the elements must be circulated between two or more production processes before they are concentrated enough to make their extraction possible, and their recovery as a metal is profitable. For this research, we will focus on the extraction and recovery of valuable metals, including Silver, Bismuth, Copper, Zinc, and Iron.

Lead is among the most ancient metallic materials utilized. It is a blue-silver element with an atomic number of 82 and an atomic mass of 207.19(amu). It is one of the metals that occur naturally in the environment. Lead exists in either sulfide or oxide form. The prevalent minerals in lead ores are galena (PbS, 86.6% Pb, 13.4% S), cerussite ($PbCO_3$, 83.5% PbO, 16.5% CO_2, 77.5% Pb), and anglesite ($PbSO_4$ 73.6% PbO, 26.4%SO_2, 68.3% Pb)(Wang, 2016).

Following the extraction of lead ore from subterranean sources by excavation and detonation techniques, it is prepared for flotation by undergoing crushing and grinding phases. Subsequently, it undergoes processing through extractive metallurgy techniques. The froth flotation technique facilitates the separation of lead from associated rock and soil particles, resulting in a concentrate that contains Pb. Lead is mostly utilized in battery production, radiation shielding, ammunition fabrication, diverse alloys, and fuel additives. Primary lead smelters generally process a combination of concentrates (e.g., PbS, $CuFeS_2$, ZnS), secondary materials, residual materials, fly ash, and waste slag. Minor constituents found in galena are currently designated as technology metals due to their utility in high-tech applications and consumer products, frequently possessing a favourable correlation with the primary mineral component, as illustrated in the Metal Wheel (Verhoef et al., 2004). These tiny elements present a metallurgical challenge: they may constitute an environmental risk, diminish the value of the final product, or be recovered as economically useful by-products, contingent upon the management of the system. Lead and copper are essential in facilitating the closure of the loop for various elements found in End-of-Life (EoL) products and leftovers.

Currently, nearly all lead-bearing minerals are transformed into metallic products by pyrometallurgical methods.

The fundamental process is the reduction and fusing of the first agglomerated lead concentrate, followed by the refining of crude metal.

An illustration of this approach is the "Imperial Smelting" method for processing lead-containing raw materials (Strunnikov & Koz’min, 2005).

However, there are lots of disadvantages attributed to the pyro-metallurgical process, which include, but are not limited to, the control needed to meet existing environmental standards for Pb emissions. Another issue is the current concern over acid rain, which could result in more stringent controls on emissions of sulfur gases (Murphy, & Haver, 1929). Furthermore, pyrometallurgical methods are high in energy consumption and cost.

With the above challenges attributed to the pyrometallurgical process, it is important to develop an alternative method. Hydrometallurgical Processes have emerged as a reliable and efficient method for obtaining pure metals. Hydrometallurgy is a branch of metallurgy that focuses on aqueous solutions to extract and purify metals from ore, concentrates, or recyclable metals. Currently, hydrometallurgical separation techniques are integral to extractive metallurgy and are employed in several metal refining facilities globally. As high-quality metal ores diminish, the metallurgical sector has shifted towards utilizing lower-grade ores, solid and liquid byproducts from metal refining facilities, and various waste materials. Hydrometallurgical separation technologies are highly appropriate for all these potential sources of raw materials. They are recognized as adaptable, highly selective, and eco-friendly techniques for processing raw materials with diverse quantities and compositions. Their energy usage is also reduced in comparison to traditional pyrometallurgical processes. Hydrometallurgical technologies are frequently regarded as having significant promise to address future issues in the environmentally and economically sustainable production of key metals (Murphy, &Haver, 1929).

As of now, lots of materials, including chalcopyrite concentrate (Turan & Altundoğan, 2013), multi-metal sulfide concentrates (Akcil & Ciftci, 2003), and Aluminum Residues (J. E. Murphy, F. P. Haver, 1929), have been worked on to recover valuable metals. Leaching for these materials was done in an autoclave system using different leaching agents like sulfuric acid, nitric acid, and hydrogen peroxide. However, there has not been enough work done with lead concentrate to recover valuable metals. While there may have been some work done using pyrometallurgical methods to leach lead concentrates, limited work has been done using the hydrometallurgical methods using both the autoclave and the glass reactor.

Therefore, this thesis aims to use hydrometallurgical methods to leach lead concentrates in a glass reactor and an autoclave for the effective recovery of valuable metals.

The specific objectives of this thesis consist of using various analytical tools such as XRD, XRF, and ICP-OES:

- To investigate and identify the most effective leaching agents (nitric acid, sulfuric acid) that selectively dissolve lead concentrate.
- To determine which metals can be effectively recovered from the leaching of Pb-concentrates.
- To maximize the best leaching parameters (temperature, leaching time, reagent concentration) for maximum selective separation efficiency and determine the effect of these leaching parameters on the leaching efficiency of various metals.

RESEARCH QUESTIONS

The following questions have been addressed in this thesis:

- What are the most effective leaching agents that can effectively dissolve lead concentrate? Will the leaching efficiency drop or increase using the glass reactor or the autoclave reactor?
- Which metal leached from Pb-concentrate has the best leaching efficiency?
- What are the suitable leaching parameters (temperature, leaching time, reagent concentration) to consider for optimizing the leaching of Pb-concentrate?
- What is the effect of temperature and leaching time on the leaching efficiency of various metals?

RESEARCH HYPOTHESIS

Based on the research questions, the following hypotheses were formulated:

- Nitric acid provides better leaching efficiency for lead concentrates than sulfuric acid due to its stronger oxidative properties
- The autoclave reactor improves leaching efficiency due to higher temperature and pressure conditions as compared to the glass reactor
- Higher temperature, longer leaching time, and increased reagent concentration enhance leaching efficiency and selectivity for specific metals

Apart from the general introduction, this thesis work is subdivided into three chapters. In the first chapter, an in-depth literature review was done. In the second chapter, the methods and materials used to conduct our experiment and verify our hypothesis were outlined. The final chapter, Chapter 3, analyzes and discusses the results of our research.

CHAPTER 1

LITERATURE REVIEW

1.0. INTRODUCTION

This chapter reviews the important literature related to the topic. It contains various sections. The first section introduces the chapter and provides the background and importance of Lead concentrates, including the overview of lead ore sources and the importance of associated valuable metals. This section also discloses the motivation of the research and the objectives of the Literature review. The second part of the chapter sheds light on the overview of the leaching system, the types of leaching, and briefly discusses the factors that affect leaching. Thereafter, in the third section of the chapter, we particularly focus on one of the valuable metals of focus, Bismuth. We reviewed available literature on bismuth leaching, separation, and recovery of bismuth from different concentrates. In the fourth section, we discussed the behaviour of silver during leaching, inclusive of forms of silver in Lead Concentrates, the solubility and recovery of silver in various leaching systems. Finally, we concluded the chapter by identifying the research gaps in current studies and the potential areas for future research.

1.01. BACKGROUND and Importance of Lead Concentrates

Lead is rather common in our daily lives and industry. Although it is not the most often used or produced nonferrous metal, it may be reasonably claimed to be the broadest in use in applications. It starts our cars, maintains engine knock-out, and gives the car bodies a beautiful, smooth form. It is in the paint on our houses and bridges, in the glues on tiles and the porcelain enamels on aluminium; it is in the best crystal and optical glass. It protects the joints from clear radiation. For us every day, it accomplishes a thousand and one things (Ziegfeld, 1964).

Lead Concentrate is one of the most crucial raw materials used worldwide in the lead industry. It is made primarily of mineral galena (PbS). Depending on the type of ore and its geological source, a range of useful by-products, including silver (Ag), bismuth (Bi), zinc (Zn), and antimony (Sb), may be recovered during the beneficiation and concentration of lead ores. Among these, bismuth and silver are especially valuable due to their key industrial uses and financial worth. Whereas bismuth is employed in pharmaceuticals, low-melting alloys, and ecologically friendly solders, silver is extensively used in electronics, photovoltaics, medicine, and jewellery (Xing et al., 2019).

1.02. Motivation of the Hydrometallurgical Treatment

The treatment of lead concentrates has always relied heavily on traditional pyrometallurgical methods. However, this method is becoming less environmentally acceptable for the treatment of bulk concentrates. These high-temperature processes are energy-intensive and generate significant environmental pollution, including sulfur dioxide emissions and hazardous solid residues. Additionally, the high capital cost associated with this method makes it even more challenging. On the other hand, hydrometallurgical treatment offers a lower-temperature, environmentally friendly alternative that enables aqueous chemistry to selectively recover important metals. The leaching agents employed, namely: sulphuric acid (lixivant) and ferric sulphate, are selective for metal sulphides. This, coupled with the fact that they create fewer environmental problems and are economical, makes this new process highly favourable (Akcil & Ciftci, 2003).

1.1. HYDROMETALLURGICAL TREATMENT OF RAW MATERIALS

The European Union in 2023 designated a list of 34 raw materials that are of economic importance and are subject to a higher risk of supply interruption. The critical raw materials are antimony, bauxite, baryte, beryllium, bismuth, boron, cobalt, fluorspar, gallium, germanium, hafnium, heavy rare earth elements, light rare earth elements, natural graphite, magnesium, niobium, platinum group metals, phosphate rock, scandium, silicon metal, strontium, Titanium metal, tantalum, tungsten and vanadium. Other minerals that do not meet the Critical Raw Materials Threshold but are included on the CRM list as strategic raw materials by the Critical Raw Materials Act include Arsenic, cooking coal, Feldspar, Helium, Lithium, Manganese, Copper, Phosphorus, and Nickel. This is due to their significant economic relevance and high relative supply risk stemming from the concentration of production of certain raw materials outside the EU. Materials of substantial importance that may become critical include bauxite, chromium, Iron, Magnesite, Manganese, molybdenum, nickel, rhenium, tellurium, vanadium, and Zinc (European Comision, 2023).

The types of raw materials available are primary high-grade ores, Primary low-grade ores, and secondary Raw materials. Minerals naturally occurring inorganic compounds with specific chemical compositions and atomic structures. An ore is a concentration of minerals in a sufficient amount for profitable extraction. The minimum metal content necessary for a deposit to be classified as an ore differs from metal to metal. Many non-ferrous ores contain less than 1% metal. Iron Ores with less than approximately 45% metals are classified as low grade. Complex ores comprise economically viable quantities of multiple precious minerals (Barry & Napier-Munn, 2006).

As mentioned earlier, hydrometallurgy has been traditionally used to recover base metals through electrolysis, including copper, lead, Zinc, and nickel, as well as for the recovery of uranium and rare earth elements (Habashi, 2005). According to *P. Hayes* in his book *Process Selection in Extractive Metallurgy*, certain hydrometallurgical techniques can effectively treat specific metals present in small amounts within the raw materials. An example of this type of smelting and electrorefining of copper is that noble metals, arsenic, antimony, bismuth, selenium, and tellurium are extracted from anode slime. The key advantage of the hydrometallurgical process is its selectivity compared to the pyrometallurgical process (Hayes, 1985). And this serves as a driving force for the advancement of the hydrometallurgical process for low-grade and secondary raw materials. **Table 1** shows a list of raw material types processed by hydrometallurgical methods. There are similarities in the processing of high-grade and low-grade primary raw materials and secondary raw materials. Some challenges will be faced in the processing of complex low-grade primary materials and secondary materials. Processing these materials is much more demanding than processing high-grade primary materials because at all process stages the separation of metals is more difficult, both by mechanical, chemical, and physical methods.

Table 1: Raw Materials that can be treated by the hydrometallurgical method(Gupta, 2006; Hayes, 1985).

Raw Materials	**Examples**
Metals:	Precious Metals
Sulfides:	Copper, nickel, zinc, lead
Oxides and hydroxides:	Bauxite, nickel laterites, copper oxide ores and nodules
Complex oxides:	Chromite, nobite-tantalite, pyrochlore, ilmenite, wolframite
Selenides and tellurides:	anode slimes from copper electrolysis
Arsenides:	Cobalt and nickel ores
Phosphates:	Phosphate rock, monazite sand
Halides:	Sodium, potassium, calcium
Spent catalysts:	Noble metals, nickel, molybdenum, vanadium
Slags, sludge, dusts:	Wastes from primary ferrous and non-ferrous metals production

1.1.1. General Hydrometallurgical Flow Sheet

In hydrometallurgy, metals are recovered using aqueous chemistry or ionic liquids, while in pyrometallurgy, metals are recovered by heat. **Figure 1** illustrates the different steps that make up a hydrometallurgical process. The unit processes all have different goals. In Figure 1, the activation or pre-treatment and leaching goals are to separate, while the solution purification goals are to move elements or make compounds, produce or purify metals (Forsén & Aromaa, 2013).

For leaching to take place, the raw materials must first be in a form that lets the leaching solution come in direct contact with valuable metals that are required to be leached. This can be achieved through both chemical and physical methods to alter the properties of the raw materials. Comminution is used to separate valuable minerals from the gangue minerals. The minerals are broken up into the largest particles possible. The objective of mineral processing is to separate the minerals into at least two different types of goods. The valuable minerals are in the concentrates, the unwanted minerals are in the tailings, and the locked particles are in the middlings (Barry & Napier-Munn, 2006). Leaching is then used to get the important metal fractions. The principle is the same for secondary raw materials, but the process is more complex as there are more materials, and they are often more interlocked. If the chemical and mechanical pretreatment is not very effective, the feed to the next process stages is comparable to the middlings of the primary raw material production; therefore, metal recovery becomes inefficient or even impossible from this kind of material.

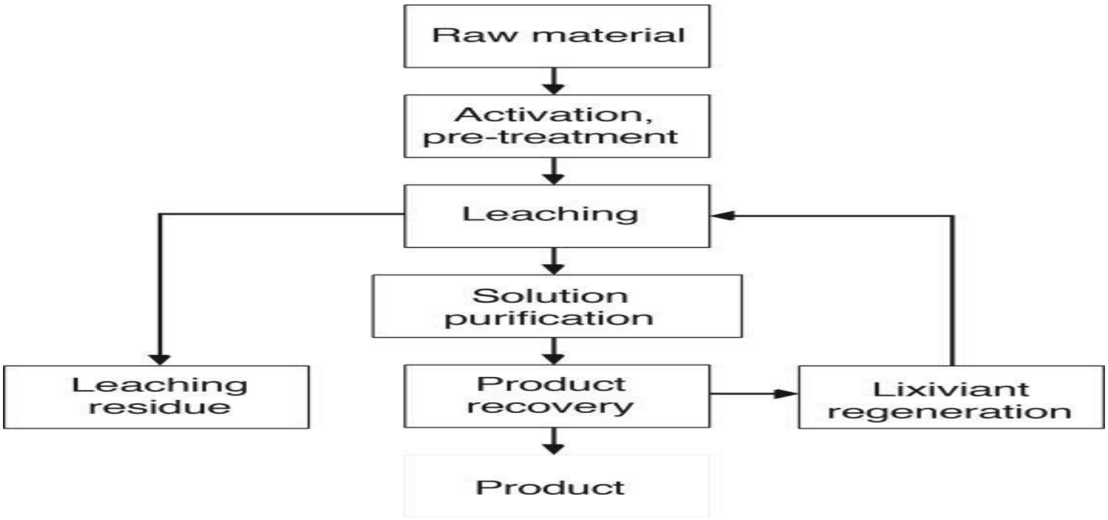

Figure 1: Stages in the processing of a hydrometallurgical process flowsheet (Forsén & Aromaa, 2013)

In leaching, solid materials come into contact with liquid, which can dissolve all or some of the metals. When you leach, it is important that the dissolving is either selective, so that only the wanted metals are brought into solution, or so that the metals have different properties that they can be separated. The loaded liquid or leachate is subjected to a separation process for purification or recovery, or both, of the wanted metals or metal compounds. The product obtained can be a concentrate, a new combination, an impure metal, a purified metal, or a semi-product, as illustrated in **Figure 2**. (Forsén & Aromaa, 2013). It is crucial to separate the wanted and unwanted fractions in the first mechanical or leaching stages.

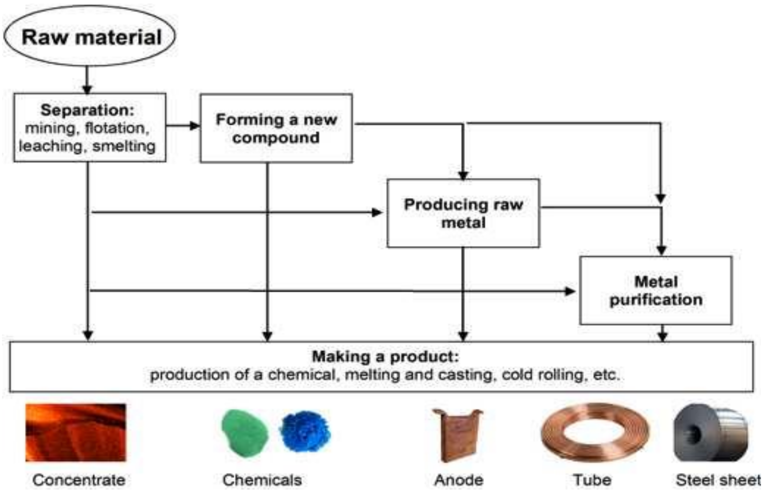

Figure 2: A diagram showing the types of metallurgical products (Forsén & Aromaa, 2013).

1.2. OVERVIEW OF LEACHING SYSTEMS

1.2.1. Theory and Principle

Leaching is an important way to get useful materials out of solid mixtures. It is also a basic process that is used in many scientific and industrial settings. In this section, we look at the theoretical foundations, experimental methods, and real-world uses of leaching in several different areas. The process involves moving parts that can dissolve from a solid matrix to a liquid medium. This is based on the materials' physical and chemical features and how they are used. This research carefully examines previous studies and established methods to provide a comprehensive understanding of leaching as both a natural phenomenon and an engineering process that has significant impacts on metals, the environment, and material processing. As an example of leaching, consider how tea dissolves in hot water. The tea leaves are the solid matrix, and the water is the leaching medium. When hot water meets tea leaves, chemicals that dissolve in water break off from their solid form and spread throughout the liquid, turning plain water into tasty tea.

1.2.2. Types of Leaching

1.2.1.1. Acid Leaching:

This type of leaching, as seen in **Figure 3**, uses strong acids like sulfuric or hydrochloric acid to dissolve the mineral matrix and release metal ions into solution for additional processing. It is a popular leaching type for extracting base metals like zinc and copper (Gunarathne et al., 2022).

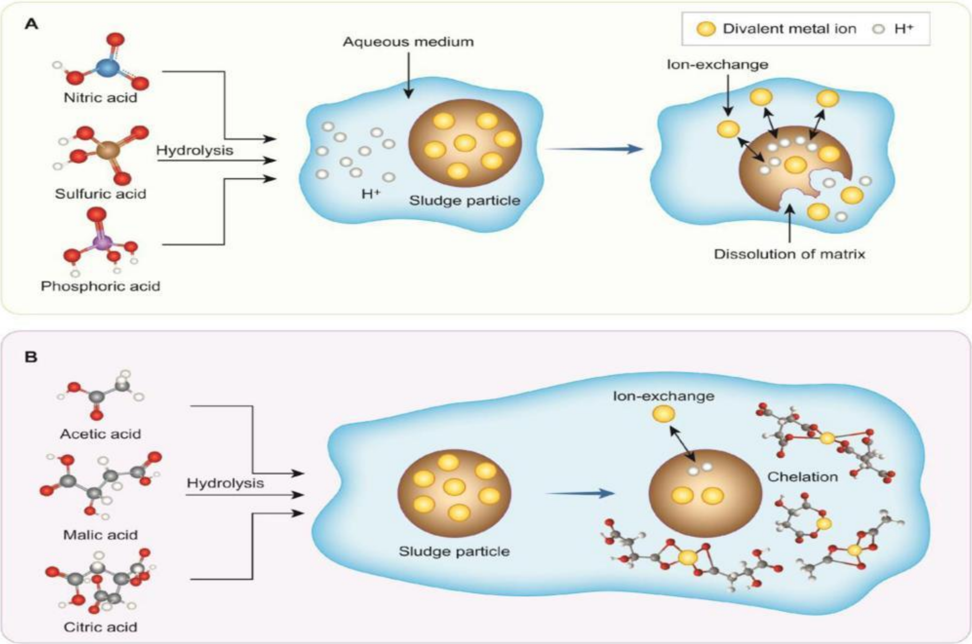

Figure 3: Release mechanisms of heavy metals via (A) inorganic acids (e.g., sulfuric acid) and (B) organic acids (e.g., citric acid) (Gunarathne et al., 2022)

1.2.2.2. Alkaline Leaching:

Using simple reagents like sodium hydroxide or ammonia, which can dissolve specific metal compounds selectively without deteriorating the host matrix. Alkaline leaching is used when acid leaching is either ineffective or inappropriate, especially when the ore contains materials that are sensitive to acid.(Gunarathne et al., 2022)

1.2.2.3. Bioleaching:

To oxidize metal sulfides and enable the solubilization of metal ions under milder, more environmentally friendly conditions, bioleaching uses the natural metabolic processes of microorganisms like acid-thiobacillus ferroxidase. This process is especially useful for low-grade ores and those that are resistant to traditional methods of chemical treatments.(Gunarathne et al., 2022)

1.2.2.4. Autoclave Leaching:

Works in a sealed reactor (autoclave) at high temperatures and pressures, speeding up the dissolution kinetics. It is particularly helpful for processing refractory ores that need more aggressive conditions to extract metal effectively. These diverse leaching methods offer versatility in handling various ore kinds and maximize metal recovery while taking environmental and financial factors into account.

1.2.3. Factors Governing Leaching

Gupta (2023) stated that there are three ways substances dissolve, namely physical, chemical, and electrochemical (Gupta, 2003). In physical dissolution, an ionic molecule breaks down into a solvent without changing its oxidation state. To dissolve a compound chemically, another compound in the solvent facilitates the dissolution of the compound.

In electrochemical dissolving, the elements will either oxidize or reduce because of an oxidant or a reducer in the solvent. This led to the structure of the raw material breaking down, letting the elements escape. In leaching, the conditions of the fluid must be just right for the metal to dissolve without changing its shape. Some tools that can be used to study thermodynamic conditions are the solubility product, PH, and redox potential (Pourbaix diagram), equilibrium potentials and mixed potential theory, and speciation. **Figure 4** illustrates an example of a Pourbaix diagram for copper sulfides. To release the metals, it is essential to select a solution that falls within the acidic and oxidizing regions.

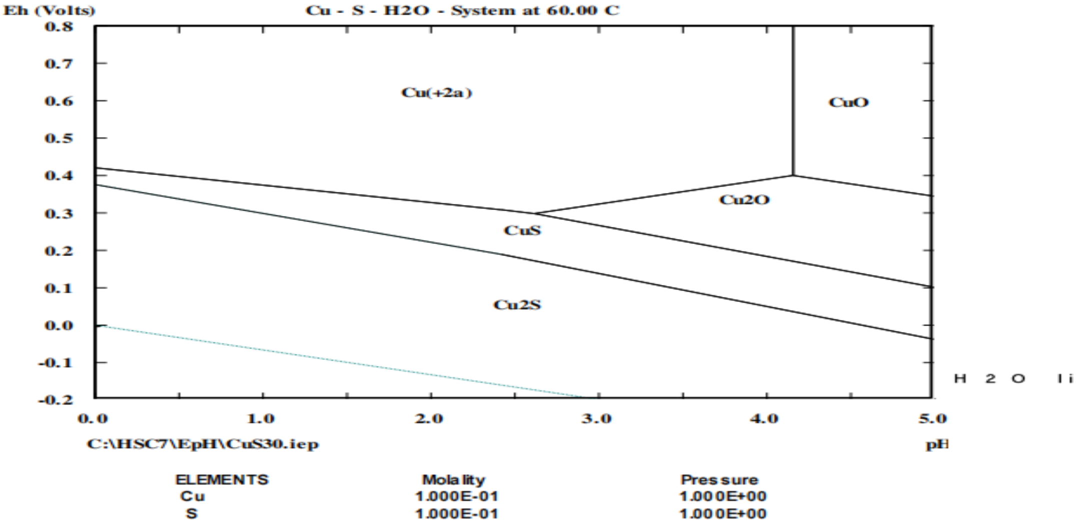

Figure 4: Pourbaix Diagram for the leaching of copper sulfides (Forsén & Aromaa, 2013)

It wasn’t until the 1930s that electrochemical dissolution mechanisms were given a theoretical study. A significant portion of the research focused on metallic corrosion. This study, conducted by U.R. Evans and his team in Cambridge, examined the effects of anodic and cathodic processes and their relationship to Faraday’s law regarding dissolution rates(U. R. E vans, L. C. Bannister, and S. C. Britton, 1931) (U. Evans, 1932), (U. R. E vans and R. B. Mears, 1934) Wagner and Traud came up with the mixed potential theory in 1939 (Wagner & Traud, 1938). Mears and Brown came up with the idea of a corrosion cell in 1941 (Mears & Brown, 1941). Pourbaix created the E-pH diagrams, which were generally known by 1949 (Pourbaix, 1949). Evans diagrams were used for 70 years (U. R. E vans, L. C. Bannister, and S. C. Britton, 1931) to show how electrochemical processes depend on each other. In 2003, they were renamed Ritchie diagrams when they were used in hydrometallurgy instead of corrosion science (Robertson et al., 2005).

The conditions for leaching are chosen so that the metal that is released is stable from a thermodynamic point of view. Reactions to dissolution should happen quickly. To separate dissolved impurities from valuable metals, the right conditions must be chosen. In addition, the lixiviant solution must be able to be made again, and it shouldn't be too expensive, harmful to health, or dangerous for the environment or workers.

Selecting the optimal leaching conditions for the primary high-grade raw materials is straightforward. This makes it easy to separate the wanted and unwanted metals. It's harder to get primary low-grade materials because the raw materials contain a lot of compounds that aren't needed. Often, the main task is to break down the host mineral to get to the valuable compounds. When leaching secondary materials, the large number of metals can make leaching technically impossible.

For example, when oxidizing electronic trash, all other metals will dissolve faster than gold, which means that too many chemicals will be used. The grade of the raw material determines which washing method is best. Any method of draining should get rid of as many unwanted metals as possible as quickly as possible while using the least amount of energy and chemicals possible. Cheap heap, dump, and vat methods are used to process low-grade products. Atmospheric reactors are used to process rich minerals. When the product is so important that an expensive method is possible, autoclaves are used.

1.3. BISMUTH LEACHING AND SEPARATION

The element Bismuth is a metallic element that is in the sixth period and lies in group 5 of the periodic table. At room temperature, Bismuth in its pure form exhibits a very low oxidation and appears as a silver-white element. Bismuth crystals are obtained because of gradual cooling and crystallization from a molten state, and the growth rate at the outer edge surpasses that of the inner edges, which leads to a spiral stair-stepped configuration. In addition, the exposure to air results in a thin and irregular coating of bismuth oxide (Bi_2O_3) being developed on the surface. This leads to different reflection intensities of light across varying wavelengths. This leads to the brilliance and iridescent spiral staircase-like quality of the crystal, as seen in **Figure 1** (Liu et al., 2016).

Bismuth (Bi) is an important by-product that can be obtained when lead concentrate is processed. It is, however, toxic in lead-based products, but is getting popular for eco-friendly applications. As a result, it is essential to remove and recover bismuth using a more environmentally friendly method. Hydrometallurgical methods are certainly the best method for the leaching and separation of bismuth.

Bismuth can be found among the chalcophilic elements. Antimony and lead can also be found there. Bismuth is 9×10^{-7} % abundant, with its concentrations increasing from ultrabasic rocks (1×10^{-7}) to acidic rocks (1×10^{-6}). The typical bismuth concentration in ores from deposits containing bismuth ranges from 0.003% to 0.06%, but in true bismuth deposits, it exceeds 0.2% (Krenev et al., 2015).

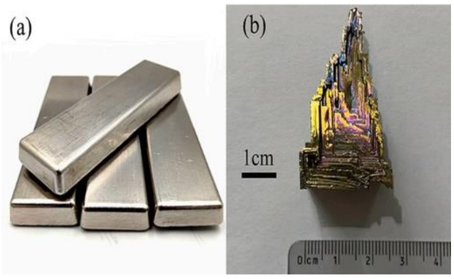

Figure 5: (a). Bismuth ingot (b). Bismuth crystal (C. Wang et al., 2025)

1.3.1. Leaching of Bismuth

Like many other metals, the leaching of Bismuth into a liquid phase is based on the specific type of Bismuth content present in the solid material. Using sulfuric acid alone does not efficiently dissolve bismuth compounds. This is because of the formation of bismuth sulfate in a diluted sulfuric acid solution, which undergoes hydrolysis and results in the precipitation of basic bismuth sulfate. On the other hand, bismuth oxide is insoluble in a Chloride medium; therefore, sufficient sulfuric acid must be introduced to the medium to change the oxides of bismuth into sulfate, which is then dissolved in the Chloride medium (Ha et al., 2015).

The chemical equations can be expressed as follows:

$$Bi_2O_{3(s)} + 3H_2SO_4 \rightarrow Bi_2(SO_{4)3(s)} + 3H_2O \qquad \text{Equation (1)}$$

$$Bi_2(SO_{4)3(s)} + \ 6NaCl \rightarrow 2BiCl_{3(aq)} + 3Na_2SO_4 \qquad \text{Equation (2)}$$

Bismuth and Molybdenum in minimum quantities can be obtained from the processing of minerals in which they are primary metals. They are mainly obtained as by-products in various metallurgical processes involving other metals. To process these minerals, we must leach with H_2SO_4 and HCl. This results in extremely acidic solutions containing base metals and bismuth.

1.3.2. Separation and Recovery of Bismuth

Bismuth may be extracted from these solutions through waste solutions. A lot of writers have written about the separation of bismuth from leaching mineral solutions using solvent extraction methods. This literature (Reyes-Aguilera et al., 2008) highlights several different approaches for recovering bismuth. They also proposed the concept of supported liquid membranes (SLM) for the recovery of bismuth from aqueous solutions in literature. (Szymanowski (1998) and Wang et al., (2016) have suggested the separation of bismuth from copper via ionic exchange and solvating extractants, employing the Acorga SBX-50 extractant in chloride media and organic phosphorus extractants, respectively.

Additionally, Yang and his colleagues in their research, to obtain the optimum recovery ratio for both metals at about 98% to 99%, went on to use a different method to separate and recover bismuth and molybdenum from a low-grade bismuth flotation concentrate using solvent extraction. They presented in their paper a laboratory-scale study that demonstrates the recovery of bismuth and molybdenum from low-grade bismuth glance can be achieved on an industrial scale using a continuous hydrometallurgical process. This results in an enriched solution suitable for producing bismuth and ammonium paramolybdate (Yang et al., 2009).

1.4. SILVER LEACHING AND SEPARATION

Mostly found as native silver (Ag^0), argentite (Ag_2S), or as isomorphic substitutions in galena (PbS), silver (Ag) is a valuable by-product in many lead concentrates. Selective and effective leaching and separation techniques are necessary for the recovery of Pb–Ag–Bi systems.

1.4.1. Leaching Methods of Silver

Silver is usually found in lead concentrates with Bismuth and other minerals. This makes it difficult to extract from the mixture of other minerals. In Lead Concentrates, Silver is often bound as sulfosalts like tetrahedrite, which are refractory to leaching or are dispersed in galena as fine inclusions or in solid solution. They are also present as AgCl or Ag° in oxidized ores and remains (Ju et al., 2011; Tuncuk et al., 2012).

The rate of leaching depends on the state of oxidation and mineral structure, particle size, and available leaching conditions. Various leaching methods are discussed next.

1.4.1.2. Thiosulfate Leaching

This method-thiosulfate ($S_2O_3^{2-}$) is a better alternative. Unlike cyanide leaching, this method is environmentally friendly and more effective in silver leaching. However, thiosulfate complexes can be unstable, especially in the presence of copper ions, and may require high reagents (Marsden & House, 2006).

$$Ag_2 + S_2O_3^{2-} \rightarrow 2Ag(S_2O3)_2^{3-} + S^{\circ} \qquad \text{Equation (3)}$$

1.4.1.3. Chloride Leaching

In chloride leaching, silver complexes like $AgCl_2^-$ in HCl-based systems, most especially when combined with oxidants, which enables the leaching of lead concentrate. This method is effective for both silver and lead, especially when integrated with solvent extraction or electrowinning (Marsden & House, 2006).

$$Ag_2S + 4Cl^- + O_2 + 2H^+ \rightarrow 2AgCl_2^- + S^{\circ} + H_2O \qquad \text{Equation (4)}$$

1.4.1.4. Nitrate and Nitric Acid Leaching

In this method, silver sulfide and metallic silver are dissolved by nitric acid due to its oxidizing potential. This method is strongly effective but highly costly and environmentally unfriendly due to the emission of NO_x gases (Tuncuk et al., 2012).

$$Ag + 2HNO_3 \rightarrow AgNO_3 + NO_3 + H_2O \qquad \text{Equation (5)}$$

$$Ag_2S + 2HNO_3 \rightarrow 2AgNO_3 + S^{\circ} + H_2O \qquad \text{Equation (6)}$$

1.5. APPLICATIONS OF BISMUTH

Bismuth is recognized as a "green metal" because of its minimal toxicity. Due to its low melting point, thermal expansion and contraction characteristics, and favourable photo and photoelectric responses of its compounds with sulfur, oxygen, and halogen elements, manufacturers frequently utilize bismuth as a substitute for toxic metals or as a primary matrix element across diverse sectors, including medicine, the nuclear industry, semiconductors, superconductors, photocatalysis, and solar cells(Chen et al., 2010; Sar et al., 2007). In recent years, high-purity metals have garnered considerable attention. High-purity metals are materials characterized by an exceptionally high concentration of the primary metal, with minimal levels of impurity elements. High-purity bismuth is a metal with a purity of 5N or greater, requiring impurity elements such as copper, magnesium, tin, and lead to below 1 ppm, and total impurities to be under 0.1%. High-purity bismuth is frequently alloyed with tellurium or sulfur to create semiconductor thermoelectric materials (Bi_2S_3, Bi_2Te_3), which mitigate lattice defects induced by impurities, thereby significantly improving charge carrier mobility and enhancing the stability and longevity of semiconductor materials. As scientific inquiry into bismuth and its compounds intensifies, alongside a growing emphasis on environmental protection and safety, the significance of metallic bismuth is poised to escalate. The United States has already designated bismuth as a critical mineral, forecasting a considerable rise in demand in the future (Sun et al., 2014; Xia et al., 2023).

Since ancient times, Bismuth has been used. With recent technological advancements over the years, it has been extensively used in other sectors of high precision and advancement, which include but are not limited to medicine, electronics, and environmental management. The metal, Bismuth, is not used in isolation; it is instead used with other elements to create high-purity materials, which bring out distinctive and superior characteristics (Deady et al., 2022).

Due to its low toxicity, Bismuth can also be used to replace certain harmful metals-thus promoting safety and environmental sustainability (Deady et al., 2022). **Table 2** outlines the uses of Bismuth across various sectors.

Table 2: Applications of Bismuth in some sectors

Application Direction	**Detailed Application**
Medicine	Bismuth subgallate, bismuth subnitrate. They are used for treating duodenal ulcers, indigestion, and diarrhea (Yuan et al., 2022).
Nuclear Industry	Lead-bismuth eutectic (LBE) alloy is the preferred material for coolant in the Fourth-generation lead-cooled fast reactors (LFR) (Zhang et al., 2013).
Alloy Additives	Adding bismuth to the Al_7SiO_4Mg alloy has been found to refine eutectic silicon, with Refinement increases as the bismuth content increases, up to 0.5 % by mass (Farahany et al., 2011).
Solar Cells	Bismuth-based halides with a perovskite structure ($C_5H_6NBiI_4BiI_3$, $AgBi_2I_7$), due to their low toxicity and good photoelectric response, are promising replacements for lead in perovskite solar cells (Eckhardt et al., 2016).

Cosmetics	Considering their notable characteristics (satiny shine, low absorption, etc.), certain bismuth compounds, notably bismuth oxychloride and bismuth vanadate, have been utilized in a range of cosmetics, such as nail polish, lipsticks, eye shadows, and hair dyes. Bismuth oxychloride is frequently used to impart a silvery luster in cosmetics and personal care items (Liu et al., 2016).

1.5.1. Resource Distribution of Bismuth Metal

The mineral Bismuth can be found in different types of ore deposits. The most important minerals are the native minerals, bismuth (Bi), bismuthinite (Bi_2S_3), and bismite (Bi_2O_3). Bismuth ores are naturally found with metals like lead (Pb), tin (Sn), and copper (Cu). Hence, extracting bismuth is a little more complicated. However, the beneficiation process is key in mining to obtain bismuth concentrations (Liguo, 1991).

The United States Geological Survey (USGS) conducted a survey covering the years 2019 to 2023. The result from the survey showed that the production of metal bismuth, as shown in Figure 6(a), places China as the largest producer of bismuth, maintaining an output of over 16,000 tonnes. This quantity exceeds that of other nations, and it constitutes about 84.21% of global bismuth production. Countries such as Laos, South Korea, Japan, Kazakhstan, as well as Mexico, Bulgaria, Canada, and Bolivia, produce the remaining 15.79% of bismuth (E.K. Schnebele, 2017); (U.S. Geological Survey, 2020). Bismuth reserves are often assessed based on the bismuth concentration in lead ores, as bismuth is frequently a by-product of lead ore processing. In 2017, the USGS identified global bismuth reserves (E.K. Schnebele, 2017), as shown in Figure 6(b), totaling 370,000 metric tons, mostly in China, Vietnam, Bolivia, Mexico, Canada, and several other nations and areas. China has the most, about 240,000 tons, or two-thirds of the world's total. Bismuth is mostly made in China and Vietnam from waste materials that are left over from processing tungsten and other metal ores. Now, only the Tasna mine in Bolivia and the Pupingling mine in Huaiji County, Guangdong Province, China, can mine bismuth as the main product. According to the national mineral resource data statistics from the Ministry of Natural Resources of the People's Republic of China, the bismuth resource reserves in China for the years 2020–2022 are illustrated in the Figure. 6(c).

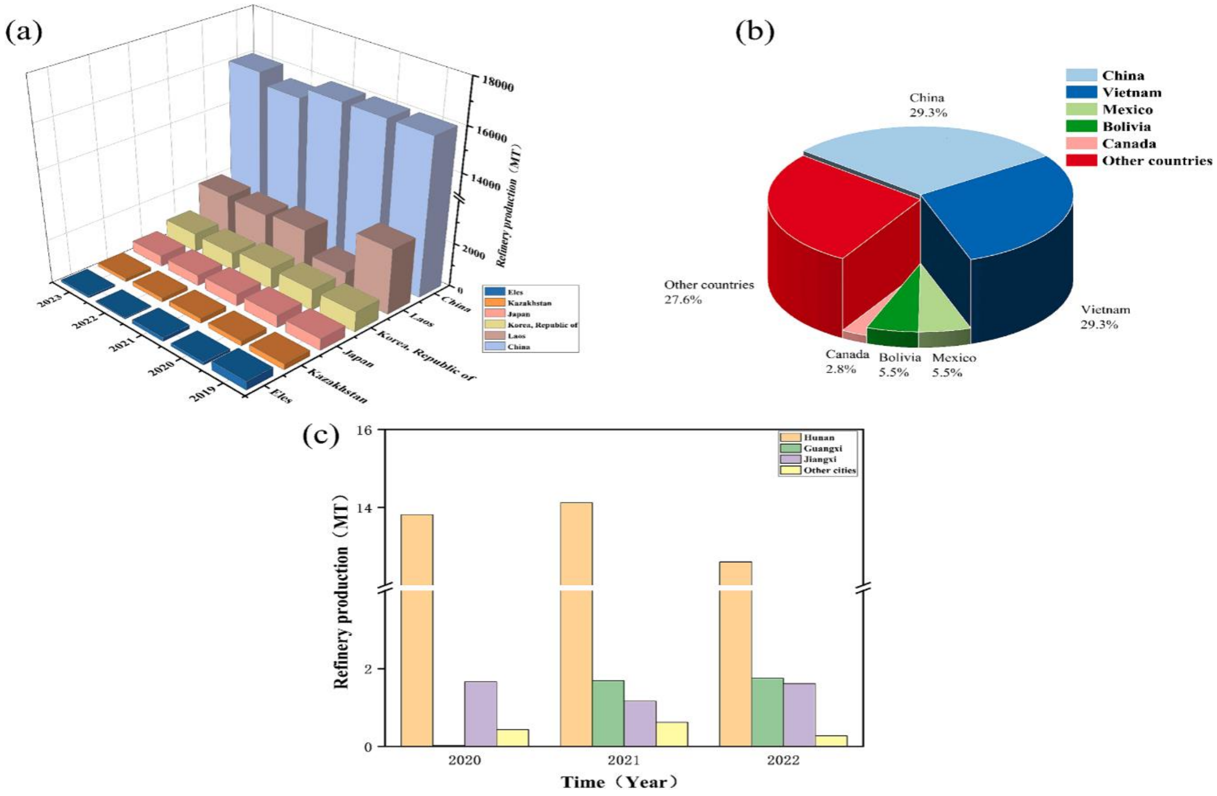

Figure 6: (a) Global Production of Bismuth Metal 2019–2023; (b) Global bismuth reserves distribution in 2017(Data from USGS); (c) Bismuth Ore Resource Reserve Statistics of China, 2020–2022.

1.6. SHRINKING CORE REACTION MODELS

The Shrinking Core Model is the most widely utilized model among the models developed for non-catalytic reactions between fluids and solids. The development of the model took into account some considerations, including the solid reactant being a non-porous material initially engulfed by a film of fluid, the gaseous or liquid reactant, through which interaction occurs (mass transfer) between the large volume of the fluid and the solid material (Gbor & Jia, 2004). The reaction between the solid particle and fluid reagent leaves behind a reacted, inert or consumed layer around an unreacted core. The equation below, adapted from (Sloman et al., 2019) is the universal or common chemical reaction (irreversible) used in the establishment of the Shrinking Core Model.

$$A_{gas} + \sigma_1 B_{solid} \rightarrow \sigma_2 C_{gas} + \sigma_3 D_{solid} \qquad \text{Equation (7)}$$

From the reaction, σ_1, σ_2 and σ_3 are stoichiometric coefficients. The model also postulates that the reaction occurs at an interface between the reacted layer and unreacted core of the solid particle and moves towards the center of the unreacted core until the reaction is complete (Melchiori & Canu, 2014; Sloman et al., 2019). As the reaction is a multi-step one, different controlling regimes, that is, steps that control how fast the overall reaction can proceed, determine the form of the rate equation of the Shrinking Core Model. The different controlling regimes or steps, as described by Gbor & Jia, (2004), Sloman et al., (2019), and Melchiori & Canu, (2014), are diffusion through the reacted or inert solid layer and chemical reaction at the interface between the reacted layer and the unreacted core of the solid particle. These controlling regimes therefore give rise to what is described as the Diffusion Shrinking Core Model and Reaction Shrinking Core Model.

1.6.1. DIFFUSION SHRINKING CORE MODEL

This is a model used to describe reactions between fluids and solids where diffusion through the solid particle is the slowest step. Since the reaction occurs in multiple steps, this implies that the overall reaction between the fluid (eg, gas) and the solid particle depends on how quickly the fluid diffuses through the inert, reacted, or product layer of the solid to encounter the unreacted core of the solid for the reaction to progress. This also hints that the chemical reaction here is faster than the diffusion process. The equation for this Shrinking Core Model, obtained from Gbor & Jia, (2004; Sloman et al., (2019) is given as:

$$kt = 1 - 3(1 - x)^{\frac{2}{3}} + 2(1 - x) \qquad \text{Equation (8)}$$

where k is the rate constant, t represents time and x is the conversion or fraction of solid transformed. Gbor & Jia, (2004) reported that this equation might be unapplicable to solid-liquid reactions because it was derived from an approximation which is valid if the ratio of the concentration of the reactant fluid to the density on a molar basis of the solid reactant is less than a fraction of $\frac{1}{1000}$ which generally applies to solid-gas reactions and not always to solid-liquid reactions. However, later studies showed that approximation is still valid for ratios greater than the above for solid-liquid reactions by considering a convective factor for mass transfer.

1.6.2. REACTION SHRINKING CORE MODEL

Just as the name suggests, this model is used to describe or determine reactions between fluids and solids where the surface chemical reaction is the controlling regime. The implication here is that the surface chemical reaction is the step that defines how the overall chemical reaction between the fluid and solid particle will proceed, and as such, the reaction process is much slower than the diffusion process. **Figure 7** illustrates a schematic of the shrinking core model. The mathematical translation for this chemical reaction, retrieved from Gbor & Jia (2004); Melchiori & Canu (2014), and Sloman et al. (2019), is stated below.

$$kt = 1 - (1 - x)^{\frac{1}{3}} \qquad \text{Equation (9)}$$

where k is the reaction rate constant, t represents time and x is the conversion or fraction of solid transformed.

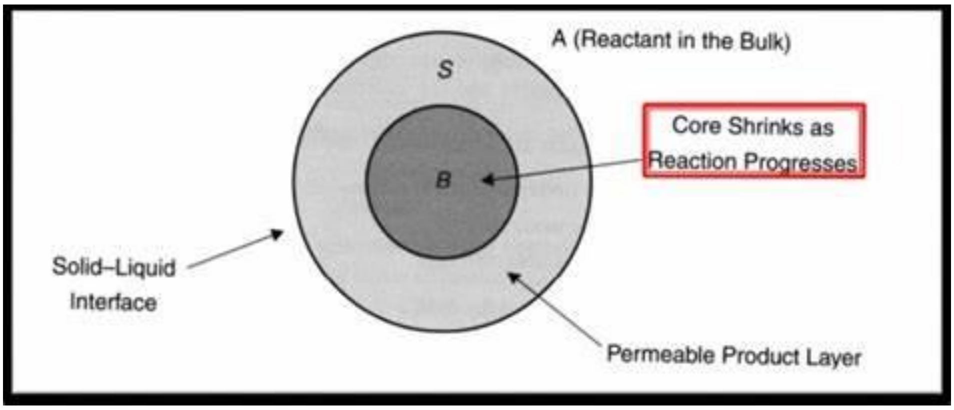

Figure 7: Schematic of the Shrinking Core Model (Paunović et al., 2019).

The Shrinking Core Model is applied to various fluid-solid reactions that occur in different chemical processes. Included in the chemical processes where these reactions are encountered are the burning of solid fuel particles, the control of gaseous pollutants, the production of catalysts, and the field of metallurgical engineering (Gbor & Jia, 2004). Typical examples of these chemical processes include oxidation of metals and reduction of metal oxides using reducing gases such as carbon monoxide or hydrogen to yield metal oxides and metals, respectively. There is also the production of synthetic gas from the reaction between carbon and water vapor, and the extraction of metals from ores through leaching by using acidic mediums such as studies form Paunović et al., (2019) and Behera & Sukla, (2016).

1.7. CONCLUSION

As of now, lots of materials, including chalcopyrite concentrate (Turan & Altundoğan, 2013), multi-metal sulphide concentrates (Akcil & Ciftci, 2003), and Aluminum Residues (J. E. Murphy, F. P. Haver, 1929), have been worked on to recover valuable metals. However, there has not been enough work done with lead concentrate to recover valuable metals. Therefore, based on this research gap, my work focuses on using hydrometallurgical methods to leach lead concentrates for the recovery of valuable metals. Henceforth, we discussed different types of leaching systems using the hydrometallurgical methods of different raw materials in this chapter.

CHAPTER 2

MATERIALS & METHODS

2.0. INTRODUCTION

In this chapter, we will focus on the research methodology, which includes the process and procedures that were used in this research to collect, analyze, and evaluate the experimental data used in the study. We will also provide a detailed explanation about how all the experiments were performed. We will start with the research design used and expand on the study area, and thereafter, we will focus on the materials used for the experiments, the origin of the material, and the detailed experimental setup and different processes for the experiments. We will conclude this section by summarizing the experimental conditions of the various experiments and showing the steps and calculations used to determine the leaching efficiency of various metals. Finally, we will briefly highlight the environmental and safety conditions under which the experiments were performed.

2.1. RESEARCH DESIGN AND STUDY AREA

This research used the experimental approach to investigate the hydrometallurgical treatment of different raw materials with a specific focus on the leaching of lead (PbS) concentrate for the selective recovery and separation of valuable metals. Two different sets of experiments were performed under different conditions of temperature, acid concentration. The first set of experiments was performed using a pressured autoclave system, and different bars of oxygen were used during this experiment. The next set of experiments was performed in a glass reactor with no oxygen pressure. The objective was to assess the effect of each of the different parameters on the leaching efficiency of lead and associated metals.

All the experiments in this research were performed in the hydrometallurgical lab of the Institute of Process Metallurgy and Metal Recycling (IME) at RWTH Aachen University in Germany. Germany is in the middle of Europe, and it is the seventh-largest country in Europe by land size and the second most populous country in Europe, after Russia. As of July 2025, the population of Germany was estimated at 84.1 million people (Worldometer, 2025). According to Worldometer elaborations of the United Nations data. The territory covers about $357{,}022 km^2$ between latitude $51°N$ and longitude $9°E$. The country shares borders with nine other countries: Denmark is to the north, Poland and the Czech Republic are to the east, Austria and Switzerland are to the south, France and Luxembourg are to the southwest, and Belgium and the Netherlands are to the northwest. The Institute of Process Metallurgy and Metal Recycling is at Intzestraße 3, 52072, in the northwest of the city of Aachen **(Figure 8).** The

Faculty of Georesources and Materials Engineering at RWTH Aachen University oversees it.

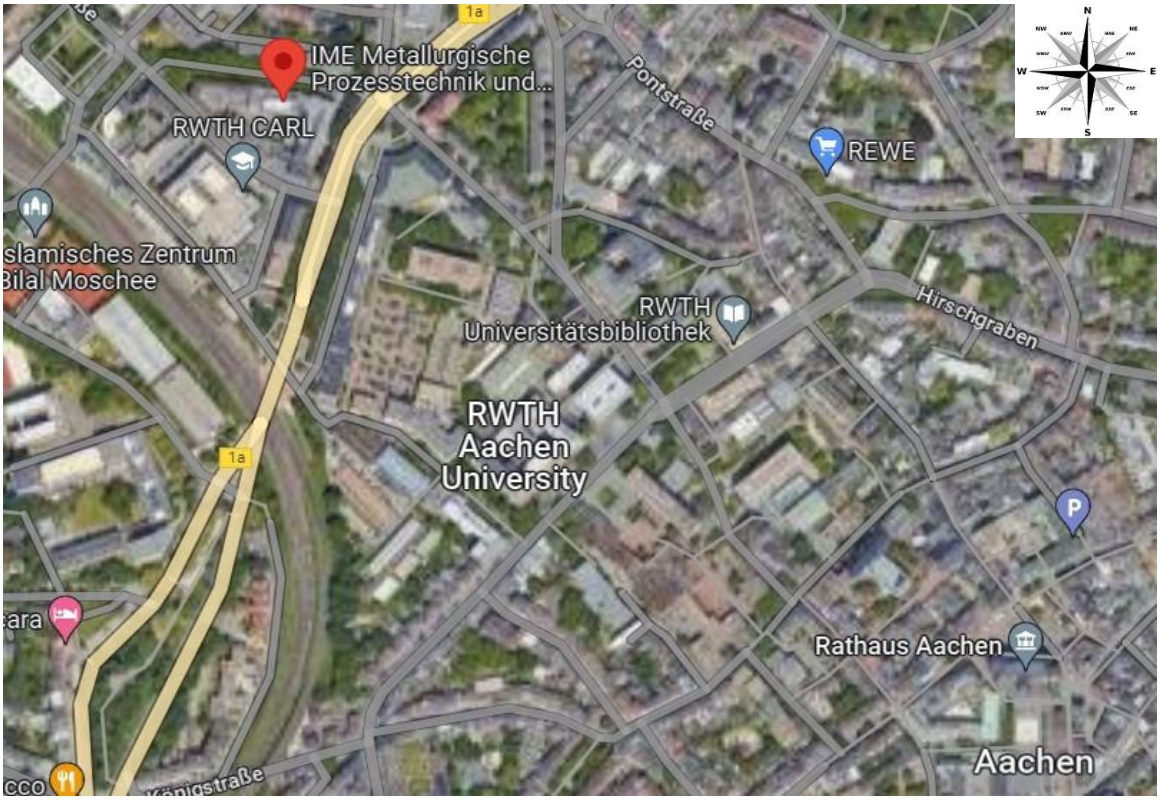

Figure 8:Geographical Location of IME (Google Map)

2.2. MATERIALS AND CHEMICALS

The lead concentrate used in the experiments was obtained from the Rudnik Mine in Serbia at the Rudnik Mountain. Pb Concentrate is one of the three products, including Zn and Cu, which is produced through the froth-flotation process of finely grained ore (Rudnik, 2025). The sample was pounded and homogenized and thereafter dried in a furnace suitable for hydrometallurgical treatment, as seen in **Figures 9 and 10**. The chemical composition of lead concentrate was analysed, and the results are shown below in **Table 3.**

Figure 9: Sample of Grounded Pb-Concentrate

Figure 10: Sample of Ungrounded Pb-concentrate

The chemicals and reagents used in the experiments are listed below:

i. Sulfuric Acid (H_2So_4) and Nitric Acid (HNO_3): about 98% purified was used to prepare the different leaching solutions of 1.0M, 2.5M, and 5.0M concentrations with deionized water.

ii. Oxygen Gas (O_2): Highly purified, about 99.5%. Oxygen was introduced into the autoclave at pressures ranging from 6 to 12 bars.

iii. Deionized water was used to prepare all the solutions and was used for leaching after leaching.

Table 3: Chemical Composition of Valuable Metals in Lead Concentrate

Element	**Concentration**
^{14} Si Silicon	9801ppm
^{16} S Sulfur	90240ppm
^{20} Ca Calcium	4493ppm
^{26} Fe Iron	35810ppm
^{29} Cu Cooper	6063ppm
^{30}Zn Zinc	7589ppm
^{47}Ag Silver	1034ppm
^{50}Sn tin	184ppm
^{82}Pb Lead	564900ppm
^{83}Bi Bismuth	3559ppm

2.3. EQUIPMENT AND INSTRUMENTS

Below are the following equipment that were used for conducting experiments.

i. Buchi Autoclave: Stainless Steel and can operate up to a temperature of 270 °C and a pressure of 30 bars.
ii. Glass Reactor: Leaching lead concentrate without oxygen
iii. Temperature Control System: Mixed at a constant rate of 600 RPM.
iv. Gas Supply System: Oxygen cylinders connected with a pressure regulator and manometer.
v. Filtration Unit: Buchner Funnel with a vacuum pump separating the solid residue from the liquid.

vi. Analytical Tools:

-ICP-OES for metal concentration analysis.

-XRD for solid residue analysis.

2.4. EXPERIMENTAL PROCEDURE

For each experiment, we weighed the required mass of the pounded and dried material and put it into the reactor with the required volume of sulfuric acid solution the required molarity.

2.4.1. Leaching Procedure for Autoclave

Leaching of the lead concentrate was performed in a Buchi autoclave from Switzerland, designed specifically for acid leaching (capacity of 1.53L, max pressure of 200bars, and maximum temperature of 270℃), as shown in **Figure 11.** Leaching was carried out using sulfuric acid. This setup includes a heat exchanger with a thermostat, a mixer, pressure adjustment probes, and the capability to extract samples during the experiment. The autoclave is connected to a computer, allowing for complete control via software that records all operational data for subsequent analysis. The pressure was monitored using both a manometer and a digital sensor.

Below is a step-by-step procedure for Leaching Using the Buchi Autoclave:

1. **Safety Precautions**

i. Wear PPE (lab coat, gloves, face shield)

ii. Ensure the ventilation upstairs is on

2. **Switching**

i. Open the water inlets and outlets

ii. Turn on all the electronic devices

iii. Switch on the computer and open the BLS 2 app.

iv. Perform leak test

3. **Leak Test**

i. Fill the reactor with distilled or demineralized water

ii. Close and seal the reactor

iii. Pump gas into the reactor and increase the pressure.

iv. Wait a little for the pressure to stabilize

v. If the pressure drops continuously, use leak test spray (soap water) to identify the leakage.

vi. Release the pressure and fix the leakage

vii. Perform another leak test if there was leakage; if not, then remove water from the reactor

4. Prepare the leaching solution

i. Prepare a known concentration and volume based on the experimental design.

ii. Pour acid solution of the desired concentration into the autoclave reactor

5. Weigh the solid phase

i. Weigh the precise amount of solid phase

ii. Pour it carefully into the reactor and close it using the handle on the side of the autoclave.

iii. Set the stirring rate and begin mixing

iv. Close the autoclave, tighten all the bolts diagonally, and ensure the reactor is appropriately tightened.

6. Run the reaction

i. Before running the reaction, pump in gas until the desired pressure is stabilized.

ii. Start recording data in the BLS app, name and save the folder.

iii. Begin heating by turning on the thermostat with a gradient of 10 maximum. Input the desired temperature, gradient, and mixing speed (rpm)

7. Monitoring

i. Monitor the pressure and temperature gauges regularly, especially when the temperature is high.

ii. Use the sampling valves to take samples when the desired temperature is reached.

iii. Begin observing the time and take a sample after every hour.

8. Sampling

i. At the beginning, all valves are closed.

ii. Open valve 1 (figure 11) briefly for a few seconds, then close it again.

iii. Then, open the valve to take a sample.

iv. After the pressure is released, open valve 3 to remove all content from the tube.

v. Finally, close all valves to complete the process.

9. After the reaction

i. Cool down: Set the temperature on the thermostat to room temperature and place the gradient at 20.

ii. Depressurize: Open the gas release valve slowly and release the pressure. Ensure no residual pressure remains.

10. Open the autoclave

i. Once it has cooled and all the pressure is released, open the autoclave reactor

ii. Collect the solution from the reactor. Carry on filtration on it to collect the leachate and the solid residue for analysis.

11. Cleaning and Shutdown of the Autoclave

i. Close the BLS app and turn off all electronic devices.

ii. Rinse the reactor well with water and dry it with paper.

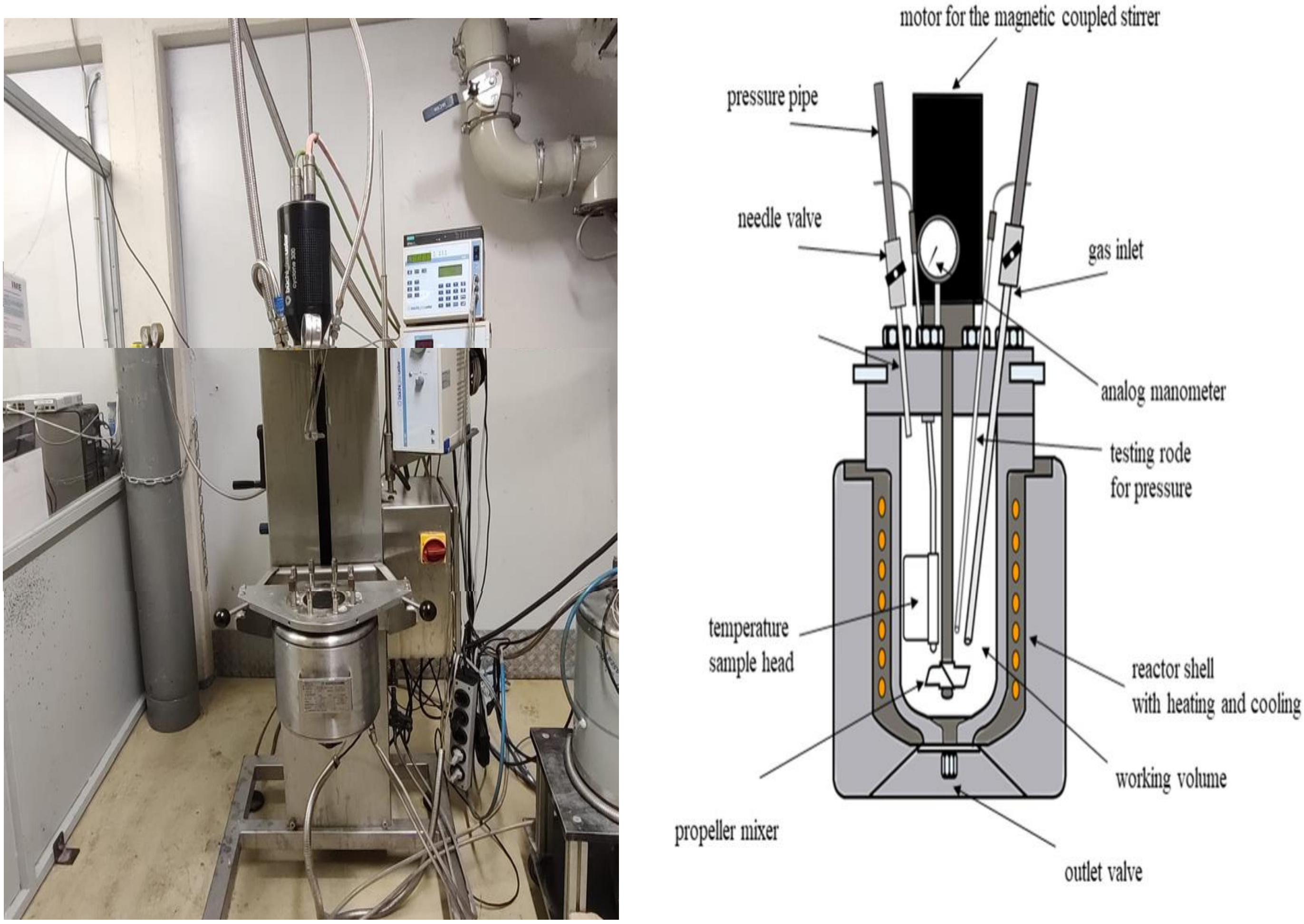

Figure 11:: Experimental Setup of Leaching and Schematic Diagram of Autoclave (Stopic & Kostic, 2024

2.4.2. Leaching Experiment Using the Glass Reactor

Three experiments were performed using the glass reactor to investigate the dissolution behaviour of PbS-rich solid residues under different conditions of nitric acid. The experimental setup for the glass reactor is seen in **Figures 12 and 13.** The glass reactor was equipped with a mechanical stirrer, temperature control, and a reflux condenser to minimize evaporation losses during a long period of heating. In the first experiment in the glass reactor, a 76.26 g solid residue from Pbs was placed into the glass reactor containing 762mL of 1M HNO_3 while in the second experiment, 60g of the same solid residue was leached using 600mL of 2M HNO_3 in the glass reactor. In the last experiment using the glass reactor, 60g of the same solid residue was leached with 600mL of 3M HNO_3.

All three experiments were performed under a constant temperature of 80℃ for 6 hours, and stirring mixing was maintained at 350RPM. After every 1 hour, a sample was taken using a syringe with a filter. At the end of each experiment, filtration was done to separate the leachate and solid residue. The leachates were analysed to determine the concentration and leaching efficiency of lead (Pb), bismuth (Bi), and other valuable metals using ICP-OES, an analytical technique used in determining the elemental composition of a sample. The solid residues were washed, dried, and subjected to X-ray diffraction (XRD) to examine the mineralogical and structural changes.

Figure 12: Experimental Set-up of Reactor

Figure 13:Sample being taken while the experiment is ongoing

2.5. FILTRATION AND DRYING PROCESS

Filtration is a process used to remove solid particles from a liquid solution by placing them on a filter. At the end of every leaching process, we performed filtration to separate the leaching solution from the solid residue. The process of filtration involves applying pressure differentials, which can be generated by a vacuum, gravity, centrifugal force, or a pressurized fluid. The force to get the suspension to the filter, filtration usually calls for a pump, as seen in **Figure 14**. A vacuum pump is employed to facilitate efficient filtration. To separate the filtrate from the glass, the pump removes the gas from the filtrate receiver. A barometric leg of at least 8 to 10 meters or a pump that can operate on snore, that is, when there is sufficient feed liquid, which causes it to tend to pull in air, are the two methods used to drain the filtration.

2.5.1. Experimental Setup of Filtration

As seen in **Figure 15**, a detailed illustration of a traditional filtration setup is shown. In this setup, we demonstrated the process of separating a combination of liquid and a solid particle into a receiving flask via a filter paper-lined funnel. The mixture is dispensed from a beaker at the top and is drawn through porous media by a vacuum pump. Usually held up by a clamp or ring stand for stability, the funnel itself is composed of either plastic or glass. To guarantee a tight seal against the funnel walls and stop particles from evading the filtering medium, the filter paper is properly folded or pre-wetted inside. Filter paper adheres better to the funnel and is less likely to channel or bypass when it is pre-wetted with a tiny amount of solvent.

Figure 14:Experimental Setup for filtration

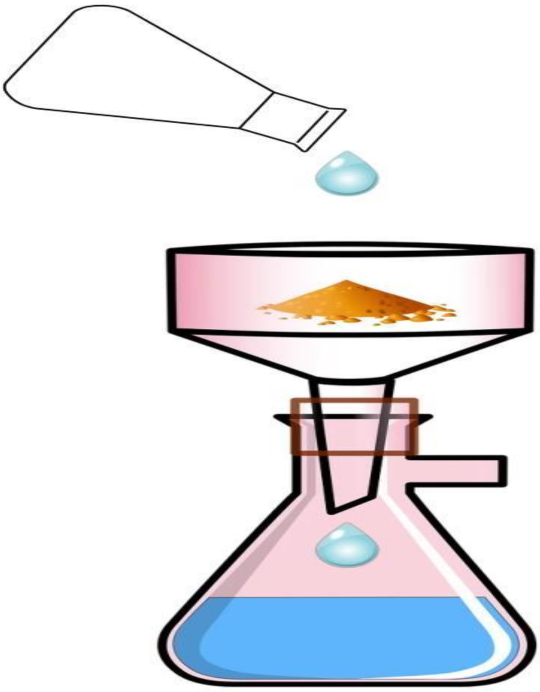

Figure 15: vacuum filtration with a Buchner funnel

2.5.2. Drying of Solid Residue

After the filtration process, the solid obtained from the solution needs to be washed, cleaned, and dried, as seen in **Figure 16.** Washing, as used here, refers to cleaning a product (filter cake); it is not the same as rinsing, which is the process of cleaning specific portions of the filter, such as the filter screen or a filter cloth, using water jets.

Washing removes liquid impurities from the filter cake's interparticle pores, while drying refers to thermal drying, where liquid is removed from the filter cake by a mechanical process.

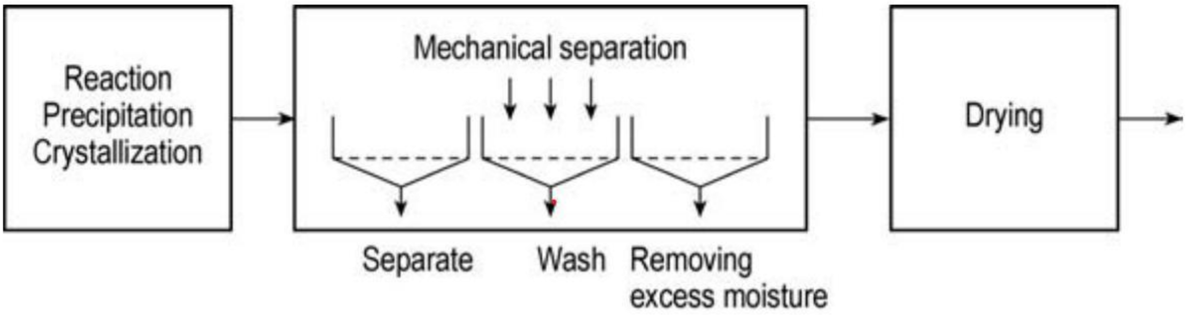

Figure 16:Solid processing chain washing, de-liquoring, and thermal drying.

2.6. SUMMARY OF EXPERIMENTAL CONDITIONS

A total of thirteen (13) experiments were performed. Ten (10) of those experiments were performed using the Buchi Autoclave, while three were performed using the glass reactors. The list of experiments performed using the autoclave is shown in **Table 4**, while the list of experiments performed in the glass reactor is shown in **Table 5.**

Table 4: Design of the experiments for the leaching of Pb-concentrate in an autoclave

Experiment	Acid Molarity (M)	Temp (° C)	O_2 Pressure (bar)	Time (h)	Stirring (rpm)
1	1.0	120	6	4	600
2	1.0	150	10	4	600
3	1.0	180	10	4	600
4	1.0	150	12	4	600
5	2.5	150	6	4	600
6	1.0	150	8	4	600
7	2.5	150	8	4	600
8	2.5	150	10	4	600
9	2.5	150	12	4	600
10	5.0	150	6	4	600

Table 5: Design of the experiments for the leaching of solid residue of Pb-concentrate in a Glass Reactor

Experiment	Residue Mass (g)	HNO_3 Concentration (M)	Volume (mL)	Temp (°C)	Time (h)	Stirring (rpm)	Reactor Type
11	76.26	1.0	762	80	6	350	Glass reactor
12	60.00	2.0	600	80	6	350	Glass reactor
13	60.00	3.0	600	80	6	350	Glass reactor

2.7. LEACHING EFFICIENCY CALCULATION

The Leaching Efficiency of each element recovered from the leaching of lead concentrate was calculated using the equation:

$$\text{Leaching Efficiency (\%)}=\frac{Mass\ of\ Element\ dissolved\ in\ Leach\ solution}{Intial\ \ Mass\ of\ element\ in\ Pb-concentrate}\times 100\% \qquad \text{Equation (10)}$$

Where:

Mass of element dissolved in Leach Solution =Concentration of element in leach solution (mg/L) X Volume of Leach solution(L)

Initial mass of element in Pb-concentrate (wt%) X mass of Pb-concentrate used in leaching (g). See how the calculation was done for each element below. A step of the calculation is shown in Appendix **1.**

2.8. CONCLUSION

This chapter provided a step-by-step method we used to perform the experiment. We also discussed the materials we used for the experiment. Additionally, we highlighted the experimental designs and briefly talked about the tools used to analyze our results.

CHAPTER 3.

RESULTS AND DISCUSSION

3.0. INTRODUCTION

This chapter aims to present results and analysis on how valuable metals were extracted and recovered from the lead concentrate. This chapter is divided into three parts. The first part will present the results obtained from the experiment performed on the leaching of Pb-concentrate with sulfuric acid (H_2SO_4) and oxygen gas (O_2) and the leaching efficiency of each of the metals recovered was analysed. In the second part, the results obtained from the leaching of solid residue with nitric acid in a glass reactor without oxygen gas will be presented and analysed. The last part highlights the effects of each leaching parameter on the leaching efficiency of Pb-concentrate.

3.1. RESULTS FROM THE LEACHING OF PB-CONCENTRATE WITH SULFURIC ACID AND OXYGEN GAS

After the experiments, the samples collected, and an elemental ICP-OES analysis was performed to establish the concentration of elements in solution after leaching. See **Tables 6 and 7** for this result.

Table 6: Results obtained from experiment 4-10

Sample	Lab. Nr	Sn	Ca	Si	Fe	Pb	Bi	Zn	Cu
M-1-1 (0min)	65081	<0.5	59	34.8	915	4.05	0.85	150	0.45
M- 1-3 (120min)	65082	<0.5	164	116	2610	4.9	209	730	37.4
M-1-5 (240min)	65083	<0.5	201	156	3240	5.1	265	855	90.5
M-3-1 (0min)	65084	<0.5	103	104	1730	5.3	59	339	4.85
M-3-3 (120min)	65085	<0.5	283	269	2570	5.15	194	629	157
M-3-5 (240min)	65086	<0.5	278	308	2910	5.1	199	636	188

Table 7: Results obtained from experiment 4-10

Probe	Lab. Nr.	Parameter (mg/l)						
		Ca	Fe	Cu	Zn	Sn	Pb	Bi
M-4-1 (0min)	65660	55	1200	2	262	0.1	4.2	< 2
M-4-2 (60min)	65661	106	1850	62	479	0.3	4.4	5.5
M-4-3 (120min)	65662	178	2560	160	702	0.4	4.6	46.5
M-4-4 (180min)	65663	212	2670	194	717	0.5	4.8	91
M-4-5 (240min)	65664	244	2820	206	743	0.5	4.8	128
M-6-1 (0min)	65665	49	801	< 1	314	< 0,1	5.7	< 1
M-6-2 (60min)	65666	158	2190	47	656	0.3	4.9	26.5
M-6-3 (120min)	65667	206	2380	102	682	0.5	4.6	75.5
M-6-4 (180min)	65668	234	2490	130	717	0.5	4.7	126
M-6-5 (240min)	65669	240	2510	142	716	0.5	5.0	145
M-7-1 (0min)	65670	157	1830	< 1	909	< 0,1	3.5	119
M-7-2 (60min)	65671	245	2650	43.5	1070	0.2	4.5	119
M-7-3 (120min)	65672	323	3090	183	1150	0.6	3.4	294
M-7-4 (180min)	65673	309	3150	210	1160	0.5	3.6	265
M-7-5 (240min)	65674	326	3340	244	1180	0.7	4.1	283
M-8-1 (0min)	65675	130	1500	43	704	< 0,1	3.0	88.5
M-8-2 (60min)	65676	186	2460	47.5	912	0.2	2.9	140
M-8-3 (120min)	65677	221	2730	97	1020	0.3	3.2	93.5
M-9-1 (0min)	65680	62	1100	< 1	528	< 0,1	3.8	16
M-9-4 (240min)	65681	102	1640	14.5	668	< 0,1	3.5	15
M-10-1 (0min)	65682	155	2250	55.5	1070	0.1	< 0,5	46
M-10-2 (120min)	65683	106	2880	1.5	1200	< 0,1	4.3	< 2

3.1.1. Leaching Efficiency and Analysis of Lead (Pb)

The amount of Pb that was recovered from dissolving Pb-concentrate is expressed **appendix 2.** We presented a graph that shows little or no variation in leaching efficiency of Pb in **appendix 3**, meaning lead is largely resistant to leaching under the conditions we performed the experiment. The leaching efficiency of lead was very low. This may have been due to several reasons, including:

i. The leaching of Pb with sulfuric acid and oxygen produces PbSO4 and elemental sulfur(S°), which may be chemically resistant to leaching. See the equation:

$$PbS + H_2SO_4 + \frac{1}{2}O_2 \rightarrow PbSO_4 + S^{\circ} + H_2O \qquad \text{Equation (11)}$$

ii. Insoluble lead compounds may have formed during leaching, which may have suppressed solubilization.

3.1.2. Leaching Efficiency and Analysis of Bismuth (Bi)

The full list of leaching efficiencies of Bismuth from all experiments is listed in **Table 8**. In **Figure 17,** a graphical analysis of the leaching efficiencies versus time is shown. From the graph, it is shown that there is no single trend across experiments. In some experiments, there is a continuous increase, while some reach an early peak and later drop. Temperature and residence time strongly affected the outcome of leaching, but process optimization is more complex than for Iron or Calcium.

3.1.3. Leaching Efficiency and Analysis of Zinc (Zn)

In **Appendix 5,** we listed the calculated leaching efficiency of Zinc from experiments 1-10, and a graph that better interprets the result in **Appendix 6.** The results shown in the graph and table show that Zinc underwent extensive leaching. All the experiments clearly show that zinc was leached rapidly; this may have been because of the availability of zinc in leachable forms. During the entire experiments, there was never a drop in leaching or a reprecipitation.

This result in zinc is indeed favorable for extracting from Pb-concentrate using a hydro-metallurgical process.

Table 8: Leaching efficiencies of Bi from experiments 1-10.

Exp No	Time (mins)	Conc. (mg/l)	Volume(ml)	Temperature (°C)	Leaching Efficiency (%)
1-1	0	0.85	661	120	0.225
1-3	120	209	661	120	55.4
1-5	240	265	661	120	70.3
3-1	0	59	706	180	16.7
3-3	120	194	706	180	55.0
3-5	240	199	706	180	56.4
4-1	0	< 2	711.5	150	-
4-2	60	5.5	711.5	150	1.57
4-3	120	46.5	711.5	150	13.3
4-4	180	91	711.5	150	26.0
4-5	240	128	711.5	150	36.6
6-1	0	< 1	636.5	150	-
6-2	60	26.5	636.5	150	6.77
6-3	120	75.5	636.5	150	19.3
6-4	180	126	636.5	150	32.2
6-5	240	145	636.5	150	37.06
7-1	0	119	589	150	28.1
7-2	60	119	589	150	28.1
7-3	120	294	589	150	69.5
7-4	180	265	589	150	62.7
7-5	240	283	589	150	66.9
8-1	0	88.5	630	150	22.39
8-2	60	140	630	150	35.42
8-3	120	93.5	630	150	23.66
9-1	0	16	631.5	150	40.66
9-4	180	15	631.5	150	3.8
10-1	0	46	538	150	9.94
10-2	60	< 2	538	150	-

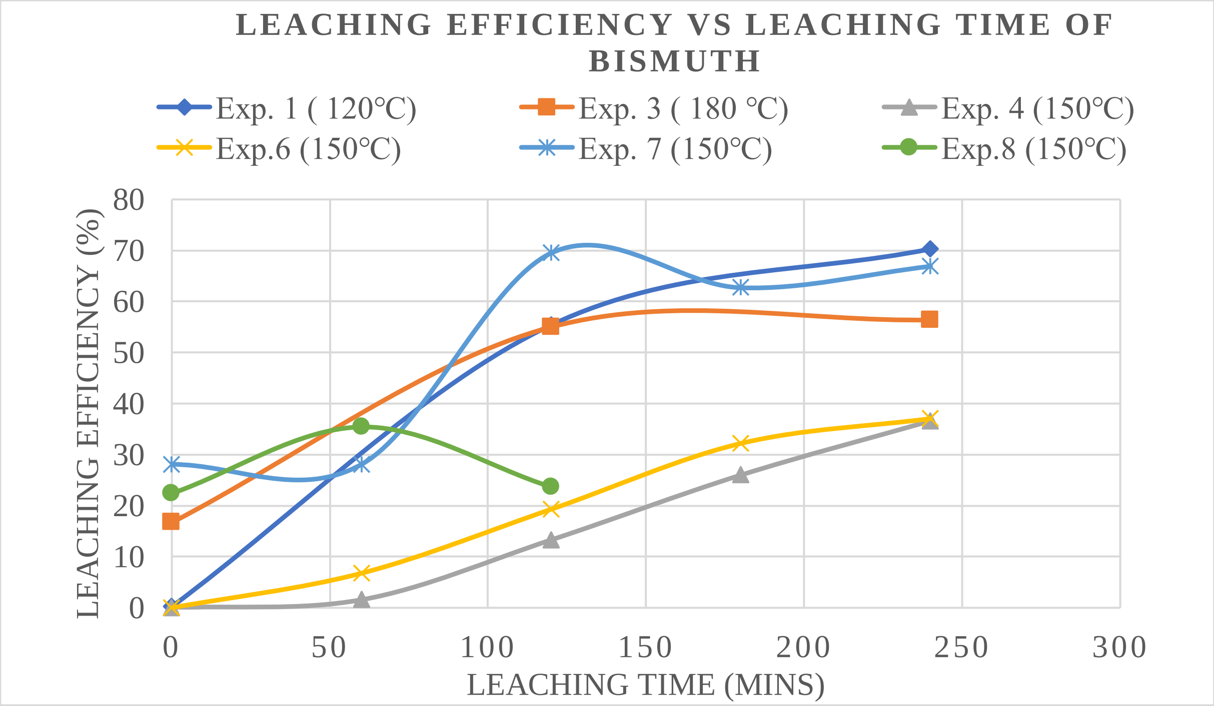

Figure 17:Leaching Efficiency vs Time of Bi from Experiment (1-8).

3.1.3. Leaching Efficiency and Analysis of Copper (Cu)

In **Table 9**, we listed the calculated leaching efficiency of copper from experiments 1-10, and a graphical representation showing the leaching efficiency of copper as a function of time is shown in **Figure 18.** The graph shown shows that copper dissolved relatively at a moderate rate. The highest copper recovery happened in experiments 4 and 7 at a temperature condition of 150 °C. The highest leaching efficiencies were 35% and 34%, respectively.

On the contrary, at an increased temperature of 180°C, there was a slight decrease in leaching efficiency. This could be because higher temperatures above 150°C do not enhance the leaching of copper. The better leaching efficiencies in experiments 4 and 7 may be due to the leaching agents applied during those experiments

Table 9: Leaching efficiencies of Cu from experiments 1-10.

Exp No	Time (mins)	Conc. (mg/l)	Volume(ml)	Temperature (°C)	Leaching Efficiency (%)
1-1	0	0.45	661	120	0.070
1-3	120	37.4	661	120	5.8
1-5	240	90.5	661	120	14.1
3-1	0	4.85	706	180	0.8
3-3	120	157	706	180	26.1
3-5	240	188	706	180	31.3
4-1	0	2	711.5	150	0.3356
4-2	60	62	711.5	150	10.4
4-3	120	160	711.5	150	26.8
4-4	180	194	711.5	150	96.3
4-5	240	206	711.5	150	34.6
6-1	0	< 1	636.5	150	-
6-2	60	47	636.5	150	7.05
6-3	120	102	636.5	150	15.3
6-4	180	130	636.5	150	19.5
6-5	240	142	636.5	150	21.3
7-1	0	< 1	589	150	-
7-2	60	43.5	589	150	6.04
7-3	120	183	589	150	25.42
7-4	180	210	589	150	29.2
7-5	240	244	589	150	33.9
8-1	0	43	630	150	6.4
8-2	60	47.5	630	150	7.06
8-3	120	97	630	150	14.15
9-1	0	< 1	631.5	150	-
9-4	180	14.5	631.5	150	2.2
10-1	0	55.5	538	150	7.04
10-2	60	1.5	538	150	0.19

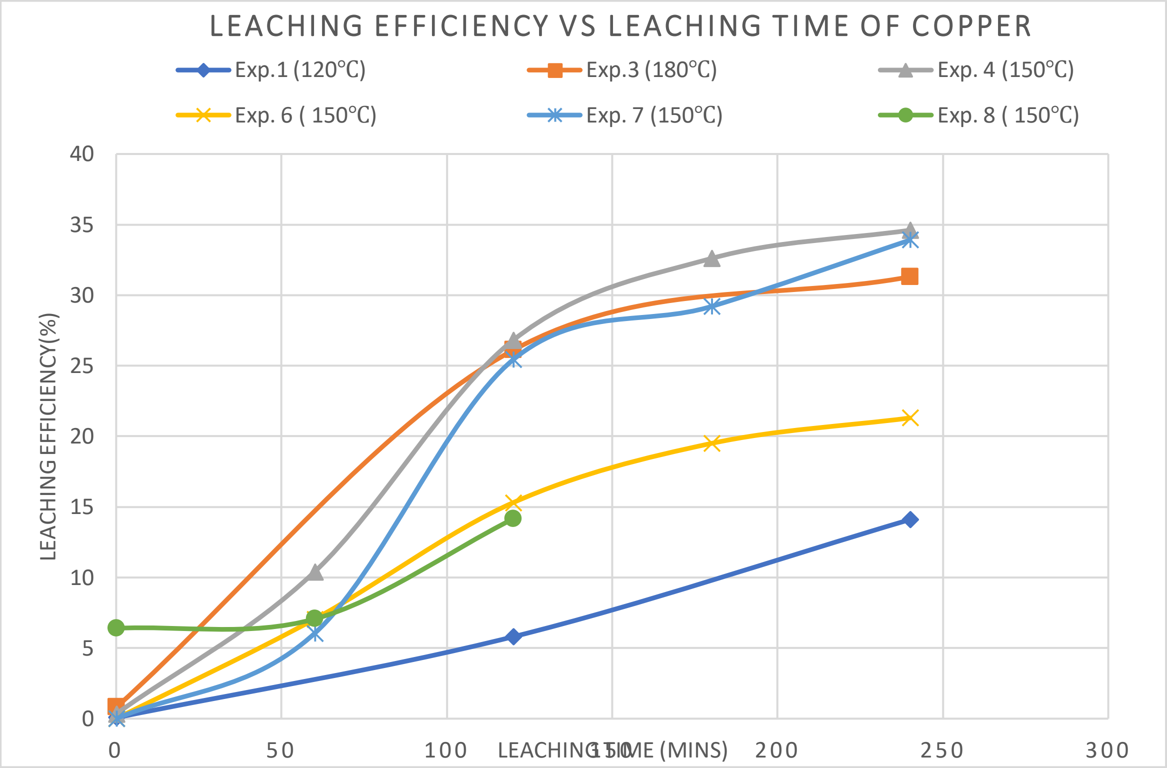

Figure 18: Leaching Efficiency vs Time of Cu from Experiment (1-8).

3.2. X-RAY DIFFRACTION ANALYSIS OF SAMPLES FROM LEAD CONCENTRATE

Three samples were taken from the first set of 10 experiments to analyse the mineralogical structure and chemical phases of Pb-concentrate before and after leaching. The first sample is considered Experiment 0, which is the un-leached Pb-concentration. In contrast, the 2nd and 3rd samples are the solid residues obtained from the leaching of Pb-concentrate from Experiments 5 and 10. The X-ray diffraction pattern before and after leaching of the lead concentrate is shown in **Figures 19, 20, and 21.** The phase pattern portrays high purity of the material before leaching, as seen in the PDF index [96-100-8294], in the upper right-hand corner of the graph. Below the 2θ region (i.e.,). The region is less than 20°. $There$ is a sharp increase in the peak, which confirms that the material is homogeneous and crystalline. Afterward, there is no increase in the peaks, which is evidenced by the fact that there were no secondary phases like oxides, carbonates, or sulfates. The material has only a single, well-defined phase.

The XRD pattern of the lead concentrate in **Figure 20** shows that the mineral lead sulfate (anglesite) $PBSO_4$ is more dominant. This can be observed from the highest peak shown in the graph and confirmed by the PDF reference [96-900-4485]. The mineral Anglesite is formed when Pb has been oxidized. This may have happened during the flotation and oxidation process of the Pb-concentrate. It is also seen that the Pb-concentrate had a high purity $PBSO_4$ because at the beginning of the graph in the range of 2θ, there is a sharp increase in peaks from 10° to 30°. Hence, it is hereby confirmed that lead exists predominantly in the form of sulfate in the Pb-concentrate, which is resistant to leaching under certain conditions. This is a clear reason why the leaching efficiency of Pb throughout the entire experiment was extremely low.

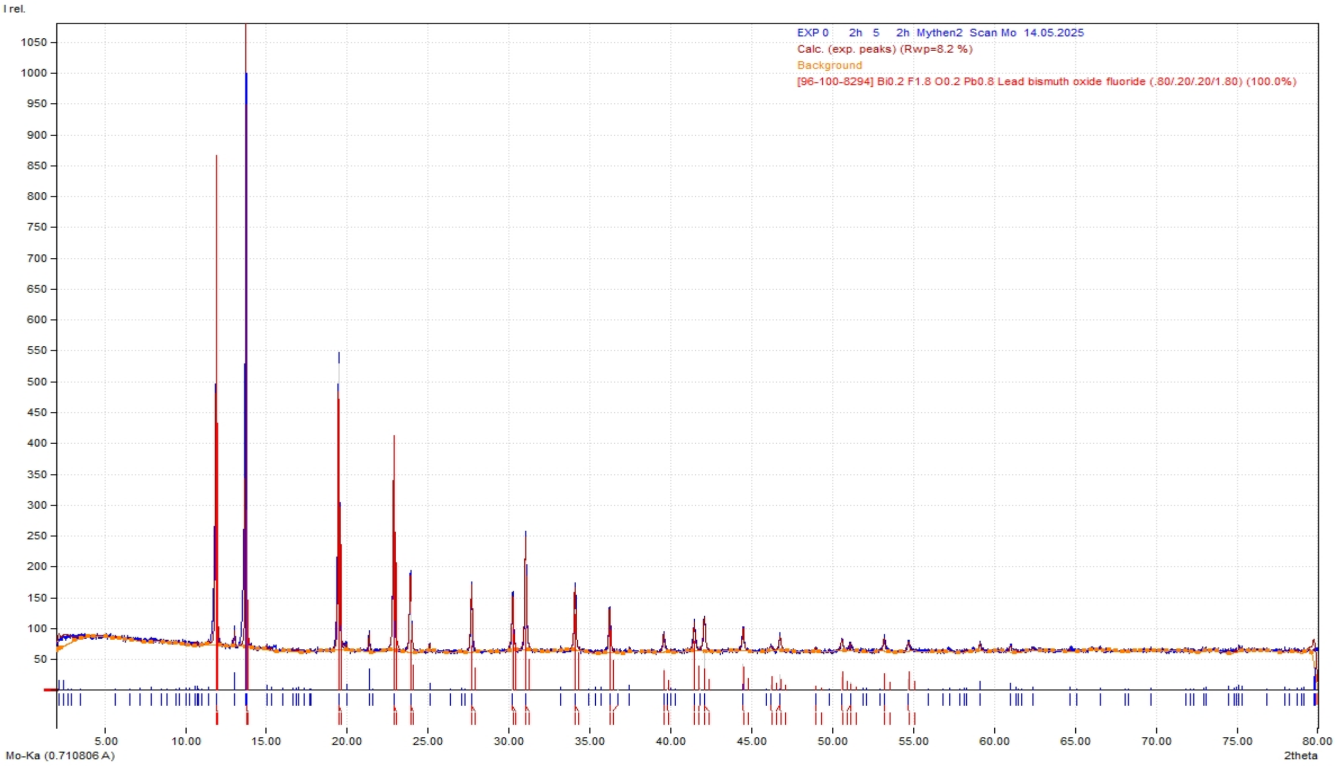

Figure 19:Diffraction Pattern of Pb-Concentrate before leaching

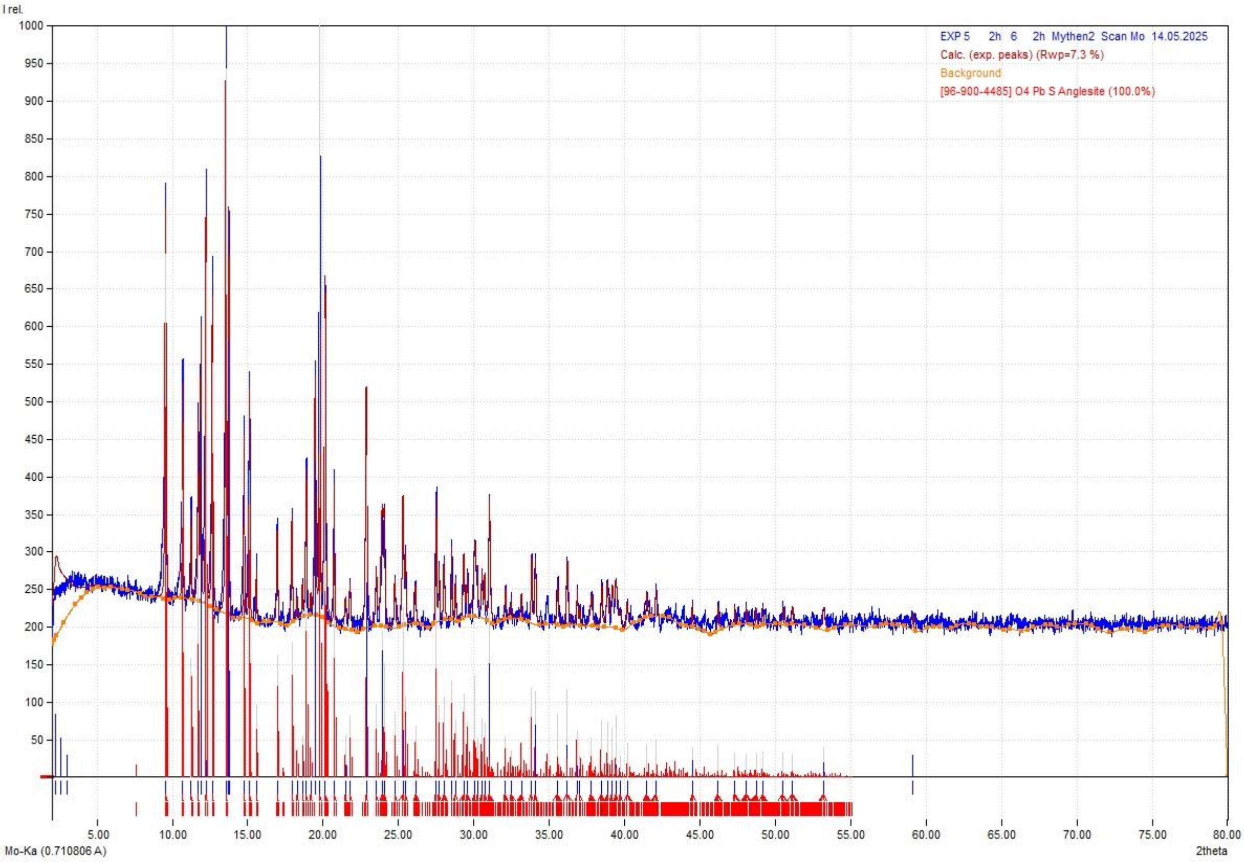

Figure 20: X-ray Diffraction Pattern of Solid Residue from Experiment 5.

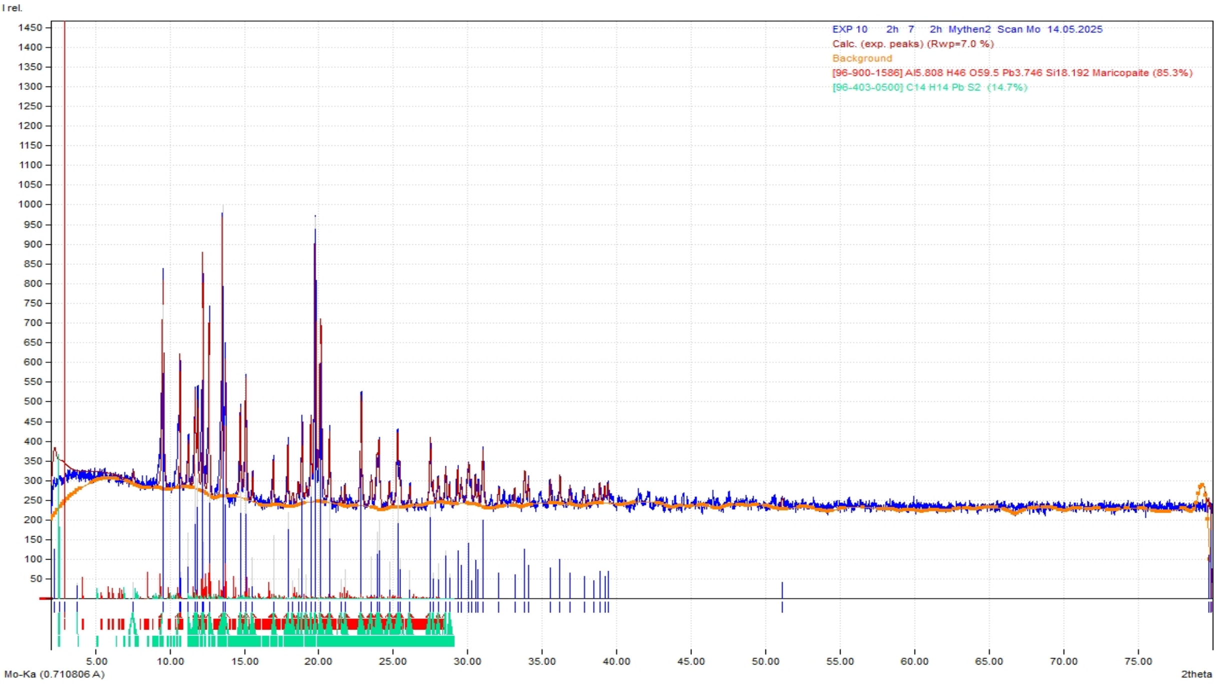

Figure 21: X-ray Diffraction Pattern of Solid Residue from Experiment 10

There are two main phases present in the XRD pattern of solid residue in this experiment, as seen in **Figure 21.** The two phases are maricopaite ($Al_{5.808}H_{46}O_{59.5}Pb_{3.746}Si_{18.192}$) and PbS_2. Macricopaite is an uncommon, complex silicate mineral that contains Pb, Al, Si, Oxygen, and Hydrogen, showing a more dominant phase with 85.3% as compared to PbS_2 which is 14.7%. Its dominant presence in the XRD may have been due to the formation of complex secondary minerals during leaching of the Pb-concentrate as a result of reactions between lead, aluminium, and silicate species. On the other hand, the presence of PbS_2 could be attributed to incomplete oxidation of lead, which remains in a sulfide form after leaching.

3.3. RESULTS AND ANALYSIS OF LEACHING OF SOLID RESIDUE IN THE GLASS REACTOR

Three experiments, numbered 11, 12, and 13, were performed using the glass reactor. The solid residue obtained from the leaching of lead concentrate in the autoclave reactor was used in this experiment. In Experiment 11, 76.26 g of solid residue was further leached in a glass reactor with 762 mL of 1 M nitric acid. In Experiments 12 and 13, 60 g of solid residue was leached with 600 mL of 2 M and 3 M nitric acid, respectively, see Table 5. All experiments in the glass reactor were done at a temperature of 80 °C for six (6) hours, and mixing was done at 350rpm. After the experiments, the leaching solution was collected as samples, and an elemental ICP-OES analysis was performed to establish the concentration of elements in solution after leaching and to calculate the leaching efficiency. The results from the analysis are shown in **Table 10**. After obtaining the results, the leaching efficiency was calculated for the metals recovered from each experiment.

3.3.1. Leaching Efficiencies of Pb Recovered from Experiments in a Glass Reactor.

The leaching efficiencies of Pb recovered from the leaching of the solid residue were calculated, and the result is shown in **Table 11.**

Table 10:Results from Experiments performed using the Glass Reactor

Sample ID/ Sample No.		Pb	Si	Sn	Ca	Fe	Cu	Zn	S	Ag	Bi
		g/L	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l
M-11 - 0min	168	7.15	31.3	<1	15.3	238	237	2.83	46.2	20.9	228
M-11 -1hr	169	16	83.2	<1	17.3	330	307	3.06	23.6	60.9	295
M-11 -2hrs	170	15.6	94.4	<1	18.7	371	321	2.92	19.7	57.7	301
M-11 -3hrs	171	15.7	97	<1	20.4	424	353	3.77	18.9	63.6	311
M-11-4hrs	172	15.4	97.6	<1	22.3	455	371	3.19	19.5	63.1	311
M-11-5hrs	173	15.1	112	<1	21.2	459	372	3.55	18.6	64.3	305
M-11-6hrs	174	15.2	132	<1	21.2	470	377	3.14	18.4	64.9	308
M-12 - 0min	174	8.14	24.5	<1	4.96	60.1	41.6	4.08	83.6	15.3	125
M-12 -1hr	176	22.8	43.5	<1	6.6	218	102	7.1	29.7	60.3	198
M-12 -2hrs	177	23.1	58.7	<1	7.92	261	111	7.95	29.3	20.7	202
M-12 -3hrs	178	22.8	71.6	<1	8.88	313	128	8.79	30.4	65.7	204
M-12-4hrs	179	22.5	79.6	<1	9.44	332	127	8.98	30.4	69	203
M-12-5hrs	180	22.2	90.5	<1	8.76	334	125	8.65	29.2	64.1	192
M-12-6hrs	181	22.5	84.4	<1	13.4	328	125	8.97	30.2	70.4	200
M-13 - 0min	182	17.8	30.4	<1	38.5	134	76	15.4	88.8	59.6	178
M-13 -1hr	183	23.2	45.2	<1	14.1	301	127	28.3	64.5	81.8	214
M-13 -2hrs	184	23.5	51.1	<1	14	348	125	29.7	66.1	83.1	214
M-13 -3hrs	185	23	53.2	<1	15.8	407	132	31.9	66	86.7	219
M-13-4hrs	186	23.5	65.4	<1	17.1	444	134	32.4	67.6	88.8	224
M-13-5hrs	187	23	69.1	<1	18.1	444	135	32.3	68.5	23.5	220
M-13-6hrs	188	22.6	80.7	<1	17.9	454	135	32.4	67.9	86.6	222

Table 11: Leaching Efficiencies of Lead-Experiment 11-13.

Exp No	Time (hr)	Conc. (g/l)	Leaching Efficiency (%)
M-11 -0min	0	7.15	10.7
M-11 -1hr	1	16	23.9
M-11 -2hrs	2	15. 6	23.3
M-11 -3hrs	3	15. 7	23.5
M-11-4hrs	4	15. 4	23
M-11-5hrs	5	15. 1	22.6
M-11-6hrs	6	15. 2	22.7
M-12 -0min	0	8.14	13.3
M-12 -1hr	1	22.8	37.1
M-12 -2hrs	2	23.1	37.6
M-12 -3hrs	3	22.8	37.1
M-12-4hrs	4	22.5	36.6
M-12-5hrs	5	22.2	36.1
M-12-6hrs	6	22.5	36.6
M-13 -0min	0	17.8	29.3
M-13 -1hr	1	23.2	38.2
M-13 -2hrs	2	23.5	38.7
M-13 -3hrs	3	23	37.9
M-13-4hrs	4	23.5	38.7
M-13-5hrs	5	23	37.8
M-13-6hrs	6	22.6	37.1

From these results, the leaching efficiency of Pb in a glass reactor is strongly influenced by nitric acid concentration and solid-to-liquid ratio. In experiment 1, where 1M of HNO_3 was used, the leaching efficiency of Pb reached up to approximately 24% after 2 hours. In experiments 12 and 13, where the concentration of Nitric acid was increased to 2M and 3M, respectively, the leaching efficiency increased up to about 37% and 39% as seen in Table 11. The leaching efficiency of Pb is also influenced by time, as seen in **Figure 22.** In the first 2hours, there is a sharp increase in the leaching efficiency of Pb in all the experiments in the glass reactor. The leaching efficiencies stabilize with slight fluctuations after 2 hours.

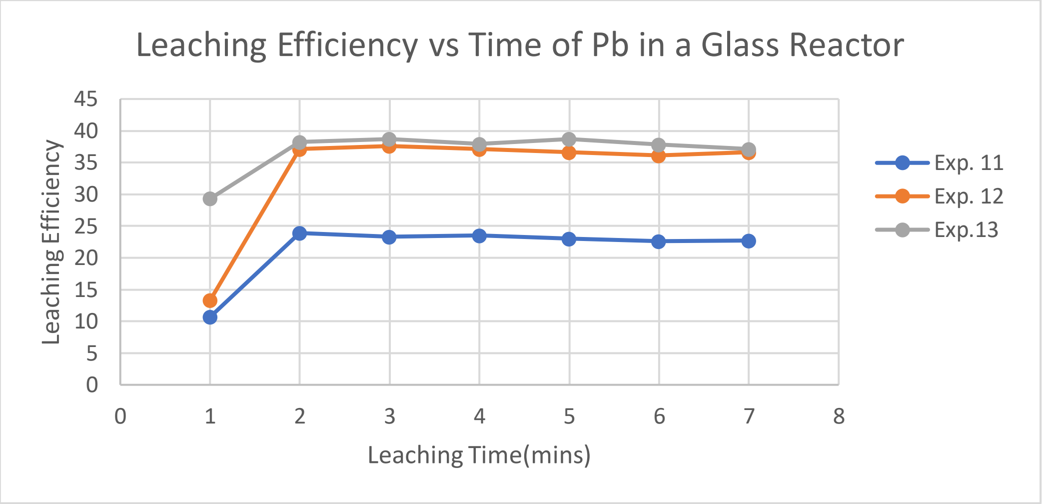

Figure 22:Leaching efficiency vs Time of Pb

3.3.2. Leaching Efficiencies of Bismuth Recovered from Experiments in a Glass Reactor.

The leaching efficiencies of Bi recovered from the leaching of the solid residue were calculated, and the result is shown in **Table 12.** The trend in leaching efficiency for Bi is quite different from Pb. The highest leaching efficiency (~74%) was obtained at 1M HNO_3 in experiment 1, whereas increasing the acid concentration (2M HNO_3 , 3M HNO_3) resulted in a reduced leaching efficiency (60% and 58%). This suggests that while stronger nitric acid improves Pb dissolution, it may not be the same for Bi. **Figure 23** suggests that the leaching of Bismuth took place within the first two hours, after which the leaching process reached near-equilibrium.

3.3.3. Leaching Efficiencies of Silver Recovered from Experiments in a Glass Reactor.

Silver (Ag) showed leaching efficiencies ranging from ~50% for 1M HNO_3 to ~80% for 3M HNO_3. See **Table 13** and **Figure 24** for the results of the leaching efficiencies of Ag. Unlike Pb and Bi, Ag leaching was characterized by strong fluctuations, most especially in experiments with higher acid concentrations. The fluctuating leaching behavior of Ag, particularly in Exp. 12 and Exp. 13, may be attributed to the reprecipitation and redissolution of Ag compounds during the process.

Table 12: Leaching Efficiencies of Bismuth-Experiment 11-13.

Exp No	Time (hr)	Conc. (mg/l)	Leaching Efficiency (%)
M-11 -0min	0	228	54.06
M-11 -1hr	1	295	69.94
M-11 -2hrs	2	301	71.37
M-11 -3hrs	3	311	73.74
M-11-4hrs	4	311	73.74
M-11-5hrs	5	305	72.31
M-11-6hrs	6	308	73.03
M-12 -0min	0	125	37.67
M-12 -1hr	1	198	59.67
M-12 -2hrs	2	202	60.87
M-12 -3hrs	3	204	61.48
M-12-4hrs	4	203	61.17
M-12-5hrs	5	192	57.86
M-12-6hrs	6	200	60.27
M-13 -0min	0	178	46.47
M-13 -1hr	1	214	55.87
M-13 -2hrs	2	214	55.87
M-13 -3hrs	3	219	57.18
M-13-4hrs	4	224	58.48
M-13-5hrs	5	220	57.44
M-13-6hrs	6	222	57.96

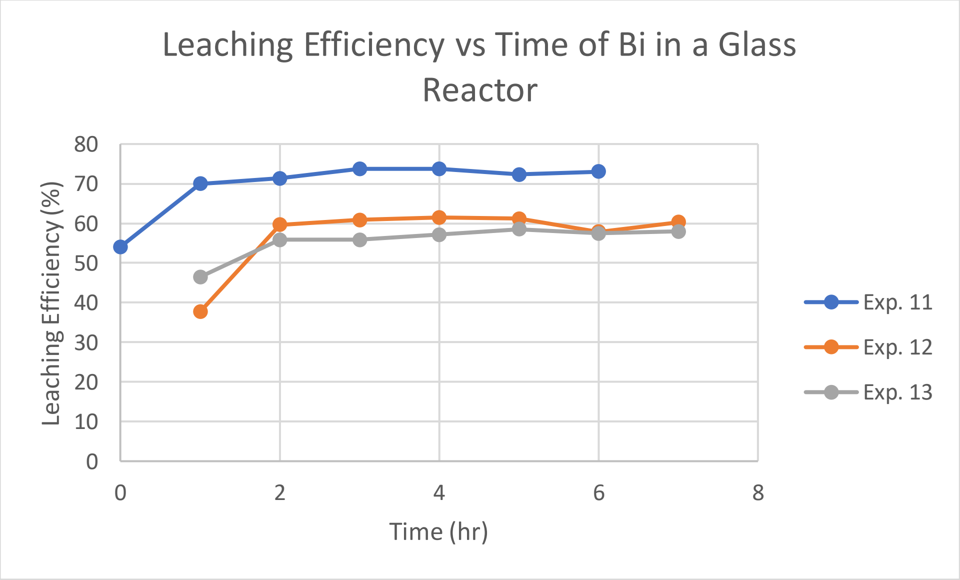

Figure 23:Leaching efficiency vs Time of Bi

Table 13:Leaching Efficiencies of Ag-Experiment 11-13

Exp No	Time (hr)	Conc. (mg/l)	Leaching Efficiency (%)
M-11 -0min	0	20.9	17.06
M-11 -1hr	1	60.9	49.69
M-11 -2hrs	2	57.7	47.09
M-11 -3hrs	3	63.6	51.9
M-11-4hrs	4	63.1	51.49
M-11-5hrs	5	64.3	52.47
M-11-6hrs	6	64.9	52.96
M-12 -0min	0	15.3	15.87
M-12 -1hr	1	60.3	62.54
M-12 -2hrs	2	20.7	21.47
M-12 -3hrs	3	65.7	68.15
M-12-4hrs	4	69	71.57
M-12-5hrs	5	64.1	66.49
M-12-6hrs	6	70.4	73.02
M-13 -0min	0	59.6	53.56
M-13 -1hr	1	81.8	73.51
M-13 -2hrs	2	83.1	74.67
M-13 -3hrs	3	86.7	77.91
M-13-4hrs	4	88.8	79.79
M-13-5hrs	5	23.5	21.12
M-13-6hrs	6	86.6	77.82

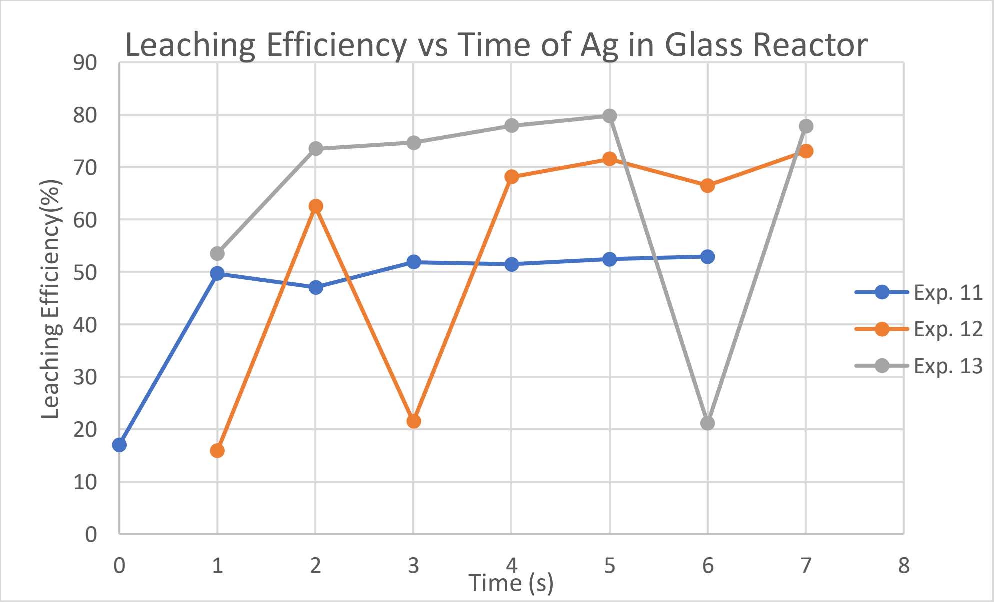

Figure 24:Leaching efficiency vs Time of Ag

3.3.4. Leaching Efficiencies of Cu Recovered from Experiments in a Glass Reactor.

The leaching behavior of Cu differed significantly from that of Pb and Bi. The maximum efficiency of Cu was obtained at a reduced acid concentration. Experiments 11 achieved over 50% Cu leaching after 6h, whereas experiments 12 and 13 had the highest leaching at ~20%. See **Table 14 and Figure 25.**

Table14:Leaching Efficiencies of Cu-Experiment 11-13

Exp No	Time (hr)	Conc. (mg/l)	Leaching Efficiency (%)
M-11 -0min	0	237	32.98
M-11 -1hr	1	307	42.73
M-11 -2hrs	2	321	44.68
M-11 -3hrs	3	353	49.13
M-11-4hrs	4	371	51.63
M-11-5hrs	5	372	51.77
M-11-6hrs	6	377	52.47
M-12 -0min	0	41.6	6.31
M-12 -1hr	1	102	15.48
M-12 -2hrs	2	111	16.84
M-12 -3hrs	3	128	19.42
M-12-4hrs	4	127	19.27
M-12-5hrs	5	125	18.97
M-12-6hrs	6	125	18.97
M-13 -0min	0	76	11.65
M-13 -1hr	1	127	19.46
M-13 -2hrs	2	125	19.16
M-13 -3hrs	3	132	20.23
M-13-4hrs	4	134	20.54
M-13-5hrs	5	135	20.69
M-13-6hrs	6	135	20.69

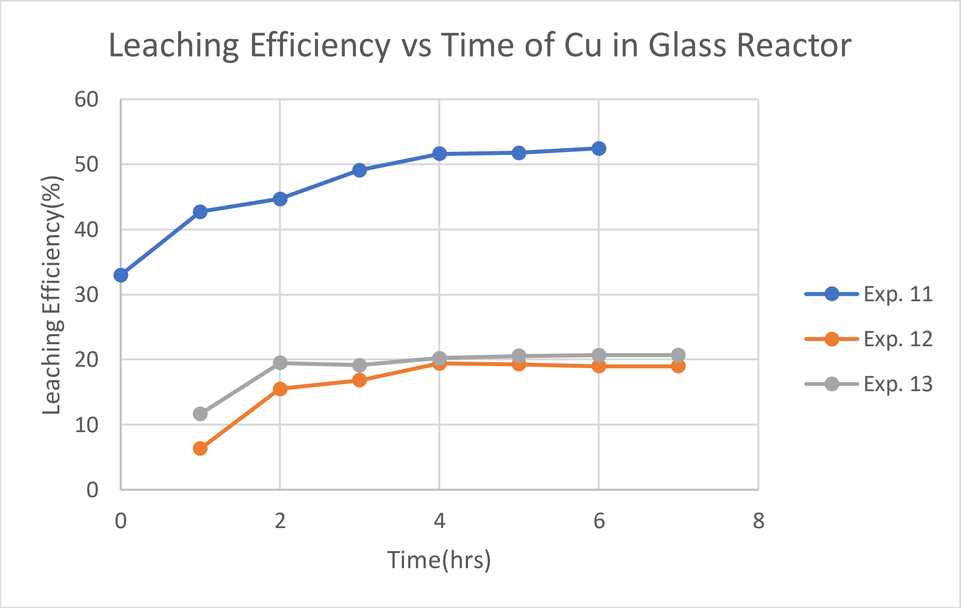

Figure 25:Leaching Efficiency vs Time of Cu

3.3.5. XRD Analysis of Solid Residue from Leaching in a Glass Reactor

The solid residue obtained from these experiments was analysed using X-ray diffraction to determine the mineralogical and elemental composition of the solid residue. See **Figures 26, 27, and 28** for each of the XRD patterns for each experiment named M-11, M-12, and M-13, respectively.

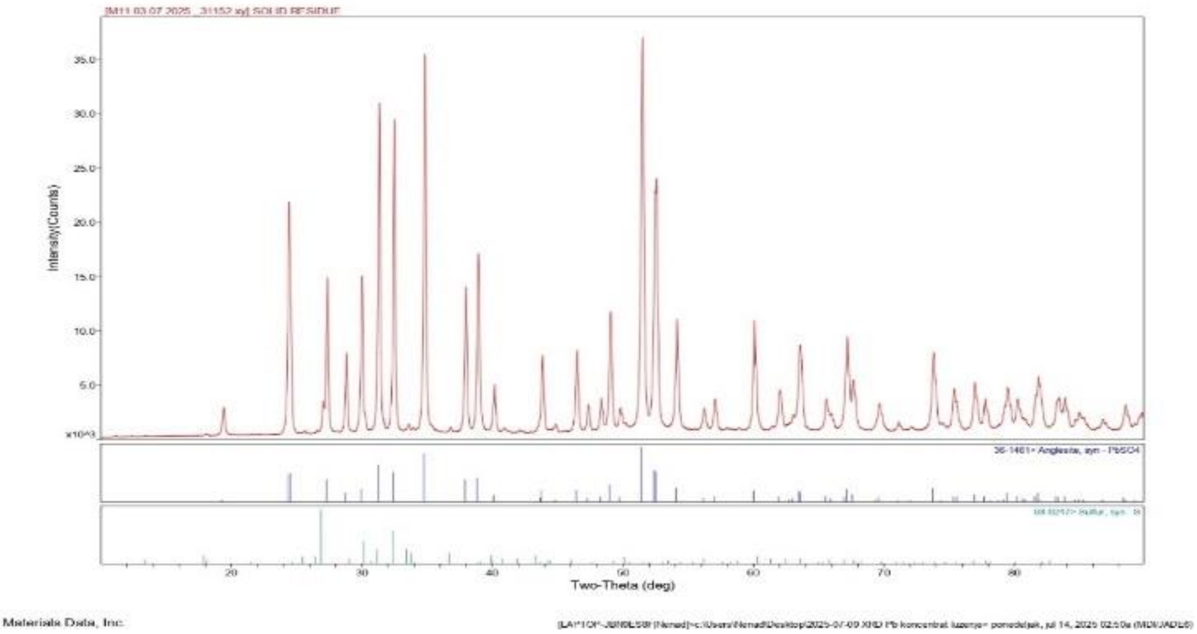

Figure 26: XRD Pattern for Experiment 11(M-11)

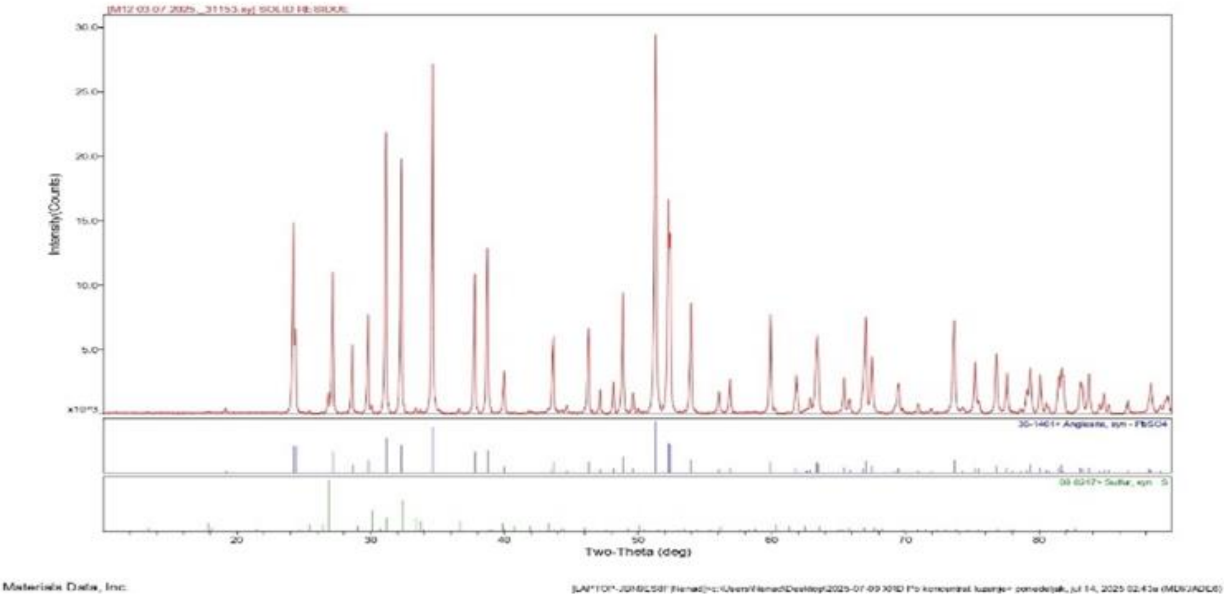

Figure 27: XRD Pattern for Experiment 12 (M-12)

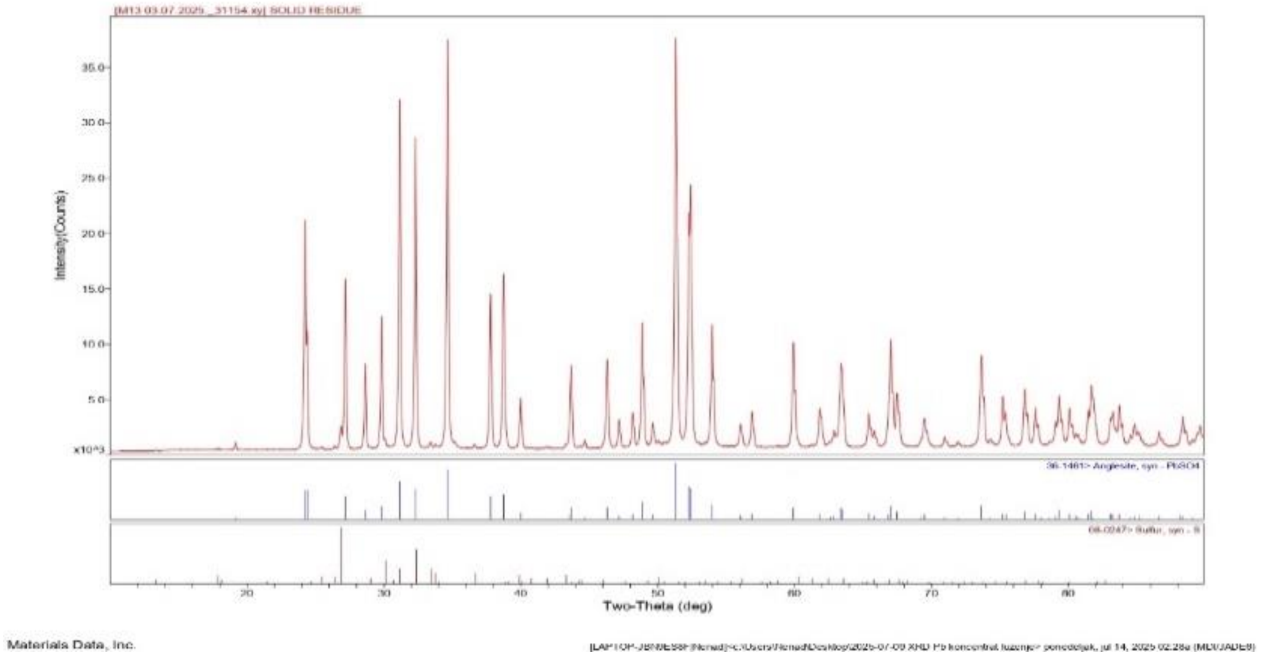

Figure 28: XRD Pattern of Experiment 13(M-13)

All samples have only two phases, namely anglesite ($PbSO_4$) which is dominant and rhombic sulfur. With samples M12 and M13, there is a complete match between these two phases, while for sample M11, the reflections were slightly shifted by the same angle. All three samples were converted into $PbSO_4$ and there is no more PbS in the concentrate. This is incomparably better than the first leaching done in the autoclave, when PbS remained in the Pb concentrate.

For a more effective leaching of the solid residue in the future, since in fact the residue is the mineral anglesite $PbSO_4$ which is a sparingly soluble salt, it can be dissolved with:

Hydrochloric Acid- Reaction: $PbSO_4$(s) + $2HCl \rightarrow PbCl_2(s)$+ $H_2SO_4(aq)$. Equation (12)

Nitric Acid- Reaction: $PbSO_4$(s) + $HNO_3 \rightarrow Pb(NO_3) \quad + HSO_4(aq)$. Equation (13)

Because $PbCl_2$ It is a sparingly soluble salt; a higher temperature will be required since it is heavier at room temperature.

Furthermore, there is a major drawback to using these two acids because the product is always sulfuric acid, which makes dissolution difficult. Hence, a higher temperature is required. But Nitric acid can decompose at a higher temperature into nitrogen oxides, so HCl would be better because it does not require an acid that is a strong oxidizing agent like nitric acid, which is far better at dissolving sulfides since there is no oxidation-reduction and change in valence state.

A complexing agent such as EDTA-

Reaction: $PbSO_4$(s) +$EDTA^{4-}$ →[PbEDTA]$^{2-}$+SO_4^{2-} Equation (14)

Dissolving with a complexing agent may be a better solution because EDTA forms stable complexes with lead, but an alkaline environment with a pH of around 8-9 will be required.

Thermal Treatment with Sodium Carbonate as a Flux-

$PbSO_4$(s) + $Na_2CO_3 \rightarrow PbO$ +Na_2SO_4 +CO_2 Equation (15)

This method produces PbO that is easily dissolved in HNO_3

3.4. REACTION MECHANISM OF EXPERIMENTS PERFORMED IN THE AUTOCLAVE

Experiments in the autoclave were performed at different temperatures (120℃, 150℃, and 180°C), and the shrinking diffusion model equation was used to calculate the activation energy for the metal recovered during the leaching process at different temperatures. The activation energy for each metal recovered was far less than 20Kj/mol, which confirmed that the reaction was diffusion-controlled. See **Figure 29** for the graph showing the Arrhenius plot of ln K plotted against (1/T) for the metal Bismuth. The slope of the straight line, as shown in the graph, is **(1935),** which, when multiplied by the universal gas constant, 8.314J/mol/K gives us the activation energy **-16.09kJ/mol**.

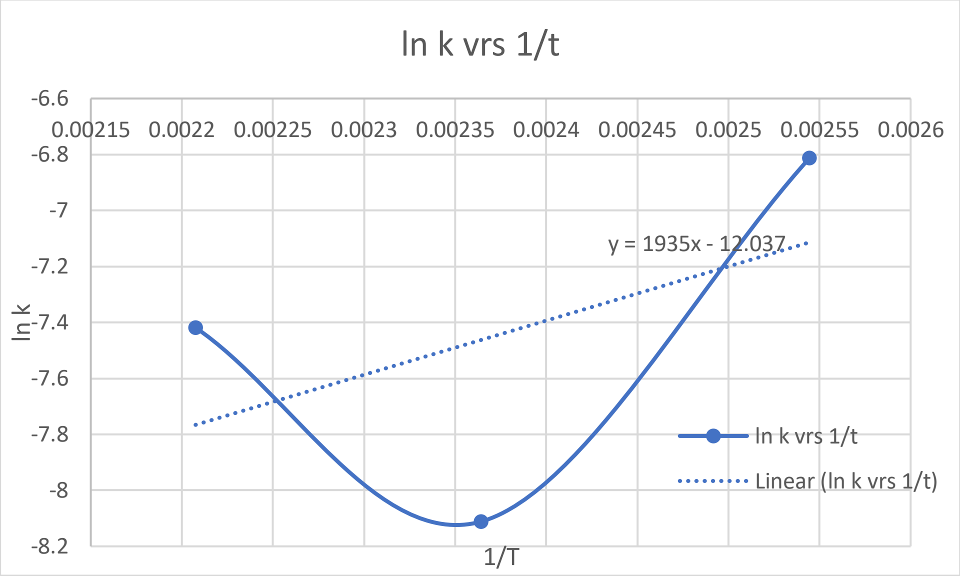

Figure 29:Arrhenius plot of ln K plotted against (1/T) for Bismuth

From the calculations of the activation energy and the graph shown, it is confirmed that the reaction is diffusion-controlled. The diffusion shrinking core model was used to describe reactions between fluids (HSO_4) and solids (Pb-concentrate), where diffusion through the lead concentrate is the slowest step. Since the reaction occurs in multiple steps, this implies that the overall reaction between the fluid (eg, gas) and the solid particle depends on how quickly the fluid diffuses through the inert, reacts, or product layer of the solid to encounter the unreacted core of the solid for the reaction to progress. This also hints that the chemical reaction here is faster than the diffusion process.

3.5. GENERAL DISCUSSION: COMPARING THE RESULTS WITH PREVIOUS WORK.

While there has been little or no work done, particularly on the hydrometallurgical treatment of Pb concentrate for the recovery of valuable metals, there has been a series of works done using high-pressure leaching and atmospheric leaching for the recovery of valuable metals. Though different materials were used for leaching, the methodology was the same as my work, and the results were consistent in some cases with my results.

The result I obtained from the leaching of Pb-concentrate with sulfuric acid was the leaching efficiency of 91% for Zinc(Appendix **3**). A similar result was obtained with the same method, where a solid residue of copper was leached with sulfuric acid in the presence of oxygen. A leaching efficiency of 92% for Zinc was obtained (Karimov et al., 2019). This result confirms that oxidation leaching in an autoclave with sulfuric acid is more effective for the recovery of zinc from different concentrates.

The leaching efficiencies I obtained for the experiments I conducted with lead concentrate using sulfuric acid under varying conditions of oxygen pressure, temperature, and leaching time, as was seen in Appendix 3, Table 8, and Table 9, were generally low. In contrast, (Stopic et al., 2024), conducted leaching experiments with slag and tionite using 5M of Sulfuric acid under similar conditions of oxygen pressure, temperature, and leaching time. They obtained high leaching efficiencies across all experiments with nearly complete extraction of Fe, Ti, and Al.

These results highlight an important difference in the leaching behaviors of the materials(lead concentrate slag and Tionite). The difference can be attributed to their distinct mineralogical properties.

Finally, the XRD result from the solid residue leached with atmospheric oxygen and nitric acid, as seen in **Figure 28**, shows that the samples have only two phases, namely anglesite ($PbSO_4$) which is dominant and rhombic sulfur. The presence of rhombic sulfur is responsible for the low leaching. On the other hand, the XRD pattern of the slag after leaching has a dominant phase of Calcium sulfate ($CaSO_4$) which implied that most elements were successfully leached. (Stopic et al., 2024).

3.6. CONCLUSION

The effective leaching and onward recovery of valuable metals from lead concentrates using hydrometallurgical methods requires pre-treatment before leaching with higher concentrations of acid. From our results, the solid residue, when further leached, obtained better leaching efficiencies compared to the Pb-concentrate that was initially leached in the autoclave.

GENERAL CONCLUSION

CONCLUSION

The focus of this work was to recover and separate valuable metals from lead concentrates using hydrometallurgical methods with a primary focus on metals such as bismuth, silver, Iron, calcium, lead, copper, and zinc. We used both an autoclave and a glass reactor to study the leaching behavior of these metals from a lead concentrate, with sulfuric acid and nitric acid serving as leaching agents.

From the experimental results of this work, we draw the following conclusions:

1. The hydrometallurgical method is a more viable alternative to the traditionally used pyrometallurgical methods when it comes to recovering valuable metals. It is environmentally friendly and consumes less energy than the latter.
2. From the leaching parameters used during the leaching, it can be said that temperature, leaching time, the amount of acid concentration, and oxygen pressure hugely influenced the leaching efficiency.
3. Under the experimental conditions in this thesis, Iron and Calcium were effectively leached in the high-pressure autoclave. Both experienced very good leaching efficiencies of 85% and 62% respectively.
4. Copper and Bismuth were moderately leached, reaching the leaching efficiencies of about 35% to 70% respectively (Table 9), in the autoclave and 59% to 88% (Table 14 and Table 12) in the glass reactor.
5. Lead could not be dissolved in the autoclave due to the leaching-resistant nature of sulfur that covers the lead during leaching, but using nitric acid as a leaching agent in the glass reactor, lead (Pb) was moderately leached, reaching up to 39%.
6. Zinc experienced rapid leaching during all the experiments in the autoclave. This may have been due to the availability of Zinc in leachable forms. This result in zinc is indeed favourable for extracting from Pb-concentrate using a hydro-metallurgical process.
7. Lastly, Silver experienced poor leaching efficiency in the autoclave but better leaching efficiencies in the glass reactor, reaching up to ~80%. Due to its complex association with other minerals in Pb-concentrates, it may require alternative or pre-treatment methods for effective leaching.

As a final conclusion, this thesis work confirms the importance of hydrometallurgical methods for selectively extracting valuable metals from Pb-concentrates, which offers several advantages in terms of energy efficiency, metal selectivity, and environmental impact.

The result of my thesis will provide further insight into the recovery of precious metals from complex sulfide ores.

Recommendations and Future Work

Based on our research findings, we would like to recommend the following for future work:

- For the hydrometallurgical treatment of lead concentrates to achieve the highest possible leaching efficiency, the Pb-concentrate must be pre-treated in a glass reactor and further leached in an autoclave with higher concentrations of acid at higher temperatures.
- The solid residue can further be leached using hydrochloric acid since the residue is the mineral anglesite $PbSO_4$ which is a soluble salt.
- Try H_2O_2 that dissolve many metals.

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APPENDIX

Lead (Pb)

Before Leaching:

Mass of Lead Concentrate: 70g

Volume of Solution: 700ml

Concentration of Pb in Pb Concentrate: 56.49%

Mass of Pb in 70g of Pb Concentrate: $70g \times \frac{56.49}{100} = 39.543g$

After Leaching:

Mass of Solid Residue 52g

Volume of Leachate=711.5ml=0.7115l

Concentration of Pb in solution after leaching =4.2mg/l

Mass of Pb in Leachate = 4.2mg/l × 0.7115l = 2.9883mg =0.0029883g

Leaching Efficiency (%)= $\frac{Mass\ of\ Pb\ dissolved\ in\ Leach\ solution}{Intial\ \ Mass\ of\ Pb\ in\ Pb{-}concentrate} \times 100$

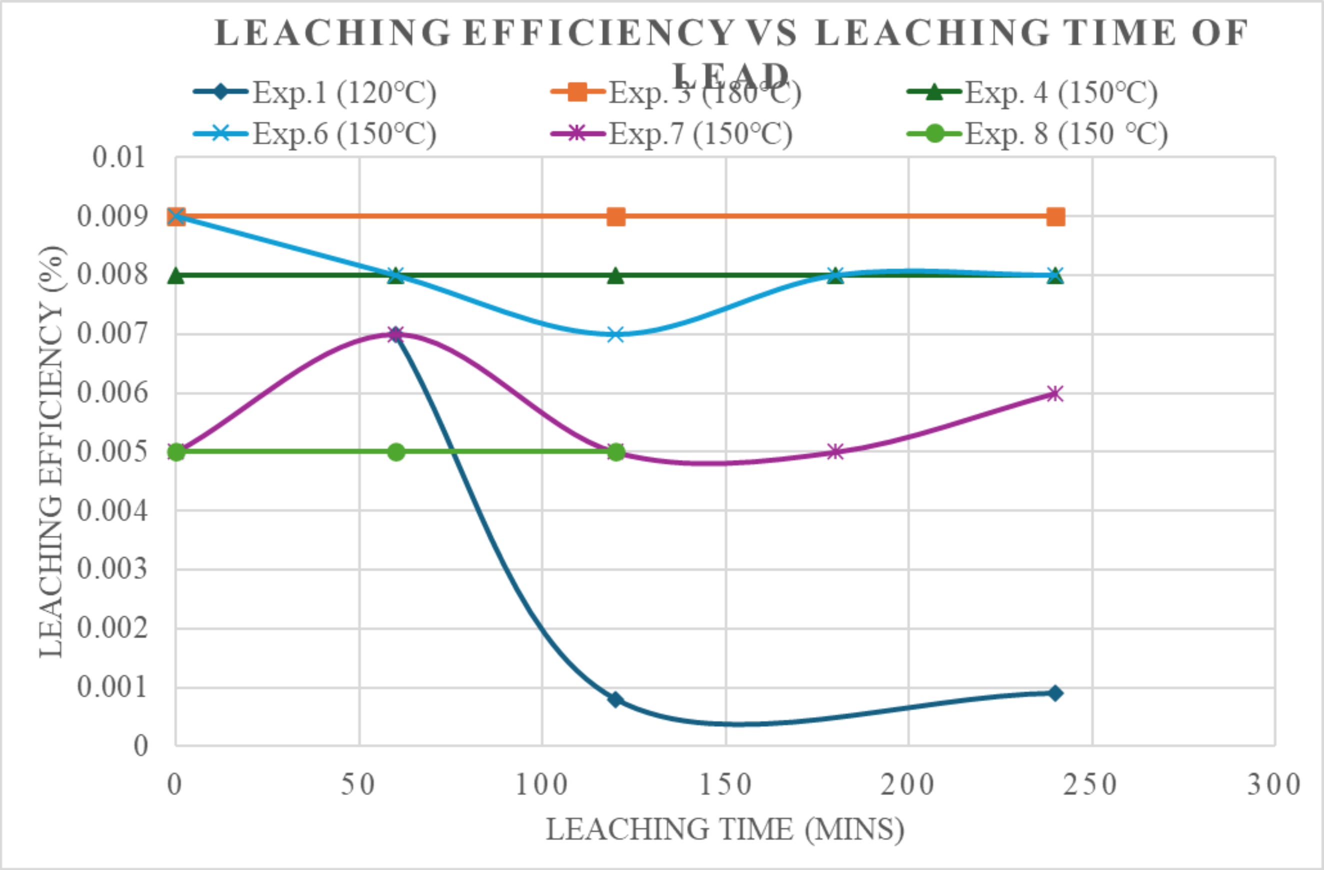
Leaching Efficiency = $\frac{0.0029883\text{g}}{39.543g} \times 100$=0.008%.

Appendix 1. Sample Calculation of Leaching Efficiencies

Appendix 2: Leaching efficiencies of Pb from experiments 1-10.

Exp No	Time (mins)	Conc. (mg/l)	Volume(ml)	Temperature (°C)	Leaching Efficiency (%)
1-1	60	4.05	661	120	0.007
1-3	120	4.9	661	120	0.0008
1-5	240	5.1	661	120	0.0009
3-1	60	5.3	706	180	0.009
3-3	120	5.15	706	180	0.009
3-5	240	5.1	706	180	0.009
4-1	0	4.2	711.5	150	0.008
4-2	60	4.4	711.5	150	0.008
4-3	120	4.6	711.5	150	0.008
4-4	180	4.8	711.5	150	0.008
4-5	240	4.8	711.5	150	0.008

6-1	0	5.7	636.5	150	0.009
6-2	60	4.9	636.5	150	0.008
6-3	120	4.6	636.5	150	0.007
6-4	180	4.7	636.5	150	0.008
6-5	240	5.0	636.5	150	0.008
7-1	0	3.5	589	150	0.005
7-2	60	4.5	589	150	0.007
7-3	120	3.4	589	150	0.005
7-4	180	3.6	589	150	0.005
7-5	240	4.1	589	150	0.006
8-1	0	3.0	630	150	0.005
8-2	60	2.9	630	150	0.005
8-3	120	3.2	630	150	0.005
9-1	0	3.8	631.5	150	0.006
9-4	240	3.5	631.5	150	0.006
10-1	0	< 0,5	538	150	-
10-2	120	4.3	538	150	0.02



Appendix 3. Graph showing the leaching efficiency of Pb vs. time

Appendix 4: Leaching Efficiencies of Iron (Fe) from Experiments 1-10.

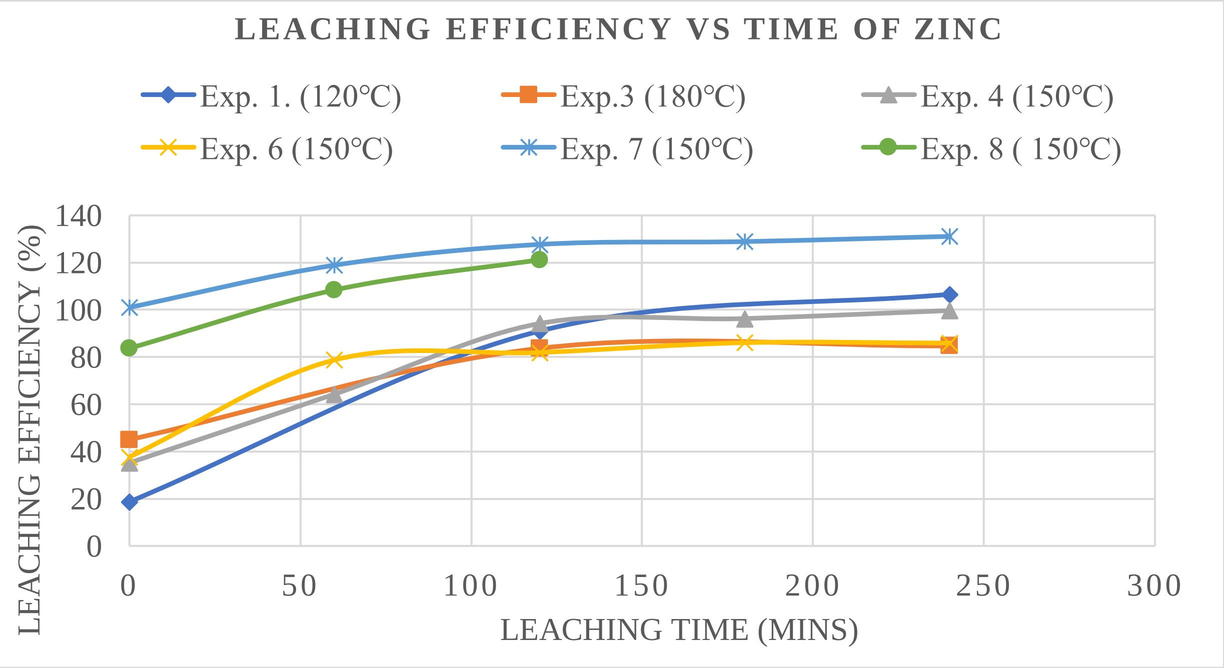
Exp No	Time (mins)	Conc. (mg/l)	Volume(ml)	Temperature (°C)	Leaching Efficiency (%)
1-1	0	915	661	120	24.1
1-3	120	2610	661	120	69.0
1-5	240	3240	661	120	85.6
3-1	0	1730	706	180	48.
3-3	120	2570	706	180	72.6
3-5	240	2910	706	180	82.2
4-1	0	1200	711.5	150	34.1
4-2	60	1850	711.5	150	52.65
4-3	120	2560	711.5	150	72.8
4-4	180	2670	711.5	150	75.9

4-5	240	2820	711.5	150	80.25
6-1	0	801	636.5	150	20.4
6-2	60	2190	636.5	150	55.8
6-3	120	2380	636.5	150	60.6
6-4	180	2490	636.5	150	63.4
6-5	240	2510	636.5	150	63.9
7-1	0	1830	589	150	43.1
7-2	60	2650	589	150	62.4
7-3	120	3090	589	150	72.8
7-4	180	3150	589	150	74.2
7-5	240	3340	589	150	78.7
8-1	0	1500	630	150	37.8
8-2	60	2460	630	150	61.9
8-3	120	2730	630	150	68.8
9-1	0	1100	631.5	150	27.8
9-4	240	1640	631.5	150	41.4
10-1	0	2250	538	150	48.42
10-2	60	2880	538	150	61.98

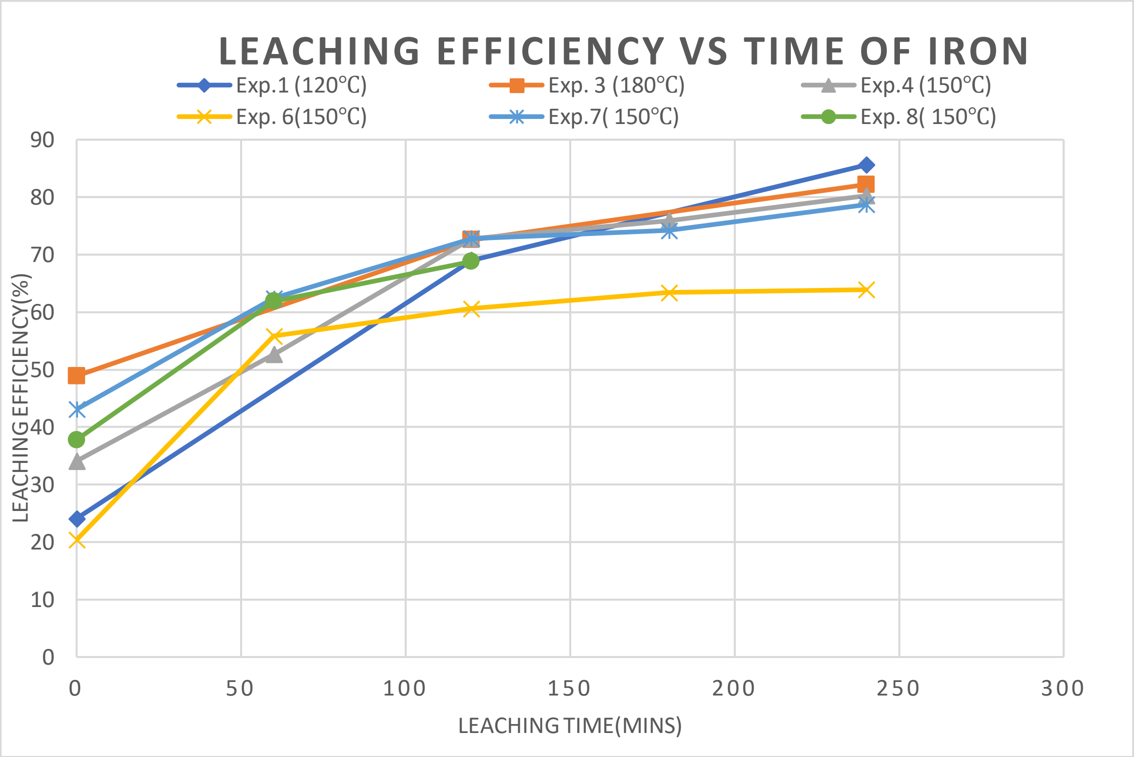
Appendix 5: Leaching efficiencies of Zn from experiments 1-10.

Exp No	Time (mins)	Conc. (mg/l)	Volume(ml)	Temperature (℃)	Leaching Efficiency (%)
1-1	0	150	661	120	18.7
1-3	120	730	661	120	91.0
1-5	240	855	661	120	106.6
3-1	0	339	706	180	45.0
3-3	120	629	706	180	83.7
3-5	240	636	706	180	84.72
4-1	0	262	711.5	150	35.2
4-2	60	479	711.5	150	64.3
4-3	120	702	711.5	150	94.2
4-4	180	717	711.5	150	96.3
4-5	240	743	711.5	150	99.7
6-1	0	314	636.5	150	37.7

6-2	60	656	636.5	150	78.78
6-3	120	682	636.5	150	81.9
6-4	180	717	636.5	150	86.1
6-5	240	716	636.5	150	85.9
7-1	0	909	589	150	101.0
7-2	60	1070	589	150	118.9
7-3	120	1150	589	150	127.7
7-4	180	1160	589	150	128.9
7-5	240	1180	589	150	131.1
8-1	0	704	630	150	83.7
8-2	60	912	630	150	108.4
8-3	120	1020	630	150	121.2
9-1	0	528	631.5	150	62.9
9-4	240	668	631.5	150	79.6
10-1	0	1070	538	150	108.6
10-2	120	1200	538	150	121.8



Appendix 6: Leaching Efficiency vs Time of Zn from Experiment (1-8).



Appendix 7: Leaching Efficiency Vs Time of Iron for Experiment 1-8.