Demineralization of Low-grade Ethiopian Coal through Alkali-acid Leaching Method to Use in Cement Industries

Chekole Demisew Tamene

A Thesis Submitted to the Department of Chemical Engineering

School of Mechanical, Chemical, and Materials Engineering

Presented in Partial Fulfillment of the Requirement for the Degree of Master of Science in Chemical Engineering (Specialization in Process Engineering)

Office of Graduate Studies

Adama Science and Technology University

February, 2025

Adama, Ethiopia

Demineralization of Low-grade Ethiopian Coal through Alkali-acid Leaching Method to Use in Cement Industries

Chekole Demisew Tamene

Advisor: Zelalem Tumsa (Ph.D.)

Co-advisor: P. Selvakumar (Ph.D.)

A Thesis Submitted to the Department of Chemical Engineering,

School of Mechanical, Chemical, and Materials Engineering

Presented in Partial Fulfillment of the Requirement for the Degree of Master of Science in Chemical Engineering (Specialization in Process Engineering)

Office of Graduate Studies

Adama Science and Technology University

February, 2025

Adama, Ethiopia

DECLARATION

I hereby declare that this Master Thesis entitled “Demineralization of low-grade Ethiopian coal through alkali-acid leaching method to use in cement industries” is my original work. That is, it has not been submitted for the award of any academic degree, diploma or certificate in any other university. All sources of materials that are used for this thesis have been duly acknowledged through proper citation.

Chekole Demisew Tamene	_____	_____
Name of student	Signature	Date

RECOMMENDATION OF ADVISORS

we, the advisors of this thesis, hereby certify that we have read the revised version of the thesis entitled “Demineralization of low-grade Ethiopian coal through alkali-acid leaching method to use in cement industries” prepared under our guidance by CHEKOLE DEMISEW submitted in partial fulfillment of the requirements for the degree of Master of Science in Process Engineering. Therefore, we recommend the submission of revised version of the thesis to the department following the applicable procedures.

Zelalem Tumsa (Ph.D.)	_____	_____
Major Advisor	Signature	Date
P. Selvakumar (Ph.D.)	_____	_____
Co-advisor	Signature	Date

APPROVAL SHEET

We, the advisors of the thesis entitled “Demineralization of low-grade Ethiopian coal through alkali-acid leaching method to use in cement industries” and developed by CHEKOLE DEMISEW, hereby certify that the recommendation and suggestions made by the board of examiners are appropriately incorporated into the final version of the thesis.

Zelalem Tumsa (Ph.D.)	_____	_____
Major Advisor	Signature	Date
P. Selvakumar (Ph.D.)	_____	_____
Co-advisor	Signature	Date

We, the undersigned, members of the Board of Examiners of the thesis by CHEKOLE DEMISEW have read and evaluated the thesis entitled “Demineralization of low-grade Ethiopian coal through alkali-acid leaching method to use in cement industries” and examined the candidate during open defense. This is, therefore, to certify that the thesis is accepted for partial fulfillment of the requirement of the degree of Master of Science in Process Engineering.

Ashenafi Hailu (Ph.D.)	_____	_____
Chair Person	Signature	Date
Melaku Tesfaye (Ph.D.)	_____	_____
Internal Examiner	Signature	Date
Ali Shemsedin (Ph.D.)	_____	24/02/2025
External Examiner	Signature	Date

Final approval and acceptance of the thesis is contingent upon submission of its final copy to the Office of Postgraduate Studies (OPGS) through the Department Graduate Council (DGC) and School Graduate Committee (SGC).

_____	_____	_____
Department Head	Signature	Date
_____	_____	_____
School Dean	Signature	Date
_____	_____	_____
Office of Postgraduate Studies, Dean	Signature	Date

ACKNOWLEDGEMENT

I would like to express my sincere gratitude and appreciation to my advisor, Dr. Zelalem for his guidance, support, and expertise throughout the research journey, and my co-advisor Dr. P. Selvakumar for his valuable support and comments on this work.

I would like to acknowledge the entire Mugher Cement Enterprise for providing a conducive environment for my research, especially, Mr. Mikiyas Tadesse, Mr. Endeshaw Mognnet, and Mr. Bizuneh Dejene for their valuable contributions and assistance in demonstrating my research there. Your technical expertise, insightful suggestions, and unwavering support have greatly enhanced the quality of my research. I am truly grateful for your patience, willingness to help, and the countless hours you dedicated.

My gratitude extended to AAiT (Addis Ababa Institute of Technology) for their special permission and hospitality to perform my experiment in their laboratory. Also for Mr. Leta Guta and Mr. Demeke of ASTU for their kind cooperation.

Lastly, I would like to express my appreciation to all the individuals who have contributed to my research in various ways but are not specifically mentioned. Your contributions, whether big or small, have played a significant role in shaping the outcome of this work.

TABLE OF CONTENTS

TABLES PAGE

LIST OF TABLES

LIST OF FIGURES AND ILLUSTRATIONS

ABSTRACT

In order to improve Ethiopian coal's qualities and lower its ash and sulfur content, this study looks into the chemical demineralization process. The demineralization efficiency is known that affected by process parameters positively or negatively. In order to investigate the effect of demineralization parameters without significantly sacrificing the organic components of the coal and to make the coal suitable for cement industries, Ethiopian coal (Boroda coal) was leached in a stepwise manner under varying process conditions including concentration, leaching temperature, leaching time, and coal particle size. The effect of these process parameters was investigated with respect to demineralization efficiency and calorific value improvement. To compare and contrast the demineralization capacity as well as the CV of coal, this inquiry tried to characterize and analyze the raw Ethiopian coal (Boroda coal) and the demineralized coal proximally and instrumentally. In order to compare the effectiveness of coal leaching and physical beneficiation, froth flotation of Boroda Coal is conducted. Although the percent demineralization and CV of the coal slightly increased after 7.5% concentration and 3hrs of contact time, the two-step NaOH-HF leaching gave 78.9% ash removal and 50.11% desulfurization and also the CV improved by 21.8% to 5207 Kcal/kg. The first stage NaOH-HF leaching was 28.8%, thus, the second stage increased the ash removal to 78.9%. The proximate analysis indicated that 52.52% of demineralization was achieved with 10.3% CV improvement to 4715 Kcal/kg.

Key words: demineralization, stepwise leaching, ash.

LIST OF ABBREVIATIONS

AAiT	Addis Ababa Institute of Technology
ASTM	American Society Testing and Materials
ASTU	Adama Science and Technology University
BSS	British Standard Sieve
C_2S	Di-calcium Silicate
C_3S	Tri-calcium Silicate
CV	Calorific Value
NCV	Net Calorific Value
NOx	Nitrogen Oxides
OFAT	One Factor At a Time
SEM	Scanning Electron Microscopy
SOx	Sulfur Oxides
VM	Volatile Matter
XRD	X-ray Diffractometer

CHAPTER ONE

1. INTRODUCTION

1.1. General Background

1.1.1. Coal and its Definition

A complex mixture of organic chemical components including carbon, hydrogen, and oxygen along with minor amounts of nitrogen, sulfur, and trace elements, is called coal. It is a combustible sedimentary organic rock that is often deep-brown to black in color. It is composed of plant remains that have undergone heat and pressure-induced compaction, hardening, chemical alteration, and metamorphosis throughout geologic time. Stated differently, it is composed of plant debris, small plant kingdoms (such as algae, fungi, and ferns), and other plant debris that has been consolidated between other rock strata and changed by biochemical and physicochemical degradation (i.e., the result of millions of years of combined bacterial action, high pressure, and high heat) *(Abraham, 2018; Usman et al., 2022a)*. This transformation of plant materials to coal is *coalification*. It is the process by which plant and tiny plant detritus is converted from peat to lignite, and subsequently to anthracite, the higher class of coal. It begins with the deposition of plant debris in low-oxygen environments, typically marshes or swamps, such as leaves, branches, and roots. With time, this organic material builds up to create a layer known as peat. Peat has a high water content and is made up of partially degraded plant material. Plant material layers build up on top of the peat, which increases the weight and pressure of the surrounding sediments. The peat becomes denser as a result of this pressure compressing it and progressively removing the water *(Yoseph, 2004)*.

The most common and widely available fuel in the world for a variety of uses, coal is the least expensive energy source whether used directly to provide heat energy or to generate electricity using a steam turbine *(S.K. Behera et al., 2018)*. Because it has a higher energy density than most other energy sources, it is essential for producing power and serving as a feedstock for the steel, iron, and cement industries, among others, to produce heat energy *(Wijaya & Zhang, 2011)*. Coal is used in the cement industry to burn raw materials at high temperatures (about 1450^{o}C) in kilns and in calcination chambers for high temperatures (around 950^{o}C) at amazing input rates *(S. K. Behera et al., 2017b)*.

The primary use of coal is the conversion of it into electricity and a heat source for the cement industry and metallurgical technologies, which results in the emissions of various air pollutants and greenhouse gases including SO_x (sulfur oxides), NO_x (nitrogen oxides), and particulate matters *(S.K. Behera et al., 2018; Wijaya & Zhang, 2011)*. The ultrafine particulates and trace metals generated from coal are potentially carcinogenic to humans *(Wijaya & Zhang, 2011)*.

1.1.2. Classification of Coal

According to American society testing and materials (ASTM) standards, coal is classified into four types as lignite, sub-bituminous, bituminous, and anthracite, despite of subdivisions in each category *(Usman et al., 2022a)*.

Lignite: This low-rank, brownish-black coal, has a high moisture and volatile matter content. Its energy and carbon contents are low, whereas its moisture content is high. The newest fossil fuel, lignite is thought to date back approximately 60 million years. Because of its brief existence, it is not exposed to high temperatures or pressures, and as a result, its energy density is only 18 MJ/kg *(Yoseph, 2004)*.

Subbituminous: Dark black coal with a moisture level of 20–30% is called subbituminous coal. Sub-bituminous coals, which date back around 251 million years, are some of the youngest types of coal. Sub-bituminous coal is the most prevalent type, making up 30% of total coal deposits. The energy content of sub-bituminous coal ranges from 16.88 to 25.32 MJ/kg. Typically, this coal has a carbon content of 35–45%, which is higher than the 25–35% found in lignite *(Demoze, 2007; Usman et al., 2022a)*.

Bituminous coal: With a high carbon concentration and a relatively high energy density of 27 MJ/kg, bituminous coal is the second-highest quality coal. It is dense and includes 45 to 86 percent carbon. It is one of the oldest and most abundant fossil fuels, having been buried for about 300 million years. It is a vital fuel and raw material for the steel and iron industries, including the cement industry, to use directly without advanced physical or chemical treatment *(Demoze, 2007)*.

Anthracite: The earliest kind of coal is anthracite, which formed from buried flora 350 million years ago. With a carbon concentration ranging from 86 to 98 percent, it is the hardest compact form of coal with low moisture content and impurities. It also has the highest metamorphic rank

of all coals. Anthracite has the potential to fire at very high temperatures *(Demoze, 2007; Yoseph, 2004).*

1.1.3. Coal Characterization and Quality Parameters

The two types of coal analysis techniques that are used to describe are proximate and ultimate analysis. An easy way to report the principal organic elemental composition of coal is to use the Ultimate Analysis of Coal. An ultimate analyzer is used for this type of analysis, where a coal sample is burned to determine the weight percentage of carbon, hydrogen, nitrogen, sulfur, and ash in the sample. On the other hand, in order to measure the coal's moisture content, volatile matter content, fixed carbon content, and ash yield, proximate analysis is used where the coal is heated under different conditions for a variable period of time. The proximate analysis include:

Moisture content: The amount of water that is contained in coal is referred to as its moisture content. Coal can contain three types of moisture: inherent moisture contained in its pores (or capillaries), free moisture on the surface of coal particles, and structural moisture that is chemically bound to organic or mineral components. Increased moisture content during coal burning can have an impact on heat transmission and combustion efficiency. Thus, low moisture content is generally preferred for steady and effective burning.

Calorific value: The term "calorific value" refers to a coal's capacity to hold heat, and it is used to calculate how much coal will be required to generate a given amount of heat. The energy content of coal is expressed by its calorific value, which is commonly expressed in British thermal units per pound (Btu/lb) or kilocalories per kilogram (Kcal/kg).

Ash: The quantity of non-combustible material (ash residue) that remains after coal is burned with aeration (oxidation) is known as the ash content of coal. A noncombustible residue that is produced when coal burns in the presence of air and is made up of mineral matter and inorganic complexes found in the original coal component. Therefore, *"the result of the determination is 'ash' and not 'ash content' as coal does not contain any ash" (Zhu, 2014).* Because it gives an indicator of the amount of incombustible material present, the ash yield is frequently used to determine the grade or quality of coal.

Volatile matter: Volatile matter (VM) refers to the products liberated as a result of thermal decomposition during heating coal at high temperatures in the absence of air. VM

content may be used to establish the rank of coals, to establish burning characteristics such as combustibility (reactivity) of coal, and ease of ignition and hence flame stability *(ASTM, 2013; Zhu, 2014).*

Sulfur content: Coal contains sulfur in the forms of organic sulfur compounds, sulfates, and iron pyrites. Increased sulfur emissions during burning from high sulfur coal can worsen air pollution and other environmental issues and technical problems is some industries.

Fixed carbon: The term "fixed carbon" describes coal's non-volatile carbon content. It stands for the carbonaceous substance that is left over after ash, moisture, and volatile materials are eliminated *(Zhu, 2014).*

Nitrogen: It is found in molecules. Coal typically contains between 0.5% and 2.5% of nitrogen by weight. Within this range, there may be notable variances, nevertheless. The main organic molecules that contain nitrogen in coal are pyridine, pyrrole, and quinoline. Nitrogen can react with coal to produce a variety of nitrogen oxides (NOx), which are recognized to cause air pollution and have negative effects on the environment and human health *(D. Wu et al., 2011).*

In addition to these listed, other parameters may be used to quantify the coal quality such as ash fusion temperature, grindability index, petrographic composition, amount of trace elements (eg. heavy metals) can be used to characterize a coal.

1.1.4. Overview of Ethiopian Coal

Ethiopia has a good potential of coal reserves to cover its local coal consumption in many industrial areas. According to the Geological Survey of Ethiopia, there are locations in which potential coal reserves have been identified with amounts of more than 430 million tons of coal *(Ashenafi, 2021; Tegegne, 2019).*

For instance, coal has been discovered and explored in some locations (coal reserves) in different parts of the country such as Yayu & Delbi-Moye (in Illubabor), Chilga (in Gonder), Mush valley (in N. Shoa), Kamashi (in Beninshangul), Wuchale (in Wollo), Arjjo, Didessa, Nejo and Mendi (in Wollega) and other areas are explored or mined (eg. Kamashi & Yayo, ...) and others are under exploration (Demoze, 2007; Yoseph, 2004). Other coal occurrences and mining are taking

place such as Gojeb, Chinda, Kindo, Halul, Lalo-Sapo, Boroda, Dawro-Tarcha, and Wake in the Southern part of the country.

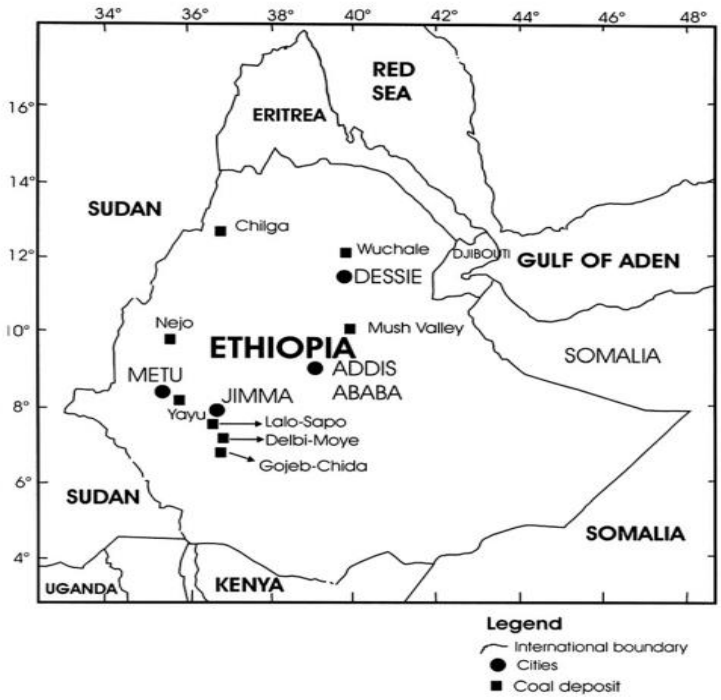

Figure 1-1: Locations of some identified coal mines & deposits in Ethiopia (Source: Demoze, 2007)

Even if Ethiopia has a large potential for coal mining, the Ethiopian coal reserves and mining sites are categorized under lignite to sub-bituminous with low heating value and high volatile matter and ash content which makes it very difficult to use directly in kiln firing or other different industries. That is why cement industries are obliged to purchase foreign coal to blend with local coal to mitigate the operational effect of local coal.

1.2. Statement of the Problem

The utilization of low-grade coal in numerous applications leads to technical difficulties, it produces a lot of ash and has low calorific value. That is a cause of environmental pollution and simultaneously reduces the production efficiency of cement industries *(Carlson & Adriano, 1993)*. One of the frequent problems that arise due to the utilization of low-grade Ethiopian coal is the disturbance of operations in cement production such as lowering the efficiency of burners, closure of the cyclone downcomers, ring formation in the kiln and snowman development at the kiln hood, low burning capacity of the raw mix and low flame characteristics leads to *rushing*.

The utilization of such coal can also be a source of sulfur and other unwanted substances that form sulfide compounds which increase the sulfate content of the clinker by decreasing the formation of C_3S in the clinkerization process. Thus, cement plants in Ethiopia uses foreign coal, mixed with the local coal to enhance the CV of a coal to burn the raw mix and to overcome technical problems.

Despite of a large quantity coal deposits in Ethiopia and such a challenges to use in cement plants, the chemical leaching to improve the quality is not examined except some physical beneficiations. Being aware that dilute HF is more effective than other acids in ash removal, the researchers didn't try the two step leaching of a coal with the combination of strong bases such as NaOH. The other challenge for most research papers is to attain high ash removal with relatively low temperatures and concentrations. Therefore, this study tried to leach Ethiopian Boroda coal as a new raw material and to combine the good characteristics of the aforementioned towards ash removal. This paper also tried to address the issues related to the temperature and concentrations in which the leaching is conducted by dilute two step NaOH-HF solutions at a low temperatures ($\leq 100^oC$). To overcome these problems, two step NaOH-HF leaching experiments of Boroda coal has been conducted in this enquiry.

1.3. Objective of the Study

1.3.1. General Objective

The aim of this work was demineralization of low-rank Ethiopian coal (Boroda Coal) to improve its quality characteristics so that to use in cement industries.

1.3.2. Specific Objectives

The specific objectives of the study was:

- Characterization of Ethiopian coal (Boroda Coal)
- Stepwise leaching of Boroda coal, and to investigate the effects of treatment parameters on demineralization.
- Physical beneficiation (froth flotation) of Boroda coal to compare with chemical leaching

1.4. Significance of the Study

Nevertheless Ethiopia has a large number of coal deposits, the demineralization idea to improve coal CV and general quality characteristics is rare or negligible. Still, low-grade coal is utilized even if it has serious effects as depicted in the problem statement. This study may be important to introduce the methods of two step chemical leaching to improve the CV of coal and reduce coal ash-bearing minerals as well as sulfur to improve low-grade Ethiopian coal quality characteristics. The study tried to investigate the possibility of demineralization at a reduced concentration of selective leaching chemicals approaching cost soundness that may empower other researchers to go through. By using two-step demineralization, this demineralization study may be '*a forward*' to keep the organic nature of the coal, which was a significant problem during chemical leaching. Although it requires further economic and methodological studies, the study may create a new thinking of effective utilization of low-grade Ethiopian coal.

1.5. Scope of the Study

This study focused on the characterization and then chemical leaching of low-grade Ethiopian coal in a stepwise method by considering factors affecting the demineralization efficiency. Moreover, the study tried to investigate the influence of leaching factors such as temperature, reagent concentration, leaching time, and size of coal particles on the demineralization and CV of coal. This coal demineralization study also extended its scope up to the characterization of coal before and after leaching to compare the effectiveness of the leaching process. Additionally, the chemical analysis of coal ash before and after demineralization was done to understand the removal efficiency of each impurity. The coal beneficiation of low-grade Boroda Coal with froth flotation is also done to make a comparison to chemical leaching. Finally, the leaching parameters were analyzed and interpreted concerning the demineralization efficiency and the CV, and for more, instrumental analysis were done.

CHAPTER TWO

2. LITERATURE REVIEW

2.1. Occurrence of Mineral Matters in a Coal

Impurities or mineral matter are the broad terms used to describe substances or compounds that reduce the calorific value of coal. Mineral materials and moisture are also included. Low-grade or low-quality coals, also referred to as brown coals, are rich in impurities and have not been used to the same degree as higher rank coals because of their unfavorable qualities and poor quality *(S. K. Behera, Chakraborty, et al., 2018)*. Low-grade coals have a number of undesirable qualities, including high ash content (usually between 30% and 50%), high moisture content (usually between 4% and 20%), high sulfur content (over 1.3%), low calorific values (between 2500 and 5000 Kcal/kg), low Hardgrove Grindability Index (HGI), which is a measure of the coal's resistance to grinding, high milling power consumption, and increased mill wear and maintenance costs of mill systems *(S. K. Behera et al., 2017a)*.

Coal is a sedimentary rock and is composed of three categories of substances *(Behera et al., 2018)*:

(1) Organic carbonaceous matter called macerals,
(2) Inorganic (crystalline type) minerals which are non-combustible resulted in the ash formation, and
(3) Fluids.

The liquid is found inside the pores of a coal or in the spaces between its solid components. The two main fluids found in coal before it is mined are moisture and methane. The moisture may come from surface or structural sources, and it comes out of the coal matrix at varying temperatures. Any inorganic element that is connected in some way to an organic component (C, H, O, N, or S) is referred to as mineral matter *(Vassilev & Vassileva, 1996)*.

Mineral materials contained in coal have been classed as inherent or incorporated minerals and extraneous by S.K. Behera, U. Kumari, and Wijaya & Zhang, (2011). Extraneous or excluded mineral matter is the term used to describe the minerals that are not a part of or connected to the coal matrix. The pollution that results from coal handling, mining, and the natural coalification

process is the cause of the extraneous mineral matter. Through coal preparation techniques, these impurities can frequently be eliminated because they are not chemically bound to the coal. Shale, sandstones, and intermediate rocks that were introduced during the mining of the coal bed are examples of extraneous mineral materials, as are partings and lenses found in the coal seam. In addition to the aforementioned, extraneous mineral materials that are deposited in the coal seam after it forms can contain pyrite, ankerite, and calcite *(Huggins, 2002; Vassilev & Vassileva, 1996)*. They consist of water, soil particles, and rocks and minerals. In the original sedimentary environment where coal developed, rocks, shale, clay, and other minerals may have been present. These elements can be found in coal. During the mining, processing, transportation, and storage activities, coal may also collect surface filth and dust, which are typically eliminated through washing and cleaning procedures. Coal typically contains moisture because of exposure to rain or high relative humidity. Moisture is seen as an exogenous contaminant even if it is not an intrinsic impurity because drying procedures can eliminate it *(Meshram et al., 2015)*.

Minerals contained inside or encircled by an organic matrix are known as inherent or included minerals. Examples of intrinsic mineral matter include the pyrite group of minerals, quartz, carbonate, and clays. They form a bond with the structure or matrix of coal. Meshram et al., (2015) and S.K. Behera, U. Kumari, (2018) also grouped these inherent minerals into *clay minerals* (which distribute widely and are major content of the coal matrix, including the abundant kaolinite, illite, sericite, montmorillonite, and others are the most common clay minerals), *sulfides* (which includes pyrite, marcasite most commonly and galena, chalcopyrite, millerite, bronite, etc. rarely.), *oxide minerals* (quartz & limonite in common and halcedony, hematite, magnetite, rutile, anatase, brookite, and others in rare amount), *phosphate minerals* (rarely bounded minerals like apatite, goyazite, gorceixite, crandallite, monazite, etc.), *carbonate minerals* (calcite & siderite in abundant amount, dolomite & ankerite in common, and witherite, dawsonite, strontionite, aragonite and magnesite of very small amount), *sulfate minerals* (including barite, gypsum, anhydrite, basanite, jarosite, szomolnokite, rozenite, mlanterite, coquimbite, rosmerite, etc. rarely), *chloride minerals* (halite & sylvite are common and bischofite rarely), *hydroxide minerals* (which include bauxite in common and gibbsite & diaspore rarely), *feldspar minerals* (incorporate plagioclase, albite, sanidine & anorthite), and other rarely found *silicate minerals* (including biotite, zircon, tourmaline, garnet, kyanite,

staurolite, epidote, augite, hornblende, topaz, prochlorite, penninite, analcime, …) and *native elements* (eg. Au, Ag, Pt, S, etc.).

2.1.1. Quality Characteristics of Ethiopian Coal

The calorific values of the coal deposits in Ethiopia range from 2490 to 6900 Kcal/g. The deposits have a low to high ash content (2.4–65%), medium moisture (2.7–21.4%), and volatile matter (3.0–46.3%). The findings of the investigation of proximate and calorific values showed that the coal reserves in Ethiopia range from lignite to sub-bituminous coal. But, because of a strong geothermal gradient, the coal seams close to the acidic volcanic intrusions underwent a metamorphosis that resulted in a semi-anthracite stage *(Ahmed, 2007; Yoseph, 2004).*

The study conducted by Ahmed Wolela (2007), confirmed that some Ethiopian coals had 11.5–46.53% volatile matter, 11.5–56.9% fixed carbon, 5.3–58.3% ash content, and sulfur contents ranging from 0.2 to 2.39% of which calorific values range from 2626 to 6743 cal/g. The elemental hydrogen content ranges from 4.2 to 6.57%, the carbon content is 60.3–80.22%, the nitrogen content of 0.8–2.27%, and the oxygen content covers the range from 15.98 to 32.69%, as he investigated.

The coals in the Delbi area are classed as lignite to high volatile bituminous coals and have low moisture content, medium to low ash percentage, and high to medium volatile matter, according to a full statement of his judgment. On the other hand, a strong geothermal gradient caused the coal seams close to the acidic volcanic intrusions to undergo a metamorphosis into a semi-anthracite stage. However, the Moye coals are typically classified as high volatile B bituminous to subbituminous. He also investigated the Chilga coals have 16.6–49.5% ash content and 2430–4599.5cal/g heating values, and the ash content of Yayu coals ranges from 3.31 to 59.3%, and the calorific value from 1173 to 5930 cal/g. Having that low to medium ash content, low to medium calorific value, and medium to high volatile matter, he grouped the Nejo, Gojeb-Chida, Wuchale, Chilga, Yayo, and Mush Valley coals as lignite to sub bituminous.

Due to their high volatile matter, low to medium moisture, low to medium sulfur, high ash content (mineral content), and low to medium calorific value, the majority of Ethiopian coals are lignite to bituminous, making them difficult and unsuitable for use in industries, particularly the cement industry, without beneficiation. Coal quarries can varies greatly in quality, which makes it challenging to control while burning the coal in burners used in the cement industry.

In spite of this, Ethiopia's government imposed a rule requiring all cement companies to utilize 80% domestic coal and 20% imported coal from outside the country in order to encourage domestic coal mining. Thus, due to their large amount of impurities and low calorific value, Ethiopian coals are not suitable to use in cement industries, causing various operational, mechanical, and quality problems.

2.2. Coal Demineralization

2.2.1. Why Coal Demineralization?

A complex mixture of both biological and inorganic components, the composition of coal varies depending on the conditions that exist during the coalification process. The inorganic substance is primarily mineral matter, while the mixture of organic materials is typically flammable. The coal may absorb various foreign materials (mineral matters) during the coalification process; they are typically referred to as "impurities" or "gangue." *(S. K. Behera, Kumari, et al., 2018; Bhatti et al., 2020).* These impurities are moistures, mineral matters, volatile matters and others *(Bilgin et al., 2021a).* Therefore, the process of separating (reducing) these impurities from raw mined coal is known as coal beneficiation or demineralization. This process improves the quality attributes of the fuel, reduces pollution, and occasionally increases its calorific value. In order for coal to be accepted as a primary energy source, it must first be beneficiated in order to reduce mineral matter, improve combustion behavior, prevent environmental pollution, improve grindability, reduce slagging and fouling, and be compatible with emission control equipment. For coal cleaning purposes, physical (beneficiation) and chemical cleaning (leaching) processes have been developed in various studies earlier *(S. K. Behera, Kumari, et al., 2018)*. In recent studies, biological (microbial) demineralization methods also investigated *(Dhawan & Kumar, 2019)* in addition to the familiar demineralization techniques.

2.2.2. Physical Coal Demineralization

The removal of coal impurities (the ash-forming components and inorganic sulfur) without changing the chemical composition of the coal or impurities is known as physical coal cleaning, and it is a commonly used commercial approach to remove impurities in high grade coals. Although it is an easy way to extract impurities (typically larger ones), it has a drawback of removing sulfur and ash-forming minerals that are attached to the coal matrix *(Meshram et al., 2015; Mukherjee & Borthakur, 2001)*. The specific gravity, surface characteristics, and

magnetic properties of mineral matter and the carbonaceous portions of the coal are the main foundations of physical beneficiation procedures. Minerals can be removed using a variety of techniques, including air dense media fluidization, oil agglomeration, magnetic separation, froth flotation, electrostatic separation, and gravity separation. *(Bhatti et al., 2020)*.

i. Gravity Separation Technique

The variations in specific gravities of coal and mineral matter (pyrite and ash-forming minerals) control the process of coal beneficiation through gravity. It is extensively utilized during the preparation and beneficiation of coal. Dense medium separation is a widely used method in gravity separation techniques. The centrifuge, jig, and landers are other gravity separation methods, etc. *(Meshram et al., 2015)*.

Beneficiation of two lignite tailings containing 66% and 53% ash, with a Multi-Gravity Separator (MGS) was reported by Oruç et al., (2010). According to their findings, the coal was beneficiated to 23% ash and had a coal recovery of 49.3% and 60.01%, respectively. For coal concentration of fine and ultra-fine materials, the Falcon concentrator—an alternative type of gravity separator—was employed. *(Oruç et al., 2010)*. As their paper mentioned, a Falcon concentrator was used to beneficiate the 66% ash coal, yielding clean coal with an ash value of 36% and a recovery of roughly 35%. When many fine coal samples were treated, the optimum concentration of coal, which was also examined by Honaker et al. (1996), generated values for ash removal ranging from 60% to 70% and recovered over 85% of the combustible material. *(Honaker et al., 1996)*. According to a recent study by Rath et al. (2011), the ash content could not be lowered to low values using the Falcon concentrator in comparison to froth flotation. Using a Falcon concentrator, a higher ash reduction of 47.5% was attained from a 60% yield of 35% ash, but froth flotation produced superior results with 34% ash at a 23% yield *(Rath et al., 2011)*. Furthermore, Das et al. (2010) found that cleaning fine coal with a combination of gravity separation and Jameson cell separation technique does not significantly increase floatability *(Das et al., 2010)*.

ii. Froth Flotation

Froth flotation is a process that involves utilizing a surface active agent to stabilize a froth that forms on the surface of an agitated solution of a substance in water in order to separate minerals with drastically varying wettability. Firstly, during the flotation process, the ash and sulfur-

containing particles in coal should stay in the tailings because they are hydrophilic. This method of beneficiation is suitable for coal particles less than 0.5 mm. The air that is added to the flotation cells as a froth is stabilized by the application of foaming reagents like kerosene or pine oil. The process's selectivity can be improved by adding surfactant compounds, also known as collectors, which selectively increase the hydrophobicity of the carbonaceous particles *(Meshram et al., 2015).*

Atesok et al. (2001) attempted to desulfurize and de-ash coals that were hard to float by using a carrier flotation method. A fine coal (-38 mm) with 16.3% ash and 2.0% total sulfur can be enhanced under ideal circumstances to produce a concentrate with 8.3% ash and 0.72% total sulfur and an 81% recovery rate *(Ateşok et al., 2001)*. The flotation investigation of pre-oxidized Indian high ash coal from the Talcher coalfield was conducted by Jena et al. (2008) in a Denver D-12 sub-aeration flotation cell using conventional reagents. After beneficiating the coal with 41–42% ash content to 31% ash content and 80.4% yield, they evaluated the effectiveness of column flotation, which allowed the ash to be further decreased to 26.6% from the same coal with a lower yield of 66.5% *(Jena et al., 2008)*. According to Ayhan et al. (2005), pH 9, a dosage of 250 g/t of kerosene, and the use of methyl isobutyl carbinol (MIBC) as a frother were the ideal flotation conditions. It eliminated 67% of the pyritic sulfur, >90% of the sulfate sulfur, and 50% of the ash content from the coal sample *(Ayhan et al., 2005)*. When kerosene and methanol were used as collectors, the coal's ash and sulfur content dropped by 40% and 30%, respectively. However, when kerosene was consumed at a rate of 125 g/t, more coal was recovered (80%) than when methanol was used *(Ehsani & Eghbali, 2007)*

iii. Oil Agglomeration

The agglomeration mechanism is predicated on the idea that coal particles are inherently hydrophobic, or at least less likely to be hydrophilic than inorganic materials. With the use of a suitable binding solvent that can efficiently coat the carbon-based components, this feature makes it possible to agglomerate and separate coal from mineral components. Baruah et al. (2000) reported on the process of cleaning Assam coal from India through agglomeration with xylene and hexane. On a dry basis, the highest organic matter recovery for xylene is 92%, while the value for hexane is roughly 55%. The maximum ash rejection percentages (90%) for xylene and hexane are nearly identical *(Baruah et al., 2000)*. Various vegetable oils were tested in order

to find the most efficient agglomerates. It was observed that the yield of agglomerates ranged from 40.0% to 87.5% and ash rejections from 13.5% to 62.0% using different coal–oil combinations *(Malik et al., 1999).*

The physical way of beneficiation is frequently less effective than other methods like chemical or thermal processes, even though there are alternative methods like magnetic, electrostatic, and microwave separations, etc. When it comes to recovering fine coals, traditional physical approaches are typically ineffective. However, although certain techniques offer excellent coal recovery, there is little increase in the calorific value of coal *(Reddy et al., 1988; Sastri et al., 1988).* It might not be able to generate coal with the required quality and standards or reach a high degree of coal recovery. Its application is also restricted to specific kinds of coal. Not all types of coal will benefit from it, particularly those with complicated mineralogical compositions or high impurity levels *(Malik et al., 1999).* Physical demineralization has several disadvantages, including high water and energy consumption, poor coal recovery, and restricted efficacy. When in operation, physical demineralization processes frequently need a significant amount of energy. Energy-intensive machinery and procedures are needed for methods including magnetic separation, froth flotation, and dense medium separation *(Meshram et al., 2015)*. The increased energy needs may partially counteract the advantages of the higher-quality coal and raise operating expenses. However, froth flotation is one of the physical demineralization techniques that needs a lot of water to separate the particles *(Dhawan & Kumar, 2019)*. This may lead to a large water consumption and create problems with the use of water resources. The other issue that renders the physical demineralization process unsuccessful is the loss of coal material. A percentage of the coal may be lost as waste or as fine particles or slurry during the separation and cleaning process *(Khoshdast & Sam, 2011)*. Physical demineralization can improve coal quality by lowering ash content and other impurities, but it can't completely remove all of the pollutants in the coal. Certain minerals and contaminants may be firmly bonded to the coal matrix, making it difficult to fully remove using only physical techniques *(Dhawan & Kumar, 2019; Rahman et al., 2017)*.

2.2.3. Chemical Demineralization of Coal

Because of its poor wash-ability qualities and the strong mineral associations within the coal matrix, low-rank coal is difficult to demineralize to below a standard limit using traditional physical treatment techniques *(Nabeel et al., 2009)*. The other alternative demineralization

method, chemical demineralization, is thought to be a solution to remove mineral matters and sulfur from coal under a variety of conditions because physical techniques only achieve low demineralization, which results in clean and ultra-clean coal (UCC, ash content <1%) *(Bilgin et al., 2021b).*

Leaching (i.e., acid leaching, alkali leaching, acid leaching followed by alkali leaching, or vice versa) and solvent extraction are among the chemical coal demineralization techniques. The first, known as chemical demineralization or leaching, tries to create upgraded coal by dissolving and removing all of the minerals from the organic coal matrix under various leaching conditions. Strong acids and alkalis can be used alone or in combination. The second method, called solvent extraction, dissolves the organic coal stuff and precipitates back the low-ash coal using organic solvents *(Rahman et al., 2013; A. Sharma & Matsumura, 2019)*. When it comes to upgrading low-grade lignite coals, solvent extraction is significantly more expensive and requires specialist equipment and high temperatures than chemical demineralization (leaching) *(Rahman et al., 2013; A. Sharma & Matsumura, 2019; Zhao et al., 2018).* In contrast, compared to physical coal cleaning, coal cleaning by leaching, or the chemical demineralization method, is a straightforward process that typically succeeds in removing all sorts of minerals from the coal under mild operating conditions *(S. K. Behera, Chakraborty, et al., 2018).*

Chemical leaching of coal with alkali and acid solutions, either alone or following physical cleaning processes, has been extensively explored and proved its effectiveness in reducing significant amounts of ash-forming minerals, pyritic sulfur, and organic sulfur from coal for the production of clean coal or UCC *(Meshram et al., 2015).*

Alkali leaching, also known as demineralization with alkali, is a successful process that removes minerals from coal by lowering the majority of the elements that are rich in minerals. Alkali reagents' synergistic action, which results from their strong affinity for coal minerals and their capacity to enter the interior of the coal matrix, may be the cause of this phenomenon *(S. K. Behera, Kumari, et al., 2018).* The leachants' strong affinity for the minerals including clay may be the reason behind the plan to target the principal minerals with alkali. These ions are called hydroxyl ions. The coal's silica, alumina, and clay-bearing minerals—mostly kaolinite and quartz—react with the alkali reagent during the alkali leaching process, converting the reaction product into hydrated alkali-bearing silicate, aluminate, and alumino-silicate complexes,

sometimes known as sodalite. A portion of pyrite and organic sulfur can also be removed through interactions with alkali solutions *(Dhawan & Kumar, 2019; Wijaya & Zhang, 2011)*.

On the other side, coal demineralization is significantly impacted by acid leaching. In a sequential leaching procedure, the acid reagent dissolves the alkali-bearing silicate complexes in addition to demineralizing certain minerals that survived alkali leaching, such as carbonates, iron oxides, and sulfides. However, most acid leaching doesn't dissociate the clay-bearing mineral except for some acids- for example, HF *(Meshram et al., 2015; Rahman et al., 2017)*.

Alkali-acid leaching works well for demineralizing coal in the majority of cases. According to multiple writers, the use of both alkali and acid leaching alone can result in a larger degree of demineralization through the combined leaching process. This may be because the unreacted portion dissolves and forms mineral complexes from the first stage of treatment *(Dhawan & Kumar, 2019)*. The principal minerals in the coal (silica, alumina, kaolinite, dolomite, quartz, etc.) and sulfur react with the treated coal using basic leaching agents (such as NaOH, $Ca(OH)_2$, or KOH) to generate hydrated alkali compounds of silicate, aluminate, and other complexes. Since the byproducts of the alkali treatment are poorly soluble, they can be readily eliminated with diluted acid *(Meshram et al., 2012)*. The unreacted product that forms during alkali leaching may cause the concentration of soluble ions to surpass that of its byproducts' solubility product, hence reducing the solubility of coal minerals. The residue of complexes that precipitated and adsorbed on the coal surface during alkali leaching can be readily dissolved in the acidic leachant and eliminated, hence limiting the process of further demineralization. Therefore, when using the alkali-followed acid leaching approach, effective demineralization will be achievable *(S. K. Behera, Kumari, et al., 2018; Dhawan & Kumar, 2019; Meshram et al., 2015)*.

The ability to achieve effective demineralization in both procedures determined the primary distinction between the application of acid-alkali and alkali-acid leaching methodologies. A significant amount of mineral matter is inherently present in low-grade coals, and this mineral matter is primarily constituted of silica, alumina, quartz, and other silica elements that are bonded to the coal matrix. Because of the strong attraction of the hydroxyl ion for the silica-alumina elements in coal, these components react strongly with the caustic leachant, forming soluble sodium hydrated silicate, aluminate, and sodium alumino-silicate compounds that

dissolve readily in an acidic solution *(S. K. Behera, Kumari, et al., 2018).* Conversely, though, the mineral contents of coal are nearly insoluble in an acidic solution; as a result, silicate and alumina complexes are subsequently generated and adsorbed on the coal surface, where they may remain intact *(Dhawan & Kumar, 2019).* Thus, reasonably, the efficient demineralization was obtained by the alkali-acid leaching rather than acid-alkali leaching.

Note that: *Alkali-acid leaching*: means the leaching of coal first by alkali solution, then after washing with water and drying the alkali-treated coal subsequently treated with acid.

Coal is typically chemically demineralized and desulfurized by leaching it in successive alkali-acid solutions or in combination with alkali and acid solutions. However, because it combines the benefits of both basic and acidic reagents, the alkali-acid sequential leaching approach is better and more efficient.

The majority of studies on the chemical leaching of coal used alkali-acid leaching reagents, which are strong acidic and basic media in diluted solutions with concentrations typically ranging from 10% to 25% based on weight *(S. K. Behera, Kumari, et al., 2018; Dash et al., 2012; Dhawan & Kumar, 2019; Meshram et al., 2012, 2015; Rahman et al., 2017).*

One of the studies conducted using strong acid/base reagents for alkali-acid leaching was tested on the Talcher coal *(D. K. Sharma & Singh, 2007).* Through the treatment of coal with 10% NaOH followed by 2% aq HCl treatment, they discovered that the degree of demineralization of Talcher coal (17% mineral matter & 38.8% volatile matter) was 75%. The same degree of demineralization was observed with 20% aqueous NaOH followed by 2% aqueous HCl treatment. This investigation of the effects of varying NaOH concentrations on coal demineralization showed that whereas concentrations from 2% to 10% increased demineralization, higher concentrations even reduced it.

Mukherjee & Borthahur (2001) additional research provided evidence in favor of the strong base/acid reagent demineralization and desulfurization of coal mentioned above. The coal samples from Boragolai, which had 8.4% ash, 4.3% sulfur, and 41.4 volatile matter contents, and Ledo, which had 10.4% ash, 4.3% sulfur, and 41.6 volatile matter contents, were ground to a size of less than 212μm. They were then leached using a solution of NaOH with varying concentrations (from 2% to 16%) and 10% HCl at 90–95ºC *(Mukherjee & Borthakur, 2001).* In accordance to their findings, the maximum levels of demineralization and desulfurization were

reached at 16% NaOH and 10% HCl concentrations. This resulted in significant increases in the calorific values of each coal, with Boragolai coal achieving 67% desulfurization and 50% demineralization and Ledo coal achieving 70% desulfurization and 44% demineralization. The Miller Blend (15.5% ash and 51.9% fixed carbon content) and Wandoan (7% ash and 52.1% fixed carbon content) coals were treated with varying quantities of NaOH solution and then 1M HCl while being stirred in the same investigation, as previously described (Wang et al., 1986). Their investigation suggested that higher demineralization of Wandoan (87%) and Miller Blend (89%) coals was discovered at a temperature of 460K with a 10M NaOH concentration followed by 1.0M HCl.

In a different study (Kumar & Shankar, 2010), Assam coal from the Beltalla region (with volatile matter of 38, ash of 6.6, and fixed carbon of 55.4 weight percent) was leached and sieved to a mesh size of -6 + 10. This study provided insight into the demineralization efficacy of HF solution. The leaching experiment (20 g of dried coal / 100 mL of 10 wt% NaOH solution) was conducted at 75 °C for one hour. This was followed by another leaching at 95 °C for approximately 20 minutes in various acids (HCl, H_2SO_4, HNO_3, and HF) with varying concentrations (10–25%). The experiment yielded a maximum demineralization of 61% for coal at a ratio of 10 ml/g of NaOH solution to coal. After that, they leached the coal with an acid concentration of 25%, and this increased the demineralization of the Assam coal to 71.25% using 10%HF solution. This investigation demonstrated a clear distinction between coal with a lower concentration and coal with a higher demineralization capacity while using an acid reagent.

Coal can also be effectively demineralized by washing it with a solution of hydrofluoric acid and then another acidic medium that can remove sulfur. Remarkably, practically all of the ash-containing mineral constituents in the coal matrix can be dissolved by the HF acid solution. Nevertheless, this solution is less reactive towards sulfur; to counteract this, both pyritic and organic sulfur can be dissolved by subsequent leaching using solutions like $Fe(NO_3)_3$ or HNO_3. To support such an innovative idea of coal demineralization, the chemical leaching of UK bituminous coal was studied *(Z. Wu & Steel, 2007)* with the treatment of Harworth (HW) coal, ground to a particle size of <52µm and have 5.3wt% ash content. The HW coal was leached with 3.5M HF for 4hrs at a temperature of 65^{o}C, followed by different concentrations of

$Fe(NO_3)_3$ at 100^oC for 6hrs. For comparison, the HF-treated coal was re-treated with H_2O_2 and HNO_3. The leaching conditions for HNO_3 and H_2O_2 were 65^oC for 4hr and 25^oC for 2hr, respectively. After two-stage treatment, the higher ash and sulfur removal was found in the HF-$Fe(NO_3)_3$ leaching with less than 990 ppm ash content and almost complete removal of sulfur. Although the calorific value was decreased, the HF-HNO_3 leaching can also remove the ash below 900ppm.

Other group of researchers *(Bilgin et al., 2021b)* also investigated the leaching potential of hydrofluoric acid, trioxoboric acid, hydrochloric acid, and sulfuric acid. Their study was conducted on the Black Sea region of Turkiye coal, ground to below 106µm particle size. From the analysis conducted, the coal composition was determined as 14.62% ash, 8.77% sulfur, 6200 Kcal/kg calorific value, 36.85% volatile matter, and 48.53% fixed carbon. The coal demineralization was conducted with varying concentrations of acid reagents (2.45%, 4.76%, 9.09%, and 13.04%) at different temperatures (20°C, 40°C, 60°C, 80°C) with different acid reagents and varying time-lapse (60min, 120min, 240min, 360min). Their laboratory result revealed that HF has a higher demineralization potential than others followed by HCl, H_2SO_4, and trioxoboric acid the last. More than 75% demineralization and over 40% desulfurization were achieved with HF leaching at 3hr leaching time, 500Kg/ton of acid reagent dosage, and 60^oC temperature.

Effective chemical leaching using strong acid/base reagents is also possible at lower concentrations of reagents to minimize the reagent uptake in order to converge the cost-effectiveness issue. Such attention-calling research was conducted by the group of researchers, Nabeel et al., (2009). This influential study was conducted and showed the possibility of coal demineralization using significantly lower concentrations of acid and alkali reagents in a stepwise leaching mechanism. They investigated the Topa coal (33.6% ash content) and power grade coals (low-grade coals obtained from thermal power stations of 43% ash content) of ash removal of chemical leaching from high concentrations of alkali and acid (20% NaOH & 10% H_2SO_4) to lower concentration (about 1% alkali and acid). They used both coals of size -60 to +120 BSS mesh and the varying leaching time from 1hr to 12hrs with a reflux leaching method at a temperature of 100^oC. After 6hrs of reaction for both alkali and acid leaching, around 74.8% demineralization was obtained. The researchers also studied the same coals with reduced alkali and acid concentrations (5% acid & 5% alkali, and 1% acid & 1% alkali) for 2hrs of leaching

time with reflux methods. This reduced concentration alkali-acid leaching was conducted in three-steps. As the study revealed, researchers obtained more than 80% and 90% demineralization after three step sequential alkali-acid treatments of both Topa and Power grade coals under reflux conditions with 1% and 5% concentrations respectively.

2.3. What Research Gaps Researchers Didn't Investigate?

Although many experimental demonstrations were conducted on chemical demineralization, there may be some research areas which need to be further studied and investigated. Having the same ash components of Ethiopian coal as others ever tested (Boroda coal ash contains more than 50% silica, more than 25% alumina, iron oxides, calcium oxides, magnesia and other metal oxides in their respective order together with some alkalis as of the preliminary investigation), the chemical leaching of Ethiopian coal has never been tested or unable to find a document. Knowing that dilute HF solution is exceptionally more effective than other mineral acids to demineralize a coal (especially for silica removal which is the major component of Boroda coal), it didn't tested for stepwise demineralization. Additionally, demineralization at higher temperature and concentrations can affect the organic nature of the coal that result calorific value reduction below the untreated coal and the volatile matter readily increases. Moreover, the combination of strong bases with dilute HF acid in two step leaching of coal will provide a good ash removal as their combination is higher in single step.

2.3.1. Factors Affecting Chemical Demineralization

To remove ash-bearing mineral matter from coal, called chemical demineralization (alkali-acid leaching), there are dominant factors to be considered and optimized for a better result. In most research ever conducted, the demineralization factors investigated are the type of alkali and acid, concentration of alkali and acid reagents, coal particle size to be demineralized, leaching time, and leaching temperature.

i. Type of reagents:

During leaching, the selection of acids and bases plays a major role in removing mineral matter from raw coal. Strong bases such as NaOH, KOH, and $Ca(OH)_2$ are efficient in removing ash-bearing minerals and sulfur by converting the mineral constituent to a hydrated mineral complex. However, the utilization of each base has a unique capacity for removal efficiency. For instance, $Ca(OH)_2$ is less corrosive to equipment and organic matter of coal but has less

capacity to remove ash-bearing minerals than NaOH and KOH at lower temperature *(Wijaya & Zhang, 2011).* $Ca(OH)_2$ leaching, to be comparable with NaOH leaching, compared to other bases it needs fairly rigorous leaching conditions: 250-300°C and 3.9-8.4MPa pressure *(Meshram et al., 2012)*. Strong mineral acids (eg. H_2SO_4, HF, HCl, HNO_3) can also remove minerals efficiently from coal and sulfur, but the clay-bearing minerals. However, some acids such as HNO_3 highly deteriorate the organic component of the coal along with ash complex dissolution. In a special case, HF can react to all ash-bearing minerals and remove them, but less effective in sulfur removal. Acidic solutions such as H_2O_2, $Fe(SO_3)_3$ are highly efficient to remove sulfur contents of coal *(Z. Wu & Steel, 2007).*

ii. Concentration of reagents:

The alkali and acid reagents for demineralization are usually used in their aqueous solution form since high concentrations of them affect the organic components of coal. In different research works before, the concentration of reagents was kept between 10% and 25%, but in some papers, it will be a bit higher up to 40% or lower than 1% concentrations. Increasing reagent concentrations favors the removal of minerals from coal due to the high affinity of hydroxyl OH^- (hydroxyl ion) towards the mineral in the coal matrix *(S. K. Behera, Chakraborty, et al., 2018)*. However, increasing the alkali concentration (NaOH) above 10% has no increasing effect, rather decreasing in some cases due to the formation of insoluble sodium salts such as sodium silicate and sodium alumino-silicates *(D. K. Sharma & Singh, 2007)*. Demineralization of coal is possible even at lower concentrations of acids and alkali with a stepwise leaching mechanism *(Nabeel et al., 2009).*

iii. Particle size of coal to be treated:

The size of coal particles affects the effectiveness of the chemical cleaning process. The percent demineralization of coal and the vulnerability of ash-bearing minerals of the raw coal varies with the particle size. The extent of demineralization increases with decreasing particle size (or increasing fineness) of coal until a certain limit. Although increasing coal fineness increases demineralization, separation of the dissolved mineral matters after demineralization will get difficult above a certain limit *(S. K. Behera et al., 2017b; D. K. Sharma & Singh, 2007; Sonmez & Giray, 2001).* Basically, the particle size should be lower than 150µm to conduct effective leaching of coal although separation difficulties arise in increasing coal fineness *(Bilgin et al., 2021a)*. In this study, the investigation aims to reduce the ash and sulfur content of low-grade

coal and improve the CV of coal to an acceptable level to use in cement industries in Ethiopia for pyro-processing. Therefore, lower coal particle sizes may not be necessary to achieve the target of cleaning, meanwhile, it will cut off the high cost of grinding and separation of fine coal from the leachant solution after chemical leaching in every step.

iv. Leaching temperature:

The solution temperature condition during leaching is one of the most influential parameters in the demineralization process. The heating effect causes the rise of activation energy of the reaction that facilitates the bond breakage that exists between the mineral and coal in the coal matrix *(S. K. Behera, Chakraborty, et al., 2018; Sonmez & Giray, 2001)*. The extent of demineralization increases since heat energy increases as reaction temperature rises which results in a higher rate of leaching. Demineralization at a higher temperature, however, is not advisable since it affects the yield of coal, increases volatile matter as well as the loss of the organic nature of coal with increasing temperature (Wang et al., 1986).

v. Leaching time

The soaking time is an important factor to be in consideration during the leaching process that decides the contact between mineral phases in the coal and the leachant. The demineralization percentage readily increases as time goes on, may be due to the greater contact time between the minerals of coal and the alkali/acid, which increases the liberation of minerals in the leaching process *(S. K. Behera, Chakraborty, et al., 2018)*. In mild conditions (reaction temperature between 60^{o}C and 100^{o}C), the optimum leaching time usually takes longer time (> 2hrs), but in actual scenario leaching time largely depends on the type of leachant and temperature *(Bilgin et al., 2021b; Nabeel et al., 2009)*. Conditions such as higher temperature, demineralization with stirring, and strong acid (eg. H_2SO_4), for example, may take a shorter time than that of lower temperature without stirring and slightly less strong acids.

CHAPTER THREE

3. MATERIALS AND METHODS

3.1. Site Description of the Study

This study "***Demineralization of high-ash Ethiopian Coal through alkali-acid leaching method to use in cement industries***" was conducted in Chemical Engineering Laboratory of Adama Science and Technology University (ASTU). However, the froth flotation experiment was accomplished at AAiT. The proximate analysis and CV determinations were carried out at Mugher Cement Factory. The chemical analysis of the raw coal and alkali-acid leached coal ashes also done at Mugher Cement Factory. Whereas the SEM scanning & XRD experiments of the raw and treated coal was conducted at the Biology Laboratory and Materials Science and Engineering laboratory of ASTU respectively.

3.2. Materials

3.2.1. Chemicals and Apparatus

The chemicals and apparatus employed in the demineralization investigation encompassed the chemicals directly utilized for demineralization, as well as those used for cleaning, disinfection, and the equipment required for conducting the experiment, characterization, and analysis. Various specific chemicals were employed for distinct purposes in this research endeavor.

Table 3-1: List of chemicals with their purposes

Name of chemicals	Purpose of the chemical
Sodium hydroxide, NaOH	NaOH-solution preparation to use in demineralization
Hydrofluoric acid, HF	HF-solution preparation to use in demineralization
Deionized water	Solution preparation and cleaning
Tap water	Cleaning and condenser cooling
HCl and H_2SO_4	Disinfecting and cleaning of experimental apparatus
Octanol and kerosene	Frother and collector respectively

The major apparatuses that were used in the research and their purpose were summarized in Table 3-2 with their respective purposes. To make it clear, the term "*apparatus*" typically refers

to a complex or specialized set of instruments, devices, or components that are designed to perform a specific scientific or technical function whereas "*equipment*" generally refers to individual tools, instruments, or devices used in a laboratory to carry out specific tasks or measurements.

Table 3-2: List of apparatus, equipments, instruments and their purposes

Apparatus name	Purpose of the equipment or apparatus
Ball mill	Size reduction of the raw coal
Sieves	Categorize size reduced coal based on particle size
Beakers	Acidic and basic solutions preparation
Water bath	Heating the reaction flask at specific temperature
Filter paper & funnel	Separation of liquid and solid particles apart
Digital balance	Measuring mass
Measuring cylinder	Measuring volume
Condenser	Vapor condensation to the reaction flask
Three neck flask	Leaching reaction to be takes place
Chiller	Circulation cold water through the condenser
Crucible	Put the sample in the hot furnace
Petri-dish	Put the sample in the heating oven for drying
Bomb calorimeter	Calorific value determination
Furnace	Investigation of ash content and volatile matter
Drying oven	Removing moisture from experimental sample
Wedag Frother machine	For froth flotation experiment
SEM	Surface morphology investigation of sample
XRD	Investigation of crystallinity

3.3. Methods

3.3.1. Raw Coal Collection and Preparation

The raw material (low-grade coal) for the experiment was collected from Mugher Cement Factory, West Shoa Zone, Oromia regional state, originally sourced from one of the coal mining areas of Ethiopia, Boroda, Gamo-Gofa Zone. Then the large-sized coal was reduced mechanically, and then the raw coal was ground with a ball mill that rotated at 620rpm.

Then the ground coal was transferred to the stack of sieves at the top that were arranged in decreasing order of sizes to the bottom. The mesh sizes 710micron, 500micron, 355micron, 180micron, and 90micron were arranged top to bottom in this order to group a sample based on size. The ground coal was put at the top of the mesh (710 microns) and the stack of meshes tightly clapped. The vibration set on for some time until the separation ended. Then each group of size of samples was carefully kept for further analysis.

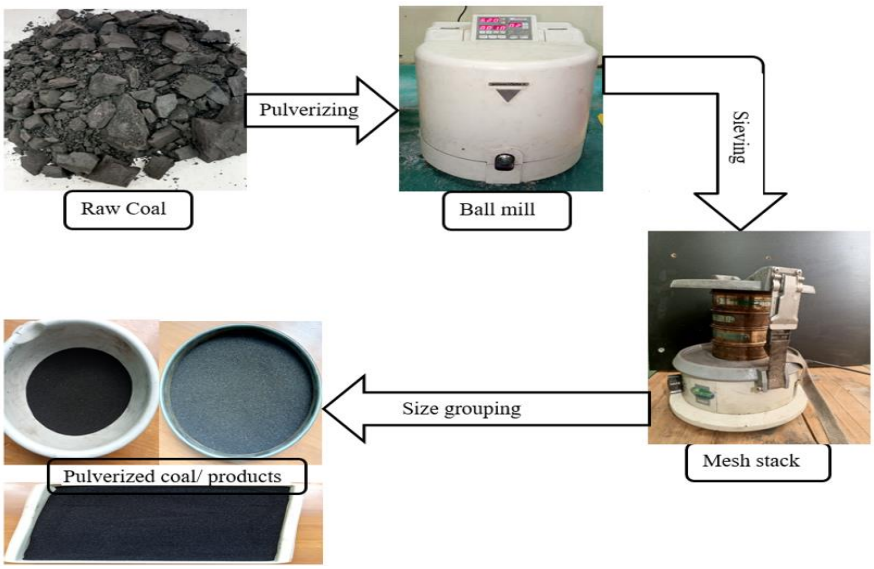

Figure 3-1: Raw coal preparation and size grouping

Table 3-3: Size analysis and grouping of the sample

Group denotation	Mesh size range in microns
A	710 to 500
B	500 to 355
C	355 to 180
D	180 to 90

3.3.2. Boroda Coal Characterization

The coal under investigation was characterized accordingly in order to know the contents of the coal once after size reduction on a dry basis. The most common and simplest method to characterize the coal is the proximate analysis, which helps to determine the moisture content,

volatile matter (VM), ash, and, by difference, the fixed carbon of the coal. Some instrumental characterizations were also conducted to determine CV (bomb calorimeter) and to compare surface morphology (SEM), and constituents of ash (chemical analysis method).

A. Moisture Content

A crucial consideration in coal analysis is the moisture content, which is necessary to determine a coal's handling qualities and net calorific value (heating value). The total moisture content, residual moisture content, or both can be found via proximate analysis of coal moisture. While residual moisture is determined on an air-dry basis, total moisture is determined on a received basis made up of surface (free) moisture. The mass lost from a sample under particular circumstances following an hour of heating in a drying oven to 105°C to 110°C provides the moisture value needed for a proximate analysis, which may be used to determine the moisture content. Using ASTM D 3173 – 03 as a reference, the moisture content was ascertained. To determine the moisture content, place the weighed samples in crucibles without covers in the drying oven and heat them at temperatures between 105°C and 110°C, or until the mass stabilizes. After the sample was dried and weighed, the mass change was estimated, and the moisture content is going to be computed.

$$\text{Moisture content (\%)} = \frac{lost\ in\ weight\ of\ sample}{initial\ weight\ of\ sample} \times 100\% \quad \ldots\ldots\ldots\ldots \text{eq. (3.1)}$$

Five grams of size-reduced coal from each sample (samples A, B, C, and D) was placed on pre-dried Petri dish plates with known mass. The samples were then dried in an oven at 105^{o}C for three hours, and the coal was weighed to ascertain the moisture content of the air-dried Boroda Coal sample. Again put in the drying oven at 105^{o}C for 30 minutes and weigh when the time is completed. The sample was dried for consecutive thirty minutes, or until there was no change from the initial mass.

B. Volatile Matter

The weight loss that results from heating a coal sample under strictly regulated conditions is used to calculate volatile matter. One can compute the percentage of volatile matter occupied in coal by applying a typical ASTM D-3175 testing protocol. The samples obtained from the moisture determinations can be used to make volatile matter determinations. A general analysis

coal sample weighing about 1g and having a top size of 250μm is heated for precisely 7 minutes to a predefined temperature in a covered crucible. The ASTM test procedure calls for heating the coal sample in a pre-weighed, covered silica crucible to 900°C ± 25°C in a furnace and holding it there for seven minutes. The atmosphere inside the furnace must be inert, ideally nitrogen. The sample is reweighed and the result is computed after it has been heated and cooled in a desiccator.

$$\text{Volatile matter (\%)} = \frac{loss\ in\ weight\ of\ sample}{weight\ of\ the\ sample\ taken} \times 100\% \quad \text{..... eq. (3.2)}$$

C. Ash Content

The ASTM D-3174 standard procedure can be used to determine the amount of ash on an oven-dried basis. A weighted analysis sample of coal (with a top size of 250μm) or a dry coal sample from the moisture determination is placed in a cold furnace and is heated, in air, gradually at such a rate that the temperature reaches 450–500°C in 1 hour. The coal sample is heated further until it reaches a final temperature of 700–750°C by the end of the second hour, and it is kept at this temperature for two more hours. After that, the sample inside the furnace is allowed to cool before being taken out. After burning, the residual ash is cooled in a desiccator, weighed once more, and the ash content is measured.

$$\text{Ash content (\%)} = \frac{weight\ of\ ash\ residue}{weight\ of\ dried\ coal\ sample\ taken} \times 100\% \quad \text{..... eq. (3.3)}$$

D. Fixed Carbon

Instead of being calculated directly, fixed carbon is computed as a mass percentage using the same moisture reference base by deducting from 100 the total of moisture, VM, and ash.

$$\text{FC (\%)} = 100 - (\text{ash} + \text{VM} + \text{moisture content}) \quad \text{..... eq. (3.4)}$$

E. Calorific Value

A bomb calorimeter was used to calculate the CV of the treated coal and the raw coal prior to treatment. In order to complete the combustion, the appropriate amount of powdered coal sample is weighed in a nickel crucible and put inside a bomb. The bomb is then filled with oxygen and pressure is increased to 25–30 atm. The known volume of distilled water is then contained in a

copper calorimeter, into which a bomb is then dropped. The water is mechanically agitated to maintain a constant temperature while the initial and maximum temperatures are recorded. The quantity of heat rising in the water is measured with a thermometer. Heat is released when the sample burns. The following empirical formula can be used to calculate the calorific value.

$$CV = \frac{e \times \Delta T - heat\ released\ due\ to\ wire}{mass\ of\ dry\ coal} \quad \text{..... eq. (3.5)}$$

Where; e is the bomb factor and ΔT is the maximum and initial temperature difference.

F. Chemical Analysis of Coal Ash

The process of analyzing coal ash chemically (classical method) is a scientific way to ascertain the composition and concentration of its constituent parts. The titration method, which involves reacting a known volume of a standardized solution (titrant) with the component of interest in the coal ash sample, is one of the most widely used chemical techniques for coal ash analysis. A change in color, a change in pH, or any other observable change that signifies the reaction's finalization is considered as the titration's endpoint. The concentration or percentage of the component in the coal ash is then determined using the volume of titrant utilized. However, the analysis process is standardized for analytical purposes.

The major component of the ash, i.e SiO_2, Al_2O_3, Fe_2O_3, CaO, and MgO determinations can be conducted by the analytical laboratory standard of ASTM D-2795 *(ASTM, 2017).*

The total sulfur content of a coal also be determined analytically by the ASTM D 3177 – 02, employing either Eschka Method or Bomb Washing Method *(D-3177, 1995).*

G. SEM Characterization

SEM, or scanning electron microscopy, is among the most effective characterization tools for examining the surface morphology of a material. SEM produces high resolution and high field depth pictures. The surface morphology of a sample, including its size, shape, structure, and alignments, is examined by SEM characterization. To determine the crystal nature of the sample, surface and texture prior to demineralization, the surface morphology of the sample coal is examined.

3.4. Batch Experiment Demineralization Study of Boroda Coal

The alkali NaOH and the acid HF used in this study were selected based on the investigations in section 2.3 that the NaOH has lower effect towards the organic matter of the coal in addition to high removal efficiency of ash bearing minerals. Additionally, dilute HF has high removal potential of ashes compared to other acids. Thus, the combinations of them in two step leaching has been investigated.

3.4.1. Alkali and Acid Solutions Preparation

The solutions were prepared based on volume by volume percentage. The alkali (NaOH) solution was prepared based on its density (2.13g/ml), then related to the volume and mass (mass is related to molar mass). Example, to prepare 10% NaOH solution of 100ml volume, one can follow;

100ml * 10% = 10ml of NaOH.

Mass of NaOH = density * volume required

= 2.13g/ml * 10ml = 21.3g.

Therefore, mass of NaOH to prepare 100ml of solution is 21.3g.

Based on this principle, 2.5%, 5%, 7.5% and 10% of NaOH solution was prepared.

The acid solution (HF, 48% conc.) were prepared based on the famous formula,

$C_1V_1 = C_2V_2$,

Where, C_1 = original concentration of HF, C_2 = final concentration of HF, V_1 = initial acid volume (48% conc.), and V_2 = final (reduced concentration) volume of solution.

The acid solution also prepared the same concentration as the NaOH solution.

3.4.2. Demineralization Experiment

Following the completion of the characterization of the raw coal, demineralization and the investigation of the impact of process variables continued. These variables include the temperature, contact time, raw coal fineness to which it is ground, and reagent (NaOH-HF) concentration. The "one factor at a time method" was used to investigate their impact on the ash removal and calorific value.

The experiment was conducted according to the "*one factor at a time method*"**.** In the first stage of leaching, 40g of raw coal (specific size) is mixed with 400 ml NaOH solution (1:10 mass by

volume ratio, an optimized dosage) of a specific concentration *(Z. Wu & Steel, 2007)*. The mixture is placed in a closed flask with reflux (condensation) at a specific temperature for a specified time elapse according to set variables for a single reagent soaking. After the leaching time was completed, the coal was separated from the solution with filter paper. Then the filtered coal was washed using hot water with stirred many times to neutralize the base. Next, the neutralized coal was transferred to the flask again and mixed with an HF solution of the same concentration and condition as the previous base demineralization. In the second stage, the first stage is done again in the same condition of process variables and sequence without changing the washing mechanism for each combination. Then after, the coal was dried in the oven and subjected to proximate analysis as explained in section 3.3.3.

3.4.3. Experimental Setup

The experiment was conducted by combining different apparatus for their different purposes. The water bath is filled with water and switched on then the temperature is set. The flask that holds the sample is partially immersed in the water in the water bath when the temperature reaches the set point. Then the condenser is mounted on the top of the flask. The chiller is connected to the condenser with tubes tightly. The chiller finally switched on to cool and circulate water. As observed in Figure 3-2, the water bath is used to heat up the sample mixture to demineralize that held in the flask (round bottom flask). The condenser is mounted on the top of the flask to reflux the vapor back to the sample mixture, and the chiller is for circulating the cooling water together with cooling it.

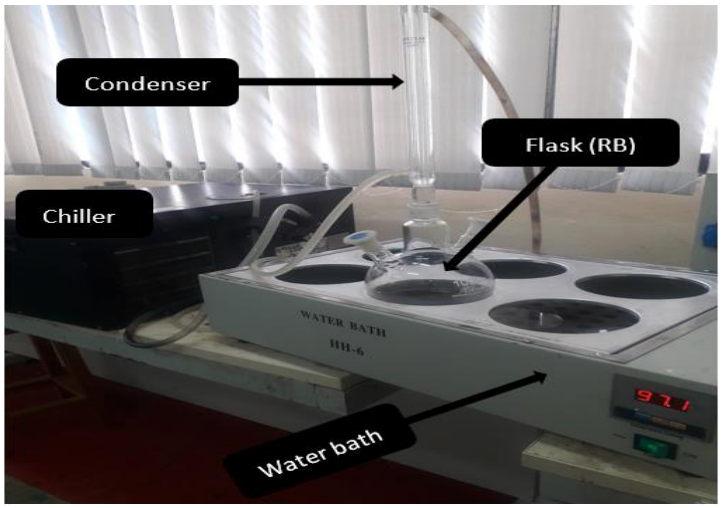

Figure 3-2: Experimental setup

3.4.4. Study of Effect of Process Variables

To study the effect of each process variable in the "*one fact factor at a time method*", the objective variable is varied while keeping the others constant at a specific value. The most important factors in the study of demineralization are the size distribution of the coal particles, the temperature to which the sample is soaked, the concentration of the alkali and acid reagents that the coal is being soaked, and the length of time that the sample wait in the given concentration and temperature.

In experimental analysis, the "*one factor at a time"* (OFAT) method is a crucial strategy. It entails controlling for other variables and evaluating the effect of a single factor at a time on a process or result. It enables researchers to carry out research with constrained time and resources, rapidly determine the effect of a certain factor on the result of an experiment, and give a large amount of data at a reasonable cost. It is advantageous when there is little to no interaction between the variables.
A known amount of ground coal is used for the demineralization and weighed after the demineralization process on a dry basis to know the coal recovery of the process.

As revealed from different works, the demineralizations conducted at sizes of [-6 +10] mesh size (>2mm) *(Kumar & Shankar, 2010),* -30+70 (or -600+212 microns) mesh size *(K. S. Behera et al., 2018).* Others tested the demineralization below 200 microns, but has lower coal recovery if it is lower than 63 microns *(S. K. Behera, Chakraborty, et al., 2018; Bilgin et al., 2021b).* The effect of size is studied by testing each of four samples of A[710-500], B[500-355], C[355-180], and D[180-90], in microns, while keeping the temperature, concentration and time at 100^{o}C, 10% and 3hrs respectively. After selecting the best size, the next parameter effect is going to be analyzed (Table 3-4).

The temperature ranges taken based on previous works that they already found their optimum value. For instance, S.K. Behera et al. (2018) took the temperature range from 60^{o}C to 100^{o}C and found the optimum demineralization at 92^{o}C.

Table 3-4: Study of size effect on coal Demineralization

Temperature (°C), ±3°C	Size group (microns)	Concentration(%)	Contact time(hrs)	VM (%)	Ash removal(%)	NCV (Kcal/kg)
100	[710-500]	7.5	3			
100	[500-355]	7.5	3			
100	[355-180]	7.5	3			
100	[180-90]	7.5	3			

The others tried to demineralize at the optimum temperature of 95-100°C *(Kumar & Shankar, 2010; Nabeel et al., 2009)*. Therefore, based on these evidences, the temperature effect was investigated at 60°C, 73°C, 86°C and 100°C with other variables kept constant and ±3°C for uncertainty of the experiment, at 7.5% concentration, 3hrs of soaking time, and C[355-180] microns of selected size (Table 3-5).

Table 3-5: Study of effect of temperature on the demineralization of coal

Temperature (°C), ±3°C	Size group (microns)	Concentration(%)	Contact time(hrs)	VM (%)	Ash removal(%)	NCV (Kcal/kg)
60	[355-180]	7.5	3			
73	[355-180]	7.5	3			
86	[355-180]	7.5	3			
100	[355-180]	7.5	3			

In mild conditions (reaction temperature between 60°C and 100°C), the optimum leaching time usually takes longer time (> 2hrs), but in actual scenario leaching time largely depends on the type of leachant and temperature *(Bilgin et al., 2021b; Nabeel et al., 2009)*. Some researchers found that the optimum temperature is 2.5hrs *(Dash et al., 2013)*. Reasonably, the selected size [355-180], the time of contact was investigated for 1.5hrs, 2hrs, 2.5hrs, 3hrs and 3.5hrs at constant concentration of 7.5% and temperature of 100°C (Table 3-6).

Table 3-6: Investigation of contact time effect on demineralization

Temperature (°C), ±3°C	Size group (microns)	Concentration(%)	Contact time(hrs)	VM (%)	Ash removal(%)	NCV (Kcal/kg)
100	[355-180]	7.5	1.5			
100	[355-180]	7.5	2			
100	[355-180]	7.5	2.5			
100	[355-180]	7.5	3			
100	[355-180]	7.5	3.5			

Demineralization of coal is possible even at lower concentrations of acids and alkali with a stepwise leaching mechanism *(Nabeel et al., 2009).* Moreover, the concentrations are already tested in many works. Thus, this work tried to address the extent of demineralization at concentrations lower than 10%. With the same concentration of NaOH solution and HF solutions, its effect was investigated at 2.5%, 5%, 7.5% and 10% by demineralizing size group C for 3hrs at 100°C (Table 3-7).

Table 3-7: Study of concentration of reagents on demineralization

Temperature (°C), ±3°C	Size group (microns)	Concentration(%)	Contact time(hrs)	VM (%)	Ash removal(%)	NCV (Kcal/kg)
100	[355-180]	2.5	3			
100	[355-180]	5	3			
100	[355-180]	7.5	3			
100	[355-180]	10	3			

3.5. Boroda Coal Beneficiation with Froth Flotation

The experiment utilized a Boroda Boal sample with a size range of D [180-90]µm and a Wedag flotation machine with a volume of 3 L (Note: smaller particle size is advisable for the froth flotation process). To begin the experiment, a fine coal sample weighing 90g/min was mixed with 2.5 L of tap water and stirred for 3 minutes at an impeller speed of 2250 rpm until the coal particles were fully wetted, achieved by closing the air valve. Subsequently, 3ml drops of kerosene were added as a collector and the mixture was agitated for an additional 2 minutes. Then, 4ml of n-octanol was introduced as a frother, and the air valve was opened to facilitate

the formation of bubble particles in the flotation cell. Once bubble formation commenced, 0.5 L of water was added to fill the cell capacity. As the bubble particles started overflowing the cell, the flow particles were collected. The collection of foam continued until the appearance of white foam, indicating that all solid particles in the cell were attached to the oil collectors. Finally, the collected particles were filtered, and dried in a hot oven at 80°C, and the flotation concentrate yield was calculated using an eq. (3.6).

$$\text{Yield, \%} = \frac{Mass\ of\ dry\ concentrate}{total\ mass\ of\ feed\ coal} \times 100\% \quad \ldots\ldots\ldots\ldots\ldots\ldots \text{ eq. (3.6)}$$

The proximate analysis of the coal after froth flotation beneficiation was done in the same manner as the chemical leached coal stated above (section 3.3.3).

Figure 3-3: Wedag Flotation Machine (left) and flotation process (right)

3.6. Characterization Boroda Coal after Treatment

The coal after demineralization (i.e. treated coal) was characterized accordingly in order to know the extent of demineralization and to make a comparison of the combination of process variables. In the same procedure and principle of raw coal proximate analysis (section 3.3.3), the moisture content, volatile matter (VM), ash, and by difference, the fixed carbon of the treated coal can be determined. Some instrumental characterizations were also conducted to determine

net CV (bomb calorimeter), the ash analysis (chemical ash analysis or the so called classical method).

The instrumental characterization of the coal sample was conducted to compare surface morphology (SEM) and to see the crystallinity alterations of the treatments (XRD). The SEM scanning of the sample was conducted with high vacuum scanning electron microscope. The sample also characterized with XRD to understand the change in crystallinity of coal sample before and after treatment. The sample was examined with XRD (made with SHIMADZU corporation, Japan with model XRD-7000) in the measurement range of 0 to 85^{o} with a scanning speed of 3^{o}/min.

CHAPTER FOUR

4. RESULTS AND DISCUSSIONS

4.1. Characterization of Raw Coal

Proximate analysis of coal is a method used to determine the moisture content, volatile matter, fixed carbon, and ash content of coal. These parameters are simple and provide valuable information about the quality and characteristics of the coal. They often used to classify coal into different ranks or types based on its composition.

4.1.1. Proximate Analysis of Raw Boroda Coal

A. Moisture Content

The moisture content that determined according to the ASTM D 3173 – 03 is tabulated in the table 4.1 (equation 3.1).

Table 4-1: Moisture content analysis (air dry basis)

	Mass (g) of sample after			
Group	3hr drying	30 min drying	30 min. drying	Total mass change (Δm)
A	4.29	4.286	4.286	0.714
B	4.28	4.27	4.27	0.73
C	4.226	4.216	4.216	0.784
D	4.275	4.275	4.275	0.725

The moisture content of the sample A: 14.28%, B: 14.8%, C: 15.68% and that of D was 14.5%. Therefore, the average moisture content of the sample was 14.82% on an air-dry basis since the next proximate analysis needs an air-dry basis. This moisture for coal is a bit higher to fire directly since moisture highly affects the heat intensity and output of heat.

Coal properties and behaviors can be significantly impacted by its moisture content in a number of ways. Some consequences include increasing the ignition temperature, and decreasing the heating value and combustion efficiency. Coal moisture requires energy to evaporate, which lowers the amount of heat that can be used for burning. Lower combustion efficiency and a reduction in total heat output are the results of moisture in the coal. The moisture must be

removed with more energy before the coal can begin to burn efficiently. Because some of the energy released during burning is spent to evaporate the moisture rather than producing heat, moisture in coal lowers its heating value.

Consequently, the calorific value of coal with a higher moisture content is lower. Additionally, it acts as a heat sink by absorbing heat from the surroundings, raising the temperature at which coal ignites and making combustion more challenging. Furthermore, moisture can decrease flame stability and slow down the rate of combustion. Handling and storing coal with high moisture content can be difficult. Because wet or high-moisture coal frequently spontaneously combusts, there is a risk of fire while it is being stored and transported. Also, because of the moisture's weight, shipping expenses may go up.

B. Volatile Matter

The test conducted according to ASTM D 3175 guideline (equation 3.2), the VM of Boroda Coal samples is averaged out of four trials:

Trial 1 = 36.35%	Trial 3 = 33.67%
Trial 2 = 32.33%	Trial 4 = 34.58%

Thus, taking the average of trials, the volatile matter of Boroda Coal is determined to be 34.23%. Since Boroda Coal is a type of lignite sometimes called “brown coal”, it had high volatile matter, largely dependent on the geological time scale of the coal formation. As the volatile matter content of coal is the proportion of combustible gases and vapors that are released when coal is heated or burned, it has some effects on the behavior of coal. Some are the combustion behavior, flame stability, and heat intensity. The volatile matter content has significant effect on coal's ignition and combustion properties. In general, higher volatile matter content facilitates easier ignition and accelerates combustion rates (i.e., coal may ignite at a lower temperature and burn quickly). However, during burning, the volatile stuff in coal helps to generate a steady flame. In order to facilitate continuous burning of coal, the release of volatiles creates a combustible environment close to the fuel surface. Burning volatile stuff releases heat energy in the form of hot gases, which raise the total calorific value but decrease its heat intensity. Higher-rank coals like bituminous or anthracite often have a lower volatile matter content than lower-rank coals like lignite. The reactivity of coal, or its ability to undergo combustion, is influenced

by the volatile matter content. Higher volatile matter content generally corresponds to greater reactivity.

C. Ash Content

The amount of ash can be evaluated using the ASTM D-3174 standard process on an oven dried basis (equation 3.3). Therefore, based on the standard procedure, the ash of Boroda Coal samples is found to be;

Trial 1 = 18.68%	Trial 3 = 17.03%
Trial 2 = 17.43%	Trial 4 = 17.60%

The average ash content of Boroda Coal was determined as 17.69% approximately. Of this ash content, the oxides listed are the major components that determined chemically.

Composition on total Ash basis	Composition total coal basis
Silica: 53.9%	9.54%
Alumina: 31.28%	5.53%
Iron-oxide: 5.81%	1.03%
CaO: 3.22%	0.57%
SO_3: 1.53%	0.27%
MgO: 0.82%	0.15%
Others (-OHs, heavy metals, rare metals,..etc.): 3.44%.	0.61%

According to the aforementioned examination of the raw Boroda Coal, silica and alumina make up more than 85% (or more than 15% of the total mass of coal) of the ash-bearing mineral substances. These materials behave as inert materials during combustion, lowering the coal overall combustion efficiency. Ash lowers the heating value of coal, resulting in low energy production per unit mass of coal burned since it is non-combustible and does not release energy during burning. Additionally, because it interferes with combustion, less oxygen is available, and the reaction between the fuel and oxidizer is hampered, it lowers the efficiency of coal's combustion. Lower flame stability, incomplete combustion, and decreased combustion efficiency can all be consequences of ash. The existence of ash in coal, as opposed to the cement

industry, requires ash handling and disposal following coal burning, which may call for specialist disposal techniques if not results in environmental damage.

Ash in coal can have both beneficial and harmful effects on cement manufacture. When mixed with calcium hydroxide in the presence of water, the ash from high silica coal often possesses pozzolanic qualities that result in the formation of cementitious compounds. When added to concrete as an additional cementitious element, ash can improve the workability, strength, and longevity of the mixture. It can increase the durability of concrete constructions and lower the amount of cement needed, both of which promote sustainability *(Singh et al., 2020)*. But, the presence of high ash in clinker or cement may not have an advantage. High ash content in coal can introduce impurities and mineral components into the cement, affecting its properties, for instance, increased alkali-silica reaction potential or corrosion of reinforcement.

D. Fixed Carbon

Fixed carbon is the remaining difference of a sample out of moisture content, VM and ash, in a mass percentage basis on the same moisture reference basis. By difference (equation 3.4), the fixed carbon content of Boroda Coal sample was 33.26% and thus, it is grouped under the lignite coal type according to the ASTM classification standard.

The fixed carbon in coal, which is a carbonaceous residue of the pyrolysis product left over after moisture and volatile matter are removed, controls the energy content and combustion properties of the coal and is typically used to identify and categorize various types of coal. Greater energy density, higher heating intensity, and improved combustion qualities, ranging from lower lignite to high anthracite, are typically associated with the fixed carbon content.

E. Calorific Value

A crucial factor in many applications, including figuring out how well combustion processes work, figuring out how much energy coal-fired power plants can produce, and evaluating the quality of various coal kinds, is the calorific value of coal.

The calorific values of various forms of coal vary because of variations in its moisture content, chemical composition, and other characteristics. A higher calorific value is typically associated with coal that has a lower moisture content and a higher carbon content. For instance, the

calorific value of anthracite coal is higher than that of lignite coal. In modern cement plants, burners used for cement clinkerization are designed to burn fuels that have a calorific value of more than 6,000 Kcal/kg and are usually taken as a standard *(Amin & Ali, 2011; Tan et al., 2023)*. But, this standard in cement plants lowered to about 5,000 Kcal/kg (even, as low as 4500 Kcal/kg in some plants) due to several reasons such as coal availability, import substitution policy, cost reduction, etc. The net calorific value of raw Boroda Coal, however, is 4275 Kcal/kg. In general, Boroda Coal has high (as received basis) moisture, high volatile matter, high ash content, low calorific value, and low fixed carbon. This proximate analysis forces to classification of Boroda Coal under lignite coal type as of ASTM standard.

4.2. Effect of Parameters on Demineralization

4.2.1. Coal Fineness Effect on Demineralization

The effect of particle size on the demineralization of Boroda Coal has been studied in four different size groups to analyze its effect (Table 4-1). The extent of demineralization increases with a decrease in particle size. Finely ground coal particles have a larger surface area, allowing for better contact with the demineralization agents *(S. K. Behera, Chakraborty, et al., 2018)*. It has been observed from the investigation, the efficient demineralization was obtained from coal C of [355-180] microns of particle size. When the fineness of the coal under demineralization increases or the size of coal particles decreases, the ash removal increases; and the same for volatile matter. As seen in Table 4-1, the ash removal and volatile matter increased when the fineness increased from [710-500] µm to [180-90] µm. But for the increase in ash removal, the calorific value doesn't increase significantly due to the increase in volatile matter. The removal of ash from coal doesn't increase significantly after the size of C [355-180].

Table 4-2: Study of size effect on coal Demineralization

Temperature (^oC), $\pm3^oC$	Size group (microns)	Concen-tration(%)	Contact time(hrs)	VM (%)	Ash removal(%)	NCV (Kcal/kg)
100	[710-500]	7.5	3	36.1	31.7	4675
100	[500-355]	7.5	3	37.2	47.3	4868
100	[355-180]	7.5	3	42.6	78.9	5207
100	[180-90]	7.5	3	46.3	81.2	5176

Even if the liberation of mineral materials is facilitated by smaller particle size, demineralization is less effective when fineness levels are further increased. For this reason, the demineralization rate (from size C to D) grew more slowly than it did for the other sizes. Additionally, as coal fineness grows, the coal particles are more susceptible to acids and bases, which alter the coal organic nature, increase its volatile matter content, and ultimately lower the coal calorific value. It may be due to the degradation of organic carbon to form carbonates and other unwanted byproducts *(S. K. Behera, Kumari, et al., 2018; Z. Wu & Steel, 2007).* The decrease in ash content is not guarantee for the increase in calorific value. For instance, researchers Z. Wu and K.M. Steel (2007) decreased the ash content of Harworth (HW) coal from 5.3% to 0.091% (more than 98% demineralization). The calorific value, however, does not improved, instead decreased from 32.3MJ/Kg to 29.1 MJ/Kg.

4.2.2. Temperature Effect on Demineralization

The temperature effect is investigated at 60^{o}C, 73^{o}C, 86^{o}C and 100^{o}C with other variables kept constant at 7.5% concentration, 3hrs of time, and [355-180] microns of the selected size. The extent of demineralization increases since heat energy increases as reaction temperature rises which results in a higher rate of leaching (Table 4-3). The demineralization of coal increased as well as the calorific value when the temperature increased from 60^{o}C to 100^{o}C. Although the ash removal increased sharply, the NCV of the coal is at decreasing rate after 86^{o}C.

Table 4-3: Study of effect of temperature on the demineralization of coal

Temperature (^{o}C), ±5^{o}C	Size group (microns)	Concen-tration(%)	Contact time(hrs)	VM (%)	Ash removal(%)	NCV (Kcal/kg)
60	[355-180]	7.5	3	36.9	46.7	4865
73	[355-180]	7.5	3	38.0	53.3	4976
86	[355-180]	7.5	3	38.8	60.8	5136
100	[355-180]	7.5	3	42.6	78.9	5207

The reaction activation energy increased as a result of the heating effect, making it simpler to break the link between the mineral and coal in the coal matrix. Nevertheless, demineralization at higher temperatures is not recommended since it reduces the amount of coal produced, increases volatile matter, and causes the coal to lose its organic content (Wang et al., 1986). The

yield of coals also reduced when demineralization is conducted at higher temperatures, even though it results in a greater degree of demineralization, particularly for finer particles *(S. K. Behera, Chakraborty, et al., 2018).*

This is due to the greater kinetics of the decomposition organic composition of the coal, which produces a high volatile matter. Because of the increase in volatile matter that occurs with demineralization at higher temperatures, there is also a decrease in the peak temperature and ignition temperature of coal following demineralization, but an increase in the burnout temperature *(Kizgut et al., 2006; Tang et al., 2022)*.

4.2.3. Effect of Contact Time on Demineralization

The length of time that affects the leaching process and the extraction of mineral stuff from coal is a significant parameter. At the selected size [355 to 180], the time of soaking is investigated for 1.5hrs, 2hrs, 2.5hrs, 3hrs, and 3.5hrs at a constant concentration of 7.5% and temperature of 100^{o}C. The ash removal increased when the residence (soaking) time increased from 1.5hrs to 3.5hrs as well as the volatile matter. But the increase in demineralization goes to insignificant as time gets longer (Table 4-4).

Table 4-4: Investigation of soaking time effect on demineralization

Temperature (^{o}C), ±3^{o}C	Size group (microns)	Concen-tration(%)	Contact time(hrs)	VM (%)	Ash removal(%)	NCV (Kcal/kg)
100	[355-180]	7.5	1.5	35.3	29.1	4653
100	[355-180]	7.5	2	37.6	43.4	4808
100	[355-180]	7.5	2.5	37.9	61.3	5046
100	[355-180]	7.5	3	42.6	78.9	5207
100	[355-180]	7.5	3.5	44.8	83.2	5228

The amount of demineralization that can be accomplished increases with the length of time the coal is exposed to the leaching solution, but the rate of removal decreases after 3hrs. That may be because it controls the point at which the mineral phases in the coal and the leachant come into contact. As the contact time increase, the concentration of mineral matters to be removed might be decreased which results decreasing in rate of removal.

More interaction between the leachant and the mineral matter is made possible by longer contact times, which increases the amount of minerals that are released from the coal matrix. Because more mineral stuff can dissolve from the coal matrix during the longer contact time, the percent demineralization tends to rise over time *(S. K. Behera, Chakraborty, et al., 2018).* The results on Table 4-4 showed that the percentage of demineralization rose over time. The longer the contact time between the minerals in the coal and the leachants, the more minerals were liberated during the leaching process, which could be the source of the higher demineralization.

4.2.4. Effect of Alkali-acid Concentration on Demineralization

With the same concentration of NaOH solution and HF solutions, its effect is investigated at 2.5%, 5%, 7.5% and 10% by demineralizing size group C for 3hrs at 100^{o}C. The demineralization efficiency readily increased as the concentrations increased from 2.5% to 10%. The decrease in ash content was noticed with an increase in concentration of both NaOH and HF as shown in Table 4-5. When the concentration rose from 7.5% to 10%, the demineralization increased noticeably, but the net CV increment did not change much. That might be because the concentration causes the VM to grow significantly, lowering the intensity of the heat. Ash removal is increased by further increasing the HF concentration, however increases in NaOH concentration above 10% have little impact because the complex sodium compound adsorbs on the reactive site of the coal surface and forms a film coating. *(S. K. Behera et al., 2017a; Dash et al., 2013).*

Table 4-5: Study of concentration of reagents on demineralization

Temperature (^{o}C), ±3^{o}C	Size group (microns)	Concen-tration(%)	Contact time(hrs)	VM (%)	Ash removal(%)	NCV (Kcal/kg)
100	[355-180]	2.5	3	36.3	24.9	4579
100	[355-180]	5	3	38.0	46.0	4837
100	[355-180]	7.5	3	42.6	78.9	5207
100	[355-180]	10	3	46.9	86.4	5237

The effect of alkali acid concentration on the demineralization of coal is an important factor to be considered in coal processing. The concentration of alkali and acid used in the

demineralization process has a significant impact on the efficiency and effectiveness of mineral matter removal from coal.

Higher quantities of alkali or acid, or both, have been found to be more effective in demineralizing coal. Numerous research have looked into the demineralization of coal utilizing a combination of alkali and acid leaching (sequential stepwise alkali-acid leaching procedures). The results revealed that the combined action of both alkali and acid leaching increased the degree of demineralization *(Dhawan & Sharma, 2024).*

Naturally, Boroda Coal incorporates a large quantity of quartz and alumina which accounts above 85% of its mineral impurities (*from preliminary test*). Usually, the *silica* is present in the separate entity as a crystalline form called quartz (SiO_2), it but may exist as a form of aluminosilicate compounds with alumina. The common aluminosilicate compounds include kaolinite ($Al_2Si_2O_5(OH)_4$), illite ($KAl_2(Si_3Al)O_{10}(OH)_2$), montmorillonite ($(Na,Ca)_{0.3}(Al,Mg)_2Si_4O_{10}(OH)_2.nH_2O$), and others rarely. CaO, the other ash content of Boroda coal, may exist commonly in the form of calcite ($CaCO_3$), dolomite ($CaMg(CO_3)_2$), and gypsum ($CaSO_4.2H_2O$). The other common oxide found in the Boroda coal ash is iron-oxide which mostly found as pyrite (FeS_2), hematite (Fe_2O_3) and magnetite (Fe_3O_4) in the coal, whereas sulfur as a pyrite and hydrogen sulfide (H_2S). Thus, the chemicals NaOH and HF will attack mechanism these impurities in the coal matrix. For this leaching process these chemical reagents diffuse from the outer surface of the coal matrix and enter through the pores to the inner part of the coal to attack the mineral matters. When an alkali solution diffused, silica, alumina, and other clay-bearing minerals readily disintegrated to create soluble sodium silicate, sodium aluminate, and sodium-aluminosilicate compounds *(Kumar & Shankar, 2010).*

The strong affinity of hydroxyl OH- (hydroxyl ion) towards the minerals in the coal matrix may account for the greater amount of dissolution of the inorganic minerals by the caustic action. Because of the action of an alkali solution, the remaining minerals were dislodged and became stuck inside the coal matrix pores *(K. S. Behera et al., 2018; S. K. Behera et al., 2017a; S. K. Behera, Chakraborty, et al., 2018; S. K. Behera, Kumari, et al., 2018).*

The following possible and selective chemical reactions, among many, which will occur during the leaching of coal with NaOH *(Batnasan et al., 2022; G.M., 1989; Habashi, 2017; Mukherjee & Borthakur, 2003; Smith, 2009; Q. Yang et al., 2020).*

$SiO_2 + 2NaOH \longrightarrow Na_2SiO_3 + H_2O$

$Al_2Si_2O_5(OH)_4 + 6NaOH \longrightarrow 2NaAlO_2 + 2Na_2SiO_3 + 5H_2O$

$KAl_2(Si_3Al)O_{10}(OH)_2 + 8NaOH \longrightarrow 3Na_2SiO_3 + 2NaAlO_2 + KOH + 4H_2O$

$(Na,Ca)_{0.3}(Al,Mg)_2Si_4O_{10}(OH)_2.nH_2O) + 10NaOH \longrightarrow 4Na_2SiO_3 + 2NaAlO_2 + Ca(OH)_2 + Mg(OH)_2 + (n+2)H_2O$

$CaCO_3 + 2NaOH \longrightarrow Ca(OH)_2 + 2Na_2CO_3$

$CaMg(CO_3)_2 + 4NaOH \longrightarrow \underline{Ca(OH)_2} + \underline{Mg(OH)_2} + 2Na_2CO_3$

$CaSO_4.2H_2O + 2NaOH \longrightarrow \underline{Ca(OH)_2} + 2Na_2SO_4 + 2H_2O$

$4FeS_2 + 16NaOH + 15O_2 \longrightarrow \underline{4Fe(OH)_3} + 8Na_2SO_4 + 2H_2O$ *(V.P., 1995)*

$Fe_2O_3 + 2NaOH \longrightarrow 2NaFeO_2 + H_2O$

$Fe_3O_4 + 4NaOH \longrightarrow 2NaFeO_2 + NaFeO_2 + 2H_2O$

$H_2S + 2NaOH \longrightarrow Na_2S + 2H_2O$

$2NaOH + R\text{-}S \longrightarrow R\text{-}SNa_2$

Here, all the demineralization products are soluble and can be removed easily by hot water washing during the experiment, except some metallic hydroxides (formed as precipitate) on the underlined.

In addition to the dissolution of sodium complexes formed during alkali leaching, HF can react with different impurities of coal such as silicates, alumina, calcite, iron oxide, pyrite, etc. When coal is subjected to demineralization using HF acid solution, several reactions can occur. The reactions below are among the major reactions involved during the dissolution of mineral components present in the coal matrix *(Dhawan & Sharma, 2024; Djomgoue & Njopwouo, 2013; G.M., 1989; Habashi, 2017; Smith, 2009).*

$SiO_2 + 4HF \longrightarrow SiF_4 + 2H_2O$

$Al_2Si_2O_5(OH)_4 + 14HF \longrightarrow 2AlF_3 + 2SiF_4 + 9H_2O$

$KAl_2(Si_3Al)O_{10}(OH)_2 + 20HF \longrightarrow 3SiF_4 + 2AlF_3 + KF + 10H_2O$

$(Na,Ca)_{0.3}(Al,Mg)_2Si_4O_{10}(OH)_2.nH_2O) + 20HF \longrightarrow 4SiF_4 + 2AlF_3 + \underline{CaF_2} + \underline{MgF_2} + (n+10)H_2O$

$CaCO_3 + 2HF \longrightarrow \underline{CaF_2} + CO_2 + 2H_2O$

$CaMg(CO_3)_2 + 4HF \longrightarrow \underline{CaF_2} + \underline{MgF_2} + 2CO_2 + 2H_2O$

$CaSO_4.2H_2O + 2HF \longrightarrow \underline{CaF_2} + H_2SO_4 + 2H_2O$

$FeS_2 + 4HF \longrightarrow FeF_2 + 2H_2S + 2H_2O$

$Fe_2O_3 + 6HF \longrightarrow 2FeF_3 + 3H_2O$

$Fe_3O_4 + 8HF \longrightarrow 3FeF_2 + 4H2O$

$H_2S + 2HF \longrightarrow SF_2 + 2H_2$

In the HF demineralization of the coal, most of the products are water soluble and gaseous and they will be easily removed, except the underlined products which are preciptates in nature.

4.2.5. Analysis of Boroda Coal

After two-step NaOH-HF demineralization, Boroda Coal is sent to Mugher Cement Factory for chemical analysis of the ash. The standard method they followed was the wet (classical) method, as depicted in section 3.3.2 (F). The result of the ash analysis is given as the following.

Table 4-6: Ash analysis of coal before and after with its removal percentage

Name of Oxide	Raw coal composition (%) (out of 17.69% ash)	Treated coal composition (%) (out of 3.73% ash)	Percent removal (out of 3.73% ash)
SiO_2	53.9	34.24	86.60
Al_2O_3	31.28	16.85	88.64
Fe_2O_3	5.81	5.79	78.99
MgO	0.82	0.82	78.91
CaO	3.22	1.37	91.03
SO_3	1.53	3.62	50.11
Others	3.44	37.31	-

The percentage composition of each oxide of the ash of the treated coal is lower than the raw coal and the unknown components are higher. This phenomenon may be due to the conversion of some oxides to salts such as SiF_4, AlF_2, FeF_3, CaF_2, MgF_2 and some organic matter of coal may also exist during ashing. The salts, the unburned coal matter, and the other components compose 37.31% out of 3.73% ash. The SO_3 composition of the treated coal is higher than the raw coal. This phenomenon is expected due to the lower capability of HF solution to remove sulfur.

Although the percent demineralization and CV of the coal slightly increased after 7.5% concentration and 3hrs of contact time, the treatment conditions to demineralize Boroda Coal are advisable to be a size of C [355-180] microns at a temperature of 100^{o}C for 3hrs of contact

time with 7.5% reagent concentrations for this two-step NaOH-HF leaching. This demineralization gave 78.9% ash removal and 50.11% desulfurization and CV improvement by 21.8%. On the above treatment conditions, the ash removal after the first stage NaOH-HF leaching was 28.8%, thus, the second stage increased the ash removal to 78.9%.

4.3. Analysis of the Concentrate of Froth Flotation

After the concentrate is dried, its mass is measured to calculate the coal yield of the process. The yield can be calculated based on the initial amount of coal used to conduct the flotation, and it is about 34.2%. The proximate analysis shows that the product from the froth flotation has a VM of 50.5%, ash content of 8.4%, and CV of 4715 Kcal/kg, it is just 10.3% CV improvement. This means that 52.52% of the ash-bearing minerals were removed by the froth flotation method.

The coal that was gained after froth flotation as a concentrate, usually called yield, was 92.32g, which is about 34.2% (equation 3.6). This result may indicate that the mixing phenomena of the coal and the mineral matter are homogeneous, i.e. the mineral matter is highly distributed through the coal matrix. But, the particle size to which the coal is ground has its effect on the percentage of the recovery. When the coal particles get finer, the coal recovery gets higher even if the CV value decreases. This may be due to the detachment of mineral matter from the coal matrix increases as fineness increases. Moreover, the density of particles decreases as their surface area to volume ratio increases. The VM of the concentrate is higher than usual which may be caused due to the higher composition of low-density particles. That also resulted lower CV of the yield of coal.

4.4. XRD and SEM Analysis Boroda Coal

4.4.1. XRD Analysis of Boroda Coal

The XRD measurement of a sample is a plot of 2θ (the angle measured in degree) versus intensity, and can show the crystallinity of a sample. The intensity of the peaks is related to the amount of molecules in that phase or with that spacing. The greater the intensity of the peak, the higher the amount of crystals or molecules with that distinct spacing. The width of the peaks is inversely proportional to the crystal size. A bigger crystal corresponds to thinner peak of the plot. A broader peak implies there may be a smaller crystal, defect of crystalline structure, or

the sample might be amorphous in nature, a solid lacking perfect crystallinity, whereas when the peaks disappeared in XRD graph responsible for the peaks in the sample indicates the transition to amorphous phase, the reduction of amount of crystallinity, or the crystal size becomes smaller *(Iowa State University, 2019; Montejo-Bernardo, 2005; Verichek technical services, 2023)*. Having the above facts, the spectra of X-ray diffraction (XRD) were performed to see if Boroda coal crystallinity was altered or disappeared by chemical or physical treatments. The X-ray diffraction spectra of raw coal, physically treated coal, chemically treated coal and for comparison, the tree samples in one graph are plotted.

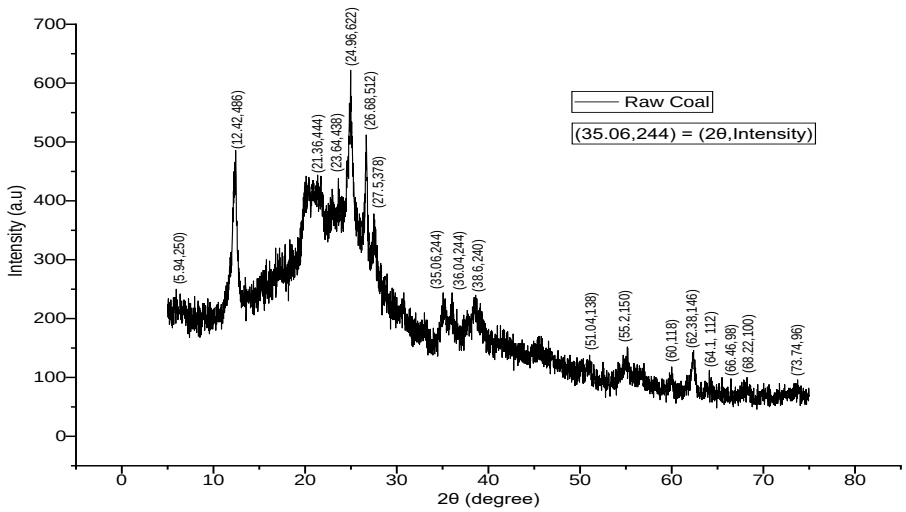

Figure 4-1: The XRD plot of raw Boroda coal

As observed on the plots, the number of peaks are increased when the raw coal was chemically treated (fig. 4-8) whereas, decreased (disappeared) when it is treated physically (fig. 4-7). This shows that the samples crystallinity is increased with chemical treatment, but decreased (gets more amorphous) with physical treatment. Therefore, the action of the chemicals on the minerals matter of the coal caused their crystallinity to increase.

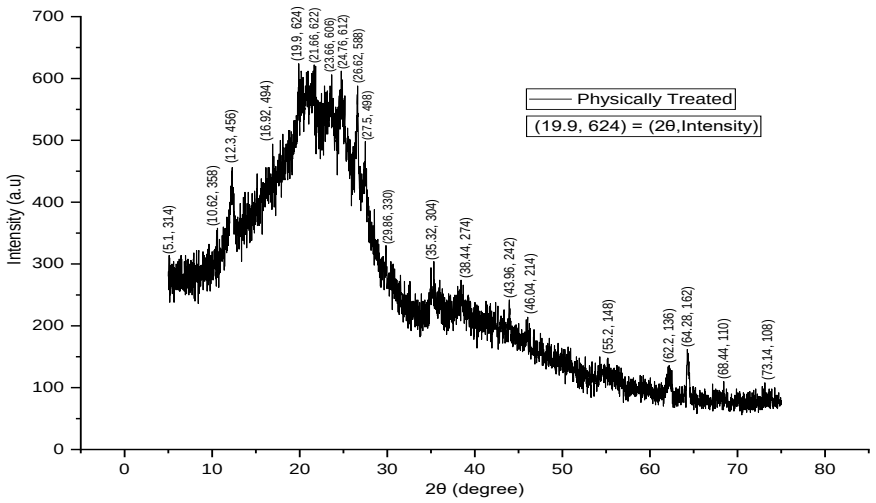

Figure 4-2: The XRD plot of physically treated Boroda coal

The peaks' width gets thinner when the coal is treated chemically. As seen in the figure (fig. 4-6), the raw coal has a few large peaks which are wide compared to the chemically treated (fig. 4-8), implies that there is an existence of bigger crystal molecules.

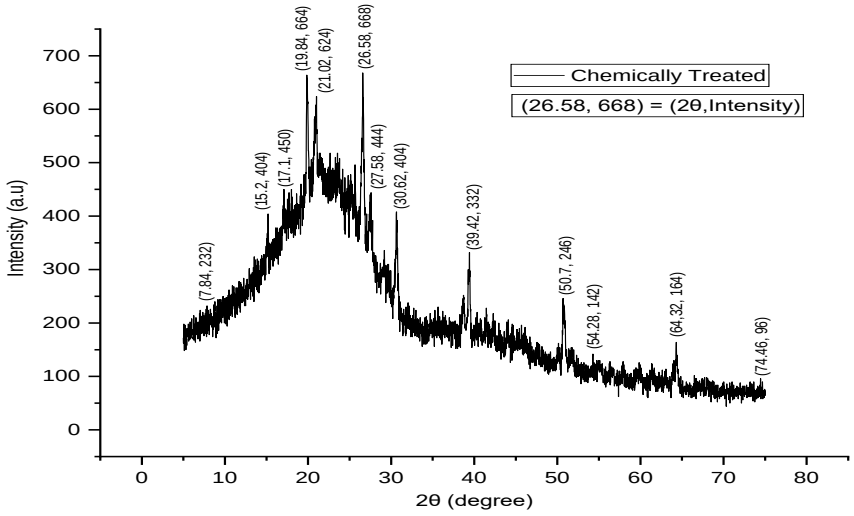

Figure 4-3: The XRD plot of chemically treated Boroda coal

Comparing the result to the literatures *(Apua & Simate, 2018; Um et al., 2009; Yu et al., 2021)*, the XRD result of raw coal sample shows that the coal particle contained the abundantly of quartz (e.g. 2θ = 12.42, 21.36, 24.96, 26.68, 51.04, etc. degrees), and iron-oxide (e.g. 35.06, 56.2, 60.1, etc. degrees), kaolinite (e.g. 23.64^{o}), mullite ($3Al_2O_3 \cdot 2SiO_2$) (e.g. 27.5, 62.0, 64.1,

73.74, etc. degrees), and alumina (e.g. 36.04, 38.6 degrees) which are responsible for ash increment.

The XRD graph of chemically treated coal (figure 4-8) indicates that the peaks are shifted with some angles, got sharp & thin, and some are disappeared (e.g. 12. 42^{o} of raw coal) after chemical treatment which might be the result of minerals removal with the treatment a conformation to chemical analysis of the ash removal (Doymaz et al., 2010; Jena et al., 2008; Usman et al., 2022b; N. Yang et al., 2016).

4.4.2. SEM Analysis and Surface Morphology of Boroda Coal

The difference in physical appearance is seen in Figure 4-6, the raw coal (A) has a nearly brown color whereas the clean coal has a black color (B). The '*light to dark brown color'* generally indicates that the coal has relatively low carbon content and high moisture content. The presence of impurities, such as minerals, can also contribute to this color. Moreover, this color of coal usually suggests that the raw coal is a younger form of coal.

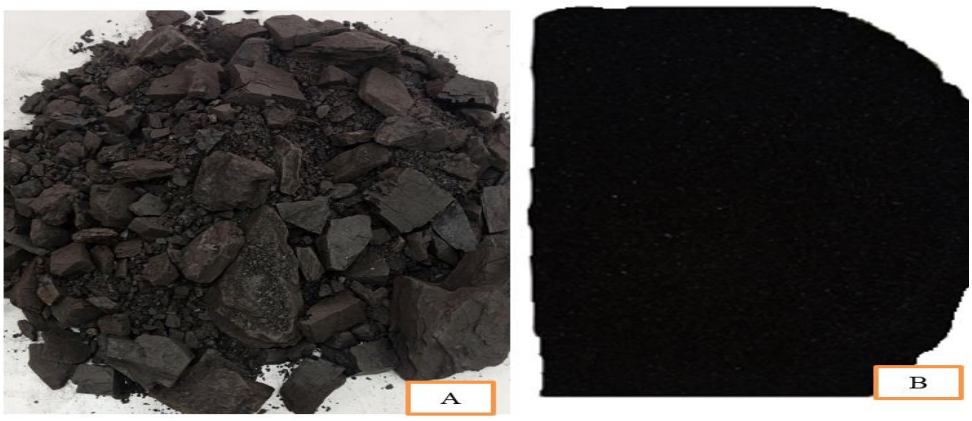

Figure 4-4: Coal appearance before demineralization (A) and after demineralization (B)

There is a color change of the coal from deep brown color to black color (Figure 4-6). The black color of the coal indicates that the coal has lower impurities, mineral matters, low moisture and higher carbon content that results a good combustion characteristics.

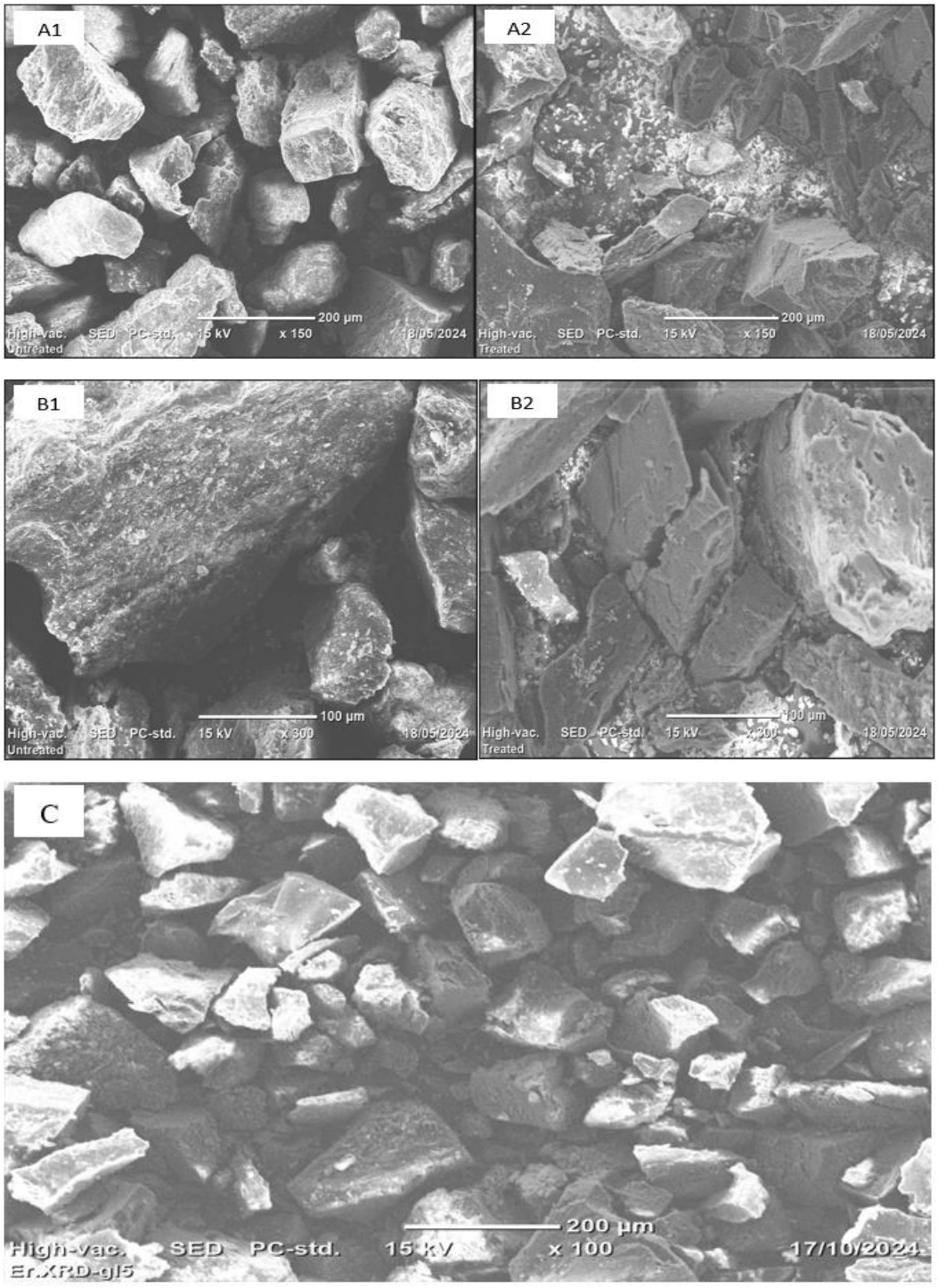

Figure 4-5: SEM images of Boroda Coal before (A1 & B1), after (A2 & B2) demineralization and froth flotation treatment (C).

The SEM image of the untreated (native) and NaOH-HF treated Boroda Coal is presented in Figure 4-7 with different resolutions. The image indicated on A1 is native coal and A2

is treated, at x150 resolution. The image indicated on B1 (native) and B2 (treated) at higher resolution of x300. The images on the left side (A1 & B1) are structurally more regular and their surface is rich in white spots. Whereas, the right ones (A2 & B2) are structurally more irregular and have lower white spots. The white spots may be the mineral matter found in the coal matrix which gets lower after demineralization. The more irregular structure acquired after treatment by NaOH-HF. The irregularity also indicates that the structure get more porous than ever before, resulted from the seeping out of mineral matters and the shape alteration of coal matter itself. However, the image in A1 (raw coal) and that of C (physically treated) are morphologically similar which indicate the physical treatment has no surface structural effect.

4.5. Coal Recovery

There is a loss of identifiable process materials during any process, including coal demineralization. Coal loss during chemical demineralization can be caused by a number of ways. Chemical demineralization can lead to some coal loss even though it is a technique that improves the grade of coal by removing mineral impurities. The main losses in coal demineralization are mechanical separation, adsorption of particles on solid objects, chemical assault (dissolution), and washout of extremely fine coal particles with the solution. *(Sriramoju et al., 2021).*

The chemical demineralization process has the ability to dissolve some minerals found in coal, including clays and carbonates. When these minerals combine with a demineralizing agent, like an acids and bases, they dissolve into soluble molecules. Some parts of the coal may also dissolve even if it is less reactive towards NaOH or HF. This means that dissolved species may be released, which could result in the loss of both the minerals and a component of the coal matrix.

Physical procedures like size classification and grinding are frequently used in chemical demineralization to improve the coal-demineralizing agent interaction. These mechanical processes have the potential to break and fracture coal particles, resulting in the loss of tiny pieces or fines that might not be successfully recovered. To get rid of a solution containing soluble mineral complexes formed by leaching, water is frequently used to wash the coal. Coal loss may occur from this procedure if some coal particles are entrained and removed

by the liquid media *(S. K. Behera, Chakraborty, et al., 2018; Bolat et al., 1998; Dash et al., 2012).*

Ash and coal slurry are examples of solid residues or byproducts that might be produced following the demineralization process. Certain coal particles that were not entirely recovered or separated during the demineralization process might be present in these residues. Coal loss could arise from the adsorption of coal particles on these solid wastes *(Meshram et al., 2012).*

In this research, the recovery of coal after demineralization was found 88.6% of C[355-180], without considering the amount of ash removed during leaching. The coal recovery decreased significantly as the coal fineness increased. This might be due to the increase in fine particles when the coal is ground finely, and the fine coal is more vulnerable to chemical attack. Also the attachment with solid materials and washout of coal increases with fineness.

CHAPTER FIVE

5. CONCLUSIONS AND RECOMMENDATIONS

5.1. Conclusions

In summary, two stage alkali-acid treatment of coal results good ash removal. At the size group C, for example, the first stage gives only 28.8% ash removal but 78.9% ash removal achieved after the second stage treatment. Thus, two stage alkali-acid treatment of coals will give a better results than single stages. The study results indicate that the utilization of HF acid reagent leads to a lower rate of organic matter decomposition in coal as both temperature and time increase compared to other works by sulfuric acid and nitric acids.

The study has achieved significant CV improvement of Boroda Coal to more than 5207 Kcal/kg at different conditions. Therefore, it can be concluded that the treated coal can be technically acceptable to utilize for cement plants, or it may take small amount of high CV coal if it is necessary to increase more.

Although it is subjective to select the optimum conditions, a chemical demineralization of a Boroda Coal sieved with [-355+180] micron treated with 7.5% concentrations for 3hrs at a temperature of 100^{o}C could be more appropriate since optimum is not always a maximum value.

On the other hand, chemical leaching is by far outshining than froth flotation in terms of demineralization, CV and coal recovery. As a result, chemical leaching of coal is advisable over froth flotation to have a better ash removal, to get high CV and for low loss of coal matter (high coal recovery) after treatment.

5.2. Recommendations

It is recommended that future studies should consider the effect of stirring and consistent heating during the leaching process. Although chemical leaching is technically effective than froth flotation, it may not be effective in terms of cost. Therefore, future studies should include cost analysis. Optimization the interaction of treatment parameters should be done to be more close to the optimum, and to understand the most important treatment parameter.

REFERENCES

Abraham, K. (2018). Characterization and evaluation of mush valley Coal for its application as a domestic energy source.

Ahmed, W. (2007). Fossil fuel energy resources of Ethiopia : Coal deposits. *Coal Geology*, *72*, 293–314. https://doi.org/10.1016/j.coal.2007.02.006

Amin, N.-U., & Ali, K. (2011). Raw Mix Designing for Coal as a Fuel in Cement Kiln as a Major Fuel and its Impact on Clinker Parameters. *Journal of Chemical Society*, *33*(2), 147–151.

Apua, M. C., & Simate, G. S. (2018). Characterization of Coal Fly Ash for the Production of Coagulant for Usage in Wastewater Treatment. *Greater Columbus Convention Center*, *2018*, 1512–1521. https://doi.org/10.7449/2018/MST

ASTM. (2013). Standard Test Methods for Proximate Analysis of the Analysis Sample of Coal and Coke by Instrumental Procedures. In *ASTM D 5142-02a*.

ASTM, S. T. (2017). *Standard Test Methods for Coal and Coke Ash _ D2795*. *05*(Reapproved), 1–7.

Ateşok, G., Boylu, F., & Çelik, M. S. (2001). Carrier flotation for desulfurization and deashing of difficult-to-float coals. *Minerals Engineering*, *14*(6), 661–670. https://doi.org/10.1016/S0892-6875(01)00058-9

Ayhan, F. D., Abakay, H., & Saydut, A. (2005). Desulfurization and deashing of Hazro coal via a flotation method. *Energy and Fuels*, *19*(3), 1003–1007. https://doi.org/10.1021/ef049747r

Baruah, M. K., Kotoky, P., Baruah, J., & Bora, G. C. (2000). Cleaning of Indian coals by agglomeration with xylene and hexane. *Separation and Purification Technology*, *20*(2–3), 235–241. https://doi.org/10.1016/S1383-5866(00)00115-5

Batnasan, A., Shibayama, A., Takeuchi, H., Haga, K., Mizutani, M., & Hihuchi, K. (2022). Removal of Silicon , Aluminum and Phosphorus Impurities from Low-grade Iron Ore by Reverse Froth Flotation and Alkaline Roasting. *International Resource Sciences*, *25*(1), 122–128.

Behera, K. S., Meena, H., Chakraborty, S., & Meikap, B. C. (2018). Application of response surface methodology (RSM) for optimization of leaching parameters for ash reduction from low-grade coal. *International Journal of Mining Science and Technology*.

https://doi.org/10.1016/j.ijmst.2018.04.014

Behera, S. K., Chakraborty, S., & Meikap, B. C. (2017a). Chemical demineralization of high ash Indian coal by using alkali and acid solutions. *Fuel*, *196*, 102–109. https://doi.org/10.1016/j.fuel.2017.01.088

Behera, S. K., Chakraborty, S., & Meikap, B. C. (2017b). Upgradation of Low Grade Coal to High Quality Coal by Chemical Beneficiation Technique. *ASME*, 1–6.

Behera, S. K., Chakraborty, S., & Meikap, B. C. (2018). Demineralization mechanism and influence of parameters on high ash Indian coal by chemical leaching of acid and alkali solution. *International Journal of Coal Science & Technology*, *5*(2), 142–155. https://doi.org/10.1007/s40789-018-0208-3

Behera, S. K., Kumari, U., & Meikap, B. C. (2018). A review of chemical leaching of coal by acid and alkali solution. *Journal of Mining and Metallurgy*, *54 A*(1), 1–24. https://doi.org/10.5937/JMMA1801001B

Bhatti, M. A., Nasir, S., & Mehmood, Z. (2020). Demineralization of a Low-Rank Coal to Produce Clean Coal for Industrial Utilization. *Insights in Mining Science and Technology*, *2*(3). https://doi.org/10.19080/IMST.2020.02.555590

Bilgin, O., Hacıfazlıo, H., & Sert, D. (2021a). Leaching of coal by trioxoboric acid for coal cleaning. *Fuel*, *57*(5), 129–136. https://doi.org/10.37190/ppmp/141489

Bilgin, O., Hacıfazlıo, H., & Sert, D. (2021b). Leaching of coal by trioxoboric acid for coal cleaning. *Physicochemical Problems of Mineral Processing*, *57*(5), 129–136. https://doi.org/10.37190/ppmp/141489

Bolat, E., Sağlam, S., & Pişkin, S. (1998). Chemical demineralization of a Turkish high ash bituminous coal. *Fuel Processing Technology*, *57*(2), 93–99. https://doi.org/10.1016/S0378-3820(98)00075-7

Carlson, C. L., & Adriano, D. C. (1993). (1993) Environmental Impacts of Coal Combustion Residues. *Journal of Environmental Quality*, *22*, 227–247.

D-3177, A. (1995). *American standard for testing materials*.

Das, A., Sarkar, B., Ari, V., & Roy, S. (2010). Efficient recovery of combustibles from coking coal fines. *Mineral Processing and Extractive Metallurgy Review*, *31*(4), 236–249. https://doi.org/10.1080/08827508.2010.508827

Dash, P. S., Kumar, S. S., Banerjee, P. K., & Ganguly, S. (2012). Mineral Processing and

Extractive Metallurgy Review : An International Chemical Leaching of High-Ash Indian Coals for Production of Low-Ash Clean Coal. *An International Journal of Coal Geology, November 2014*, 37–41. https://doi.org/10.1080/08827508.2012.656775

Dash, P. S., Kumar, S. S., Banerjee, P. K., & Ganguly, S. (2013). Chemical leaching of high-ash indian coals for production of low-ash clean coal. *Mineral Processing and Extractive Metallurgy Review*, *34*(4), 223–239. https://doi.org/10.1080/08827508.2012.656775

Demoze, E. A. (2007). *Utilization of coal in metal industries*.

Dhawan, H., & Kumar, D. (2019). Advances in the chemical leaching (inorgano-leaching), bio- leaching and desulphurisation of coals. *International Journal of Coal Science & Technology*, *6*(2), 169–183. https://doi.org/10.1007/s40789-019-0253-6

Dhawan, H., & Sharma, D. K. (2024). Process engineering of demineralisation of moderate to high ash Indian coals through NaOH-HCl leaching and HF leaching. *International Journal of Coal Science and Technology*, *11*(1), 1–12. https://doi.org/10.1007/s40789-024-00679-9

Djomgoue, P., & Njopwouo, D. (2013). FT-IR Spectroscopy Applied for Surface Clays. *Journal of Surface Engineered Materials and Advanced Technology*, *3*(October), 275–282. https://doi.org/http://dx.doi.org/10.4236/jsemat.2013.34037

Doymaz, I., Gulen, J., Piskin, S., & Toprak, S. (2010). Energy Sources , Part A : Recovery , Utilization , and Environmental Effects The Effect of Aqueous Caustic and Various Acid Treatments on the Removal of Mineral Matter in Asphaltite The Effect of Aqueous Caustic and Various Acid Treatments on the Removal. *Energy & Fuels*, *October 2014*, 37–41. https://doi.org/10.1080/15567030600819882

Ehsani, M. R., & Eghbali, F. (2007). Reduction of sulfur and ash from tabas coal by froth flotation. *Iranian Journal of Chemistry and Chemical Engineering*, *26*(2), 35–40.

G.M., R. (1989). Taillings management, problems and solutions in the mining industry. In *Energy, Mines and Resources* (1st ed.). Elsevier Sciences Publisher.

Habashi, F. (2017). *A Textbook of Hydrometallurgy* (2nd ed., Vol. 6875, Issue November 2000). https://doi.org/10.1016/S0892-6875(00)00127-8

Honaker, R. Q., Wang, D., & Ho, K. (1996). Application of the Falcon Concentrator for fine coal cleaning. *Minerals Engineering*, *9*(11), 1143–1156. https://doi.org/10.1016/0892-6875(96)00108-2

Huggins, F. E. (2002). Overview of analytical methods for inorganic constituents in coal. *International Journal of Coal Geology*, *50*, 169–214.

Iowa State University, C. I. F. (2019). X-RAY ABSORPTION AND DIFFRACTION. In *Diffraction Basics*. https://www.cif.iastate.edu/acide/xrd-tutorial/xrd (accessed January, 2024)%0D

Jena, M. S., Biswal, S. K., & Rudramuniyappa, M. V. (2008). Study on flotation characteristics of oxidised Indian high ash sub-bituminous coal. *International Journal of Mineral Processing*, *87*(1–2), 42–50. https://doi.org/10.1016/j.minpro.2008.01.004

Khoshdast, H., & Sam, A. (2011). Flotation Frothers : Review of Their Classifications , Properties and Preparation. *The Open Mineral Processing Journal*, *4*, 25–44.

Kizgut, S., Baris, K., & Yilmaz, S. (2006). Effect of chemical demineralization on thermal behavior of bituminous coals. *Journal OfThermal Analysis and Calorimetry*, *86*, 483–488.

Kumar, M., & Shankar, R. H. (2010). Removal of Ash from Indian Assam Coking Coal Using Sodium Hydroxide and Acid Solutions. *Energy Sources*, *22*(2), 187–196. https://doi.org/10.1080/00908310050014153

Malik, A., Singh, D. P., Sharma, S., Dastidar, M. G., & Roychoudhury, P. K. (1999). Oil agglomeration for recovery of coal fines: Effect of vegetable oil and bacterial pretreatment. *Coal Preparation*, *20*(3), 247–268. https://doi.org/10.1080/07349349908945603

Meshram, P., Purohit, B. K., Sinha, M. K., Sahu, S. K., & Pandey, B. D. (2015). Demineralization of low grade coal – A review. *Renewable and Sustainable Energy Reviews*, *41*, 745–761. https://doi.org/10.1016/j.rser.2014.08.072

Meshram, P., Sinha, M. K., Sahu, S. K., & Pandey, B. D. (2012). Chemical benefication of low grade coal-a review. *16th International Conference on Non-Ferrous Metals*, 1–13.

Montejo-Bernardo, S. G.-G. and J. M. (2005). X-ray Absorption and Diffraction. In *Encyclopedia_of_Analytical_Science* (Second_Edi). Elsevier Ltd.

Mukherjee, S., & Borthakur, P. C. (2001). Chemical demineralization / desulphurization of high sulphur coal using sodium hydroxide and acid solutions. *Fuel*, *80*, 2037–2040.

Mukherjee, S., & Borthakur, P. C. (2003). Effect of leaching high sulphur subbituminous coal by potassium hydroxide and acid on removal of mineral matter and sulphur q. *Fuel*, *82*, 783–788.

Nabeel, A., Khan, T. A., & Sharma, D. K. (2009). Energy Sources , Part A : Recovery ,

Utilization , and Environmental Effects Studies on the Production of Ultra-clean Coal by Alkali- acid Leaching of Low-grade Coals Studies on the Production of Ultra-clean Coal by Alkali-acid Leaching of Low-grade Coals. *Energy Sources*, *31*(November 2014), 37–41. https://doi.org/10.1080/15567030701743684

Oruç, F., Özgen, S., & Sabah, E. (2010). An enhanced-gravity method to recover ultra-fine coal from tailings: Falcon concentrator. *Fuel*, *89*(9), 2433–2437. https://doi.org/10.1016/j.fuel.2010.04.009

Rahman, M., Pudasainee, D., & Rajender, G. (2017). Review on chemical upgrading of coal : Production processes , potential applications and recent developments. *Fuel Processing Technology*, *158*, 35–56. https://doi.org/10.1016/j.fuproc.2016.12.010

Rahman, M., Samanta, A., & Gupta, R. (2013). Production and characterization of ash-free coal from low-rank Canadian coal by solvent extraction. *Fuel Processing Technology*, *115*, 88–98. https://doi.org/10.1016/j.fuproc.2013.04.008

Rath, R. K., Singh, R., & Bhattacharyya, K. K. (2011). Processing of Coal Waste by Enhanced Gravity Seperation and Froth Flotation. *Proceedings of International Conference on Coal and Coke*.

Reddy, P. S. R., Kumar, S. ., Bhattacharyya, K. K., S.R.S, S., & Narasimhan, K. S. (1988). Flotation column for fine coal beneficiation. *International Journal of Mineral Processing*, *24*, 161–172.

Sastri, S. R. S., Reddy, P. S. R., Bhattacharyya, K. K., Kumar, S. G., & Narasimhan, K. S. (1988). Recovery of coal fines using column flotation. *Minerals Engineering*, *1*(4), 359–363. https://doi.org/10.1016/0892-6875(88)90026-X

Sharma, A., & Matsumura, A. (2019). A comparative study on demineralization of coals by acid-washing and solvent-extraction methods for low temperature catalytic coal gasi fi cation application. *Carbon Resources Conversion*, *2*(3), 175–181. https://doi.org/10.1016/j.crcon.2019.09.001

Sharma, D. K., & Singh, S. K. (2007). Advanced Process for the Production of Clean Coal by Chemical Leaching Technique Advanced Process for the Production of Clean Coal by Chemical Leaching Technique. *Energy Sources*, *17*(March 2015), 37–41. https://doi.org/10.1080/00908319508946096

Singh, N., Shehnazdeep, & Bhardwaj, A. (2020). Reviewing the role of coal bottom ash as an

alternative of cement. *Construction and Building Materials*, *233*, 117276. https://doi.org/10.1016/j.conbuildmat.2019.117276

Smith, P. (2009). Hydrometallurgy The processing of high silica bauxites — Review of existing and potential processes. *Hydrometallurgy*, *98*(1–2), 162–176. https://doi.org/10.1016/j.hydromet.2009.04.015

Sonmez, O., & Giray, E. S. (2001). The influence of process parameters on desulfurization of two Turkish lignites by selective oxidation. *Fuel Processing Technology*, *70*, 159–169.

Sriramoju, S. K., Dash, P., Suresh, A., & Ray, T. (2021). Integrated process for coal chemical demineralization and spent caustic regeneration- A pilot scale study. *Journal of Cleaner Production*, *327*, 129497. https://doi.org/10.1016/j.jclepro.2021.129497

Tan, T. H., Mo, K. H., Lin, J., & Onn, C. C. (2023). *Review Article An Overview of the Utilization of Common Waste as an Alternative Fuel in the Cement Industry*. *2023*.

Tang, L., Xiao, J., Mao, Q., Zhang, Z., Yao, Z., Zhu, X., Ye, S., & Zhong, Q. (2022). Thermogravimetric Analysis of the Combustion Characteristics and Combustion Kinetics of Coals Subjected to Different Chemical Demineralization Processes. *ACS Omega*, *7*(16), 13998–14008. https://doi.org/10.1021/acsomega.2c00522

Um, N., Han, G., You, K., & Ahn, J. (2009). Immobilization of Pb , Cd and Cr by Synthetic NaP1 Zeolites from Coal Bottom Ash Treated by Density Separation Immobilization of Pb , Cd and Cr by Synthetic NaP1 Zeolites from Coal Bottom Ash Treated by Density Separation. *Resources Processing*, *56*(September), 130–137. https://doi.org/10.4144/rpsj.56.130

Usman, T., Abicho, S., Meshesha, D., & Adam, G. (2022a). Froth flotation beneficiation and physiochemical characterization of coal from Achibo-Sombo-Dabaso area, Southwestern Ethiopia. *Heliyon*, *8*(August), e11313. https://doi.org/10.1016/j.heliyon.2022.e11313

Usman, T., Abicho, S., Meshesha, D., & Adam, G. (2022b). Heliyon Froth fl otation bene fi ciation and physiochemical characterization of coal from Achibo-Sombo-Dabaso area , southwestern Ethiopia. *Heliyon*, *8*(October), e11313. https://doi.org/10.1016/j.heliyon.2022.e11313

V.P., E. (1995). *Pyrite Oxidation* (1st ed.). CRC Press Inc.

Vassilev, S. V, & Vassileva, C. G. (1996). Occurrence , abundance and origin of minerals in coals and coal ashes. *Fuel Processing Technology*, *48*, 85–106.

Verichek technical services. (2023). *Verichek technical services, inc. All about X-Ray Diffraction (XRD) Analysis, Metal Analysis Testing.* https://verichek.net/why-xrd-is-used.html

Wang, Z. Y., Ohtsuka, Y., & Tomita, A. (1986). Removal of mineral matter from coal by alkali teratment. *Fuel Processing Technology*, *13*, 279–289.

Wijaya, N., & Zhang, L. (2011). A Critical Review of Coal Demineralization and Its Implication on Understanding the Speciation of Organically Bound Metals and Submicrometer Mineral Grains in Coal. *Energy & Fuels*, *25*(12), 1–16. https://doi.org/10.1021/ef1008192

Wu, D., Lei, J., Zheng, B., Tang, X., Wang, M., Hu, J., Li, S., Wang, B., & Finkelman, R. B. (2011). Nitrogen in Chinese coals. *Chinese Journal of Geochemistry*, *30*(2), 248–254. https://doi.org/10.1007/s11631-011-0506-6

Wu, Z., & Steel, K. M. (2007). Demineralization of a UK bituminous coal using HF and ferric ions. *Fuel*, *86*, 2194–2200. https://doi.org/10.1016/j.fuel.2007.02.038

Yang, N., Tang, S., Zhang, S., & Chen, Y. (2016). *Mineralogical and Geochemical Compositions of the No . 5 Coal in Chuancaogedan Mine , Junger Coalfield , China*. *5*. https://doi.org/10.3390/min5040525

Yang, Q., Zhang, F., Deng, X., Guo, H., Zhang, C., & Shi, C. (2020). Extraction of alumina from alumina rich coal gangue by a hydro-chemical process. *Royal Society Open Science*, *7*(192132), 1–12. https://doi.org/http://dx.doi.org/10.1098/rsos.192132

Yoseph, D. (2004). *School of Graduate Studies The Utilization of Indigenous Coal as Energy Substitute in Cement Industry*.

Yu, Q., Deng, Y., Feng, Y., & Li, Z. (2021). Phase Transformation of Alumina , Silica and Iron Oxide during Carbothermic Reduction of Fly Ash for Ceramics Production. *Metals*, *11*(1165).

Zhao, J., Zuo, H., Beijing, T., Wang, J., Xue, Q., & Beijing, T. (2018). *Extraction and Thermal Dissolution of Low-Rank Coal by N-Methyl-2- Extraction and thermal dissolution of low-rank coal by N- 1 Introduction*. *February*. https://doi.org/10.1007/978-3-319-72362-4

Zhu, Q. (2014). Coal sampling and analysis standards standards. *IEA Clean Coal Centre, April 2014*.

APPENDIX: A

Designation: D 3177-02

Standard Test Methods for Total Sulfur in the Analysis Sample of Coal and Coke

This standard is issued under the fixed designation D3177; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last re-approval.

1. Scope

1.1 These test methods cover two alternative procedures for the determination of total sulfur in samples of coal and coke. Sulfur is included in the ultimate analysis of coal and coke.

1.2 The procedures appear in the following order:

Method A—Eschka Method
Method B—Bomb Washing Method

1.3 The values stated in SI units are to be regarded as the standard.

2. Summary of Test Methods

2.1 *Eschka Method* — A weighed sample and Eschka mixture are intimately mixed and ignited together. The sulfur is dissolved in hot water and then precipitated from the resulting solution as barium sulfate ($BaSO_4$). The precipitate is filtered, ashed, and weighed.

2.2 *Bomb Washing Method* — Sulfur is precipitated as $BaSO_4$ from oxygen-bomb calorimeter washings, and the precipitate is filtered, ashed, and weighed.

3. Significance and Use

3.1 Determination of sulfur is, by definition, part of the ultimate analysis of coal.

3.2 Sulfur analysis results obtained by these methods are used to serve a number of interests: evaluation of coal preparation, evaluation of potential sulfur emissions from coal combustion or conversion processes, evaluation of the coal quality in relation to contract specification, and other purposes of commercial or scientific interest.

4. Sample

4.1 The sample shall be the material pulverized to pass No. 60 (250-µm) sieve in accordance with Method D2013 or Method D346.

4.2 A separate portion of the analysis sample should be analyzed for moisture content in accordance with Test Method D3173, so that calculation to other than the as-determined basis can be made.

4.3 Procedures for converting as-determined sulfur values obtained from the analysis sample to other bases are described in Practice D3176 and Method D3180.

4.4 Standard Reference Material (SRM), such as SRM Nos. 2682 through 2685—Sulfur in Coal[1] which consist of four different coals that have been individually crushed and ground to pass a No. 60 (250-µm) sieve, and bottled in 50-gunits, or other commercially available reference material coals with a certified sulfur content of ±0.0*xx* precision can be used. Sulfur values obtained by analyzing these coals, using any of the methods described in this test method, may be used for checking the accuracy of analytical results.

ALTERNATIVE PROCEDURES
TEST METHOD A—ESCHKA METHOD

5. Apparatus

5.1 Gas or Electric Muffle Furnace, or Burners, for igniting the sample with the Eschka mixture and for igniting the barium sulfate ($BaSO_4$).

5.2 Crucibles or Capsules—Porcelain capsules, 22 mm (7⁄8 in.) in depth and 44 mm (13⁄4 in.) in diameter, or porcelain crucibles of 30-mL capacity, high or low form, or platinum crucibles of similar size shall be used for igniting the sample with the Eschka mixture. Porcelain, platinum, alundum, or silica crucibles of 10 to 15-mL capacity, shall be used for igniting the $BaSO_4$.

6. Reagents

6.1 Purity of Reagents—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Available Reagents of the American Chemical Society[2], where such

[1] Available from National Institute of Standards and Technology, Gaithersburg, MD 20899.

[2] *Reagent Chemicals, American Chemical Society Specifications*, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see *Analar Standards for Laboratory Chemicals*, BDH Ltd., Poole, Dorset, U.K., and the *United States Pharmacopeia and National Formulary*, U.S. Pharmaceutical Convention, Inc. (USPC), Rockville, MD

specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

6.2 Purity of Water — Unless otherwise indicated, references to water shall be understood to mean reagent water, Type IV, conforming to Specification D 1193.

6.3 Barium, Chloride Solution (100 g/L)—Dissolve 100 g of barium chloride ($BaCl_2 \cdot 2H_2O$) and dilute to 1 L with water.

6.4 Eschka Mixture—thoroughly mix 2 parts by weight of light calcined magnesium oxide (MgO) with 1 part of anhydrous sodium carbonate (Na_2CO_3). Both materials should be as free as possible from sulfur. Eschka mixture is also available commercially.

6.5 Hydrochloric Acid (1 + 1) — Mix equal volumes of concentrated hydrochloric acid (HCl, sp gr 1.19) and water.

6.6 Hydrochloric Acid (1 + 9) — Mix 1 volume of concentrated hydrochloric acid (HCl, sp gr 1.19) with 9 volumes of water.

6.7 Methyl Orange Indicator Solution (0.2 g/L)—Dissolve 0.02 g of methyl orange in 100 mL of hot water and filter.

6.8 Sodium Carbonate, Saturated Solution—Dissolve approximately 60 g of crystallized sodium carbonate ($Na_2CO_3 \cdot 10H_2O$) or 22 g of anhydrous sodium carbonate (Na_2CO_3) in 100 mL of water, using a sufficient excess of Na_2CO_3 to ensure a saturated solution.

6.9 Sodium Hydroxide Solution (100 g/L)—Dissolve 100 g of sodium hydroxide (NaOH) in 1 L of water. This solution may be used in place of the Na_2CO_3 solution.

7. Procedure

7.1 Preparation of Sample and Mixture—thoroughly mix on glazed paper approximately 1 g of the sample, weighed to nearest 0.1 mg and 3g of Eschka mixture. The amount of sample to be taken will depend on the amount of $BaCl_2$ solution required in accordance with 7.3. Transfer to a porcelain capsule, or porcelain crucible, or a platinum crucible and cover with about1g of Eschka mixture.

7.2 Ignition—Heat the crucible over an alcohol, gasoline, or gas flame as described in 7.2.1, or in a gas or electrically heated muffle as described in 7.2.2 for coal and in 7.2.3 for coke. The use of artificial gas for heating the sample and the Eschka mixture is permissible only when the crucibles are heated in a muffle.

7.2.1 Open Flame—Heat the crucible, placed in a slanting position on a triangle, over a very low flame to avoid rapid expulsion of the volatile matter that tends to prevent complete absorption of the products of combustion of the sulfur. Heat the crucible slowly for 30 min, gradually increase the temperature, and occasionally stir until all black particles have disappeared, which is an indication of the completeness of the procedure.

7.2.2 Muffle (Coal)—Place the crucible in a cold-vented muffle and gradually raise the temperature to 800 6 25°C in about 1 h. Maintain this maximum temperature until, on stirring, all black particles have disappeared (about 1.5 h).

7.2.3 Muffle (Coke)—Place the crucible in a warm-vented muffle (about 200°C) and gradually raise the temperature to 800 ± 25°C in about 30 min. Maintain this maximum temperature until, on stirring, all black particles have disappeared.

7.3 Subsequent Treatment—Remove the crucible and empty the contents into a 200-mL beaker and digest with 100 mL of hot water for *1/2* to *3/4* h, while stirring occasionally. Decant the solution through filter paper, retaining as much insoluble material in beaker as possible. Thoroughly wash the insoluble matter in the beaker with hot water. After several washings in this manner, transfer the insoluble matter to the filter and wash five times with hot water, keeping the mixture well agitated. Make the filtrate, amounting to about 250 mL, just neutral to methyl orange with NaOH or Na_2CO_3 solution; then add 1 mL of HCL (1+9). Boil and add slowly from a pipet, while stirring constantly, 10 mL or more of $BaCl_2$ solution. The $BaCl_2$ solution must be in excess. If more than 10 mL of $BaCl_2$ solution is required, reduce the weight of sample to about 0.5 g and repeat the ignition and digestion. Continue boiling for 15 min and allow to stand for at least 2 h, or preferably overnight, at a temperature just below boiling. Filter through a fine ashless paper, such as Whatman No. 42 or similar, and wash with hot water until 1 drop of silver nitrate ($AgNO_3$) solution produces no more than a slight opalescence when added to 8 to 10 mL of filtrate.

7.3.1 Place the wet filter containing the precipitate of barium sulfate ($BaSO_4$) in a weighed platinum, porcelain, silica, or alundum crucible, fold the paper loosely over the precipitate to allow a free access of air but prevent spattering.

APPENDIX: B

Designation: D 2795 - 95

Standard Test Methods for Analysis of Coal and Coke Ash

This standard is issued under the fixed designation D 2795; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision.

1. Scope

1.1 These test methods cover the analysis of coal and coke ash for the commonly determined major elements.

1.2 The test methods appear in the following order:

	Sections
Silicon Dioxide (SiO_2)	9 to11
Aluminum Oxide (Al_2O_3)	12 to14
Ferric Oxide (Fe_2O_3)	15 to17
Calcium Oxide (CaO), and Magnesium Oxide (MgO)	25 to 28

1.3 The values stated in SI units (Practice E 380) shall be regarded as the standard. The values given in parentheses are for information only.

2. Summary of Test Methods

2.1 The coal or coke to be analyzed is ashed under standard conditions and ignited to constant weight. Two solutions are prepared from the ash. Solution A is obtained by fusing the ash with sodium hydroxide (NaOH) followed by a final dissolution of the melt in dilute hydrochloric acid (HCl). Solution B is prepared by decomposition of the ash with sulfuric (H_2SO_4), hydrofluoric (HF), and nitric (HNO_3) acids. Solution A is used for the analysis of SiO_2 and Al_2O_3, and Solution B for the remaining elements.

2.2 The two solutions are analyzed by a combination of methods: (1) spectrophotometric procedures are used for SiO_2, Al_2O_3, and Fe_2O_3, (2) chelatometric titration for CaO and MgO.

3. Significance and Use

3.1 A compositional analysis of the ash is often useful in the total coal quality description. Knowledge of the ash composition is also useful in predicting the behavior of the ashes and slags in combustion chambers. Utilization of the coal combustion ash by-products sometimes depends on the chemical composition of the ash. 4.2 It should be noted that chemical composition of laboratory prepared coal ash may not exactly represent the composition of mineral matter in the coal, or the composition of the fly ash and slags resulting from the commercial scale burning of the coal.

4. Apparatus

4.1 *Balance*, sensitive to 0.1 mg.

4.2 *Crucibles*-Nickel crucibles of 50-cm^3 capacity shall be used for NaOH fusion of the ash, and platinum crucibles of 30-cm^3 capacity shall be used for decomposition of the ash with HF.

4.3 *Emission Flame Photometer*.

4.4 *Muffle Furnace*-Electrically heated muffle furnace with good air circulation and capable of maintaining a temperature of approximately 750°C.

4.5 *Absorption Spectrophotometer*, visible region 380 to 780 nm.

4.6 *Sieves*, 150 and 250-µm (No. 100 and No. 60) U.S.A. standard.

5. Purity of Reagents and Materials

5.1 *Purity of Reagents*-Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available[3]. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 *Purity of Water*-Unless otherwise indicated, references to water shall be understood to mean Type II reagent water as defined in specification D 1193.

6. Sample

[3] *Reagent Chemicals, American Chemical Society Specifications, American Chemical Society, Washington, DC. For suggestions on the testing of reagents not listed by the American Chemical Society, see Analar Standards for Laboratory Chemicals, BDH Ltd., Poole, Dorset, U.K., and the United States Pharmacopeia and National Formulary, U.S. Pharmaceutical Convention, Inc. (USPC), Rockville, MD.*

6.1 Prepare the analysis sample in accordance with Test Method D 2013 or Practice D 346 by pulverizing the material to pass 250 µm (No. 60) sieve.

6.2 Analyze separate test portions for moisture and ash contents in accordance with Test Methods D 3173, D 3174, or D5142 so that calculations to other bases can be made.

7. Preparation of Coal Ash and Coke Ash

7.1 *Procedure*-Prepare 3 to 5g of ash from the analysis sample. Spread the coal or coke in a layer not over 6 mm (1/4 in.) in depth in a fireclay or porcelain roasting dish. Place in a cold muffle furnace and heat gradually so that the temperature reaches 500°C in 1 h and 750°C in 2 h. Ignite to constant weight (±0.001 g precision), at 750°C. Allow the ash to cool, transfer to an agate mortar, and grind to pass a 150-µm (No. 100) U.S.A. standard sieve. Reignite the ash at 750°C for 1 h, cool rapidly, and immediately weigh portions for analysis. If samples are stored, reignite the ash before weighing or deter mine loss on ignition at 750°C on a separate sample weighed out at the same time as the analysis sample. Thoroughly mix each sample before weighing.

8. Preparation of Analysis Solutions (Sample, Standards, and Blank)

8.1 *Reagents and Materials*:

8.1.1 *Hydrochloric Acid* (1 + 1)-Mix 1 volume of concentrated hydrochloric acid (HCl, sp gr 1.19) with 1 volume of water.

8.1.2 Hydrofluoric Acid (sp gr 1.15)-Concentrated hydrofluoric acid (HF).

8.1.3 National Institute of Standards and Technology (NIST) Sample No. 99a Soda Feldspar.[4]

8.1.4 Nitric Acid (sp gr 1.42)-Concentrated nitric acid (HNO_3).

8.1.5 Sodium Hydroxide (NaOH) pellets.

8.1.6 Sulfuric Acid (1 + 1)-Mix carefully while stirring 1 volume of concentrated sulfuric acid (H_2SO_4, sp gr 1.84) into 1 volume of water.

8.2 *Procedure*:

8.2.1 The methods described are for typical ash samples; however, different dilutions or aliquots than those specified may be preferable to attain suitable concentrations for proper intensities for various constituents. Colors developed as specified are stable unless otherwise stated. Although the methods are described for a single sample, a group of ten or more can be processed at the same time. Each numbered step should be completed for the group of samples being analyzed before proceeding to the next step.

8.2.2 *Solution A for SiO_2 and Al_2O_3 Determination*-Weigh 0.0500 g of sample and transfer to a 50-mL nickel crucible. Add 1.5 g of NaOH, cover the crucible, and heat in a gas flame to melt the NaOH. Swirl gently to ensure that no particles of sample float on the surface of the melt. Continue fusion for about 5 min at dull red heat; then remove the crucible from the flame and swirl the melt, while cooling, to coat the crucible wall. Add about 25 mL of water to the melt and let stand for at least1horovernight if convenient. Pour the contents of the crucible into a 600-mL beaker containing 400 mL of water and 20 mL of HCl (1+1). (Do not allow the nickel crucible to come in contact with the acid.) With a rubber policeman, remove any residue from the crucible and wash it into a beaker. Clean a 1000-mL volumetric flask with HCl (1 + 1), rinse with water, and then transfer the solution in the beaker to it. Dilute with water to the 1000-mL mark and mix.

8.2.2.1 *Standard Solution for SiO_2 and Al_2O_3 Determination*-Prepare duplicate standard solutions in the same manner (see 8.2.2) using 0.0500-g portions of NIST Sample No. 99a, Soda Feldspar.[i] Also prepare a blank solution as in 8.2.2, but omit the soda feldspar. Store the standard and blank solutions in plastic bottles.

8.2.3 *Solution B for Fe_2O_3, TiO_2, P_2O_5, CaO, MgO, Na_2O, and K_2O Determinations*-Treat 0.400 ± 0.0005 g of sample in a 30-mL platinum crucible with 3 cm^3 of H_2SO_4 (1 + 1) and 10 mL of HF. Evaporate on an air bath until most of the HF is removed then add 1 mL of HNO_3, and continue heating until strong fumes of sulfur trioxide (SO_3) evolve. Cool the crucible and contents, add water to dissolve the residue, and digest on an air bath for 1/2 h. Transfer the contents of the crucible to a 250-mLvolumetric flask. Cool to room temperature then dilute to the 250-mL mark and mix. Also prepare a blank Solution B (8.2.3), omitting the sample. Because of the possibility of alkali contamination from the glass from which the flask is made, determine sodium and potassium the same day that Solution B is prepared, or withdraw 25 mL with a pipet and store in a plastic bottle.

SILICON DIOXIDE (SiO_2)

9. Reagents

9.1 *Ammonium Molybdate Solution* (7.5 g/100 mL)-Dissolve 7.5 g of ammonium molybdate ($(NH_4)_6Mo_7O_{24}.4H_2O$) in 75 mL of water. Add 10 mL H_2SO_4 (1 + 1) and dilute to 100 mL. Store in a plastic bottle.

9.2 *Reducing Solution*-Dissolve 0.7 g of sodium sulfate ($Na_2SO_3.7H_2O$) in 10 cm^3 of water. Add 0.15 g of 1 amino-2-naphthol-4-sulfonic acid and stir until dissolved. Dissolve 9.0 g of sodium metabisulfate ($Na_2S_2O_5$) in 90ml of water, and add this solution to the solution above and mix. Store in a plastic bottle. Unless this solution is freshly prepared, check the reducing properties of the solution against a known standard.

[4] *National Institute of Standards and Technology Sample No. 99a, soda feldspar contains 65.2 % SiO_2 and 20.5 % Al_2O_3. This reagent is used for standardization purposes only*

9.3 *Tartaric Acid Solution* (10% in water)-Store in a plastic bottle.

10. Procedure

10.1 Pipet a 10-ml aliquot of blank solution and 10 ml of each standard solution and Sample Solution A into separate 100-ml volumetric flasks. Dilute each solution to 50 or 60 ml with water and mix. Add 1.5 ml of ammonium molybdate solution with a measuring pipet, mix, and let stand 10 min. Pipet 4 ml of tartaric acid solution followed immediately by 1 ml of reducing solution into the first flask, mixing during the additions. Dilute contents of this flask immediately to the 100-ml mark and mix before proceeding to the next flask. Let each solution stand 1 h; then determine its absorbance at 650 nm, using the blank solution as a reference, assumed to have zero absorbance.

11. Calculation

11.1 Compute factors f_1 and f_2 for each standard solution as follows:

$f_1 = Cs / A_1$ and $f_2 = Cs / A_2$

Where: Cs = concentration of SiO_2 in the standard sample, %, and

A_1 and A_2 = absorbance for replicate standard solution each containing 50 mg of standard sample.

11.2 Calculate the percent of silica in the ash as follows:

SiO_2, % = FA

Where: $F = (f_1+f_2)/2$, and

A = absorbance of the sample solution containing 50 mg of ash.

ALUMINUM OXIDE (Al_2O_3)

12. Reagents

12.1 *Acetic Acid, Glacial* (CH_3COOH).

12.2 *Alizarin Red-S Solution* (0.1 % in water).

12.3 *Calcium Chloride Solution* ($CaCl_2$) (7 g/500 mL)-Transfer 7 g of calcium $_2$carbonate ($CaCO_3$) to a 250-mL beaker. Add about 50 mL of water and HCl (1 + 1) in drops until the $CaCO_3$ is dissolved. Boil the solution for 1 to 2 min, cool, and dilute with water to 500 ml.

12.4 *Buffer Solution*-Dissolve 70g of sodium acetate ($CH_3COONa.3H_2O$) in water, add 30 mL of CH_3COOH, and dilute to 500 ml.

12.5 *Hydroxylamine Hydrochloride Solution* (10% in water)-Prepare fresh.

12.6 *Thioglycollic Acid* (5%)-Dilute 5 ml of thioglycollic acid to 100 ml with water. Prepare fresh.

13. Procedure

13.1 Pipet a 10-ml aliquot of Sample Solution A, 20 ml of each Standard Solution A, and 20 ml of blank solution into separate 100-ml volumetric flasks. Then pipet 10 ml of blank solution to the flask containing 10 ml of sample solution to maintain correct pH. For ash samples that contain less than 20 % Al_2O_3 take a 20-ml aliquot directly from Sample Solution A. Add from pipets, in the following order, mixing thoroughly after addition of each reagent, $1cm^3$ of $CaCl_2$ solution, 1 ml of hydroxylamine hydrochloride solution, and 1 ml of thioglycollic acid solution. From a graduated cylinder add 10 ml of buffer solution to each flask and allow to stand 10 min. Add 5 ml of alizarin red-S solution with a pipet, dilute to 100 ml, and mix. Allow each solution to stand for 1 h, and measure absorbance at 475 nm using the blank solution as a reference, assumed to have zero absorbance.

14. Calculation

14.1 Compute factors f_1 and f_2 for each standard test as follows:

$f_1 = CA/A_1$ and $f_2 = CA/A_2$

Where: CA = concentration of Al_2O_3 in standard feldspar sample, %, and

A_1 and A_2 = absorbance for replicate standard solutions.

14.2 Calculate the percent Al_2O_3 as follows: For 10-mL aliquot of Sample Solution A:

Al_2O_3, %in ash = 2 FA

For 20-mL aliquot of Sample Solution A:

Al_2O_3,% in ash = FA

Where: $F = (f_1+f_2)/2$, and

A = absorbance of sample solution.

15. Reagents (Fe_2O_3)

15.1 *Hydroxylamine Hydrochloride Solution* (10%)-Prepare a 10 % solution of hydroxylamine hydrochloride ($NH_2OH.HCl$) in water.

15.2 *Orthophenanthroline* (0.1%)- Prepare a 0.1 % solution in water.

15.3 *Sodium Citrate* (10%)-Prepare a 10% solution of sodium citrate ($Na_3C_8H_5O_7.2H_2O$) in water.

15.4 *Iron, Standard Solution* (1mL = 0.1mg Fe_2O_3)-Dissolve 0.2455 ± 0.0005 g of ferrous ammonium sulfate $Fe(NH_4)_2(SO_4)_2.6H_2O$ in water, add 3 mL of H_2SO_4(1 + 1), and dilute to 500 mL.

16. Procedure

Dilute 10 mL of Sample Solution B to 50 mL in a volumetric flask. Pipet 10 cm3 of diluted sample solution into a 100-mL volumetric flask, pipet 5 cm3 of standard iron solution into another 100-mL flask, and add nothing to a third flask for reagent blank. Add 5 mL of hydroxylamine hydro chloride solution with a graduated cylinder to each flask, and allow to stand for 10 min. Then add 10 mL of orthophenan-throline solution with a graduated cylinder to each flask and mix. Finally, add 10 mL of sodium citrate solution with a graduated cylinder to each flask, dilute to 100 mL with water, and mix. After 1 h measure absorbance at 510 nm, using the reagent blank as reference, assumed to have zero absorbance.

17. Calculation

17.1 Calculate the percent Fe_2O_3 as follows:

Fe_2O_3, % = $(AC_F / A_1B) \times 100$

Where: A = absorbance of sample solution. A_1 = absorbance of standard iron solution, B = sample contained in the final dilution of Solution B (9.23 and Section 16), mg, and C_F = Fe_2O_3 in aliquot taken for standard iron solution, mg.

NOTE 4-For the dilutions given, 5 mL of standard iron solution contains 0.5 mg of Fe_2O_3 (C_F) and the diluted sample solution contains 3.2 mg of sample (B). For samples containing more than 15 % of Fe_2O_3, take a 5-mL aliquot of the diluted sample solution which contains 1.6 mg of sample.

CALCIUM OXIDE (CaO) AND MAGNESIUM OXIDE (MgO)

18. Reagents

18.1 *Ammonium Hydroxide* (sp gr 0.90)-Concentrated ammonium hydroxide (NH_4OH).

18.2 *Calcein Indicator*-Mix 0.2 g of calcein, 0.12 g of thymolphthalein, and 20 g of finely ground potassium chloride (KCl).

18.3 *EDTA Solution*-Dissolve 3.720 g of the disodium salt of ethylenediaminetetraacetic acid (EDTA) in water and dilute to 1000 mL. Standardize against the standard calcium solution using calcein or phthalein purple indicator.

18.4 *Hydrochloric Acid* (sp gr 1.19)-Concentrated hydro chloric acid (HCl).

18.5 *Hydrochloric Acid* (1 + 1)-Mix 1 volume of concentrated HCl (sp gr 1.19) with 1 volume of water.

18.6 *Phthalein Purple Indicator*-Mix 0.1 g of phthalein purple, 0.005 g of methyl red, and 0.05 g of naphthol green B with 10 g of finely ground KCl.

18.7 *Potassium Hydroxide Solution* (224.4 g/L)-Dissolve 224.4 g of potassium hydroxide (KOH 85%) in water and dilute to 1000 mL. Store in a plastic bottle.

18.8 *Calcium Standard Solution* (1.000 g/L) (1 mL50.00056 g CaO)-Dissolve 1.000 g of calcium carbon ate (CaCO3) in water with 4 mL of HCl (1 + 1). Heat to boiling to expel carbon dioxide (CO2), cool, and dilute to 1000 mL.

18.9 *Triethanolamine Solution*-Dilute 500 mL of triethanolamine with water to 1000 mL and mix.

19. Procedure for CaO

19.1 Pipet 25 mL of Sample Solution B and 25 mL of the blank solution into separate 500-mL Erlenmeyer flasks. Dilute with water to approximately 100 mL. Add 20 drops of concentrated HCl, 5 mL of the triethanolamine solution, 5 mL of NH_4OH, and 10 mL of KOH solution in that order, mixing after addition of each reagent. Dilute with water to about 200 mL. Add approximately 40 mg of calcein indicator and titrate with standard EDTA solution until the color changes from a green fluorescence to purple. Observe the color change in diffused light looking down through the flask to a black surface.

20. Procedure for MgO

20.1 Pipet 25 mL of Sample Solution B and 25 mLof blank solution into separate 500-mL Erlenmeyer flasks. Dilute with water to about 100 mL. Add 20 drops of concentrated HCl, 20 mL of triethanolamine solution, and 25 mL of NH_4OH, mixing after addition of each reagent. Dilute with water to approximately 200 mL. Add a volume of standard EDTA solution slightly less than the calcium titer; then add about 40 mg of phthalein purple indicator. Continue the titration until the color changes from pale purple to colorless or pale grey. A slight excess of EDTA solution produces a green coloration. Observe the color change in diffused light looking down through the flask to a white surface.

21. Calculations

21.1 Calculate the percent CaO as follows:

$$\text{CaO, \%} = \frac{V1 \times F(250/A)}{W} \times 100$$

Where:

V_1 = volume of EDTA solution required for the calcium titration, minus the volume of EDTA solution required for the blank titration, mL,

F = grams of CaO=1mL EDTA,

W = grams of sample, and

A = volume of aliquot, mL.

NOTE: If W=0.4 g, F=0.0056 g, and A =25 mL, then percent of CaO 51.4 V_1.

21.2 Calculate the percent MgO as follows:

$$\text{MgO, \%} = \frac{(V2-V1)(0.719\ F)(250/A)}{W} \times 100$$

Where: V_2 = volumes of EDTA required for calcium plus magnesium titration minus volume of EDTA solution required for blank titration, mL, and

0.719F = grams MgO = 1mL EDTA. Remaining symbols are the same as for computing percent CaO.