

ADDIS ABABA UNIVERSITY
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***“PRODUCTION, OPTIMIZATION AND CHARACTERIZATION OF
FERROUS SULFATE FROM LOCAL IRON ORE”***

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.

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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 the degree at this or any other university, and that all resources of materials used in this thesis have been duly acknowledged.

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68 Abstract

Iron sulfate has a diversified uses in agriculture, chemical industries and waste water treatment plants. Although Ethiopia has a huge deposits of iron ore. Therefore, this study investigates the potential of the country to produce iron sulfate from local iron ore and sulfuric acid.

Iron samples has been taken from two ores namely Horu Guduru and Melkasedi in Oromia regional state characterized, 77% and 66% weight based iron oxide composition obtained from Horu Guduru and Melkasedi respectively. The sample from high iron oxide composition ore, Horu Guduru was reacted with sulfuric acid and hydro chloric acid subsequently by varying three process variables: temperature, reaction time and particle size.

From the analysis the optimum iron sulfate yield obtained is 97.75% at temperature of (75°C), reaction time 60 min and particle size 1.00(which is <0.125mm).

Lastly, after iron sulfate characterization its production economics evaluated. The total investment cost of the project is estimated to be 1,830,822 birr. The project is financially viable with an internal rate of return (IRR) of 17.68 % and a Net annual profit of Birr 6,144,677.5birr/yr, at discounted rate of 10%. From the result, it is possible to conclude that establishment of such factory in the country saves foreign exchange, contributes for the economy, creates job opportunities, assures product availability and enhances input and output chain in the country.

List of Acronyms

AAS: Atomic absorption spectroscopy

ASTMA: American Society for Testing and Materials association

BIF: Banded iron formations

Df: degree of freedom

F: degree Fahrenheit

FCI: fixed capital investment

FFD: Full Factorial Design

GSE: Geological Survey of Ethiopia

HF: Hartree–Fock

ISTM: International Society of Travel Medicine

OL: Operating Labor

PEC: Purchased equipment cost

Q: Heat transfer vaper

TCI: total capital investment

TPC: Total production cost

Uv: ultra-violate analysis

VIF: variance inflation factor

WC: working capital

XRD: X-ray crystallography

1. INTRODUCTION

Ethiopia is one of the few African countries without active public geological survey. Accordingly, the mineral potential of the country is known only partly and selectively. The country's mineral exploration is ongoing process and the available deposit data is old. [1]

The iron ores hitherto known in Ethiopia are oxides only. Even if there is no clear information about smelting history, there is legendary information from local farmers. Using deposit indicatives, Wollega province has stood the leading iron potential location in the country. Even though the exact deposit amount is not known, Ethiopia is expected to be one of high iron having country in the continent. Besides lack of clarity in the deposit level and the ores composition, the country has no factory that manufactures any type of iron compounds. So all iron sulfate consumers forced to import.

Generally there are two types of iron sulfate formulations, which are ferrous sulfate FeSO_4 and ferric sulfate $\text{Fe}_2(\text{SO}_4)_3$. Each have its own property and uses. Iron (III) sulfate (or ferric sulfate), is the chemical compound with the formula $\text{Fe}_2(\text{SO}_4)_3$, the sulfate of trivalent iron. Usually yellow, it is a rhombic crystalline salt and soluble in water at room temperature. It is used in dyeing as a mordant, and as a coagulant for industrial wastes. It is also used in pigments, and in pickling baths for aluminum and steel. [2]

Iron (II) sulfate (ferrous sulfate) is chemical compound with the formula FeSO_4 . It can be found in various states of hydration, and several of these forms exist in nature. Known since ancient times as copperas and as green vitriol, the blue-green heptahydrate is the most common form of this material. All iron sulfates dissolve in water to give the same aqua complex ($\text{Fe}(\text{H}_2\text{O})_6$.)



Figure 1-1: Iron sulfate

Iron (II) sulfate is used medically to treat iron deficiency, and also for industrial applications it is mainly used as a precursor to other iron compounds. It is a reducing agent, mostly for the reduction of chromate in cement. Also Iron sulfate used as fungicide, the oxalate of iron in photographic development, limonite, goethite, hematite as pigments and abrasives, magnetite in the production of industrial electrodes and also for washing coal.

1.1. Problem Statement

Ethiopia is one of Agrarian country whose 75 percent of its population lives mainly depends on traditional farming. This outdated farming is being challenged with crop diseases and low crop yield. The low yield is caused either by crop diseases or deficiency of minerals. One of these minerals is iron. Except in modern farming, the traditional farmers are not aware of the importance of each mineral. The mechanized farming users import iron sulfate to correct the deficiency problem. Even though Ethiopian's soil contains different types of iron minerals, iron sulfate is the only absorbable iron compound by the plant root. So, low total Fe doesn't mean iron deficiency and low total iron is seldom relative to iron deficiency. Iron deficiency is mostly observed on high pH calcareous soils, but may also occur on acid soils that are very low in total Fe (this is in the central high lands of the country). Irrigation water and soils which is high in bicarbonate may aggravate the situation also. Fe deficiencies, such a problem observed in the eastern Ethiopia low lands where cotton and sugar cane is produced in high quantity.

Ethiopia will have than 10 sugar factories in the next few years. These factories need iron sulfate to supplement iron deficiency in their sugarcane cultivation soil. According to the research conducted by the Haramaya university and Debreziet agricultural research center on sugar cane

by using ferrous sulfate as foliar sprays at rate of 15 kg/hect increased cane length and commercial sugar by 33 and 44 % over the control respectively [3]. The booming demand in sugar cane, fruits, vegetables and flower plantation give a picture of the promising huge future market opportunities for iron based fertilizer use.

In addition to serve as supplementing micro mineral nutrition, ferrous sulfate is used to treat many plant fungal diseases which cause crop yield reduction. This is another use of the chemical if it is easily available in the country. Even the pastoralists need it to grow better animal feed plants.

Since all of the raw materials are abundant and cheap, it is possible to supply affordable product that enables all economic level customer (farmers) to use it.

Leather and leather products are among the main manufacturing export products. The annual volume of liquid waste discharge from the 15 tanneries based on their annual production capacities is estimated to vary between 2,000,000 and 2,500,000 cubic meters. To meet the environmental regulations set to control pollution; the sector is forced to invest heavily in pollution abatement. Iron sulfate is one the most known chemicals in waste water treatment [4]. According to the research conducted by Debre Birhan university research center iron sulfate had a good coagulation capacity to remove chrome and suspended solid particle from leather factory waste water. [5]

Furthermore, Iron sulfate is used in pharmaceuticals, dyes, pigments and other product producing industries which are common in the country. However, in all industries iron sulfate requirement is met through import.

Even though both the required raw materials are locally available the country spend huge amount of foreign currency to import Iron sulfate. So, studying production potential and technology for iron sulfate from locally available iron ore will be the main aim of this project work.

1.2 Objectives

1.2.1 General objective

The General Objective of this research work was to produce iron sulfate from local iron ore and to evaluate its economic potential.

1.2.2 Specific objectives

Specific Objectives of the research were the following:

- ✓ To characterize iron ore and select the ore with the better grade
- ✓ To prepare iron sulfate by using sulfuric acid
- ✓ To optimize process parameters (reaction temperature, reaction time and particle size) in order to maximize iron sulfate yield.
- ✓ To characterize the produced iron sulfate
- ✓ To conduct a preliminary economic analysis for iron sulfate production from local iron ore

1.3. Significance of the study

If this project becomes realized practically, it will have several contributions for the scientific, economic and social development in the country. In academic perspective, the outcome of this study can serve as background for next studies in the area. Economically, if the project becomes realized it substitutes the import and saves the foreign currency. The investigation will also create forward linkage with the manufacturing sector and backward linkage with the mining and chemical manufacturing sub sector. Beyond all it will generate income for the Government in terms of tax revenue and payroll tax.

1.4. Scope of the Study

This research work covered collection of iron ore from different locations in the country, characterization of ore's iron content, production of iron sulfate and it also optimized the operating conditions for the reaction. Finally after the characterization of the product, preliminary economic evaluation was done.

1.5. Limitation of the study

The limitation of the study was the following

- This study select Horo Gudurus iron ore by comparing only the iron ores from two different places. But there are several iron ores sources in Ethiopia which may have high grade of iron.
- The amount of iron ore around Horo Guduru didn't studied. So it is impossible to predict the project life time of the plant if the plant will build around Horo Guduru.

2. REVIEW OF LITERATURE

2.3. Iron ore

Iron ores are rocks and minerals from which iron can be economically extracted. The ores are usually rich in iron oxides and vary in color from dark grey, bright yellow, deep purple, to rusty red. The iron itself is usually found in the form of magnetite (Fe_3O_4), hematite (Fe_2O_3), goethite ($\text{FeO}(\text{OH})$), limonite ($\text{FeO}(\text{OH}) \cdot n(\text{H}_2\text{O})$) or siderite (FeCO_3).

Metallic iron is virtually unknown on the surface of the Earth except as iron-nickel alloys from meteorites and very rare forms of deep mantle xenoliths. Although iron is the fourth most abundant element in the Earth's crust, comprising about 5%, the vast majority is bound in silicate or more rarely carbonate minerals. The thermodynamic barriers to separating pure iron from these minerals are formidable and energy intensive, therefore all sources of iron used by human industry exploit comparatively rarer iron oxide minerals, primarily hematite. Iron ore mining methods vary by the type of ore being mined [6].



Figure 2-1 Iron ore form Horo Guduru

2.4. Geology of Iron-Ore Resources

Currently, there are four main types of iron ore deposits depending on their mineralogy. These are magnetite, titan magnetite, massive hematite and pisolitic ironstone deposits.

Based on the geological setting, the varieties of Iron-ore deposits can be grouped as described in the following subheadings.

2.4.1. Banded iron deposits

Banded iron formations (BIF) are metamorphosed sedimentary rocks composed predominantly of thinly bedded iron minerals and silica (quartz). The iron mineral present in such Formation may be the carbonate iron- siderite, but those used as iron ores contain the oxides magnetite or hematite.

2.4.2. Magmatic magnetite ore deposits

Occasionally granite and ultrapotassic igneous rocks contain segregated magnetite crystals and form masses of magnetite suitable for economic concentration.

2.4.3. Hematite ore

Hematite iron ore deposits are currently exploited in all continents, with the largest intensity in South America, Australia and Asia. Most large hematite iron ore deposits are sourced from metasomatically altered banded iron formations and rarely from igneous accumulations .Hematite iron is typically rarer than magnetite bearing BIF or other rocks which form its main source or protolith rock, but it is considerably cheaper to process as it generally does not require beneficiation due to its higher iron content. However, hematite ores are harder than magnetite ores and therefore require considerably more energy to crush and grind if beneficiation is required. [7]

2.5. Types of iron ores

The major rock types of metallic iron are massive hematite, pisolitic goethite/limonite, which provide a 'high-grade' ore. Banded metasedimentary ironstone, magnetite-rich metasomatite, rocks rich either in siderite or chamosite provide a 'low-grade' ore.

High-grade ore

Currently most of the iron ore mined in the world comes from large deposits of massive hematite rock formed by the in situ enrichment, most commonly a banded iron formation (BIF). High-grade ore generally has a cutoff grade of 60% Fe. Historically it has provided a direct feed to smelters either as a raw lump or fines, also in a processed form such as sinter or pellets.

Low-grade ore

Low-grade ore is a term applied to iron-rich rocks with cut-off grades in the range of 25–30% Fe. It was the main supply of iron ore for many centuries of the World's early history of production of iron. Since the 1950's North America's main supply has been low grade ore. The dominant economic iron mineral in low-grade ore is magnetite. [8]

2.6. Iron Resources in Ethiopia

Iron ore production in Africa is dominated by South Africa, Mauritania and Algeria; Zimbabwe and Morocco produce ore for use within the country. Many countries possess iron ore deposits that are as yet unmined.

In Ethiopia there are many occurrences which discovered by geological survey of Ethiopia. But also there are some indications of iron occurrence that have no study. [9].

Iron ore occurrences of Ethiopia can be classified based on the geological setting as follows:

- Metamorphic type is of primary sedimentary origin, altered mineralogically and texturally by subsequent regional metamorphism.
- Combined metamorphic-contact metasomatic type that was formed by a combination of sedimentation, metamorphism and metasomatic.
- Residual concentration type, having resulted from decomposition and leaching of extrusive or other ferruginous siliceous rocks.

- Magmatic type which is genetically related to the emplacement of igneous rocks [10]. [11].

The Geological Survey of Ethiopia (GSE) identified many iron occurrences in Wollega, Bikilal, Gordana, Worakalu, Chago, Yubdo, Nejo, Kata, Tsoli, Sirba Korkandi, Kiltukara and Wobera Kiltu), Bale, (Melka Arba), Kefa (Mai Gudo and Ghimira) and ararghie (Cherecher and Jijiga) regions . [1]

The following are the major iron occurrences and deposits so far discovered in Ethiopia.

Bikilal

A total ore reserve of about 57.8 million tons with average grade of 23.3% magnetic iron and 41% total iron was calculated for 27 identified ellipsoidal ore bodies, which are intimately related to a metagabbro and amphibolite complex. [12]

According to [Contech, 1995] the iron ore reserve is calculated to be 22Mt with an average grade of 40.7% total iron and 28% of Magnetic iron.

The iron ore bodies occur as veins with 200m-1400m length, 2-6m width, and 200-300m depth. The ore contains on average 30% limonite, 40% magnetite and 30% silicate and accessory sulfides (pyrite, pyrrhotite and apatite).

The average chemical composition has been given as 41.1% total iron, (23.3%Fe in magnetic minerals), 16.7%TiO₂, 0.24%V₂O₅, 36%P₂O₅ and 0.77%S. [13] [14]

Gordana

The iron deposits of the Wollega region include the Gordana, Koree, Dima, Worakalu, and Chago occurrences, which were investigated in 1963 under a contract agreement between the Mining Industrial Association of the then Yugoslavia and the Ethiopian government.

The ore reserve of the main exposure was inferred to be about 250,000 tons of both probable and possible ores, at an average grade of 66.95% total iron to a depth of nearly 100m.

Koree

The ore outcrop has a length of 200m, with an assumed extension of 100m. The ore consists of magnetite and martite blocks with quartzite lamination. Chip samples showed 71.6% total iron. The possible reserve was inferred to be 150,000-200,000 tons, taking the depth as half the length of the ore body on surface.

Chago

The iron ore lenses are composed of magnetite and hematite, and are believed to be syngenetic with the intercalated ferruginous quartzite bands. They occur in a sequence of pelitic and arenaceous Proterozoic rocks the ferruginous quartzite and iron lenses occupy the core of an anticline. The maximum lens width, as outlined by trenching, reaches 2m over the full extent of the ore zone extending for 280m. A reserve of 440,000 tons of high-grade ore (57-68% iron) for 400m length and 5m width, which is underlain by low-grade ore (33% iron content) was inferred. Later, the ore reserve is reduced to 12,000 tons of high grade and 27,000 tons of low grade ore. A more recent magneto metric survey suggested that this occurrence was non-profitable for even medium-scale mining operations.

Tsole

The iron extends to about one km strike length and the exposed width is from 4m to 4.5m. The iron in the Tsole area is of magnetite-hematite composition that grades to localized limonite due to strong weathering.

Belowteoist locality

The iron ore is banded, fine grained and dark gray. Ferruginous quartzite may occur to the northeast and southwest of the area. On the northwestern slope of the hill fragments of iron rich ores (limonite –hematite) are encountered. Possible reserves of ferruginous quartzite of the locality can be estimated at 2,500,000 tons per 100m depth.

Werfedo

Iron ore occurrence spots of magnetite and iron sulphide minerals (0.1cm-0.3 cm in size) are distributed within the rock. The average grade of the iron is 42% and the reserve under C2 category is estimated to be 20,911 tons.

Other Iron ore occurrences

There are also minor occurrences at Dime that is derived from volcanics, brown to purple and free of quartz. At depth it is richer in iron, containing 40% to 50% Fe₂O₃.

Iron ore is also known to be found around Adwa, the ore type is supposed to be magnetite, limonite with inferred resource of 5Mt, and that of Enticho is 14.23Mt.

The Iron ore occurrence of Kaffa region is mainly associated with magnetite, hematite and limonite, at the localities of Gamalucho, Garo, Mai Gudo, Ghimira basin, Kurkura valley, Melka Sedi and Dombowa with total inferred resource of 47Mt of iron ore. [15]

2.7. Sulfuric acid in Ethiopia

Sulfuric acid is currently being produced by Melkasa Aluminum Sulfate and Sulfuric Acid factory at Melkasa Factory. In Ethiopia, the aluminum sulfate and sulfuric acid factory, situated in Melkassa , 130km east of Addis Abeba, is the only plant producing sulfuric acid using imported Sulphur even if plenty Sulphur deposits occur in Ethiopia.

Currently, the factory's production capacity is not fully employed due to the absence of a demanding market. Of course the rate of consumption of sulfuric acid is a measure of one country's industrialization; hence the prevailing low consumption of sulfuric acid in Ethiopia reflects nothing but Ethiopian's level of industrialization. [16]

2.8. Iron sulfates properties and uses

Both ferric and ferrous sulfate are soluble in water. But they have their own properties.

2.8.1. Properties of iron sulfate

Table 2-1: properties of ferrous sulphate [10] [17]

Properties	
Molar mass	151.91 g mol ⁻¹
Appearance	Blue/ green or white crystals
Odor	Odorless
Density	3.65 g/cm ³ (anhydrous)

Melting point	680 °C (anhydrous)
Solubility in water	Monohydrate: 44.69 g/100 mL (77 °C)
Solubility	Negligible in alcohol
Solubility in ethylene glycol	6.4 g/100 g (20 °C)
Vapor pressure	1.95 kPa (heptahydrate)

Table 2-2: Properties of ferric sulfate [18]

Molecular formula	$\text{Fe}_2(\text{SO}_4)_3$
Molar mass	399.88 g/mol (anhydrous) 489.96 g/mol (pentahydrate) 562.00 g/mol (nonahydrate)
Appearance	grayish-white crystals
Density	3.097 g/cm ³ (anhydrous) 1.898 g/cm ³ (pentahydrate)
Melting point	480 °C (anhydrous) 175 °C (nonahydrate)
Solubility in water	slightly soluble
Solubility	sparingly soluble in alcohol negligible in acetone, ethyl acetate insoluble in sulfuric acid, ammonia

2.8.2. Uses of iron sulfate

Uses of ferric sulfate

Horticultural: In horticulture it is used for treating iron chlorosis. Although not as rapid-acting as iron chelate, its effects are longer-lasting. It can be mixed with compost and dug into to the soil to create a store which can last for years. It is also used as a lawn conditioner, and moss killer.

Colorant:-Ferrous sulfate was used in the manufacture of inks, most notably iron gall ink, which was used from the Middle Ages until the end of the eighteenth century. Chemical tests made on the Lachish letters showed the possible presence of iron. It is thought that oak galls and copperas may have been used in making the ink on those letters. It also finds use in wool dyeing as a mordant. Hardwood, a material used in marquetry and parquetry since the 17th century, is also made using ferrous sulfate. Woodworkers use ferrous sulfate solutions to color maple wood a silvery hue. [19]

Nutritional supplement:-Together with other iron compounds, ferrous sulfate is used to fortify foods and to treat iron-deficiency anemia. Constipation is a frequent and uncomfortable side effect associated with the administration of oral iron supplements. Stool softeners often are prescribed to prevent constipation.

Other uses

In the second half of the 19th century, ferrous sulfate was also used as a photographic developer for collodion process images. Ferrous sulfate is sometimes added to the cooling water flowing through the brass tubes of a turbine condenser. It forms a corrosion-resistant, protective coating on the inside of the tube. [20]

It is used as a gold refining chemical to precipitate metallic gold from auric chloride solutions (gold that has been dissolved into solution with aqua regia).

It has been applied for the purification of water by flocculation and for phosphate removal in municipal and industrial sewage treatment plants to prevent eutrophication of surface water bodies. [21]

It is used as a traditional method of treating wood panel on houses, either alone, dissolved in water, or as a component of water-based paint. Green vitriol is also a useful reagent in the identification of mushrooms.

Uses of ferric sulfate

Especially in recent years, a ferric sulfate solution has occupied the attention as a useful Water treatment agent and, particularly, a ferric sulfate solution and a basic ferric sulfate solution have a quick sedimentation speed for the resulting flocs and show good deodorizing ability as compared With a Water treatment agent of an aluminum type such as an aluminum sulfate solution and la basic aluminum chloride solution Whereby they have been Widely used as a Water treatment agent for Waste Water from paper Manufacturing industry, from food industry, from chemical industry, leather industry. Etc. or as a dehydrating aid for sewage sludge. It also used in dyeing as a mordant, pigments, and in pickling baths for aluminum and steel. Medically it is used as an astringent and styptic. [22]

2.9. Review of Iron sulphate production technologies

There are many journals which state about different ways of iron sulfate production. The methods are differ each other by their raw material, product or by process condition. So generally there are four types of iron sulfate production process those are

- Ferrous sulfate from iron metal
- Ferrous sulfate from iron ore
- Ferric sulfate from iron metal
- Ferric sulfate from iron ore

2.9.1. Ferrous sulfate production process

Ferrous sulfate from iron metal

Iron is a fairly active metal and can easily displace hydrogen from mineral acid solutions. It reacts vigorously and exothermically with sulfuric acid to produce iron (II) sulfate: [23] [24]



Drying the solution produces green vitriol: blue-green crystals of $\text{FeSO}_4 \cdot 7 \text{H}_2\text{O}$. Air oxidizes iron (II) salts to iron (III), and the crystals are soon crusted with brown iron (III) hydroxides and sulfates. [25] [26]

Ferrous sulfate from pickling baths

In the finishing of steel prior to plating or coating, the steel sheet or rod is passed through pickling baths of sulfuric acid. This treatment produces large quantities of iron (II) sulfate as a by-product. [27] [28] [29]

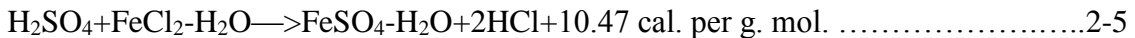
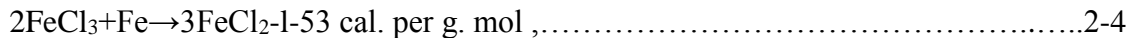
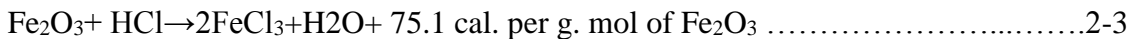
Ferrous sulfate from oxidation of pyrite

Another source of large amounts results from the production of titanium dioxide from ilmenite via the sulfate process. Ferrous sulfate is also prepared commercially by oxidation of pyrite:



Ferrous sulfate from iron ore (Fe₂O₃)

An improved method of producing ferrous sulfate which comprises gradually feeding iron ore in comminuted form into a relatively deep body of liquid comprised of an aqueous solution of hydrochloric acid and during the descent of the ore in the solution reducing the ore to ferric chloride, feeding additional hydrochloric acid into the lower portion of the body of liquid and, by such feeding of additional hydrochloric acid plus said feeding of ore, effecting the rise of said ferric chloride solution and the low thereof from the upper portion of said body of liquid into contact with a mass of metallic iron and thereby converting the ferric chloride solution to a ferrous chloride solution, and removing the excess liquid from the latter solution to provide crystalline ferrous chloride, gradually delivering the ferrous chloride crystals to a pool of sulfuric acid and thereby producing ferrous sulfate, with an accompanying release and rise of hydrochloric acid gas from the pool of sulfuric acid, and feeding the said gas with added water into said acid solution to provide the said additional hydrochloric acid therefor.



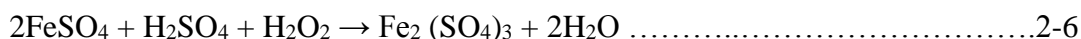
The hydrochloric acid gas released in the reaction escapes through pipe which conducts it into the top of the enclosed compartment of the leaching tank. It will be understood that this process is

cyclic; the acid first used is recovered and re-used repeatedly in the continuous separation of the iron from the gangue of the ore. [31]

2.9.2. Ferric sulfate production process

Ferric sulfate from ferrous sulfate

Ferric sulfate is produced on a large scale by adding sulfuric acid and an oxidizing agent (e.g., nitric acid or hydrogen peroxide) to a hot solution of iron (II) sulfate. [32]



Processes comprising slurring ferrous sulphate in a sulfuric acid solution, oxidizing the ferrous sulphate with nitric acid at a temperature above about 60°C.



Ferric sulfate from iron ore (FeOOH)

The invention by Toshihiko Kakio, and Tatsuo Tsukamoto, have found that, when iron ore containing FeOOH is calcined, there is a further improvement in its solubility. The calcination temperature is 200-600° C. and, more preferably, 400-500° C. Although, the reason why the solubility in sulfuric acid is improved by calcination is not clear, it is likely that FeOOH is dehydrated by calcination resulting in an increase in a specific surface area whereby the solubility is improved. According to the experiment by the present inventors, there is no improvement in the solubility when the temperature is lower than 200° C. Also, there is no improvement in the solubility when it is calcined at higher than 600° C.

Although the reason therefor is not clear, it is presumed that FeOOH is changed to a stable Fe₂O₃ Whereby the solubility is not improved. With regard to the time for the calcination, one hour or shorter is sufficient. Even when calcination is carried out for longer time than one hour, there will be no significant improvement in the solubility and, if the time is longer than one hour, a calcination furnace of a big scale is necessary in an industrial case whereby the cost for the calcination becomes high. Although there is no particular limitation for raising and lowering of the temperature, it is desirable to rise within about 30 minutes and to lower within about one hour.

With regard to sulfuric acid, concentration of the sulfuric acid used is preferably 30-50% by Weight. When it is less than 30% by Weight, long time is needed for dissolving the iron oxide. While, When it is more than 50% by Weight, solubility of the iron oxide usually becomes low depending upon the adding order of the materials, ratio of iron oxide to sulfuric acid used, dissolving temperature, etc. With regard to the ratio of sulfuric acid used, it is adjusted so as to make the ratio of sulfuric acid to total iron within a range of 1:1.5 SO_4 and Fe respectively. When the ratio is less than 1.0, solubility of iron oxide is not sufficient and economy is poor. While, when it is more than 1.5, pH of the resulting ferric sulfate solution is low and its use is significantly restricted.

In the manufacturing method according to the present invention, the above-mentioned materials are poured into a reactor and the order of addition is that, at first, sulfuric acid of a predetermined concentration is poured into a reactor and then the ground iron ore is added. Incidentally, it is also possible to use concentrated sulfuric acid in the present invention. In that case, ground iron ore is added to water and then concentrated sulfuric acid is added thereto with stirring. When concentrated sulfuric acid is used, it is also possible to maintain the reaction temperature utilizing the exothermic reaction. Anyway, ratio of the materials is to be within the above mentioned range. With regard to the reaction temperature, it is recommended to be 70° C. or higher and, more preferably, 90° C. or higher. The most preferred reaction temperature is about the boiling point. Of course it is also possible to use an autoclave.

Reaction time varies depending upon the molar ratio of sulfuric acid to iron, concentration of sulfuric acid and other reaction conditions and, although it is not decided readily, three hours is usually sufficient. When iron ore is well dissolved by the above method, the solution is cooled by allowing to stand, by means of Water, etc. and then filtered by any filtering means such as a filter press or a centrifuge. [33]

It is easy to recognize from the literatures there are many ways to produce ferrous and ferric sulfate.

From this different methods the best methods can be chosen by considering the following criteria

1. It is better to produce iron sulfate from the ore other than the metal iron. Because the ore is cheapest and continues resource.

2. Most of the ore in Ethiopia occur in form of hematite (Fe_2O_3) rather than other iron ores.
3. Ferrous sulfate is more important than ferric sulfate.

3. MATERIALS AND METHODS

3.3. Raw Materials and Chemicals

3.3.1. Raw material collection and preparation

Materials which were used for iron sulfate production were local iron ore from two different places, 98% sulfuric acid, and 35% hydrochloric acid. The disposal of local iron ore which is necessary for iron sulfate preparation is investigated using the data which is study by the geological survey of Ethiopia. [34]. It is supposed to accomplish the following specific tasks to access data of local raw material which is important for iron sulfate production;

- Iron ore explored which is available in Ethiopia from different literatures, journals and farmers who was locally made plough plow knife and other tools from the soil.
- Then the best production process and useful raw materials which are necessary for the preparation of iron sulfate would be presented. For this purpose different published literatures would be applied, especially the method which investigate in [35] is dominant source for this task. This work paves the way to show way of iron sulfate preparation from the mentioned local iron ore (Fe_2O_3).

The Geological Survey of Ethiopia (GSE) identified many iron occurrences in Oromia and Tigray regions. But for this research iron ore were collected from Horo Guduru, Wallaga zone, Abe Dengoro woreda, walage kebele special place FALLE and Melkasedi, Oromia .

3.3.2. Chemicals

Other Chemicals were bought from Neway Private Limited Company; in Addis Ababa. And the chemicals which used for different activates were listed below:

Table 3-1: Chemicals which used for different activates

Activities	Chemicals used
Characterization of iron ore	Lithium etaborate(LiBO ₂),Nitric acid (HNO ₃), Lanthanum chloride (LaCl ₃),potassium chloride KCl ₂ ,distele water(H ₂ O)
Iron sulfate Production	iron ore(Fe ₂ O ₃) ,sulfuric acid(H ₂ SO ₄) and hydrochloric acid (HNO ₃)
Characterization of iron sulfate	Ethanol(CH ₃ CH ₂ OH),phenophitaline(C ₂₀ H ₁₄ O ₄),sodium hydroxide (NaOH),toluene, sulfuric acid (H ₂ SO ₄),phosphoric acid (H ₃ PO ₄),potassium permanganate

3.3.3. Equipment's

The equipment used to run the experiments are listed below:

- Safety goggles
- Jaw crusher, Secondary crusher, Miller and Pulverizer
- Sieves with shaker
- Rubber or vinyl gloves
- Lab apron & lab coat
- Electronic balance
- Water bathe
- Beaker, glass
- Steel pan or glass dish

- Droppers and Laboratory oven
- Funnel and filter paper; better yet, a vacuum filtration setup
- pH meter

3.4. Methodology

3.4.1. Determination of iron Content and Characterization of iron ore

The experimental work was done in Geological Survey of Ethiopia (around Mekanisa) laboratory. The iron ore were characterized by LiBO₂ FUSION, HFattack, GRAVIMETERIC, OLORIMETIC and AAS methods.



Figure 3-1: Atomic absorption spectroscopy.

3.4.2. Experimental works to prepare iron sulfate

Experimental works were done in Chemical Engineering Department Laboratory. In addition, characterization of the product was done in Addis Abeba university chemistry department Laboratory.

From the characterization result the Horo gudurus' ore were selected because it has high amount of iron oxide than Melkasedis' ore.

Iron ore sample preparation

Before the reaction the ore were cleaned and prepared. The sample were crushed by jaw crusher and motor mill Followed by sieve analysis in Chemical Engineering Size Reduction Laboratory. Then the sample with the size $< 2\text{mm}$ was ready for next the reaction.

3.2.3. Experimental setup

First iron ore(Horo Gudurus') and hydrochloric acid was reacted to give ferric chloride. Then some amount of iron scrape is added to get ferrous chloride.

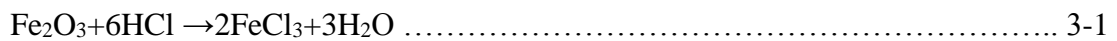
The next reaction was done using water bath. The measured amount of iron chloride were placed in the jar at available temperature. Then sulfuric acid was titrated. At that moment the byproduct of the reaction (hydrochloric gas) was pass through the pipe and dissolve in water.



Figure3-2: experimental setup

Reaction of iron ore with acid

The ore from Horo Guduru were crushed in jaw crusher and motor mill with a particle size of < 2mm. Then the crushed sample was divided in three different groups depending on particle size. Those are particle size 1(which are <0.125mm), particle size 2 (<0.85mm and >0.125mm), particle size 3 (<2 mm and >0.85mm) Then, the crushed and sieved ore were placed in the beaker with concentrated (35%) hydrochloric acid.



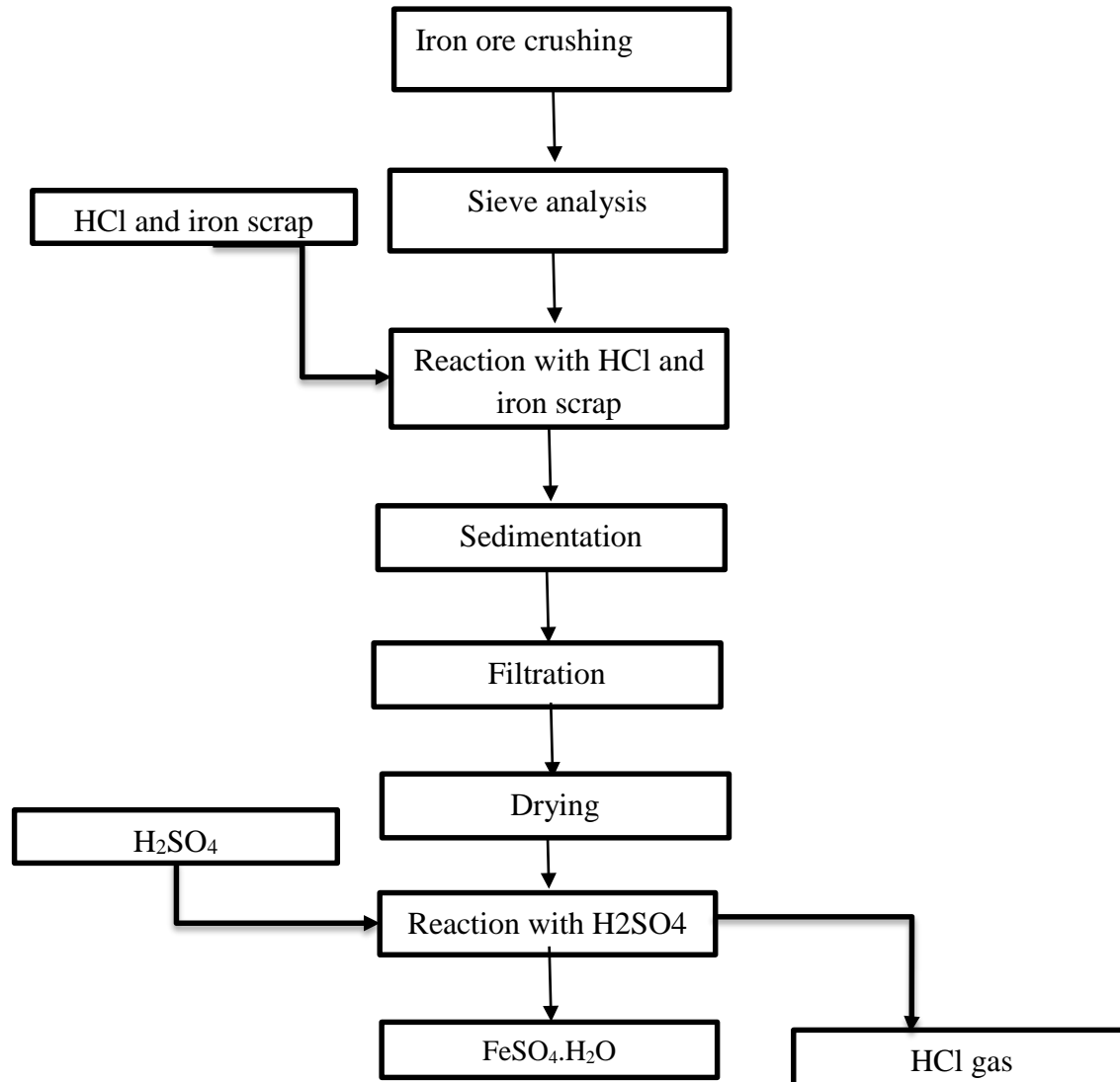


Figure 3-3: Experimental steps

Then unreacted solid ore and ferric chloride was separated by sedimentation followed by a vacuum filtration. If we react ferric chloride directly with sulfuric acid it gives ferric sulfate. So first we put equivalent amount of porous mass of iron scrap in the solution, and the ferric chloride (FeCl_3) is reduced to ferrous chloride (FeCl_2) in accordance with the following exothermic reaction:



Then FeCl₂ solution was dried in the oven. After drying ferrous chloride crystals was crushed and react with sulfuric acid. The mixture of the powdered sample and acid were heated at constant temperature of (50°C, 75°C, 95°C) for 30, 60, 90 minutes to produce iron sulfate.

3.5. Characterization of iron sulfate (Physicochemical properties)

3.5.1. Determination of Acid value

Acid value is a numerical value equivalent to the number of milligrams of potassium hydroxide required to neutralize the acids present in 1 gram of the product. The determination was performed as follows. 25ml of Toluene and 25ml of ethanol was mixed in a 250ml beaker. The resulting mixture was added to 2grams of sample in a 250ml conical flask and few drops of phenolphthalein were added to the mixture. The mixture was titrated with 0.1M KOH to the end point with consistent shaking for which a dark pink color was observed and the volume of 0.1M KOH (V₀) was noted. The required solutions were prepared with the required concentration as shown below. Preparation of 80 percent ethyl alcohol: 19.6ml distilled water was added into 80.4ml 99.5 percent absolute ethanol. And Preparation of 0.5N sodium hydroxide solutions: 10.1grams of 99 percent NaOH was dissolved in 500ml distilled water.

3.5.2. Determination of Moisture Content

Moisture content was determined by drying the samples in an oven until a constant weight obtained. The 500 grams of samples and 6grams of the aluminum foil; total of 506 grams were accurately weighed and put in kettle and dried at the 105°C temperatures. The process was repeated until a constant weight obtained. The moisture content was determined using following equation.

$$MC (\%) = \frac{W_1 - W_2}{W_2} \dots\dots\dots 3.3$$

Where: W₁ = weight of the sample before drying

W₂ = weight of the sample after drying

3.5.3.Determination of specific gravity

The density of iron sulfate was measured by a standard pycnometer of 25ml capacity. First empty pycnometer was weighed then weighed with half full iron sulfate; the pycnometer with iron sulfate crystal was filled with toluene and weighed. Knowing mass of toluene and density of toluene, volume of toluene was calculated and from this result volume of iron sulfate in the pycnometer calculated by deducting volume of toluene from volume of pycnometer. The density of iron sulfate calculated as follows:

$$\text{Density} = \frac{\text{Mass of iron sulphate}}{\text{Volume of iron sulphate}} \dots\dots\dots 3-4$$

3.5.4.Determination of pH

5 g of the iron sulfate was weighed and transferred to a 250ml beaker of resistant glass. 100 ml of distilled water was added stirred well and set aside for a short while. The pH of the solution was determined by a potentiometric instrument (pH meter).

3.5.5.Determination of insoluble matter in water

20 g of the material was weighed accurately, dissolved in 150 ml of water and heated on a water bath for about an hour. A filter paper was taken and washed it well with water, dried to constant weight at 105°C. Any insoluble matter was filtered, washed it with water and dried at 105⁰C±2°C to constant weight. Matter insoluble in water, percent by weight was calculated using the formula:

$$\text{Matter insoluble in water, percent by weight} = \frac{W_1}{W_2} * 100 \dots\dots\dots 3-5$$

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

W2 = weight in g of the material taken for the test.

3.5.6.X-Ray Diffraction Structure Analysis

The method of X-ray diffraction (XRD) was used to investigate the material structure of iron nanoparticles. So according to the XRD of the particle indicated in figure 4.7, the broad peak reveals the existence of crystal phase of iron sulfate.

3.6. Experimental work design

During this work the iron sulfate was produced using local iron ore with hydrochloric and sulfuric acid. Experimental design was analyzed and done by the Design Expert 7.0.0 software application. Experimental design selected for this study is full factorial design and the output measured is iron sulfate yield gained. Process variables revised are reaction temperature, reaction time and particle size. The operating limits of the iron sulfate production process conditions are reasons to choose levels of the variables.

Three level three factors full factorial design was made use of in the optimization study, needing 27 experiments to be done. Reaction temperature, reaction time and particle size were the independent variables selected to optimize the conditions for iron sulfate production by using. Twenty seven experiments were done and the data was statistically analyzed by the Design Expert 7.0.0 software and to get suitable model for the percentage of iron sulfate as a function of the independent variables.

Table 3-2: complete experimental design of full factorial design

Variables	Factor coding	Unit	Levels		
			-1	0	+1
Reaction temperature	A	°C	50	75	95
Reaction time	B	Minute	30	60	90
Particle size	C	No	1	2	3

Table 3.3 Indicates the complete experimental design matrix of full factorial design for the factorial design. Order in which the runs were made was randomized to avoid errors which are caused by systematic.

Table 3-3: Experimental setup

Run	Temperature (A)	Time (B)	Particle size (C)
1	75.00	60.00	3.00
2	50.00	90.00	2.00
3	75.00	30.00	3.00
4	50.00	60.00	3.00
5	50.00	60.00	1.00
6	100.00	60.00	1.00
7	50.00	30.00	1.00
8	100.00	90.00	3.00
9	50.00	30.00	3.00
10	50.00	90.00	3.00
11	75.00	90.00	3.00
12	100.00	90.00	1.00
13	75.00	60.00	2.00
14	100.00	30.00	1.00
15	75.00	60.00	1.00
16	100.00	60.00	3.00
17	75.00	90.00	1.00
18	100.00	60.00	2.00
19	75.00	90.00	2.00
20	75.00	30.00	1.00
21	100.00	90.00	2.00
22	100.00	30.00	3.00
23	75.00	30.00	2.00
24	50.00	60.00	2.00
25	50.00	30.00	2.00
26	50.00	90.00	1.00
27	100.00	30.00	2.00

4. RESULTS AND DISCUSSION

4.3. Characterization of the Raw Materials

4.3.1. Physical Characterization

The raw material collected was first characterized physically with a visual observations, touching.

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

Table 4-1: Physical characterization of the raw materials

Properties	Type/amounts
Color	dull to bright red
Density	5.567 g/cm ³

Table 4-2: Particle size characterization of iron ore from sieve analysis

Sieve size (mm)	Passing (g)	Group name (No)
2	1.3	1
1.8	1.1	
0.850	179	
0.500	184	2
0.250	94	
0.125	243	
0.090	82.6	3
0.045	175	
Pan	98	

4.3.2. Chemical Characterization

The samples were collected from two different sources (from Horo guduru Wallag and, melkasedi) tested at the central laboratory of the Geological Surveys of Ethiopia (GSE) around mekanisa.

To determine the quality of the potential target, the samples were tested for its composition and the following values were obtained as in Table

Table 4-3: Compositional analysis of Horo gudurus' ore

Compound	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	MnO	P ₂ O ₃	TiO ₂	H ₂ O	LOI
Amount (%)	7.64	4.28	77.2	1.84	0.36	0.36	<0.01	0.24	0.08	0.09	0.47	6.81

Table 4-4: Compositional analysis of Melkasedi 'sore

Compound	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	MnO	P ₂ O ₃	TiO ₂	H ₂ O	LOI
Amount (%)	1.6	3.57	65.55	-	0.75	-	-	1.24	0.86	-	0.97	1.35

4.4. Experimental Design analysis

The experimental design selected for this study is Full Factorial Design (FFD) and the response measured is the yield of iron sulfate. The three process variables studied are reaction temperature, reaction time and particle size. The Design Expert 7.0.0 program 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 full factorial design conditions and responses, and the statistical analysis of the ANOVA are given in Tables 4.5 and 4.6, respectively. The multiple regression coefficients were obtained by employing a least square technique to predict a quadratic polynomial model for the reaction content (Table 4.5). The actual yield of iron sulfate produced at different process parameters was calculated and is given in table 4.5. 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 (R^2), adjusted R Squared and predicted R-Squared having a value of 0.7578, 0.6296 ,0.3203 respectively with an adequate precision of 9.999. Adequate precision measures the signal to noise ratio. A ratio greater than 4 is desirable. Adequate precision of 9.999 indicates an adequate signal or minimal noise interference during the experiment.

Table 4-5: Yield of iron sulfate yield

Run	Reaction temperature (A)	Reaction time(B)	Particle size (C)	Yeild
1	75.00	60.00	3.00	77.125
2	50.00	90.00	2.00	71.87
3	75.00	30.00	3.00	73.625
4	50.00	60.00	3.00	63.875
5	50.00	60.00	1.00	61.93
6	100.00	60.00	1.00	95.9375
7	50.00	30.00	1.00	74.62
8	100.00	90.00	3.00	56.08
9	50.00	30.00	3.00	64.68
10	50.00	90.00	3.00	32.64
11	75.00	90.00	3.00	71.81
12	100.00	90.00	1.00	84.64
13	75.00	60.00	2.00	77.12
14	100.00	30.00	1.00	76.31
15	75.00	60.00	1.00	97.75
16	100.00	60.00	3.00	70.125
17	75.00	90.00	1.00	89.25
18	100.00	60.00	2.00	71.875
19	75.00	90.00	2.00	78.18
20	75.00	30.00	1.00	79.5
21	100.00	90.00	2.00	73.125
22	100.00	30.00	3.00	68.68
23	75.00	30.00	2.00	76.00
24	50.00	60.00	2.00	63.875
25	50.00	30.00	2.00	69.625
26	50.00	90.00	1.00	81.375
27	100.00	30.00	2.0	1.56

4.4.1. Development of Model Equation

The regression model equation that correlates the response variable, yield of iron sulfate, 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.

$$\text{Yield} = 82.01 + 4.71 * A - 0.92 * B - 9.04 * C + 1.61 * A * B - 0.44 * A * C - 5.94 * B * C - 10.38 * A^2 - 3.59 * B^2 + 0.64 * C^2 \dots \dots \dots 4-1$$

Where A= Reaction Temperature

B= Reaction time

C= particle size

The multiple regression coefficients were obtained by employing a least square technique to predict quadratic polynomial model for the iron sulfate (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 as suggested by the DOE software.

Table 4-6: Regression coefficients and significance of response

Factor	Coefficient Estimate	Df	Standard Error	95% CI Low	95% CI High	VIF
Intercept	82.01	1	3.87	73.85	90.17	
A-temperature	4.71	1	1.79	0.94	8.49	1.00
B-time	-0.92	1	1.79	-4.70	2.85	1.00
C-particle size	-9.04	1	1.79	-12.81	-5.26	1.00
AB	1.61	1	2.19	-3.02	6.24	1.00
AC	-0.44	1	2.19	-5.07	4.19	1.00
BC	-5.94	1	2.19	-10.57	-1.31	1.0

4.4.2. Model Adequacy Check

The model that was developed by using Design Expert 7.0.0 has to be checked for its consistency and quality how it correlates 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 0.7578. It implies that 75.78 % of the total variation in the yield of iron sulfate 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.

Design-Expert® Software
Yield

Color points by value of
Yield:

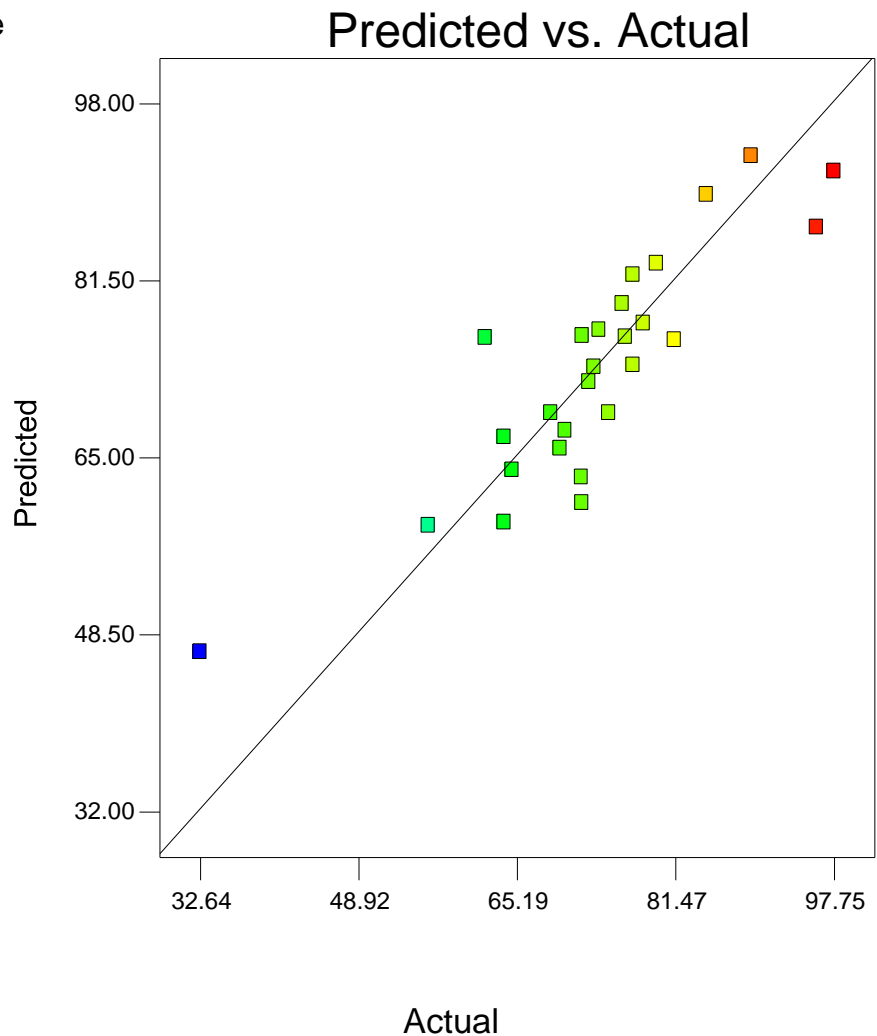
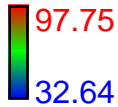


Figure 4-1. Predicted verses actual responses

The statistical analysis of the ANOVA for the response value iron sulfate yield was analyzed using DOE and the result is given in Tables 4.

Table 4.7 A quadratic model Analysis of variance (ANOVA) for iron sulfate yield

Source	Sum of Squares	Df	Mean Square	F Value	p-value Prob > F	
Model	3069.11	9	341.01	5.91	0.0009	Significant
A-temperature	399.90	1	399.90	6.93	0.0175	
B-time	15.36	1	15.36	0.27	0.6125	
C-particle size	1470.13	1	1470.13	25.48	< 0.0001	
AB	31.15	1	31.15	0.54	0.4725	
AC	2.32	1	2.32	0.040	0.8436	
BC	423.52	1	423.52	7.34	0.0149	
A2	646.86	1	646.86	11.21	0.0038	
B2	77.41	1	77.41	1.34	0.2628	
C2	2.45	1	2.45	0.042	0.8393	
Residual	980.94	17	57.70			
Cor Total	4050.05	26				

The coefficients of the response surface model, as provided by the above quadratic model equation, were also evaluated. From the ANOVA of response surface quadratic model for iron sulfate conversion, the Model F-value of 5.91 and Prob > F of <0.0009 implied that the model was significant. For the model terms, values of Prob>F less than 0.05 indicated that the model terms were significant. In this case A, B, C and BC are significant model terms (all have Prob > F less than 0.050) where A (Temperature), B (Reaction time), C (particle size). This tells us that the reaction temperature, reaction time, particle size, and the interaction term BC affect the yield much significantly.

4.5. Effect of process variables on yield of Iron Sulphate

Based on the analysis of variance, the iron sulfate reaction was significantly affected by various interactions between the process variables. On the other hand, significant individual process variables that affect the iron sulfate preparation is reaction temperature, A, reaction time, B, and reaction time, C. This result demonstrated the advantage of using design of experiments in capturing the interaction between variables that affects the iron sulfate preparation.

The statistical analysis of DOE software indicated that the iron sulfate yield was significantly affected by the individual process variables and by their interaction. The individual process variables that significantly affected the response value was the reaction temperature (A), reaction time (B), particle size (C), and the interaction term reaction temperature and reaction time (AB) , reaction time and particle size(BC). This detailed parameter effect analysis result shows that DOE software is a best tool in examining the experimental findings. The individual and interaction effects of the variables are well discussed below:

4.5.1. Effect of Temperature on the yield of Iron sulphate

Figure 4.2 shows the effect of reaction temperature on the yield of the iron sulfate preparation. It can be seen that with an increase in reaction temperature, the yields of iron sulfate increased significantly. Usually conducting a reaction at a higher temperature delivers more energy into the system and increases the reaction rate by causing more collisions between particles, as explained by collision theory. However, the main reason that temperature increases the rate of reaction is that more of the colliding particles will have the necessary activation energy resulting in more successful collisions.

Disparate, as it can be seen from figure 4.2, further increase in temperature above 83⁰C seems incident decreases the FeSO₄ yield; High Reaction temperature tend to produce trivalent iron or hydrated complex sulfur compounds instead of FeSO₄. In addition it can cause higher energy consumption, which is extra cost.

Design-Expert® Software

Yeild

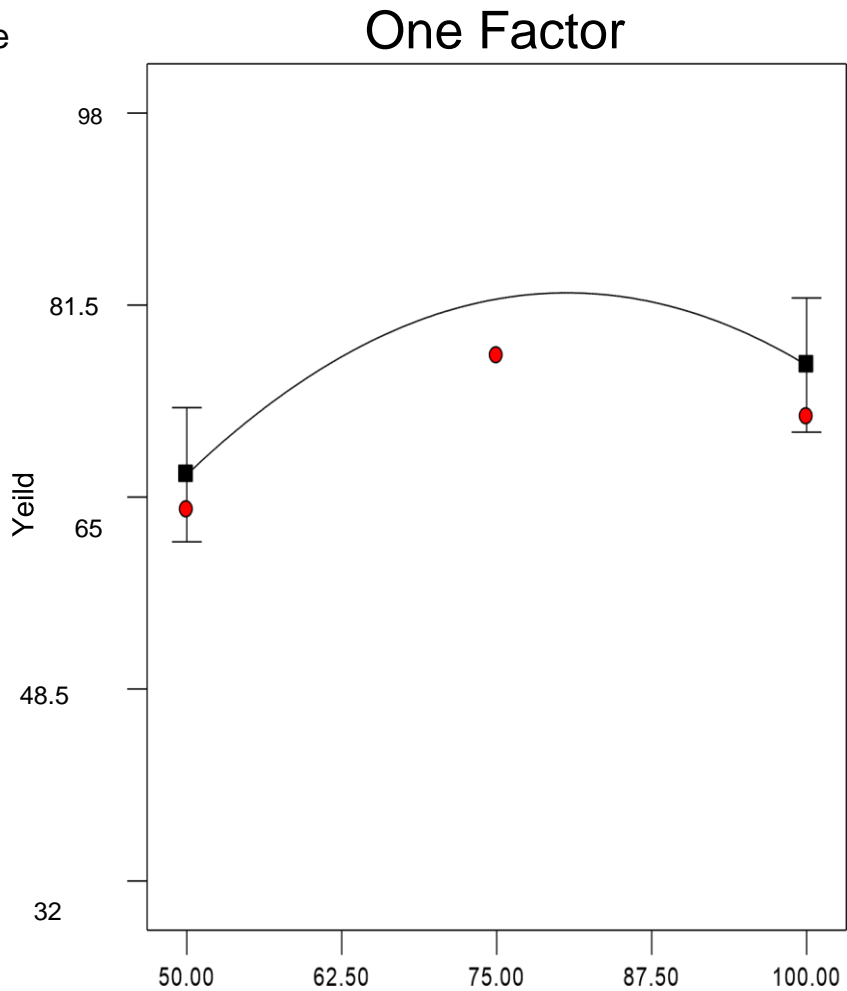
● Design Points

X1 = A: temperature

Actual Factors

B: time = 60.00

C: particle size = 2.00



A: temperature

Figure 4-2: Effect of reaction temperature on the yield of Iron Sulphate

4.5.2. Effect of Time on the yield of Iron sulphate

The reaction time affects the iron sulfate yield positively. As it is easily be observed from Fig.4.3, the time increases, and the iron sulfate also increases. This is because that at a longer time the rate of reaction is greater so that the reaction facilitated and the yield will be good. As it is well reported almost in all reaction journals and literatures, the rate of the chemical reaction is positively affected by time. At a lower time the reaction fully didn't completed. The ore and acid gets enough time for the reaction in the long time.

But as shown from the Figure (4.3) below the effect of one factor which is the reaction time is not highly significant compared to the reaction temperature and particle size of the ore.

Design-Expert® Software

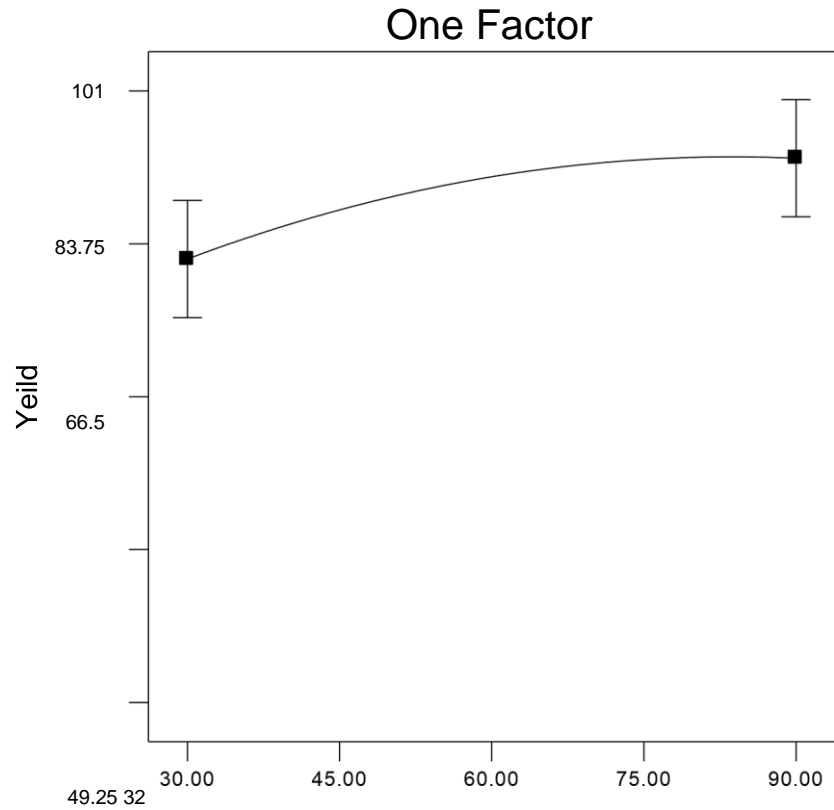
Yeild

X1 = B: time

Actual Factors

A: temperature = 87.84

C: particle size = 1.03



B: time

Figure 4-3: effect of reaction temperature

4.5.3. Effect of particle size on the yield of Iron sulphate

Unlike reaction time, particle size of iron ore is inversely proportional with product yield. Because when the particle size decreases the surface area for the reaction will increase. This means the rate of reaction increases as the surface area does. That is because more particles of the solid are exposed and can be hit by reactant molecules.

Design-Expert® Software

Yeild

● Design Points

X1 = C: particle size

Actual Factors

A: temperature = 75.00

B: time = 60.00

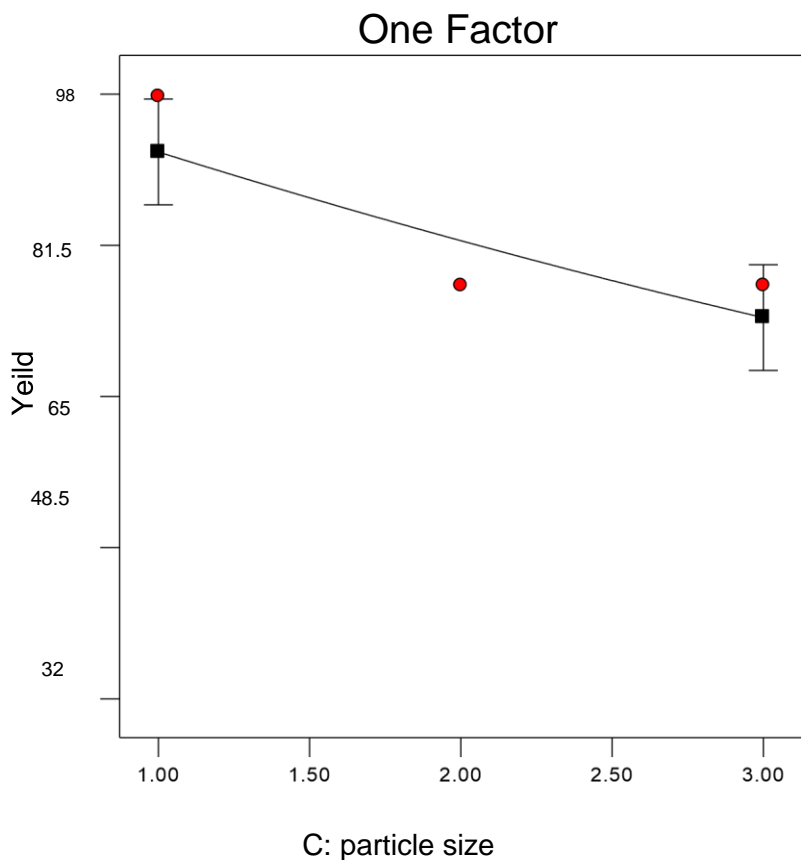


Figure 4-4: effect of particle size on the yield of Iron sulphate

4.5.4.Effect of Interaction between Process Variables

The process variable were found to have significant interaction effects was only reaction time and particle size (BC). Figure 4.5 show the interaction between reaction time and particle size on the yield of iron sulfate.

Reaction temperature and reaction time (AB), reaction temperature to particle size (AC) had not significant interaction. But generally, increase in reaction temperature is found to increase the yield of iron sulfate up to some pointe but after that there will be a decrease in all time points. This is due to similar explanation given in the previous section.

At smaller range of particle size, longer reaction time give higher yield of iron sulfate and it decrease as the time was smaller. However, at larger range of particle size, totally opposite is

observed. Longer reaction time give lower yield of iron sulfate and it increase as the time was smaller.

At smaller range of particle size, longer reaction time give higher yield of iron sulfate and it decrease as the time was smaller. However, at larger range of particle size, totally opposite is observed.

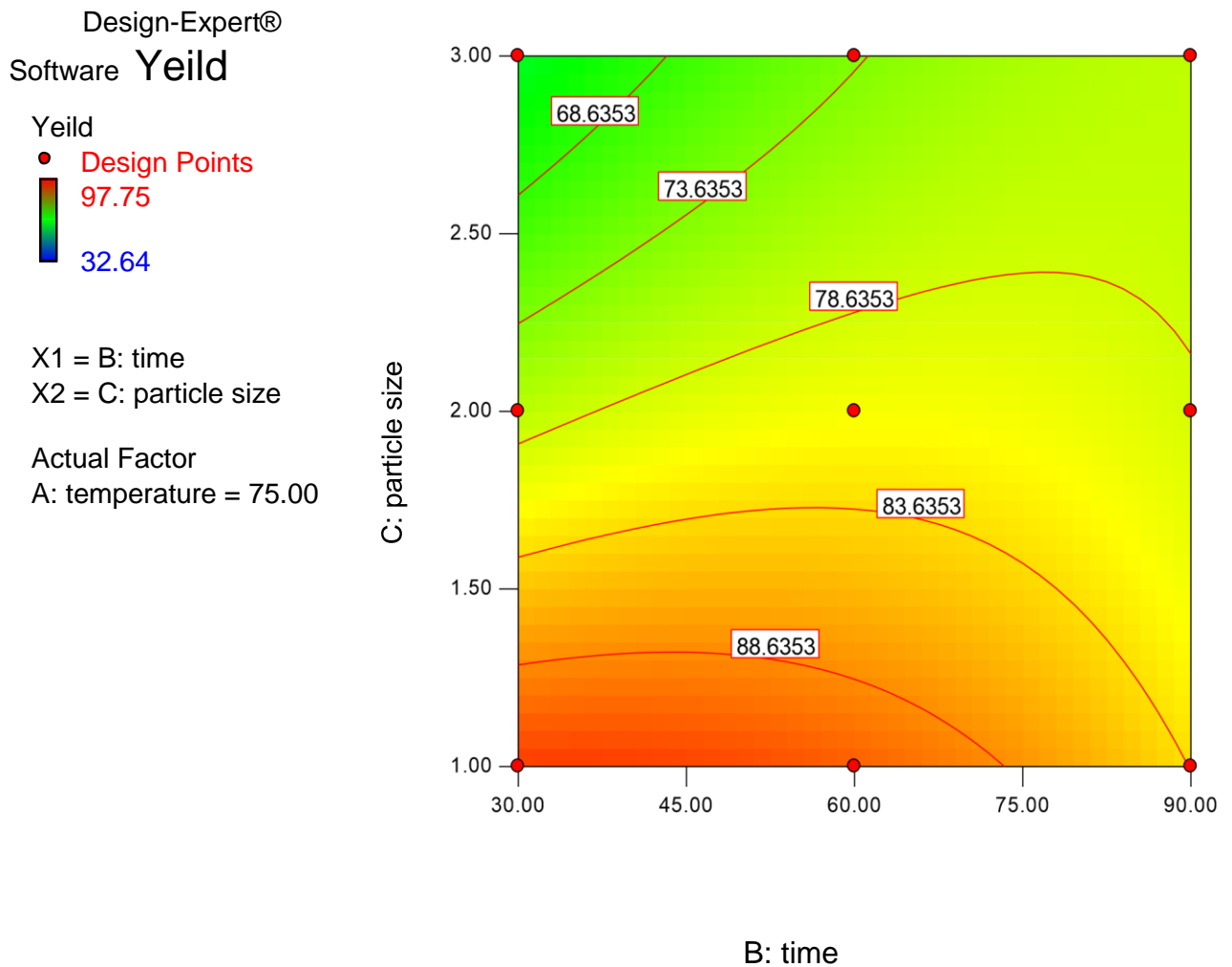
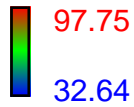


Figure 4-5: Effect of Interaction between time and particle size

Design-Expert® Software

Yeild



X1 = B: time

X2 = C: particle size

Actual Factor

A: temperature = 75.00

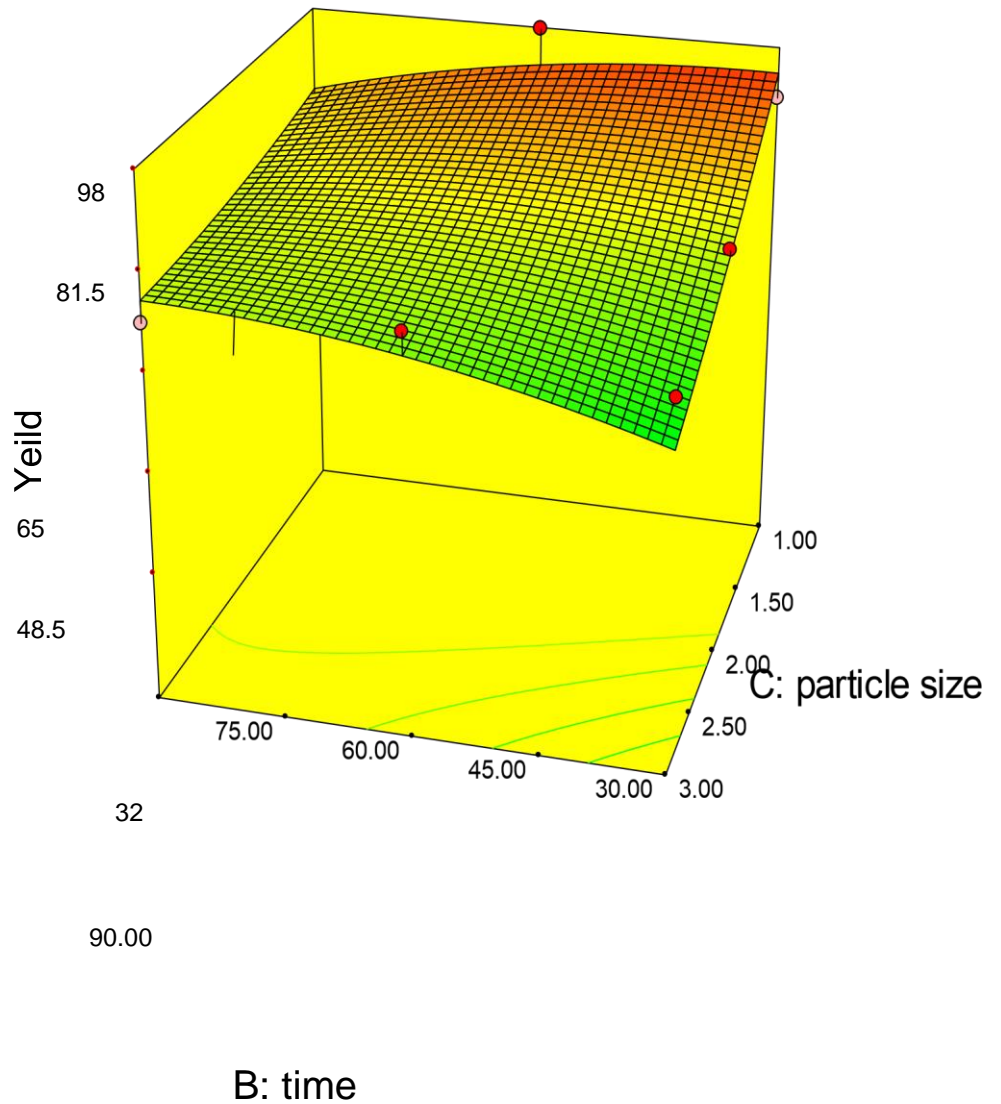


Figure 4-6: Effect of Interaction between time and particle size

This phenomena is further supported by the fact that reaction temperature and particle are the only significant process variable that affect the yield of the iron sulfate as indicated by the highest F value in the ANOVA (Table 4.5).

4.6. Optimization of Process Variables

The results above have shown that the three process variables and the interaction among the (BC) variables affect the yield of iron sulfate. Therefore, the next step is to optimize the process variables in order to obtain the highest amount of iron sulfate using the model regression developed.

Using the optimization function in Design-Expert, it was predicted that at conditions of 75°C reaction temperature, 60 min reaction time and <0.125mm of particle size, an optimal yield of 97.75% can be obtained. In order to verify this prediction, experiments were conducted and the results were comparable with the prediction. It was found that the experimental value of 94.4024% yield of iron sulfate agreed well with the predicted value. Therefore, this study shows that Fe₂O₃ and acid reaction is a potential reaction process for the production of iron sulfate from local iron ore, hydrochloric acid and sulfuric acid. The optimization result also tells the same result as the ANOVA output. The ANOVA output shows that the reaction between iron ore and acid is significantly affected by the temperature, reaction time and the particle size of the ore also the interaction between the reaction time and particle size.

4.7. Physico - chemical properties of iron sulfate

The physical and chemical properties of the iron sulfate from local iron ore was characterized by the methods indicated in chapter three under section 3.3 are summarized as follow.

Acid value

Acid values, the triplicated results for iron sulfate obtained is summarized in table below.

Table 4-6 Acid values

Run	Titration volume (ml)	AV of FeSO₄
1	0.11	0.61
2	0.14	0.78
3	0.08	0.44
Mean		0.61
		+_0.17

From the table above the average acid value of iron sulfate 0.61 which is relatively small. The low acidity of the product is an indication of the iron sulfate which is free from hydrolytic rancidity and enables the direct use of such product without further neutralization. Therefore, the result obtained indicated that iron sulfate can be used directly without further neutralization. So this can be an advantageous that iron sulfate cannot develop high acidity in the soil during fertilization or waste water treatment.

Moisture content

Table 4-7: Moisture content

Run	Weight of the sample before drying (g)	Weight of the sample after drying (g)	Weight Difference (g)	Moisture content (% w/w)
1	500	304.04	195.96	39.192
2	500	304.98	195.02	39.004
3	500	305.23	194.77	38.954
Mean value	500 ±0.00	304.75±0.627	195.25 ±0.627	39.05±0.125

The moisture content of iron sulfate was performed and observed to be in the range of 38.940 - 39.192 wt. %. When we compare the average of the results with the theoretical amount (38.84%) ASTMA, maximum is acceptable.

Specific gravity (Density)

The density of the iron sulfate produced was performed and observed to be in the range 1.6 to 1.9g/cm³ at different process parameters. When we compare the average of the results 1.898 g/cm³ with the ASTMA for iron sulfate it is acceptable.

Table 4-8 specific gravity

Run	Density (g/cm³)
1	1.64
2	1.93
3	1.88
Mean value	1.816667 +_0.155027

pH determination

The pH value of iron sulfate was measured using pH meter three times and the results obtained are summarized in table 6 below.

Table 4-9: pH determination

Run	p^H values
1	4.94
2	5.12
3	4.96
Mean value	5.007 +_0.098658

From the table above the pH value of iron sulfate was slightly acidic. The preferable pH value is in the range of 4.94-5.12. The obtained pH value of iron sulfate is in the range to be used in ASTMA standard.

Matter insoluble in water

The insoluble matter of iron sulfate produced was performed and observed to be in the range of 0.018-0.062wt % at different process parameters. So almost it is soluble in water. This property makes it easy soluble and absorbable by plant as a fertilizer.

Table 4-10: determination of matter insoluble in water

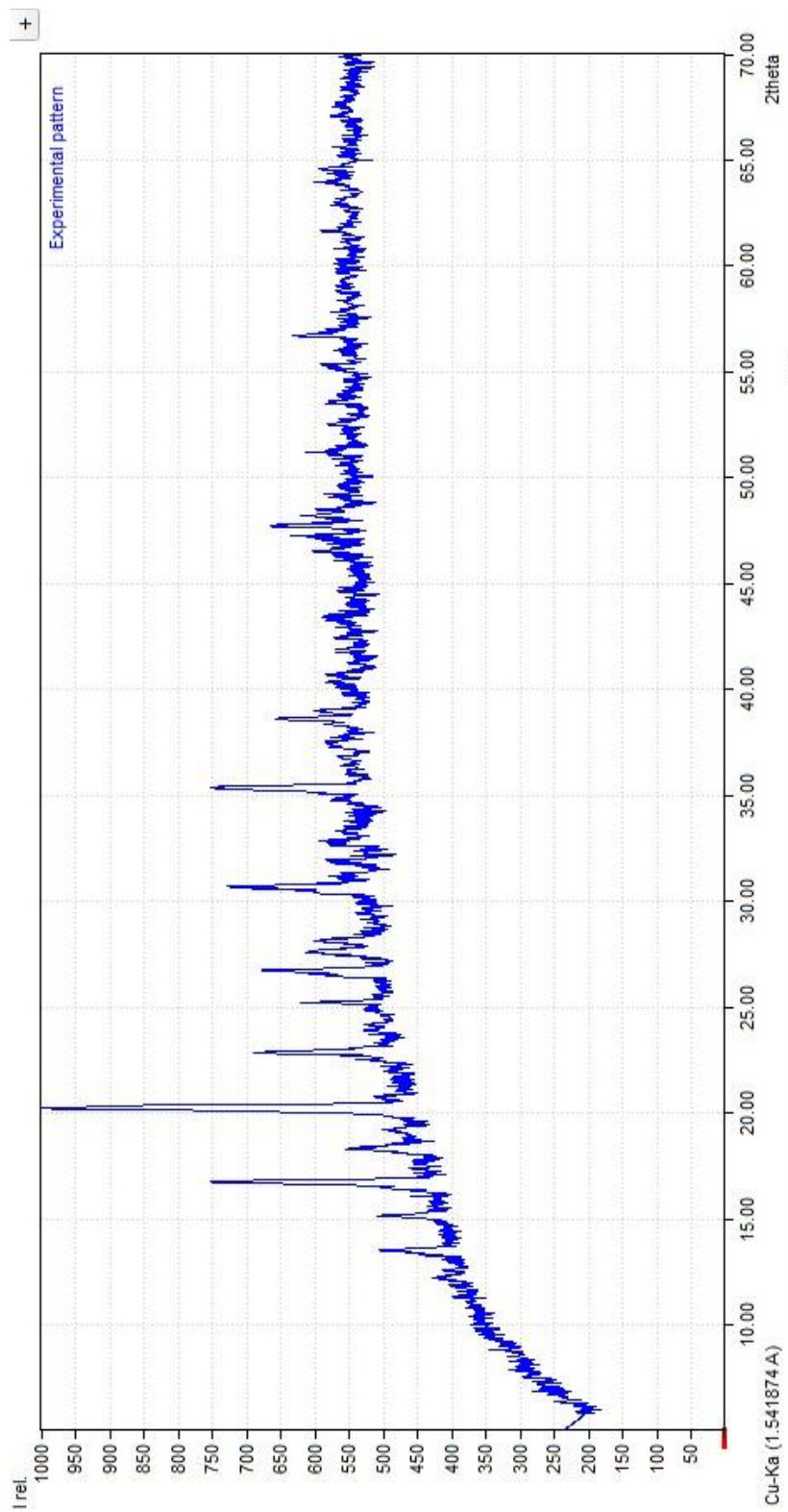
Run	Water soluble matter (wt. %)
1	0.018
2	0.032
3	0.062
Mean value	0.0373 +_0.02248

X-Ray Diffraction Structure Analysis

X-ray crystallography is a tool used for identifying the atomic and molecular structure of a crystal, in which the crystalline atoms cause a beam of incident X-rays to diffract into many specific directions. By measuring the angles and intensities of these diffracted beams, a crystallographer can produce a three-dimensional picture of the density of electrons within the crystal. From this electron density, the mean positions of the atoms in the crystal can be determined, as well as their chemical bonds, their disorder and various other information. [36]

The oldest and most precise method of X-ray crystallography is single-crystal X-ray diffraction, in which a beam of X-rays strikes a single crystal, producing scattered beams. When they land on a piece of film or other detector, these beams make a diffraction pattern of spots; the strengths and angles of these beams are recorded as the crystal is gradually rotated. Each spot is called a reflection, since it corresponds to the reflection of the X-rays from one set of evenly spaced planes within the crystal. For single crystals of sufficient purity and regularity, X-ray diffraction data can determine the mean chemical bond lengths and angles to within a few thousandths of an angstrom and to within a few tenths of a degree, respectively. The atoms in a crystal are not static, but oscillate about their mean positions, usually by less than a few tenths of an angstrom. X-ray crystallography allows measuring the size of these oscillations. [37]

The results of the iron sulfate analyses by XRD are presented in Figure 4.7 XRD analysis detected the following Iron crystalline phases Melanterite ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), Szomolnokite ($\text{FeSO}_4 \cdot \text{H}_2\text{O}$) and Rozenite ($\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$).



Please run raw data processing (e.g. press <Ctrl+A>):

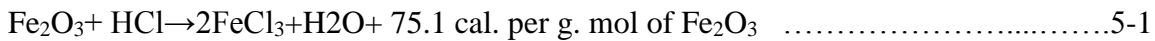
Figure 4-7: XRD result

5. ECONOMIC EVALUATION

5.3. Process description and technology selection for iron sulfate production from local iron ore

Iron ore (hematite) are finely crushed to pass a screen < 0.125mm mesh. The reactor 1 is filled up to the bottom of the filter with a body of concentrated hydrochloric acid (35% by weight). The relatively deep body of acid is heated to 60° C.

The particles of ore are fed through the interstices of the screen into the column of acid in the reactor 1. The acid reacts exothermically with the ore, as follows:



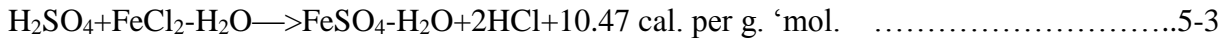
The acid flows downwardly through the reactor 1 and maintains a high concentration of acid at the bottom of reactor, while the fine ore admitted through the screen at the top of such tank maintains the solution produced, a solution comprised essentially of ferric chloride, nearly at neutral value as it overflows through the filter into the other reactor 2 that contains the body of ferrous metallic scrap.

In second compartment any free acid in the solution is quickly neutralized while it flows downwardly through the porous mass of scrap, and the ferric chloride (FeCl₃) is reduced to ferrous chloride (FeCl₂) in accordance with the following exothermic reaction:



Then to get pure product the solution was filtered after sedimentation. When the solution in tank delivers to a spray nozzle of an evaporator or drier, which is heated by hot gases delivered through a duct. The evaporation of the water from the solution sprayed into the evaporator leaves dry ferrous chloride crystals. The ferrous chloride salt retains from the time of its formation one molecule of water of crystallization at 450° F., represented by the formula FeCl₂·H₂O. The crystalline chlorides collect in a hopper provided at the bottom of the evaporator, whence they are fed by a screw conveyor into a reaction chamber. In the chamber a pan is provided, the pan containing a pool of concentrated (66°) sulfuric acid. In consequence the salt and acid are thoroughly mixed and react endothermically, to form ferrous sulfate and hydrochloric acid gas is

released in accordance with the following reaction, it being noted that the ferrous chloride coming from the hot evaporator adds sufficient heat to the acid in pan to make-up for the heat lost in the reaction.



The hydrochloric acid gas released in the reaction escapes through pipe which conducts it into the top of the enclosed compartment of the leaching tank.

The operation is done by Batch-Continuous Operation (semi batch) this operation endeavors to obtain the advantages of both of batch and continuous operations. It is based on reactors that feed the feedstock at once and continuously discharging the product or continuously adding the feedstock and discharging the product at once, a continuous separation and purification process. It used to control the reaction process and change feed stocks more rapidly than the continuous and batch operations.

5.4. Basic assumptions

- Any type of available raw materials, both iron ore and sulfuric acid are locally available
- Daily production will be about 48 quintals.
- 5 working days per week about 260 days per year
- Income tax will be about 35% of the gross profit and will be paid starting from the second year of the project

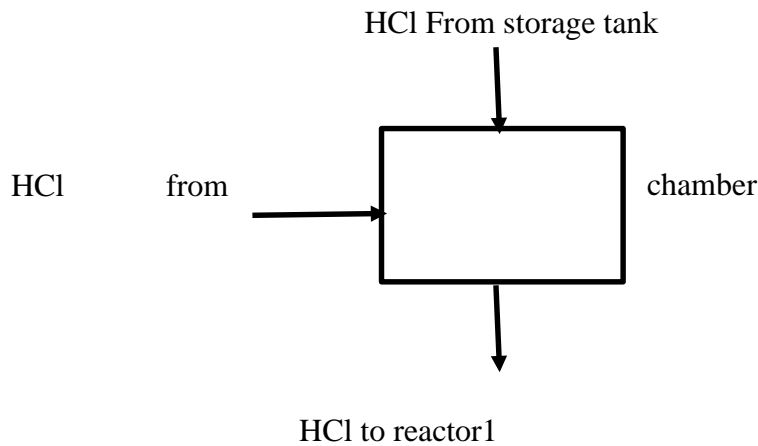
5.5. Material and energy balance on major unit operations

5.5.1. Material balance on major unit operations

Capacity: Daily production will be about 4800kg. Daily requirements of chemicals will be 2000 kg of 80%(w/w) iron ore (hematite Fe_2O_3)ore 1600kg of pure iron ,2785 kg of pure H_2SO_4 and 1200kg HCl.

1. Acid storage tank 1

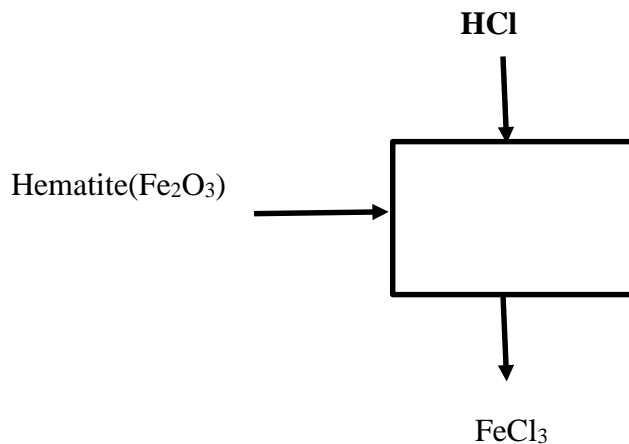
Let's assume 80% of hydrochloric acid will be recycled

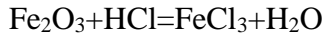


$\text{HCl From storage tank} = 0.2 \times 6000 \text{kg} = 1200 \text{kg}$

$\text{HCl to Reactor1} = 6000 \text{kg}$

2. Reactor 1





$$160\text{g} + 600\text{g} = 322\text{g} + (384 + 54\text{g}) = 322\text{g FeCl}_3 + 438\text{g H}_2\text{O}$$

General reactor mole balance as

accumulation = flow in - flow out + generation by reaction

$$\frac{dn_j}{dt} = F_{j,0} - F_j + \int_V r_j dV$$

Mole balance for batch reactor

Accumulation = generation by reaction

$$\frac{dn_j}{dt} = \int_V r_j dV$$

$$r_j V_f = \frac{dn_j}{dt}$$

$$V_f = - \int_{n_{j,0}}^{n_j} \frac{dn_j}{r_j}$$

Where: V_f = volume of reactor

N_j = number of mole

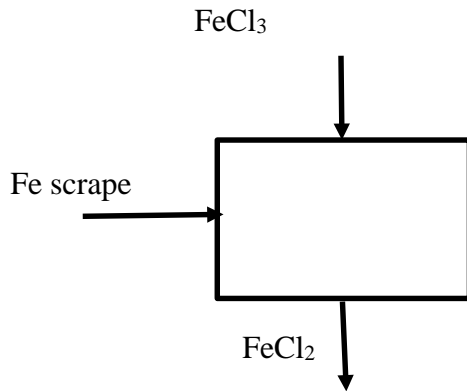
t_r = time

r_j = rate of reaction (which get from the experiment)

$$V_f = 0.01584\text{m}^3 \text{ density} = 5260\text{kg/m}^3$$

So the amount of hematite required = **2000kg hematite**

3. Reactor



$$V_f = - \int_{n_{j,0}}^{n_j} \frac{dn_j}{\text{tr}(-r_j)}$$

Where: V_f = volume of reactor

N_j = number of mole

t_r = time

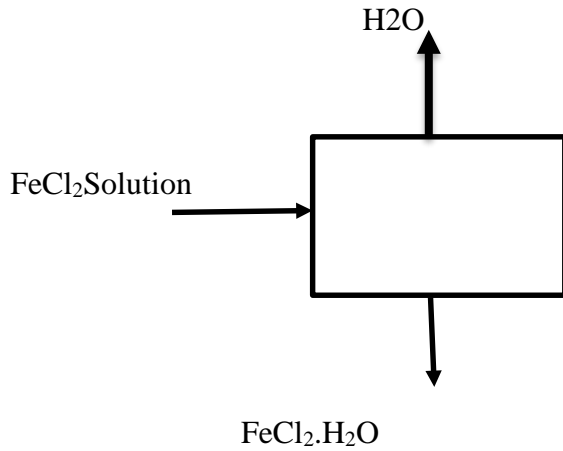
r_j = rate of reaction (which get from the experiment)

$$V_f = 0.14224 \text{m}^3 \text{ density} = 3937 \text{kg/m}^3$$

So the amount of iron scrape required

$$= 560 \text{kg iron scrape}$$

4. Drier



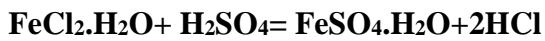
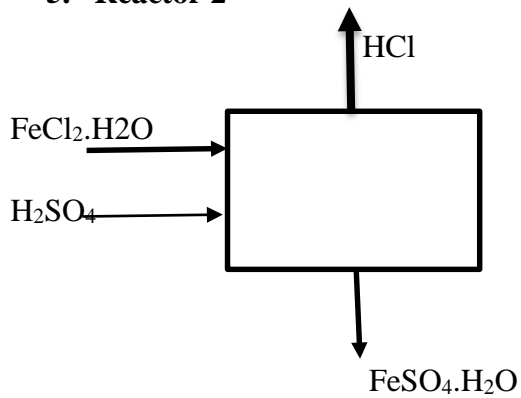
In one molecule of $\text{FeCl}_2 \cdot \text{H}_2\text{O}$ there is 126g FeCl_2 and 18g H_2O

So with 3580kg FeCl_2 there will be

$$= (3580\text{kg} \times 18\text{g}) / 126\text{g} = 511.4\text{kgH}_2\text{O}$$

The amount of water evaporated = 4380kg - 511.4kg = 3868.57kgH₂O

5. Reactor 2



$$144 + 98 = 170 + 72$$

$$(3580\text{kg} + 511.4\text{g}) + X = Y + Z$$

$$V_f = - \int_{n_{j,0}}^{n_j} \frac{dn_j}{r_j}$$

Where: V_f = volume of reactor

N_j = number of mole

t_r = time

r_j = rate of reaction (which get from the experiment)

Volume of HCl $V_f = 1.37 \text{ m}^3$ density = 1490 kg/m^3

So the amount of HCl produced

$$= 2045 \text{ kg}$$

Volume of FeSO_4 $V_f = 1.61 \text{ m}^3$ density = 3000 kg/m^3

So the amount of FeSO_4 produced

$$= 4830 \text{ kg}$$

5.3.2 Energy balance on major unit operations

Energy balance on dryer

$$Q_s = 3580 \text{ kg} \cdot 100.6 \text{ J/mol} \cdot \text{K} (323\text{K} - 298\text{K})$$

$$Q_s = 2322007.8 \text{ kJ/hr}$$

$$Q_{\text{FeCl}_2} = M_{\text{FeCl}_2} C_{p_{\text{FeCl}_2}} (T_{\text{FeCl}_2} - T_{\text{ref}})$$

$$Q_{\text{FeCl}_2} = 4091.4 \cdot 394.5 \text{ J/mol} \cdot \text{K} (505.2\text{K} - 298\text{K})$$

$$Q_{\text{FeCl}_2} = 334109861.1 \text{ kJ/hr}$$

$$Q_{\text{water vapor}} = M W \lambda_{\text{water vapor}}$$

$$Q_{\text{water vapor}} = 3868.57 \text{ kg} * 2,256 \text{ kJ/kg}$$

$$Q_{\text{water vapor}} = 8726208 \text{ kJ/kg}$$

$$Q_{\text{electric heating}} + Q_{\text{solution}} = Q_{\text{water vapor}} + Q_{\text{FeCl}_2} \dots\dots\dots 5-4$$

$$Q_{\text{electric heating}} = Q_{\text{water vapor}} + Q_{\text{FeCl}_2} - Q_{\text{solution}}$$

$$Q_{\text{electric heating}} = 872620.8 \text{ kJ} + 33410.98611 \text{ kJ} - 23220.078 \text{ kJ}$$

$$Q_{\text{electric heating}} = 882811.7 \text{ kJ/hr}$$

5.6. Design of Equipment

The main objective of this design is to determine volume of the equipment and material for construction.

1) hydrochloric acid tank

Mass feed rate of hydrochloric acid = 1200 kg/day = 150 kg/hr and density = 1178.9 kg/m³

Volumetric flow rate of hydrochloric acid = (150 kg/hr) / (1178.9 kg/m³)

Volumetric flow rate of hydrochloric acid = **0.1272 m³/ hr**

Let the HCl will store for 1 day

The volume of storage tank = Volumetric flow rate of the tank * storage time

The volume of storage tank = 0.1272 * 24hr = **3.0536 m³**

Assuming 15% safety margin m³ = 3.05369 * 0.15 = 0.458 m³

Therefore total volume of the mixer = 3.05369 m³ + 0.458 m³ = **3.5119 m³** From the geometry of

material with cylindrical form, the volume = π (R²) h

From physical space of the plant let the height of the mixer be 1.5 m.

Then, the radius of the mixer can be calculated as 3.5119 m³ = π (R²) h

$$R^2 = 3.5119\text{m}^3 / 1.5 \pi = 3.5119\text{m}^3 / 4.712\pi = 0.7453\text{m}^2$$

$$\Rightarrow R = 0.8633\text{m}$$

$$\text{Diameter of the tank, } D = 2R = 1.7266\text{m}$$

2) Reactor 1

Mass feed rate of hematite = **2000kg /day = 83.333kg/hr** and density = **5260kg/m³**

Mass feed rate of hydrochloric = **6000 kg/day = 250 kg/hr** and **Density = 1178.9kg/m³**

Volumetric flow rate of hematite = **0.01584m³/hr**

Volumetric flow rate of hydrochloric acid = **0.212m³/hr**

Volumetric flow rate of the mixture = **0.01584m³/hr + 0.212m³/hr = 0.22784m³/hr**

If the reaction takes 1 hour

The volume of mixer = Volumetric flow rate of the mixture * reaction time = **0.22784m³**

Assuming 15% safety margin $m^3 = 0.22784\text{m}^3 * 0.15 = 0.034176\text{m}^3$

Therefore total volume of the mixer = **0.22784m³ + 0.034176m³ = 0.262016m³**

From the geometry of material with cylindrical form, the volume = $\pi (R^2) h$ From physical space of the plant let the height of the mixer be 1.5 m.

Then, the radius of the mixer can be calculated as $0.262016\text{m}^3 = \pi (R^2) h$

$$R^2 = 0.262016\text{m}^3 / 4.712389\pi = 0.0556 \Rightarrow R = 0.2358\text{m}$$

$$\text{Diameter of the mixture, } D = 2R = 0.4716\text{m}$$

3) Reactor 2

Volume of iron scrupe = mass/ dencity = $560\text{kg} / 3937\text{kg/m}^3 = 0.14224 \text{m}^3$

Volume of reactor 2 = Volume of iron scrupe + Volume of reactor 1

$$=0.14224 \text{ m}^3+0.22784\text{m}^3=0.370086\text{m}^3$$

Assuming 30 % safety margin

$$\text{Volume of reactor 2} =0.370086\text{m}^3*1.3=\mathbf{0.4811118\text{m}^3}$$

4) Settling tank

$$\text{Volumetric flow rate of the settling tank} = 0.01584\text{m}^3/\text{hr} + 0.212\text{m}^3/\text{hr} = 0.22784\text{m}^3/\text{hr}$$

If sedimentation needs 2 hour

$$\text{The volume of settling tank} = \text{Volumetric flow rate of settling tank} * \text{settling time} = \mathbf{0.45568\text{m}^3}$$

5) Chamber (Reactor 3)

$$\text{The volume of FeSO}_4\cdot\text{H}_2\text{O} = 4830.12\text{kg} /3000\text{k g/m}^3=1.61\text{m}^3$$

$$\text{The volume of HCl} =1490 \text{ kg/m}^3 /2045.69=1.37\text{m}^3$$

$$\text{The volume the chamber} =1.61\text{m}^3 +1.37\text{m}^3 =2.98 \text{ m}^3$$

Assuming 30 % safety margin

$$\text{The volume the chamber} =2.98*1.3=\mathbf{3.874 \text{ m}^3}$$

5.7. Financial Analysis

Experimentally and engineering wise it has been seen that investing iron sulfate production for the plant is feasible. But, its feasibility should be checked financially. In this section, the proposed project to be analyzed financially depending on the proposed and designed iron sulfate production plant. [38]

Total Capital Investment

The total capital investment (TCI) for the production of iron sulfate is estimated by summing up the fixed capital investment (FCI) and working capital. [39]

$$\mathbf{TCI = FCI + WC \dots\dots\dots 5-5}$$

1. Purchase equipment cost estimation Purchased cost for some basic plant equipment's are estimated from the internet. [40].

1. Machinery

Table 5-1: Purchased Equipment Cost estimation

Equipment	Amount	unit Cost(\$)	Total Cost(\$)
Storage tanks			
HCl storage tank	1	6300	6300
H ₂ SO ₄ storage tank	1	6800	6800
Process equipment			
Reactor 1	1	2900	2900
Reactor 2	1	11568	11568
Reactor 3	1	9315	9315
Settling tank	1	4784	4784
Dryer	1	9000	9000
Pump	6	100	600
Filter system	2	3750	7500
Heavy duty balances	2	700	1400
Total			60,167\$ =1,383,841birr

2. Building

The engineering estimates of the built are not yet available. However, the following estimates were taken by considering the fact that the type of building required will be types that can be built on cheaper materials without compromising the quality product.

Table 5-2: Estimation cost of building

No.	Building type	Number	Dimension	Total cost birr
1	Office	10	5m x 5m	600000
2	Store	5	10m x10m=2 20m x20m=2 30m x30m=1	1000000
3	Production hall	6	30m x10m=1 10m x10m=5	1000000
4	Shower and toilet	10		200000
5	Water well	1		400000
6	Parking shade	1		4000
7	Guard house	1		4000
8	Fence			100000
9	Drainage system			10000
10	Water supply lines			10000
11	Water treatment tanks		5m x 5m x 3m	100000
12	Electrical supplylines			200000
Sub total				3448,000 birr

Estimation of Fixed Capital Investment

Table 5-3: Estimation of Fixed Capital Investment

	Components	Factors	Cost(birr)
1.Direct cost	Purchased equipment cost(PEC)	PEC	1,383,841
	Equipment erection	0.05PEC	69192.05
	Piping	0.02PEC	27676.82
	Electricity	0.01PEC	13838.41
	Building	0.05PEC	69192.05
	Utilities	0.025PEC	34596.025
	Storage	0.025PEC	34596.025
	Total direct cost		
2.Indirect cost	Design and engineering	0.02PEC	27676.82
	Contractors fee	0.05PEC	69192.05
	Contingency	0.01PEC	13838.41
	Total indirect cost		
3.Fixed Capital Investment	FCI =Direct Cost + Indirect Cost= 1,743,640		
4.Working Capital (WC)	0.05FCI = 87,182		
5.Total Capital Investment	FCI+WC=1,743,640+87182= 1,830,822		

Estimation of Total Production Cost

Cost of raw materials

The cost of each raw material per year is estimated by multiplying the raw material required per day by 260 working days per year and 8 working hours per day, and then multiplying by raw material unit price.

Table 5-4: Cost of raw materials

No.	Item	Unit	Quantity	Unit price birr	Total price birr
1	iron ore	Kg	420000	10	420,000
2	H ₂ SO ₄	Kg	588000	40	23,520,000
3	HCl	Kg	360000	20	7,200,000
Sub total					31,140,000

Annual utility cost estimation

Annual utility cost estimation can be determined from energy balance by calculating the total amount of steam, water and electricity cost.

Current price one tonne of steam=850.00 Birr/tonne

Total amount of steam required per year =45 tonne/yr

Cost of steam =38250 Birr/yr

Current price of electricity=0.46cents/kWh

Total power used annually = 60,000kWh/yr

Cost of current = birr 27,600 Birr/yr

Water current price = 0.26 birr per 20 liter

Total amount of water required per year = 4,372,662/yr

Cost of water = 56844.606birr/yr

Total utility cost 122694.6 birr/yr

Operating labor cost estimation

Table 5-5: Operating labor cost estimation

Work specification	No. Required	Monthly salary (birr)	Yearly salary (birr)
Manager	1	9000.00	10800.00
Production head	1	4000.00	48000.00
Quality head	1	5200.00	63000.00
Purchasing and sales head	1	4600.00	55200.00
Accountant	1	3000.00	36000.00
Secretary	1	2200.00	26400.00
Laboratory technician	1	3000.00	36000.00
Mechanics	1	2200.00	26400.00
Production line worker	4	1400.00	67200.00
Raw material storage are workers	1	1200.00	14400.00
Final product storag area workers	1	1200.00	14400.00
Drivers	1	1600.00	19200.00
Security guard	3	1200.00	18800.00
Cleaners	1	1200.00	18800.00
Total			454600.00

Table 5-6: Estimation of Total Product Cost

Components		
A. Direct production cost		.
1.Raw material cost		31,140,000
2.Operating Labor (OL)		454600.00
3.Direct supervision	10%OL	45460.00
4. Utilities		122694.6
5. Maintenance and repair	0.4% FCI	697456
6. Laboratory charges	1%OL	4546.00
Direct production cost	32,464,757	
B. Fixed charges		
1.Depreciation	8%FCI	139491.2
2.Capital charge	1%FCI	17436.4
3.Insurance	1%FCI	17436.4
Fixed charges	174364	
C. plant overhead	5%OL	22730
A+B+C=manufacturing cos	32,661,851	
1.Adminstrative cost	2%TPC	
2.Distribution and selling cost	2%TPC	
3. R&D	2%TPC	

Total production cost (TPC) = Manufacturing cost + General expenses

$$\text{TPC} = 32,661,851 + 6\% \text{TPC}$$

$$\text{TPC} - 0.06\text{TPC} = 32,661,851 \text{ birr}$$

$$\text{TPC} = 34,746,650 \text{ birr/year}$$

$$\text{Unit cost of iron sulfate} = 50 \text{ birr/kg}$$

$$\text{Annually earning of iron sulfate} = 44,200,000 \text{ birr/yr}$$

Gross annual profit = Total Annual sales price- Total Annual operating cost
=44,200,000birr/yr -34,746,650 birr/yr

$$=9,453,350\text{birr/yr.}$$

Assume 35% of income tax for Ethiopia case

Net annual profit

$$\text{Net annual profit} = 9,453,350 - (0.35 * 9,453,350) = 6,144,677.5\text{birr/yr}$$

Annual depreciation = 10% of fixed capital cost

$$= 0.1 * 1,743,640$$

$$= 174,364\text{birr/year}$$

Rate of return on investment (ROR)

$$\text{ROR} = \text{Net profit} / \text{Total Capital Investment} \dots\dots\dots 5-6$$

$$= 6,144,677.5 / 34,746,650$$

$$= 17.68 \%$$

Payback period

It is the minimum length of time theoretically necessary to recover the original investment in the form of cash flow to the project based on total income minus all cost except depreciation

Payback period = depreciable fixed capital / (average profit + average depreciable / year)

$$= (1,743,640 - 174,364) / (6,144,677 + 174,364)$$

$$= 1,569,276 / 6,319,041.5 = 2.48\text{years}$$

6. CONCLUSION AND RECOMMENDATION

Conclusion

In this project, iron sulfate is prepared and characterized from local raw materials. Iron sulfate was produced using local iron ore with sulfuric and hydrochloric acid. Different parts of Ethiopia are rich in iron ore especially Oromia and Tigray Region. Iron sulfate is produced by reacting iron ore with sulfuric acid in the presence of hydrochloric acid.

Production was performed by batch process system at atmospheric pressure. And then the effects of reaction temperature, reaction time and particle size were investigated using Design expert 7.0.0 software. The statistical analysis showed that the three process variables reaction temperature, reaction time and particle size, and the interaction between this reaction time and particle size had significant effects on the yield of iron sulfate preparation. Three levels and three factors central composition design with full type calibration is used. Increasing reaction temperature, reaction time causes increase in the yield of iron sulfate until the optimal reached. However, further addition of temperature results in reduction of iron sulfate yield due to high reaction temperature tends to produce trivalent iron or hydrated complex sulfur compounds instead of FeSO_4 . The result also gives the optimum value for the three processing variables: temperature, time and particle size which are 75°C , 60 min and 1.00(which is $<0.125\text{mm}$) respectively. The corresponding yield is 97.75%.

The physicochemical properties of the produced iron sulfate were tested against ASTM specifications and most of them were in a good agreement with the standard. The test results showed that iron sulfate produced from local iron ore has almost the same quality as compared with other imported iron sulfate products.

Based on the existing production process and using current values for reagents, equipment's, and raw material costs the economic analysis is evaluated. It estimated that the production cost of iron sulfate from local iron ore approximately to be 37.52 birr/kg. Thus, the preliminary economic evaluation result suggests that the project is feasible. Therefore, local iron ore can be used as a less expensive supplementary feedstock for iron sulfate by curing the environment and increasing the agricultural earning.

Recommendation

Iron sulfate can be produced both from iron metal and iron ore; but iron metal was very expensive and imported material. At the same time, many mineral exploration finding shows that Ethiopia is gifted with abundant iron ores. Detailed surveys of the aforementioned exploration projects outlined the presence of iron rock in different iron oxide forms .For these reasons, using local iron ore for production of iron sulfate is choice less option. In addition, sulfuric acid is locally available (from Awash Melkasa aluminum sulfate and sulfuric acid factory).

Crushing the iron ore, reacting with acid at optimum temperature and drying are the main unit operations to produce iron sulfate.

Having technology for production of ferrous sulfate is preferable than for ferric sulfate due to its multipurpose uses and diversified product uses. Ferrous sulfate is useful both in agricultural and industrial purpose than ferric sulfate. But for waste water treatment purpose ferric sulfate is preferred. In this case, the ferrous sulfate plant can produce ferric sulfate by excluding one unit operation (which is addition of iron scrape).

There are many factors that affect the yield of iron sulfate; but for this study only the three main factors are considered (reaction temperature, reaction time and particle size). It is possible to test the other factors such as types of iron ore, pressure level and iron content of the ore.

Production of iron sulfate from iron ore in Ethiopia is studied for the first time. Therefore extensive researches need to be done.

Finally, this study shows as Ethiopia has a great unused and untouched iron resource potential which has to be exploited to produce usable products so as the country can benefited from it.

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Preparation :-200 MESH
 Number of Sample: 1 Element to be determined Major Oxides & Minor Oxides
 Analytical Method: LiBO2 FUSION , HFattack,GRAVIMETRIC,COLORIMETRIC and AAS

Analytical Results in PERCENT

FIELD NO	Lab No	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	MnO	P ₂ O ₅	TiO ₂	H ₂ O	LOI
B.G.01	0981/17	7.64	4.28	77.20	1.84	0.36	0.36	<0.01	0.24	0.08	0.09	0.47	6.81

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