ADDIS ABABA UNIVERSITY

ADDIS ABABA INSTITUTE OF TECHNOLOGY

SCHOOL OF CHEMICAL AND BIO-ENGINEERING

Thesis Title:

“SYNTHESIS AND CHARACTERIZATION OF α-FERRIC OXIDE FROM LOCAL IRON ORE IN ETHIOPIA”

By: **DAWIT DILALLAH ADEM**

SUBMISSION DATE: 25 OCT, 2021

ADDIS ABABA, ETHIOPIA

ADDIS ABABA UNIVERSITY

SCHOOL OF GRADUATE STUDIES

ADDIS ABABA INSTITUTE OF TECHNOLOGY

SCHOOL OF CHEMICAL AND BIO ENGINEERING

“SYNTHESIS AND CHARACTERIZATION OF α-FERRIC OXIDE FROM LOCAL IRON ORE IN ETHIOPIA*”*

A final thesis Submitted to the School of Chemical and Bio Engineering, ADDIS ABABA INSTITUTE OF TECHNOLOGY in Partial Fulfillment of the Requirements for the Degree of Master of Science in Process Engineering.

By : DAWIT DILALLAH ADEM

ADDIS ABABA UNIVERSITY
ADDIS ABABA INSTITUTE OF TECHNOLOGY
SCHOOL OF CHEMICAL AND BIOENGINEERING

This is to certify that the thesis is prepared by **Dawit Dilallah**, entitled: **Synthesis and characterization of α-ferric oxide from local iron ores in Ethiopia.** and submitted in partial fulfillment of the requirements for the Degree of Master of Science in Process Engineering fulfills with the regulations of the University and meets the accepted standards with respect to originality and quality.

Signed by the Examining Committee:

Dr. Beteley T.	______________	___________
Advisor	Signature	Date
Dr. Abubeker Y.	______________	___________
Internal Examiner	Signature	Date
Dr. Shimelis K.	______________	___________
External Examiner	Signature	Date

____

School Dean/ or Graduate Programs Coordinator

DECLARATION

I declare that, this thesis for the M.Sc. Degree at Addis Ababa University, hereby submitted by me, is my original work and has not previously been submitted for any degree programs in Addis Ababa University or any other university, and that all resources of materials used in this thesis have been duly acknowledged.

Name: Dawit Dilallah

Signature: __________

Date of Submission: ____________

ACKNOWLEDGEMENTS

In the beginning, I would like to thank the almighty **God** for giving me health, strength and patience to complete this thesis successfully.

- I want to express my gratitude to my advisor Dr. Beteley T. (Assistant prof.), for his understanding and guidance through the entirety of this thesis.
- I want to wish my appreciation to the whole geological survey of Ethiopia employees, for their willingness to support.
- I wish to express my sincere gratefulness to my former teacher and colleague, Dr. Albert Selvakumar, whose encouragement, inspiration, intelligence, and hopes are critical to my accomplishments.
- My deepest thank and respect goes to my class mate Ms. Setty T. for her Honesty and help, I owe you, my gratitude.
- I extend my thankfulness to AASTU, Chemical Engineering Laboratory Staffs for their willingness support to my laboratory work.
- I need to thank Kadisco Asian paints, especially Eng. Daniel for their willingness and supportive helps.
- I also would like to recognize, AAiT, the department of Chemical and Bio Engineering for the provided great chances and their continuous support.

Last but not least, my special gratitude goes to my family members and my friends for their deepest encouragement and love to accomplish my thesis.

TABLE OF CONTENTS **PAGE**

LIST OF FIGURES

List of Figures **page**

LIST OF TABLES

List of Tables **page**

ABSTRACT

*Ethiopia has a huge deposits of iron ore and α-ferric oxide, (α-Fe_2O_3) has received great interest and extensively used in agriculture, chemical industries, paint industries, as catalysts, magnetic materials, gas sensors, lithium-ion batteries and waste water treatment plants. Therefore, this study is to synthesize α-ferric oxide from local iron ore in Ethiopia. Iron ore samples has been studied from two different regions (Sekota and Axum) and characterized in geological survey of Ethiopia laboratory with the grade of 46.56% and 65.81% of iron oxide composition found from Sekota and Axum respectively. The sample from Axum was reacted with hydrochloric acid and ammonium hydroxide by fluctuating three process variables: particle size, calcination temperature and calcination time. The effect of these different particle size (0.125mm – 2mm), calcination temperature (500 – 600 °C) and calcination time (90 – 150 minutes) towards the yield of α-ferric oxide, (α-Fe_2O_3) synthesis were investigated by using design of expert (DOE) version 12.0 software and Box-Behnken design method. Based on analysis of variance (ANOVA), the determination coefficient, R^2 obtained was 0.9878. Optimization processing condition that synthesizes highest yield of 77.103 % was at particle size (<0.125mm), calcination temperature (500 °C) and calcination time, (*126.73 *minutes). Characterization of α-ferric oxide, (α-Fe_2O_3) powder samples were investigated by means of numerous characterization methods like; X-Ray Diffractometer (XRD), Fourier Transform Infrared (FTIR) and Major and minor oxide analysis. From FTIR spectrum Iron-oxide group (Fe-O) and atmospheric carbon dioxide (CO_2) were found. The characteristic peak occurring at $2\theta = 33.4°$ indicated presence of α-Fe_2O_3 in the samples with 14 nm particle size. The synthesized particles confirmed 91.56% of Fe_2O_3 by Major and minor oxide analysis which is acceptable purity. Last of all, From the result it is conceivable to say that producing of such chemical from local raw materials can help as upbringing idea for next studies.*

ACRONOMY

AAIT	Addis Ababa Institute of Technology
AAS	Atomic Absorption Spectrophotometer
AASTU	Addis Ababa Science and Technology University
AAU	Addis Ababa University
ANOVA	Analysis of Variance
ASTMA	American Society for Testing and Materials Association
ASTU	Adama Science and Technology University
BIF	Banded Iron Formations
CFMC	Cross Flow Micro Filtration
DOE	Design of Expert
FTIR	Fourier Transform Infrared
GIF	Granular Iron Formations
ISO	International Organization for Standardization
LOI	Loss On Ignition
NOM	Non-Organic Matter
REE	Rare Earth Elements
SEM	Scanning Electron Microscope
THM	TriHaloMethanes
XRD	X-Ray Diffraction

CHAPTER ONE

1.1 Introduction

Iron oxides are commonplace compounds which are vast in nature and effectively synthesized inside the laboratory. they are found in almost all the different compartments in: atmosphere, pedosphere, biosphere, hydrosphere and lithosphere. And participate in the manifold interrelationships among these compartments as shown in Fig. 1.1

Initially, formation of Fe (III) oxides predominantly includes aerobic weathering of magmatic rocks (especially in the ground) in each terrestrial and marine environment; redistribution procedures between the numerous global booths may additionally observe. Such techniques may additionally involve mechanical shipping by way of wind/water erosion from the pedosphere into the hydrosphere or surroundings, or, greater importantly, reductive dissolution followed via migration of Fe (II) and oxidative reprecipitation in a brand-new compartment. Presently adays, metallic oxides, like iron oxide, including hematite, magnetite, and maghemite, has been drawing in expanding consideration as they utilized in an alternate electrical, optical and attractive properties for quite a long time like combination of inorganic shades, attractive capacity media, advancement of gas sensors just as electronic and optical gadgets, data stockpiling, shading imaging, magneto caloric refrigeration, bioprocessing, ferrofluid innovation and wastewater treatment adsorbents [2]. Iron ore formation and iron oxide precipitation in biota are crucial examples of redistribution. guy participates in those strategies no longer best as a dwelling organism, however also as a consumer of iron steel and Fe oxides for numerous commercial purposes. the general result of these types of processes is a continuous internet growth in Fe oxides within the worldwide system at the expense of iron in magmatic rocks[1]. Iron (III) oxide is a suitable compound for the versatile study of the polymorphism and the mutual polymorphous changes in nanoparticles. The presence of amorphous Fe_2O_3 and four of its phases (alpha, beta, gamma, and epsilon) has been founded [3].

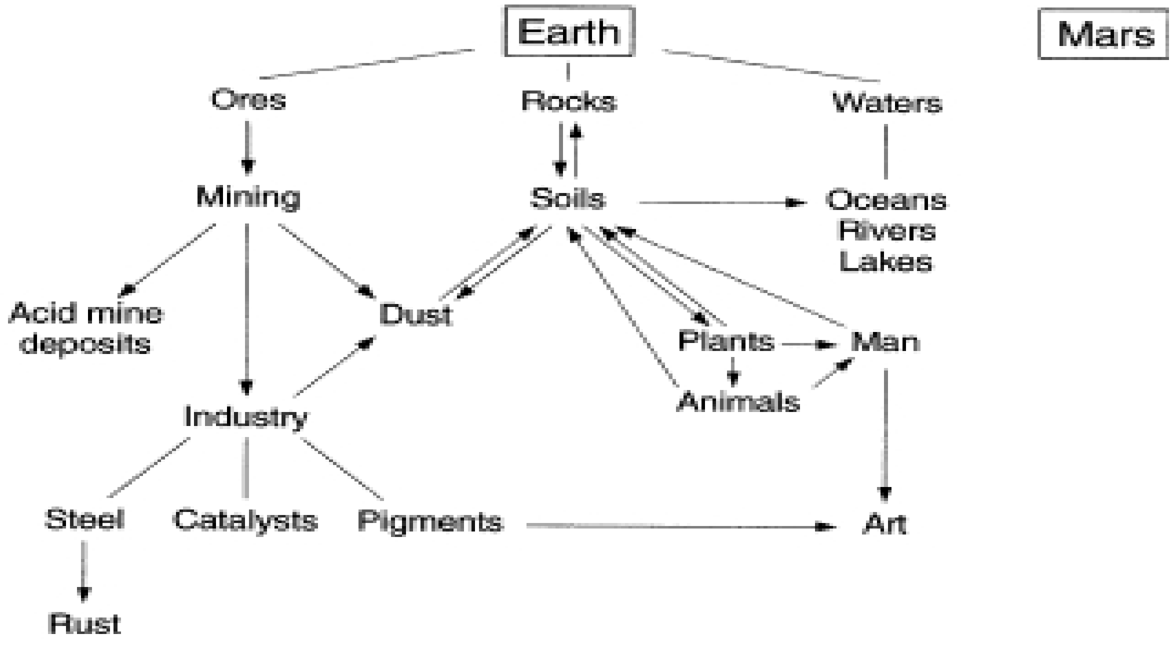


Figure 1.1: presence of iron oxide[1].

On account of its polymorphism magnetite (Fe_3O_4) is one of the most intriguing crystallographic periods of iron oxide, explicitly in its nanosized structures. It shows four stand-out glasslike polymorphs with remarkable attractive homes. The primary paperwork, α-ferric oxide (α-Fe_2O_3) and maghemite (γ- Fe_2O_3), occur in nature and the alternative oxides inside the forms are beta (β- Fe_2O_3) and epsilon (ε- Fe_2O_3) are nanometric systems which might be normally synthesized in laboratory. Hematite, α- Fe_2O_3, is the maximum known of iron oxides and the maximum common polymorph which exists in nature as mineral, going on broadly in rocks and soils. it's miles an oxide with a vulnerable antiferromagnetic or ferromagnetic property at room temperature. moreover, above 956K (Curie or Curie temperature or Neel temperature or Curie-Weiss law [2], it is paramagnetic. α-Fe_2O_3 exhibits corundum type and rhombohedral shape that's made from an ion O^{-2} particle as a close-packed hexagonal crystallographic machine and Fe^{+3} ions occupying two-thirds of the octahedral interstices in trade layers. α-ferric oxide is less complicated to synthesize than the opposite forms of oxide as it's miles the give up made from different iron oxide forms of transformation and is likewise extraordinarily stable underneath environmental situations [3].

In this study it will be discussed the leaching of iron ore with hydrochloric acid (37%), co-precipitation process using ammonia hydroxide (30%) to Synthesize α-ferric oxide, finding an optimum process parameter (particle size, calcination temperature and calcination time) for co-Precipitation reaction and also characterization of Synthesized α-ferric oxide.

Figure 1.2: α-ferric oxide (α-Fe_2O_3).

1.2 Problem Statement

Ethiopia is one in all Agricultural country, which greater than 70 percent of its populations lives depends on outmoded farming. This consequences farming is being difficult with crop sicknesses and low crop yield. The low yield is prompted either via crop diseases or deficiency of minerals. One of the minerals is iron.

Ethiopia have more than 20 paint factories within the country, these factories need α-ferric oxide as a pigment to synthesize paints. in step with the studies carried out by the Ethiopian revenues and customs authority" The countries requirement of α-ferric oxide is met through import. The past year (2012) demand for α-ferric oxide is estimated at 693 tons. The demand for the product is predicted to be 1,228 tones and 1,978 tones with in the years 2018 and 2023, respectively"[4].

Further to the irresistible application of α-ferric oxide is as feedstock Iron industry, Polishing and coating, as the most common m magnetic storage and recording media, Photocatalysis, Pharmaceutical, cosmetics, Waste water treatment, Adsorptive removal of metal ions and also allowed for use as food additives

An excellent powder of α-ferric oxide is known as "gem dealer's rouge", its miles used to put the absolute keep going shine on steel hoops and focal points, and generally as a marvel. Rouge cuts more leisurely than a couple of current shines, which incorporates cerium (IV) oxide, however is as yet utilized in optics manufacture and through gem dealers for the predominant end it could orchestrate.

Presently adays, metallic oxides, like iron oxide, including hematite, magnetite, and maghemite, has been drawing in expanding consideration as they utilized in an alternate electrical, optical and attractive properties for quite a long time like combination of inorganic shades, attractive capacity media, advancement of gas sensors just as electronic and optical gadgets, data stockpiling, shading imaging, magneto caloric refrigeration, bioprocessing, ferrofluid innovation and wastewater treatment adsorbents [2].

However, in Ethiopia in all industries α-ferric oxide requirement is met through import. Even if the main required raw materials are locally available. Therefore, finding a way for the synthesis technology of α-ferric oxide from a local iron ore will solve many problems.

1.3 Objectives

1.3.1. General objective

The General Objective of this research work is to synthesize and characterize α-ferric oxide from local iron ores in Ethiopia.

1.3.2. Specific Objectives

Specific Objectives of the research will be the following:

- To select and characterize the grade of iron ores (from AXUM and SEKOTA) to identify the ore with better oxide composition.
- To synthesize α-ferric oxide by co-precipitation method.
- To investigate the optimum process parameters (particle size, calcination temperature and calcination time) using statical optimization to get a better α-ferric oxide yield and to characterize the synthesized α-ferric oxide.

1.4 Significance of the study

It will have many advantages for the economic, social and most importantly for the knowledge creation. In educational way, the result of this research can help as upbringing idea for next studies. Since, the country have a huge deposit of iron ore this research will be an incentive idea for further studies.

1.5 Scope of the Study

This research will cover the leaching of iron ore with hydrochloric acid (37%), co-precipitation process using ammonia hydroxide (30%), Synthesis of α-ferric oxide, finding an optimum process parameter (particle size, calcination temperature and calcination time) for the reaction and also characterization of Synthesized α-ferric oxide.

CHAPTER TWO

2. REVIEW OF LITERATURE

2.1. Iron ores

Iron ores are oxide or carbonate rocks and minerals from which metal iron can be economically extracted. Iron ore is a fundamental raw material for making crude steel, pig-iron, sponge iron, steel and alloy metal. Iron ore lumps or pellets have excessive iron content, low gangue content, excellent mechanical strength and are quite simply reducible. Iron accounts for approximately 95% of all metals utilized by modern-day industrial society. The iron ore minerals are characterized by way of excessive volume of extraction, high over burden with gangs, transportation and intake[5].

Iron ores are rocks and minerals from which metal iron can be economically extracted. The ores are typically rich in iron oxides and range in color from darkish gray, shiny yellow, or deep pink to rusty red. The iron is typically discovered in the form of magnetite (Fe_3O_4), hematite (Fe_2O_3), goethite ($FeO(OH)$), limonite ($FeO(OH)\cdot n(H_2O)$), ilmenite ($FeTiO_3$), pyrite (FeS_2), pseudobrookite (Fe_2TiO_5), chamosite ($(Fe,Mg)_5Al(AlSi_3O_{10})(OH)_8$) or siderite ($FeCO_3$)[6]. Ores containing very high portions of hematite or magnetite (more than approximately 60% iron) are called "natural ore" or "direct transport ore", meaning they can be fed at once into iron-making standard furnaces. Iron metal is the natural substance used to make pig iron, which is one of the really unrefined components to make steel—98% of the mined iron mineral is utilized to make steel [7]. In 2011 the financial instances have speculated that iron ore is "extra integral to the global economic system than another commodity, besides perhaps oil". steel iron is certainly unknown at the floor of the Earth besides as iron-nickel alloys from meteorites and really rare sorts of deep mantle xenoliths. some iron meteorites are idea to have originated from accreted our bodies 1,000 km in diameter or larger[7].

2.2. Iron Formations

Iron developments ought to be essentially 15% iron in creation, similar as ironstones and all iron-rich sedimentary rocks. However, iron developments are essentially Precambrian in age which implies that they're 4600 to 590 million years of age. they're a lot more established than ironstones. It tends to be cherty, even though chert cannot be used as a manner to classify iron formations because it is a not unusual element in many varieties of rocks. they may be well banded and the banding may be anywhere from a few millimeters to tens of meters thick. The layers have very awesome banded successions that are made from iron rich layers that change with layers of chert. Iron formations are often associating with dolomite, quartz-wealthy sandstone, and black shale. They every now and then grade locally into chert or dolomite. they could have numerous particular surfaces that take after limestone. some of these surfaces are micritic, pelleted, intraclastic, peloidal, politic, pisolitic, and stromatolitic. In poor quality iron developments, there are extraordinary predominant minerals subject to the particular assortments of facies. Siderite is the dominant mineral inside the carbonate facies. Pyrite is the dominant mineral within the sulfide facies. most iron formations are deformed or metamorphosed actually because of their notably antique age, but they nonetheless maintain their particular unique chemical composition; even at excessive metamorphic grades. The higher the grade, the extra metamorphosed it is. Low grade rocks might also only be compacted at the same time as excessive grade rocks often cannot be identified. They regularly include aggregate in BIF's and GIF's. Iron formations may be classified into two groups such as: Banded iron formations (BIFs) and Granular iron formations (GIFs)[8].

2.2.1. Banded Iron Formations

Banded Iron Formations (BIFs) were initially compound muds and contain all around grew dainty cover. They can have this overlay because of the absence of burrowers in the Precambrian. BIFs show ordinary substituting layers that are wealthy in iron and chert that reach in thickness from a couple of millimeters to a couple of centimeters. The arrangement can proceed continuous for tens to many meters stratigraphically. These developments can contain sedimentary designs like cross-sheet material, evaluated bedding, load projects, swell imprints, mud breaks, and disintegration channels. In contrast with GIFs, BIFs contain a lot bigger range of iron minerals, have more diminished facies, and are more bountiful. BIFs are divided into type categories based on the characteristics related to the nature of their formation and unique physical and chemical properties. Some categories of BIFs are the Rapitan type, the Algoma type, and the Superior type.

2.2.1.1. Rapitan Type

Rapitan kinds are associated with the glaciogenic sequences of the Archean and Early Proterozoic. the type is exclusive as the hydrothermal-input has significantly less impact on this formation's rare earth elements (REE) chemistry than different formations at some point of this term.

2.2.1.2. Algoma Type

Algoma types are tiny lentiform iron deposits which could be found in volcanic rocks and turbidites. Iron content material on this magnificence type hardly ever exceeds 1010 tons. They thickness could be from 10-99 meters. Island arc/back arc basins and intracratonic rift zones are the main deposition of Algoma type.

2.2.1.3. Superior Type

Superior kinds are big, thick, giant iron deposits throughout strong shelves and in broad basins. total iron content on this magnificence type exceeds 1013 tons. they are able to make bigger to over 105 km^2 Deposition happens in extraordinarily shallow marine conditions under transgressing seas.

2.2.2. Granular Iron Formations

Granular iron formations (GIFs) have been in the beginning properly-taken care of chemical sands. They lack even, non-stop bedding that takes the form of discontinuous layers. Discontinuous layers probable constitutes bedforms that were generated through storm waves and currents. Any layers which can be thicker than some meters and are uninterrupted, are uncommon for GIFs. They comprise sand-sized clasts and a finer grained matrix, and commonly belong to the oxide or silicate mineral facies[6].

2.3. Types of iron ore

There are four foremost kinds of iron ore deposits available presently, based on the geological arrangement and mineralogy pattern of the mineral deposits. those are magnetite, titanomagnetite, hematite and pisolitic iron ore deposits.

A. **Magnetite** is a rock mineral and one of the primary iron ores, with the chemical components Fe_3O_4. it's far one of the oxides of iron, and is ferrimagnetic; it's far attracted to a magnet and may be magnetized to grow to be a permanent magnet itself. it's miles the maximum magnetic of all the evidently-occurring minerals on this planet.

B. **Titanomagnetite** is a mineral containing oxides of titanium and iron, with the formulation Fe^{2+} (Fe^{3+}, Ti_2O_4). it's also known as titaniferous magnetite. it's miles a part of the spinel institution of minerals. The Curie temperature for titanomagnetite has been discovered to have a extensive variety of 200 to 580°C.

C. **Hematite**, also spelled as haematite, is a commonplace iron oxide with a system of Fe_2O_3 and is great in rocks and soils. Hematite crystals belong to the rhombohedral lattice machine that's specific the alpha polymorph of Fe_2O_3. It has the identical crystal shape as corundum.

D. **Pisolite** is a sedimentary rock made from pisoids, which might be concretionary grains – typically of calcium carbonate which resemble ooids, however are more than 2 mm in diameter. these grains are about spherical and feature concentric layers reaching 10 mm in diameter. magnetite has been found to have a wide range of 200 to 580°C.

The fundamental rock styles of steel iron are massive hematite, pisolitic goethite/limonite, which provide a 'high-grade' ore. Banded metasedimentary ironstone, magnetite-rich metasomatite, rocks rich both in siderite or chamosite offer a 'low-grade' ore.

A. **High -grade ore**

Presently most of the iron ore mined in the world comes from massive deposits of massive hematite rock formed through the in-situ enrichment, most typically a banded iron formation (BIF). high-grade ore usually has a cutoff grade of 60% Fe. traditionally it has provided a right away feed to smelters either as a raw lump or fines, also in a processed shape along with sinter or pellets.

B. **Low-grade ore**

Low-grade ore is a time period implemented to iron-wealthy rocks with cut-off grades in the variety of 25–30% Fe. It turned into the main supply of iron ore for plenty centuries of the arena's early history of production of iron. for the reason that 1950's North the United States important supply has been low grade ore. The dominant monetary iron mineral in low-grade ore is magnetite.

2.4. Availability /Occurrence of Iron Ore in Ethiopia

Sufficient knowledge about available iron ore and other input materials in the country enables to put strategic perspectives on alternatives raw material provisions and selecting appropriate process technologies for upstream processes. Survey of indigenously available iron ore indicate limited exploration and characterization effort to generate geoscience data, especially before two decades, while there is no effort in recent years. Numerous iron deposit and occurrence documented in different parts of the country. In Ethiopia there are about three different types of iron ore deposits: it includes magmatic iron of Precambrian era from Melka Arba and Bikilal areas, banded iron formation (BIF type) of Precambrian era from Koree, Gordoma, Chago areas, and lateritic (also gossan related) iron deposits (residual type) from Melka Sedi, Garo, Gato, Billa, Gambo, and Gammalucho areas. Low-to-High grade ore deposit exist in the western Ethiopia forming a continuous zone, in Akobo-Tulu Dimitu and Assosa Gisien belt, Metti-Nejo and Assosa Gesine. Tsoli_Bildegule, Dalati, Afoda and Gidami; other minor iron deposit exists as lenticular and discontinuous bodies within central zone [29].

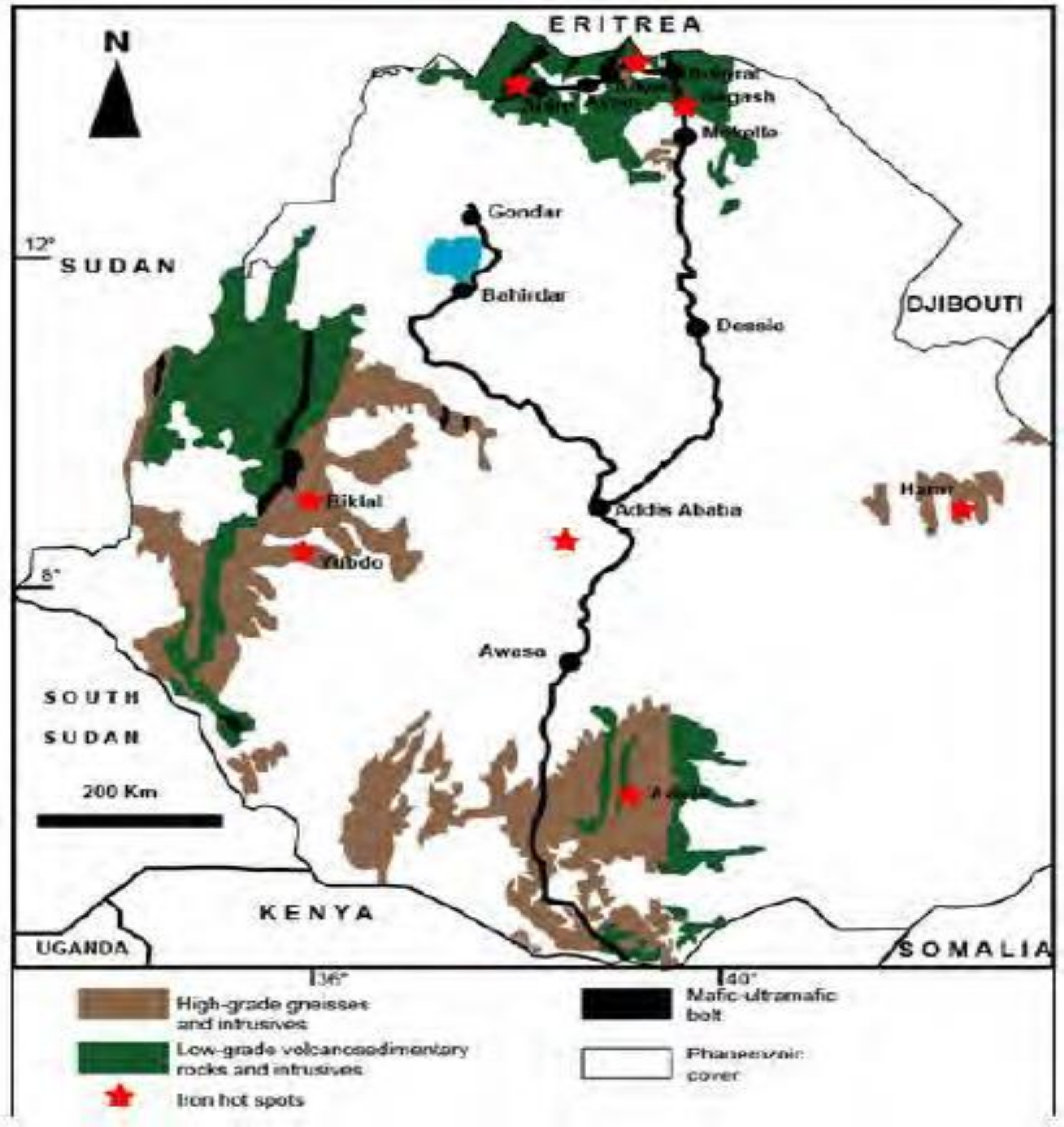


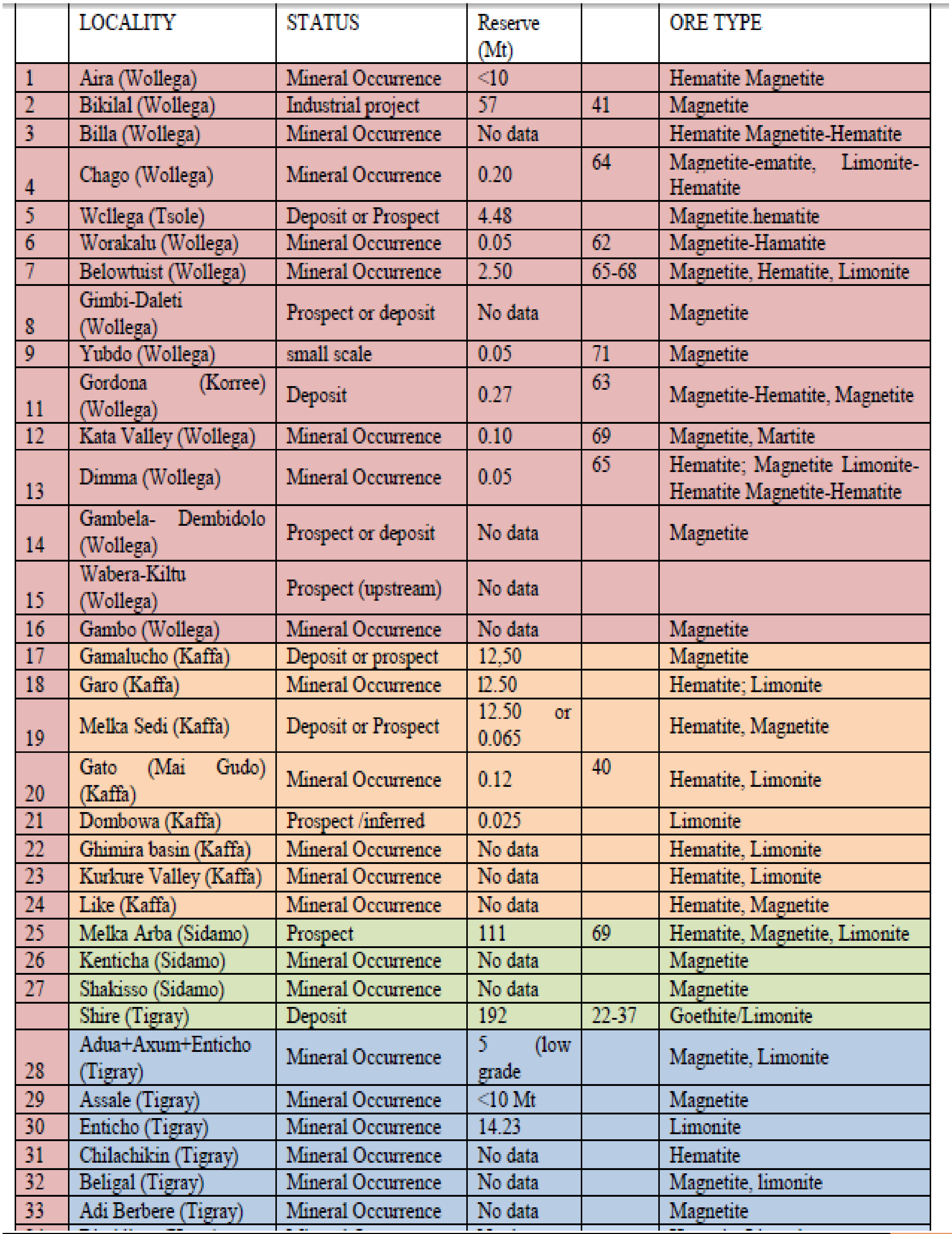
Figure 2.1: depicts location map of iron ore occurrences[5].

2.5. Iron Ore Characterization

Maximum iron incidence and deposit sorts, size, form and other ore traits aren't sufficiently explored, which constraints viability analysis for better choice in funding. The occurrences may be sub grouped into medium-large deposit and small scale. Ethiopian iron ore has incredibly low iron content material. The deposit of Shire, Bikilal, Melka Arba and little place in Kaffa are notably studied. the whole acknowledged iron ore inside the United States aggregates to approximately 350mt.

According to prefeasibility take a look at carried out on Bikilal iron ore by Boliden Contech AB of Sweden in 1995, the entire ore reserve is expected to be 57.8million tons. The ore kinds are: I) Ilmeno-magantite (fundamental rocks), II) Apataite-ileminite and III) Limonite type, elongated for about 1-1.5 Km wide and 15Km length. similarly, to Bikilal, there are different iron ore places within the location of Wollega quarter, which offers an opportunity to make the most them in a centralized plant with exceptionally less transport effort and cost. The Bikilal phosphate capability, that is 127Mt of apatite with 21.8% overall iron, appears secondary derived deposit of titano-ferrous iron ore. moreover, similarly exploration may additionally monitor greater useful resource location at the time of the Bikilal studies, the feasibility was not proved. Bikilal ore has approximately 41% Fe content. this is close to the minimal iron content material of 40-50% for use in blast furnace iron manufacturing. China ‘s iron ore has handiest 30% iron content material however China exploits this low-grade ore and import high grade ore for blending. See Table3 for iron ore incidence, type, place and status in Ethiopia. ability deposits for iron making inclusive of coal, limestone/dolomite and others are located in lots of regions at approximately overall amount of 700M[5].

Table 2.1: Iron ore occurrences in Ethiopia [5].



	LOCALITY	STATUS	Reserve (Mt)		ORE TYPE
1	Aira (Wollega)	Mineral Occurrence	<10		Hematite Magnetite
2	Bikilal (Wollega)	Industrial project	57	41	Magnetite
3	Billa (Wollega)	Mineral Occurrence	No data		Hematite Magnetite-Hematite
4	Chago (Wollega)	Mineral Occurrence	0.20	64	Magnetite-ematite, Limonite-Hematite
5	Wcllega (Tsole)	Deposit or Prospect	4.48		Magnetite.hematite
6	Worakalu (Wollega)	Mineral Occurrence	0.05	62	Magnetite-Hamatite
7	Belowtuist (Wollega)	Mineral Occurrence	2.50	65-68	Magnetite, Hematite, Limonite
8	Gimbi-Daleti (Wollega)	Prospect or deposit	No data		Magnetite
9	Yubdo (Wollega)	small scale	0.05	71	Magnetite
11	Gordona (Korree) (Wollega)	Deposit	0.27	63	Magnetite-Hematite, Magnetite
12	Kata Valley (Wollega)	Mineral Occurrence	0.10	69	Magnetite, Martite
13	Dimma (Wollega)	Mineral Occurrence	0.05	65	Hematite; Magnetite Limonite-Hematite Magnetite-Hematite
14	Gambela- Dembidolo (Wollega)	Prospect or deposit	No data		Magnetite
15	Wabera-Kiltu (Wollega)	Prospect (upstream)	No data		
16	Gambo (Wollega)	Mineral Occurrence	No data		Magnetite
17	Gamalucho (Kaffa)	Deposit or prospect	12,50		Magnetite
18	Garo (Kaffa)	Mineral Occurrence	12.50		Hematite; Limonite
19	Melka Sedi (Kaffa)	Deposit or Prospect	12.50 or 0.065		Hematite, Magnetite
20	Gato (Mai Gudo) (Kaffa)	Mineral Occurrence	0.12	40	Hematite, Limonite
21	Dombowa (Kaffa)	Prospect /inferred	0.025		Limonite
22	Ghimira basin (Kaffa)	Mineral Occurrence	No data		Hematite, Limonite
23	Kurkure Valley (Kaffa)	Mineral Occurrence	No data		Hematite, Limonite
24	Like (Kaffa)	Mineral Occurrence	No data		Hematite, Magnetite
25	Melka Arba (Sidamo)	Prospect	111	69	Hematite, Magnetite, Limonite
26	Kenticha (Sidamo)	Mineral Occurrence	No data		Magnetite
27	Shakisso (Sidamo)	Mineral Occurrence	No data		Magnetite
	Shire (Tigray)	Deposit	192	22-37	Goethite/Limonite
28	Adua+Axum+Enticho (Tigray)	Mineral Occurrence	5 (low grade		Magnetite, Limonite
29	Assale (Tigray)	Mineral Occurrence	<10 Mt		Magnetite
30	Enticho (Tigray)	Mineral Occurrence	14.23		Limonite
31	Chilachikin (Tigray)	Mineral Occurrence	No data		Hematite
32	Beligal (Tigray)	Mineral Occurrence	No data		Magnetite, limonite
33	Adi Berbere (Tigray)	Mineral Occurrence	No data		Magnetite

2.6. Hydrochloric acid

Hydrochloric acid, (HCl), is an aqueous solution of hydrogen and chlorine gas. Hydrochloric acid is synthesized inside the United States of America mainly via four simple techniques: the chlorination of natural chemical compounds; the reaction of hydrogen(H_2) and chlorine (Cl), the salt-sulfuric acid production method; and, as a co-product in the manufacture of silica. maximum hydrochloric acid is comprised of the chlorination of natural chemical compounds with a lot smaller quantities from the alternative approaches.

Hydrochloric acid is generally prepared industrially through liquifying hydrogen gas and chloride in water. Hydrogen chloride may be generated in many approaches, and as a result plentiful study to hydrochloric acid exist. The large-scale production of hydrochloric acid is nearly usually incorporated with the industrial scale manufacturing of different chemical substances, including inside the chloralkaline system which synthesizes hydroxide, hydrogen, and chlorine, the latter of which may be mixed to provide HCl.

The ensuing hydrogen chloride gasoline is then absorbed in de-mineralized water to yield a high purity hydrochloric acid. This fabric is also a co-product from the manufacturing of different chemical substances [9].

Uses of Hydrochloric Acid

Hydrochloric acid (HCl) is an important and commonly applicable chemical. the largest give up advantage of hydrochloric acid are metal pickling, oil nicely acidizing, meals production and ore processing. it's used industrially to technique metal, the cloth of choice for suspension bridges and automobiles and vehicles. Hydrochloric acid is likewise used inside the production of batteries, photoflash bulbs and fireworks. it is even used to manner sugar and make gelatin.

Common Uses of Hydrochloric Acid

1. Manufacture of Organic Compounds
2. Manufacture of Inorganic Compounds
3. Removing metal stains
4. Oil manufacture
5. Refinement of Table Salt, and pH Control

Physical and chemical properties of hydrochloric acid

physical properties of hydrochloric acid, the physicochemical properties depend on the molarity of HCl within the aqueous solution. Hydrochloric acid as the binary (two-component) combination of HCl and H_2O has a constant-boiling azeotrope at 20.2% HCl and 108.6 °C (227 °F).

Table 2.2: chemical properties of hydrochloric acid

Properties of 37% HCl	**Value**
Molar mass	36.458 g mol−1
Appearance	Colorless gas-liquid
pH	1.1
Density	1.18 g/cm3
Melting point	1539 °C (anhydrous)
Solubility in water	Highly soluble

2.7. Ammonium hydroxide

The ammonium hydroxide is also called the Aqua Ammonia, solution of the ammonia gasoline within the water, and additionally a common industrial form of ammonia.it is a liquid that has no coloration and has a sturdy function smell.in the focused shape, ammonium hydroxide can result in burns on coming in touch with the pores and skin. Moreover, with the regular household ammonia, useful as a purifier, is dilute ammonium hydroxide. The water solution is largely represented through the formulation i.e., NH4OH, although no considerable quantity of the molecular species NH4OH is gift over there[10].

Uses and properties of Ammonium hydroxide

Ammonium hydroxide is widely applied as a pH controlling agent in food and beverage manufacture. It serves as a precursor to a few alkyl amines and is likewise used within the tobacco industry for flavor enhancement and as a processing resource. at some point of fixtures making, it combines with tannic acid to dye wood by using making it iron salts. In chemical laboratories, it used for qualitative inorganic analysis, as a complexant and as a base. Applicable in smoothing gold, silver and platinum earrings. it is an active thing of Tollens' reagent (which include a solution of silver nitrate and ammonia) and is used to control the occurrence of aldehyde or alpha-hydroxy ketone functional groups[10].

Properties of Ammonium hydroxide

Ammonium hydroxide is a colorless liquid that has a highly pungent odor. Ammonium hydroxide has a density of 0.91 g/mL-1. The melting point is -57.5^{o}C and a boiling point of 37^{o}C. It is highly miscible with the water.

Table 2.3: chemical properties of Ammonium hydroxide

Properties	Value
Molar mass	35.04 g mol−1
Density	0.91 g/cm3
Melting point	-57.5 °C
boiling point	37 °C

2.8. Iron oxides

Iron oxides are common compounds which can be full-size in nature and comfortably synthesized within the laboratory. they are found in almost all the different compartment of the global system: atmosphere, pedosphere, biosphere, hydrosphere and lithosphere and take part within the manifold interrelationships between those compartments. to start with, formation of FeIII oxides predominantly includes aerobic weathering of magmatic rocks (particularly on this planet's floor) in each terrestrial and marine environment; redistribution processes between the numerous worldwide cubicles may comply with. Such methods can also contain mechanical transport by way of wind/water erosion from the pedosphere into the hydrosphere or ecosystem, or, more importantly, reductive dis- solution accompanied by migration of FeII and oxidative reprecipitation in a new compartment. Iron ore formation and iron oxide precipitation in biota are important examples of redistribution. man participates in those tactics now not simplest as a residing organism, however also as a patron of iron metal and Fe oxides for various industrial functions. the general result of all these approaches is a continuous net increase in Fe oxides within the global system on the rate of iron in magmatic rocks[1].

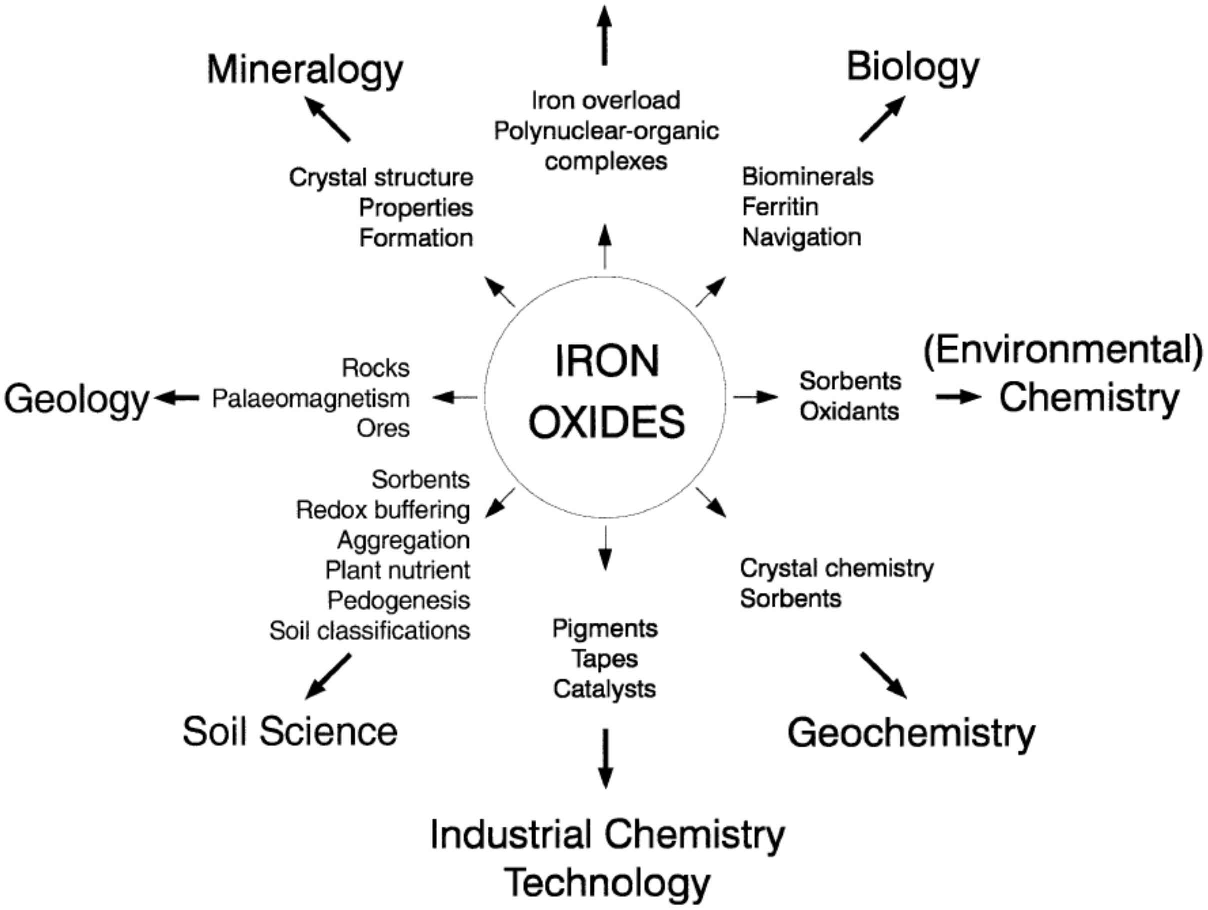


Figure 2.2:The multidisciplinary nature of iron oxide research[1].

The logical consequence of this widespread distribution of Fe oxides is that many different scientific disciplines (Figure 2.2) have an interest in Fe oxides. There are 16 iron oxides (Table 2.4). These compounds are either oxides, hydroxides or oxide-hydroxides, collectively referred as iron oxides. The iron oxides are composed of three compounds FeO, $Fe(OH)_2$ and Fe_3O_4 which contain Fe(II) in common.

Table 2.4: The iron oxides and hydroxides

Oxide-hydroxides and hydroxides	**Oxides**
Goethite α-FeOOH	Hematite α-Fe_2O_3
Lepidocrocite γ-FeOOH	Magnetite Fe_3O_4
Akaganeite β-FeOOH	Maghemite γ-Fe_2O_3
Schwertmannite $Fe_{16}O_{16}(OH)y(SO_4)z$	β-Fe_2O_3
γ-FeOOH	ε-Fe_2O_3
Feroxyhyt δ-FeOOH	Wustite FeO

High pressure FeOOH	
Ferrihydrite $Fe_5HO_8+7H_2O$	
Bernalite $Fe(OH)_3$	
$Fe(OH)_2$	

2.8.1 Main types of iron ore

There are four major forms of iron ore deposits available presently, based on the geological arrangement and mineralogy pattern of the mineral deposits. These are magnetite, titanomagnetite, massive hematite and pisolitic iron ore deposits.

Magnetite

Magnetite is composed of Fe(II) and Fe(III) oxide typically denoted by 'Fe_3O_4' but more appropriately expressed by its full notation '$Fe(II)Fe(III)_2O_4$'. Magnetite is one of the most usually happening, ferromagnetic minerals on Earth. It is a member of the class of minerals known as the 'spinels. Those minerals have the general formulation 'A^{2+}, A and B can be divalent, trivalent, or quadrivalent cations, including magnesium, zinc, iron, manganese, aluminum, chromium, titanium, and silicon. The anion is typically oxide, and A and B can also be the identical metal under unlike charges, such as the case of magnetite 'Fe(II)Fe(III)'. Spinels form in the isometric/cubic crystal system. Magnetite is typically initiate in natural terrestrial environments ranging from igneous and metamorphic rocks to all varieties of sedimentary environments. Magnetite is also be in intracellularly in several lineages of life: The Bacteria, the Protozoa, and the Animals. Additionally, magnetite has also been found in materials believed to be of extraterrestrial origin[11].

Figure 2.3: magnetite

Titanomagnetite

Titanomagnetite is a mineral containing oxides of titanium and iron, with the formula $Fe^{2+}(Fe^{3+},Ti)_2O_4$. It is also known as titaniferous magnetite. It is miles a part of the spinel institution of minerals. The Curie temperature for titanomagnetite has been decided to have a massive sort of 200 to 580°C.

Titanomagnetites are not unusual magnetic minerals in igneous and metamorphic rocks. Titanomagnetites shape a whole strong answer above 923K good enough amongst end-members magnetite (Fe_3O_4) and ulvo ¨ spinel (Fe_2TiO_4).

properties of titanomagnetites, together with saturation magnetization, Curie temperature, magneto crystalline anisotropy, magnetostriction, and electrical conductivity rely upon an expansion of interrelated crystal chemical properties. those encompass chemical composition, cation ordering, and sickness content, each of which can be changed at some point of preliminary petrogenesis or subsequent thermal records. The impact of Ti substitution motives both the MS and TC to lower approximately linearly with the x-parameter. Titanomagnetites with x extra than about zero. it has Curie temperatures under 273k and consequently are paramagnetic at ambient temperatures. Cations apart from Ti additionally may be substituted into the spinel crystal shape and herbal titanomagnetites additionally commonly incorporate minor portions of Al_3þ, Mg_2þ, and, Mn_2þ the principle results of those greater cations are to decrease both TC and MS from the rate in the perfect stoichiometric titanomagnetite[12].

Figure 2.4: titanomagnetite

pisolite

A **pisolite** is a sedimentary rock product of pisoids, which are concretionary grains – typically of calcium carbonate which be like ooids, but are more than 2 mm in diameter. These grains are approximately sphere-shaped and have concentrical layers reaching 10 mm in diameter. The term originates from the Hellenic word for pea. Bauxites, limonite and siderites often have a pisolitic structure.

Figure 2.5: pisolite

Hematite

Hematite, α-Fe_2O_3, is the oldest acknowledged iron oxide mineral and is widespread in rocks and soils. Its color is blood-red (Greek haima = blood) if finely divided and black or a glowing grey if coarsely crystalline. Hematite has the corundum (α-Al_2O_3) structure which is based on a hcp anion packing. Like goethite, it is extremely solid and is frequently the stop member of differences of different iron oxides. Hematite is an important pigment and a treasured ore; it is a first-rate constituent of the so- referred to as, banded iron formations. other names for hematite encompass iron III oxide, ferric oxide, iron sesquioxide, crimson ochre, specularite, specular iron ore, kidney ore, crocus martis and martite[1].

Fe_2O_3 is a ferromagnetic mineral in darkish crimson coloration and without problems infected by acids. Fe_2O_3 has diverse polymorphs of more than one crystal structure paperwork. a couple of phases of crystal shape in Fe_2O_3 which includes α and γ seek advice from the octahedral coordination geometry, wherein Fe on the middle bounds to six oxygen ligands. The α-Fe_2O_3, additionally known as hematite, has a rhombohedral shape just like the corundum shape (α-Al_2O_3). This shape is the maximum commonplace form in the metallic industry. Hematite mineral is as the primary extraction detail of naturally taking place iron. The γ-Fe_2O_3 generally takes place as a magnetite mineral with cubic shape. This mineral is metastable and convertible from the alpha segment at high temperatures. The β level is a cubic body part that is focused, metastable, and equal to the alpha section at temperatures above 500°C (930°F)[13].

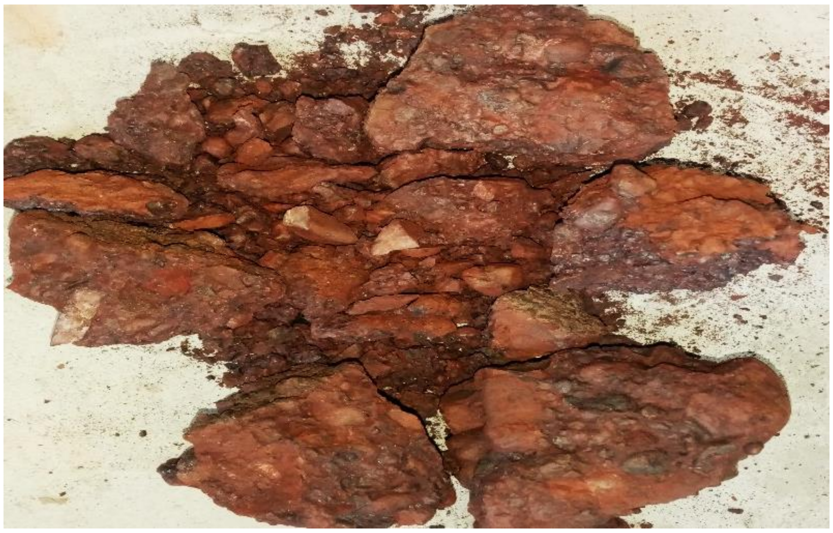


Figure 2.6: hematite

2.8.2 Composition of α-ferric oxide

pure α-ferric oxide has a composition of about 70% and 30% for iron and oxygen respectively by means of weight. Like most natural materials, it is not often discovered with that pure composition. that is particularly proper of the sedimentary deposits where α-ferric oxide paperwork by means of inorganic or organic precipitation in a body of water.

Applications of α-ferric oxide (α-Fe_2O_3)

α-ferric oxide gets a great deal interest because of its promising traits for lots programs in electronic, optical, and photonic devices. The hobbies focus on research of α-ferric oxide and α-ferric oxide as photoelectric chemical sun mobile cloth. except, it is a fee-powerful, environmentally friendly, and relatively green approach, additionally demonstrating chemical balance above a wide pH range appropriate for photocatalytic packages[13]. α-ferric oxide (α-Fe_2O_3), the maximum strong iron oxide, with n-type semiconducting homes underneath ambient situations, is of medical and technological importance because of its utilization in catalysts, pigments, magnetic materials, gasoline sensors, and lithium-ion batteries. The diameter length and porosity of α-ferric oxide nanorods also have an effect on the magnetization residences, which have high sensitivity in less than 20nm particle size[14].

Synthetic iron oxide powders are used ordinarily for his or her pigmentary and magnetic properties (even though not all kinds of oxide aren't ferromagnetic). The category of iron oxide powders consists of all types of artificial iron oxides (α-ferric oxide, magnetite, maghemite, and so forth.) and ferrite powders additionally, because the latter substances have as their essential constituent ferric oxide (Fe_2O_3). Iron oxide powders are the most broadly used of all colored inorganic pigments, utilized in concrete products, paints, plastics, and other media. due to their chemical and magnetic homes, iron oxide powders also locate vast business usage in electromagnetic additives, catalysts, toners, magnetic recording media, and different programs[15].

Ferric oxides, and impurities, inclusive of manganese, clay, or organics. those impurities can once in a while impose obstacles on its applicability. artificial iron oxide pigments are one of the most famous coloration pigments worldwide for coloring concrete merchandise, along with ready-blended and stamped concrete, concrete blocks, bricks and paving stones, roofing tiles, architectural precast merchandise, colored mortar cement, stucco and grout. different applications encompass pigments for inks, paints, cosmetics, wood, tiles, ceramics, and anticorrosive coatings used within the manufacture of automobiles and ships.

A full variety of color pigments, inclusive of yellows, reds, blacks and browns, is synthesized for a variety of programs. artificial iron oxides may be synthesized in diverse approaches, together with thermal decomposition of iron salts, including ferrous sulfate, to provide reds; precipitation to provide yellows, reds, browns, and blacks (e.g., the Penniman-Zoph manner); and discount of organic compounds by using iron (e.g., nitrobenzene reduced to aniline in the presence of specific chemicals) to supply yellows and blacks. Reds may be synthesized with the aid of calcining either yellow or blacks[15].

α-ferric oxide (α-Fe_2O_3) colloids have the tendency to form complexes with natural count (NOM) which can be precursor compounds that shape with the aid of-merchandise like risky trihalomethanes (THMs). stated the utility of hematite (α-Fe_2O_3) colloids as a flocculent in go-float microfiltration (CFMF) which is a totally beneficial system for putting off colloids and suspended solids in water. software of iron oxide nanoparticles-based totally nanomaterials for elimination of heavy metals is famous adsorbents for remediation of water. free chlorine can react with several organic substances inclusive of amino acids, humus, environmental pollution in raw floor water to yield halogenated organics[16].

Ferric oxide is especially used in a paint manufacturing facility as a pink pigment which used for the manufacturing of pink anti-rust and in addition to the overpowering software of iron (III) oxide is as the feedstock of the metallic and iron industries, such as, the manufacturing of iron, metal, and lots of alloys.

An exceptionally agreeable powder of ferric oxide is classified "goldsmith's rouge", "red rouge", or genuinely rouge. it is utilized to put the last clean on steel studs and focal points, and generally as a corrective. Rouge cuts more noteworthy gradually than a couple of cutting the edge shines, alongside cerium (IV) oxide, but keeps on being used in optics creation and by utilizing goldsmiths for the predominant completion it might blend. when cleaning gold, the rouge scarcely stains the gold, which adds to the appearance of the finished piece.

Physical and chemical properties of α-ferric oxide

α-ferric oxide has an extremely flexible presence. Its color can range from rocky to metallic. Its shade levels consist of pinky to brownie and black to grayish to metallic. It happens in lots of paperwork that encompass micaceous, large, crystalline, botryoidal, fibrous, politic, and others. even though hematite has a particularly variable appearance, it constantly synthesizes a reddish streak. The reddish streak is the maximum crucial clue for figuring out α-ferric oxide. α-ferric oxide isn't always magnetic and need to its anti-ferromagnetic properties. however, many samples of α-ferric oxide contain small magnetite that they can’t be attracted to any metals. this may cause an incorrect hypothesis that α-ferric oxide is magnetite or the ferromagnetic type of iron ore.

Table 2.1: properties of α-ferric oxide[17]

Properties	Value
Molecular formula	α-Fe_2O_3
Molar mass	159.6871 g mol−1
Appearance	Black to steel-gray to silver; red to reddish brown to black
Odor	Odorless
Density	5.25 g/cm3
Melting point	1539 °C (anhydrous)
Solubility in water	Insoluble
Solubility	Soluble in diluted acid

2.9 Ammonium chloride (NH_4Cl)

NH4Cl is an inorganic compound with chemical name Ammonium Chloride. It has diuretic and expectorant results. In its pure form, its far crystalline salt, white. This compound is fairly water-soluble and mildly acidic. it is utilized in veterinary medicinal drug inside the prevention of urinary stones in sheep, goats, and livestock. when ammonium sulfate and NaCl solutions react, NH_4Cl is synthesized. whilst a 5% solution of ammonium chloride (through weight) is blended with water, the resulting answer has a pH price ranging from 4.6 – 6.0.

Ammonium chloride is an acidifying agent that can be found inside the urine. Ammonium chloride uses in pH regulation in almost any industries. This acid-forming salt additionally is a medical purpose for traumatic the mucous membranes, and also as a fertilizer for agriculture because it can be high source of nitrogen for the soil. Ammonium chloride is a crystalline white substance.

Physical and chemical properties of Ammonium chloride

Table 2.7: chemical properties of ammonium chloride

Properties of Ammonium Chloride	**Value**
Molar mass	53.491 g mol−1
Appearance	White crystals
pH	4.6 – 6.0
Density	1.53 g/cm3
Melting point	338 °C
Boiling point	520 °C
Solubility in water	Highly soluble

Uses of Ammonium Chloride

- it is used as a fertilizer for nitrogen source.
- its miles used in medicine (specifically in cough medicine) as an expectorant.
- it's far utilized in glue which allows to bond plywood.
- it's far used in meals additives – in bread making as a yeast nutrient.
- it's far used as an acidifier.
- it is utilized in cooling baths to create low temperatures.
- they may be used as buffer answers together with ammonia.
- it is given to cattle as feed dietary supplements.

2.10 Methods of α-ferric oxide synthesis

In this few years numerous method synthesis have been established to synthesize iron oxides, α-Fe_2O_3, Fe_3O_4, and γ-Fe_2O_3, on nanometric and micro level for different useful applications. One of the most common methods includes sol-gel, microemulsion, co-precipitation, and thermal decomposition methods. These reaction processes are significantly influenced by reaction process parameters and it may have a serious effect on physicochemical properties of the products.

SOL-GEL

Sol-gel synthesis procedures typically involve the hydrolysis and condensation of metal alkoxides or alkoxide precursors, resulting in oxide particle dispersions in "sol," which is subsequently dried or gelled by removing the solvent. Magnetic iron oxide nanoparticles have high surface energies due to their huge surface-to-volume ratio, and so tend to agglomerate and form clusters, resulting in increased particle size.

MICROEMULSION

Microemulsion research began in 1943, but it wasn't until 1959 that Hoar and Schulman popularized the notion, and its application has risen since then. Microemulsions, according to the authors, are a transparent system generated spontaneously when an oil phase and an aqueous phase are combined with a medium chain alcohol ionic surfactant in relatively significant concentrations.

Because it produces particles with a narrow pore size distribution spanning from 4 to 15 nm, a cubic or spherical shape, and a high surface area (315 $m^2.g^{-1}$), the microemulsion approach has been widely utilized to create catalytic iron oxide. The production of magnetic iron oxide nanoparticles with precise size and morphology.

CO-PRECIPITATION

Hematite (α-Fe_2O_3) magnetic nanoparticles can be made by co-precipitating a stoichiometric combination of Fe (II) and Fe (III) salts in a basic aqueous medium of sodium hydroxide (NaOH) or ammonium hydroxide (NH_4OH).

This synthesis process can produce particles with diameters ranging from 5 to 20 nm. The type of ion salt-chlorides, sulphates, nitrates, or perchlorates as well as the Fe^{2+} / Fe^{3+} concentration ratio are crucial experimental conditions. In order to alter the size of magnetic iron oxide nanoparticles, other synthesis factors such as pH, ionic force of the medium, and reaction temperature can be modified during the synthesis.

THRMAL COMBUSTION

Iron oxides are often used as ballistic additions in composite solid propellant formulations to speed up combustion at the burning surface and hence boost the burn rate and thrust-time curve of the propellant. They may tune the burning rate to meet a given grain design this way. Because the decomposition of ammonium perchlorate is so important to propellant combustion, several studies have looked at the catalytic influence of nanosized ferric oxide on the oxidizer's thermal decomposition. Nanosized transition metallic oxides like as iron oxide, hematite (α-Fe_2O_3), and maghemite (γ-Fe_2O_3) are materials that can be used in solid propulsion.

Because of its speed, simpleness and high productivity, the co-precipitation method is the most promising and cost-effective approach for synthesizing α-Fe_2O_3 particles.

2.11 Review of α-ferric oxide synthesis technologies

There are numerous papers/literatures which states about distinctive strategies of α-ferric oxide manufacturing. each approach is extraordinary both via their uncooked fabric, product or by way of their method situation. those are 4 extraordinary kinds of α-ferric oxide synthesis method those are

A. The preparation of α-ferric oxide of pigment quality from mill scale iron waste[18][32].
B. The preparation of A-ferric oxide xerogels through sol-gel technology, using Iron(III) nitrate nonahydrate as precursor[19].
C. The preparation of α-ferric oxide from iron ore.
D. The preparation of α-ferric oxide from ferrous sulphate heptahydrate.

A. The preparation of α-ferric oxide of pigment quality from mill scale iron waste

Plant scale iron waste has been utilized to set up some iron oxide colors through explicit forerunners. Magnetite and goethite were encouraged from their separate antecedents in watery media. Different red shades of α-ferric oxide were ready by the calcinations of the encouraged goethite at temperatures going from 600 to 900 °C [32].

B. The preparation of α-ferric oxide xerogels through sol-gel technology, using Iron (III) nitrate nonahydrate as precursor

α-ferric oxide xerogels were ready through sol-gel innovation, utilizing iron (III) nitrate nonahydrate as forerunner, ethanol as dissolvable and ammonium hydroxide as gelation specialist. This base is utilized for propylene oxide replacement, which was the gelation specialist in past works. The union of a gel utilizing the NH4OH gelation specialist is a progressive outcome with this type of forerunner, considering the way that with metal salts the expansion of a tough base normally brings about precipitation of the strong. The gel blend changed into performed with the guide of controlling the base expansion time [9].

C. The preparation of α-ferric oxide from iron ore

Some grams of crushed and sieved ore will be placed in the beaker with concentrated hydrochloric acid (HCl) while stirring and heated on hot plate magnetic stirrer at about 120 °c to synthesize ferric chloride ($FeCl_3$) and it will be followed by Precipitation process with ammonium hydroxide (NH_4OH) into the solution until the pH reaches 6 and formed a cake and filtrate in the reaction. Then the cake will be washed and dried in a dryer/oven for 19 hours at 105 ºC, Next calcination [35] will be conducted using the muffle furnace to synthesize a α-ferric oxide.

D. The preparation of α-ferric oxide from ferrous sulphate heptahydrate

α-ferric oxide can be synthesized by thermal decomposition method of ferrous sulphate heptahydrate ($FeSO_4.7H_2O$). the ferrous sulphate heptahydrate sample is decompose to the monohydrate and then calcined at a temperature above 500 °C in furnaces. The final color synthesized can be adjusted to by fluctuating the temperature, pressure and time of calcination. Relatively short calcination durations (7-8 hours) and lower temperatures synthesize lighter shade pigments, whereas longer calcination durations (11-12 hours) and higher temperatures synthesize deeper blue/red shades[20][31].

As there are different studies being studied in the synthesis of α-ferric oxide, there are many methods to synthesize α-ferric oxide. But, from these different methods the best methods can be selected by considering the following measures,

1. It is better to synthesize α-ferric oxide from the ore other than other chemicals and even from waste iron sources. Because the ore is cheapest and continues resources.
2. In Ethiopia one of the most deposited mineral is iron ore.
3. in Ethiopia Most of the iron ores occur in form of α-ferric oxide (Fe_2O_3) rather than other forms.

Many researches had been conducted to produce α-ferric oxide by using different raw materials such as; chemicals (ferrous sulphate heptahydrate, ferrous nitrate), iron ore and also waste materials from iron industries. In Ethiopia some researches were conducted in this previous five years. For instance, In 2017 "Production, optimization and characterization of ferrous sulfate from local iron ore" had been studied by Birhan Getachew in Addis Ababa Institute of technology (AAiT) and iron ore from Horu Guduru was selected for the study and 97.75% iron sulfate yield was obtained [29]. In 2020 "Production of magnetite nanoparticles from Ethiopian iron ore using solvent extraction and studying parameters that affect crystallite size." was studied by dr. Kebede S. and dr. Abubuker Y. The iron ore sample from wollega region was selected for the study. And Magnetite nanoparticle was synthesized using the iron ore from wollega region, by solvent extraction method and it was confirmed by XRD analysis, EDS, and FTIR spectra [37]. But synthesizing α-ferric oxide from iron ore located in Ethiopia had never been studied.

CHAPTER THREE

3. METHODOLOGY AND MATERIALS

3.1. Raw Materials, chemicals and Equipment

3.1.1. Raw material collection and preparation

Materials which were used for α-ferric oxide synthesis were local iron ore from two different locations. Those iron ore samples were collected from geological survey of Ethiopia (GSE) sample library because of the instability of the road to the northern regions of Ethiopia. After collection of the samples the selection of local iron ore which is used for α-ferric oxide synthesis was analyzed using different analyzing methods by the geological survey of Ethiopia (appendix A). It is supposed to achieve the following specific responsibilities to access data of local iron ore which is important for α-ferric oxide synthesis;

Iron ore deposits which is available in Ethiopia from different literatures, journals and with the help of the employees in geological survey of Ethiopia the iron ore deposits were identified.

Then the best synthesis line and raw materials which are required for the preparation of α-ferric oxide would be presented. For this aim, different literatures would be covered. This work covers the best possible way to show method of α-ferric oxide preparation from the available local iron ore (Fe_2O_3) in Ethiopia. The Geological Survey of Ethiopia (GSE) acknowledged many irons (Fe) occurrences in two locations in Ethiopia, those are from AXUM and SEKOTA regions.

3.1.2. Chemicals

Other Chemicals and equipment's were bought from RANCHEM® industrials and trading Private Limited Company; in Kirkos shopping center, Addis Ababa. And the chemicals which used for different activities were listed below:

For the synthesis; Local iron ore (from Axum region, 65.81% grade), Hydrochloric acid (HCl, 37% conc.), Ammonium hydroxide (NH_4OH, 30% conc.), Distilled water and for characterization; Nitric acid (HNO_3, 15%), Lanthanum chloride, Potassium chloride (KCl), Ethanol (C_2H_5OH, 98%), Toluene, Potassium hydroxide (KOH, 0.1M), Phenolphthalein (1%), Phosphoric acid (H_3PO_4, 98%) Potassium permanganate, Sulfuric acid (H_2SO_4, 98%), Sodium hydroxide (NaOH, 0.1M) and all these chemicals were used without further purification

3.1.3. Materials / Equipment

Major Equipment used for synthesis and characterization were; Crusher, Sieve analyzer, Weighting balance, Beakers, PH meter, Magnetic stirrer with heater, Ash less filter paper, Funnels, clay crucible flasks, Spatula, dryer/oven, Pipette, Vacuum pump, Titration column, Flasks, Aluminum foil, Warm water bath, Filter paper, Pycnometer, XRD and FT-IR.

3.2. Methodology

3.2.1. Characterization of iron ore

Characterization of the ores was performed by major and minor oxides analysis which analyzed by wavelength dispersive X-ray fluorescence spectrometry (XRFS) was used. Trace elements were determined on loose-powder specimens by energy-dispersive XRFS using procedures and algorithms of Johnson and King[21]. Major and minor oxides analysis was prepared by fusing the standard reference samples with pure lithium tetraborate flux. An 800-mg portion of powder (dried at 105°C) was ignited to 20 min or longer in a muffle furnace at 925°C. The ignitions were done in a muffle furnace with its window removed. After the loss on ignition (LOI) was determined gravimetrically, the residue was mixed with 8 g of anhydrous $LiB0_2$ flux. A 0.250-ml aliquot of LiBr solution [21].

This major and minor oxide analysis and trace elements was done in Geological Survey of Ethiopia (Addis Ababa around SARBET) laboratory. The iron ore were characterized by LiBO2 FUSION, HFattack, GRAVIMETERIC, CALORIMETIC and AAS methods.

3.2.2. Experimental steps to synthesize α-ferric oxide

The Experiments were conducted in Chemical Engineering Department PG Laboratory. Furthermore, characterization of the product (α-ferric oxide) was done in Addis Ababa university (AAU) chemistry department Laboratory, in Addis Ababa science and technology University (AASTU) food engineering department laboratory and Adama science and technology University (ASTU). From the iron ore characterization result the AXUM iron ore were selected because it has high amount of iron oxide than SEKOTA iron ore.

Iron ore sample preparation

Before starting the reaction, the ores were cleaned, prepared and crushed by jaw crasher and RETSCH (5657 HAAN) miller Followed by sieve analysis in Chemical Engineering Size Reduction Laboratory in AAiT. Then the crushed sample will be divided into three different groups depending on particle size.

A. Particle size 1. (X < 0.125mm),
B. Particle size 2. (<0.85mm X >0.125mm), and
C. Particle size 3. (<2 mm X >0.85mm).

Then, those samples were ready for next the reaction.

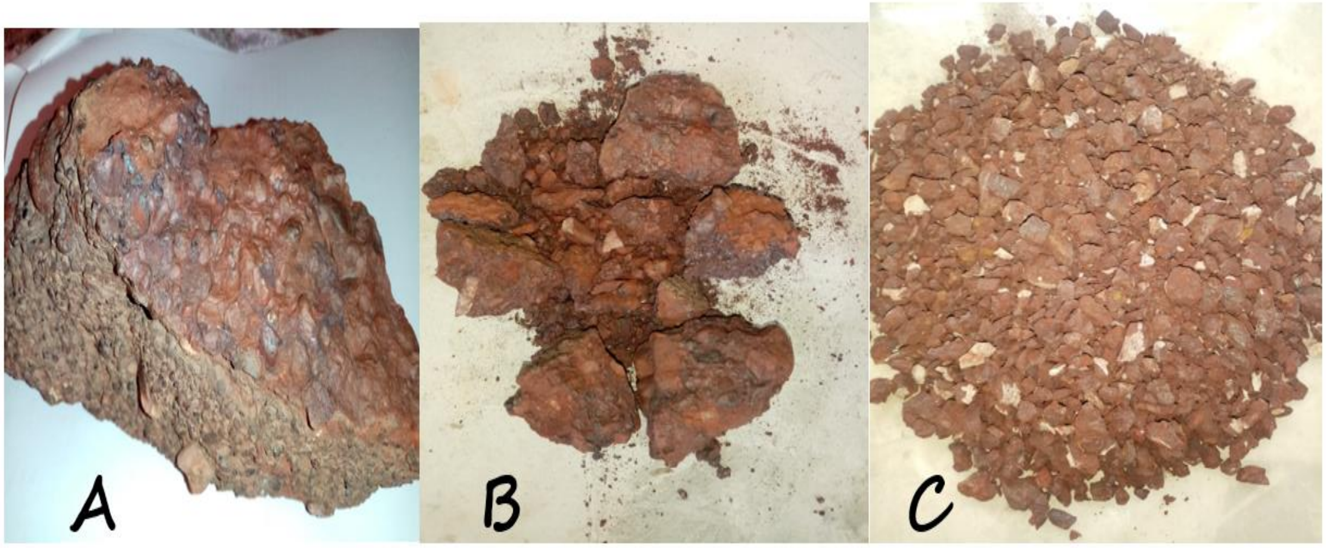


Figure 3.1: size reduction stages of iron ore from AXUM region.

3.2.3. Experimental setup

First, leaching of iron ore (AXUM) in hydrochloric acid (37%) was done to get ferric chloride. Then, the next reaction was called co-precipitation reaction [33]. Which is the reaction between ferric chloride and ammonium hydroxide (30%). In detail, 77g of the crushed sample by using crusher (7311 Dietz-motoren) and sieved by Retsch AS-200 sieve analyzer then, it was placed in beaker (Lasany B. glass) and reacted with concentrated (37%) hydrochloric acid (HCl) while stirring and heated on hot plate (MS-H280-PRO) [28] magnetic stirrer for about 2 hours at 120 ºC to synthesize ferric chloride ($FeCl_3$) and filtered by a vacuum pump (MZ-2C NT) to separate the ferric chloride and unreacted substances. then, the liquid yellowish red colored ferric chloride solution followed by adding concentrated (30%) ammonium hydroxide (NH_4OH) into the solution until the pH reaches 6 by measuring the pH by PH meter (Hanna

HI-98194) repeatedly and at pH = 6±0.2 it formed a precipitation (cake and filtrate) in the reaction. Then, the precipitates were filtered by vacuum pump (MZ-2C NT) to separate the ferric hydroxide (FeOOH) and ammonium chloride (NH_4Cl), the cakes were washed and dried in an oven (PRI/150/A) for 19 hours at 105±5 ºC, Next calcination were conducted using the muffle furnace at three different time (90, 120 and 150 min) and temperature (500, 550 and 600 ºC) values to synthesize α-ferric oxide.

$$\textbf{Iron ore} + 6HCl \longrightarrow 2FeCl_3 + 3H_2O$$

$$2FeCl_3 + 3H_2O + 6NH_4OH \longrightarrow 2Fe\,(OH)_3 + 6NH_4Cl + 3H_2O$$

$$2Fe(OH)_3 \longrightarrow \mathbf{Fe_2O_3\ (\alpha\text{-ferric oxide}) + 3H_2O}$$

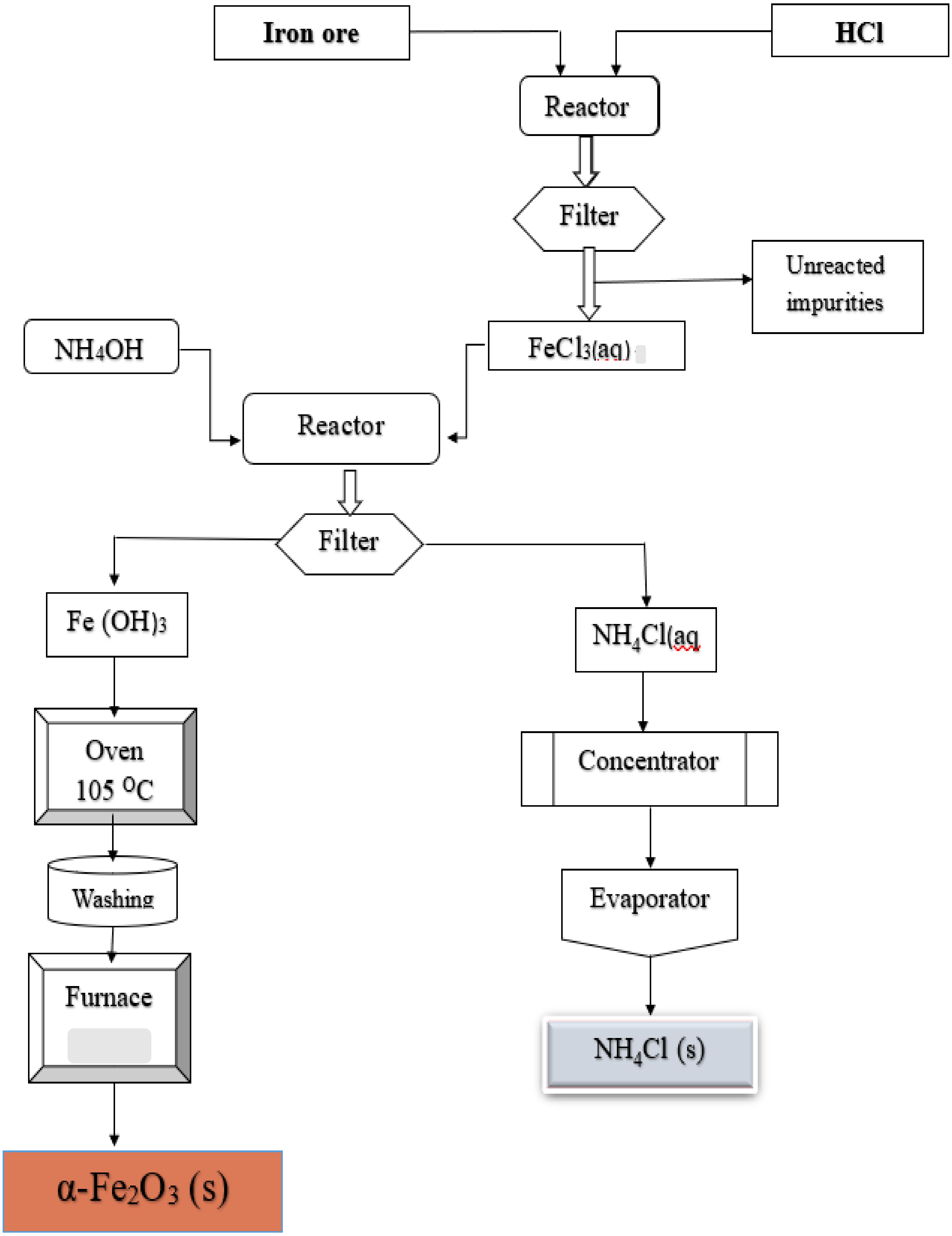


Figure 3.2: block flow diagram for synthesis of α-ferric oxide

Figure 3.3: A) α-ferric oxide (Product) and B) Ammonium chloride (Byproduct)

3.3. Characterization of α-ferric oxide (Physicochemical properties)

The characterization of ferric oxide was made to make sure the resulting product's physicochemical properties are the same with desired to synthesize or market ferric oxide. Therefore, in this research the following physicochemical properties will be characterized.

A. Acidic value
B. Moisture content
C. PH
D. Specific gravity
E. Insoluble matter in water
F. XRD (X-Ray Diffraction)
G. FT-IR (Fourier Transform Infrared)
H. Major oxides Analysis

3.3.1. Determination of Moisture Content

The test According to ISO 1248:2006(E), 2008, the moisture content was determined by drying the samples in an oven until a constant weight obtained. Amount of sample was weighed properly and put in a crucible and dried at the 105^{O}C temperatures. The moisture content was determined using following equation.

$$\text{MC (\%)} = \frac{W1 - W2}{W2} \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots \text{(Eq. 1)}$$

Where: W1 = weight of the sample before drying
W2 = weight of the sample after drying

3.3.2. Determination of density

The test According to ISO 1248/2006/cor. 2/2008-E, 2007, The density of the product was measured by a standard Pycnometer of 50 ml capacity. First Empty Pycnometer was measured on digital balance and mass was recorded. The half of the Pycnometer filled with the product and weighted. Then, the remaining volume of Pycnometer was filled with distilled water and weighted. Mass of water was determined, the volume of water, volume of the product and the density of the product was obtained from equation below.

volume water = $\frac{\text{mass of water}}{\text{density of water}}$………………………………………………………….. (Eq. 2)

Density of water in g/cm^3 and mass in gram (g), then volume of water in cm^3

Volume of product = total volume of Pycnometer minus volume of water………………. (Eq. 3)

Density of product = $\frac{mass\ of\ sample}{volume\ of\ sample}$……………………………………………………… (Eq. 4)

3.3.3. Determination of pH

Some weight (2 grams) of product was weighed and transferred to a beaker and some amount of diluted sulfuric acid and distilled water was added and stirred well and put for an hour. The pH of the solution was read by a PH meter.

3.3.4. Determination of soluble matter in water

The test According to ISO 15528:2013(E), 2013, Some amount of the product was weighed accurately and dissolved in water and then heated up on a water bath for about an hour. A filter paper was used to wash it well with water, then dried up to constant weight at 105°C in an oven**.** Any insoluble matter was filter out.

Matter insoluble in water, percent by weight is calculate as follow:

Matter insoluble in water, percent by weight = $\frac{W1}{W2} * 100\%$ ……………………………… (Eq. 5)

Where, W1 = weight in g of the residue, and

W2 = weight in g of the product

3.3.5. Determination of volatile matter/ Loss on Ignition (LOI)

The test according to ISO 787/2/1981-E, 2000, 3 grams of product were oven-dried at 105 °C for 24 hours. Then the dried sample were fired at 1050 °C. Loss of Ignition (LOI) was determined by measuring the weight loss of the sample between the drying and firing stages as described in Eq. 6 [22].

$$\text{LOI\%} = \frac{(\text{Wd}-\text{Wf})}{\text{Wd}} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{(Eq. 6)}$$

Where Wd is the mass of oven-dried specimens (g), and

Wf is the mass of fired specimens (g).

3.4. External Methods/Tests

3.4.1. X-Ray Diffraction Structure Analysis

X-Ray Diffraction investigation (XRD) is a method utilized in materials science to decide the crystallographic design of a material. XRD works by lighting a material with occurrence X-ray and afterward estimating the powers and dispersing points of the X-ray that leave the material.

The technique for X-ray diffraction (XRD) was utilized to decide the material's crystal structure and particle size of synthesized α-ferric oxide.

3.4.2. Fourier Transform Infrared (FT-IR)

Fourier change infrared spectroscopy (FTIR) utilizes the numerical interaction (Fourier change) to decipher the crude information (interferogram) into the real range. FTIR technique is utilized to get the infrared range of transmission or ingestion of a fuel test. FTIR distinguishes the presence of natural and inorganic mixtures in the example. Contingent upon the infrared ingestion recurrence range 600–4000 cm−1, the particular sub-atomic gatherings winning in the example not set in stone through range information in the robotized programming of spectroscopy.

It is one of the analytical methods which used to reveal the functional groups present in the given sample and also to determine the microcrystalline nature of the particles.

3.4.3. Major Oxides and trace elements Analysis

For major and minor oxides analysis by wavelength dispersive X-ray fluorescence spectrometry (XRFS) was used. Trace elements were determined on loose-powder specimens by energy-dispersive XRFS using procedures and algorithms of Johnson and King[21]. Major element analysis was prepared by fusing the standard reference samples with pure lithium tetraborate flux. An 800-mg portion of powder (dried at 105°C) was ignited to **20** min or longer in a muffle furnace at 925°C. The ignitions were done in a muffle furnace with its window removed. After the loss on ignition (LOI) was determined gravimetrically, the residue was mixed with 8 g of anhydrous $LiB0_2$ flux. A 0.250-ml aliquot of LiBr solution [21].

This major and minor oxide analysis will be done in Geological Survey of Ethiopia (Addis Ababa around SARBET) laboratory. The synthesized α-ferric oxide will be characterized by LiBO2 FUSION, HFattack, GRAVIMETERIC, CALORIMETIC and AAS methods.

The next step was to optimize the process variables with the purpose of finding the maximum yield possible of α-ferric oxide using the experimental data's, design expert 12.0.0 software and the model regression methods.

3.5. Experimental Design

The laboratory experiment will be based on box-Behnken where the different operating variables will be analyzed for the different combinations of experiment. Randomization of the experimental runs as well as appropriate analysis technique will be safeguarded through proper use of software – Design – Expert ® version 12.0. Results from experiment will be the foundation to conclude this research.

Experimental operating variables/ factors are;

1. Particle size of raw material
2. Calcination Temperature and,
3. Calcination Time.

3.6. Experimental work design

During this study α-ferric oxide was prepared using local iron ore with hydrochloric acid and ammonium hydroxide. The Experimental design was analyzed by the Design Expert version 12.0.0

software. Experimental design selected for this study is Box-Behnken design and the output measured was α-ferric oxide yield found. Process variables studied are reaction temperature, reaction time and particle size. The operating limits of the α-ferric oxide synthesis process conditions are explanations to pick levels of the variables.

Three level and three factors Box-Behnken design was made use of in the optimization study, requiring 17 runs with 5 centers of points to be conducted. Reaction temperature, reaction time and particle size were the independent variables studied to optimize the conditions for α-ferric oxide preparation. seventeen experiments were done and the data was statistically analyzed by the Design Expert 12.0.0 software and to get suitable model for the percentage of α-ferric oxide as a function of the independent variables.

Table 3.4: complete experimental design of Box-Behnken design Variables

Variables	Factor coding	Unit	Levels		
			-1	0	+1
Particle size	A	-	1	2	3
Calcination temperature	B	^{O}C	500	550	600
Calcination time	C	Minute	90	120	150

Table 3.5: The complete (17 runs) experimental design of Box-Behnken design for the factorial design.

Run no.	Particle size	Calcination Temp. (°C)	Calcination time (min)	Yield (%)
1	P.S 1	550	150	
2	P.S 1	600	120	
3	P.S 2	550	120	
4	P.S 2	550	120	
5	P.S 1	550	90	
6	P.S 2	500	150	
7	P.S 2	550	120	
8	P.S 3	600	120	
9	P.S 3	550	150	
10	P.S 2	600	150	
11	P.S 2	550	120	
12	P.S 3	550	90	
13	P.S 2	550	120	
14	P.S 2	500	90	
15	P.S 2	600	90	
16	P.S 1	500	120	
17	P.S 3	500	120	

CHAPTER FOUR

4. RESULTS AND DISCUSSION

4.1. Characterization of the Raw Materials

4.1.1. Physical Characterization

The raw material collected was characterized both physically with a visual observation, touching and chemically by different analyzing mechanisms.

The physical characterization of the raw materials was as in Table 4.1

Table 4.1: Physical characterization of the raw materials

Properties	**Values/amounts**
Color	dull to bright red
Density	5.5 g/cm^3

4.1.2. Chemical Characterization

The samples were collected from two different sources (from AXUM region and SEKOTA region) was analyzed in Geological Survey of Ethiopia (Addis Ababa around SARBET) central laboratory. To determine the quality of the iron and other contents in the ore, the samples were tested for its composition by LiBO2 FUSION, HFattack, GRAVIMETERIC, CALORIMETIC and AAS methods and the following values were obtained as in Table.

Table 4.2: Compositional analysis of the ore (in %)

Code	SiO2	Al2O3	**Iron oxide**	CaO	MgO	Na2O	K2O	H2O	LOI
AXUM	12.68	14.96	**65.81**	2.81	0.24	0.01	0.01	0.04	3.39
SEKOTA	33.48	12.46	**46.56**	0.01	0.12	0.01	0.01	1.24	4.98

The above iron oxide percentages are indicators of purity states. In ores, the Fe content is lowered refers to the number of impurities existing. Generally, the quality of iron ore is primarily decided based on the Fe content. More specifically, ores with Fe contents above 65% are regarded as high-grade ores; 62–64% medium- (or average) grade ores and those below 58% Fe are considered as low-grade ores [30].

Based up on the above characterization result, the AXUM region ore have high grade purity of iron oxide (65.81%) than the Sekota region iron ore. Therefore, all the synthesis and characterization will be done by using iron ore from Axum region.

4.2. . Experimental Design analysis

4.2.1. Experimental analysis

The experimental design nominated for this study is Box-Behnken design method and the response measured is the yield of hematite. The three process variables studied are particle size, reaction temperature, and reaction time. The Design Expert 12.0 software was used in the regression analysis and analysis of variance (ANOVA). The Statistical software program was used to generate surface plots, using the fitted equation obtained from the regression analysis, holding one of the independent variables' constant. The Box-Behnken design conditions and responses, and the statistical analysis of the ANOVA are given in Tables 4.3 and 4.6, respectively. The actual yield of α-ferric oxide synthesized at different process parameters was calculated and is given in table 4.4. The model was tested for adequacy by ANOVA. The regression model was found to be significant with the correlation coefficients of determination of R-Squared (R2), adjusted R Squared and predicted R-Squared having a value of 0.9878, 0.9722 ,0.8052 respectively with an adequate precision of 23.3571. Adequate Precision measures the signal to noise ratio. A ratio greater than 4 is desirable. Your ratio of 23.357 indicates an adequate signal. This model can be used to navigate the design space.

Table 4.3: Fit statistics

Std. Dev.	1.04	**R^2**	0.9878
Mean	71.07	**Adjusted R^2**	0.9722
C.V. %	1.47	**Predicted R^2**	0.8052
		Adeq Precision	23.3571

Table 4.4: Yield of α-ferric oxide from each run.

Run no.	Particle size	Calcination Temp. (^oC)	Calcination time (min)	Yield (%)
1	P.S 1	550	150	77.3
2	P.S 1	600	120	78.3
3	P.S 2	550	120	75.74
4	P.S 2	550	120	76.1
5	P.S 1	550	90	69
6	P.S 2	500	150	71.6
7	P.S 2	550	120	76.34
8	P.S 3	600	120	65.2
9	P.S 3	550	150	62
10	P.S 2	600	150	71.8
11	P.S 2	550	120	76.23
12	P.S 3	550	90	59
13	P.S 2	550	120	76.71
14	P.S 2	500	90	69
15	P.S 2	600	90	63
16	P.S 1	500	120	76.7
17	P.S 3	500	120	64.8

4.2.2. Development of Model Equation

The regression model equation that correlates the response variable, yield of α-ferric oxide, with the process variables, in terms of actual values by excluding the non-significant variables and variable interactions are given by the following equation in terms of coded factors.

$$\text{Yeild} = 76.1 - 6.26*A - 0.475*B + 2.84*C - 0.300*AB - 1.32*AC + 1.55*BC - 3.44*A^2 - 1.41*B^2 - 5.84*C^2 \quad \text{4-1}$$

Where A= particle size
B= Reaction Temperature
C= Reaction time

The equation in terms of coded factors can be used to make predictions about the response for given levels of each factor. By default, the high levels of the factors are coded as +1 and the low levels are coded as -1. The coded equation is useful for identifying the relative impact of the factors by comparing the factor coefficients.

The multiple regression coefficients were obtained by employing a least square technique to predict quadratic polynomial model for the α-ferric oxide (Table 4.5) hence, the best fitting model was determined. The model was selected based on the highest order polynomial where the additional terms were significant and the model was not aliased.

Table 4.5: Regression coefficients and significance of response

Factors	Coefficient estimate	df	Standard error	95% Cl LOW	95% Cl HIGH	VIF
Intercept	76.10	1	0.4665	75.00	77.20	
A-PARTICLE SIZE	-6.29	1	0.3688	-7.16	-5.42	1.00
B-CALCINATION TEMP.	-0.4750	1	0.3688	-1.35	0.3971	1.00
C-CALCINATION TIME	2.84	1	0.3688	1.97	3.71	1.00
AB	-0.3000	1	0.5216	-1.53	0.9334	1.00
AC	-1.32	1	0.5216	-2.56	-0.0916	1.00
BC	1.55	1	0.5216	0.3166	2.78	1.00

The coefficient estimate represents the expected change in response per unit change in factor value when all remaining factors are held constant. The capture in a symmetrical plan is the general normal reaction of the multitude of runs. The coefficients are changes around that normal dependent on the factor settings. At the point when the elements are symmetrical the VIFs are 1; VIFs more noteworthy than 1 demonstrate multi collinearity, the higher the VIF the more serious the relationship of elements. As a rough rule, VIFs less than 10 are tolerable.

4.2.3. Model Adequacy Check

The model that was developed by using Design Expert 12.0 has to be checked for its uniformity and quality how it relates the experimental variables to the response variables. The model quality can be evaluated from its coefficients of correlation (R2). The value of R-squared for the developed correlation is 0.9878. It indicates that 98.78% of the total variation in the α-ferric oxide yield is attributed to the experimental variables studied. The graph of the predicted values (obtained using the developed correlation) versus actual response values is shown in Figure 4.1.

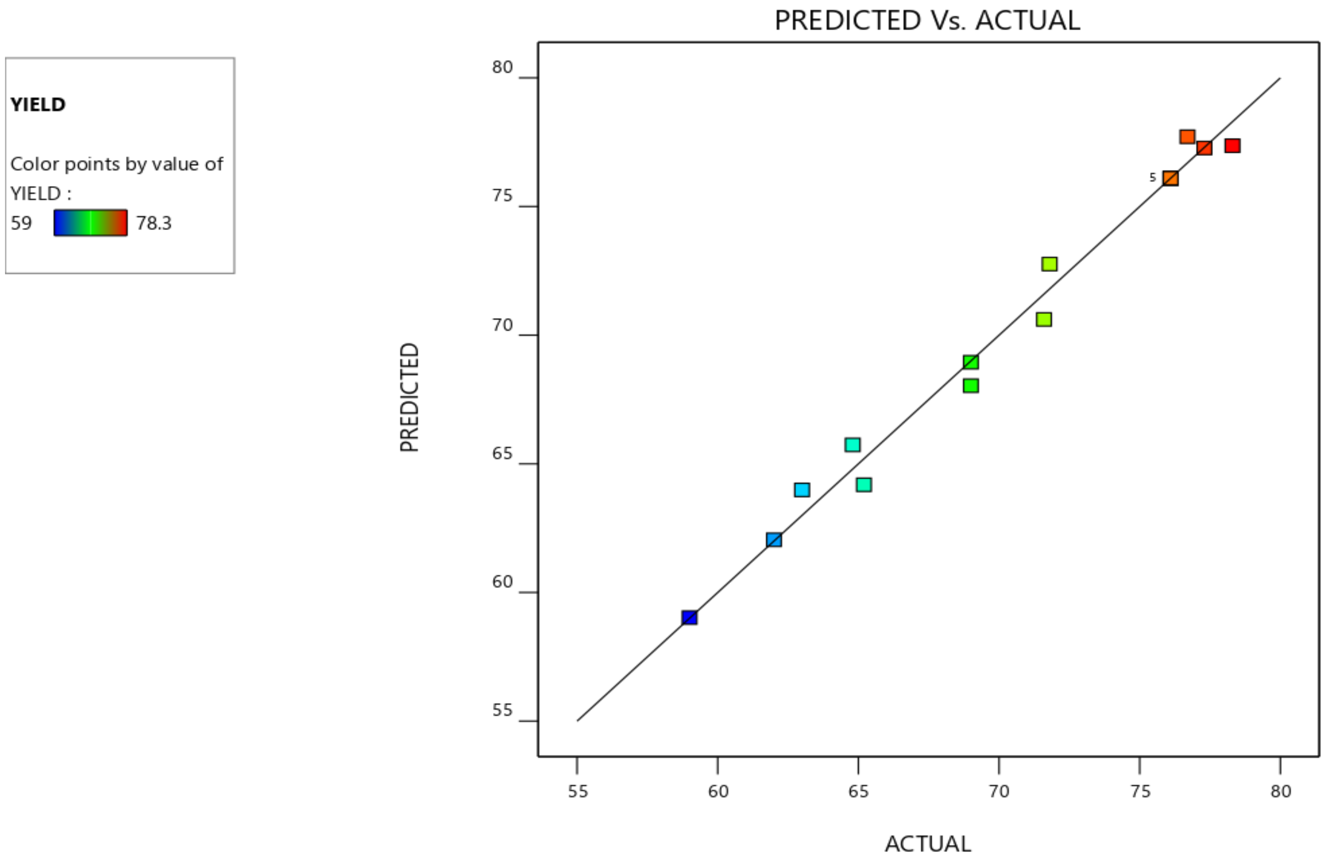


Figure: 4-1. Predicted verses actual responses

4.3. ANOVA for Quadratic model

The statistical analysis of the ANOVA for the response value of α-ferric oxide yield was analyzed using DOE and the result is given in Tables 4.6.

Table 4.6: A quadratic model Analysis of variance (ANOVA) for α-ferric oxide yield

Source	Sum of Squares	df	Mean Square	F-value	p-value	
Model	617.90	9	68.66	63.09	< 0.0001	significant
A-PARTICLE SIZE	316.26	1	316.26	290.62	< 0.0001	
B-CALCINATION TEMP.	1.81	1	1.81	1.66	0.2387	
C-CALCINATION TIME	64.41	1	64.41	59.19	<0.0001	

AB	0.3600	1	0.3600	0.3308	0.5832
AC	7.02	1	7.02	6.45	< 0.0001
BC	9.61	1	9.61	8.83	< 0.0001
Residual	7.62	7	1.09		
Lack of Fit	7.62	3	2.54		
Pure Error	0.4993	4	0.1248		
Cor Total	625.52	16			

The **Model F-value** of 63.09 implies the model is **significant**. There is only a 0.01% chance that an F-value this large could occur due to noise.

P-values less than 0.0500 indicate model terms are significant. In this case A, C, AC, BC are significant model terms where A (particle size), B (calcination Temperature), C (calcination Time). Values greater than 0.1000 indicate the model terms are not significant. If there are many insignificant model terms (not counting those required to support hierarchy), model reduction may improve your model. This tells us that the, particle size, calcination time, and the interaction term AC and BC affect the yield much significantly.

4.4. Effect of process variables on α-ferric oxide yield

Based on the analysis of variance, the α-ferric oxide reaction was significantly affected by numerous interactions between the process variables. Alternatively, significant individual process variables that affect the α-ferric oxide preparation is particle size, A, calcination temperature, B, and calcination time, C. This result proved the advantage of using design of experiments in showing the interaction between variables that affects the α-ferric oxide production.

The analysis of DOE software showed that the α-ferric oxide yield was significantly affected by the individual process variables and by their interaction. The individual process variables that significantly affected the response value was particle size, (A) calcination temperature, (B) and calcination time (C), and the interaction term particle size and calcination time (AC), calcination temperature and calcination time (BC). The individual and interaction effects of the variables are discussed below:

4.4.1. Effect of particle size on the α-ferric oxide yield

As the Figure 4.2 shows the effect of particle size on the α-ferric oxide synthesis yield. It can be seen that with an increase in particle size, the yields of α-ferric oxide decreased significantly. Therefore, it can be said that particle size of iron ore is inversely proportional with the α-ferric oxide yield. Because when the particle size increased the surface area for the reaction will be decreased. This means the rate of reaction also decreased as the surface area decreased.

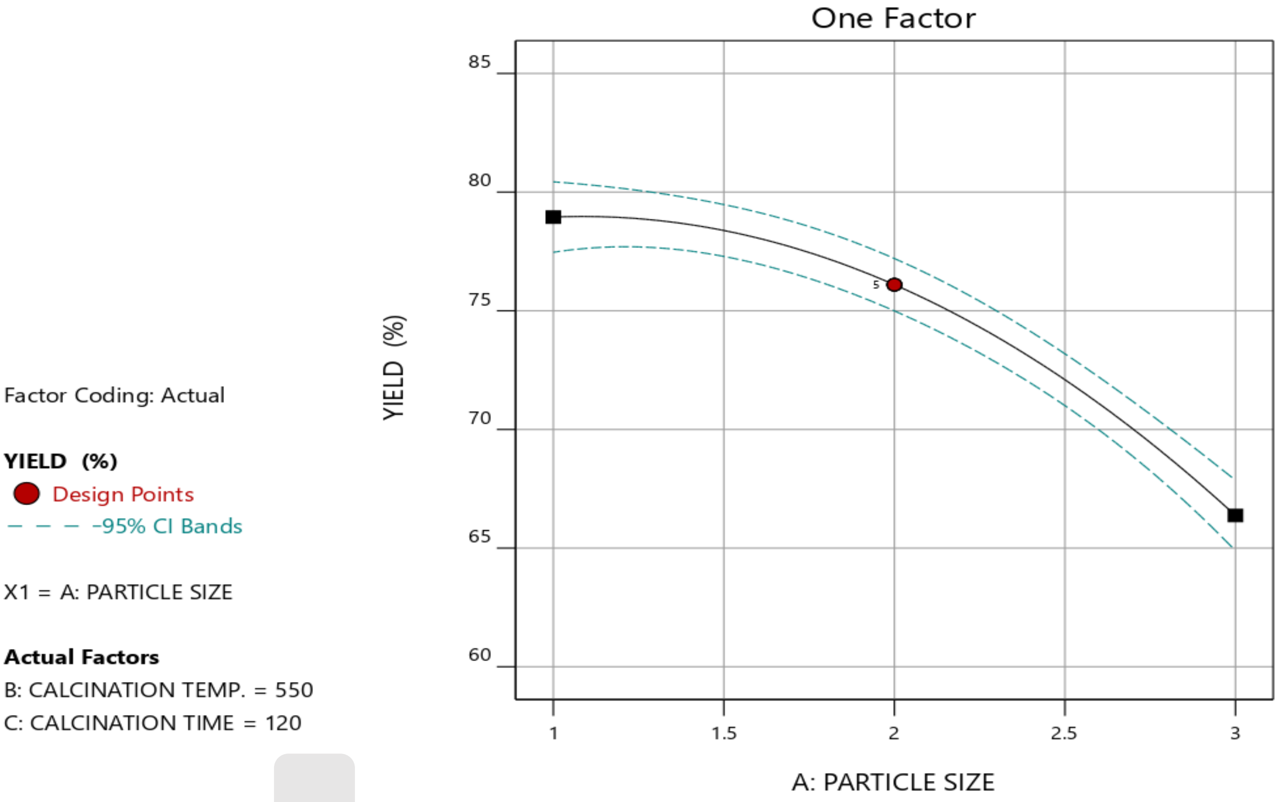


Figure 4.1: the effect of particle size on the α-ferric oxide synthesis yield

4.4.2. Effect of Calcination Temperature on the α-ferric oxide yield

As the Figure 4.2 shows the effect of calcination temperature on the α-ferric oxide synthesis yield. It can be seen that with an increase in calcination temperature, the yields of α-ferric oxide are almost negligible. Therefore, it can be said that calcination temperature has no significance effect on the α-ferric oxide yield [34].

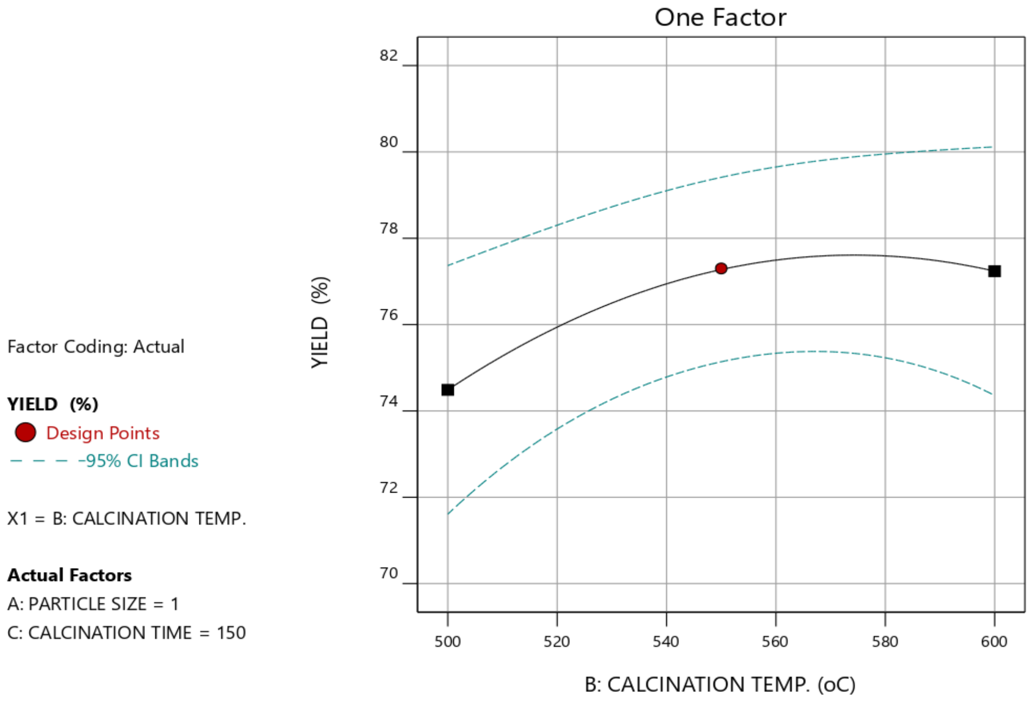


Figure 4.2: the effect of calcination temperature on the α-ferric oxide synthesis yield

4.4.3. Effect of Calcination Time on the α-ferric oxide yield

As the Figure 4.3 shows the effect of calcination time on the α-ferric oxide synthesis yield. It can be seen that with an increase in calcination time, the yields of α-ferric oxide increased significantly. Therefore, it can be said that calcination time is directly proportional with the α-ferric oxide yield. Because, as the reaction takes longer time the rate of reaction is greater so that the reaction speeded up and the yield will be maximum as possible. But, as it can be seen from figure 4.3, additional increase in time above 130 min appears significant decreases on the α-ferric oxide yield, because high calcination time will result to the formation of another unnecessary reaction and products.

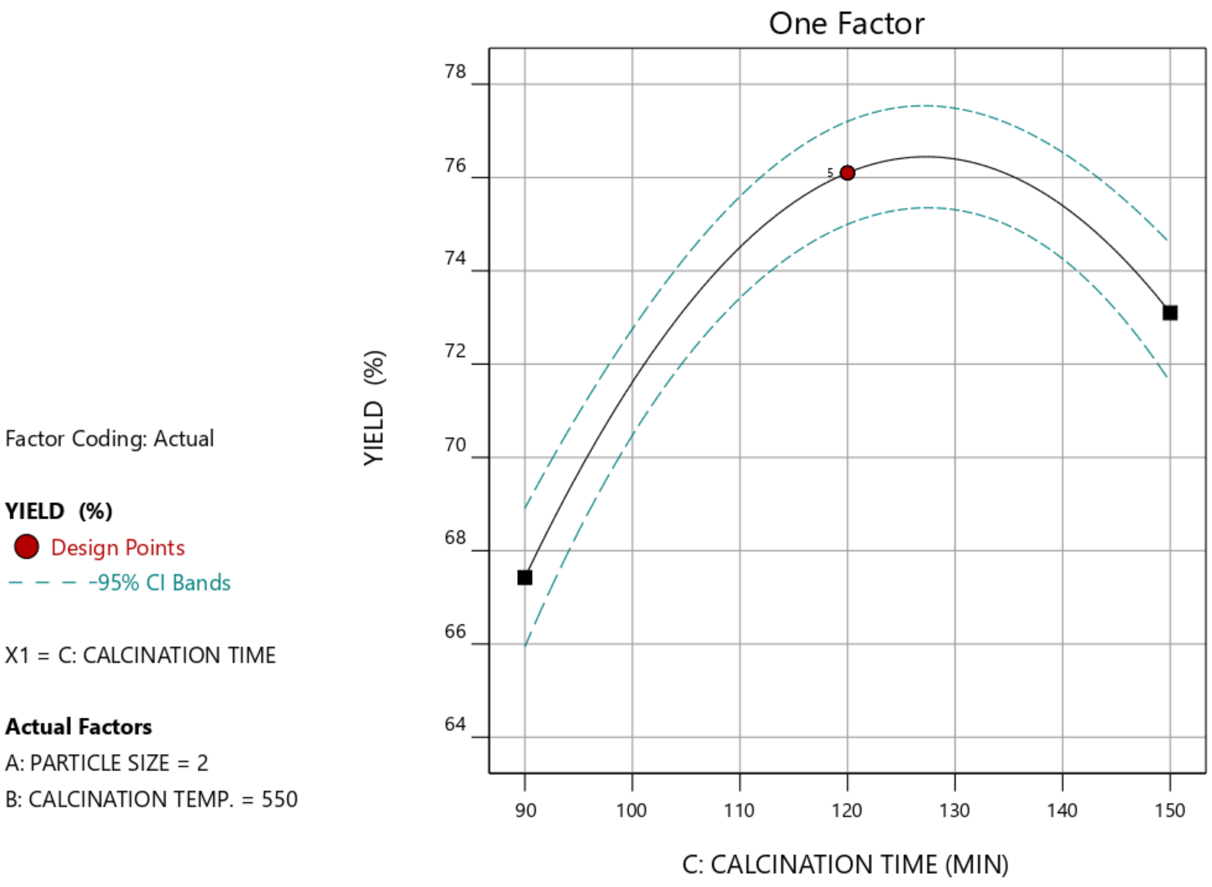


Figure 4.3: the effect of calcination time on the α-ferric oxide synthesis yield

4.4.4. Effect of Interaction between Process Variables

The process variables were found to have significant interaction effects on both particle size and calcination time (AC) and calcination temperature and calcination time (BC). Figure 4.4 show the interaction between particle size and calcination time (AC) on the α-ferric oxide yield.

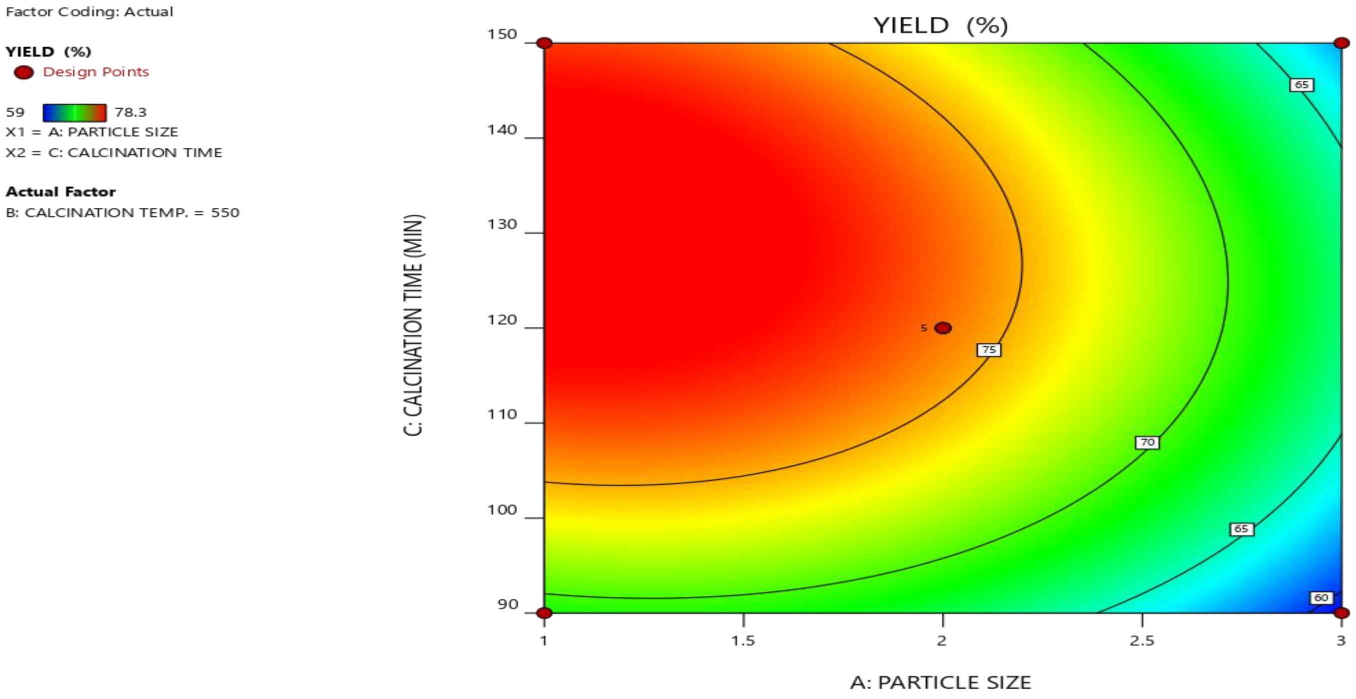


Figure 4.4: Effect of Interaction between Process Variables (particle size vs calcination time)

As shown in the above figure, decreasing particle size and increasing calcination time (AC) will led to found a good yield.

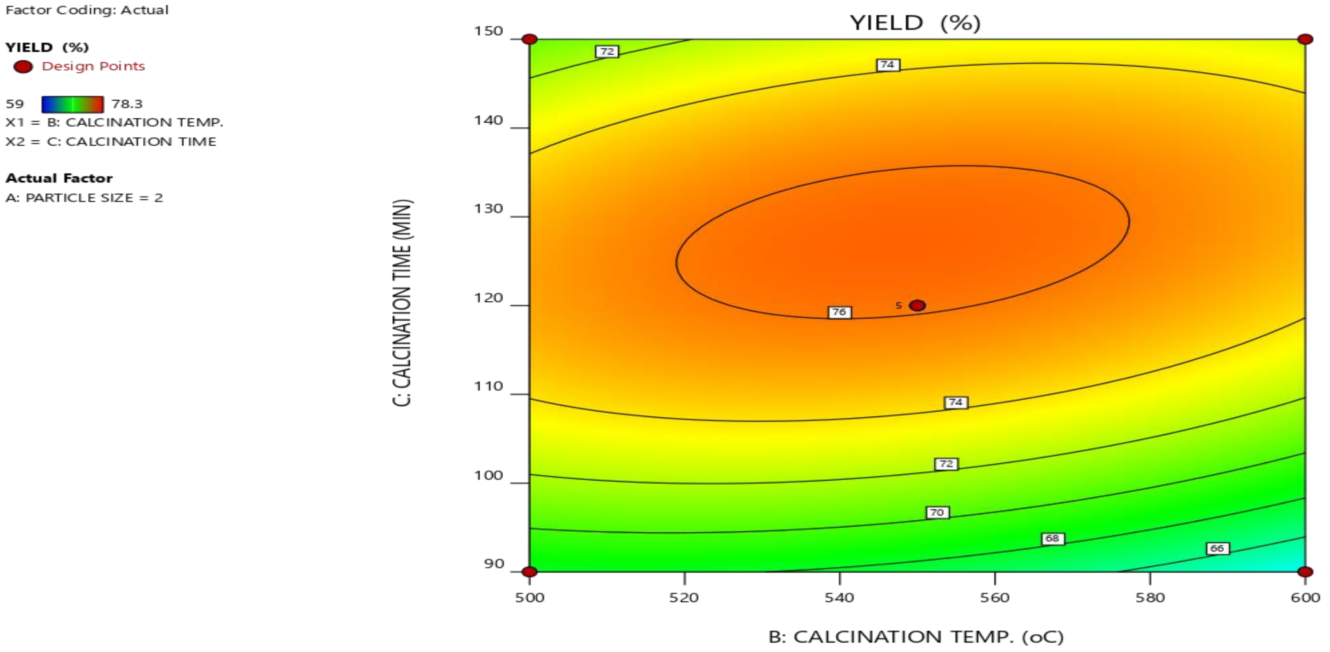


Figure 4.5: Effect of Interaction between Process Variables (calcination temperature vs time)

Figure 4.5 show the interaction between calcination temperature and calcination time (BC) on the α-ferric oxide yield.

As shown in the above figure, calcination temperature and calcination time (AC) process variables will affect the synthesis of α-ferric oxide yield. But, controlling the variables to optimized points will led to found a good yield. But, particle size to calcination temperature (AB) had not significant interaction.

4.5. Optimization of Process Variables

The results above have shown that the three process variables (A, B and C) and the interaction among the (AB, AC and BC) variables affect the α-ferric oxide yield. Therefore, the next step is to optimize the process variables with the aim of obtaining the highest α-ferric oxide synthesis yield using the model regression developed in the previous section.

By using the Design-Expert 12.0 software optimization, it was predicted that at conditions of <0.125mm of particle size, 500 °C reaction temperature and 126.73 minutes reaction time, an optimal yield of 78.005 % can be achieved. To validate this prediction, three experiments were conducted and the average results were equivalent with the prediction. It was found that the average experimental value of 77.103 % yield of α-ferric oxide production.

Table 4.7: Optimization of Process Variables (constraints and solutions)

Constraints

Name	**Goal**	**Lower Limit**	**Upper Limit**	**Lower Weight**	**Upper Weight**
A: Particle Size	Minimize	1	3	1	1
B: Calcination Temp.	Minimize	500	600	1	1
C: Calcination Time	Is in Range	90	150	1	1
Yield	Maximize	59	78.3	1	1

Solutions

Number	**Particle Size**	**Calcination Temp.**	**Calcination Time**	**Yield**	**Desirability**	
1	**1.000**	**500.000**	**126.731**	**78.005**	**0.995**	**Selected**
2	1.000	500.001	126.401	78.004	0.995	
3	1.000	500.001	127.136	78.004	0.995	
4	1.000	500.000	126.051	78.002	0.995	
5	1.000	500.000	127.708	77.998	0.995	

4.5.1. Validation of experimental model

Table 4.7 demonstrate the desired goals for the factors and response of yield of synthesized α-Fe_2O_3 whereas Table 4.8 show the validation test result for optimization verification. Based on Table 4.7, the selected solution generated by Design Expert Software represented the optimum condition to synthesize the highest yield of synthesized α-Fe_2O_3. The avarage yield of synthesized α-Fe_2O_3 obtained was 77.103 % at particle size 1 (<0.125 mm), 500 °C and for 126.73 minutes. The average error or difference between the value of predicted yield (78.005%) and actual experimental value was only small percentage error of 1.161 %. Since the percentage error was less than 5 %, it can be concluded that designated solution condition has been validated.

Table 4.8: Validation test result for optimization verification.

Run	A: Particle size	B: Calcination temperature (°C)	C: Calcination time (Min.)	Current response of yield of synthesized α-Fe_2O_3		
				Predicted	experimental	Error (%)
1	PS 1	500	126.73	78.005 %	77.41 %	0.778 %
2	PS 1	500	126.73	78.005 %	76.82 %	1.519 %
3	PS 1	500	126.73	78.005 %	77.08 %	1.185 %
Average					**77.103 %**	1.161 %

Since, temperature has no significance effect using high temperature leads to high energy usage and it makes it expensive. Therefore, we should use minimum temperature (500 °C), minimum particle size and calcination time in the range.

4.6. Physco-chemical properties of α-ferric oxide

The physical and chemical properties of the α-ferric oxide from local iron ore was characterized by the methods directed in chapter three under section 3.3 as follow.

4.6.1. Moisture content

The moisture content of the α-ferric oxide was theoretically expected to be less than 10%w/w. The average moisture content of the synthesized α-ferric oxide is 2.655 % according to ISO 1248:2006(E), 2008, it's acceptable [27].

Table 4.10: Moisture content

Run	Weight of the sample in crucible before drying (g)	Weight of the sample in crucible after drying (g)	Weight Difference (g)	Moisture content (%w/w)
1	12.524	12.21	0.314	2.571
2	12.524	12.30	0.224	1.821
3	12.524	12.092	0.432	3.572
Mean value	**12.524**			**2.655**

4.6.2. Density

The density of the α-ferric oxide was theoretically expected to be in the range 4.0 - 5.25 g/cm3 at different process parameters. The average density of the synthesized α-ferric oxide is 5.183 g/cm3 with the ISO 1248/2006/cor. 2/2008-E, 2007 for α-ferric oxide, it is acceptable [25].

Table 4.11: specific gravity/ density

Run	**Density (g /cm3)**
1	5.43
2	4.97

3	5.15
Mean value	**5.183**

4.6.3. pH determination

The preferable theoretical pH value of synthesized α-ferric oxide is in the range of 6.0-7.0. and the average PH of the synthesized α-ferric oxide is 6.48 with the ISO 1246/2008-E,2007 for α-ferric oxide, it is acceptable.

Table 4.12: pH determination

Run	**pH values**
1	6.15
2	6.87
3	6.43
Mean value	**6.48**

4.6.4. Matter soluble in water

The soluble matter of the α-ferric oxide was theoretically expected to be less than 1% at different process parameters. The average soluble matter of the synthesized α-ferric oxide is0.0373% with the ISO 15528:2013(E), 2013 for α-ferric oxide, it is acceptable [26].

Table 4.13: determination of matter soluble in water

Run	Water soluble matter (wt. %)
1	0.018
2	0.032
3	0.062
Mean value	**0.373**

4.6.5. Loss On Ignition

The LoI of the α-ferric oxide was theoretically expected to be less than 0.5% at different process parameters. The LoI of the synthesized α-ferric oxide is 0.373% with the ISO 787/2/1981-E, 2000 for α-ferric oxide, it is acceptable [24].

Table 4.13: determination of LoI (loss on ignition)

Run	LoI (wt. %)
1	0.18
2	0.32
3	0.62
Mean value	**0.374**

4.6.6. X-Ray Diffraction Structure Analysis of synthesized α-Fe_2O_3

X-Ray Diffraction investigation (XRD) is a method utilized in materials science to decide the crystallographic design of a material. XRD works by lighting a material with occurrence X-ray and afterward estimating the powers and dispersing points of the X-ray that leave the material.

The technique for X-ray diffraction (XRD) was utilized to decide the material's crystal structure and particle size of synthesized α-ferric oxide. Determination of crystallite size and phase composition was generated by using wavelength of Cu-Kα at ($\lambda = 1.5406$ nm) over 2θ range of 20^o to 70° proceed with scanning rate of 2°/min. Figure 4.7 shows the typical XRD patterns of the as-prepared samples. It can be seen clearly from Figure 4.8 that the reflection peaks of synthesized α-Fe_2O_3 sample can be perfectly distributed.

According to Scherrer, if the crystallites in a powder are sufficiently small, the maxima of diffraction pattern are broadened by an amount inversely proportional to the crystallite size, and measurement of additional broadening thus gives a means of estimating the size through the formula. By using Scherrer equation, crystallite size of synthesized α-Fe_2O_3 was calculated with the use of full width at half maximum at the peak broadening of diffraction reflection which occurred at $2\theta = 33.40°$.

The major phase observed in the XRD scans of the synthesized sample is α-Fe_2O_3 (the main peaks appearing at 2θ of 33.40^o [30].

$$D = \frac{k * \lambda}{FWHM * Cos\theta}$$

Where, D is the apparent crystallite size,

λ is the wavelength radiation for Cu-Kα,

FWHM is full width at half maximum of diffraction peak (rad), and

θ is the Bragg angle.

The calculated crystallite size using Scherrer formula of the synthesized α-ferric oxide is approximately 14nm. And the diffraction peaks were seen at $2\theta = 24.38, 30.14, 33.40, 35.92, 41.14$.

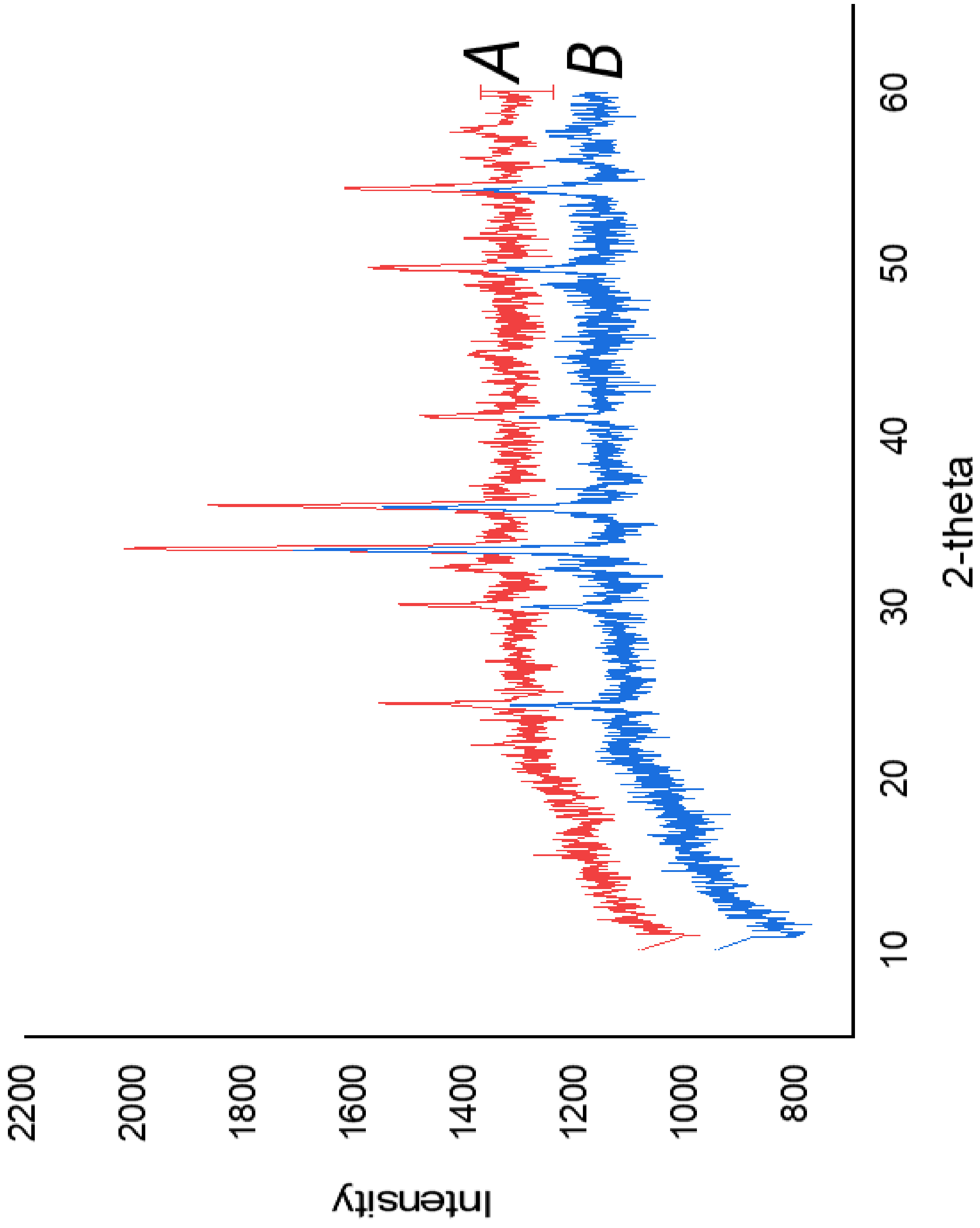


Figure 4.7: α-ferric oxide A) XRD analyzed in AAU and B) XRD analyzed in ASTU

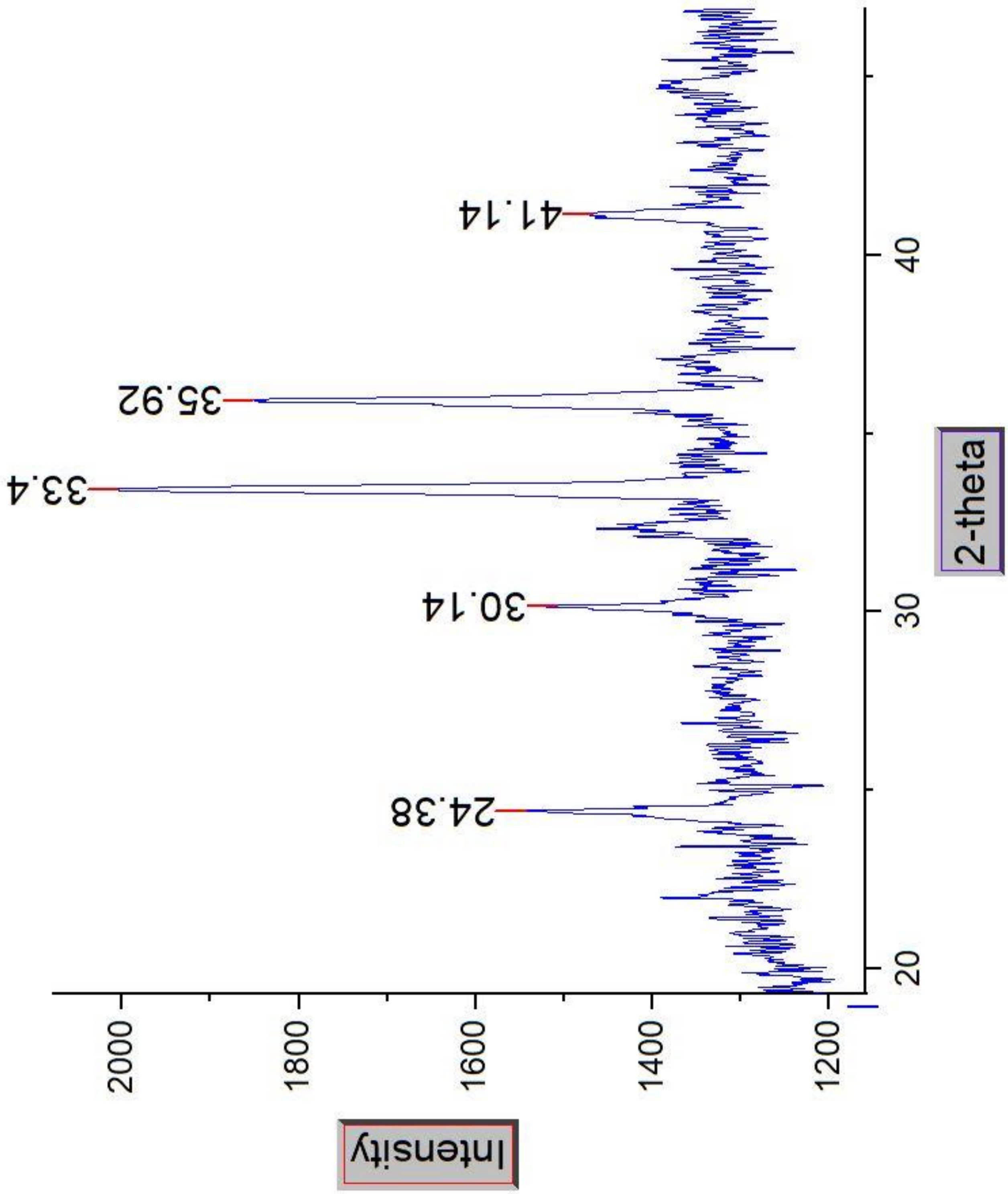


Figure 4.8: α-ferric oxide XRD pattern and found peaks

4.6.7. Fourier Transform Infrared (FT-IR)

Fourier transform infrared spectroscopy (FTIR) utilizes the numerical interaction (Fourier change) to decipher the crude information (interferogram) into the real range. FTIR technique is utilized to get the infrared range of transmission or ingestion of a fuel test. FTIR distinguishes the presence of natural and inorganic mixtures in the example. Contingent upon the infrared ingestion recurrence range 600–4000 cm−1, the particular sub-atomic gatherings winning in the example not set in stone through range information in the robotized programming of spectroscopy. It is one of the analytical methods which used to reveal the functional groups present in the given sample.

A Comparison of the FTIR spectra of the synthesized α-ferric oxide could give information regarding the functional groups of the α-ferric oxide particles. The prominent bands at 450 cm^{-1} and 615.3 cm^{-1} observed in the spectrum in figure 4.9 can be attributed to Fe–O functional groups. Therefore, the synthesized particles which is α-ferric oxide have a Fe-O functional group[23]. And a small bend around 1646.9 cm^{-1} indicates a small portion of atmospheric carbon dioxide (CO_2).

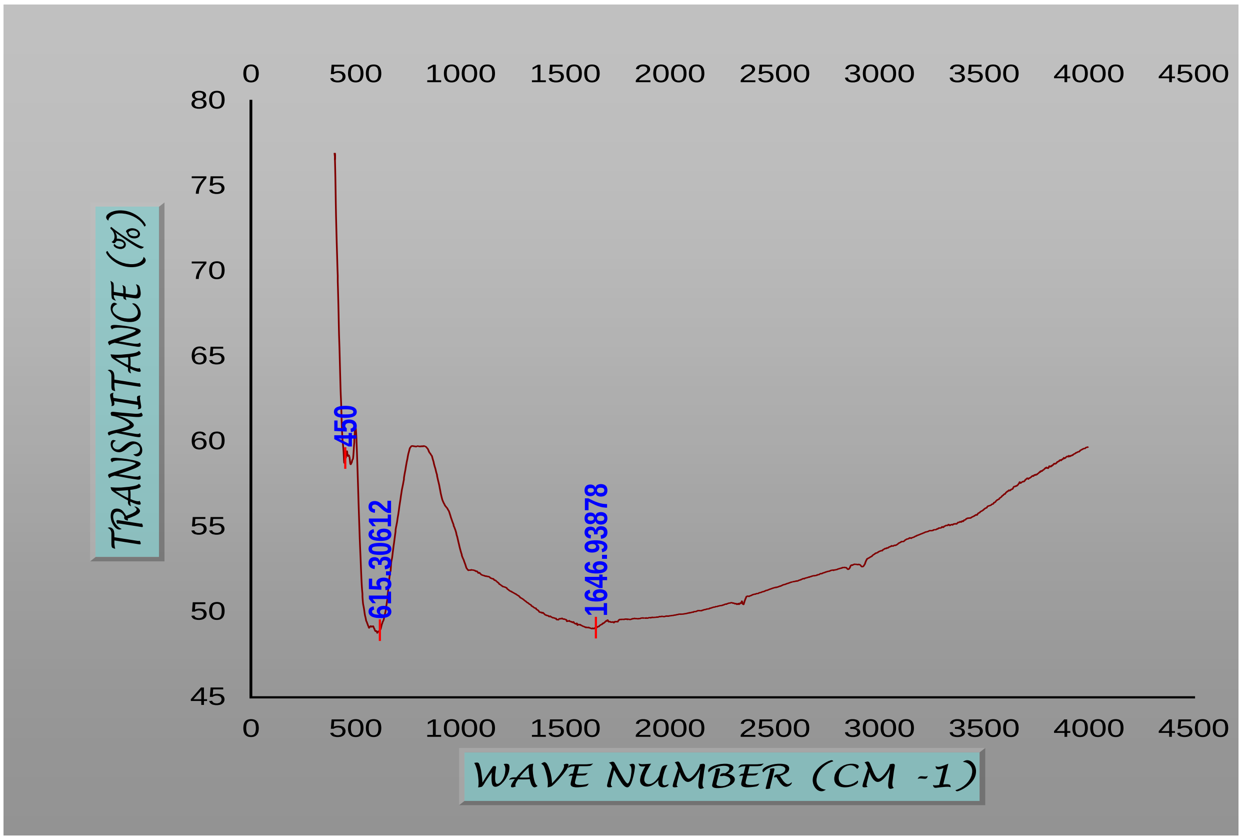


Figure 4.9: Fourier Transform Infrared (FT-IR) of synthesized α-ferric oxide particles

4.6.8. Major and minor oxides analysis

For major and minor oxides analysis by wavelength dispersive X-ray fluorescence spectrometry (XRFS) was used. Trace elements were determined on loose-powder specimens by energy-dispersive XRFS using procedures and algorithms of Johnson and King[21]. Major element analysis was prepared by fusing the standard reference samples with pure lithium tetraborate flux. An 800-mg portion of powder (dried at 105°C) was ignited to **20** min or longer in a muffle furnace at 925°C. The ignitions were done in a muffle furnace with its window removed. After the loss on ignition (LOI) was determined gravimetrically, the residue was mixed with 8 g of anhydrous $LiB0_2$ flux. A 0.250-ml aliquot of LiBr solution [21].

This major and minor oxides analysis was done in Geological Survey of Ethiopia (Addis Ababa around SARBET) laboratory. The synthesized α-ferric oxide was characterized by LiBO2 FUSION, HFattack, GRAVIMETERIC, CALORIMETIC and AAS methods. And the result showed in appendix C which found 91.56% of Fe_2O_3, 1.81% SiO_2 and 6.96 Al_2O_3 this result is acceptable according to the ISO standard.

CHAPTER FIVE

5. CONCLUSION AND RECCOMONDATION

CONCLUSSION

In this study, α-ferric oxide is prepared and characterized from local raw materials available in Ethiopia. α-ferric oxide was synthesized using local iron ore with hydrochloric acid and ammonium hydroxide. As known, different parts of Ethiopia are rich in iron ore especially Oromia (wollega) and Tigray Region (Axum).

The Synthesis was performed by batch process system at atmospheric pressure. And then, the effects of particle size, calcination temperature and calcination time were studied using Design expert version 12.0.0 software. The statistical analysis showed that the effects of particle size, calcination temperature and calcination time, and the interaction between those variables had significant effects on the yield of α-ferric oxide production. Three levels and three factors in box-Behnken design method with full type calibration is used. The result from the design expert data gives the optimum value for the three processing variables: A: particle size <0.125mm, B: calcination temperature = 500 °C and C: calcination time =126.73 minutes. At these parameters value the yield found is 77.103%.

The physicochemical properties of the synthesized α-ferric oxide were tested against ISO and ASTM specifications and according to the standards, the results are acceptable. Which means the results proved that the synthesized α-ferric oxide from local iron ore has nearly similar physicochemical properties as compared with other imported α-ferric oxide.

The determination coefficient (R2) obtained was 0.9878. The model F-value obtained was 63.09 and p-value < 0.0001 indicated this model was statistically significant. The optimization of the α-ferric oxide synthesis was completed successfully to achieve higher yield.

The result of Fourier Transform Infrared Spectroscopy (FTIR) analysis showed the synthesis of the α-ferric oxide by using local iron ore discovered two main functional groups Fe-O group and atmospheric CO_2. X-ray Diffraction (XRD) analysis has confirmed the presence of α-Fe_2O_3 occurred at the peak of $2\theta = 33.4°$. In addition, Major and minor oxide analysis showed 91.56% of Fe_2O_3 which is acceptable purity.

RECOMMENDATIONS

The main discovery of this research is α-ferric oxide from abundantly available iron ore in Ethiopia. This synthesized α-ferric oxide used for the different applications but in this research, it is used as a pigment for paint industries. Therefore, if some further research work is carried out recommended studies are:

- There are many factors that affect the yield of α-ferric oxide; but for this study only the three main factors are considered (particle size, calcination temperature and calcination time). It is promising to test other factors like, iron ore from different location, hydrochloric acid concentrations, ammonium hydroxide concentration and PH of the mixture.
- It is recommended to perform preliminary design, economic feasibility study and set up mini scale plant for production of α-ferric oxide.

- It is recommended to analyze the synthesized α-ferric oxide's oil absorption behavior and particle shape.
- Finally, this study confirm that Ethiopia has a lot of iron ore deposits which has to be used to synthesize useful products like α-ferric oxide.

REFERENCES

[1] R. M. Cornell and U. Schwertmann, The Iron Oxides, Structure, Properties, Reactions, Occurences and Uses, 2nd ed, WILEY-VCH GmBh &Co.KGaA, 2003, pp. 1-7.

[2] E. A. Campos, D. V. B. S. Pinto, J. I. S. de Oliveira, E. da C. Mattos, and R. de C. L. Dutra, "Synthesis, characterization and applications of iron oxide nanoparticles - A short review," J. Aerosp. Technol. Manag., vol. 7, no. 3, pp. 267–276, 2015, doi: 10.5028/jatm.v7i3.471.

[3] R. Zboril, M. Mashlan, and D. Petridis, "Iron (III) Oxides from Thermal Processes Synthesis ," Chem. Mater., vol. 14, no. Iii, pp. 969–982, 2002.

[4] "Profile on the Production of RED OXIDE PAINT," 2012.

[5] Idris Zeherudin (PhD), Alem Baraki (Msc) and Hadush Berhe (Msc), "Study of development of iron ore and metallurgy industries : challenges , prospects and policy / strategy Addis Ababa , Ethiopia FDRE," 2017.

[6] Osama R. Shaltamia, Daniela de Moraisb, Fares F. Faresa, Farag M. EL Oshebia, Hwedi Errishic and Ilas Bustanyd, "IRON ORES: A REVIEW" 22 th International Conference on Ore Deposits University of Dar es Salaam (UDSM) Proceeding Book GOLD-BEARING VEINS, September, 2020.

[7] J. I. Goldstein, E. R. D. Scott, and N. L. Chabot, "Iron meteorites: Crystallization, thermal history, parent bodies, and origin," Chemie der Erde, vol. 69, no. 4, 2009, pp. 293–325. doi: 10.1016/j.chemer.2009.01.002.

[8] INESON,J.R. & SURLYK, F., "Geological Survey of Denmark and Greenland Bulletin", Printed in the United Kingdom in 2004 Cambridge University Press., vol. 141, no. 6, 2004,p p. 739–740 doi: 10.1017/s0016756804210019.

[9] OxyChem, "Hydrochloric Acid Handbook, Introduction to hydrochloric acid,", october, 2012, pp. 1–47.

[10] L. E. West and A. Wilson, "The preparation of ammonium hydroxide for laboratory use," J. Chem. Educ., vol. 19, no. 9, 2012, , pp. 418–419. doi: 10.1021/ed019p418.

[11] R. Onyenwoke and J. Wiegel, "Magnetite : Structure , Properties and Applications," no.

January 2011, 2014.

[12] B. M. Moskowitz, M. Jackson, and V. Chandler, Geophysical Properties of the Near-Surface Earth: Magnetic Properties, Elsevier B.V, vol. 11., 2015.

[13] M. Muhajir, P. Puspitasari, and J. A. Razak, “Synthesis and Applications of Hematite α-Fe_2O_3 : a Review,” J. Mech. Eng. Sci. Technol., vol. 3, no. 2, 2019, pp. 51–58, doi: 10.17977/um016v3i22019p051.

[14] C. Wu, P. Yin, X. Zhu, C. OuYang, and Y. Xie, “Synthesis of hematite (α-Fe2O3) nanorods: Diameter-size and shape effects on their applications in magnetism, lithium ion battery, and gas sensors,” J. Phys. Chem. B, vol. 110, no. 36, 2006, pp. 17806–17812. doi: 10.1021/jp0633906.

[15] Horiba Instruments, Inc., "Particle Size Distribution Analyzer on iron oxide, Application note", Irvine, CA 92614 USA, internet: www.horiba.com, 2004.

[16] A. A. Almarasy, S. A. Azim, and E. Zeiny, “The application of hematite (α - Fe 2 O 3) nanoparticles in coagulation and flocculation processes of River Nile Rosetta branch surface water,” SN Appl. Sci., vol. 1, no. 1, 2019. pp. 1–6, doi: 10.1007/s42452-018-0006-y.

[17] U. T. Lam, R. Mammucari, K. Suzuki, and N. R. Foster, “Processing of iron oxide nanoparticles by supercritical fluids,” Ind. Eng. Chem. Res., vol. 47, no. 3, 2008, pp. 599–614, doi: 10.1021/ie070494+.

[18] M. Legodi, “The preparation of magnetite , goethite , hematite and maghemite of pigment quality from mill scale iron waste,” no. December 2007, 2018, doi: 10.1016/j.dyepig.2006.01.038.

[19] L. Durães., “Sol-gel synthesis of iron (III) oxyhydroxide nanostructured monoliths using Fe (NO)* 9HO / CHCHOH / NHOH ternary system,” no., 2012, doi: 10.1016/j.jpcs.2011.02.020.

[20] S. parker, X. Zhu, “Scientific Opinion on the re-evaluation of iron oxides and hydroxides,” vol. 13, no. 12, 2015, pp. 1–57, doi: 10.2903/j.efsa.2015.4317.

[21] Davison V. VIVIT and Bi-Shia Wang KING “the determination of major oxide and trace element concentrations in eighteen chinese standard reference by x-ray fluorescence

spectrometry," U.S. Geological Survey, 345 Middlefield Road, Menlo Park, California 94025, U.S.A vol. 12,2008, pp. 363–370.

[22] O. Heiri, Andre Lotter and Gerry Lemcke Swiss "Loss on Ignition as a Method for Estimating Organic and Carbonate Content in Sediments : Reproducibility and Comparability of Results" Article in Journal of Paleolimnology · January 2001 no., January 2016, DOI: 10.1023/A:1008119611481.

[23] A. Rufus, N. Sreeju, and D. Philip, "Synthesis of biogenic hematite (a-Fe2O3) nanoparticles for antibacterial and nanofluid applications," journal by royal society of chemisry, vol. 3, pp. 94206–94217, september 2016, doi: 10.1039/c6ra20240c.

[24] International Organization For Standardization Information Handling Services, "general method of test for pigment and extenders, part 2, determination of volitile matter", firt edition, ref. no. ISO 787/2/1981-E, 2000.

[25] International Organization For Standardization "Iron oxide pigments - Specifications and methods of test, paint and varnishes " ref. no. ISO 1248/2006/cor. 2/2008-E, 2007.

[26] International Organization For Standardization and I. H. S. Licensee, "Paints, varnishes and raw materials for paints and varnishes — Sampling," 2nd edition, ef. no. ISO 15528:2013(E) ,2013.

[27] International Organization For Standardization "Iron oxide pigments - Specifications and methods of test, paint and varnishes " 2nd edition, Reference number ISO 1248:2006(E), 2008.

[28] Ali Mufida and Mochamad Zainuri, "The Influence of Calcination Temperature on Quantitative Phase of Hematite from Iron Stone Tanah Laut", Trans Tech Publications, Switzerland, Vol. 1112, pp 489-492, 2015.

[29] B. Getachew," Production , optimization and characterization of ferrous sulfate from local iron ore" By : Birhan Getachew ,Addis Ababa University" pp. 48-54, 2017.

[30] A. J. B. Muwanguzi, A. V Karasev, J. K. Byaruhanga, and G. J, "Characterization of Chemical Composition and Microstructure of Natural Iron Ore from Muko Deposits," vol. 2012, 2012, doi: 10.5402/2012/174803.

[31] J. A. Selvakumar and R. Thirumalaikumar, "Removal of Sulphur Dioxide by Ferric Oxide In Packed Bed And Analyze Break Through Curves And Mass Transfer Zone," International Journal of Engineering Research & Technology vol. 1, no. 9, pp. 1–9, 2012.

[32] L. Rahman, S. Bhattacharjee, S. Islam, F. Zahan, B. Biswas, and N. Sharmin, "particles from iron-containing waste materials A study on the preparation and characterization of maghemite (γ -Fe 2 O 3) particles from iron-containing waste materials," J. Asian Ceram. Soc., vol. 00, no. 00, pp. 1–12, 2020, doi: 10.1080/21870764.2020.1812838.

[33] S. K. Vishwanath, D. Kim, J. Kim, and C. Chen-tao, "Hematite from Natural Iron Stones as Microwave Absorbing Material on X-Band Frequency Ranges," IOP Conference of Materials Science and Engineering 2016 ,2017, doi: 10.1088/1757-899X/196/1/01.

[34] U. Islam et al., "Synthesis of Hematite Pigments (α -Fe2O3) by Thermal Transformations of Synthesis of Hematite Pigments (α -Fe 2 O 3) by Thermal Transformations of FeOOH," no. March, 2013.

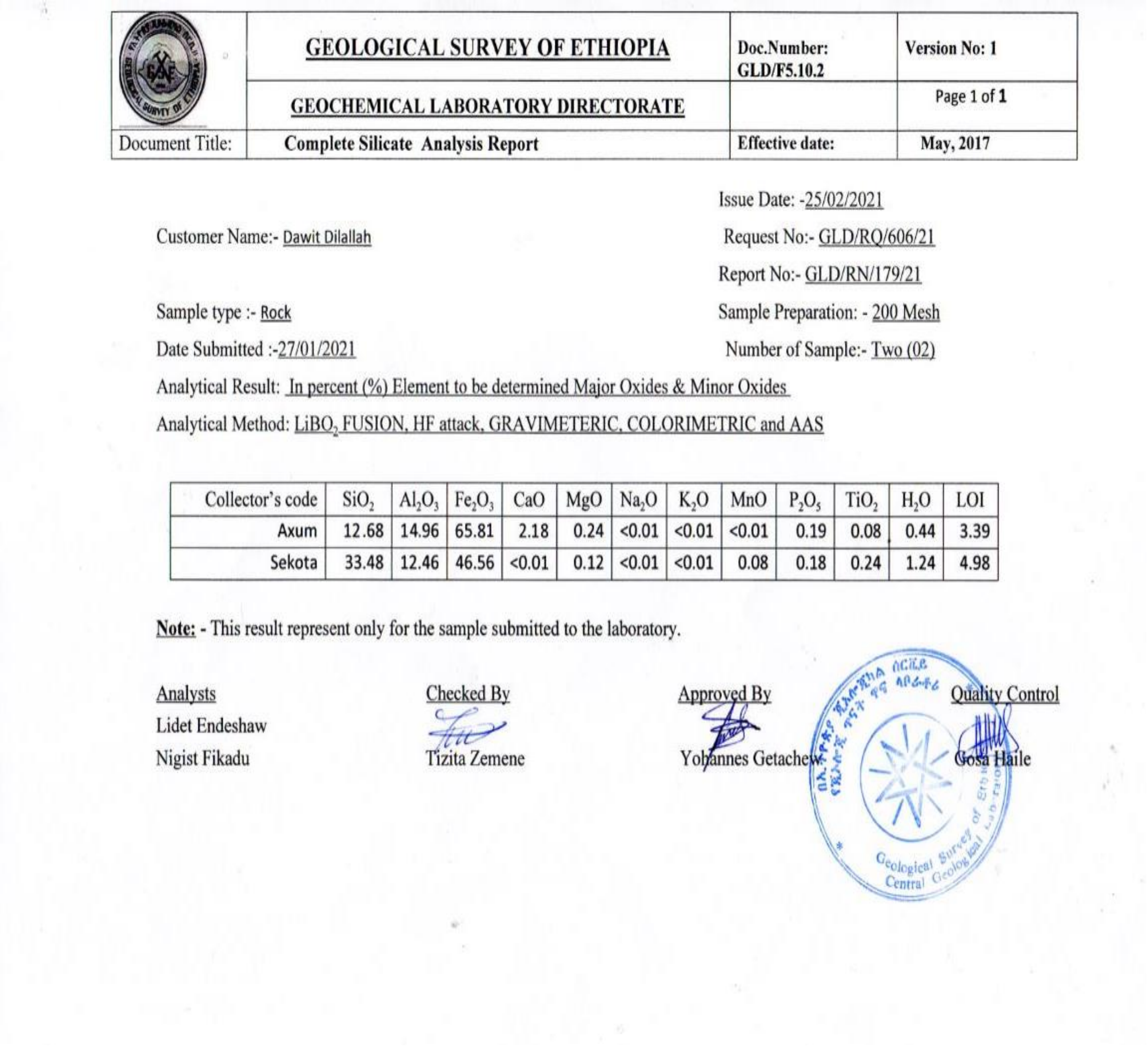
[35] Alafara Abdullahi Baba and Folahan Adekola "Quantitative Leaching of a Nigerian Iron Ore in Hydrochloric Acid", Article in Journal of Applied Sciences and Environmental Management, November 2006. DOI: 10.4314/jasem.v9i3.17346.

[36] Joan J. Kiptarus, Alex M. Muumbo, Augustine B. Makokha and Stephen K. Kimutai, "Characterization of Selected Mineral Ores in the Eastern Zone of Kenya: Case Study of Mwingi North Constituency in Kitui County", International Journal of Mining Engineering and Mineral Processing, 2015.DOI: 10.5923/j.mining.20150401.02

[37] K. G. Sebehanie, A. V. Del Rosario, A. Y. Ali, and O. E. Femi, "Production of magnetite nanoparticles from Ethiopian iron ore using solvent extraction and studying parameters that affect crystallite size," *Mater. Res. Express*, vol. 7, no. 10, 2020, doi: 10.1088/2053-1591/abc2df.

APPENDICES

Appendix A: complete major and minor oxides analysis of raw materials



	GEOLOGICAL SURVEY OF ETHIOPIA	**Doc.Number: GLD/F5.10.2**	**Version No: 1**
	GEOCHEMICAL LABORATORY DIRECTORATE		Page 1 of **1**
Document Title:	**Complete Silicate Analysis Report**	**Effective date:**	**May, 2017**

Issue Date: -25/02/2021

Customer Name:- Dawit Dilallah

Request No:- GLD/RQ/606/21

Report No:- GLD/RN/179/21

Sample type :- Rock

Sample Preparation: - 200 Mesh

Date Submitted :-27/01/2021

Number of Sample:- Two (02)

Analytical Result: In percent (%) Element to be determined Major Oxides & Minor Oxides

Analytical Method: $LiBO_2$ FUSION, HF attack, GRAVIMETERIC, COLORIMETRIC and AAS

Collector's code	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	MnO	P_2O_5	TiO_2	H_2O	LOI
Axum	12.68	14.96	65.81	2.18	0.24	<0.01	<0.01	<0.01	0.19	0.08	0.44	3.39
Sekota	33.48	12.46	46.56	<0.01	0.12	<0.01	<0.01	0.08	0.18	0.24	1.24	4.98

Note: - This result represent only for the sample submitted to the laboratory.

Analysts	Checked By	Approved By	Quality Control
Lidet Endeshaw Nigist Fikadu	Tizita Zemene	Yohannes Getachew	Gosa Haile

Appendix B: some pictures during the research

Sample of Iron ore from SEKOTA region

Sample of iron ore from AXUM region

Milling the iron ore by RETSCH (5657 HAAN) miller

Sieve shaker analyzer

Cont.

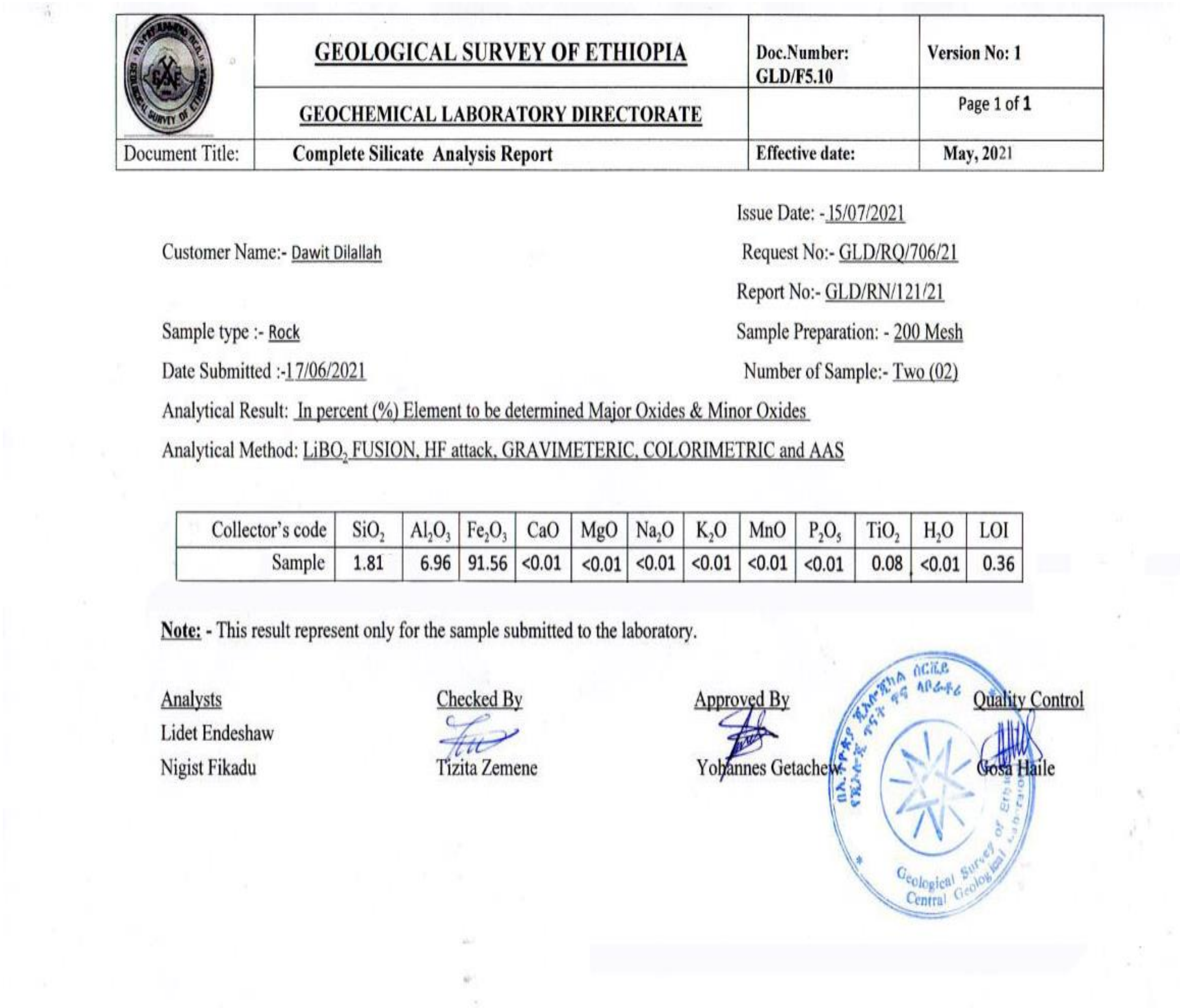
Reacting the ore with HCl in heater with magnetic stirrer

Filtering the cake formed in Vacuum pump

Drying the filtered cake in Oven and incubator at 105°C

Calcining FeOOH in Muffle furnace at 550°C

Appendix C: complete major and minor oxides analysis of synthesized α-ferric oxide



	GEOLOGICAL SURVEY OF ETHIOPIA	**Doc.Number: GLD/F5.10**	**Version No: 1**
	GEOCHEMICAL LABORATORY DIRECTORATE		Page 1 of **1**
Document Title:	**Complete Silicate Analysis Report**	**Effective date:**	**May, 2021**

Issue Date: - 15/07/2021

Customer Name:- Dawit Dilallah

Request No:- GLD/RQ/706/21

Report No:- GLD/RN/121/21

Sample type :- Rock

Sample Preparation: - 200 Mesh

Date Submitted :-17/06/2021

Number of Sample:- Two (02)

Analytical Result: In percent (%) Element to be determined Major Oxides & Minor Oxides

Analytical Method: $LiBO_2$ FUSION, HF attack, GRAVIMETERIC, COLORIMETRIC and AAS

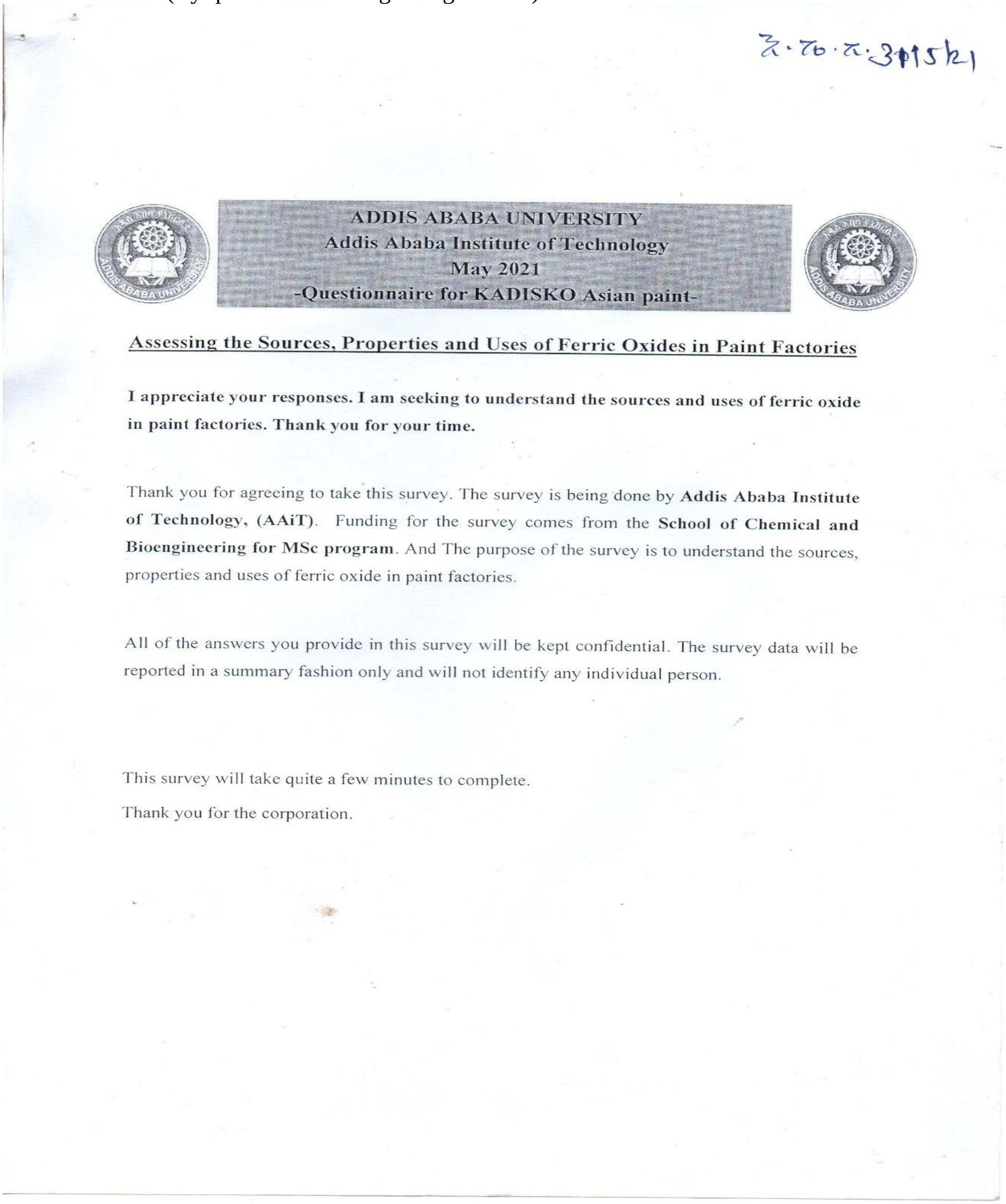
Collector's code	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	MnO	P_2O_5	TiO_2	H_2O	LOI
Sample	1.81	6.96	91.56	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.08	<0.01	0.36

Note: - This result represent only for the sample submitted to the laboratory.

Analysts	Checked By	Approved By	Quality Control
Lidet Endeshaw Nigist Fikadu	Tizita Zemene	Yohannes Getachew	Gosa Haile

Appendix D: questionnaires filled by Kadisco Asian Paints

(By: production manager Eng. Daniel)



[illegible] 3/15/21

ADDIS ABABA UNIVERSITY
Addis Ababa Institute of Technology
May 2021
-Questionnaire for KADISKO Asian paint-

Assessing the Sources, Properties and Uses of Ferric Oxides in Paint Factories

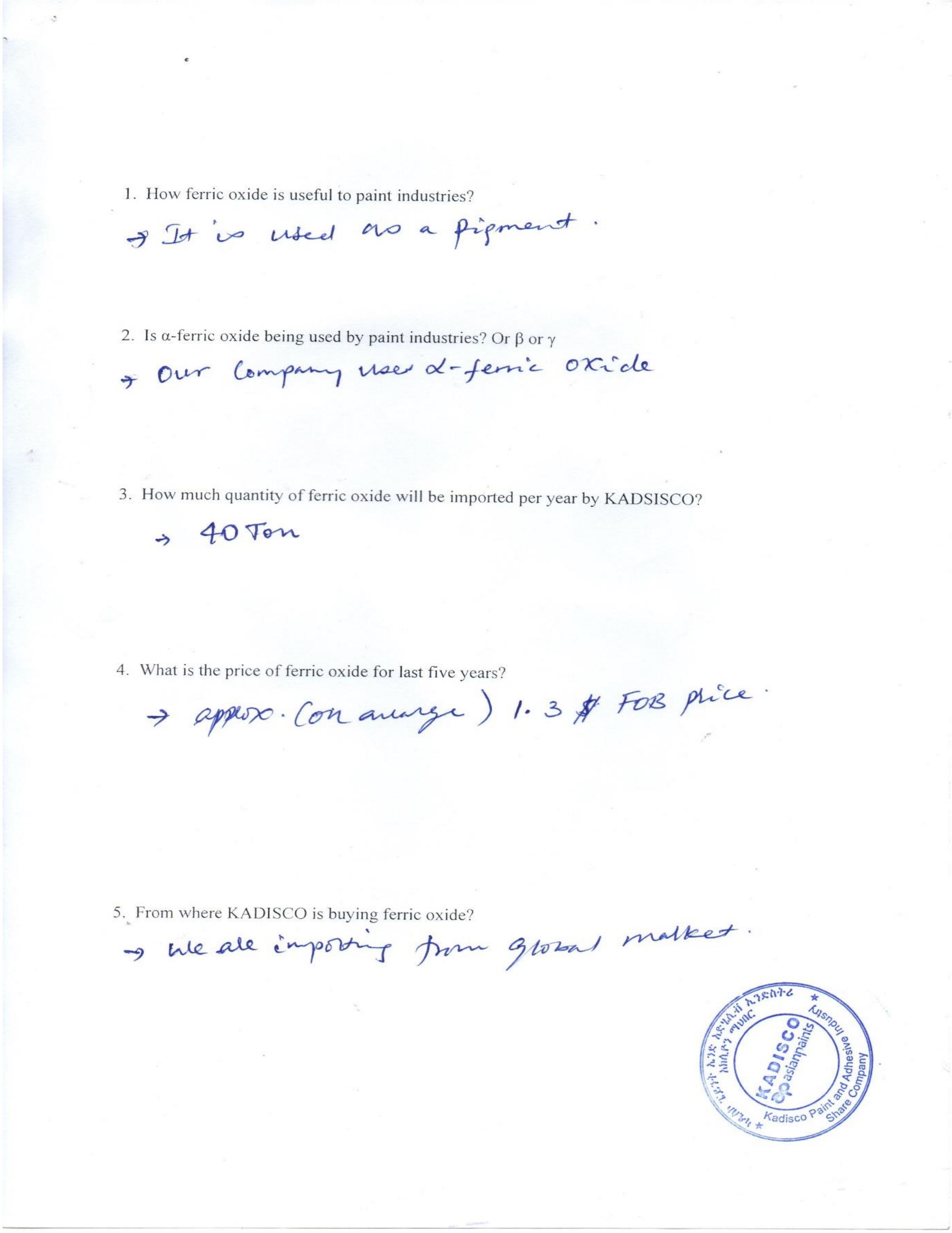
I appreciate your responses. I am seeking to understand the sources and uses of ferric oxide in paint factories. Thank you for your time.

Thank you for agreeing to take this survey. The survey is being done by **Addis Ababa Institute of Technology, (AAiT)**. Funding for the survey comes from the **School of Chemical and Bioengineering for MSc program**. And The purpose of the survey is to understand the sources, properties and uses of ferric oxide in paint factories.

All of the answers you provide in this survey will be kept confidential. The survey data will be reported in a summary fashion only and will not identify any individual person.

This survey will take quite a few minutes to complete.

Thank you for the corporation.



1. How ferric oxide is useful to paint industries?

→ It is used as a pigment.

2. Is α-ferric oxide being used by paint industries? Or β or γ

→ Our Company uses α-ferric oxide

3. How much quantity of ferric oxide will be imported per year by KADSISCO?

→ 40 Ton

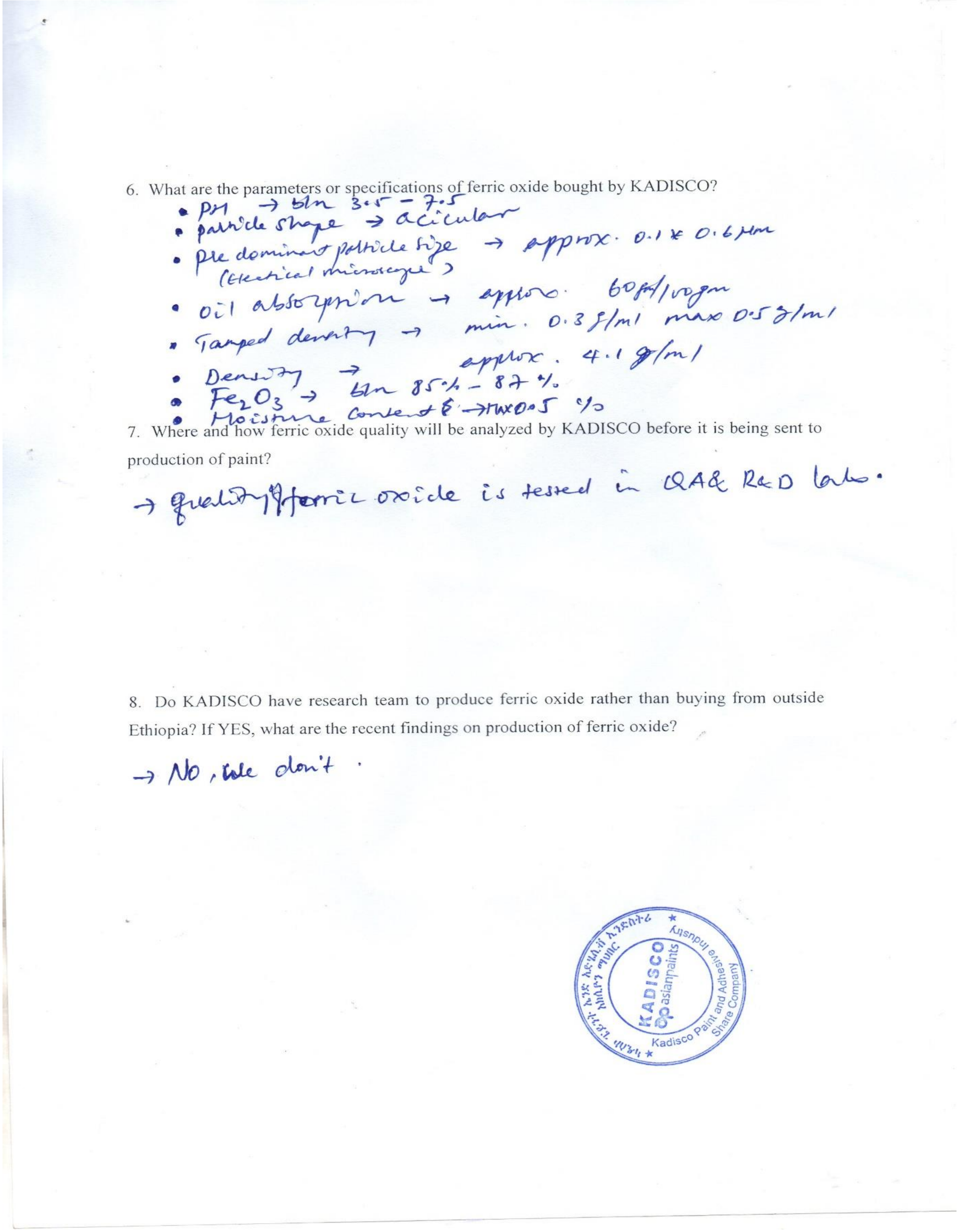
4. What is the price of ferric oxide for last five years?

→ approx. (on average) 1.3 $ FOB price.

5. From where KADISCO is buying ferric oxide?

→ We are importing from global market.

KADISCO asianpaints
Kadisco Paint and Adhesive Industry Share Company



6. What are the parameters or specifications of ferric oxide bought by KADISCO?

- PH → b/n 3.5 – 7.5
- particle shape → acicular
- pre dominant particle size → approx. 0.1 × 0.6 μm (Electrical microscope)
- oil absorption → approx. 60gm/100gm
- Tamped density → min. 0.3 g/ml max 0.5 g/ml
- Density → approx. 4.1 g/ml
- Fe_2O_3 → b/n 85% – 87%
- Moisture content → max 0.5 %

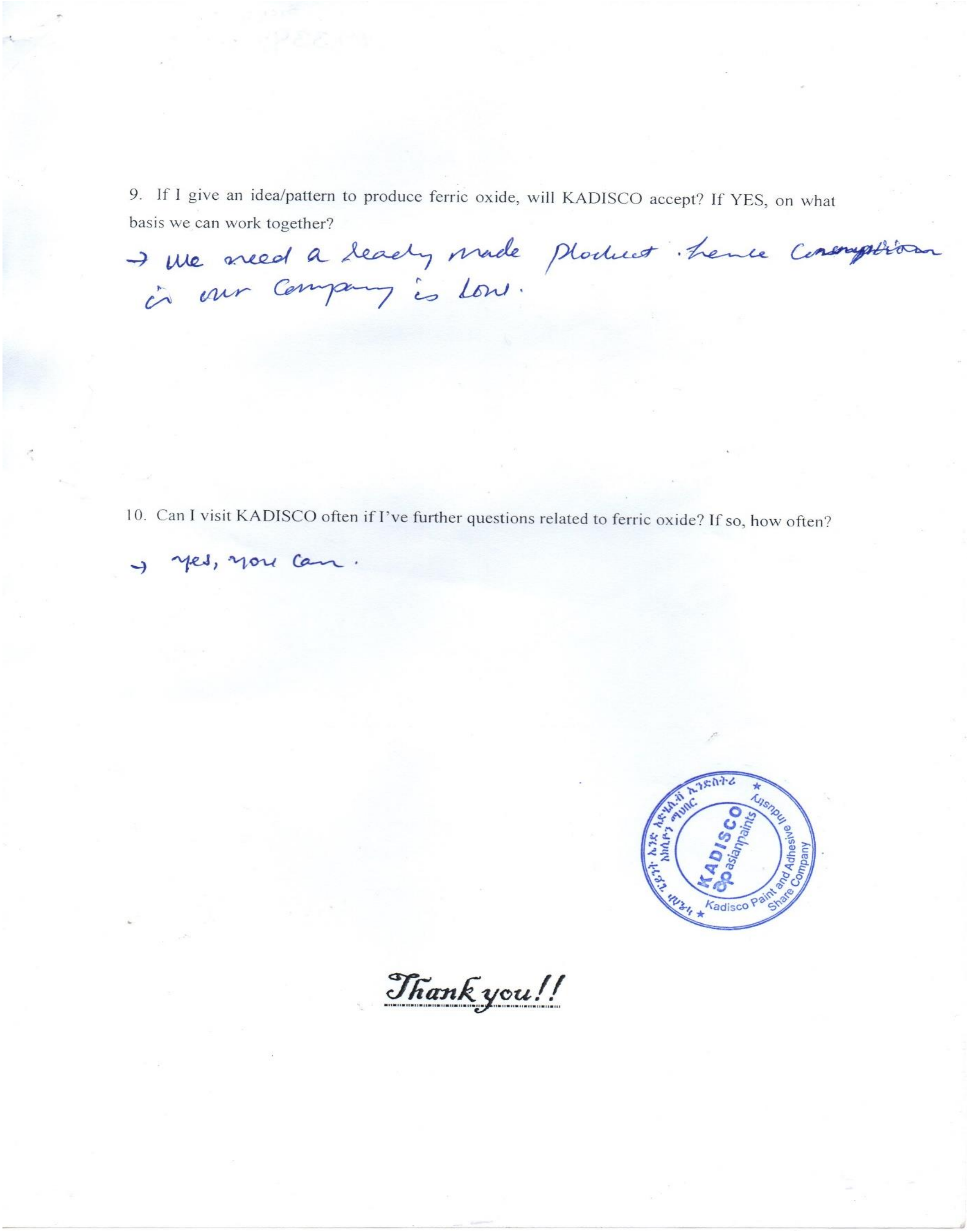
7. Where and how ferric oxide quality will be analyzed by KADISCO before it is being sent to production of paint?

→ quality of ferric oxide is tested in QA& R&D labs.

8. Do KADISCO have research team to produce ferric oxide rather than buying from outside Ethiopia? If YES, what are the recent findings on production of ferric oxide?

→ No, we don't.

KADISCO asianpaints
Kadisco Paint and Adhesive Industry Share Company



9. If I give an idea/pattern to produce ferric oxide, will KADISCO accept? If YES, on what basis we can work together?

→ we need a ready made product. hence Consumption in our Company is low.

10. Can I visit KADISCO often if I've further questions related to ferric oxide? If so, how often?

→ yes, you can.

Kadisco Paint and Adhesive Industry Share Company

Thank you!!

Appendix E: Mole and Mass Balance

Mole and Mass balance

Mole balance is the number of moles of a generated or consumed by the system. And Mass balance is it's also called material balance is an application of conservation of mass. Most of the analysis of physical system. by accounting for material entering and leaving a system mass flow can be identified which might have been unknown or difficult to measure without this technique.

Mole and material balance of the first reaction;

Iron ore (Fe_2O_3) + 6HCl $\longrightarrow$ $2FeCl_3 + 3H_2O$

As it shown from appendix A or from the raw material characterization, the processed ore from AXUM region have 65.81% of Fe_2O_3. Therefore, these experiments were done by using 77 grams of iron ore which have approximately equivalent to 50 grams of Fe_2O_3.

Mol of Fe_2O_3 = $\frac{MFe2O3}{M.wt} = \frac{50g}{159.69g/mol}$ = 0.319 mol

In order to find the amount of HCl added to the reaction, it's necessary to calculate the mole balance of HCl

Mol of HCl = Mol of Fe_2O_3 * $\frac{6\ mol\ HCl}{1\ mol\ Fe2O3}$

= 0.319 mol * 6 mol

= 1.9146 mol

Now, let's calculate the mass of HCl

Mass of HCl = Mol of HCl * M.wt of HCl

= 1.9146 mol * 36.46 g/mol

= 69.806 g

Since, HCl is in aqueous solution, the mass should be converted in to volume by using density

Volume of HCl = $\frac{\text{Mass of HCl}}{\text{Density of HCl}}$

$= \frac{69.806g}{1.19\ g/ml3}$

$= 58.661\ ml^3$

To calculate the moles of the product from the reaction above first it's necessary to know/ identify the limiting reagent.

Determining limiting reactant /reagent

determining limiting reactant /reagent is done by dividing number of moles of the reactants by stochiometric coefficients.

For Fe2O3 = $\frac{\text{Mol of Fe2O3}}{1}$ = 0.319 mol

For HCl = $\frac{\text{Mol of HCl}}{6}$ = 1.9146 / 6 = 0.319 mol

Therefore, it's possible to take/assume one of the reactants as a limiting reactant.

Now, calculate the moles and mass of ferric chloride using HCl as limiting reactant.

Mol of $FeCl_3$ = Mol of HCl * $\frac{mol\ FeCl3}{6\ mol\ HCl}$

= 1.9146 mol *$\frac{2\ mol}{6\ mol}$ mol

= 0.6382 mol

Mass of $FeCl_3$ = Mol of $FeCl_3$* M.wt of $FeCl_3$

= 0.6382 mol * 162.19 g/mol

= 103.510 g

And also, calculate the moles and mass of H_2O using HCl as limiting reactant.

Mol of H_2O = Mol of HCl * $\frac{mol\ \text{H2O}}{6\ mol\ HCl}$

= 1.9146 mol *$\frac{3\ mol}{6\ mol}$ mol

= 0.9573 mol

Mass of H_2O = Mol of H_2O * M.wt of H_2O

= 0.9573 mol * 18.0 g/mol

= 17.2314 g

Mole and material balance of the second reaction;

$2FeCl_3 + 3H_2O + 6NH_4OH \longrightarrow 2Fe(OH)_3 + 6NH_4Cl + 3H_2O$

First, let's calculate the moles of ammonium hydroxide to know how much amount of ammonium hydroxide required to the reaction.

Mol of NH_4OH = Mol of $FeCl_3$ * $\frac{6\,mol\ \mathrm{NH4OH}}{2\,mol\ \mathrm{FeCl3}}$

= 0.6382 mol *$\frac{6\,mol}{2\,mol}$ mol

= 1.9146 mol

And now, mass of ammonium hydroxide;

Mass of NH_4OH = Mol of NH_4OH * M.wt of NH_4OH

= 1.9146 mol * 35.0 g/mol

= 67.011 g

Since, NH_4OH is in aqueous solution, the mass should be converted in to volume by using density

Volume of NH_4OH = $\frac{\mathrm{Mass\ of\ NH4OH}}{\mathrm{Density\ of\ NH4OH}}$

= $\frac{67.011g}{0.9\ g/ml3}$

= 74.4566 ml^3

To calculate the moles of the product from the reaction above first, it's necessary to know/ identify the limiting reagent.

Determining limiting reactant /reagent

determining limiting reactant /reagent is done by dividing number of moles of the reactants by stochiometric coefficients.

For $FeCl_3 = \frac{\text{Mol of FeCl3}}{2} = 0.319$ mol

For $H_2O = \frac{\text{Mol of H2O}}{3} = 0.319$ mol

For $NH_4OH = \frac{\text{Mol of NH4OH}}{6} = 0.319$ mol

Therefore, it's possible to take/assume one of the reactants as a limiting reactant.

Now, calculate the moles and mass of ferric hydroxide using NH_4OH as limiting reactant.

Mol of $Fe(OH)_3$ = Mol of NH_4OH * $\frac{2\,mol\ \text{Fe(OH)3}}{6\,mol\ \text{NH4OH}}$

$= 1.9146\text{mol} * \frac{2\,mol}{6\,mol}$ mol

= 0.6382 mol

Mass of $Fe(OH)_3$ = Mol of $Fe(OH)_3$ * M.wt of $Fe(OH)_3$

= 0.6382 mol * 106.845 g/mol

= 68.188 g

And also, calculate the moles and mass of ammonium chloride (byproduct) using NH_4OH as limiting reactant.

Mol of NH_4Cl = Mol of NH_4OH * $\frac{6\,mol\ \text{NH4Cl}}{6\,mol\ \text{NH4OH}}$

$= 1.9146\text{mol} * \frac{6\,mol}{6\,mol}$ mol

= 1.9146 mol

Mass of NH_4Cl = Mol of NH_4Cl * M.wt of NH_4Cl

= 1.9146 mol * 53.45 g/mol

= 102.335 g

And, calculate the moles and mass of water which removed from the ammonium chloride(aq) by using concentrator and evaporator.

Mol of H_2O = Mol of NH_4Cl * $\frac{3\,mol\ \mathrm{H2O}}{6\,mol\ \mathrm{NH4Cl}}$

= 1.9146 mol *$\frac{3\,mol}{6\,mol}$ mol

= 0.9573 mol

Mass of H_2O = Mol of H_2O * M.wt of H_2O

= 0.9573 mol * 18.0 g/mol

= 17.2314 g

Mole and material balance of the third reaction;

$$2Fe(OH)_3 \longrightarrow \boldsymbol{\alpha\text{-}Fe_2O_3}\ \textbf{(α-ferric oxide)} + \boldsymbol{3H_2O}$$

First, let's calculate the moles of α-ferric oxide to know how much amount of α-ferric oxide will be found from this process or to know the theoretical yield.

Mol of **α-Fe_2O_3** = Mol of $Fe(OH)_3$ * $\frac{1\,mol\ \boldsymbol{\alpha-\mathrm{Fe2O3}}}{2\,mol\ \mathrm{Fe(OH)3}}$

= 0.6382 mol *$\frac{1\,mol}{2\,mol}$ mol

= 0.3191 mol

Now, calculate the theoretical yield of the product.

Mass of **α-Fe_2O_3** = Mol of **α-Fe_2O_3** * M.wt of **α-Fe_2O_3**

= 0.3191 mol * 159.69 g/mol

= 50.657 g

And, calculate the moles and mass of water which removed by calcination process.

Mol of H_2O = Mol of NH_4Cl * $\frac{3\,mol\ \mathrm{H2O}}{6\,mol\ \mathrm{NH4Cl}}$

= 1.9146 mol *$\frac{3\,mol}{6\,mol}$ mol

= 0.9573 mol

Mass of H_2O = Mol of H_2O * M.wt of H_2O

= 0.9573 mol * 18.0 g/mol

= 17.2314 g

Finally, the general mass balance will be;

$$2Fe(OH)_3 \longrightarrow \boldsymbol{\alpha\text{-}Fe_2O_3\ (\alpha\text{-ferric oxide}) + 3H_2O}$$

$$68.1887\text{ g} \longrightarrow 50.657\text{ g} + 17.2314\text{ g}$$

$$68.1887\text{ g} \longrightarrow 68.1887\text{ g}$$

Therefore, from this mole and mass balance it's observed that to process 77 gram of iron ore;

58.661 ml^3 of hydrochloric acid (37% by wt.) and 74.4566 ml^3 of ammonium hydroxide (30% by wt.) are required. And it results 50.657 grams of **α-Fe_2O_3** which is called theoretical yield.

$$\text{Yield of synthesized } \boldsymbol{\alpha\text{-}Fe_2O_3} = \frac{(\boldsymbol{theoretical\ yield - actual\ yield\ from\ each\ experiment})}{\textbf{theoretical yield}}$$