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ADDIS ABABA INSTITUTE OF TECHNOLOGY
CENTER FOR ETHIO-MINES DEVELOPMENT

A MASTERS PROJECT ON
UTILIZATION AND QUALITY ENHACEMENT OF LOCAL KAOLIN CLAY MINERALS THROUGH BENEFICIATION

BY: Abiyot Ayalew Bekele

A project submitted to the center for Ethio-mines development in partial fulfillment of the requirement for the degree of masters of engineering in mineral engineering.

Advisor: Anteneh Marlign (PhD)
Co-Advisor: Meseret Aregahegn (PhD cand)

Feb 2023
Addis Ababa, Ethiopia.

Approval sheet

This Project paper entitled “**UTILIZATION AND QUALITY ENHANCEMENT OF LOCAL KAOLIN CLAY MINERALS THROUGH BENEFICIATION**” prepared and submitted by Abiyot Ayalew Bekele in partial fulfillment of the requirements for the subject project work for Master of Engineering in the University of Addis Ababa; Center for Ethio-mines development in department of mineral engineering has been examined and is hereby recommended for acceptance and approval for final oral defense.

Student Name:- Abiyot Ayalew Bekele

Signature -----------------------

Approved by Examining Committee Members:

	Name	Academic Rank	Signature	Date
Advisor	-----------------------------------	-----------------------	-------------	------/------/------
Co-Advisor	-------------------------------	-----------------------	---------------	------/------/-------
Examiner (Int)	----------------------------	-----------------------	---------------	-----/-------/------
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Signature DGC chair person

Name Academic Rank Signature Date

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Dean/ Associate

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Dean for graduate programs

Name	Academic Rank	Signature	Date
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Declaration

I, Abiyot Ayalew Bekele, declare that this project work is the result of my own work and that all source and material used for this project work have been duly acknowledged. This project is submitted in partial fulfillment of the requirement for master of engineering in Center for Ethio-mines development in department of mineral engineering at Addis Ababa University. I confidently declare that this project has not been submitted to any other institutions anywhere for the award of any academic degree, diploma, or certificate.

Student Name: - Abiyot Ayalew Bekele

Signature -----------------------

Date-----------------------------

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Abstract

Recently, some researchers labeled industrial minerals as ‘Development Minerals ‘because of their crucial role for fast local economic development and their necessity in the industrialization. The commercial term “Kaolin “is one of the most versatile industrial clay minerals composed essentially of kaolinite ($Al_2O_3.2SiO_22H_2O$). Kaolin What we call it as “China clay” have been found in Ethiopia as huge reserve estimated (20 million tons), throughout in the different parts of country. However, manufacturing industries import commercially value-added Kaolin from foreign countries due to the low qualities of local kaolin which have major impurities. The impurities of Kaolin from literatures and from XRF characterization of Raw Kaolin (RK) are quartz, mica, feldspar, iron oxide and titanium oxide minerals. Here my interest was to improve the qualities of this local kaolin through physical, thermal and chemical beneficiation to substitute imported commercial Kaolin. The two principal objectives of kaolin refining were the removal of impurities and the production of the desired particle-size distributions. Possibly to meet some industrial requirements, the coloring impurities (mainly iron oxides and other small amounts of fuxing components) must be removed. Based on the XRF analysis, the raw kaolin ore from AlemTena, Ethiopia containing 64.135 wt% SiO_2, 25.747 wt% Al_2O_3, 4.838 wt% Fe_2O_3, and 8.22 wt% loss of ignition (LOI). Then it was physically beneficiated, chemically leached, and thermally treated for possible industrial use, especially for ceramic applications. The leaching experiments were carried out using oxalic acid solutions as leaching reagents for the iron extraction and colour enhancement process. A substantial reduction of iron oxide (4.838 to 3.107 wt %) and silica (64.135 to 57.285 wt%) SiO_2 on the other hand a substantial increment of alumina (25.747 to 33.662 wt%) Al_2O_3 from the raw kaolin was observed at operating conditions of 2.0 M oxalic acid, the temperature of 90 °C, and contact time of 120 min. From Chemically leached kaolin we observed a significant whiteness and brightness. In other way the thermally treated kaolin was observed an increment of iron oxide (4.838 to 6.605 wt %) and also it lost its crystalline structure and becomes an amorphous phase but still its alumina and silica contents improved. Generally, from my study I understood that, the physically beneficiated, chemically leached, and thermally treated kaolin raw material can used to fabricate low-cost kaolin-based ceramic products.

Table of Contents

List of figures

List of Tables

List of abbreviations

ISO	International Organization for Standardization) Standard
MER	Main Ethiopia Rift Valley
EARS	East Africa Rift System
SPNNRS	South People Nation Nationalities and Regional State
USGS	United States Geological Survey
EIGS	Ethiopian Institute of Geological Survey
XRF	X-ray fluorescent spectrometer
XRD	X-Ray diffraction
FT-IR	Fourier-Transform Infra-Red
ISO	International Standards Organization
MIDI	Mineral Industry Development Institute
RK	Raw Kaolin
CK	Calcined kaolin
AK	Acid leached Kaolin
JCPDS	The Joint committee on powder diffraction standards
ICDD	International center for diffraction data

CHAPTER ONE

1. INTRODUCTION

1.1. **Background of kaolin clay minerals**

Industrial minerals including Clay minerals are the critical input materials to manufacturing industries. Recently the demands and their economic values of Industrial minerals becoming increased. Some researchers labeled Industrial minerals as ‘Development Minerals ‘because of their crucial role for fast local economic development and their necessity in the industrialization. Those of the conditions make Industrial minerals more important are, the relatively low investment cost, less sophisticated extraction and processing and also their potential to support the livelihood of low-income population. Therefore, due to these conditions, exploration and extraction(processing) of such deposits is important for developing countries like our country Ethiopia. Ethiopia is developing country which has a number of industrial mineral occurrences some of which are under exploitation (Gezahegn and Getaneh 2020).

Clay is one of the most important groups of Industrial minerals. Georgius Agricola (1494–1555), the founder of geology, who gave the first definition of clay in 1546. His first definition has been modified several times due to which the clay definition raises the questions related of constituents of clay and implicitly which was very important. The latest definition which answered all these issues was done by the Joint Nomenclature Committees (JNCs) of the Association Internationale pour l’Etude des Argiles (AIPEA) and the Clay Minerals Society (CMS). According to these societies, the term "clay" refers to naturally occurring material, composed mainly of fine-grained minerals, become plastic in presence of water and become hard when dried or fired(Al Ani and Sarapää 2008; Kumari and Mohan 200ADa). By this definition of clay, engineered clays and clay-like materials can be distinguished as clay (fine grained minerals) exhibiting plasticity in presence of water and become hard on drying and firing(Kumari and Mohan 200ADa).

The term “clay mineral” refers to aluminosilicate layers or phyllosilicates minerals (leaf like or plate like structure) in which, formed by the combination the basic structural unit of tetrahedral and octahedral sheets. It is a soft, freely bound, fine grained natural rock or earthy material having diameter less than 0.005 mm and composed essentially of clay particles (Kumari and

Mohan 200ADa). Based on the standard definition of mineral, clay minerals are mainly inorganic materials except peat, muck, some soils, etc. that contain huge number of organic/natural materials. The clay minerals are formed due to the weathering and erosion of rocks containing soil, ceramic clays, clay shales, glacial clays (including great volume of detrital and transported clays) the mineral group feldspar (known as the ‘mother of clay’) over vast spans of time. During weathering, the content of feldspar is distorted by hydrolysis process results in formation of clay minerals such as kaolinites (the primary minerals in kaolin clays) and smectite (the primary minerals in bentonite clays). Clay minerals can incorporate with one or more clay minerals even in presence of minute quantities of quartz (SiO_2), metal oxides (Al_2O_3, MgO etc.) and organic matter. The plasticity of clay minerals is due to their particle size, geometry as well as content of water and become hard, stiff, coherent and non-plastic upon drying or firing. Plasticity and hardness are greatly affected by the chemical composition of the material present in the clay. Clays can be molded in any form when they retain water. Clays are easily molded into a form that they retain when dry, and they become hard and lose their plasticity when subjected to heat(Al Ani and Sarapää 2008; Kumari and Mohan 200ADa).

Grain size classification scheme

All researchers in their definition of clay emphasize particle size of the clay. the particle size is a key parameter, no generally upper limit is accepted till now(Kumari and Mohan 200ADa).According to(Al Ani and Sarapää 2008)(Kumari and Mohan 200ADa)Although clays can be distinguished from other fine-grained soils (sand and silt) on the basis of their size difference and mineralogy. Clay and sand both indicate a specific grain size; it is often used to refer to a specific mineralogical composition of sediments (Al Ani and Sarapää 2008).The particle sizes of silts (fine-grained soils that do not consist of clay minerals) is larger than clays. Individual clay particles are always smaller than 0.004 mm (Al Ani and Sarapää 2008)Kumari & Mohan, 200 C.E.a). The difference between silt and clay varies by discipline. Geologists and soil scientists usually consider a particle size of 2μm (clays being finer than silts) for the separation, sedimentologists apply 4–5μm, and colloid chemists use 1 μm. According to Geotechnical engineers, differentiation between silts and clays can be done on the basis of the plastic characteristics of the soil, as measured by the soils’ Atterberg limits. The combination of silts, sand and clay (<40%) are called loam (Kumari and Mohan 200ADa).Figure 1 shows the classification of siliciclastic sediments (unconsolidated, loose) that are based on average grain size. An important point in this figure is that the boundary between sand and silt is 0.06mm and smaller than 0.004mm is clay. The current ISO (International Organization for Standardization) Standard 14688:1996 placed the boundary at 0.06 mm between sand and silt (Al Ani and Sarapää 2008).

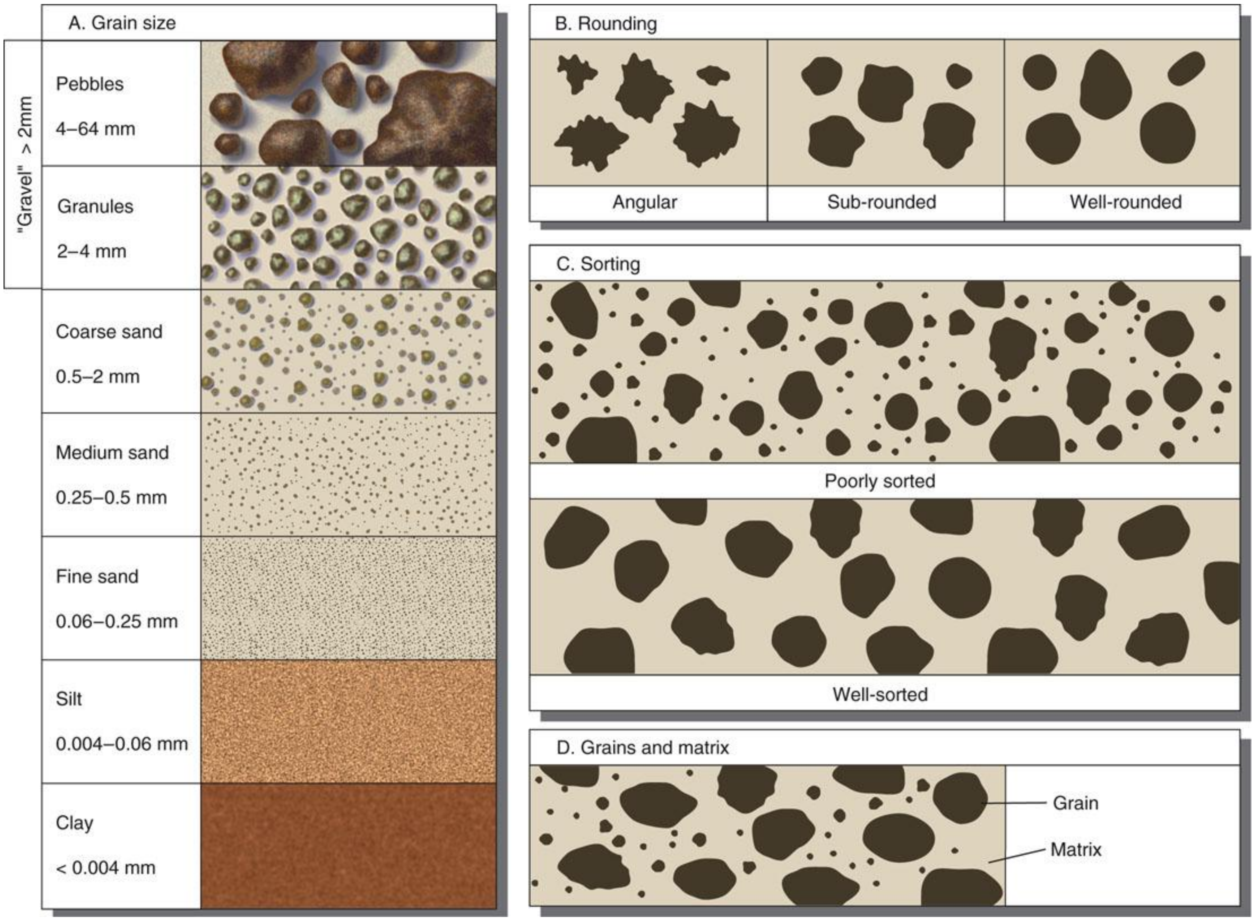


Figure *1. Grain size classification scheme (Al Ani and Sarapää 2008)*

1.2. Classification of clay minerals

Based on the way that the tetrahedral and octahedral sheets are packed into layers, Clay minerals can be classified into four major groups. These major groups of clay minerals present in the soil environment include:1) layer, 2) chain silicates, 3) sesquioxide's, and 4) other inorganic minerals as shown in Figure 2(Kumari and Mohan 200ADa). Layer silicates: A silicate comprising of planar octahedral layer bound to tetrahedral layer above and below with a distinctive repeating distance between t-o-t layers. These are the primary component of soils and are known as excellent trappers of water held between layers. Minerals within these groups are further categorized into dioctahedral and trioctahedral (Kumari and Mohan 200ADa). On the other hand, based on the number and arrangements of tetrahedral and octahedral sheets present in clay, the layer silicates are divided into three categories: I) 1:1 type of clay mineral, II) 2:1 type of clay mineral and III) 2:1:1 type of clay mineral (Kumari and Mohan 200ADa).

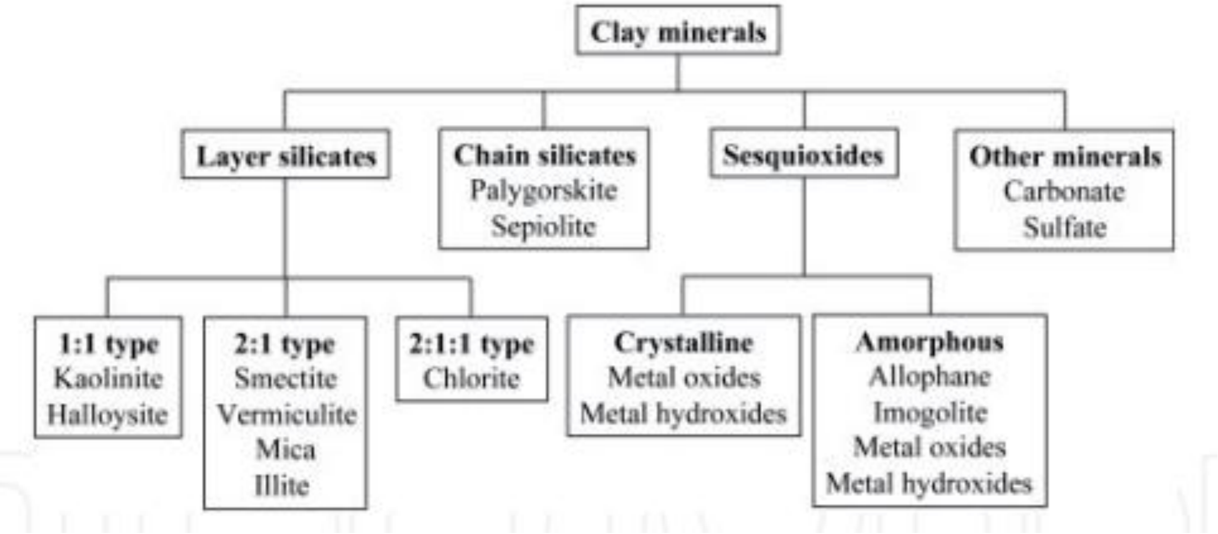


Figure 2. Classification of clay minerals (Kumari and Mohan 200ADa)

1:1 Layer silicate

This is aluminosilicate layers comprises of the basic structural units of phyllosilicates which is formed by the combination of tetrahedral and octahedral sheets bound by shared oxygen atoms(Kumari and Mohan 200ADa).Each individual layer is assembled from one tetrahedral (SiO_4) and one octahedral sheet (AlO_6). The sheets are bonded together by sharing of O^{2-} ions. Kaolinite and Halloysite are examples under this category (Bedassa,Getaneh,and Hailu 2019)(Kumari and Mohan 200ADa).

The word "kaolin," also referred to as "china clay," comes from the Chinese word "Kauling," which means "high ridge." This hill is located close to Jauchau Fu, China, and is where the material was mined for ceramics centuries ago.

Experts from different disciplines have their own meaning for the term “**kaolin**”. Kaolin in terms of geologists has a rock term meaning: they defined it as a rock comprised primarily of one of the kaolin groups of clay minerals. On the other hand, in terms of mineralogist the term is given to the group name for the kaolin minerals (kaolinite, halloysite, dickite, and nacrite). And also, ceramist use interchangeable term “china clay" which is synonymous words with " kaolin " meaning that it is a white firing ceramic raw material(Murray 1980a).Basically, the meaning of term “kaolin” Industrially defined as a clay consisting of substantially pure kaolinite or related clay minerals, which is naturally or can be beneficiated to be white or nearly white; will fire white or nearly white; and is amenable to beneficiation by known methods to make it suitable for use in white ware, paper, rubber, paint, and other uses(Murray 1980a). In mineralogy, the term "kaolin" is used interchangeably with "kaolinite group" minerals to refer to a group of clay minerals, such as kaolinite, nacrite, deckite, and halloysite (Al Ani and Sarapää 2008;Murray 1980b,1980a). With the exception of the hydrated form of halloysite, all minerals in this group share a nearly identical ideal chemical formula: $Al_2Si_20_5$ $(OH)_4$ and the theoretical chemical composition of pure kaolinite consists of 46.54% SiO2, 39.50% Al2O3, and a 13.96% loss on ignition attributed to structurally bonded hydroxyls. In reality, commercial kaolins differ to some extent from the aforementioned pure value due to the presence of accessory minerals and potential substitutions of other elements within the crystal lattice (Mathur, 2002). Halloysite, in its fully hydrated form, has the ideal chemical formula$Al_2Si_20_5$ $(OH)_4.2H_20$[1,4,18]. This kaolinite group has a 1:1 layered structure, that is, each layer consists of one tetrahedral silicate sheet and one octahedral sheet, with two-thirds of the octahedral sites occupied by aluminum. A perfectly ordered kaolinite crystal exhibits a pseudo-hexagonal shape; however, the degree of ordering can vary significantly, leading to poorly ordered crystals where the shape is indeterminate (Bedassa, Getaneh, and Hailu 2019). The kaolin group minerals are among the most common clay minerals in nature. It is one of extremely important industrial raw material, which is used in a number of different industrial applications. Within the kaolin group minerals, kaolinite is the most abundant and one of the most versatile industrial materials that has received most attention in terms of its structure, properties and industrial applications (Bedassa, Getaneh, and Hailu 2019). Kaolin is chemically stable across a broad pH spectrum, exhibits a white hue, and provides excellent opacity when utilized as a pigment or extender. It is characterized by its softness and non-abrasive nature, along with low thermal and electrical conductivity. Certain applications of kaolin, including its use in paper coatings and as fillers in paints and plastics, demand stringent specifications regarding particle size, color, brightness, and viscosity, while other applications may not require such detailed criteria (Bedassa, Getaneh, and Hailu 2019).

The only difference in kaolin polymorphs is the mode of their structural arrangement. Halloysite shares the same composition as kaolinite, but it contains an additional layer of oriented water molecules interspersed between its layers (Bedassa, Getaneh, and Hailu 2019).

Kaolin clay mineral deposits are categorized into two types: residual deposits, referred to as 'primary deposits', and sedimentary deposits, known as 'secondary deposits'. Primary kaolin deposits typically originate from the in situ transformation of aluminosilicate-rich crystalline parent rock through weathering, hydrothermal activity, and, less frequently, volcanic processes. Secondary kaolin deposits are found in sedimentary rocks, resulting from the erosion of primary deposits, or through the transportation and deposition of kaolinite derived from these primary sources.

The majority of clay minerals globally are extracted using open-pit methods. While there are some underground mines, the high production costs and unfavorable roof conditions generally prevent the underground mining of clay deposits (Bloodworth et al. n.d.). The mined raw kaolin is not used direct as raw material in the manufacturing industry. It passes through a consecutive beneficiation process to upgrade the quality and commercial value. The two principal objectives of kaolin refining are the removal of impurities and the production of the desired particle-size distribution (Bloodworth et al. n.d.).Physical properties, mineralogical, and chemical compositions are employed to assess the quality and commercial value of the kaolin deposit (Bloodworth et al. n.d.; Kogel 2014a; Prasad, Reid, and Murray 1991; G. Abdykirova et al 2022). The key properties of kaolin are opacity, electrical and mechanical property, whiteness and brightness, and particle shape and size distribution (Bloodworth et al. n.d.; Kogel 2014a; Prasad, Reid, and Murray 1991; G. Abdykirova et al 2022).To improve the quality of kaolin deposits to possibly meet some industrial requirements, the coloring impurities (mainly iron oxides and other small amounts of fuxing components) must be removed (Ayalew and Demir 2023). Many beneficiation techniques can be used for upgrading the quality and the production of a desired particle shape and size distribution of kaolin clay (Zewdie et al. 2021). The mined kaolin is processed by adopting various physical and chemical processes like sieving, magnetic separation, selective flocculation, etc. Application of ultrasound, leaching with various chemicals like oxalic and other organic acid (Saikia et al 2003).

1.3. Location and Geology of Study Area

The study area is found in the part of the Main Ethiopia Rift Valley (MER). Specifically located within latitudes 80 9’28.91” N and 8 0 16’1.95” N, and longitudes 380 58’30.14” E and 390 7’20.22” E in the area of small town known as “Alem Tena”. This area is surrounded by Lake Koka to the north and by Wonji Sugar plantation and Gademsa caldera to the north-east. The area AlemTena can be accessed through two main asphalted high ways, Mojo - AlemTena and Nazret - Assela road (Gezahegn and Getaneh 2020; Oluwadebi AG 2015).

The Main Ethiopian Rift (MER) represents to the northernmost part of the East Africa Rift System (EARS). It is a tectonically active rift situated between the northwestern and southeastern Ethiopian Plateaus (Bedassa, Getaneh, and Hailu 2019). The MER has been of interest to many geoscientists for many decades because it extends or connects the two old rift segments of the EARS: The Oligocene–Miocene Red Sea rift in the north, and the early Miocene Turkana rift in the south(Gezahegn and Getaneh 2020).Like the rest of the East African Rift System, the Main Ethiopian Rift (MER) has experienced an extremely complex tectonic history(Kussbilo, Bheemalingeswara, and Hagosi 2024). It is the least evolved of the three arms of the triple junction, and it is ∼18Ma younger than the Gulf of Aden and Red Sea rifts (Gezahegn and Getaneh 2020).The evolution of rifting in the MER is related to the long-term kinematics of the major Nubia and Somalia plates (Bedassa, Getaneh, and Hailu 2019). The axial zone, or rift axis, of the MER is the youngest portion. It overlaps with the Wonji Fault Belt, which primarily originated during the Quaternary epoch. Active NNE-SSW-trending extension fractures and normal faults with a right-stepping en-echelon layout are features of the Wonji fault belt. Two primary Pleistocene magmatic episodes are known along these faults: (1) basaltic flows that erupted between 2 and 1 Ma, followed by ignimbrites and a few silicic centers, and (2) axial silicic volcanic and basalts that erupted in the last~650 Ka (Kussbilo, Bheemalingeswara, and Hagosi 2024).

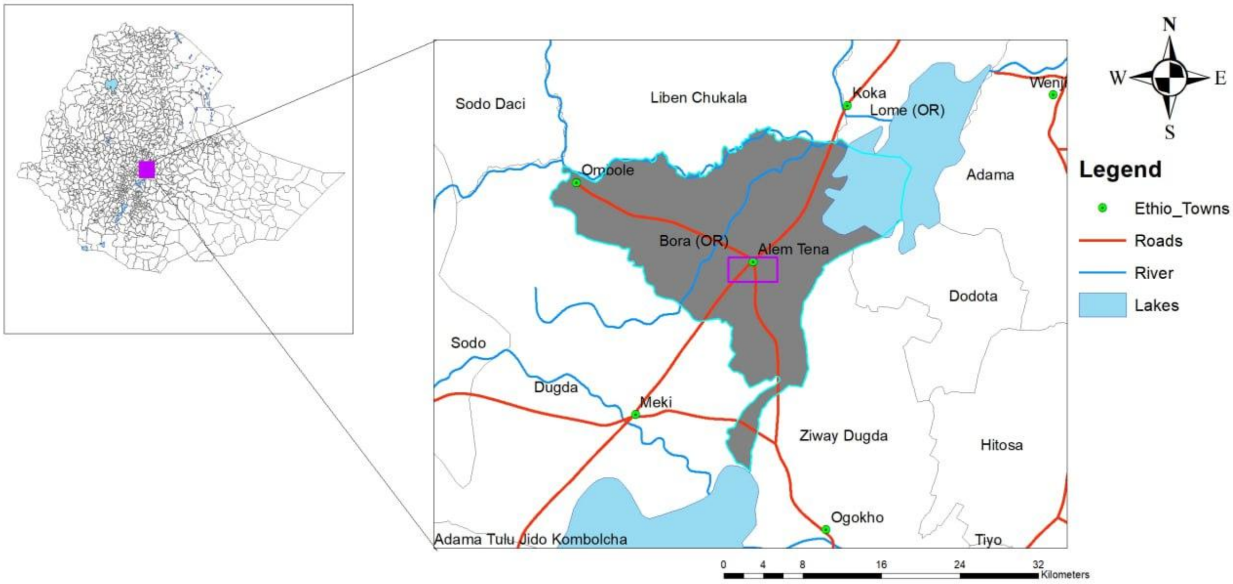


Figure 3. Location map of the study area (AlemTena).

The geology of the MER is categorized into three lithostratigraphic sequences: pre-rift, syn-rift and main rift sequences. The pre-rift units are constituted by Precambrian metamorphic; Mesozoic sedimentary and Oligocene to Late Miocene plateau flood basalts. The syn-rift units are Upper Miocene-Quaternary volcanics constituted by Nazret pyroclastic rocks of welded to partially welded pyroclastic flows and rhyolitic and trachytic lava domes. Syn-rift volcanism has bimodal character with predominant acid products and associated basalts. These units have an age of 8 Ma years. Main rift units comprise Quaternary-Holocene young central volcanoes, basaltic and obsidian lava flows, trachyte, rhyolitic domes, and pyroclastic flow and fall deposits. Pyroclastic and pumice fall deposits of Bora-Bericha group in which the AlemTena is situated is related to the main rift units(Gezahegn and Getaneh 2020).The volcanic rocks of the Main Ethiopian Rift (MER) are one of the most important hosts of the kaolin deposits in Ethiopia(Gezahegn and Getaneh 2020). Regionally, The Main Ethiopia Rift is divided into three different segments: Northern, Central and Southern part (Bedassa, Getaneh, and Hailu 2019).Alemtena area exists in the central part of the MER valley which is mostly covered by ignimbrite rock. The ignimbrite is the youngest unit out of the three ignimbritic units of the volcanic complex which belongs to a bimodal magmatic suite erupted between 830 Ka and 20 Ka (thousand years)(Oluwadebi AG 2015). The recent felsic products of the Berecha (AlemTena) unit consist of obsidian lava domes and flows as well as pantelleritic ignimbrites ranging from 240 - 20 Ka. The pyroclastics are unwelded pumice flows and ashes, which are referred to as the final products. Alemtena area consist of Pleistocene - Holocene (< 500 Ka)10. Figure2 shows the geological map of the study area (Gezahegn and Getaneh 2020).

In terms of economic potential, the MER has been of interest only for geothermal resources to date. However, the region does have huge industrial mineral reserves, including potash, salt, gypsum, limestone, diatomite, clay, and pumice, as well as some metallic mineral commodities, such as Au, Fe, and Mg, are present in this rift. Among the industrial mineral resources in MER, kaolin is the most common and important. Investigations by geologists from the Ethiopian Ministry of Mines led to the discovery of many kaolin occurrence such as Belessa, Alem Tena and other deposits(Bedassa, Getaneh, and Hailu 2019).This resource is also used in the production of cosmetics, fertilizers, insecticides, pigment, cement, ceramics, glass, floor tiles, bricks, and pottery(Kussbilo, Bheemalingeswara, and Hagosi 2024).

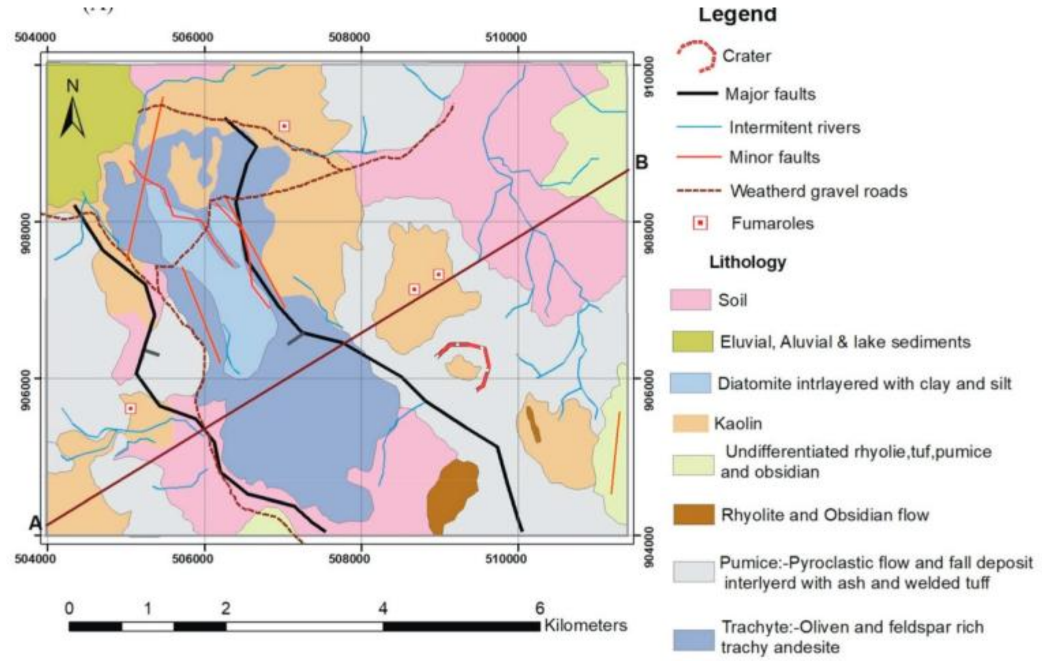


Figure 4. *Shows the geological map of the study area (Gezahegn and Getaneh 2020).*

1.4. Mineralogy of the kaolin deposit

The geology of the deposit consists of the most important volcanic hosts rocks of pumice, rhyolitic tuff, rhyolite, and trachy-andesite. The kaolin deposit of the area is related to the above acidic volcanic rocks of pumice, tuffs, rhyolite and trachy-andesites. The deposit occurs as an irregularly shaped patch (blanket) of kaolin. The thickness of the kaolin deposit varies from about 4m to 11m. The deposit is found exposed or covered by overburden of up to about 2 m(Gezahegn and Getaneh 2020).As far as the reserve of the deposit is concerned, a total of nearly 85 million tons of probable reserve is calculated(Gezahegn and Getaneh 2020).

1.5. Statement of the Problem

The mineral resource is one of the pillars and the backbones for the fast economic growth of many countries in the world, which leads their *sustainable* development and better living standard of their society. But by itself the presence of this resource is not enough for economic growth unless it farther more processed since it contains mineral impurities which make its commercial applications not viable. To convert this resource to economically viable it needs continuous and progressive research on the deposits, occurrence, and their physicochemical properties in order to select and design the processing methods.

Many published and unpublished research papers indicated that Ethiopia has a huge reserve of kaolin deposits estimated to 20 million tons, which spreads in different localities of the country. The fast-growing kaolin consuming manufacturing industry demands it as raw mineral for the production of a variety of appliances. But the Raw kaolin minerals cannot be used as raw materials for industries, unless it upgraded the quality. Because raw kaolin has some impurities, such as iron oxide, soluble salts, feldspar, quartz, mica, and titanium oxide, which directly impact the chemical composition, optical, and mineralogical properties. So, to meet some possibly industrial requirements here the quality of kaolin must be upgraded through a consecutive refining technique. even if, there is a huge reserve and demands of raw kaolin minerals in Ethiopia still know there is no kaolin producer companies which can supply and fulfill these needs or demands of raw material for these kaolin consuming industries. Due to this reason, investors on kaolin demanding industries in Ethiopia imports kaolin raw material from kaolin producer countries such as china, India etc. for the production of paper, ceramics paint, rubber and plastics. Importing kaolin raw minerals is not economically viable because it requests foreign currency in addition to high price of appliances produced by these industries. And also discourage the country’s economic growth from mining sector through losing income from huge reserve of kaolin deposits. In major kaolin producing countries such as USA, Brazil, UK, Czech Republic, Germany etc. The kaolin producing companies plays a great roll in the total economic growth of the country’s GDP by supplying and exporting the processed kaolin raw materials to the local and global markets. So, to fill this gap and use these resources appropriately the government through the ministry of mines and the private companies has to play the grate roll on the production and processing of kaolin raw minerals by founding processing plants. Kaolin producing company’s needs the technical skill coupled with and financial strength to produce good quality kaolin raw minerals. Since the improved quality determines “the commercial value of kaolin minerals. As all researchers stated that “the commercial value of kaolin depends on whiteness and fine particle size” (Zewdie et al. 2021).For the future to cover the needs of this fast-growing demands of kaolin raw mineral locally, the laboratory scale beneficiation method is necessary because the commercial processing methods is scale up from laboratory scale beneficiation method. Here this mineral processing sector requests Professionals in its own sector, advanced technology, financial strength, and technical skill because the commercial processing methods very complex and sophisticated multistage processing units are available. So as a mineral processing engineering student, I tried to enhance the quality of local kaolin minerals through a consecutive beneficiation technique. A0s some researchers stated, wet physical beneficiation of kaolin was more effective in removing kaolin impurities (Al Ani and Sarapää 2008; Ayalew and Demir 2023; Bloodworth et al. n.d.; Mesele et al. 2021). Therefore, in this project I tried to improve the quality of local kaolin deposits to possibly meet some industrial requirements, through wet beneficiation, chemical bleaching and calcination.

1.5.1. Research question

1. Why not the kaolin mineral demanding industries use the local kaolin instead of imported kaolin?
2. Why need the beneficiation and what are the major impurities of raw kaolin minerals removed?
3. Which physicochemical properties of kaolin are improved through beneficiation technology?
4. Which beneficiation methods preferentially used economically and environmentally eco-friendly to improve its commercial value?
5. What is the recommended standard quality and chemical composition of kaolin in some kaolin consuming manufacturing industry?

6. What is the recommended particle size distribution and shape for kaolin demanding industries?

1.6. Objective

1.6.1. General Objective

The General Objective of this project was to improve the grade (quality) of local kaolin minerals through a consecutive beneficiation process possibly to meet some industrial requirements.

1.6.2. Specific Objectives

To improve the commercial value of local kaolin minerals through enhancing the purity of aluminum oxide (Al_2O_3) and silicon (SiO_2) oxide by removing some chemical and physical impurities (soluble salts, feldspar, quartz, gris, muscovite, mica, titanium oxide, and iron oxide).

- Investigate the effect of Wet beneficiation processes on the quality improvement and the removal of major impurities of the local kaolin minerals.
- Investigate the effect of thermal treatment (calcinations) on the quality improvement of the local kaolin minerals.
- Investigate the effect of chemical leaching on the quality improvement of the local kaolin minerals.
- Compare and contrast the chemical composition and structural arrangement of raw, beneficiated and calcined kaolin using analytical instruments.
- Identify the percentage of major oxide and lose of ignition of raw, beneficiated and calcined kaolin through characterization.

1.7. Scope of the project

Upgrading the quality of local kaolin minerals taken from Alemtena cite which is one of the reserve deposit localities in the Main Ethiopian Rift (MER) (Oromia regional states) by removing chemical and physical impurities through physical, chemical and thermal processing methods, i.e. (wet beneficiation, chemical leaching and calcinations techniques) to possibly meet some industrial requirements (ceramic industries) was the primary interests of this project work). To achieve the appropriate quality requirements to meet some industrial applications (in this case for ceramic industries) of this mineral in the given timeline through using the preferential beneficiation techniques in the locally accessible laboratory according to the permitted budget was the boundary of this project.

1.8. Significance of the study

Many different exploration reports of the Geological Institute of Ethiopia indicated that Ethiopia has enormous minerals including kaolin clay. The Kaolin clay estimated to (20 million tons) (Zewdie et al. 2021) was surveyed and found across different regions such as SPNNRS (Belessa Kaolin, Ansho Kaolin), Amhara regional states (Debre Tabor Kaolin, Awzet kaolin, Gypsite-Mariam Kaolin, Kerker Kaolin,) Oromia regional states (Bombowha Kaolin, Kombelcha Kaolin, Alemtena) and so on. But still now it is not used enough comparatively the amount of its deposits as commercial raw material for industrial applications due to its high level of impurities in the local kaolin clay (low quality of local kaolin minerals). Because of this reason the most of kaolin demanding industries imports kaolin clay minerals for various industrial productions. As a mineral processing engineering to solve these problems the use of kaolin minerals for different applications requires knowledge and study of the physiochemical properties. However, slight consideration was given to the chemical, physical, mineralogical and morphological properties (Ayalew and Demir 2023), due to these very limited studies on the synthesis and characterization of Ethiopian kaolin have been reported in the literature. Here my research work is important to examine the physiochemical properties of local kaolin which will have evidence to the sector as a preliminary investigation about the grade (quality) of the clay to insight and to encourage the beneficiated kaolin for the manufacture of low-cost kaolin-based for various applications. (Aragaw and Angerasa 2020).Also the findings of this project may serve as an initial paper for the project investigated on the substitution of ceramic raw material launched by mineral industry development institution provide insight into how to improve the quality of local kaolin up to the quality required by manufacturing industries.

1.9. Limitation of the study

The Limitation of this study was in the case of budget, the budget permitted to implement this project was not sufficient for different activity and payments for laboratory and to access laboratory chemicals due to high cost and the depreciation value of Ethiopian birr with respect to USD. Another limitation of this project was the un-stability in different part of the country also an obstacle to collect samples from different areas of the country. Another limitation of this project was the accessibility and functionality of laboratory apparatus or equipment’s.

CHAPTER TWO

2. LITERATURE REVIEW

2.1. Geological Occurrence

The mode of formation of the kaolin may have considerable influence on the mineralogy, chemistry and morphology of the clay and may dictate the type of mining and beneficiation process employed to achieve a commercial product (Bloodworth et al. n.d.).

2.2. Classification of Kaolin deposits

Generally, Kaolin deposits are classified into two Classes according to the nature of their deposits: These are as residual deposits known as *"primary deposits* "and sedimentary deposits known as *"secondary deposits*"(Bloodworth et al. n.d.).

Primary kaolin deposits are generally formed by in situ alteration of aluminosilicate-rich crystalline parent rock (such as granite or granitic gneiss) by surface weathering, hydrothermal Solution of rocks, and, more rarely, volcanic processes and are found in the location where they were formed(Bloodworth et al. n.d.). Humid tropical weathering of granitic rocks is a major process in kaolinite formation through the intense leaching of alkalis from aluminosilicate minerals. Kaolin deposits form as residual mantles at or near the surface. Occasionally they may occur in association with bauxite deposits (Bloodworth et al. n.d.). The abundance and nature of iron-bearing minerals is particularly important (Bloodworth et al. n.d.). The kaolinite concentration in primary kaolins can fluctuate between 15% and 30% of the overall ore composition. The remaining portion of the ore is made up of unmodified granite, which includes minerals such as quartz, muscovite, and feldspar (Bloodworth et al. n.d.; Prasad, Reid, and Murray 1991). Hydrothermal alteration of aluminosilicate-bearing rocks is an important kaolinization process. The host rock must be sufficiently fractured to allow the circulation of hot groundwater. High-heat-flow granites may provide optimum thermal conditions required to drive groundwater convection cells. High-quality kaolins are produced from granitic host rocks which are relatively low in iron-bearing minerals such as biotite (Bloodworth et al. n.d.). Potassium feldspars and muscovite represent the predominant primary minerals among all kaolin polymorphs, which undergo transformation into kaolinite through the leaching of potassium and silica during weathering or hydrothermal alteration processes (Awad et al. 2017). Significant amounts of quartz, feldspars, muscovite, tourmaline, zircon, rutile and pseudo rutile are common

(Awad et al. 2017). The kaolin resources of south west England are an example of Primary deposits of kaolin.

Secondary kaolin deposits are generated in new and potentially remote locations from the source of primary deposits through the processes of erosion and the subsequent deposition of kaolinite materials derived from these primary deposits. This process typically occurs within sedimentary rock formations (Kumari and Mohan 200ADa). As the eroded materials are transported downstream, separation occurs due to gravity and particle size. The lighter and finer kaolin particles are carried further away and ultimately settle in lakes, estuaries, and lagoons, where secondary deposits may form. These secondary deposits are significantly richer in kaolinite, with the deposits in Georgia containing 85-95% kaolin. In this context, the contaminants consist of small amounts of silt to clay-sized particles from other minerals such as quartz, illite, and anatase, as well as smectite, hematite, goethite, pyrite, graphite, muscovite, and marcasite (Awad et al. 2017; Bloodworth et al. n.d.; Prasad, Reid, and Murray 1991). Kaolinite typically forms as a secondary mineral through various sedimentary deposition processes, while halloysite is often produced as in situ alteration products of aluminous felsic igneous and metamorphic rocks, resulting from hydrothermal or weathering processes that lead to residual (saprolite) deposits; dickite and nacrite are generally limited to primary hydrothermal deposits (Awad et al. 2017).

2.3. Structure and chemical composition of kaolin clay minerals

The properties that define the composition of clay minerals are derived from chemical compounds present in clay minerals, symmetrical arrangement of atoms and ions and the forces that bind them together. Kaolinite normally appears as stacked pseudo hexagonal platelets, < 2 μm in size, with a common booklet-like shape (Fig. 5) (Awad et al. 2017). Each platelet is considered as an arrangement of several layers (Awad et al. 2017).The two surface planes to form Kaolinite as stacked pseudo hexagonal platelets which considered as an arrangement of several layers of surface planes are: Tetrahedral silica sheet (“siloxane surface”) and Octahedral alumina sheet (“aluminol surface”).

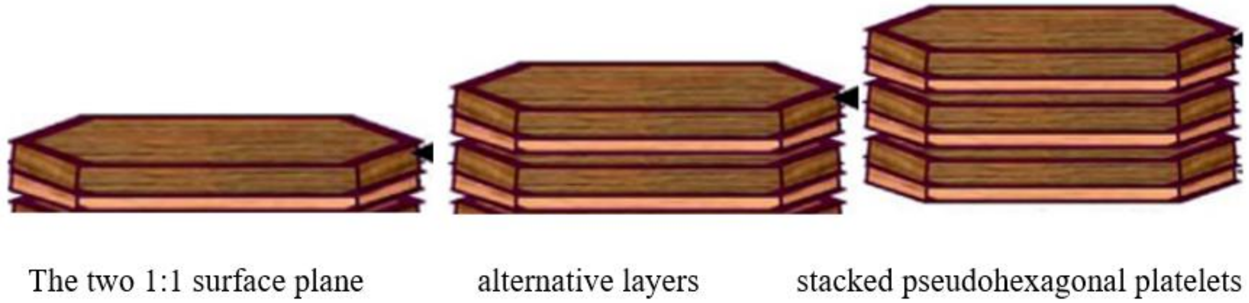
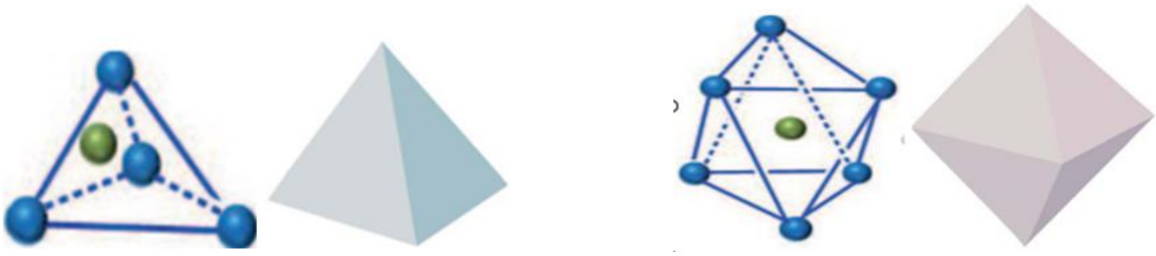


Figure 5.Structural appearance of Kaolinite (Awad et al. 2017)

Each of surface planes which consists of two basal (001) planes: the tetrahedral silica sheet, with O atoms bonded to Si atoms, and called the “siloxane surface”, and the octahedral alumina sheet, with OH groups bonded to Al, called the “aluminol surface”. The clay minerals are mainly known as the complex silicates of various ions such as aluminum, magnesium and iron. On the basis of the arrangement of these ions, basic crystalline units of the clay minerals are of two types are: Silicon – oxygen tetrahedron and Aluminum or magnesium octahedron (Awad et al. 2017).

The first structural unit to form tetrahedral silica sheet (“siloxane surface”) is Silicon – oxygen tetrahedron. This first structural unit is the basic building block units of tetrahedral sheet in which the Si atom at the Centre of a tetrahedron is surrounded by four oxygen atoms at each of the four corners known as silica tetrahedral(Awad et al. 2017).

The second structural unite to form Octahedral alumina sheet (“aluminol surface”) is Aluminum or magnesium octahedron. This octahedron (Al, Mg, Fe) (O, OH)6 is the basic building block units of octahedral sheets in which usually aluminum (Al^{3+}), iron (Fe^{3+}), and magnesium (Mg^{2+}) atoms at the Centre of an octahedron surrounded by six oxygen atoms or hydroxyl group at the corners known as octahedral alumina sheet (Kumari and Mohan 200ADb). This octahedral sheet is known as gibbsite sheet If aluminum is main dominating atom and brucite sheet If magnesium is main dominating atom (Dondi et al. 2008).



a) Tetrahedron structural unit (T). *b) Octahedron structural unit (O)*

Figure 6. The two basic crystalline units of the clay minerals: (Al Ani and Sarapää 2008).

2.3.1. Tetrahedral silica sheet ("siloxane surface")

The tetrahedral sheet is the first structural surface plane in the kaolinite layer. The "siloxane surface" is the tetrahedral silica sheet that has O atoms bound to Si atoms. The Si^{4+} cation is the primary dominating atom in the tetrahedral sheet. The fundamental component of a tetrahedral sheet is the silicon-oxygen tetrahedron (silica tetrahedral). As seen in Figure 7, the tetrahedral sheet is created by sharing three of each tetrahedron's oxygen atoms with the three closest tetrahedral. These oxygen atoms, referred to as basal oxygen, join pairs of all tetrahedral elements (more or less) in a single plane, while the fourth oxygen stays free and forms as apical oxygen bond with other polyhedral elements. The octahedral and tetrahedral sheets are connected by apical oxygen's, which are all in a different plane. Each tetrahedral shares a corner with an octahedron in the octahedral sheet since each tetrahedron only has one apical O. Due to the isomorphous substitution of Al^{3+} for Si^{4+}, which creates a charge deficit in the tetrahedral sheet, the tetrahedral sheet is carrying a negative charge. The tetrahedral cat ions Si4+, Al^{3+}, and Fe^{3+} are frequently found. With four O having two charges and four Si having four+ charges, the isolated tetrahedron has a net negative charge of -4. The composition and charge of each atomic plane in the sheet are distinct. The sheet has a net charge of -4 and is composed of Si$_4$O$_{10}$ (Al Ani and Sarapää 2008).

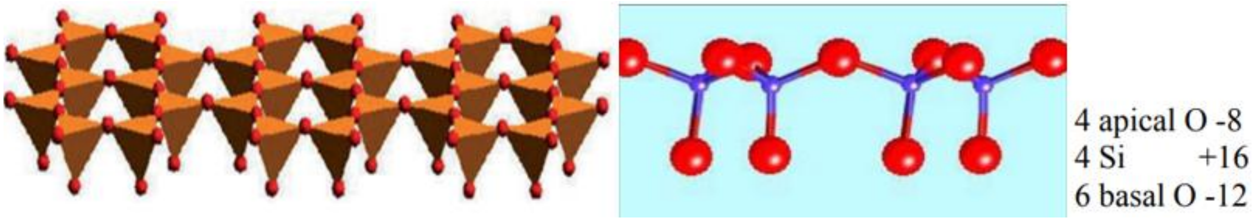


Figure 7. Side view showing the tetrahedral sheets (Al Ani and Sarapää 2008).

2.3.2. Octahedral alumina sheet (“aluminol surface”)

The second structural surface plane in the kaolinite layer is the octahedral sheet. The octahedral alumina sheet, with OH groups bonded to Al, called the “aluminol surface”. The octahedral sheet is comprised of closely packed oxygen’s and hydroxyls in which Al, Fe, and Mg atoms are arranged in octahedral coordination. The net charge on an isolated Al-OH octahedron is -3 (Al^{3+} and six OH with 1- charge). In the octahedral sheet the charge is reduced through the sharing of anions by adjacent octahedral. A single octahedron can be recognized by following the bonds from the small blue balls (Al atoms). Three of them are directed upwards and are each connected a hydroxyl group as indicated by the arrows (Fig.4). The remaining three bonds are directed downwards to other hydroxyl groups. Since, octahedral sheet is present in two forms: dioctahedral or trioctahedral sheet (Kumari and Mohan 200ADb). When aluminum with positive valence of three (Al^{+3}) is present in the octahedral sheet, only two-thirds of the possible positions are filled in order to balance the charges. When only two octahedral sites filled with trivalent cat ions is a dioctahedral sheet. When magnesium with a positive charge of two (Mg^{+2}) is present, all three positions are filled by divalent cat ions is a trioctahedral sheet (Al Ani and Sarapää 2008). The octahedral sheet is formed by sharing all hydroxyl groups at the corners of an octahedron with neighboring octahedral. When you view the octahedral sheet from the side (Figure 8), they contain four aluminum atoms, six lower plane hydroxyls, and six upper plane hydroxyls. These rectangles are the same size as the planar motif outlined for the tetrahedral sheet. The formula for this unit is: Al$_4$ (OH)$_{12}$ and the net charge are ZERO (Al Ani and Sarapää 2008).

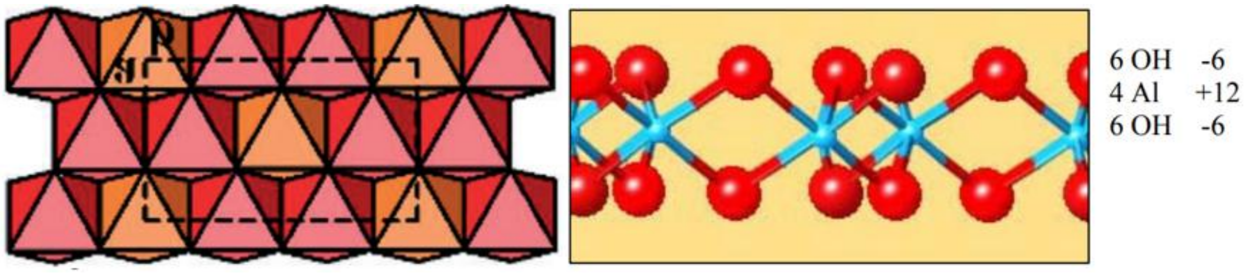


Figure 8. Side view showing the octahedral sheets (Al Ani and Sarapää 2008).

2.3.3. Kaolinite layer

To create a 1:1 layer silicate structure, the octahedral alumina sheet (O) and the silica tetrahedral sheet (T) share apical O atoms. One hydroxyl of the octahedral sheet is replaced by the apical oxygen of the tetrahedral sheet in the 1:1 layer silicate structure, 1(T) +1(O) sheet, creating what is known as the 1:1 clay mineral layer as kaolinite (Fig.8). Every kaolinite layer is regarded as a strong dipole, with the aluminol surface exhibiting positive charges and being hydrophilic and the siloxane surface being hydrophobic and dominated by negative charges (Bloodworth et al. n.d.). As a result, hydrogen and dipolar interactions create strong bonds between the individual kaolinite layers. (None)$(Al_4)(Si_4)O_{10}$ $(OH)_8$ is the typical result for a 1:1 dioctahedral mineral without substitution. Pure hydrous aluminum silicates are not the only minerals found in clay. In the octahedral sheet, Mg could take the place of Al, and other ionic substitutions could also occur. The main restriction is that the radius of the replacing ion must not necessitate a different coordination or significantly alter the sheet's structure. It's possible that the substituting element has a different ionic charge. Changes in composition could change the clay's physicochemical characteristics. The two most frequent isostructural substitutions are the interchange of Mg, Al, ferrous Fe, ferric Fe, and Mn in the octahedral sheet and the substitution of Al and ferric Fe for Si in the tetrahedral sheet. Common substitutions in the tetrahedral sheet substitute an ion with a lower valence for Si. When figuring out the charge on the cation plane of the tetrahedral sheet, you need to keep this in mind. The cation plane of a tetrahedral sheet containing Si_3Al or Si_3Fe (one of the four Si^{4+} atoms substituted by Al^{3+} or Fe^{3+}) will have 15+ charges instead of 16+. Similar charge reductions take place in the octahedral sheet when Mg^{2+} or Fe^{2+} is substituted for Al^{3+}. On the other hand, an additional + charge results when Mg^{2+} is swapped out for Al^{3+} or Fe^{3+}. The total charge connected to the cation plane of an octahedral sheet with (Al_3Fe^{3+} 0.5Mg 0.5) would be +11.5.

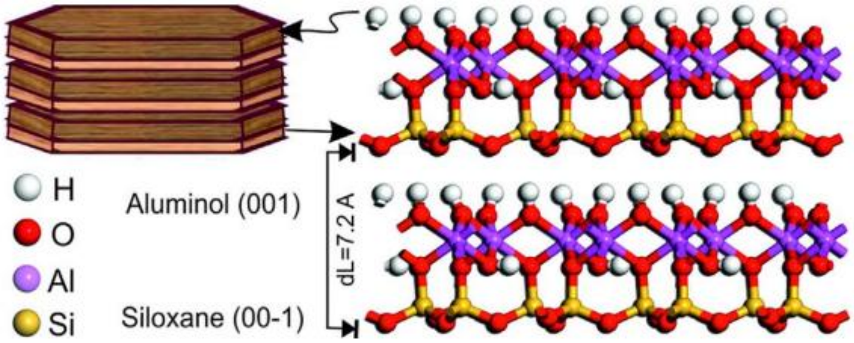


Figure 9. Structure of 1:1 layer silicate (kaolinite) illustrating the connection between tetrahedral and octahedral sheets (Awad et al. 2017)

2.4. Kaolin deposits in the world

Only a limited number of countries dominate the global processed kaolin market, as they possess substantial deposits of high-quality kaolin along with the technical expertise and financial resources of leading production companies (Bloodworth et al. n.d.; Prasad, Reid, and Murray 1991). The United States, Brazil, and England are the three leading countries in the global kaolin market. The extensive and high-quality secondary kaolin deposits span a region approximately 25 miles wide and 150 miles long, stretching from Andersonville, Georgia, to Aiken, South Carolina. This kaolin belt positions the United States as the leading producer and a dominant force in the global market. The deposits in this belt are characterized by their exceptional purity and substantial size, originating from granitic and phyllitic rocks found on the Piedmont plateau. These deposits have undergone significant weathering over extensive geological time, resulting in an average kaolin content of 90% in the raw material, with only trace amounts of quartz and mica as impurities. To date, more than 400 million tons of kaolin have been extracted from the deposits in Georgia. The primary kaolin deposits, which have formed through hydrothermal and weathering processes affecting Permian granites, are predominantly found in residual deposits that are extensively exposed in Cornwall and Devon, located in southwest England, making the country the second-largest producer after the United States. In Brazil, secondary kaolin deposits are found along the Jari River in the State of Amapá and the Capim River in the State of Pará. These deposits are a result of the weathering of granites from the Guyana Shield, yielding kaolin of exceptionally high quality, with an average purity of 98%. The substantial size of these deposits is projected to sustain production for 500 years, positioning Brazil as one of the largest owners and producers of kaolin globally (Awad et al. 2017). Other significant deposits of commercial relevance include the primary deposits located in Czechoslovakia, which were created through the weathering of crystalline rocks from the Bohemian Massif, as well as the German deposits found in Bavaria and Saxony, the Ukrainian deposits in the former USSR, the primary origin deposits near Pittong, and the secondary deposits dating from the late Cretaceous period in Australia, specifically near Weipa. In Africa, significant deposits of kaolinite are primarily found in Egypt, Nigeria, South Africa, Eritrea, and Uganda. Conversely, the principal global commercial deposits of halloysite are located in the North Island of New Zealand and the Dragon halloysite mine in the Tintic district of Utah, USA, with smaller amounts found in Morocco, Japan, Korea, and the Czech Republic; pure dickite is extracted in Russia (Awad et al.

2017).The major world production of kaolin was estimated by the USGS to be 37,800,000 tons, in 2007. The major production by country is shown as in Table (1).

Table 1.The major world production of kaolin (USGS)(Al Ani and Sarapää 2008).

USA	7,330,000	China	600,000
Brazil(beneficiated)	2,500,000	Mexico	490,000
UK	2,100,000	Spain	460,000
Czech Republic	1,049,225(beneficiated)	Turkey	450,000
Czech Republic	5,183,000 (raw)	Argentina	300,000
Germany	3,800,000	France	300,000
South Korea	2,400,000	Ukraine	300,000
Commonwealth of Independent States (CIS)	6,000,000	Indonesia	250,000
Iran	900,000	Australia	250,000

China was the largest producer of kaolin worldwide in 2022, with a production volume of more than 8.5 million metric tons. The world's second-largest producer of kaolin that year was the United States and amounted to 4.6 million metric tons.

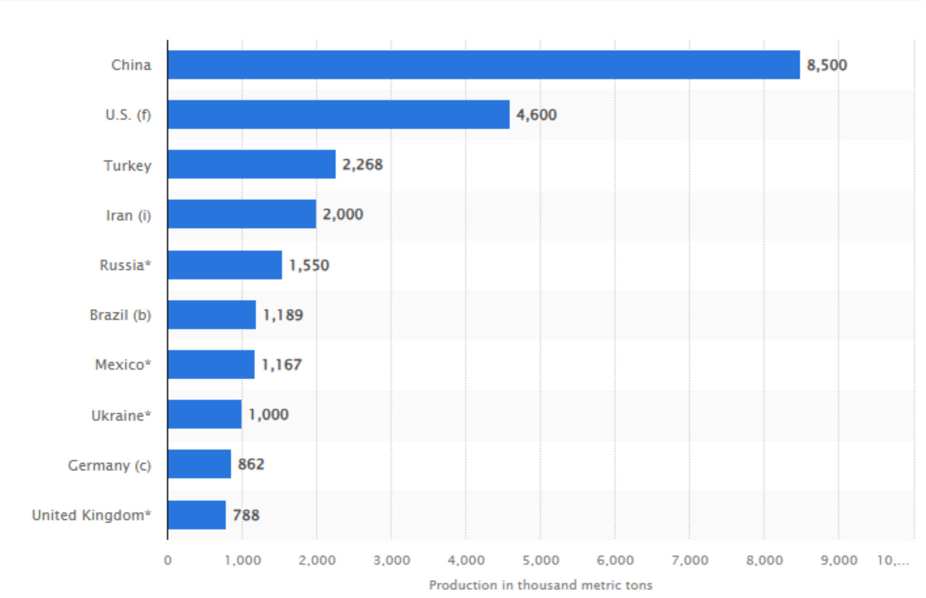


Figure 10. Kaolin production volume worldwide 2022, by leading country (M. Jaganmohan, 2024)

2.5. Kaolin deposits of Ethiopia

Many geologists have undertaken studies and found many kaolin suites such as Kombolcha, Ammacio Belessa, Ansho, Bensa, Debre Tabor, including the Alemtena kaolin and they investigated the genesis, mineralogy, and geochemistry and industrial use of these kaolin minerals(Kussbilo, Bheemalingeswara, and Hagosi 2024).The Ethiopian Institute of Geological Survey founded in 1983.since this time it has led to the discovery of raw materials for various industries (ceramics, cement, glass, soda ash, etc.).As different research papers Surveyed by this Institute and other researchers indicates that, Ethiopia has a huge reserve of kaolin, some of them estimates (20 million tons), which spreads in different parts of the country such as Tigray, Amhara, Oromia and Southern Nations, Nationalities, and Peoples Regions (Zewdie et al. 2021). The volcanic rocks of the Main Ethiopian Rift (MER) are one of the most important hosts of the kaolin deposits in Ethiopia (Gezahegn and Getaneh 2020).my study area (Alemtena Kaolin) is a part of this (MER) area. Some researcher reports the reserve of kaolin in a different specific locality as follow. Many kaolin deposit areas investigated in Ethiopia are shown below in different parts of the country.

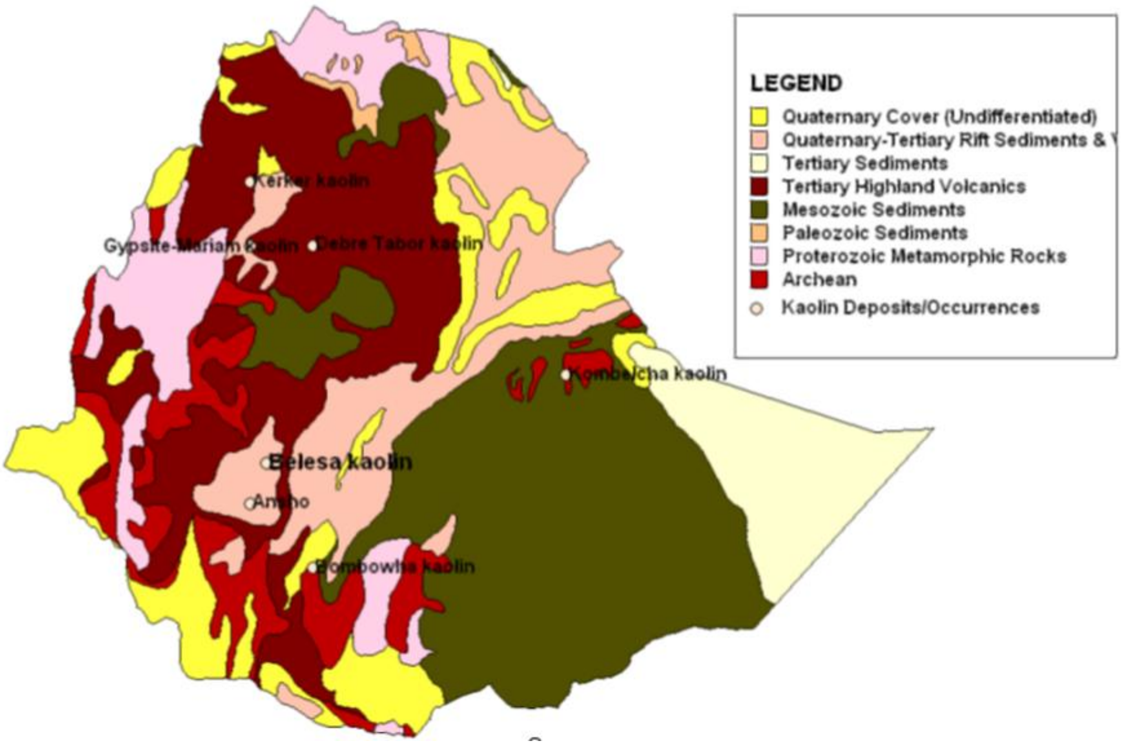


Figure 11.*General Geology and Kaolin Occurrences of Ethiopia (Shiferaw Ayele 2011)*

2.5.1. Bombowha kaolin deposit

Bombowha kaolin deposit is located in Southern Ethiopia, Borena Zone, Bore District, at the locality called Bombowha. Geographically the area is bounded between 6° 04' 38"N to 6 0 5' 20"N latitude and 38° 45' 25"E to 38°46' 10"E longitude which is found between Bore and Kiberemengist towns (i.e. 40km south of Bore town and 40km north of Kiberemengist town) which is 430km in the south far from the capital Addis Ababa. Bombowha kaolin deposit produced by in-situ weathering of pegmatites and granites. The color pinkish near the surface and brownish yellow, and grey to white with depth. The Proven reserves of 150,000 ton of kaolin had been identified in 1992, at which time open-pit mining operations began. Moreover, recently it is reported that several hundred thousand tons of good quality kaolin is known to be hosted by the kaolinized granites (Shiferaw Ayele 2011).

2.5.2. Kombolcha kaolin deposit

The Kombolcha kaolin deposit is located in the East Hararghe Zone of Oromia Regional State, Kombolcha is found at about 16 kilometers to the north of Harar town along all-weather road from Harar to Ejersa Goro town. The primary deposit of kaolin in Kombolcha originated from the in situ weathering of the parent rock, which consists of pegmatite and granite. These occurrences of kaolinized granite are distributed within a radius of 4 to 10 kilometers from the town of Kombolcha. They vary light pinkish to whitish and sometimes light grayish in color. The kaolin deposit occurs as blankets extending over a large aerial coverage and overlying the granite rocks. Residual/in situ kaolin deposits are formed by the weathering of feldspar and other aluminum silicate bearing rocks (Shiferaw Ayele 2011).

2.5.3. Belessa kaolin deposit

The Belessa kaolin deposit is located in Southern People Nations and Nationalities Regional National State. Specifically, in north east of Hosanna town, near the village of Belessa, which is 230 km south of the capital Addis Ababa. The kaolin occurrences of Belessa area are associated with acidic volcanic rocks of rhyolites and ignimbrites. The kaolinized horizon contains alternating layers of extremely fine-grained and purely kaolinitic layers and medium to fine grained quartz bearing kaolinitic layers. Kaolinite and halloysite can be formed by the alteration of volcanic glasses and feldspars in the parent rhyolite by hydrothermal process (Shiferaw Ayele 2011).

2.5.4. Ansho kaolin deposit

The Ansho kaolin deposit is located in SPNNRS, Hadiya zone, Duna Woreda. Geographically the deposit is bounded between latitude 350000m E & 352000m E and longitude 811000m N & 814000m N and 232 km far from south of the capital Addis Ababa. The deposit is located around 1 km distance from the center of the Ansho town. Trachyte rocks are the largest rock units in the Ansho area. Kaolinite and halloysite can be formed by the alteration of volcanic glasses and feldspars in the parent rhyolites by hydrothermal process. Most of the kaolin occurrences are derived from residual (in-Stu) weathering or hydrothermal alteration of trachyte and rhyolite. The color variation ranges from light grey, brownish grey and white when weathered. It is medium to fine grained in rare cases and it is coarse grained. The total reserve of kaolin deposit is estimated to be 960, 062tons while pure kaolin is calculated as 291, 355 tons (Shiferaw Ayele 2011).

2.5.5. Debre Tabor kaolin deposit

Debre tabor kaolin deposit located in Amhara national regional state, south Gondar zone at south west of Debre tabor town on a mountain called Eyesus. It is the alteration product of feldspar rich trachytic rocks. The kaolin is soft, unbedded and yellowish white in colour (Shiferaw Ayele 2011). The deposit lies at about 2km far from the Debre tabor town, over 5 million tons estimated of kaolin deposit occurs at Debre Tabor (Zewdie et al. 2021). The thickness of this deposit varies depending on the topographic feature, from 2 to 3 m in flat, and 3 to 4 m in the sloppy exposure (Mesele et al. 2021).

2.5.6. Kerker kaolin deposit

kerker kaolin deposit located in Amhara national regional state, central Gondar zone, At Kerker, on the foot of a mountain called Ayemba which is situated to the North-West of Gondar. There occurs a deeply weathered light yellow colored agglomerate tuff which is highly kaolinized. It is unbedded and highly friable, with abundant quantity of weathered feldspar particles which are in a state of being changing into clay. It also contains some weathered basaltic rock. There the same tuff attains a maximum thickness of 3 meters (Shiferaw Ayele 2011).

2.5.7. Genet Terrara kaolin deposit

Genet Terrara kaolin located in Amhara national regional state, central Gonder zone, this deposit found at the foot of a mountain called Genet Terrara. The mountain is entirely covered with basalt, and the tuff occurs as an interbedded layer within the basalt. It is light reddish brown coloured, silty, friable and elight1y kaolinitic. Its thickness and length were found to be 1.50 and 5.50 meters respectively. According to the 10cal information, the tuff used to be quarried by a former ceramist (Japanese) for the use of ceramic making (Shiferaw Ayele 2011).

2.5.8. Gypsite Marriam kaolin deposit

A deposit of localized well bedded rhyolitic tuff with insignificantly developed clay soil occurs near the village of Gypsite Marriam. It is highly dissected by the effect of erosional phenomena and forms small grooves and hills. The tuff consists of two main alternating layers, which are varying in composition and texture. The first layer is coarse grained and light grey coloured, composed of dominantly rock fragments, feldspar and quartz particles binded together by clayey materials. Its thickness varies from 15 to 56cm. whereas the second layer is light yellowish coloured and fine-grained glassy rock, having a thickness of from 24 to 30cm. Unlike to the other occurrences of kaolinitic tuffs, this one is very fresh and highly compacted. Gypsite Mariam can be reached from Hamusit on 15 km. of all weather road,(Shiferaw Ayele 2011).

And also other unknown amount of potential clay deposit such as Refractory bond clays and clays suitable for cement manufacturing occur in Gondar (Chelga) and Showa (Koka)(Tadesse, Milesi, and Deschamps 2003), Alluvial clay deposits for brick, tile, pottery and pipe industries occur in Showa (Addis Ababa area), near Debre Zeit, Akaki, Kaliti and Sululta, between Debre Sina and Debre Berhan, and at Zega Wodel, Keffa (Bebeka), Sidamo (Kebre Mengist area), Wollega (Dilla), Hararghe (Dire Dawa area), Abay River valley and the Rift valley lake regions(Tadesse, Milesi, and Deschamps 2003), Clay materials for the manufacture of pigment occur in Gondar and Kaffa, Ceramic clays are common in Ambo, Showa, Harar and Sidamo (Bombowha or Bwambwa Weha) and Kaolin results from the weathering of granite occur in Kombelcha. But mining at depth, continuous and progressive research on kaolin deposits and their occurrences, an increased level of mineral impurities makes commercial applications not viable (Zewdie et al. 2021).

2.6. Characterization of clay minerals

Currently, modern analytical techniques such as Nitrogen Adsorption Isotherm, X-Ray diffraction (XRD), Fourier-Transform Infra-Red (FT-IR), Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), Zeta potential and Thermal Gravimetric Analysis

(TGA) used to identify and characterize of clay minerals in easier ways (Kumari and Mohan 200ADb). The nitrogen adsorption isotherm used for analyzing the specific surface area, pore volume and pore size distribution by characterizing the porous materials like clay minerals. XRD is mainly used for identification of crystallinity of clay minerals. The characteristic peaks clay minerals like illite, kaolinite, chlorite, smectite etc. can be identified using XRD pattern which further gives information about the interlayer space. The interlayer space is determined using Bragg's equation ($n\lambda = 2d\sin\theta$). FT-IR technique is used for identification of functional group like hydroxyl group, Si-O, Al-O group etc. Scanning electron microscopy used to study the surface topology of clay minerals such as the size of platelets and their shape mainly describes the surface morphology. Transmission electron microscopy (TEM) is used for studying microstructure and micromorphology of clay minerals by observing the stacking of layers and interlayer space and it can provide useful data on size, shape, and aspect ratio of kaolinite crystals in fine-grained products from beneficiation trials. TEM imaging also allows the positive identification of halloysite. Zeta potential mainly used to study the surface charge of clay minerals. Zeta potential holds the information about electric double layer of charged particles whose magnitude is proportional to particle charge adhere on outer surface of clay minerals. Thermogravimetric analysis used for determination of thermal stability of clay minerals. The curve obtained during analysis at various temperatures indicates the dehydration, dehydroxylation and phase transformation of clay minerals (Kumari and Mohan 200ADb).

2.7. Mining and refining

2.7.1. Mining methods of kaolin

The majority of clay mined worldwide is done so in open pits. Although there are a few underground mines, most clay deposits cannot be mined underground due to poor roof conditions and production costs(Bloodworth et al. n.d.).

Open-pit mining method

This kind of mining technique uses mechanical mining tools like load trucks, backhoes, and shovels to remove the overburden from the site. The cost of removing overburden determines how much capital is needed for this mining technique. Scrapers and dozers, which are typically assisted by large draglines, may be used if the overburden is more than sixty feet. Following the removal of the overburden, small draglines are used to excavate the clay, which is then fed into plungers where a dispersing agent helps it stay suspended in water. Pumping the dispersed clay slurry to central degritting stations allows for the removal of mica and coarse sand using hydrocyclones and gravity settling, followed by screening. Until testing determines the necessary blending for feeding into the main processing plant, any additional processing needed will result in the product from this initial beneficiation being stored separately in large tanks. Over distances of 10–32 km or more, the clay slurry is transported by pipelines with a diameter of 15–30 cm to the main processing facility (Bloodworth et al. n.d.). In the Georgia-South Carolina sedimentary belt, kaolin is extracted using traditional open-pit techniques (Bloodworth et al. n.d.).

Hydraulic mining method

The preconcentration technique employed in hydraulic mining aids in minimizing the handling of excessive waste rock. The resilient, unkaolinised rock remains after the softer kaolin is preferentially extracted from the matrix using water jets that operate at pressures reaching 250 psi. Due to the variability of the deposits, selective mining is essential. The kaolin slurry, which contains suspended particles, is directed to the lowest point of the pit as the rock face undergoes washing. Initially, spiral classifiers eliminate the coarser particles from the slurry, after which hydrocyclones are employed to separate the finer sand and mica particles. Subsequently, the slurry is thickened in a large-diameter thickener before being processed in centrifuges for fine sizing (Bloodworth et al. n.d.). In the kaolin mining operations located in Devon and Cornwall, in the southwest region of England, water jets are utilized.

Critical issues involved in the mining of kaolin

The disposal of the waste material produced in the processing and the disposal of the 80 to 85% of the host rock from which the kaolin is extracted by hydraulic methods.

- The depth of the ore body as mining progresses because these deposits are funnel shaped and become smaller in circumference with depth (fig.9).
- Their relatively high viscosity in comparison with the Georgia and Brazil sedimentary kaolin’s, example in Southwestern England.

- The heavy rains, which flood the mines during the rainy season. Also, the remoteness of the mines from population centers creates difficulties in labour and management turnover, example In Brazil.
- The availability of high quality, low viscosity kaolins are rapidly disappearing, example In Georgia (Bloodworth et al. n.d.).

As long as the fine particle dust is kept under control, kaolin is a material that is safe for the environment and does not pose any health risks. In Georgia and Brazil, open pit mines are reclaimed to make way for recreational, forestry, or agricultural endeavors (Al Ani and Sarapää 2008).

2.7.2. Refining (beneficiation) of natural kaolin

Many kaolin deposits are essentially pure and require little concentration during preparation for market. While other deposits contain small percentages of kaolinite, and these must be washed and concentrated to recover marketable kaolin (Murray 1980a).The geological history of a kaolin deposit has a significant impact on the processing technology needed to beneficiate kaolin minerals. Therefore, it is essential to have a comprehensive understanding of the mineral composition. Therefore, the type of deposit and the products' intended uses determine which process is best. Kaolin can be processed using either a wet process or a dry method (Bloodworth et al. n.d.; Murray 1980a).

The initial phase of kaolin processing entails the separation of abrasive minerals, such as quartz, and undesirable minerals like mica. This process is more straightforward in secondary deposits that have undergone natural sorting during their transport. Conversely, extracting kaolin from primary deposits presents greater difficulties due to the substantial presence of abrasive minerals that persist through the alteration process (Bloodworth et al. n.d.).

Beneficiation refers to the process of enhancing quality. The primary goals of refining kaolin are to eliminate impurities and achieve the desired distribution of particle sizes(Bloodworth et al. n.d.). Currently, industries utilizing kaolin favor materials that contain the maximum kaolinite content while minimizing the presence of other minerals, including quartz, potassium feldspar, mica, and titaniferous oxide minerals such as anatase, brookite, rutile, ilmenite, goethite, hematite, and magnetite.(Awad et al., 2017). Kaolin ore undergoes processing to improve or regulate various properties within a certain range, as dictated by the intended application

(Bloodworth et al. n.d.). The presence of iron and titanium oxide minerals is detrimental as they reduce whiteness and lower brightness. An excess of silica, whether in the form of quartz or cristobalite, often results in abrasion problems during paper application. The inclusion of micas and feldspar can influence the rheological properties, brightness, and abrasion characteristics. Furthermore, the viscosity of the kaolin slurry is affected by the presence of smectite (Prasad, Reid, and Murray 1991).In the world market, the commercial value of kaolin depends on whiteness and fine particle size. Therefore, the removal of colouring oxides is essential if high-brightness saleable grades are to be produced (Bloodworth et al. 1993).To produce commercially marketable kaolin, the raw material must first go through a beneficiation process (Mussel et al. 2008).Hereby the purpose of kaolin raw materials beneficiation process is to increase the content of valuable clay rocks (kaolinite, halloysite, diquite), by reducing the major amounts of impurities (quartz, mica, feldspar, titanium oxide and iron oxide) and other ore minerals through using different processing techniques. To improve the quality of kaolin deposits to possibly meet some industrial requirements, the coloring impurities (mainly iron oxides and other small amounts of fluxing components) must be removed through efficient, economical, and environmentally friendly beneficiation methods (Bloodworth et al. n.d.). Various beneficiation methods are available for enhancing the quality and achieving the desired particle shape and size distribution of kaolin clay. The choice of process is influenced by the characteristics of the deposit and the specific applications for the products. Kaolin can be processed primarily through two methods: a dry method and a wet process (Kogel 2014b; Prasad, Reid, and Murray 1991).

Dry Processing

In other contexts, dry processing is referred to as air flotation, a method that separates clay from impurities. This process involves relatively simple or fewer steps, less expensive or has lower costs, Low quality of the product or has poorer color and higher grit content, significant losses of kaolin in waste (produces a less refined products), low productivity of beneficiation plants, heterogeneity of beneficiated kaolin properties limit the use of dry beneficiation method (Al Ani and Sarapää 2008).(Bloodworth et al. n.d.; Kogel 2014a; Prasad, Reid, and Murray 1991; G. Abdykirova et al 2022) In the dry process operation, a deposit must be chosen with desirable properties of color and relatively low content of grit (> 44 µm). The primary characteristic of the dry process is to dehydrate the raw clay to enable its pulverization (G. Abdykirova et al 2022).

Upon entering the storage shed, the raw clay is subjected to shredding or crushing by roll crushers, reducing it to pieces approximately the size of an egg. At this point, the crude material contains 20-25% moisture, which is subsequently eliminated using a rotary dryer. After drying, the crushed kaolin is processed in a roller mill, where it is pulverized and then directed into the grinding section of the mill. Here, plows elevate the clay into the zone where the rollers grind it against the grinding ring. The disintegrated kaolin can subsequently undergo air classification, where the finely milled product is elevated through the upper section of the machine to the outlet duct. Within the outlet duct, particles interact with the whizzer, which sorts them by size. The lighter particles ascend through the whizzer and are collected separately, while the heavier particles that do not possess sufficient velocity to exit the whizzer are expelled through the side ports of the mill. This material may undergo further grinding to extract additional quantities of previously unliberated clay (Murray n.d., n.d.).

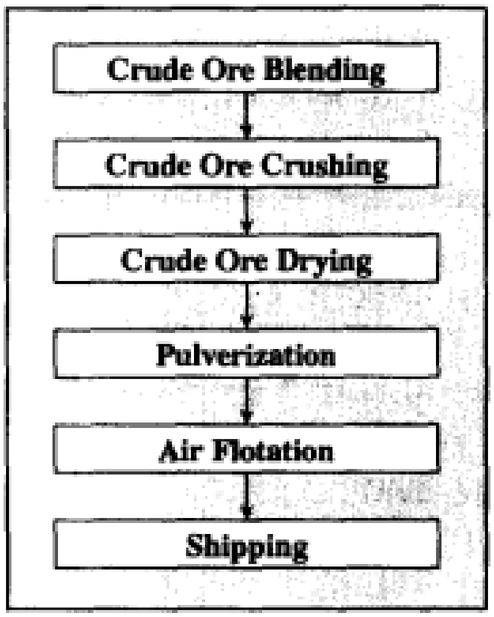


Figure 12. Schematic diagram for dry processing of kaolin.(Prasad, Reid, and Murray 1991)

Wet process

Typically, the wet processing method referred to as the water wash process for kaolin is significantly more intricate than the dry processing; however, this technique is more commonly employed and yields superior results in its wet form (Bloodworth et al. n.d.; Kogel 2014a; Prasad, Reid, and Murray 1991; G. Abdykirova et al 2022). Wet processing commences with the formulation of a dispersed mineral water suspension, which essentially transforms the raw clay into a slurry. This slurry should comprise distinct mineral particles that are separated and suspended in water. The kaolin particles display opposing charges on the edges and surfaces of their plates, leading to mutual attraction and the formation of flocs. To separate the particles in the flocs, a dispersion reagent (0.75%) such as sodium polyphosphate, sodium hexametaphosphate, sodium silicate, tetra sodium polyphosphate, and sodium polyacrylate is added.(Kogel 2014b; Prasad, Reid, and Murray 1991). The next stage following dispersion involves eliminating the larger grit particles (> 44 µ) through settling methods and then processing them with vibrating screens, hydro separators, or hydro cyclones. The resulting degritted slurry is processed in centrifuges to segregate the kaolin into fine, medium, and coarse particle size groups. After the fractionation process, the slurry is subjected to brightness enhancement to eliminate impurities that cause discoloration, including iron oxides, iron hydroxides, anatase. Usually, there are various beneficiation techniques used to improve kaolin brightness. These techniques include size classification methods, high-intensity magnetic separation, selective flocculation, froth flotation, and bleaching (Kumari and Mohan 200ADa; Mathur 2002). The kaolin is subsequently dewatered using a filtration method, dried in rotary, apron, or spray dryers, and readied for shipping. This procedure is employed to create highly refined kaolins with specific attributes, such as viscosity in a water suspension, particle size distribution, color, and brightness (Kogel 2014b; Mathur 2002; Prasad, Reid, and Murray 1991). Wet grinding is utilized to manipulate the shape of particles by separating stacked kaolinite crystals, resulting in single particles that have a high aspect ratio. Before being shipped, the kaolin slurry is either dewatered or dried, depending on the method of delivery chosen for the customer (Kogel 2014b; Prasad, Reid, and Murray 1991).

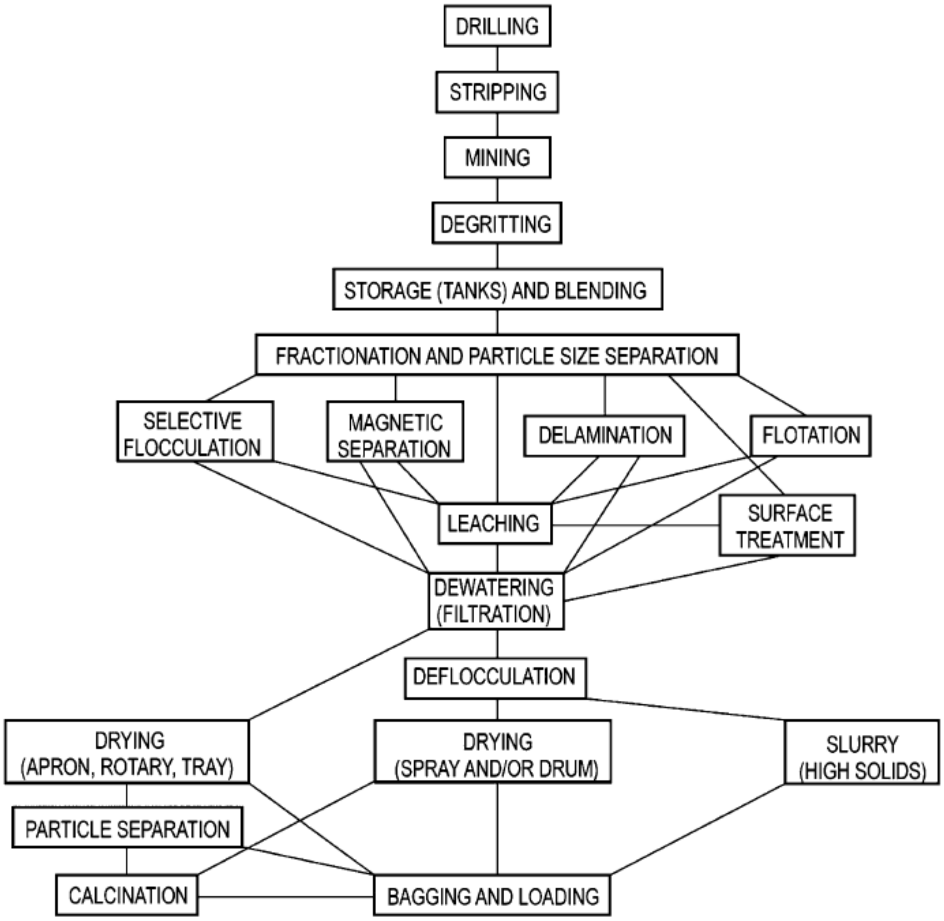


Figure 13.Typical flow sheet used for wet processing of kaolin (Murray, 2006)

Thermal Treatment

Thermal Treatment (calcination) is a procedure utilized to create special grade kaolin products, involving the high-temperature firing of wet- or dry-processed kaolin in either a rotary kiln or a vertical kiln. The calcinations process enhances whiteness and hardness, improves electrical characteristics, and modifies the size and shape of the kaolin particles. The firing temperature and duration are adjusted based on the intended outcome of the product. Two distinct grades of calcined kaolin are produced, depending on the treatment temperature (Kogel 2014b; Prasad, Reid, and Murray 1991). Calcinations processes conducted at temperatures between 650 and 700°C eliminate structural hydroxyl groups, and the resulting water vapor leads to the formation of metakaolin. This material is utilized in paint and specific paper applications that demand high bulk and optically enhanced aggregated particles. Additionally, products generated at this temperature are employed in PVC cable insulation to enhance dielectric properties and serve as a pozzolanic additive in concrete (Kogel 2014b; Prasad, Reid, and Murray 1991). Firing kaolin's at a high temperature range (1000-1050°C), causes mullite formation. at this range of temperature, the improvement of brightness of 92-95% can be obtained, even though the abrasiveness is increased. Products fired in this temperature range are used in rubber compounds and may be coated with silane to enhance mechanical properties and chemical resistance. Silane treatment also improves rigidity, toughness, and dimensional stability in polyamide moldings. High-temperature firing is also used to manufacture high-strength ceramic proppants for hydraulic fracturing (Kogel 2014b; Prasad, Reid, and Murray 1991).

Chemical beneficiation methods involve the removal of mineral impurities from kaolin clay by organic and inorganic acids such as oxalic acid, citric acid, thiourea dioxide, sodium dithionite, sulfuric acid, and hydrochloric acid (Kogel 2014b; Prasad, Reid, and Murray 1991). The effect of different organic acids and their concentration in iron removal from kaolin ore indicates that the iron removal efficiency of oxalic acid is the most promising organic acid. Similarly, oxalic acid solution is the best iron leaching reagent because of its acid strength, good complexing characteristics, and high reducing and bleaching power over those of other organic acids leachants (malonic, citric, and ascorbic acid) (Kogel 2014b; Prasad, Reid, and Murray 1991).

In recent decades, biological beneficiation methods have been also used to remove mineral impurities from kaolin clay. Several studies have been applied biological beneficiation techniques for removing mineral impurities from kaolin clay by using different kinds of fungi and bacteria (Kogel 2014b; Prasad, Reid, and Murray 1991).Biological purification techniques are more economical, eco-friendly, not energy-intensive, and maintains the crystal structure of kaolin clay to a large extent but a very slow process for industrial mass production (Kogel 2014b; Prasad, Reid, and Murray 1991).

Physical beneficiation methods are preferentially used to improve the quality of raw kaolin due to the less economical, while biological beneficiation of kaolin is non-eco-friendly, energy intensive, poorly maintained crystal structure, and very slow process for industrial mass production. Physical beneficiation methods are preferentially used to improve the quality of raw kaolin. The removal of gravel, sand, and other matter during the wet beneficiation of kaolin involves centrifugal separation, chemical bleaching, filtering, selective flocculation, gravity separation, magnetic separation and flotation(Bloodworth et al. n.d.; Kogel 2014a; Prasad, Reid, and Murray 1991; G. Abdykirova et al 2022).

2.7.3. The critical properties of kaolin clay

The evaluation of the kaolin deposit's quality and commercial worth is based on its physical properties, including grain size, bulk density, and specific gravity, as well as its mineralogical and chemical compositions (Bloodworth et al. n.d.; Kogel 2014a; Prasad, Reid, and Murray 1991; G. Abdykirova et al 2022). The primary characteristics of kaolin include its opacity, electrical and mechanical properties, whiteness and brightness, as well as the distribution of particle shape and size (Bloodworth et al. n.d.; Kogel 2014a; Prasad, Reid, and Murray 1991; G. Abdykirova et al 2022).

The industrial uses of kaolin primarily rely on its physical properties, with various applications requiring unique combinations of these functional characteristics. Consequently, specific grades are seldom appropriate for all uses. Aside from kaolin intended for ceramics, the chemical composition is typically not a crucial factor (Bloodworth et al. n.d.; Kogel 2014a; Prasad, Reid, and Murray 1991; G. Abdykirova et al 2022).

The economic worth of kaolin is influenced by its whiteness and fine particle size. This latter characteristic also affects viscosity, color, abrasiveness, and the ease of dispersion. Additional significant attributes include its lamellar particle shape, which enhances opacity or hiding power, its soft and non-abrasive texture resulting from the lack of coarser impurities, and its chemical inertness across a broad pH range. The existence of surface charges contributes to properties that ensure the mineral is flocculated at low pH and deflocculated at high pH, a feature that is leveraged during processing and application. Kaolin exhibits favorable rheological properties, enabling it to be readily dispersed in water to create slurries with low viscosities, both under low and high shear conditions, and at high solids content, which is critically important in the paper industry (Bloodworth et al. n.d.; Kogel 2014a; Prasad, Reid, and Murray 1991; G. Abdykirova et al 2022).

Physical and Chemical Properties

The physical characteristics of kaolin are crucial for determining their appropriateness for various applications. The primary variation in the chemical composition of kaolin found in secondary deposits lies in the levels of iron and titanium, whereas for clays in primary deposits, the significant differences are observed in the kaolin content and the amounts of free silica (Bloodworth et al. n.d.; Kogel 2014a; Prasad, Reid, and Murray 1991; G. Abdykirova et al 2022). Key physical constants of kaolin include: specific gravity of 2.60, an index of refraction of 1.56, a hardness rating of 2 on the Mohs scale, a fusion temperature of 1850° C, and a dry brightness ranging from 78 to 92 percent (Murray n.d.).

Particle size determination

The particle size is represented as e.s.d. (equivalent spherical diameter) and is measured using sedimentation techniques from a deflocculated clay suspension in water. The shape and size distribution of kaolin significantly influence various properties, including brightness, viscosity, opacity, gloss, ceramic strength, and shrinkage. These factors also impact the filling and coating properties of paper, affecting the mechanical, optical, and printing attributes of the final paper sheet (Bloodworth et al. n.d.; Kogel 2014a; Prasad, Reid, and Murray 1991; G. Abdykirova et al 2022). The 2µm point serves as the standard control point in commercial applications. Coarser kaolins are typically utilized as filler clays, while finer materials are predominantly employed in coating products. The particle shape is intricately linked to its size; filler clays generally consist of a high quantity of stacked particles, whereas coating clays are characterized by a predominance of thin plates (Bloodworth et al. n.d.; Kogel 2014a; Prasad, Reid, and Murray 1991; G. Abdykirova et al 2022).

Brightness and whiteness

Brightness and whiteness are distinct characteristics that should not be conflated. Brightness refers to the percentage of reflectance in comparison to a standard of smoked magnesium oxide, which is set at 100% at a wavelength of 457 millimicrons. In the paper industry, kaolin typically exhibits brightness levels ranging from 80 to 90, with filler grades usually between 80 and 85 and coating grades from 85 to 90. Conversely, whiteness pertains to the color perceived by the human eye. This measurement can be determined by assessing reflectivity at wavelengths of 400 and 700 millimicrons. A smaller discrepancy between these values indicates a whiter product (Murray 1980a).

The optical characteristics of kaolin are crucial for various commercial uses. These properties are typically analyzed through the absorption coefficient (k) and the scattering coefficient (s) based on K-M theory. The absorption coefficient can be altered through chemical treatments or beneficiation processes aimed at eliminating colored impurities. Standard brightness values for kaolin are established by assessing the diffuse reflectance of light at a specific wavelength, usually 457 nm, and are compared against a reference standard calibrated in a laboratory recognized by the International Standards Organization. Additionally, the presence of other minerals such as micas, tourmaline, and titaniferous impurities significantly affects light absorption, as do hydrated iron oxide coatings on kaolinite particles (Bloodworth et al. n.d.; Kogel 2014a; Prasad, Reid, and Murray 1991; G. Abdykirova et al 2022).

Rheology

The rheological characteristics of kaolin slurries are crucial at both low and high shear rates. The relationship between the bulk properties of kaolin and the rheology of coating slurries is intricate. Key factors appear to include specific surface area, particle morphology, and particle arrangement. Ideally, clay would exhibit Newtonian flow behavior, maintaining consistent viscosity across varying shear rates. However, all clays exhibit dilatant behavior, indicating that the viscosity of the slurries rises with increasing shear rate. Viscosity measurements of clay-water slurries are conducted at specific solid concentrations, typically 67% for delaminated clays and either 70% or 71% for ultrafine clays. The surface area of the clay influences the low shear viscosity at a defined solids concentration. Coarse clays generally exhibit lower Brookfield viscosities compared to fine clays. High shear rheology is more influenced by particle shape. Most standard coating clays maintain viscosities of 300 cp or less at 20 rpm. At elevated shear rates, as assessed using a Hercules Viscometer, coating clays can vary from 18 dynes cm X 10^5 at a bob speed of 700 rpm to 3 or 4 dynes cm X 10^5 at 1100 rpm (Welch and Dahlquist, 1984). For coating clay slurries to be easily pumpable, they must possess low viscosity at high shear rates. Delaminated clays, due to their shape and aspect ratio, exhibit higher high shear viscosity. The presence of contaminants and soluble salts negatively impacts rheology. Expanding minerals like smectite, which swell upon contact with water, are advantageous for drilling mud but detrimental for aqueous slurries used in paper coating. Techniques have been established to eliminate these minerals from raw clay through continuous centrifugation or chemical modification. Alternatively, they can be transformed into a non-swelling form by introducing positively charged aluminum-hydroxyl species to a kaolin suspension and subsequently increasing the pH to approximately 7. Under these conditions, the smectite layers bond with each other and with the kaolinite platelets (Bloodworth et al. n.d.; Kogel 2014a; Prasad, Reid, and Murray 1991; G. Abdykirova et al 2022).

pH

The pH level of coating clays varies between 6.5 and 7.5. A higher pH typically suggests the existence of soluble salts, which may lead to significant issues in various applications (Bloodworth et al. n.d.; Kogel 2014a; Prasad, Reid, and Murray 1991; G. Abdykirova et al 2022)..

Screen residue

The residue observed on the screen signifies the existence of larger particles that are captured by a 325-mesh screen. Retained on the screen are quartz, mica, feldspar, and clusters of densely packed clay, as well as the most prevalent minerals. This characteristic is crucial to assess in both the dry and wet processing of clay (Bloodworth et al. n.d.; Kogel 2014a; Prasad, Reid, and Murray 1991; G. Abdykirova et al 2022).

Sheet properties

Paper sheets may be coated with kaolin and a binder in accordance with the established protocols set forth by the Technical Association of the Pulp and Paper Industry. To assess the suitability of specific clay for coating applications, the coated sheets must undergo conditioning, calendaring, drying, and the evaluation of various properties. The subsequent properties are of significance (Bloodworth et al. n.d.; Kogel 2014a; Prasad, Reid, and Murray 1991; G. Abdykirova et al 2022).

Opacity is affected by the arrangement of particles and is primarily determined by the size and shape of the particle distribution. The inclusion of ultrafine particles measuring 0.1 µm or smaller diminishes opacity, while the ideal opacity or covering capacity of coating clay is achieved with particles sized between 0.3 and 1.5 µm (Bloodworth et al. n.d.; Kogel 2014a; Prasad, Reid, and Murray 1991; G. Abdykirova et al 2022).

The presence of fine particles enhances the gloss of coated paper. Gloss is typically associated with a high pore volume, which strengthens specular reflectance. The presence of ultrafine particles influences gloss. In contrast, smoothness is not influenced by optical phenomena; rather, the development of smoothness relies on the presence of fine, thin, and small-diameter particles (Bloodworth et al. n.d.; Kogel 2014a; Prasad, Reid, and Murray 1991; G. Abdykirova et al 2022).

Film strength is influenced by the preferential migration of the adhesive into the substrate and the orientation of kaolin particles. Well-dispersed coating clay with fine particle size and low relative sediment volume will yield optimal film strength (Bloodworth et al. n.d.; Kogel 2014a; Prasad, Reid, and Murray 1991; G. Abdykirova et al 2022).

Ink receptivity varies among different clay grades. Particles with a small diameter that are randomly oriented exhibit superior ink receptivity. Additionally, the presence of minor amounts of smectite enhances ink receptivity but reduces ink holdout because of its large surface area and significant sorptive ability. Generally, a decrease in clay particle size leads to an increase in ink holdout (Bloodworth et al. n.d.; Kogel 2014a; Prasad, Reid, and Murray 1991; G. Abdykirova et al 2022).

Adhesive demand

Adhesives like starch or latex serve to unite the clay particles with each other and with the paper sheet. The amount of adhesive needed is directly proportional to the clay's surface area and must be meticulously regulated, as it also affects opacity, brightness, color, and smoothness (Bloodworth et al. n.d.; Kogel 2014a; Prasad, Reid, and Murray 1991; G. Abdykirova et al 2022).

2.7.4. Industrial applications kaolin clay

Numerous researchers have explored the industrial uses of kaolin, demonstrating that this mineral is a crucial raw material utilized across various industrial sectors, each requiring specific combinations of kaolin's functional properties (Bloodworth et al. n.d.; Kogel 2014a; Prasad, Reid, and Murray 1991; G. Abdykirova et al 2022). The Critical properties of kaolin which makes it suitable for industrial application includes its color, softness, particle size, particle shape and chemical inertness.

The whiteness (white color) and fine particle size (has a bearing on viscosity, gloss, colour, abrasiveness and ease of dispersion depend on particle size), lamellar particle shape (which increases opacity or hiding power), its soft and non-abrasive texture (due to the absence of coarser impurities), and its chemical inertness over a wide range of pH and the presence of surface charge (which ensures that the mineral is flocculated at low pH and deflocculated at high pH) improves the commercial value of kaolin(Bloodworth et al. n.d.; Kogel 2014a; Prasad, Reid, and Murray 1991; G. Abdykirova et al 2022).

Kaolin forms the basis of an industry of worldwide importance with output being in excess of 20 Mt in 1990 valued at about $2000 million. In terms of value, about 75% is used in papermaking, 10% in ceramics and 15% in the paint, rubber and plastics industries; the latter category also includes a range of miscellaneous applications. The grain size distribution is used to identify the possible field of industrial applications. The grain size specification of kaolin used for fillers requires 40– 60% of it to be<2 μm. In high-quality ceramics, more than 85% of the grains should be <2 μm (Bloodworth et al. n.d.; Kogel 2014a; Prasad, Reid, and Murray 1991; G. Abdykirova et al 2022).

Paper industry

The paper industry primarily utilizes white Kaolin mineral, with approximately 1,200,000 tons consumed in 1958(Bloodworth et al. n.d.; Kogel 2014a; Prasad, Reid, and Murray 1991; G. Abdykirova et al 2022). Globally, over 10 million tons per year are consumed. The paper sector is among the largest consumers of white kaolin, representing 5,902,367 tons, or 59.7%, of the 9,891,135 tons of kaolin sold or utilized by U.S. producers in 1988(Bloodworth et al. n.d.; Kogel 2014a; Prasad, Reid, and Murray 1991; G. Abdykirova et al 2022). Kaolin mineral serves two distinct roles in paper and board production: first, as a filler, it is added to the paper web to lower costs while also improving opacity, brightness, and printability; second, as a coating pigment, it enhances the surface characteristics of the paper, including brightness, smoothness, glossiness for magazines, and ink receptiveness, and can also act as a substitute for pulp (Bloodworth et al. n.d.; Kogel 2014a; Prasad, Reid, and Murray 1991; G. Abdykirova et al 2022). Opacity is a crucial characteristic in the paper industry, and the flow properties or rheology of kaolin clays, particularly the kaolin coating clays utilized in this sector, play a significant role due to their impact on coat weight, smoothness, texture, and other attributes. This ensures precise color reproduction in printing. The proportion of kaolin incorporated in different types of paper, including Newsprint, Uncoated, Coated, and Lightweight Coated, ranges from 3% to 10%, 10% to 20%, 35% to 40%, and up to 40%, respectively (Bloodworth et al. n.d.; Kogel 2014a; Prasad, Reid, and Murray 1991).

Kaolin possesses several advantageous characteristics as a paper filler, such as a fine, uniform, and controllable particle size, ease of dispersion in water, softness, and low abrasiveness (which minimizes wear on papermaking equipment), high brightness that enhances light reflectance and opacity, as well as chemical inertness (Bloodworth et al. n.d.; Kogel 2014a; Prasad, Reid, and Murray 1991). The control parameters for filler kaolins include particle size, powder brightness, and abrasiveness.

Brightness is characterized as the percentage ratio of radiation reflected by a material compared to that reflected by a $BaSO_4$ standard, which is approved by the International Standards Organization (ISO) and measured at an effective wavelength of 457 nm using a Carl Zeiss photoelectric reflection photometer. Yellowness is quantified as the difference in percentage reflectance between 570 nm and 457 nm. The ISO standard for brightness is predominantly utilized in Europe, while alternative systems may be employed in other regions. Enhancements in brightness can be achieved through methods such as fine grinding, magnetic separation, froth flotation, and chemical bleaching (Bloodworth et al. n.d.; Kogel 2014a; Prasad, Reid, and Murray 1991; G. Abdykirova et al 2022).

Kaolinite exhibits softness with a Mohs hardness ranging from 2 to 2.5; however, the presence of other minerals in the clay, such as quartz and feldspar, can greatly enhance its abrasiveness. The particle size of the mineral is crucial, as abrasiveness diminishes with smaller particle sizes. Various instruments can be employed to assess abrasiveness, and these specialized methods typically evaluate the abrasiveness of clay by measuring the weight change of a standard bronze wire that has been abraded by clay slurry over a predetermined duration (Bloodworth et al. n.d.; Kogel 2014a; Prasad, Reid, and Murray 1991; G. Abdykirova et al 2022).

Smaller particle sizes enhance brightness, opacity, and gloss; however, their increased surface area disrupts fiber bonding, which consequently diminishes the strength of the paper. Additionally, finer particles exhibit lower retention. The control parameters for kaolin fillers include particle size, powder brightness, and abrasiveness (Bloodworth et al. n.d.; Kogel 2014a; Prasad, Reid, and Murray 1991; G. Abdykirova et al 2022).

For coating purposes kaolin is applied to the surface of the finished paper as a thin film of finely divided mineral suspended in water with an adhesive mixture. Machine-made paper has a relatively rough substrate which can be masked to produce a smoother, brighter, glossier surface, more receptive to ink transfer and ideal for high-quality printing. Particle size exerts the most influence on coating performance, contributing not only to the smoothness, gloss and printability of the coated sheet, but also to the rheological properties of the coating slurry. Coating clays are mainly controlled in terms of particle size, powder brightness and rheology. Gloss, brightness, opacity and smoothness all generally improve with decreasing particle size, although very finely-sized kaolin's may give other problems (Bloodworth et al. n.d.; Kogel 2014a; Prasad, Reid, and Murray 1991; G. Abdykirova et al 2022).

Combinations of properties required for filler and coating grades of kaolin are significantly different. Coating demands the highest qualities of clay which are brighter and whiter with better glossing properties than filler grades. Since finer kaolinite particles have improved brightness, gloss characteristics and superior hiding power, coating grades are much finer than filer grades, with typically >75% -2 µm compared with >30% -2 µm for filler grades. As a general rule the relative cost of kaolin pigment increases as pigment brightness increases and particle size decreases. As a result, coating clays command a higher price than filler grades. Particle-size distribution of kaolin products is generally measured using a gravity sedimentation technique such as Andreasen pipette or X-ray sedigraph (Bloodworth et al. n.d.; Kogel 2014a; Prasad, Reid, and Murray 1991; G. Abdykirova et al 2022).

Typical values for coating clays and filler clays are 30 and 60-70 dm^2 respectively. Apparatus for measurements of this kind is rarely seen outside the specialist laboratories of major kaolin producers and consumers.

Ceramics

Until the end of the 19th century, kaolin was used almost exclusively in the manufacture of ceramics. Although the tonnages used in this application are now greatly exceeded by those consumed in paper making, white ware ceramics and refractoriness remain a major market for kaolin. Kaolin forms an important constituent of a number of ceramic body formulations. By definition, non-plastic kaolin’s have low plasticity and low dry strength (due mainly to their relatively coarse particle size). Kaolinitic ball clay is added to most ceramic bodies to confer both plasticity and green/dry strength. The main function of non-plastic kaolin in ceramics is to confer whiteness on the body, therefore fired (as distinct from natural) brightness is the critical property in kaolin’s intended for this application. Low iron content (~0.9%) is necessary in order to achieve fired brightness values in excess of 83% at 1180°C. The absence of iron-bearing minerals such as biotite and tourmaline are also important to prevent specking on the surface of the fired product.

As in kaolin’s intended for paper manufacture, the rheological properties of ceramic-grade kaolin’s are an important consideration. The main controls on these properties are the particle-size distribution of the clay and the presence of smectite. The overall effect of increasing smectite concentration on the rheological behavior of ceramic grade kaolin may be summarized as follows *in the Table*:

Particle-size distribution and the presence of small amounts of smectite also influence properties such as modulus of rupture (strength) and shrinkage of the clay. Dry strength of the kaolin component is important in bone china and some porcelain bodies where ball clay is absent. These bodies utilize fine grades of kaolin which exhibit a higher dry strength. Coarser grades are used in sanitary ware bodies where a considerable thickness of clay must dewater quickly into the plaster mould. The high SiO_2, Al_2O_3, and LOI in kaolin make it more favorable with the standards for ceramics and refractory and moderately suitable for Paper (coating and filler) and paint. Kaolin used in the ceramic industry requires high Al_2O_3 content ranging from 20 to 35 wt. %(Bloodworth et al. n.d.; Kogel 2014a; Prasad, Reid, and Murray 1991; G. Abdykirova et al 2022).

Paint, rubber and plastics

The paint, rubber, and plastics industries use calcined and natural kaolins as useful extenders and fillers. Clay is used to improve the end product's qualities and lower its cost. Features like kaolin's size, shape, and surface qualities are crucial for various uses. Additionally, the mineral can react with specific organic compounds to produce surface layers that are compatible with the polymer. As a result, the product's mechanical qualities increase.

Paint

Kaolin is commonly employed in water-based paints and undercoats due to its high oil absorption capacity. It not only enhances opacity or hiding power, thereby reducing the overall cost of the paint, but also improves the optical properties of the product. The lamellar structure, fine particle size, excellent dispersibility, and the presence of electrostatic charges on the edges (positive) and faces (negative) of kaolinite particles contribute additional advantageous rheological properties to the paint. These characteristics enable kaolin to function as a suspension aid, preventing pigment from settling within the container. The use of calcined clays in paint formulations is on the rise, as this material can partially substitute the more expensive TiO2 pigment due to its superior opacity and increased brightness (up to 90%). Furthermore, calcinations results in harder particles, which enhance the durability of the paint coating. The primary parameters that are controlled include brightness and particle size. The grades of kaolin used in paint are comparable to those used in filling paper applications.

Rubber

The most widely used non-black reinforcing filler in the rubber sector is kaolin. Particle shape, particle-size distribution, and surface characteristics are essential characteristics of kaolin for usage in rubber. There are two types of kaolin used in rubber: semi-reinforcing "hard" clays and non-reinforcing "soft" clays. High-quality kaolin (75–80% 2 µm) has useful reinforcing qualities. These give the product abrasion resistance and strong tensile strength. These materials' high brightness makes them suitable for usage in colored composites. Although they contribute less to reinforcement, coarser grades (20–45% <2 µm) can be employed at high loadings, which lowers costs. Certain surface areas of kaolin exceeding 10 m^2/g have quantifiable reinforcing qualities, whilst those below do not. Improved brightness and enhanced electrical resistance are two notable distinctions between calcined kaolin and natural clay. This material is most frequently used in cable insulation compositions.

Plastics

Kaolin is frequently used in PVC flooring materials, which are polymers. In the cable business, clays that are calcined at relatively low temperatures are used as fillers in PVC for insulation and sheathing. Calcined clay's high-volume resistivity makes it ideal for high-voltage insulation compounds that need a high level of electrical resistance. The standards for quality in the polymer and paper filling sectors are similar.

Other uses

With the notable exception of pharmaceutical items, kaolin has a wide range of other applications where quality criteria are typically less strict. The mineral is utilized as a low iron, low alkali source of alumina in the production of glass fiber, as well as an anti-caking agent in the production of fertilizer prills, a pesticide carrier, and a source of alumina without iron in the manufacturing of white cement. The total world production of kaolin in 2007was estimated 39 million tons per year as distributed in Table (2)

Table 2. The total world production of kaolin per year (USGS)(Al Ani and Sarapää 2008).

Paper Filling and Coating	45%
Refractories	16%
Ceramics	15%
Fiberglass	6%
Cement	6%
Rubber and Plastics	5%
Paint	3%
Catalyst	2%
Others	2%

Source *Roskill Information Services, Ltd. A The Economics of Kaolin@ 10th Edition (Al Ani and Sarapää 2008)

CHAPTER THREE

3. EXPERIMENTAL METHODOLOGY

3.1. Materials and Methods

3.1.1. Sample Material and Chemicals.

In this project, the studied local raw kaolin was collected from the local area Alemtena kaolin deposits, located, Bora (OR) Woreda in east shoa Zone in the state of the Oromia Region, Ethiopia. The sample was collected by the Mineral Industry Development Institute (MIDI) researchers for further investigation in order to substitute the imported industrial raw material by using our own resources. Laboratory grade chemicals sodium hexametaphosphate was used as dispersant reagents and oxalic acid was used as leaching chemicals. Distilled water was used in the slurry formation and to wash lab Equipment and Apparatus to avoid cross-contamination among different samples or from other sources for this project study.

3.1.2. Equipment and Apparatus

According to literatures reported by different researchers, kaolin beneficiation processes in the laboratory uses different size reduction equipment's, screens, particle size fractionations, attrition cells, driers, measuring instruments and analytical apparatus etc.(Bloodworth et al. n.d.; Kogel 2014a; Prasad, Reid, and Murray 1991; G. Abdykirova et al 2022). Here in my study, laboratory scale mechanical size reduction equipment's such as jaw crusher, ball mill, cut mill, mortar and pestle was used to reduce the size of the sample, standard sieves (for size fractionation), classical thermal equipment's (Hot air oven and muffle furnace) were used to prepare sample for further beneficiation and characterization. Also, analytical equipment and glassware such as analytical mass balance, Attrition cell, measuring cylinder and water bath and condenser were Equipment's used to process kaolin mineral ore in laboratory frequently used for batch beneficiation experiments by referring (Bloodworth et al. n.d.; Kogel 2014a; Prasad, Reid, and Murray 1991; G. Abdykirova et al 2022).

3.2. Methods

3.2.1. Mineral processing methods

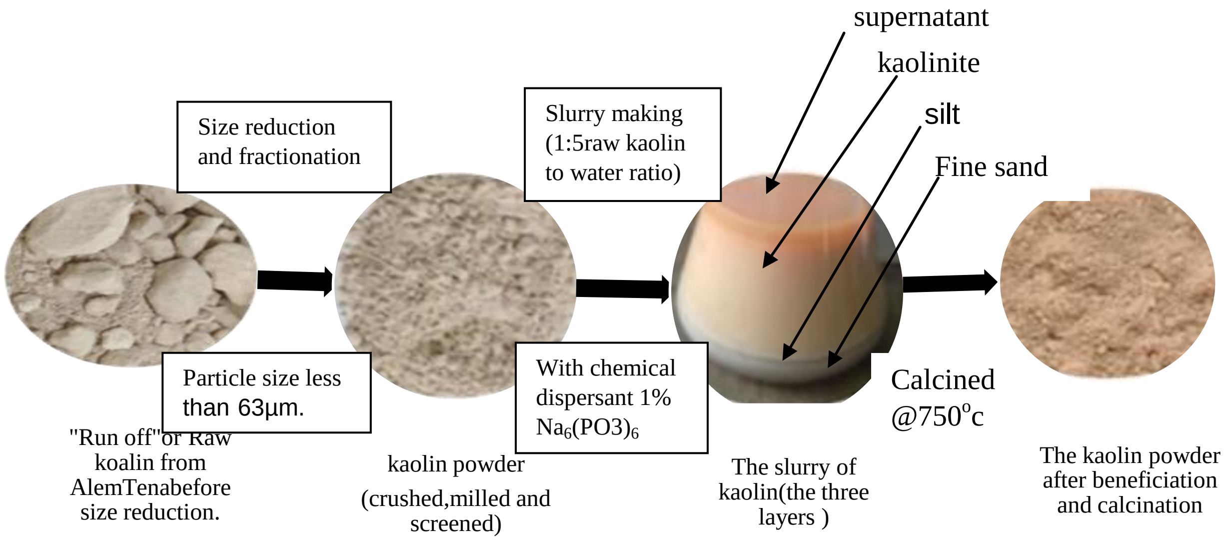
Crude or "run-of-mine" or raw kaolin which consists of valuable minerals (kaolinite) and gangue (impurities) taken from Alemtena was prepared for processing. In the discipline of Mineral engineering, the term Mineral processing, in other words known as ore dressing, mineral dressing or milling follows mining and prepares the ore for extraction of the valuable minerals and produces a commercial end product (Wills and Napier-Munn 2015). In addition to regulating the size of the ore, it was also the process of physically separating the grains of valuable minerals from the gangue minerals, to produce an enriched portion, or concentrate, containing most of the valuable minerals, and a discard, or tailing, containing predominantly the gangue minerals. The two fundamental operations in mineral processing are liberation, of the valuable minerals from their waste gangue minerals and separation of these values from the gangue which is known as concentration (Wills and Napier-Munn 2015).

Liberation of the valuable minerals from the gangue was accomplished by comminution, which involves crushing, grinding, and milling to such a particle size that the product is a mixture of relatively clean particles of mineral and gangue. In order to produce clean concentrates with little contamination with gangue minerals, it was necessary to grind and milled the ore finely enough to liberate the associated metals (Wills and Napier-Munn 2015).

Concentration valuable minerals: The object of mineral processing, regardless of the methods used, is always the same, i.e. to separate the minerals into two or more products with the values in the concentrates, the gangue in the tailings, and the "locked" particles in the middling. Such separations are, of course, never perfect, so that much of the middling’s produced are, in fact, misplaced particles, i.e. those particles which ideally should have reported to the concentrate or the tailings. This is often particularly serious when treating ultra-fine particles, where the efficiency of separation is usually low. In such cases, fine liberated valuable mineral particles often report in the middling and tailings. The technology for treating fine-sized minerals is, as yet, poorly developed, and, in some cases, very large amounts of fines are discarded (Wills and Napier-Munn 2015).

3.2.2. Experimental design

This lab experiment was done in the laboratory of Addis Ababa institute of technology in the chemical engineering department. “Run-off-mine" or raw kaolin ore contains valuable minerals(kaolinite) and gangue (impurities) is Collected from Alemtena was beneficiated to improve its aluminum oxide (Al_2O_3) and silicon oxide (SiO_2) by removing mineral impurities (feldspar, quartz, mica, muscovite, iron oxide, titanium oxide, and clay) with a sequential beneficiation (Wet-beneficiation, Chemical Leaching and Thermal treatment) process. According to the fineness of its particle size mostly <4µm in the literature, Kaolinite is generally concentrated in the fine fraction; Therefore, beneficiation can be achieved by simple size separation. Some researcher reports that, A cut at between 10 and 20 µm removes all of the quartz and most of the mica and for many years this was the only form of beneficiation used by the industry (Bloodworth et al. n.d.; Kogel 2014a; Prasad, Reid, and Murray 1991;G. Abdykirova et al 2022).In Both laboratory beneficiation and commercial processing are essentially size fractionation processes which utilize the tendency of kaolinite to concentrate in the fine fraction. 'Wet' processing is generally preferred since this method is more efficient in concentrating kaolinite and is much more commonly used commercially as many researchers proved. Wet processing of kaolin began with the dispersion of the kaolin powder in water in an attrition cell after size reduction and sieved below 63µm. This was generally carried out using a heavy-duty laboratory stirrer rotating at a rate of 1000 rpm for 15 minutes. This method has been used effectively dispersed the kaolin powders in water and liberating kaolinite to suspension. This was followed by wet screening through sieves ranging from 500-63 µm to produce a kaolinite-rich <63 µm suspension.



A) Calcination process

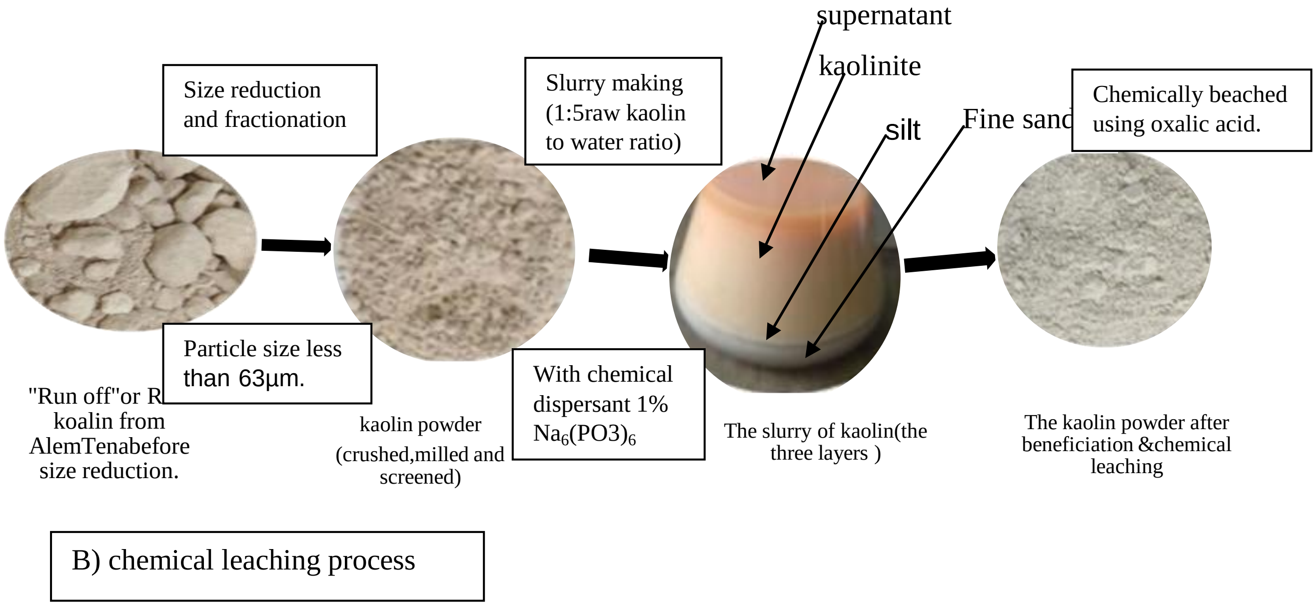


Figure 14. *Beneficiation process of Alemtena kaolin clay*

Size Reduction and screening

Some of the coarse impurities were removed from raw kaolin by physical separation of dirt and before comminution (crushing, milling), some of the coarse impurities were removed from raw kaolin by physical separation of dirt, then followed by size reduction through comminution techniques. First it was crushed using laboratory scale jaw crusher into controllable particle size followed ball milling and cut milling into smaller particle size less than 500µm. Then it was screened to produce fine powder using Standard sieves less than 63µm. The fine kaolin powder less than 63µm, was used for batch experiment and characterization as a ‘‘raw kaolin sample’’ without further treatment.

Wet-Beneficiation Procedure

After mechanical size reduction of kaolin powder with the particle size of 63µm, it was subjected to water wash or wet treatment (wet beneficiation) using distilled water in the cylindrical shape glassware of 1L capacity, the raw kaolin was suspended in distilled water (1:5 kaolin to water ratio) in the presence of a chemical dispersant (1% of sodium hexametaphosphate, $Na_6(PO_3)_6$) and then stirred using laboratory stirrer at 1000 rpm for 15 min and then allowed to settle for

48h. After 48 h sedimentation time, the dispersed clay was settled by gravity and fractionated into three layers: The first layer was kaolin clay (top); The second layer was silt (middle), and the third layer was fine sand and mica (bottom). The water was decanted and the kaolin clay was separated from residue and dried in an oven at 105°C for 24 h to obtain the dried beneficiated cake-like product (hydrous kaolin) was ground with mortar and pestle, milled, and sieved for less than 63 μm and prepared for further treatment (Chemical bleaching and Thermal treatment).(Bloodworth et al. n.d.; Kogel 2014a; Prasad, Reid, and Murray 1991; G. Abdykirova et al 2022).

Chemical bleaching

Leaching of hydrous kaolin by oxalic acid was carried out in a 500 ml round bottom flask placed in a water bath at a temperature of 90^oC. The hydrous kaolin material from wet beneficiated and dried was mixed with the oxalic acid solution at a concentration of 2.0 M acid solution in the ratio of 1:10 solid to solution by shaking and stirring manually for 10 minutes. The flask contained acid to kaolin mixed solution was placed in a water bath at a temperature of 90^oC and it was continuously stirred manually for two hours. After two hours get out round bottom flask contained Leached acid to kaolin solution from water bath and allowed to cooled down for 30 minutes. There was crated a clear layer between the leached kaolin at the bottom and acid water solution at the top. Then the leached kaolin product was filtered and repeatedly washed with distilled water to remove any unspent oxalic acid and dried at 80°C for 24 finally this was powdered with mortar and pestle then used this powdered kaolin for further analytical characterization by symbolized it as a ‘‘bleached kaolin sample (AK)’ ’.Oxalic acid solution is the best iron leaching reagent because of its acid strength, good complexing characteristics, and high reducing and bleaching power over those of other organic acids leachant (malonic, citric, and ascorbic acid). Due to the relatively low cost, availability, and very good potential for industrial applications, oxalic acid was chosen as a leachant for the leaching experiments in this work (Kogel 2014b; Prasad, Reid, and Murray 1991).

Figure 15*. Chemically bleached kaolin's intended for high-value applications.*

Thermal treatment

Mechanically size reduced (63 μm), and wet beneficiated and dried kaolin powder, was used for thermal activation or thermal treatment in other word "calcinations" to get Metakaolin. Metakaolin can be produced with a range of calcinations temperatures depending on the age, and formation of kaolin clay. Commonly, the dehydroxylation process can occur from 550 ^{0}C to 850 ^{0}C to produce disordered Metakaolin. The wide range of calcinations is due to a complex amorphous structure that can maintain because of the heaping of the nature of hexagonal layers. Dehydroxylation occurs up to 750 ^{0}C by referring the literatures (Bloodworth et al. n.d.; Kogel 2014a; Prasad, Reid, and Murray 1991; G. Abdykirova et al 2022). Thus, beneficiated Hydrous powder (63 μm) was calcined at 750 ^{0}C for 3 h using Muffle Furnace and used this powdered Metakaolin for further analytical characterization by symbolized it as a ‘‘calcined kaolin sample (CK)’’.

CHAPTER FOUR

4. RESULT AND DISCUSSION

Beneficiation is necessary for practically all commercial kaolin's to yield a product that can be sold. The kind of raw material, the requirements of the industries that use it, the amount of capital available, and regional circumstances (such as water availability) all influence the kind and quantity of processing that is needed.(Bloodworth et al. n.d.).Here why need beneficiation process of raw kaolin is that currently, kaolin-consuming industries use materials with maximum content of kaolinite minerals and minimum content of all other minerals (quartz, potassium feldspar, mica, minerals of iron and titanium oxides)(Gezahegn and Getaneh 2020). Moreover, each manufacturing industries have its own requirements for the quality of beneficiated kaolin. As almost all researchers agree, Wet beneficiation is more widely used methods than dry beneficiation methods. There are many wet beneficiation methods starting from grinding to gravity beneficiation in hydrocyclones and centrifuges used at different deposits all over the world. The wet beneficiation technology for kaolin raw materials refers to the classification process for kaolinite and quartz grains by size, where highly dispersed kaolinite grains are separated from the larger grains of other minerals. When kaolin is processed, hydrocyclones are the preferred devices for selective separation of fine particles (kaolin) and coarse particles (sand) but here in my project I used Hydraulic classification (wet gravity concentration) is based on different velocities of falling particles in the liquid stream due to unavailability of hydrocyclones. In this regard, most of the extracted natural kaolin clays was beneficiated (removal of sand and silty particles), and concentrate with high kaolinite minerals content was obtained. The purpose of kaolin raw materials beneficiation process is to increase the content of valuable clay rocks (kaolinite, halloysite, diquite) and reduce the amount of Gange (quartz, iron and other ore) minerals Which enables to have Bright and white kaolin raw materials for manufacturing industries. Brightness and whiteness are also important quality measurement properties of kaolin clay. These two terms are different properties. Brightness is the measurement of percent reflectance compared to a standard of smoked magnesium oxide, which is 100%, at a wavelength of 457 mill microns. Kaolin's for the paper industry range from 80 to 90 brightness with filler grades generally ranging from 80 to 85 and coating grades from 85 to 90. Whiteness, on the other hand, is the color as seen by the eye. This value can be quantified by taking reflectivity measurements at 400 and 700 mill microns. The smaller the difference in these values the whiter the product (Murray 1980a).As visually observed, there was colour changes between the three samples (raw, beneficiated acid leached and beneficiated & calcined) kaolin’s which is due to the amount and types of impurities present in each sample. Simply by visually observe the colour changes using our naked eye and by comparing their colour difference we can guesses how much this whiteness becomes. ‘’.

Dispersion and flocculation.

Kaolinite particles display opposing charges on the edges and surfaces of their plates, leading to mutual attraction and the formation of flocs. When kaolin is stirred and combined with water, the resulting slurry typically undergoes flocculation, causing the particles to aggregate into flocs. To effectively separate kaolinite from mineral contaminants like quartz and mica, and to classify it into fine, medium, and coarse grades, the slurry must contain individual mineral particles that are distinct and suspended in water. The introduction of dispersing agents, which ionize and adhere to the charged kaolin plates, results in similarly charged particles that repel one another, thereby producing a highly fluid and well-dispersed slurry suitable for efficient processing. Commonly used dispersing agents include sodium polyphosphates and silicates (Murray, 1980a) In this instance, sodium poly hexametaphosphate powder was employed as a dispersing agent. The advancement of methods for dispersing and deflocculating kaolin slurries has facilitated the use of more efficient processing techniques. The variation in fluidity of the dispersed slurry at the same solids concentration is significant and is associated with a crucial physical property known as viscosity (Murray,1980). After being dispersed, the kaolin slurry can undergo flocculation through the addition of chemicals such as sulfuric acid, aluminum sulfate (alum), or calcium hydroxide.

Chemically bleached kaolin’s

Brightness (or whiteness), is one of the critical importance qualities in the economic evaluation of kaolin products. Natural brightness is crucial in assessment of kaolin for the paper and filler markets, where as fired colour is important in kaolin’s for use in ceramics (Bloodworth et al. n.d.). Researchers and industrial experts confirm that, chemical bleaching is a standard industrial used to improve the brightness of kaolin’s intended for high-value applications. The brightness technique of a clay product can be improved by chemical treatment (see figure 13). Bleaching was carried out by the addition of a strong reducing agent (generally oxalic acid) which reduces ferric iron coating the surfaces of the kaolinite particles to the ferrous form. The process whitens the clay and allows a small proportion of the total iron to be removed in solution. Figure 13 show the effect of this treatment on the brightness of kaolin from Alemtena.

The color of chemically treated sample is expressed as a wavelength against reflected intensity in the reflectance spectrophotometer which can be used in variety of ways. The overall reflectivity of a pure white sample remains constant across a range of wavelengths. But here it is not tested by spectrophotometer Ruther than observing the physical color change through our naked eye.

The raw kaolin clay appears in slightly white with a brownish red color as shown in the figure14. This is due to impurity present in the raw kaolin such as iron oxide, titaniferous, and pyrite /ilmenite. Having the less whiteness relative to the chemically leached. The beneficiated and acid leached kaolin is essentially white, having the highest whiteness compared to the other two samples. A similar observation was obtained by (Zewdie et al. 2021). After the beneficiated and calcined process, more brownish red color pigment was appeared in the sample here (see figure (b)). This is due to the presence of iron-stained titania. As shown in the figure14(c) the acid leached sample also not enough white. This observation indicates that oxalic acid leaching has not completely removed the titanium dioxide (TiO_2) content.

Figure 16. *Powder Samples of (a) raw kaolin ;(b) wet beneficiated and calcined kaolin; (d) wet beneficiated and acid leached.*

The Figure14 shows the color changes of the kaolin before and after beneficiation; In the raw kaolin sample, a beige coloration is evident that indicates darker colour to the white kaolin, the beneficiated and acid leached kaolin is essentially white (high brightness) discolor enhancement indicates the removal of discoloration of titaniferous impurities, while imparts color to beneficiated and calcined kaolin (low brightness due to iron oxide impurity).In my project the following equipment was used for the studies of kaolin: X-ray diffractometer (XRD), X-ray fluorescent spectrometer (XRF), Spectrometer (FTIR).

4.1. Chemical Composition Analysis (XRF)

The chemical composition of raw, beneficiated and acid leached and also beneficiated and calcined kaolin's samples was determined by using x-ray fluorescence (XRF), as sown in the Table3. Based on the XRF result, the main (major) composition of Alemtena kaolin was obtained as SiO_2 and Al_2O_3 those covers more than 87% also other some elements expressed in the form of their oxides like K_2O, Na_2O, Fe_2O_3, TiO_2, CaO, MnO, and MgO with its LOI values for raw, beneficiated & acid leached and beneficiated & calcined kaolin. As shown in the table, SiO_2 and Al_2O_3 were the greatest part of kaolin and the result confirms that kaolin is predominantly composed of kaolinite ($Al_2Si_2O_5(OH)_4$).

Table3: Chemical composition in wt. % of raw kaolin (RK), Wet beneficiated and Acid leached kaolin (AK), and Wet beneficiated and calcined kaolin (CK) (XRF)

Che. Com (%)	Al_2O_3	SiO_2	CaO	MgO	Fe_2O_3	Na_2O	K_2O	MnO	TiO_2	P_2O_5	LOI
RK	25.747	64.135	<0.01	<0.01	4.838	<0.01	<0.01	<0.01	3.25	0.10	8.22
CK	32.313	55.135	<0.01	<0.01	6.605	<0.01	<0.01	<0.01	2.45	0.15	13.96
AK	33.662	57.285	<0.01	<0.01	3.107	<0.01	<0.01	<0.01	3.49	0.02	14.55

The XRF characterization result as shown in the table 3 indicated that The Chemical composition of raw, beneficiated acid leached and beneficiated & calcined kaolin's are varied. This variation of Chemical composition becomes because of the consecutive beneficiation process. The chemical composition of SiO_2 varied between 64.135, 55.135 and 57.285 and whereas the chemical composition of Al_2O_3 varied between 25.747, 32.313 and 33.662, RK, CK and AK respectively. The major oxide SiO_2/Al_2O_3 ratio are 1.7063, 1.7018 and 1.6424 for RK, AK and CK respectively which are higher than the ratio of ideal kaolinite, 1.18. According to the XRF analysis, the high SiO_2, Al_2O_3, and LOI in the Alemtena raw kaolin make it more favorable with the standards for ceramics and refractory and moderately suitable for Paper (coating and filler) and paint. Kaolin used in the ceramic industry requires high Al_2O_3 content ranging from 20 to 35 wt-%(Bloodworth et al. n.d.). Here The XRF analysis result indicated that the Al_2O_3 content ranging from 25.747to 33.662 (RK to AK). So, the concentrations of the studied kaolin fulfill the specification for ceramic, agriculture, pharmaceutical, textile, brick clay, refractory brick, paper coating, and filler industries similar results provided (Gezahegn and Getaneh 2020). On the other hand, according to(Bloodworth et al. n.d.)the silica SiO_2 content of this raw material should be less than 50 wt-%, Fe_2O_3 < 1 wt-%, CaO (1–2 wt-%), MgO (0.7–1 wt-%), and K_2O (3–4 wt-%). Here also Alemtena kaolin is ranges from 55.135to 64.135 (CK to RK) in which the beneficiated was less than 50 wt-%. CaO, MgO, and K_2O are (<0.01 wt-%). but the amount of Fe2O3 (3.107 to 6.605) and TiO_2 (3.25 to 3.49 wt-%) are greater than 1wt-% which indicates still it needs further beneficiation for some specific applications such as paper filler and paper coating applications.

The existence of low titanium and alkali concentration makes the deposit relatively good in quality, but the concentration of iron is relatively high, which could limit its applications for different industries so it needs further additional beneficiations. This XRF analysis result indicated that the composition of SiO_2 and Al_2O_3 varying between 49.605 and 64.135%, and 30.202 and 33.662%, respectively. But the Theoretical of SiO_2 and Al_2O_3 are 46.3 and 39.8 respectively. On the other hand, the loss on ignition was varied between 8.22 and 10.87%.

4.2. X-Ray Diffraction (XRD) Analysis

The primary aim of mineralogical analysis of potential kaolin’s is to confirm the presence of kaolinite. Effective mineralogical analysis can be carried out by X-ray diffraction (XRD). The XRD patterns determine the qualitative and mineralogical phase composition of the materials (Ayalew and Demir 2023). In this project, The XRD mineralogical analysis of potential kaolin’s was done in the laboratory of organic chemistry in Addis Ababa university at 4 kilo campus. The raw, beneficiated & acid leached and beneficiated & calcined kaolin clay indicates well-defined diffraction at 2-theta values of 11.42^0,12.4^0,20.38^0,21.5^0,24.94^0,25.14^0,35.24^0,38.54^0 and 55.18^0 these major peaks are characteristically matching to the kaolinite (Ayalew and Demir 2023). Whereas, other peaks are equivalent to the 2-theta values of 21.5°, 26.94°, and 45° typically corresponding to quartz. The obtained XRD showed that the beneficiated kaolin material is rich in kaolinite and quartz. This is an endorsement that the level of quartz in the kaolin was not entirely removed during the beneficiation process. Thus, the existence of quartz in the beneficiated kaolin results in an increase in the content of silicon dioxide (SiO_2) (Ayalew and Demir 2023).

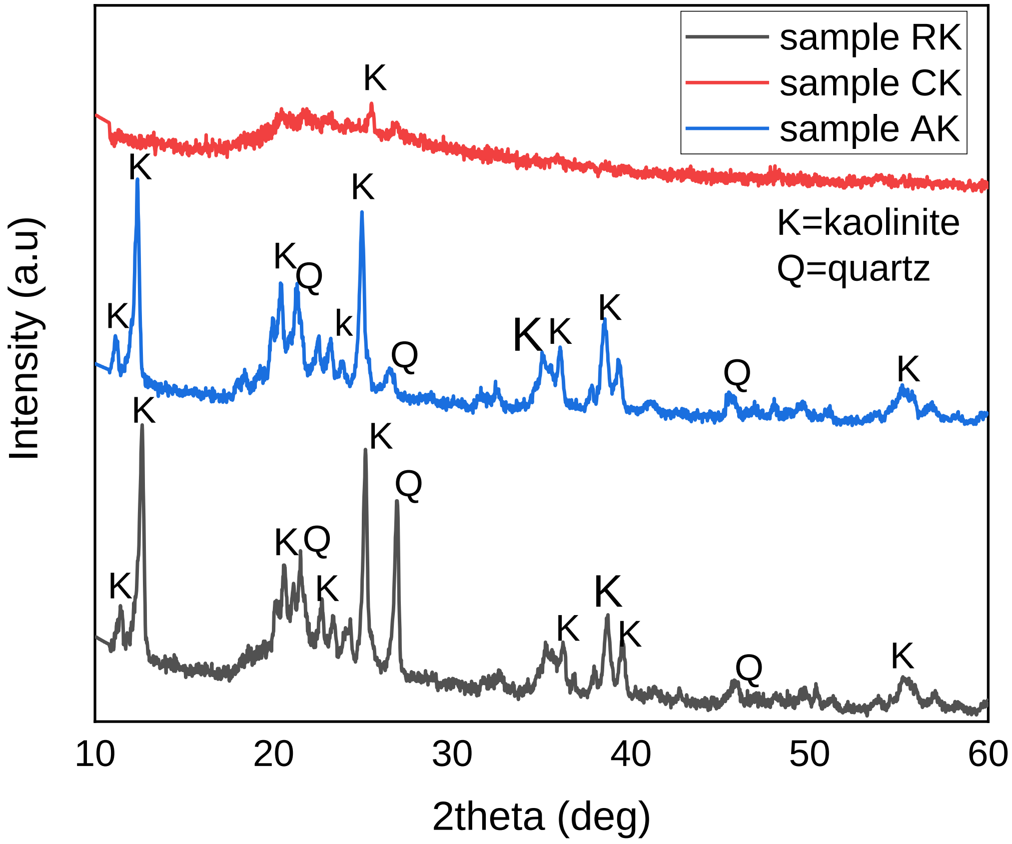


Figure 17.*X-ray diffraction (XRD) patterns of (RK) raw kaolin; (AK) beneficiated and acid leached kaolin; (CK) beneficiated and calcined kaolin.*

4.3. FTIR Spectroscopy

The crystal structures, functional groups, and other structural flaws in the samples were all identified using FTIR. Figure 19 shows the FTIR spectra of the beneficiated, calcined, acid-leached, and raw materials. It is evident that the peaks of the acid-leached, raw, and beneficiated kaolin exhibit sharpness at those bands. Moreover, a negligible peak is seen in the calcined, acid-leached, and beneficiated kaolin. The bands at 797 cm−1 and 695 cm^{-1} were associated with Si-OH vibrations that were perpendicular. Iron (Fe^{3+}) and aluminum (Al^{3+}) cat ions were connected to OH deformation, which was responsible for a band at 914 cm^{-1}.

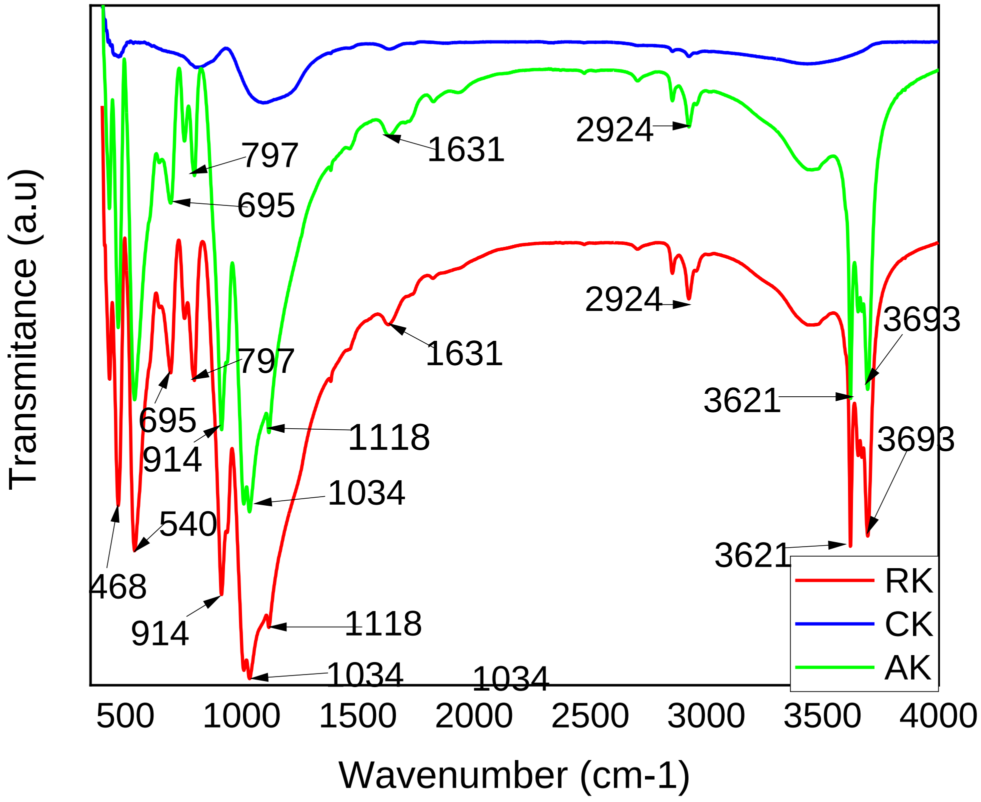


Figure 18. (FTIR) patterns of raw kaolin (RK); beneficiated and acid leached kaolin (AK); beneficiated and calcined kaolin (CK).

Bands at 1118 cm^{-1} and 1034 cm^{-1} were identified as the symmetric stretching vibrations of Si-O-Si bonds and the stretching vibrations of Si-O and/or Al-O. This demonstrates that a significant amount of silicon oxide was present in the kaolin under investigation. In comparison to the raw, beneficiated, and calcined kaolin spectra, the spectra of the acid-leached and beneficiated kaolin (figure 6(AK)) exhibit new, tiny intensity peaks around 1631 cm−1, which may be characterized as H-O-H bending modes of water.

In raw, beneficiated, and acid-leached kaolin, bands at 3621 cm−1 and 3693 cm−1 were attributed to the OH stretching of water. Because the calcination process causes the structural hydroxyl group to be lost (calcination leads to the dehydroxylation at temperatures in the range of 400 °C to 750 °C), the calcined and benefited do not contain OH− and Al-O. However, Si-O bands formed during the calcination process (figure 6 (CK)). The FTIR data demonstrates that sufficient heat treatment was used to transform kaolin into Metakaolin. The disappearance of several bands in the FTIR spectra of kaolin in the wave number range of 3600–3700 cm^{-1} indicates the development of Metakaolin.

CHAPTER FIFE

5. CONCLUSION AND RECOMMENDATION

5.1. Conclusion

As all researchers agree that kaolin clay is one of the most versatile industrial minerals which play a great roll in economic growth of the developing countries. Even if there is the variation of the quality all most, in all countries these minerals have been found. Although there are so many deposits are investigated (explored) in different regions in our country which can be processed and used as raw material for different products. The commercial values of the kaolin depend on the amount of SiO_2 and Al_2O_3 and also its brightness and witness. To have this quality it needs some processing methods. In this study, the main goal of the study was how much the quality of the local kaolin specifically (Alemtena kaolin) was improved through consecutive beneficiation whether it can be substitute or not the imported raw materials for different manufacturing industries. Here, I tried to increase the amount of SiO_2 and Al_2O_3 through wet beneficiation and also enhance the color through thermal and chemical treatment to improve the commercial values of kaolin for local manufacturing industries. As shown in the table from XRF results the chemical composition of SiO_2 and Al_2O_3 was increased and closet to the specification needed by ceramics, industries similar results also reported by(Wang et al. 2011).

5.2. Recommendation

Based on this study, the Wet beneficiation process of local kaolin can be used as raw material for ceramic industries. According to the results of Analytical analysis (based on the XRF results) of processed local kaolin (Alem Tena) the primary components were SiO_2 and Al_2O_3. These results showed that after some beneficiation the local kaolin can used for many industries. Even if the XRF results shows improvement of SiO_2 and Al_2O_3 but still it needs further treatment for some industries until the percentage of Fe_2O_3 and TiO_2 becomes below 1%. because the specification for paper industry the percentage of Fe_2O_3 and TiO_2 must be less than 1%. Also, further analysis such as thermal gravimetric analysis (TGA) or differential thermal gravimetric metric analysis (DTA), atomic absorption spectroscopic (AAS), SEM Observation are recommended for detailed information. Finally, this paper may serve as a reference for researchers, investors and students those interested to do their thesis or project research on clay especially kaolin clay in Ethiopia.

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