ADDIS ABABA UNIVERSITY

SCHOOL OF GRADUATE STUDIES

ADDIS ABABA INSTITUTE OF TECHNOLOGY

SCHOOL OF CHEMICAL AND BIO-ENGINEERING

Optimization and Characterization of Magnesium Chloride Production from Magnesium Carbonate using HCl

By

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By

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Acronyms

A	Acid concentration
Al_2O_3	Aluminum oxide
ANOVA	Analysis of Variance
ASTM	American Standards Tests and Materials
B	Liquid to solid ratio
C	Reaction time
$CaCO_3$	Calcium carbonate
CaO	Calcium oxide
C_{AO}	Initial molar concentration species A (mol/L)
C_A	Molar concentration species A (mol/L)
N_B	Moles of species B
N_{BO}	Initial moles of fluid reactant
N_A	Moles of species A
DCFR	Discounted Cash Flow Return
EDTA	Ethylene diamine tetra acetic acid
FCI	Fixed Capital Investment
Fe_2O_3	Iron oxide
GTP	Growth transformation period
L.O.I.	Loss on ignition
$MgCl_2.6H_2O$	Magnesium chloride hexahydrate
$MgCO_3$	Magnesium carbonate
N_{AO}	Initial moles of species A
X_A	Fractional conversion of species A
NPV	Net Present Value
PEC	Purchased equipment cost
Rpm	Revolution per minute
SiO_2	Silica dioxide
TCI	Total Capital Investment
TPC	Total production cost
WC	Working Capital

Abstract

The objective of the study was, Optimization and Characterization of Magnesium Chloride Production from locally available Magnesium Carbonate using HCl. The reaction of magnesite in aqueous hydrochloric acid solution was studied in a batch reactor. Complexometric method was used for chemical analysis using EDTA. According to result obtained magnesite has composition of: 46.77% MgO, 0.78% SiO_2, 3.03% CaO, 0% Fe_2O_3, 0.2% Al_2O_3, 49.12%L.O.I and the maximum amount of $MgCO_3$ that could possibly be present in the sample is 94.4%. The experimental design was done by using the Design Expert 7.0.0 software three levels; three factor general factorial design with full type in the study. The experimental parameters were, acid concentration, liquid to solid ratio and reaction time. The results showed that optimum parameters were: 180 min reaction time, 7M acid concentration and 2.07ml/g liquid-to-solid ratio. Under these optimum conditions, the maximum magnesium chloride yield was 94%w/w. In contrast, the minimum magnesium chloride yield was 58% w/w at 4M acid concentration, 1.88 ml/g liquid to solid ratio and 60 min reaction time.

Keywords: *magnesite powder, reacting hydrochloride acid, magnesium chloride, $MgCl_2$*

1. INTRODUCTION

1.1. Back ground

A wide range of building materials and construction facilities are required by modern society, including residential and commercial properties, manufacturing facilities, schools, hospitals, transport, infrastructure etc. Chemical manufacturing Industries sector has been identified as a priority sector for the achievement of the Growth and Transformation Plan of the country for 2010-2015 (GTP I) and GTP II for the period of 2016-2020. One of the inputs required and used to lower the overall cost of the houses is magnesium board partition walls. Magnesium board partition wall is mainly produced from magnesium oxide and magnesium chloride. Magnesium oxide is being produced locally however, the next important ingredient, which is magnesium chloride, is not produced in Ethiopia in spite of the magnitude of demand at present. With the ever increasing demand for magnesium chloride for the manufacture of partition walls, the import volume is also increasing thereby contributing to the outflow of foreign exchange. In order to fulfill the country demand a considerable quantity of this chemical is imported annually from abroad. The demand for magnesium chloride in Ethiopia is mainly a derivative demand of Agro Stone production. The demand for Agro Stone in return is dependent on building construction, particularly low cost housing construction [1].

The attempts of the various agencies such as the Ethiopian Mineral Development Enterprise Share Company under the joint guidance of the Ministry of Industry and The Ministry of Construction & Urban Development to produce magnesium chloride from the bitterns of salt works at Afdhera lake in Afar Region has not been successful so far.

This project aims to utilize an alternative mineral resource which is magnesite found in Kenticha area in the South East Ethiopia in tandem with the possible conversion of the Zeway Caustic Soda plant into a chlor-alkali process by abandoning the lime-soda process. It shall pave the way for import substitution of magnesium chloride saving foreign expenditure and ensure its availability for the booming construction sector specifically in the manufacture of partition boards for low cost housing construction by producing magnesium chloride from local. The total reserve of the mineral as an indicated resource of 1.5 million tonnes [1]. The mineral at present, is being mined to serve as raw materials for the production of MgO.

1.2. Statement of Problem

Ethiopia has a vibrant economy which has been registering a double digit growth rate of 10.1% on the average during the last decade. The Government of the Federal Democratic Republic of Ethiopia has formulated and implemented the first five year Growth and Transformation Plan (GTP) from 2010/11-2014/15 and has just launched the second GTP that would run in the next five years starting from September 2015. During the 1st GTP a total of 150,000 houses in Addis Ababa and 101,022 houses for the new sugar projects under construction were planned whereby most of them have been completed and handed over to dwellers. The keen interest of the government for providing decent houses to its citizens is reported to continue with vigour also during the 2nd GTP period.

One of the inputs required and used to lower the overall cost of the houses is magnesium board partition walls. These boards are made mainly from magnesium oxide and magnesium chloride. The Housing Construction Agency established a 30,000 tonne per annum magnesium oxide plant at Kenticha but magnesium chloride is being imported.

On the other hand, the existing Caustic Soda Plant found at Zeway has ceased its operation because of outdated process. Hence, there is a desire by the Government to convert the technology of the plant to a salt electrolysis one in order to meet the rising demand of caustic soda by domestic production. However, the challenge of utilizing the co-product chlorine could not be overcome due to the low level of demand for chlorine and its derivatives such as hydrochloric acid and hypo-chlorites. For every tonne of caustic soda produced almost an equivalent quantity of chlorine is produced that has to be commercialized. Therefore, the amount of chlorine and its derivatives that can be marketed has become a limiting factor for establishing an electrolytic caustic soda plant of reasonable capacity to meet local demand. The production of hydrochloric acid in the chlor-alkali plant for its utilization in the production of magnesium chloride would give an opportunity to establish an economic scale electrolytic caustic soda plant as well as enable the production of magnesium chloride from local resources and substitute imports [Addis Ababa House construction and Urban development].

1.3. Objectives

1.3.1. General Objective

To optimize the production of magnesium chloride from magnesium carbonate and Hydrochloric acid

1.4. Specific objectives

- To characterize Raw material (magnesite)
- To analyze the Yield
- To determine optimal parameters for the reaction of $MgCO_3$ with HCl for production of magnesium chloride
- To characterization the product
- Finally, production cost analysis for the production of magnesium chloride from locally available magnesium carbonate and compare the result with import price

1.5. Significance of the study

Most of the magnesium chloride used in many parts of the world is obtained from the fractional crystallization of various salts from the bitterns of salt works. The attempt made by the Ethiopian Mineral Development Enterprise by the behest of the Ministry of Urban Development & Construction to investigate the possibility of production of magnesium chloride from Lake Afdhera in the Afar Region could not proceed due to the percolation of bitterns through the earth pond based design of the majority of the salt works from which bittern cannot be collected for further processing.[Feasibility study for Rehabilitation and renovation caustic soda share company]. The significance of this study is therefore to see the possibility of producing magnesium chloride from magnesite with the reaction of HCl with high anticipation of the establishment of a chlor-alkali plant in Ethiopia and thereby substitute the present importation as well as augment the scale of production of caustic soda plant[1].

The other method of obtaining $MgCl_2$ by fractional crystallization of salt work bitterns beyond the lack of the availability of the inputs would pose challenges of pure magnesium chloride due to the existence of several other salts such as NaCl, KCl, $CaCl_2$, K_2SO_4, $MgBr_2$, $MgSO_4$ etc. Therefore, pioneering and showcasing experimentally the production of $MgCl_2$ from locally available magnesite mineral will pave the way for large scale production of magnesium chloride and thereby result in import substitution and foreign exchange saving.

The other benefits of the local production of magnesium chloride, creation of job opportunities for achievement of self-sufficiency in the production of magnesium boards and independence from foreign import and creation of outlet avenue for hydrochloric acid and contribution to the enabling of the development of a chlor-alkali plant.

2. LITERATURE REVIEW

2.1. Introduction

Magnesium chloride is the name for the chemical compounds with the formulas $MgCl_2$ and its hydrates $MgCl_2(H_2O)_x$. These salts are typical ionic halides, being highly soluble in water.

It is an inorganic salt, which has the chemical formula of $MgCl_2$ and molecular weight 95.210 g/mol and Predominantly magnesium chloride exists as various hydrates, particularly hexahydrate $MgCl_2.6H_2O$ having the molecular weight of 203.301 g/mol. Magnesium chloride hexahydrate occurs as a natural mineral Bischofite named after a German geologist Karl Gustav Bischo [15]. It is a constituent of many salt lakes and natural brines. Sea salt contains 17% magnesium chloride salt deposits contains the important mineral canalite $KCl.MgCl_2.6H_2O$, bischofite $MgCl_2.6H_2O$ and occasionally the double salt anhydrites in which the magnesium chloride is combined with calcium chloride ($CaCl_2.2MgCl_2.12H_2O$).Magnesium chloride is obtained from mineral salt deposited by processing the spent liquors remaining after extraction of potassium chloride and also by direct solution mining; it is also recovered from salt lakes and sea water. $MgCl_2$ crystallizes in the cadmium chloride, which features octahedral Mg. In the hexahydrate, the Mg^{2+} remains octahedral, but coordinated to six water ligands. Magnesium chloride is one of the most important magnesium compounds and forms hydrate with 2, 4, 6, 8, and 12 molecules of water. A variety of hydrates are known with the formula $MgCl_2(H_2O)x$, and each loses water with increasing temperature: x = 12 (-16.4 0C), 8 (-3.4 0C), 6 (116.7 ^{0}C), 4 (181 0C), 2 (300 ^{0}C). As suggested by its tendency to form octahedral complexes, $MgCl_2$, especially when anhydrous, is a weak Lewis acid [2]. Magnesium salt is typically extracted from salt water, particularly high salt content sources like the Dead Sea and the Great Salt Lake in Utah, US. Available in both anhydrous and multiple hydrated crystal forms, magnesium chloride is most commonly used, particularly in the US, for de-icing treatments for roads and as a means of stabilizing dust in crumbly soils or to resist the effects of wind erosion. It also finds its way into a whole host of applications as a component of fertilizer, in the production of paper and textiles, and for fireproofing and fire extinguishing. A construction board is mainly formed from composition of magnesium oxide, magnesium chloride. MgO Board Composition are, Magnesium oxide [MgO] (40%), Magnesium chloride [$MgCl_2$] (35%), Wood chips (15%), Perlite [SiO_2] (5%) (volcanic glass), Small glass cloth (1%) and Linking composite materials (4%) [1,2,3]. Both the anhydrous and hexahydrate salt are deliquescent and need to be stored

under dry cool conditions.Magnesium chloride is very soluble in water 54.6 g/100 mL, and the hexahydrate is the only stable hydrate between 0 and 100^0C. The anhydrous salt is also soluble in methanol (20.4 g at 60^0C) and ethanol (15.9 g at 60^0C). On cooling, these solutions crystallize the alcoholate addition compound, such as magnesium chloride hexamethanolate, $MgCl_2.6CH_3OH$, and magnesium chloride hexaethanolate, $MgCl_2.6C2H_5OH$. Anhydrous magnesium chloride can also form addition compounds with ammonia, that is, $MgCl_2.6NH_3$, $MgCl_2.2NH_3$, and $MgCl_2.NH_3$. Magnesium chloride can be produced by reacting magnesium oxide, carbonate, or hydroxide in hydrochloric acid and cooling the solution to crystallize $MgCl_2.6H_2O$ (bischofite). It can also be produced from naturally occurring brines and seawater by solar evaporation, using fractional crystallization of other salts such as potassium chloride, sodium chloride, and magnesium sulfate. Anhydrous $MgCl_2$ can be made by the direct chlorination of magnesium oxide in the presence of a reducing agent such as coke or coal [4].

2.2. Raw materials for Production of Magnesium Chloride

2.2.1. Hydrochloric Acid

The main byproduct in the caustic soda industry is chlorine. Chlorine is produced almost as much as caustic soda in the chlor - alkali industry in all the available usable technologies today. HCl is produced as a gas from the combustion of hydrogen and chlorine gases collected from the electrolysis plant, which is then absorbed in water and cooled. It is assumed that HCl for the process will be obtained from the chlor-alkali plant that will be established in Zeway Caustic Soda Plant.

2.2.2. Magnesium Carbonate

Natural magnesite($MgCO_3$) is one of the major sources of magnesium and its compounds. These compounds are widely used in the manufacture of refractories, metallurgical, chemical, ceramic and pharmaceutical industries. Magnesium carbonate is considered as one of the most important compounds of the magnesium industry. It has been widely used in various industries, such as toothpaste, painting, cosmetic manufacturing, plastic, rubber, and as precursors for other magnesium-based chemicals [5]. Basic magnesium carbonate can also be used as the chemical coolant when the heat is absorbed during the thermal decomposition [6]. In recent years, a series of $xMgCO_3 \cdot Mg(OH)_2 \cdot yH_2O$ with different morphologies have been obtained via different synthesis method or in different preparation conditions. Magnesium carbonate ($MgCO_3$) has a theoretical magnesium oxide contents of 47.7%. Dolomite is calcium carbonate magnesium

carbonate mineral ($CaCO_3.MgCO_3$) that has a theoretical magnesium content of 22% Brucite, magnesium hydroxide [$Mg(OH)_2$], contains up to 69% magnesium, and olivine ($MgFe_2SiO_4$) contains up to 19% magnesium. Of these minerals, magnesite and dolomite are the largest sources of magnesium and magnesium compounds.

2.2.3. Occurrence of Magnesite

Magnesite is partially derived from rock formation materials and it mostly occurs together with dolomite and forms deposits, which are generally very old (>400 million years old). The magnesite occur in two physical forms, crystalline and cryptocrystalline. The crystalline form typically has a crystallite size in the range 50-200μm. Most crystalline magnesite are intimately associated with dolomite, which may occur as discrete bands or lenses. Cryptocrystalline are very fine-grained (≤20μm) magnesite which are usually associated with serpentinites, from which they are believed to have been formed. The deposits are usually quite pure and normally off-white in color [7].

Magnesium carbonate occurs in nature in several minerals as hydrated, basic and double salts, as shown above. The two principal minerals are magnesite, $MgCO_3$ and dolomite, a double salt, $CaCO_3 \bullet MgCO_3$. Both minerals are used as source materials in the production of magnesium metal.Other applications of magnesium carbonate are in flooring, fireproofing and fire-extinguishing compositions; as a filler material and smoke suppressant in plastics; as a reinforcing agent in neoprene rubber; as a drying agent and for color retention in foods; in cosmetics; in dusting powder; and in toothpaste. The high purity magnesium carbonate is used as an antacid in medicine; and as an additive to table salt.

2.2.4. Resources of magnesium carbonate in Ethiopia, Kenticha area

The Kenticha is located in the eastern Adola area that forms a segment of the north-south trending Mozambique orogenic belt of Pan-African (710-530 Ma) age in southern Ethiopia.

Magnesite is found with dolomite marble in Kenticha (Adola Belt), as white, fine to medium grained crystalline rocks. The width of the occurrence varies from few meters to about 50m. Magnesite is the cheapest sources of magnesia (MgO) and the release of CO_2 from this source during firing produce MgO which reacts with $MgCl_2$ and used for industrial applications.

$$MgCO_{3(S)} \xrightarrow{\text{heating}} MgO_{(s)} + CO_{2(g)}$$

$$MgO_{(s)} + 2HCl_{(aq)} \longrightarrow MgCl_{2(aq)} + H_2O_{(l)}$$

Samples collected from this magnesite occurrences indicated Magnesite is found with dolomite marble in Kenticha, with a $MgCO_3$ content above 95% can be selectively mined and be used for the production of $MgCl_2$ and high MgO (40-46%), low Fe_2O_3 (0.04-0.08 %) and $A1_2O_3$ (<0.1%). The magnesite marbles at Kenticha extends for few kilometers. It runs nearly north-south with structural closures at the south. The width of individual bands is generally less than 100 meters. The total indicated resource is about 1.5 million tonne. Other occurrence of magnesite are in Harar (Gara Jabe, Kunni), Sidamo, Moyale, Wallega and Assosa in close association with basic and ultrabasic rocks. Systematic exploration activities are required to assess the economic potential of the magnesite occurrences [1].

At present, the magnesite deposit is being used to produce magnesium oxide (MgO) a quality sufficient enough for the production of magnesia boards. Production of local MgO with a capacity of 10,000 tons/year has a net saving of about 20 millions birr per year as compared to the imported MgO. Moreover, it has a saving of about 4kg of MgO for every board of production by using locally produced MgO due to its better quality and reactivity. Currently, the plant has increased its production capacity of MgO from 10,000 tons/year to 30,000 tons/year [1].

Figure :2. 1 Magnesite block from the magnesite deposit of Kenticha, Adola

2.2.5. **Decomposition of Magnesium Carbonate**

At high temperatures $MgCO_3$ decomposes to magnesium oxide and carbon dioxide. The process is important in the production of magnesium oxide [8]. This process is called calcining:

$$MgCO_3 \rightarrow MgO + CO_2 \ (\Delta H = +118 \text{ kJ/mol}$$

The decomposition temperature is given as 350 °C (662 °F) [9,10]. However, calcination to the oxide is generally not considered complete below 900 °C due to interfering readsorption of liberated carbon dioxide .

2.3. Magnesium Chloride Production Technologies

There are different technologies which are employed in the production of magnesium chloride. Magnesium chloride is produced from lake brines such as the Dead Sea in Jordan Valley & Great Salt Lakes in North America. It is also solution mined from the naturally occurring bischofite mineral and will also anticipated that $MgCl_2$ be extracted from the bitterns of salt production processes around the Afdhera Lake in the Afar Region if fractional crystallization from several other associated salts can be carried out successfully. Magnesium chloride is produced from lake brines such as the Dead Sea in Jordan Valley & Great Salt Lakes in North America. It is also solution mined from the naturally occurring bischofite mineral and will also anticipated that $MgCl_2$ be extracted from the bitterns of salt production processes around the Afdhera Lake in the Afar Region if fractional crystallization from several other associated salts can be carried out successfully [1]. A number of methods have been followed in the past for the production of magnesium chloride hexahydrate. One of the most common techniques involves the evaporation of sea water and natural brines, but this has heretofore only been economical where the dilute solutions can be preconcentrated by solar evaporation. In one specific example of this process, brine from the Great Salt Lake containing approximately 35% by weight $MgCl_2$ solution (nominally $MgCl_2.12H_2O$) is first subjected to solar evaporation, followed by vacuum evaporation until the 6-hydrated form of $MgCl_2$ and $MgSO_4$ are precipitated.

Thereafter, the precipitated crystals are heated to 120-150 ^{0}C to redissolve the $MgCl_2.6H_2O$ and allow removal of magnesium sulfate. The $MgCl_2.6H_2O$ can then be crystallized out. Alternately, the initially evaporated solution can be maintained at 120 ^{0}C until the magnesium sulfate content decreases to less than 20 g/L as a result of crystallization of kieserite. The $MgCl_2.6H_2O$ is then crystallized by vacuum evaporation at 90 ^{0}C [1].

The prime difficulty with evaporative processes of this type steams from the high energy input and hence costs associated with the ultimate production of $MgCl_2.6H_2O$. Indeed, the cost of brine dehydration is by far the most significant expense associated with production of the desired product. It has also been known to manufacture magnesium chloride as a by-product of the potash industry or by direct chlorination of magnesium oxide in the presence of an organic reducing agent. However, these methods are generally even more expensive than those involving evaporation of brines. In a similar fashion, salts such as calcium chloride have been produced in commercial quantities by a number of processes including the refining of natural brines, reaction

of calcium hydroxide with ammonium chloride in Solvay soda ash production, and the reaction of hydrochloric acid with calcium carbonate. Here again, the brine processes are relatively expensive, and involve multiple steps such as reaction of the brines with lime and subsequent concentration. There is therefore a need in the art for a simplified, low cost process for the production of alkaline earth metal salts, and particularly $MgCl_2.6H_2O$, which avoids multiple, energy intensive evaporation and/or chemical separation steps. As mentioned above, the direct production of $MgCl_2$ from seawater or brines by evaporation is only economical where the dilute solutions can be preconcentrated by solar evaporations. If sea water cannot be preconcentrated by solar energy, magnesium chloride salt or solution can only produced in large scale by precipitation as the hydroxide, followed by conversion to the chloride with hydrogen chloride [11]. That is in the Dow process, magnesium chloride is regenerated from magnesium hydroxide using hydrochloric acid:

$$Mg(OH)_2(s)+2HCl \rightarrow MgCl_2(aq)+2H_2O(l)$$ [11].

Method for production of magnesium chloride, also to be used for production of magnesium metal, by leaching of magnesite in hydrochloric acid. The magnesium chloride containing solution is led to a reactor, where finely ground magnesite or hydrochloric acid is added to obtain approximate equivalence between magnesium and chlorine. To precipitate the impurities an excess of magnesium oxide or magnesium hydroxide is added in one or several purification stages.

Magnesium chloride, as the natural mineral bischofite, is also extracted (via solution mining) out of ancient seabeds; for example, the Zechstein seabed in northwest Europe. Some magnesium chloride is made from solar evaporation of seawater. Anhydrous magnesium chloride is the principal precursor to magnesium metal, which is produced on a large scale. Hydrated magnesium chloride is the form most readily available.

Magnesium chloride is prepared by treating magnesium carbonate, hydroxide or oxide with hydrochloric acid followed by crystallization by evaporation. The hexahydrate of the salt $MgCl_2 \bullet 6H_2O$ is obtained upon crystallization process. In most commercial processes, the compound is either derived from, the sea water or from the natural brines, the latter both of which are rich sources of magnesium chloride.

The basic raw materials for production of magnesium with electrochemical process are generally divided into two: salts containing chloride and raw materials that must be transformed into salts

containing chloride. Eventually, all the materials will become either bischofite or carnallite prior to drying and feeding into the electrolysis cells.

The production process employed by Dead Sea Magnesium (DSM) is based on raw material obtained directly from the Dead Sea through processes of dehydration and crystallization. This process is thought to be the most efficient and economic of all the production processes for raw materials, since it is based on evaporation with the help of solar energy on open ponds [6]. Magcorp uses a similar method with the water of the Great Salt Lake, from which it produces magnesium chloride-rich solutions. Various manufacturers from the former Soviet Union produce artificial carnallite from bischofite or magnesium sulphate. The artificial carnallite is produced thought addition of spent electrolyte from the electrolysis process, which containing about 70% KCl to magnesium chloride-rich solutions [9]. With this process, the carnallite settles, and is separated, by means of crystallizers, back to the production process. The production of magnesium directly from raw materials containing chloride is advantageous, since for each ton of magnesium, 2.5t of chloride, which are produced during the electrolysis process can be sold. With all other production processes, it is necessary to manufacture HCl with an intermediate process in order to complete the process of preparation the raw materials for the electrolysis [8-9]. T he Dow process of production of magnesium chloride was originally based on the roasting of dolomite in kilns and its addition to seawater containing magnesium ions (this fundamental process is still used today at hydro magnesium plant in Norway). The process is carried out according to the following equation[9].

During the history of magnesium production there were a number of additional processes with which attempts were made to produce directly anhydrous magnesium chloride, attempting to bypass the drying stage. The process is carried out at temperature of 800^0C, and the melted magnesium chloride flowed from the bottom of the reactor[1].

I) Magnesium Chloride production From Sea Water

On industrial scale, magnesium chloride is prepared from sea water. The sea water on treatment with lime gives precipitate of magnesium hydroxide. The precipitate is separated and dissolved in hydrochloric acid. The solution upon crystallization and cooling gives crystals of $MgCl_2.6H_2O$ [12].

$$Mg(OH)_{2(aq)} + 2HCl_{(aq)} \longrightarrow MgCl_2\,(aq) + 2H_2O(l)$$

In the sea water process, the water is treated with lime or calcined dolomite (dolime), CaO•MgO or caustic soda to precipitate magnesium hydroxide. The latter is then neutralized with hydrochloric acid. Excess calcium is separated by treatment with sulfuric acid to yield insoluble calcium sulfate.

II) Magnesium Chloride production From Brine

To recover magnesium chloride from brines, using the Great Salt Lake brines as an example, the water is pumped to a series of solar evaporation ponds where water evaporates to concentrate the brine. The first salt to precipitate as the water evaporates is sodium chloride. The next group of salts to precipitate is a mix of double salts containing potassium and magnesium. Depending on brine concentration, temperature, and other factors, kainite (MgSO4•KCl•3H2O), schoenite (MgSO4•K_2SO4•6H2O), and carnallite (KMgCl•6H2O) may be precipitated. Sodium sulfate is then precipitated from the cooled brine in the winter (even though it is no longer harvested for sale). The final product remaining dissolved in the brine is magnesium chloride. In general, equilibrium is reached at about 35% magnesium chloride ($MgCl_2$) concentration by weight in the brine. Although most of the sodium and potassium have been removed from the brine at this stage, it still contains some dissolved sulfate. The purity of this brine is sufficient for some applications, but if necessary, it may be purified further. Purified brine then may be further processed to produce the hexahydrate solid formula. The overall production cycle takes about 2 years to complete [5].

When produced from underground brine, brine is first filtered to remove insoluble materials. The filtrate is then partially evaporated by solar radiation to enhance the concentration of $MgCl_2$. Sodium chloride and other salts in the brine concentrate are removed by fractional crystallization. The crude product containing magnesium oxide or hydroxide is purified by heating with chlorine.

2.3.1.Magnesium Chloride production from Magnesium Carbonate and Hydrochloric Acid

Magnesium chloride is prepared by treating magnesium carbonate, with hydrochloric acid solutions followed crystallization by evaporation. The hexahydrate of the salt $MgCl_2 \cdot 6H_2O$ is obtained upon crystallization process.

The reaction of magnesium carbonate ($MgCO_3$) with hydrochloric acid (HCl) is according to the following reaction [2] :

$$MgCO_3(_s) + 2HCl(_{aq}) \longrightarrow Mg^{+2}(_{aq}) + 2Cl^{-}(_{aq}) + CO_2(_g) + H_2O(_l)$$

$$MgCO_{3(s)} + 2HCl(aq) \longrightarrow MgCl_{2(aq)} + CO_{2(g)} + H_2O(_l)$$

Chou et al. [13] investigated the dissolution of various carbonates (including calcite, magnesite and dolomite) in HCl solutions at 25 °C using a continuous fluidized bed reactor and samples of a relatively coarse particle size.

Harris et al. [14] studied the production of magnesium from concentrated magnesium chloride solutions. In addition, Abali et al.[15] investigated the optimum conditions for the dissolution of magnesite with H_2SO_4 solutions. They reported that the optimum conditions were 65 °C, 5/100 g/cm^3, 2M, 60 min and 300 rpm. Abdel-aal et al. [16] analyzed Egyptian magnesite ore (43.32% MgO) from the Eastern Desert leached with aqueous hydrochloric acid. They reported that the optimum conditions of leaching were: ore particle size 0.79 mm, temperature 60°C, leaching time 15 min, HCl-to MgO molar ratio 1.06, and liquid/solid ratio of 2.5:1 cm^3/g. These conditions led to a recovery of approximately 99.1% MgO. Abali et al. [17] also investigated the Taguchi method to determine the optimum conditions for leaching dolomite ore in hydrochloric acid solutions. The experimental parameters were leaching temperature, solid-to-liquid ratio, acid initial concentration, leaching time and stirring speed. The optimum leaching parameter levels were found to be temperature 50°C, solid-to-liquid ratio 2%, acid concentration 20 g/cm^3 (2 mol/dm^3), stirring speed 450 rpm, leaching time 5 min. Under the optimum process conditions, the dolomite ore leaching efficiency was approximately 83%.

Ozdemir et el.[18] investigated the recovery of magnesium from magnesite in aqueous hydrochloric acid solutions in a batch reactor using hydrochloric acid solutions. Subsequently, they also investigated production of magnesium chloride hexahydrate ($MgCl_2 \cdot 6H_2O$) from leaching solution. The parameters were temperature, acid concentration, solid-to-liquid ratio, particle size and stirring speed on the leaching process . According to Ozdemir et al., the pseudo-second-order reaction model seems to be appropriate for the magnesium chloride leaching. The

experimental plan was based on parameters and their levels to determine the leaching rate of magnesite powder in HCl solutions. The maximum leaching performance of the magnesite powder is predicted from the calculation of the optimum conditions. Results showed that optimum leaching parameters were: temperature of 70°C, 180 min leaching time, 130 cm^3 acid consumption, 3.6 cm^3/g liquid-to-solid ratio, 10.17 M acid concentration, 79µm average particle size and a mixing speed 60 rpm. Under these optimum conditions, the leaching yield was 96.72%.

In the laboratory, magnesium chloride is prepared by the action of hydrochloric acid on magnesium oxide or magnesium carbonate. It is prepared by treating magnesium carbonate, with hydrochloric acid followed crystallization by evaporation. The hexahydrate of the salt $MgCl_2 \bullet 6H_2O$ is obtained upon crystallization process[16].

$$MgO + 2HCl\ (aq) \longrightarrow MgCl_2(aq) + H_2O$$

$$MgCO_3 + 2HCl \longrightarrow MgCl_2\ (aq) + CO_2 + H_2O$$

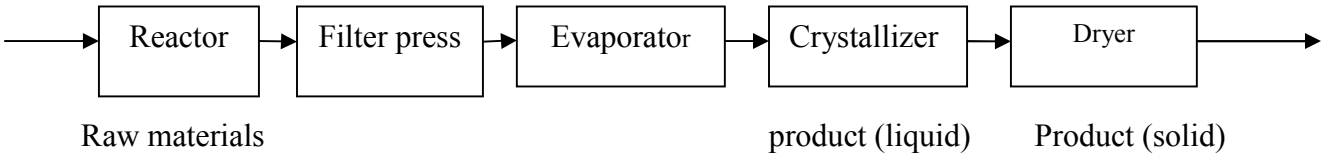


Fig 2.2. Magnesium Chloride Production Process

2.4. Magnesium Chloride in Ethiopia

The economic development strategy landscape of Ethiopia has entered a new phase with the launching of a new five-year development plan i.e. the Growth and Transformation Plan (2011-2015) GPT I and (2015-30 GTP) II. The plan envisages the transformation of the country's economy from agrarian to industrial. Chemical industries are crucial to the development of any modern economy and Major industrial economies are characterized by the existence of strong and vibrant chemical industries. Cognizant of this situation, the government of Federal Democratic Republic of Ethiopia (FDRE) has made the chemical manufacturing sub-sector one of the priority industrial subsectors and has been exerting at most effort to create a conducive business environment to support the growth of the sub sector[Addis Ababa house construction and Urban development]. Magnesium chloride is one of the most important in manufacturing industries. But, there is no local producer of magnesium chloride inspite of demand.

2.4.1. Demand of magnesium chloride in Ethiopia

The demand for magnesium chloride in Ethiopia at present is in the manufacturing of magnesium boards used for partition walls. The major component of magnesium boards is magnesium oxide which is being produced locally. However, the next important ingredient, which is magnesium chloride, is not produced in Ethiopia at present. With the ever increasing demand for magnesium chloride for the manufacture of partition walls, the import volume is also increasing thereby contributing to the outflow of foreign exchange.

The quantity and value of magnesium chloride annually imported in to the country covering the period 2006-2014 is shown in the Table below.

Table 2.1:Import of Magnesium Chloride (Quantity in Tonne and Value in 000 Birr)

Y ear	Quantity	Value	Growth Rate(%)
2006	2,336	4,010	
2007	1,707	5,923	47.7
2008	5,216	20,224	241.4
2009	24,719	82,197	306.4
2010	1,346	6,155	-92.5
2011	2,322	14,990	143.5
2012	1,636	12,310	-17.9
2013	3,769	26,445	114.8
2014	12,241	72,199	173.0
Total	55,292	244,453	304.1
Average	6,144	27,161	38.0

Source: Ethiopian Revenue & Customs Authority

The demand for magnesium chloride showed an average growth rate of 38% during 2006 to 2014. According to the market survey conducted on magnesium chloride, it was found that the main consumers of magnesium chloride are agro stone panel and magnesium board producers, namely Agro stone Production Centers of Addis Ababa (with two plants), Bahir Dar, Dessie, Adama, Hawassa as well as YEBEL Industrial PLC. Furthermore, IPS made a projection that the demand for magnesium chloride ($MgCl_2$) will increase from 12,533 tonne in the year 2016 to 17,051 tonnes and 25,054 tonne by the years 2020 and 2025, respectively [table2.1]. As can be

seen from table 1, import of magnesium chloride during the period 2006–2014 was fluctuating from year to year although it shows a general increasing trend. For instance, the yearly average imported quantity during the period 2006-2008 was about 3,086 tonne. However, an exceptionally high import figure is registered during year 2009, which amounts to 24,719 tonne. This means that the quantity imported during year 2009 alone is higher by 8 fold compared to the average quantity imported during the three preceding years i.e. 2006-2008. Although what was imported in the year 2009 might not be consumed in the same year, the huge growth in the import of $MgCl_2$ is due to a finding of new application for Magnesium Chloride in the Ethiopian market. The major driver for the increase of import is, mainly because of the increasing demand in the production of agro-stone (Magnesium Oxychloride cement) by Federal and Regional Housing Development Agencies and other construction materials producers [1]. The demands of magnesium chloride per year from year, 2016 to 2030 is represented in the table 2.2.

In order to assess the prevailing demand in Ethiopia potential users of magnesium chloride have been interviewed. Manufacturing industries of plastics, tanneries, pulp and paper, textiles, ceramics, soap and detergents and agro stone production centers has been visited in different localities including Adama, Mojo, Debrezeit, Awassa, and Burayou. According to the market survey conducted on magnesium chloride, it was found that the main consumers of magnesium chloride are agro stone panel and magnesium board producers., namely Agro stone Production Centers of Addis Ababa (with two plants), Bahir Dar, Dessie, Adama, Awassa as well as YEBEL Industrial PLC. Among this the two largest magnesium chloride consumers are Addis Ababa Agro Stone Production Center and YBEL Industrial plc. Addis Ababa Agro Stone Production Center and YBEL Industrial plc have consumed 5,763 tonne and 2,000 tons respectively, representing a total demand of 7,763 tonne. The rest of agro stone production centers, according to experts involved for years in the production of agro stone, share 40% of the total supply of government sector agro stone production. Thus, magnesium chloride consumption of Adama, Bahir Dar, Desssie and Awassa production centers is estimated to be 3,842 tonne. Adding this to the first two largest consumers, the total current effective demand for magnesium chloride is estimated at 11,605 tonne [source: table 2.1, 2.2 and Addis Ababa and Ministry of construction and Urban development]

Table:2.2 Forecasted Demand for Magnesium Chloride (Ton)

Year (G.C)	2016	2017	2018	2019	2020	2021	2022	2023
Magnesium chloride	12,533	13,536	14,619	15,788	17,051	18,416	19,889	21,480
Year	2024	2025	2026	2027	2028	2029	2030	
Magnesium chloride	23,198	25,054	27,059	29,223	31,561	34,086	36,813	

Source: Ethiopian Revenue and Custom Authority

As indicated in the table above the demand for Magnesium Chloride will increase from 12,533 tonne in the year 2016 to 36,813 tonne by the years 2030, respectively.

2.4.2. Market Share Analysis for Magnesium Chloride

Locally magnesium chloride is one of the basic chemicals that are imported in considerable quantity for different applications. The main local user of magnesium chloride is textile, magnesium board factory and paper industry. There is no local production of magnesium chloride in spite of the magnitude of demand. In order to fulfill the country demand a considerable quantity of this chemical is imported annually from abroad [source : Ministry of Construction and Urban Development].

Since the Ethiopian market for chlorine is extremely narrow there will not be direct sale to end user industries. Hence, the chlorine to be produced by the Zeway Caustic Soda S.C will be utilized to diversify its own product mix by producing magnesium chloride and hydrochloric acid which used for substitution of magnesium chloride from abroad. The byproduct, chlorine gas which is evolved from the electrolysis process is considered to be converted to most marketable products namely hydrochloric acid and magnesium chloride. Currently the demand for magnesium chloride is met from import.

According to literatures magnesium chloride can be produced from different source, but most of them are energy intensive to obtain pure magnesium chloride. Therefore pure magnesium chloride can be produced from magnesium carbonate using hydrochloric acid compared to others methods based on the literatures. The demand of magnesium chloride is increasing from time to time due to construction sectors which influences production of magnesium chloride locally.

2.5. Applications of Magnesium Chloride

Magnesium chloride powder dissolves with water and mix to admixtures to enhance the resistance of magnesia cement to water, fire, acid, thermal.

Magnesium Chloride Hexahydrate is an excellent water soluble crystalline Magnesium source for uses compatible with chlorides. Chloride compounds can conduct electricity when fused or dissolved in water. Magnesium chloride is used for the manufacture of magnesia cement which resembles marble and is used for making tiles, used in the preparation of magnesium by electrolytic method, and as a gauging solution for Sorel cement, used as a fireproofing agent for wood, as a de-dusting agent for roads and in mines, road deicing, in textiles, water treatment, and sugar production from sugar beets. Magnesium chloride is used primarily in, magnesium board, paper, textile industries, production of magnesium metal, it is also used as a fireproofing agent for wood, a de-dusting agent for roads and in mines etc. The compound is also used to make Oxychloride cement, or what is known as Sorel cement for flooring, fire-resistant panel, and fireproofing of steel beams and other materials. Other applications are: as a dust binder on roads; as a flocculating agent in water treatment; for dressing cotton and woolen fabrics; as a fire-extinguishing agent and a fireproofing material; in processing of sugar-beets; and as a catalyst and magnesium board partition production with magnesium oxide.

Magnesium chloride is a widely used reagent in chemistry and molecular biology as a source of magnesium ion. Magnesium chloride is easily assimilated and metabolized in the human body. Magnesium chloride is used primarily in: Agrostone panel uses Magnesium Oxychloride Cement (MOC), also known as Sorel cement as a binder. MOC is non-hydraulic cement which is formed by mixing powdered Magnesium Oxide, MgO with concentrated solution of Magnesium Chloride [16].

The $MgCl_2$ powder dissolves with water and mix to admixtures to enhance the resistance of magnesia cement to water, fire, acid, thermal**.** Magnesium Chloride Hexahydrate is an excellent water soluble crystalline Magnesium source for uses compatible with chlorides. Chloride compounds can conduct electricity when fused or dissolved in water. Magnesium chloride is used for the manufacture of magnesia cement which resembles marble and is used for making tiles, used in the preparation of magnesium by electrolytic method, and as a gauging solution for Sorel cement, used as a fireproofing agent for wood, as a de-dusting agent for roads and in mines, road deicing, in textiles, water treatment, and sugar production from sugar beets.

The compound is also used to make Oxychloride cement, or what is known as Sorel cement for flooring, fire-resistant panel, and fireproofing of steel beams and other materials. Other applications are: as a dust binder on roads; as a flocculating agent in water treatment; for dressing cotton and woolen fabrics; as a fire-extinguishing agent and a fireproofing material; in processing of sugar-beets; and as a catalyst and magnesium board partition production with magnesium oxide [18].

3. MATERIALS AND METHODS

3.1. Materials

I) **Raw Materials and Chemicals**

For the experiments the sample of magnesite was obtained from South Eastern part of Ethiopia located in Kenticha area in Guji Zone and the others hydrochloric acid (35.4%w/w), sodium hydroxide, phenolphthalein, Eriochrome black-T indicators, EDTA and ammonia-ammonium chloride were purchased from chemical suppliers.

II) **Equipments**

The equipments used to conduct this study were, measuring cylinders of 5ml, 50ml, 100ml, conical flask of 250 ml, beakers of 100ml, 200ml and 250ml, funnel, micro pipette of 5ml, burette of 50ml, volumetric flasks of 250ml and 500ml, pH meter, Digital weighing balance (precision, ±0.0001 gm), what man filter paper, Pycnometer, Thermometer, Plate heater (max. 2400 rpm), Water bath, Sample milling machine and micro sieve (ASTM , NO. 170 Mesh).

3.1.1. Raw Material Characterization for Production of Magnesium Chloride

Before proceeds to production and optimization process, the sample collected must be, characterized. Characterization of magnesium carbonate includes: size reduction, moisture content determination, density determination and composition analysis.

3.1.2. Yield Analysis/ Determination from Produced Magnesium Chloride

The percentage yield of the production can be determined based on the produced magnesium chloride. The yield is calculated based on theoretical and actual (experimentally obtained result) yield.

3.1.3. Optimum Parameters Estimation for Production of Magnesium Chloride

The parameters selected for production of magnesium chloride were:

Acid concentration, liquid to solid ratio and reaction time. The others parameters taken as constant based on literature were reaction temperature, particle size and mixing speed.

The parameters were prepared/selected according to the following ranges.

Acid concentration was prepared from 4 to 10 M

Reaction time selected from 60 to 180 min and

Liquid to solid ratio was prepared from 1.88 to 2.07ml/g according to stiochiometric relation.

3.1.4. Product Characterization

Product characterization was carried out after, raw material characterization, yield determination and optimum parameters estimation.

3.2. Methods

3.2.1. Raw Material Characterization

I) Size Reduction

The sample that was acquired had to be prepared for determination of the sample purity before the reaction carried out for the production. Sample preparation process included, magnesite size reduction. Sample size reduction was carried out at laboratory of Addis Ababa Cement Factory using sample milling machine (appendix C).

After Magnesium carbonate undergo size reduction at required size, in order to determine the optimum particle size, according to [10] magnesite powder, sieve analysis was carried out using 79μm sieve.

II) Moisture contents determination

30 g of magnesium carbonate sample was weighed into a tared dish and placed in an oven at a temperature of 105°C for one hour. After one hour, it was removed to a desiccator, cooled and weighed. Similar procedure was repeated until constant weight was obtained and finally the weight was taken and compared with the initially recorded weight. The percentage weight in the magnesium carbonate was calculated using the formula:

$$\text{Moisture content (w/w \%)} = \left(\frac{w_1 - w_2}{w_1}\right) \text{----------} (3.1)$$

Where, w_1 = original weight of the sample before drying;

W_2 = Weight of the sample after drying.

III) Density determination

The density of magnesium carbonate was measured by a standard Pycnometer of 50 ml capacity. First Empty Pycnometer was measured on digital balance and mass was recorded. The sample was filled halve of the Pycnometer and weighted. The mass of magnesium carbonate was determined according to equation below. Then the remaining volume of Pycnometer was filled with distilled water and weighted. Mass of water was determined, the volume of water obtained

from equation below (3.2). The density of the sample was determined from total volume of Pycnometer (50 ml) minus volume of water equation (3.4).

Density of water = $\frac{\text{mass of water}}{\text{volume of water}}$, volume water = mass of water /density of water----(3.2)

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

Volume of sample = total volume of Pycnometer minus volume of water ----------(3.3)

Density of magnesium carbonate $= \frac{\text{mass of sample}}{\text{volume of sample}}$----------(3.4)

IV)Composition Analysis by Acid Titration Method

The purpose of titration was to determine the composition of magnesium carbonate in the sample and percentage of purity.

Titration is a common laboratory method of chemical analysis which can be used to determine the concentration of a known reactant and its composition. Back acid titration method was used for the experiments titration. The reason behind for back titration method:-

The reaction of HCl with $MgCO_3$ is not instantaneous, and as acid is consumed in the reaction, its concentration decreases, so the rate of reaction slows dramatically.

It would be difficult or impossible to accurately determine the endpoint of the titration if we tried to add only the stechiometric amount of acid needed.

The titration with acid was carried out and magnesium carbonate was dissolved in excess hydrochloric acid according the following paragraphs. The magnesium carbonate reacted with the acid as follows:

$$MgCO_3(s) + 2HCl(aq) \longrightarrow MgCl_2(aq) + CO_2(g) + H_2O(l)$$

Then the solution was titrated with NaOH against the excess hydrochloric acid appendix (C).

3.2.2. Yield Analysis/Determination

Stechiometric calculations allows us to calculate the amounts of reactant required or amounts of products generated from a chemical reaction.

I) Magnesium Chloride Production Procedure

In modeling a batch reactor, it is assumed that there is no inflow or outflow of material during the reaction. The reactor is well mixed, the density change with reaction is usually small and can be neglected.

Based on stiochiometric relation, initially, about 63.12ml HCl was poured into a 250ml glass reactor. The reactor was connected to a water bath thermostat which was capable of controlling the temperature of the system. The reactor assembly was then heated to the desired temperature by using thermostat to make acid hot. A measured 30 g of magnesium carbonate was added to the reactor. The reaction parameters were chosen as follows: acid concentration 4, 7 and 10 M, liquid to solid ratio 1.88, 1.97 and 2.07 ml/g and reaction time 60, 120 and 180 min. The others parameters 70^0C temperature, 79μm particle size and 60rpm rotation speed were selected at the optimum point based on [10]. Finally, after the reaction was carried out, unreacted magnesium carbonate and impurity was removed by filter paper. The end product, magnesium chloride solution was obtained by evaporating the liquid from the solution using plate heater as evaporator and the solid form of magnesium chloride was obtained by drying the solution using oven as dryer. These procedures were used for each experiments executed at different parameters using the general full factorial design.

Chemical reaction:- $MgCO_3 + 2HCl \longrightarrow MgCl_{2(aq)} + HO_2 + CO_2$

The percent yield of a reaction measures the reaction's efficiency. It is the ratio between the actual yield and the theoretical yield

The Percent yield is calculated as follows [20]:

$$\text{Percent Yield} = \frac{\text{Actual conversion(obtained experimentally(g))}}{\text{theoretical conversion (determined from stiochiometeric(g))}} \text{ x } 100\ \% \quad \text{----------(3.6)}$$

3.2.3. Optimum Parameters Estimation For Production of Magnesium Chloride

In the production of magnesium chloride the number of operating parameters such as acid concentration, liquid to solid ratio and reaction time are important in the reaction. This thesis research work covers the effect of acid concentration, liquid to solid ratio and reaction time on the yield of magnesium chloride in its scope. Hence, effects of the following parameters on the yield of magnesium chloride production: acid concentration to liquid-solid ratio, acid concentration to reaction time, and liquid-solid ratio to reaction time on magnesium chloride yield were the specific objectives. The selected process parameters were acid concentration, liquid to solid ratio and reaction time each with three levels and two replicates. The variables were prepared as: Acid concentration at 4,7 and 10M, liquid to solid ratio 1.88, 1.97 and 2.07g/ml and reaction time 60, 120 and 180min and the others parameters selected as constant

were, reaction temperature, particle size and rotation speed at optimum magnesium chloride yield was produced. Acid concentration was prepared from stock solution containing 35.4%w/w and has concentration of 11.44M. Liquid to solid ratio was prepared based on stiochiometric relations between chemical reaction of magnesium carbonate and hydrochloric acid

The reaction temperature, particle size and rotation speed were taken at fixed optimum points at which magnesium chloride production becomes maximum. Hence, the reaction temperature, particle size and rotation speed were 70^0C, 79μm and 60rpm respectively to achieve the maximum yield.

Table 3.1. selected parameters for magnesium chloride production [3]

Parameters	Values
Reaction temperature ^{0}C	70
Acid concentration (M)	4-7-10
Liquid to liquid ratio (ml/g)	1.88-1.97-2.07
Reaction time (min)	60- 120- 180
Mixing speed (rpm)	60
Average particle size (μm)	79

3.2.4. Product Characterization

I) Determination of pH

pH meter was used to measure the pH of magnesium chloride solution at 20^0C specified. The pH meter was washed first by distilled water. The sample solution were taken with intervals of 30 min to adjust the pH of the solution/ product to desired one. To neutralize the solution, a little amount of magnesium carbonate was weighted and added to the solution in order the complete the reaction with HCl.

II) Density determination

The density of magnesium chloride was measured by a standard Pycnometer of 50 ml capacity. First empty Pycnometer with 50 ml was measured on digital balance and mass was recorded. The sample of magnesium chloride was filled halve of the Pycnometer and weighted. The mass of magnesium chloride was determined form total mass of Pycnometer and sample. Then the remaining volume of Pycnometer was filled with distilled water and weighted. After mass of water was determined, the volume of water obtained from equation below. The density of the

sample was determined from total volume of Pycnometer (50 ml) minus volume of water equation below.

$$\text{Density of water} = \frac{\text{mass of water}}{\text{volume of water}}$$, volume water = mass of water /density of water - (3.7)

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

$$\text{Volume of sample} = (\text{total volume of Pycnometer} - \text{volume of water})$$ ----------(3.8)

$$\text{Density of magnesium chloride} = \frac{\text{mass of sample}}{\text{volume of sample}}$$ ----------(3.9)

III) **Composition of Magnesium Chloride determination**

the percentage of $MgCl_2$ was calculated according to H. Gulensoy [19].

$$\%\ MgCl_2 = \frac{\text{Volume of EDTA consumed} * C_{EDTA} * MgCl_{2\ \text{equivalent}}}{\text{sample weight}} * 100$$ -----(3.10)

where C= concentration of EDTA

IV) **Determination of total Calcium and Magnesium ions**

In this method, a Complexometric titration, was used to find the total calcium and magnesium content of magnesium carbonate solid materials. The method uses a very large molecule called EDTA which forms a complex with calcium and magnesium ions. A blue dye called Eriochrome Black T was used as the indicator. This blue dye also forms a complex with magnesium ion, changing colour from red to blue in the process for magnesium concentration. The colour change represents the end point of the titration for determination of ions. The dye–metal ion complex is less stable than the EDTA–metal ion complex and complexed with the metal ions to release ions from EDTA.

The indicator used for calcium ion determination is murexide. It react only with calcium metal and gives the colour change when all of the calcium has been complexed by EDTA at a pH of 12-13.The amount of magnesium and calcium in the solution was analyzed volumetrically by EDTA method at pH 10.7 for magnesium and Ph 12 for calcium [19] and calculated based on the volume of EDTA consumed and relation between one to one ratio of EDTA and magnesium ion, EDTA and calcium ion respectively.

EDTA was added from the buret to solution containing calcium and magnesium ions, it reacted with the calcium before the magnesium.

The indicator was added and remains blue as all the Ca^{2+} and Mg^{2+} ions present were complexed with the EDTA. A back titration was carried out using a solution of magnesium chloride. This forms a complex with the excess EDTA molecules until the end-point, when all the excess EDTA has been complexed. The remaining magnesium ions of the magnesium chloride solution then started to complex with ErioT indicator, immediately changing its colour from pink to blue for magnesium concentration.

a) For total Magnesium and Calcium

About 0.93 g of EDTA was weighted to determine concentration of EDTA (0.1 M) and EDTA was prepared into 500 ml which concentration is 0.1 M. Accurately about 0.3 g of sample was Weighted and dissolved in water to make exactly 100 ml. Exactly 20 ml of this solution was measured. 50 ml of water was added to 20 ml of the solution. From this solution,25 ml was measured into conical flask and 5 ml of ammonia- ammonium chloride buffer (pH 10.7), Two drops of indicator (eriochrome black T) were added to the solution respectively. EDTA was pipetted from the buret for the titration (0.1 M EDTA). The colour was changed from red to the blue and the volume of EDTA consumed was recorded.

b) Only for Calcium ion

accurately about 0.3 g of sample was Weighted and dissolved in water to make exactly 100 ml. Exactly 20 ml of this solution was measured and 50 ml of water added. From this solution,25 ml was measured into conical flask, 5 ml (1M) of sodium hydroxide solution (Ph = 12) few drop of murexide indicator were added respectively. Then the titration was carried out with 0.1mol/L EDTA. For calcium ion the end point was from pink to purple and the volume of EDTA consumed was recorded.

Milligram of calcium ion per liter of magnesium chloride was calculated as:

$$Ca^{2+}(mg/L) = V * C * 1.0165 * 40.1 * \frac{1000}{\text{mass of sample(g)}} \quad \text{----------(3.11)}$$

Milligram of magnesium ion per liter of the solution

$$Mg^{2+}(mg/L) = (V_H - V) * C * 24.32 * 1.0165 * \frac{1000}{\text{mass of sample(g)}} \quad \text{----------(3.12)}$$

V) **Melting and Boiling point determination**

a) **Melting Point**

Melting point and boiling point both describe temperatures at which phase changes occur in substances. Melting point describes the temperatures at which phase changes occur in substances. At this temperature that a solid will start melting to become a liquid. the molecules forming the substance are gaining enough kinetic energy to overcome the intermolecular forces which hold them in fixed positions and they gain the ability to move around. From the sample 5 ml of the solution was taken to determine the melting point of the sample. For magnesium chloride, the melting point is 117 ^{0}C and 300 ^{0}C for hexahydrate and anhydrous respectively.

b) Boiling Point

Boiling point can be defined for a liquid as the temperature at which its vapour pressure of the substance is equal to external pressure. At this temperature, the substance in liquid phase enters the gas phase. The normal boiling point is defined as the temperature at which the vapour pressure of the liquid is equal to 1atm, i.e. the temperature at which liquid would boil when the external pressure is equal to 1 atm. From the literature the boiling point of magnesium chloride is 1412 ^{0}C hexahydrate.

VI) **Determination of Heat of reaction**

A calorimeter is an object used for calorimetry, or the process of measuring the heat of chemical reactions or physical changes as well as heat capacity. Differential scanning calorimeters, isothermal micro calorimeters, titration calorimeters and accelerated rate calorimeters are among the most common types. A simple calorimeter just consists of a thermometer attached to a metal container full of water suspended above a combustion chamber. To find the enthalpy change per mole of a substance A in a reaction between two substances A and B, the substances are added to a calorimeter and the initial and final temperatures (before the reaction started and after it has finished) are noted. Multiplying the temperature change by the mass and specific heat capacities of the substances gives a value for the energy given off or absorbed during the reaction. Dividing the energy change by how many moles of A were present gives its enthalpy change of reaction.

3.3. Experimental Design and Statistical Data Analysis

During this work magnesium chloride was produced using the two raw materials magnesium carbonate and hydrochloric acid. Experimental design was analyzed and done by the Design Expert 7.0.0 software application. Experimental design selected for this study is general factorial design and the output measured is magnesium chloride yield gained. Process variables revised are acid concentration, liquid to solid ratio and reaction time. To get maximum conversion; reaction temperature, rotation speed and particle size were selected at70^0C, 60rpm and79μm respectively and at atmospheric pressure. The operating limits of the magnesium chloride production process conditions are reasons to choose levels of the variables. For three factors with thee level general full factorial design was used. Acid concentration, liquid to solid ratio and reaction time were the independent variables selected to optimize the conditions for magnesium chloride production. Fifty four experiments were done and the data was statistically analyzed by the Design Expert 7.0.0 software to get suitable model for the percentage of magnesium chloride of the independent variables.

4. RESULT AND DISCUSSION

4.1. Raw material Characterization

I) Size Reduction

Magnesium carbonate size reduction was carried out at laboratory of Addis Ababa Cement Factory using sample milling machine. The particle size was milled to less than 100μm and after Magnesium carbonate undergo size reduction at required size, in order to determine the optimum particle size, magnesite powder, sieve analysis was carried out using 79μm sieve. Then 79μm particle size was taken as constant for all runs. According to[12,18] a particle size has not a significant effect on the leaching process.

II) Moisture Content Determination

30 g of magnesium carbonate sample was weighed into a tared moisture dish and placed in an oven at a temperature of 105°C for one hour. After one hour, it was removed to a desiccator, cooled and weighed. Similar procedure was repeated until constant weight was obtained and finally the weight was taken and compared with the initially recorded weight. The final weight was 29.95g and the percentage of moisture content was determined according to eq (3.1) and the result was 0.17% (w/w)

III) Density Determination

The density of magnesium carbonate was measured by a standard Pycnometer of 50 ml capacity. First Empty Pycnometer with 50 ml was measured on digital balance and mass was recorded. The sample was filled halve of the Pycnometer and weighted. The mass of magnesium carbonate was determined according to equation below. Then the remaining volume of Pycnometer was filled with distilled water and weighted. Mass of water was determined, the volume of water obtained from equation below (3.2). The density of the sample was determined from total volume of Pycnometer (50 ml) minus volume of water equation (3.4).

The mass of water is equal to the volume of the water, because density of water is g/cm^3 and the volume of the water is 43.8 cm^3 from eq, (3.1).

Therefore from equation (3.2) volume of the sample was 6.2 cm^3 and from eq (3.4) density of the sample was 2.85 ~ 2.9 g/cm^3

IV) **Composition Analysis by Acid Titration Method**

The purpose of titration was to determine the composition of magnesium carbonate in the sample and percentage of purity.

The magnesite sample (triplicates) 0.25 g was dissolved in 50 ml amounts of hydrochloric acid (con. 0.5 M). The metal carbonate reacted with the acid to give the water soluble chlorides. An excess amount of acid that is somewhat in excess of the maximum stechiometric amount needed to dissolve the maximum possible amount of $MgCO_3$,was added to the sample. It was allowed to react with a sample and the solution was heated using bussen burner and gently boiled over five (5 min) minute to speed up the reaction. The residue carbon dioxide liberated can interfere with the subsequent determination and is therefore expelled by boiling the solution. The solution was cooled to room temperature and two drop of phenolphthalein indicator was added to the solution and the excess hydrochloric acid was then titrated with standardized sodium hydroxide (con. 0.5 M) solution to neutralize un reacted /excess HCl. The volume of NaOH consumed was represented in the following table. The end point was detected by colour change. The experiments were repeated three times to obtain the same result. The complete chemical analysis was carried out at laboratory of Mugher Cement Factory for all composition analysis, equipments and chemicals used were presented in appendix (E)

Table 4.1. composition analysis for Magnesium Carbonate

No. titration	Mass of sample (g)	Volume of HCl (0.5 M)	Volume of NaOH (0.5 M)	Colour changes
1	0.25	50 ml	38.6 ml	White to red
2	0.25	50 ml	39.5 ml	White to red
3	0.25	50 ml	38.4 ml	White to red
Average	0.25	50 ml	38.8 ml	

The maximum amount of $MgCO_3$ that could possibly be present in the sample was calculated according to stechiometric ratio from eq.(3.6).Result was 94.43 $\%MgCO_3$. Detailed calculation is represented under appendix (C).

Table:4.2 results of Chemical analysis of magnesite for all compositions

Compounds	MgO	CaO	SiO_2	Al_2O_3	SO_3	Fe_2O_3	L.O.I	Total
Weights %	46.77	3.03	0.78	0.2	0.02	0	49.12	100.0

Impurities present with magnesite like metal oxide which causes problem for complete reaction between magnesium carbonate and HCl it reduce the yield of production. According to the experimental result from table 4.1 and 4.2, the magnesite mineral contains different chemical composition such as: 0.78% SiO_2, 0.2%Al_2O_3, 0.02% SO_3 and 0% Fe_2O_3. These minerals are reacted with HCl which has a problem on the yield of magnesium chloride.

4.2. Percent of Yield Determination

Stechiometric calculations allows us to calculate the amounts of reactant required or amounts of products generated from a chemical reaction.

Chemical reaction:- $MgCO_3 + 2HCl \longrightarrow MgCl_{2(aq)} + HO_2 + CO_2$

Based on stiochiometric relation the theoretical yield of magnesium chloride was determined using 30 g of magnesium carbonate. From stiochiometric relation, theoretically 33.87g of magnesium chloride is produced, but from experimental result the actual yield was 31.84 g. The percentage yield of magnesium chloride was calculated using eq (3.6).

Table 4.3.Yield of Magnesium Chloride

Run No.	Acid concentration (M)	Liquid to solid ratio (ml/g)	Time (min)	Yield (% w/w)
1	10	1.88	60	68
2	4	1.97	60	61
3	7	1.97	60	73
4	4	1.88	60	59
5	10	2.07	120	71
6	10	2.07	120	80.3
7	7	1.88	180	70
8	7	1.97	60	74
9	4	2.07	120	68
10	4	2.07	60	64
11	7	1.97	180	80
12	10	1.88	60	70
13	4	2.07	60	65
14	10	1.88	120	66
15	7	2.07	60	78
16	7	2.07	60	80
17	7	1.88	60	65
18	4	1.97	120	63
19	10	1.97	60	75
20	10	1.97	120	80
21	4	1.97	60	60
22	4	2.07	120	67.6
23	10	1.88	120	65
24	7	2.07	180	94.1
25	10	1.97	180	76
26	7	1.88	60	64

Table 4.3 continued.

27	4	2.07	180	61
28	4	1.88	180	62
29	10	1.97	120	79
30	4	1.97	180	65
31	4	1.88	120	59.8
32	10	2.07	180	86
33	10	1.97	60	76.5
34	4	1.88	180	63
35	10	2.07	180	84.9
36	7	1.88	120	64
37	7	2.07	180	94
38	10	1.88	120	64
39	10	1.97	180	75
40	10	1.97	180	75.3
41	4	2.07	180	62
42	7	1.88	180	69
43	7	1.88	120	65
44	4	1.97	120	63
45	7	1.97	120	75
46	10	2.07	60	74
47	4	1.88	120	60
48	4	1.88	60	58
49	7	1.97	180	79
50	4	1.97	180	66
51	7	1.97	120	77.1
52	7	2.07	120	88
53	7	2.07	120	87
54	10	2.07	120	80

From Table 4.3, the maximum yield was 94% (w/w), at experiment number 24 and 37, while the minimum yield was 58 % (w/w), at experiment number 48. Also from the table experiment numbers 52 and 53 were related to the maximum amount of yield gained. Therefore it was concluded that the maximum amount of magnesium chloride yield was gained at 7 M acid concentration, 2.07 ml/g liquid to solid ratio and 180 min reaction time.

4.3. Optimal Parameters and Experimental Result for Magnesium Chloride

In section 3.2.3,the selected process parameters were acid concentration, liquid to solid ratio and reaction time each with three levels and two replicates and the reaction temperature, particle size and rotation speed were taken as constant. According to the experimental results from table 4.3, the point at which maximum yield of magnesium chloride obtained were: at 7M acid concentration, 2.07ml/g liquid to solid ratio and 180 min reaction time. Therefore the optimum point at which the maximum yield of magnesium chloride obtained were, at 7 M acid concentration, 2.07ml/g liquid to solid ratio and 180 min reaction time, 70^0C reaction temperature, 79µm particle size and 60 rpm rotation speed. While the minimum yield was 58 % (w/w) at 4 M acid concentration, 1.88 ml/g liquid to solid ratio and 60 min reaction time.

Table 4.4. Optimum parameters for magnesium chloride production

Parameters	Values	Optimum	Units
Reaction temperature	70	70	^{0}C
Acid concentration	4-7-10	7	M
Liquid to solid ratio	1.88-1.97-20.7	2.07	ml/g
Mixing speed	60	60	Rpm
particle size	79	79	µm
Reaction time	60-120-180	180	Min
Yield	-	94	%

4.4. Product Characterization

I) pH adjustment

pH meter was used to measure the pH of magnesium chloride solution at 20^0C specified. The pH meter was washed first by distilled water. The 3ml sample solution was taken with intervals of 30 min to adjust the pH of the solution/ product to desired one. To neutralize the solution, a little 0.5 g of amount of magnesium carbonate was added to the solution in order the neutralize HCl. Then the Ph of the solution was adjusted to 7.5 according to [16], the pH of magnesium chloride is range from 6.5 to 8.

II) Density determination

The density of magnesium chloride was measured by a standard Pycnometer of 50 ml capacity. First Empty Pycnometer was measured on digital balance and mass was recorded. The sample of magnesium chloride was filled halve of the Pycnometer and weighted. The mass of magnesium chloride was determined form total mass of Pycnometer and sample. Then the remaining volume of Pycnometer was filled with distilled water and weighted. After mass of water was determined, the volume of water obtained from equation eq(3.2). The volume and density of the sample was determined from eq (3.3) and (3.4) respectively. Therefore from equation (3.3) volume of the sample is 9.52 cm^3 and from equ. (3.4) density of the sample is 1.56 g/cm^3

III) Determination of Magnesium Chloride Composition

In order to determine the quality/composition of the magnesium chloride produced, chemical analysis was carried out using Complexometric method using EDTA. The amount of magnesium chloride was determined according to eq (3.5) in section 3.4.3 and appendix(D). In order to determine amounts of compounds present in the product complete chemical analysis was carried out using Complexometric using EDTA and gravimetric method at laboratory of Mugher Cement Factory and results in table 4.5

Table 4.5 Amount of Magnesium Chloride in Magnesium Chloride Hexahydrate

No.	Volume of EDTA consumed	Colour change	%$MgCl_2$
1	46.9	Red to black (dark)	44.18
2	46.63	Red to black (dark)	43.92
3	46.62	Red to black (dark)	43.9
Average	46.87		44.0

Table 4.6. Chemical analysis results of the magnesium chloride.

Compounds	CaO	Al_2O_3	SiO_2	Fe_2O_3	SO_3	$MgCl_2$	L.O.I	Total
Weight %	3.99	0.05	0.62	0	0.03	44.1	51.2	100

According to the results of the chemical analysis given in Table 4.6, the product of magnesium chloride contained, 0.62%SiO_2, 3.99 % CaO, 0% Fe_2O_3, 0.05 % Al_2O_3,0.03%SO_3 , 44.1% $MgCl_2$ and 50.2% L.O.I. Thus, results show that impurities were existed both in raw material and in the product of magnesium chloride. Due to these the yield of magnesium chloride was reduced and further purification will be advised to obtain maximum yield of magnesium chloride .

IV) **Determination of total calcium and magnesium ion content (EDTAtitrimetric- method)**

a) For total Magnesium and Calcium

About 0.93 g of EDTA was weighted to determine concentration of EDTA (0.1 M) and EDTA was prepared into 500 ml which concentration is 0.1 M. Accurately about 0.3 g of sample was Weighted and dissolved in water to make exactly 100 ml. exactly 20 ml of this solution was measured. 50 ml of water was added to 20 ml of the solution. From this solution,25 ml was measured into conical flask and 5 ml of ammonia- ammonium chloride buffer (pH 10.7) [14], Two drops of indicator (eriochrome black T) was added to the solution respectively. EDTA was pipetted from the buret for the titration (0.1 M EDTA). The colour was changed from red to the blue and the volume of EDTA consumed was recorded.

b) Only for calcium ion

Accurately about 0.3 g of sample was Weighted and dissolved in water to make exactly 100 ml. Exactly 20 ml of this solution was measured and 50 ml of water added. From this solution,25 ml was measured into conical flask, 5 ml (1M) of sodium hydroxide solution (Ph = 12) few drop of murexide indicator were added respectively. Then the titration was carried out with 0.1 mol/l

EDTA. For calcium ion the end point was from pink to purple and the volume of EDTA consumed was recorded.

Calculations:

V_H = volume of EDTA consumed for total (Ca+2 +Mg^{+2}) = 14.415 ml

V = volume of EDTA consumed only for calcium ion Ca^{+2} ion = 3.25 ml

Mg^{+2} = volume of EDTA consumed for magnesium ion = V_H - V = 11.09 ml

Concentration of EDTA (C) = 0.1 mol/L

formula weight of calcium = 40.1g/mol

formula weight of magnesium = 24.32 g/mol

Mass of the sample = 0.3g

volume of sample = 250 ml

Density of EDTA= 1.0165 g/ml

Milligram of calcium and magnesium ions per liter was calculated from eq(3.8) and (3.9) respectively as follows [2]:

$$Ca^{2+}(mg/L) = V * C * 1.0165 * 40.1 * \frac{1000}{\text{mass of sample}}$$

$$= 44000mg/L = 44.03g/L$$

$$(Mg^{2+}(mg/L) = (V_{EDTA} * (C_{EDTA} * 24.32 * 1.0165 * \frac{1000}{\text{mass of sample(g)}}$$

$$= 687960mg/L = 687.97g/L$$

V) Melting and Boiling point determination

a) **Melting Point**

As discussed in section 3.4.5, melting point and boiling point both describe temperatures at which phase changes occur in substances. Melting point describes the temperatures at which phase changes occur in substances. 5 ml of sample was taken to determine the melting point of the sample. The melting point of magnesium chloride hexahydrate is, 117 ^{0}C. But, the melting point of the sample was started to decompose at 96 ^{0}C. It was conclude that the sample has impurities which reduce the normal melting point of the product. Therefore the produced magnesium chloride is not pure as experimental result due to impurities.

b) Boiling Point

according to the literature, the boiling point of magnesium chloride hexahydrate is 1412 ^{0}C. To check experimentally this boiling point of the sample, the sample was taken to 4 Kilo and Mugher Cement Factory, however there was no at laboratory scale equipment that used for this material due to its higher boiling point. Therefore the literature value was taken for boiling point.

VI)Determination of Heat of reaction

A calorimeter is an object used for calorimetry, or the process of measuring the heat of chemical reactions or physical changes as well as heat capacity. There is a bomb calorie meter used to measure heating value or heat of reaction in laboratory of Chemical Engineering. But there is no oxygen in the equipment and bomb calorie meter cannot work without oxygen gas again I asked another place and I didn't bomb calorie meter filled with oxygen. Due to this problem the heat of reaction was calculated based on [15] and standard heat of reaction between chemical reaction for magnesium chloride production. Enthalpy of reaction ΔH = -50.4kJ/mol and used under energy balance.

4.5. Experimental Design and Effects of Parameters on the Yield

4.5.1. Statistical data Analysis using Design expert® 7.00 software

In this study statistical experimental design techniques were used to determine the effects of acid concentration, liquid to solid ratio and reaction time on production of magnesium chloride. A total of 54 experiments were conducted for optimization of process parameters purpose and the effect of each factor was determined in section below.

To determine whether or not the modified model is significant, it was crucial to perform analysis of variance (ANOVA), table 4.7. The probability (P-values) values were used as a device to check the significance of each coefficient, which also showed the interaction strength of each parameter. The smaller the P-values are, the bigger the significance of the corresponding coefficient.

Table 4.7. Analysis of variance (ANOVA) for the modified model

Source	**Sum of square**	**Degree of freedom**	**Mean square**	**F-value**	**P -value Prob>F**
Model	3727.61	10	372.76	28.71	< 0.0001**
A-Acid concentration	1418.12	1	1418.12	109.23	< 0.0001**
B-Liquid to solid ratio	1298.64	1	1298.64	100.03	< 0.0001**
C-Time	222.21	1	222.21	17.12	< 0.0002**
AB	72.82	1	72.82	5.61	0.0224
AC	6.57	1	6.57	0.51	00.4807
BC	24.74	1	24.74	1.91	0.1746
A^2	622.75	1	62.75	47.97	< 0.0001**
B^2	20.57	1	20.57	1.58	0.2149
C^2	0.43	1	0.43	0.033	0.8563
ABC	66.53	1	66.53	5.12	0.0287
Residual	558.24	43	12.98		
Lack of fit	542.41	16	33.90	57.81	0.0001*
Pure error	15.83	27	0.59		
Cor total	4285.86	53			
Where * significant, ** highly significant on the process					

F- Value is a test for comparing model variance with residual (error) variance. If the variances are close to the same, the ratio will be close to one and it is less likely that any of the factors have a significant effect on the response. It is calculated by Model Mean Square divided by Residual Mean Square. Here the Model F-value of 28.71 implies the model is significant. There is only a 0.01% chance that a "Model F-Value" this large could occur due to personal error or disturbance. Probability values and/or "Prob > F" values less than 0.0500 indicate model terms are significant. In this case A (acid concentration), B (liquid to solid ratio), C (time), A^2, AB and ABC are significant model terms. Values greater than 0.1000 indicate the model terms are not significant.

This shows that the main effects are highly significant(acid concentration, liquid to solid ratio, reaction time) and interaction between acid concentration and liquid to solid ratio, acid concentration, liquid to solid ratio and time have significant affect on the yield.

The lack of fit F-value of 57.81 implies the lack of fit is significant relative to the pure error. There is a 0.01% chance that a lack of fit F-value this large could occur due to noise. Significant lack of fit is bad-we want the model to fit. Non significant lack of fit is good. Coefficient of Variation, the standard deviation expressed as a percentage of the mean; Predicted Residual Error Sum of Squares, which is a measure of how the model fits each point in the design; the R-Squared, measure of the amount of variation around the mean explained by the model; Adj R-Squared that is a measure of the amount of variation around the mean explained by the model, Pred R-Squared, a measure of the amount of variation in new data explained by the model, and Adequate Precision, this is a signal to disturbance ratio due to random error, presented in the table 4.8, below, are used to decide whether the model can be used or not.

Table 4.8. Model adequacy measures

Standard deviation	3.6	R-squared	0.8697
Mean	71.21	Adj R-squared	0.8395
C.V.%	2.78	Pred R-squared	0.7860
PRESS	916.99	Adeq Precision	20.67

The "Pred R-Squared" of 0.7860 is as close to the "Adj R-Squared" of 0.8395 in less than 0.0535difference as one might expect. "Adeq Precision" measures the signal to disturbance ratio due to random error. A ratio greater than 4 is desirable. Here ratio of 20.67 indicates an adequate signal. Therefore, this model can be used to navigate the design space. The regression coefficients and the corresponding 95%CI (Confidence Interval) High and Low were presented in table 4.9 below. If zero is in the range High and Low 95% Confidence Interval, the factors has no effect. From the 95% CI High and Low values of each model term, it could be concluded that the regression coefficients of acid concentration and the interaction terms of time and acid concentration have highly significant effect on magnesium chloride production.

Table 4.9 Regression coefficients and the corresponding 95% CI High and Low

Factors	Coefficient of Estimation	Standard error	95%CI low	95%CI high
Intercept	76.87	1.30	74.25	79.49
A	6.28	0.60	5.07	7.49
B	6.01	0.60	4.80	7.22
C	2.49	0.60	1.27	3.70
AB	1.74	10.74	0.26	3.22
AC	0.52	0.74	-0.96	2.01
BC	1.01	0.74	-0.47	2.50
A^2	-7.20	1.04	-9.30	-5.11
B^2	-1.31	1.04	-3.42	0.79
C^2	0.19 1	1.04	-1.91	2.29
ABC	2.04 1	0.90	0.22	3.85

A = acid concentration, B = liquid to solid ratio and C= time

By the designed experimental data from table 4.9, the modified polynomial model for magnesium chloride production from magnesium carbonate by reacting it with HCl was retreated and shown as below:

Equation in terms of coded factors:

Yield of magnesium chloride = +76.68 +6.28*A + 6.01*B + 2.49*C +1.74*A*B +0.52*A*C +1.01*B*C -7.2*A^2* +-1.13*B^2*C+0.19*C^2 +2.04*A*B*C ----------(4.1)

where, A = acid concentration, B = liquid to solid ratio and C = reaction time

Equation in terms of actual factors:

Yield of magnesium chloride=742.48587 +29.13383*Acid concentration +647.16308*Liquid to solid ratio +1.30469*Time -08.19444*Acid concentration*Liquid to solid ratio-0.23250 *Acid concentration*Time -0.65633* Liquid to solid ratio *Time – 0.80043*Acid concentration^2 – 14.55556* Liquid to solid ratio^2 +5.26265E-005*Time^2 +0.11920*Acid concentration *Liquid to solid ratio*Time ----------(4.2)

Equation4.1 and 4.2 represent the yield of magnesium chloride resulted from Design expert® 7.00 software in terms of coded factors and interms of actual factors respectively.

To see how well the model satisfies the assumptions of the analysis of variance (ANOVA), the plots of residuals versus predicted were analyzed. In the analysis of variance, it is usually more effective (and straight forward) to do this with the residuals. This shown below resembles a straight line.

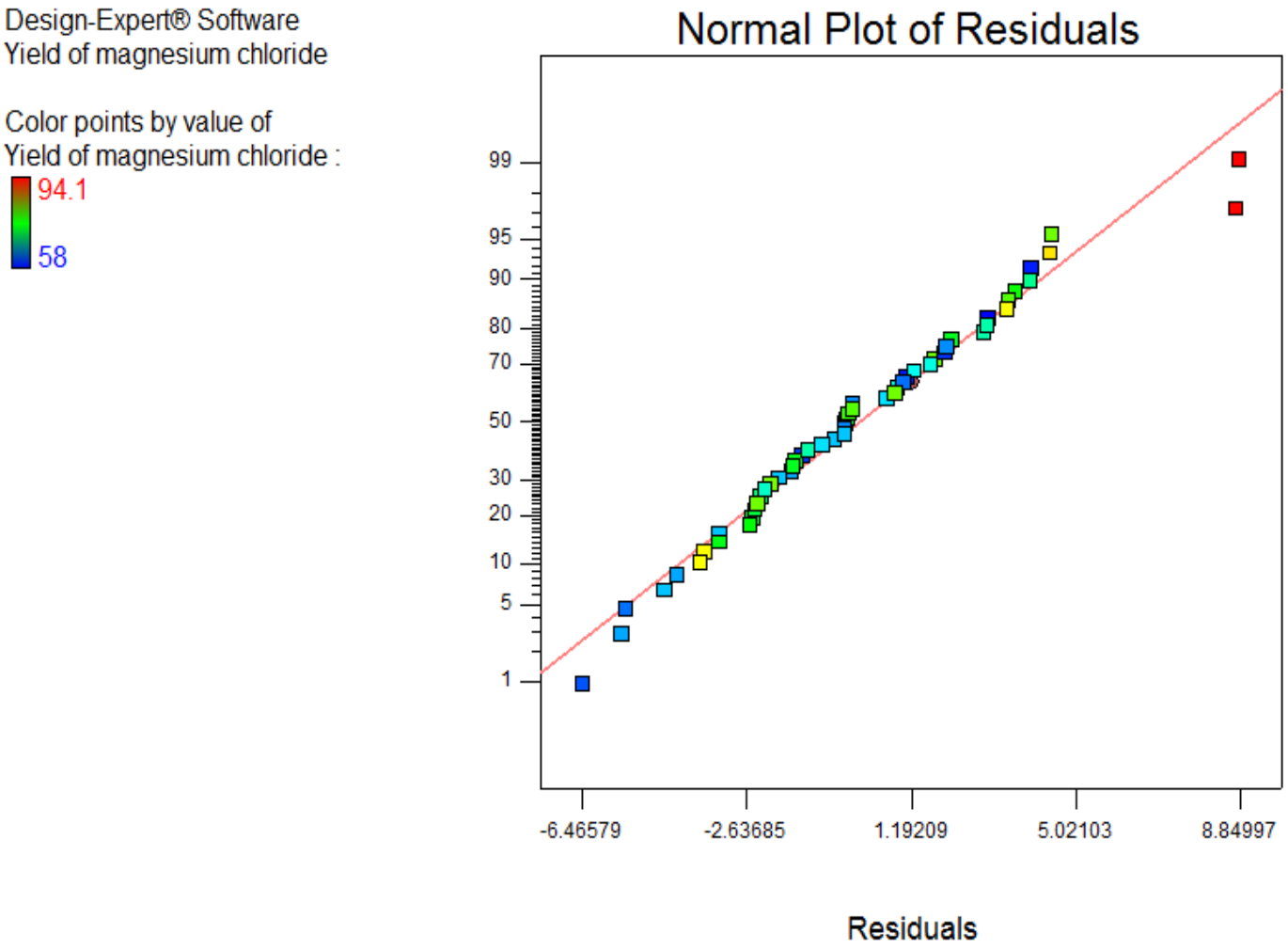


Fig. 4.1 Normal plots of residuals

Fig. 4.1 Normal plots of residuals from the plot as shown above, the normal probability plot indicates the residuals following a normal distribution, in the case of this experiment the points in the plots shows fit to a straight line in the figure, this shows that the modified polynomial model satisfies the assumptions analysis of variance (ANOVA) i.e. the error distribution is approximately normal.

4.5.2. Effects of Individual Process Variables on the Yield of Production

The yield can be affected by individual and interaction parameters. The best method to identify whether or not the yield can be affected by individual or interaction are to generate individual and interaction plots.

4.5.2.1. Effect of Acid Concentration

Setting reaction temperature 70^0C, mixing rate 60 rpm and particle size 79µm respectively for all the runs. The effect of acid concentration at 4M, 7 M and 10 M on magnesium chloride yield for 2.07ml/g liquid to solid ratio and time180 min is indicated in figure 4.2

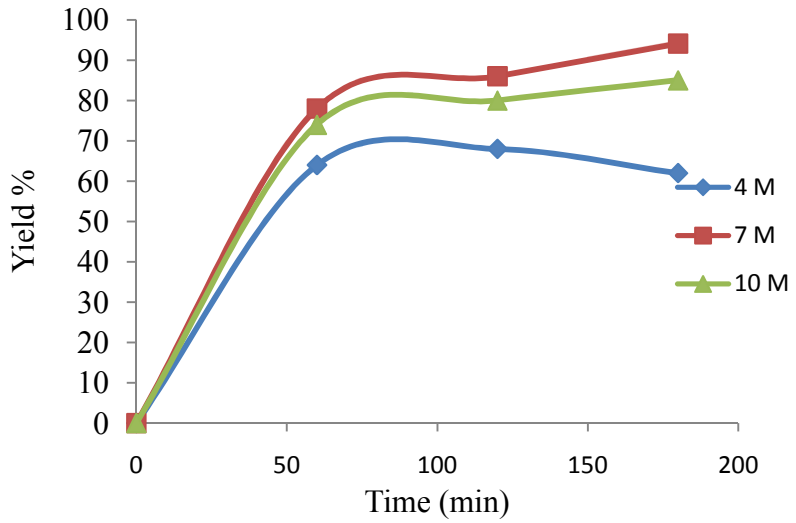


Fig. 4.2 Effect of acid concentration on the magnesium chloride yield (reaction time : 180 min, liquid to solid ratio:2.07 ml/g, average particle size: 79µm, stirring speed: 60 rpm).

In order to determine the effect of the hydrochloric acid concentration on the dissolution rate, the experiments were carried out in the concentrations of 4,7 and 10 M while the reaction time, temperature, particle size, stirring speed and liquid to solid ratio were kept constant at 180 min,70˚C, 0.079 mm, 60 rpm and 2.07ml/g, respectively. The results in Figure 4.2 show the positive effect of the hydrochloric acid concentration of 7 M on the dissolution of magnesium carbonate. Similar results were reported by [5]. They also reported that the amount of dissolved magnesium carbonate decreased when the acid concentration exceeded the maximum point to leach. Since the appearance rate of the product increased as the product approached to the saturation value on the surface of the solid particle and it forms a difficultly soluble solid film

layer around the particle. For the acid concentration range of 4–7 M, the yield of production was increased.

4.5.2.2. Effect of Solid to Liquid Ratio

To determine the effect of liquid to solid ratio on the yield of magnesium chloride, the experiments were performed at 1.88, 1.97 and 2.07 ml/g under the conditions of 7 M acid concentration, 60 rpm stirring speed, 70˚C reaction temperature and 0.079 mm particle size and 180 min reaction time. Figure 4.3 shows the results of the leaching experiments carried out with various liquid to solid ratio. According to the results, the leaching rate decreased as the liquid to solid ratio decreased. This might be explained by the fact that the amount of reagent is not sufficient to leach magnesium from magnesite ore when liquid to solid ratio is low or solid to liquid ratio is high. The same results were also found by [16] and [19].

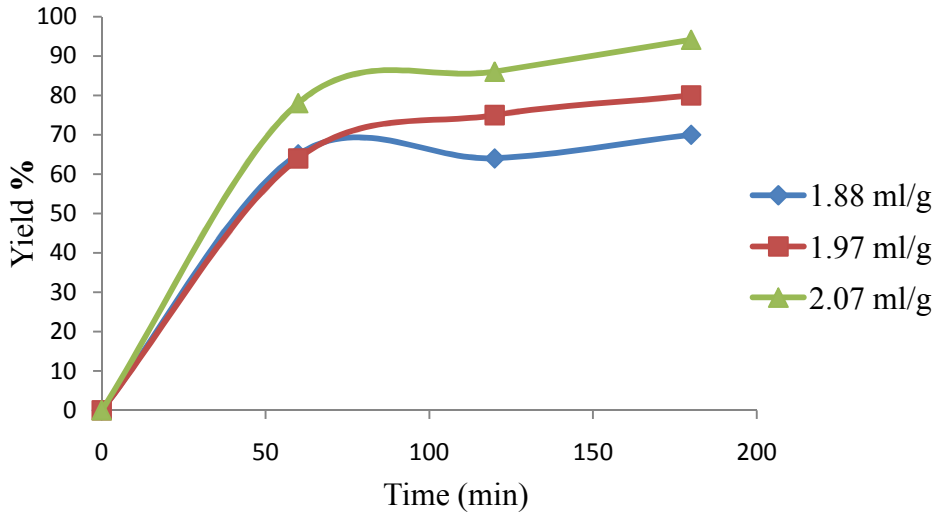


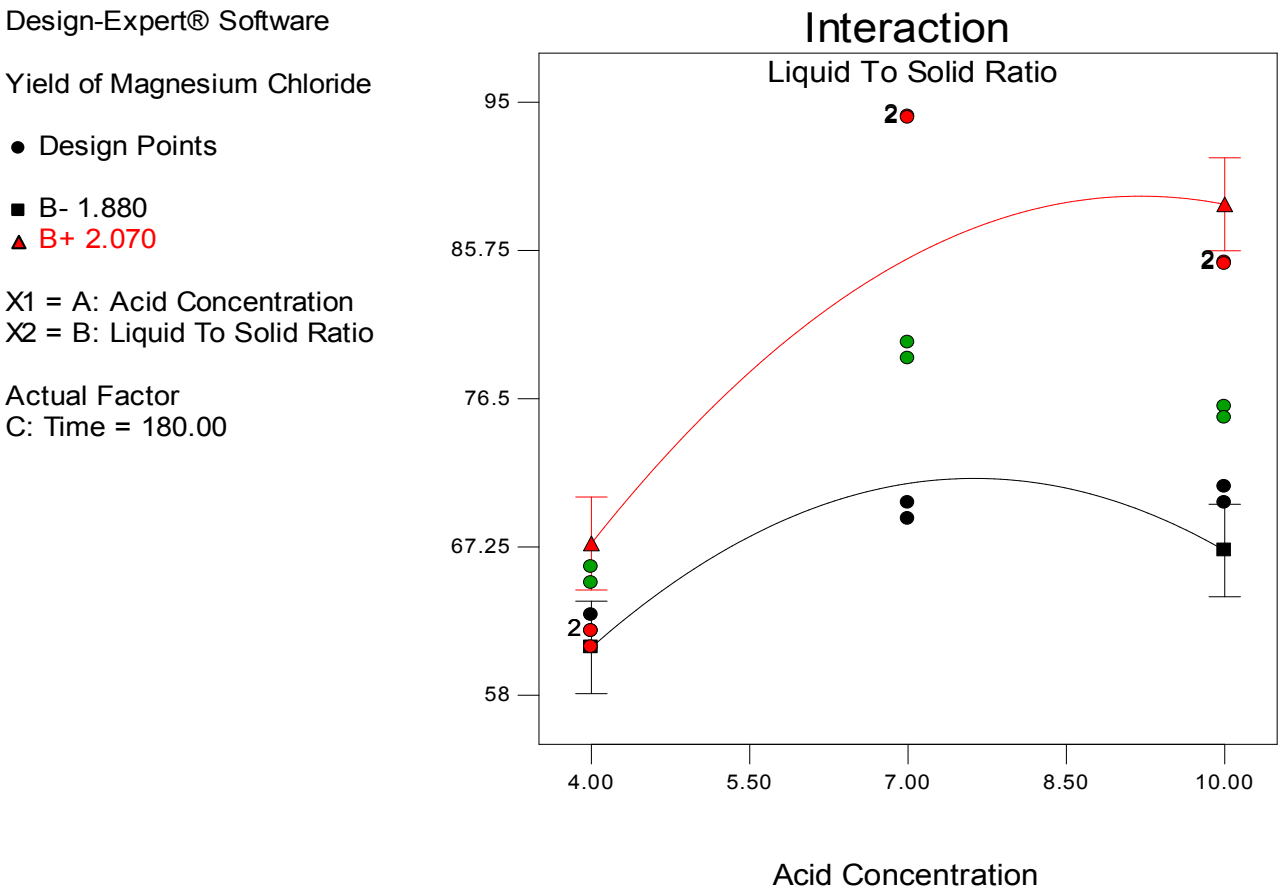
Fig. 4.3 Effect of liquid to solid ratio on the magnesium chloride yield (reaction time : 180 min, acid concentratio:7 M, average particle size: 79µm, stirring speed: 60 rpm).

4.5.2.3. Effect of Reaction Time

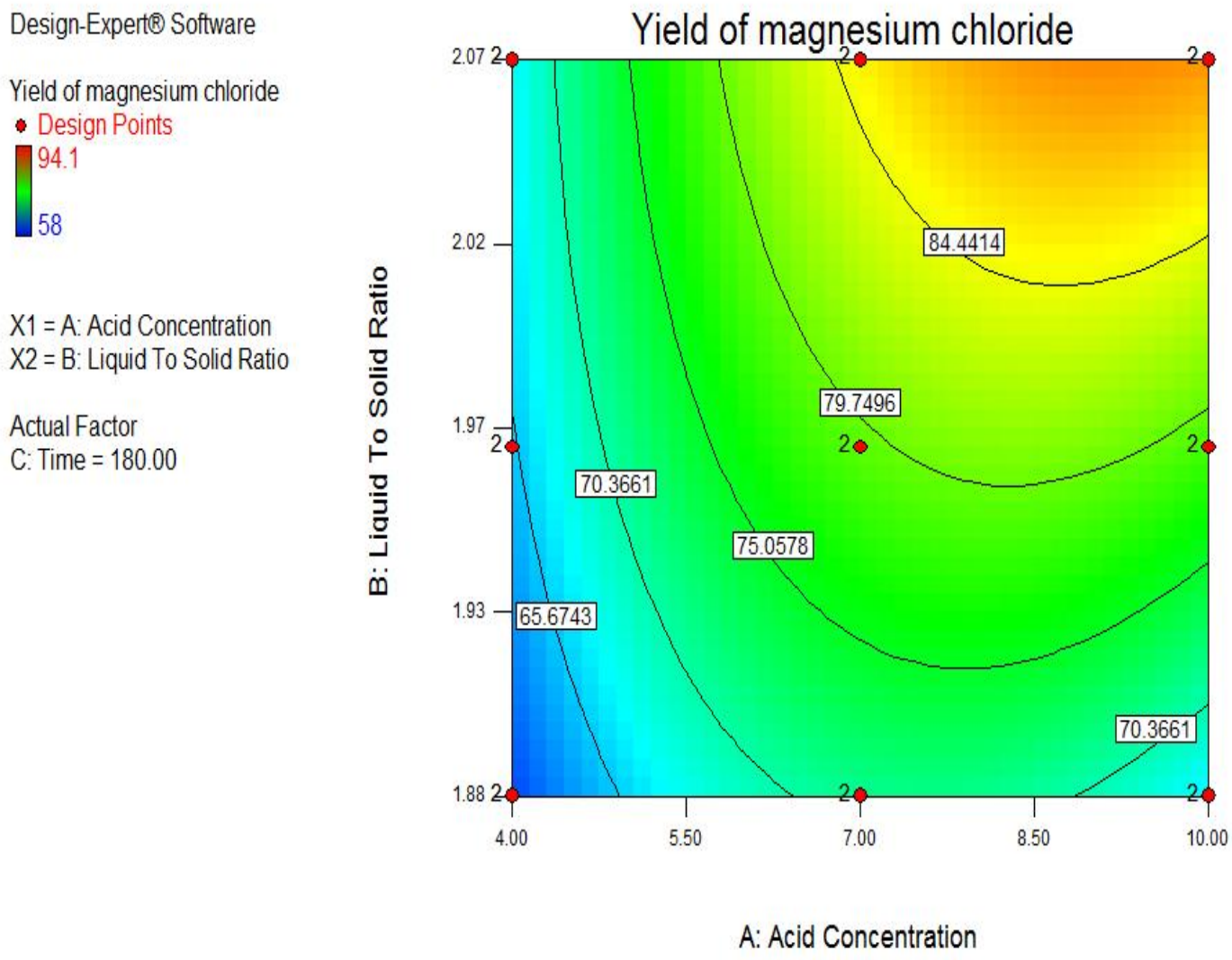
Reaction time has positive effects on the yield of magnesium chloride, as reaction time increased, in all cases percentage yield of magnesium chloride at acid concentration 4, 7, and 10 M and liquid to solid ratio 1.88, 1.97 and 2.07 g/ml.

4.5.3. Effect of Interaction Between Process Variables

The process variables were found to have significant interaction effects. Figure 4.4, 4.5 and 4.6 shows the interaction between acid concentration and liquid to solid ratio, acid concentration, liquid to solid ratio and time respectively, on the yield of magnesium chloride. an increase acid concentration increases the yield of magnesium chloride up to 7 M and started to decrease above it as discussed under main effect. Generally, an increase in liquid to solid ratio and reaction time is found to increase the yield of magnesium chloride up to some optimal value in all three cases. For the interaction figures black, green and red line indicates low, middle and high level of parameters respectively.



a)



b)

Fig.4.4 the effect of acid concentration and liquid to solid ratio on magnesium chloride yield s at 180 min**. a** interaction plot **b** counter plot.

Design-Expert® Software

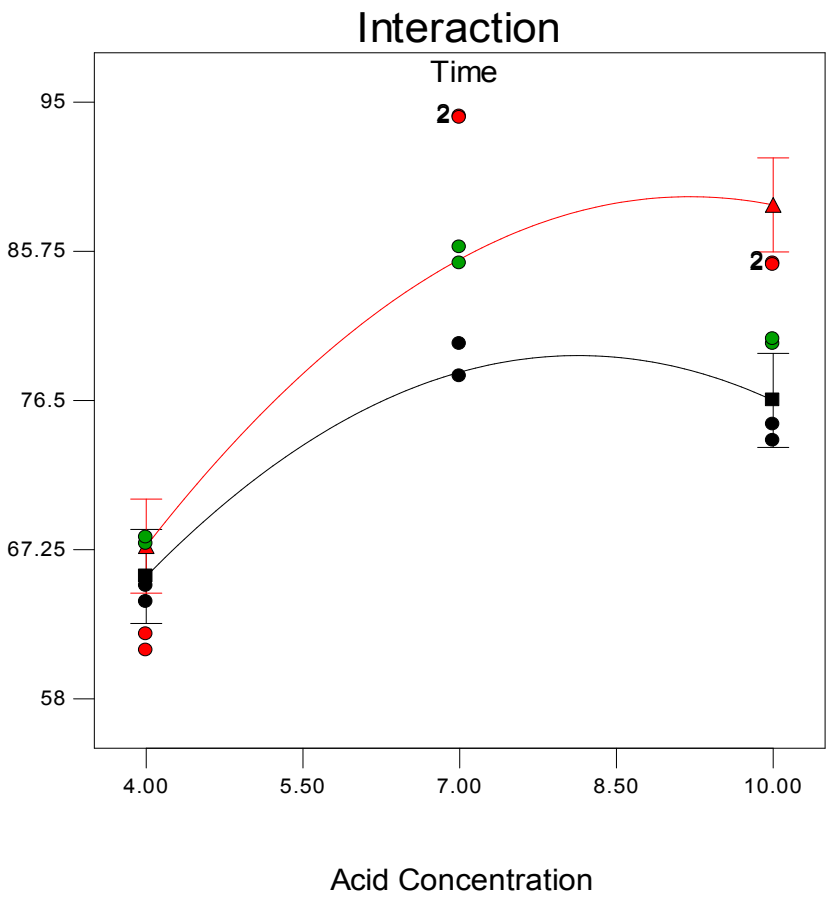
Yield of Magnesium Chloride

● Design Points

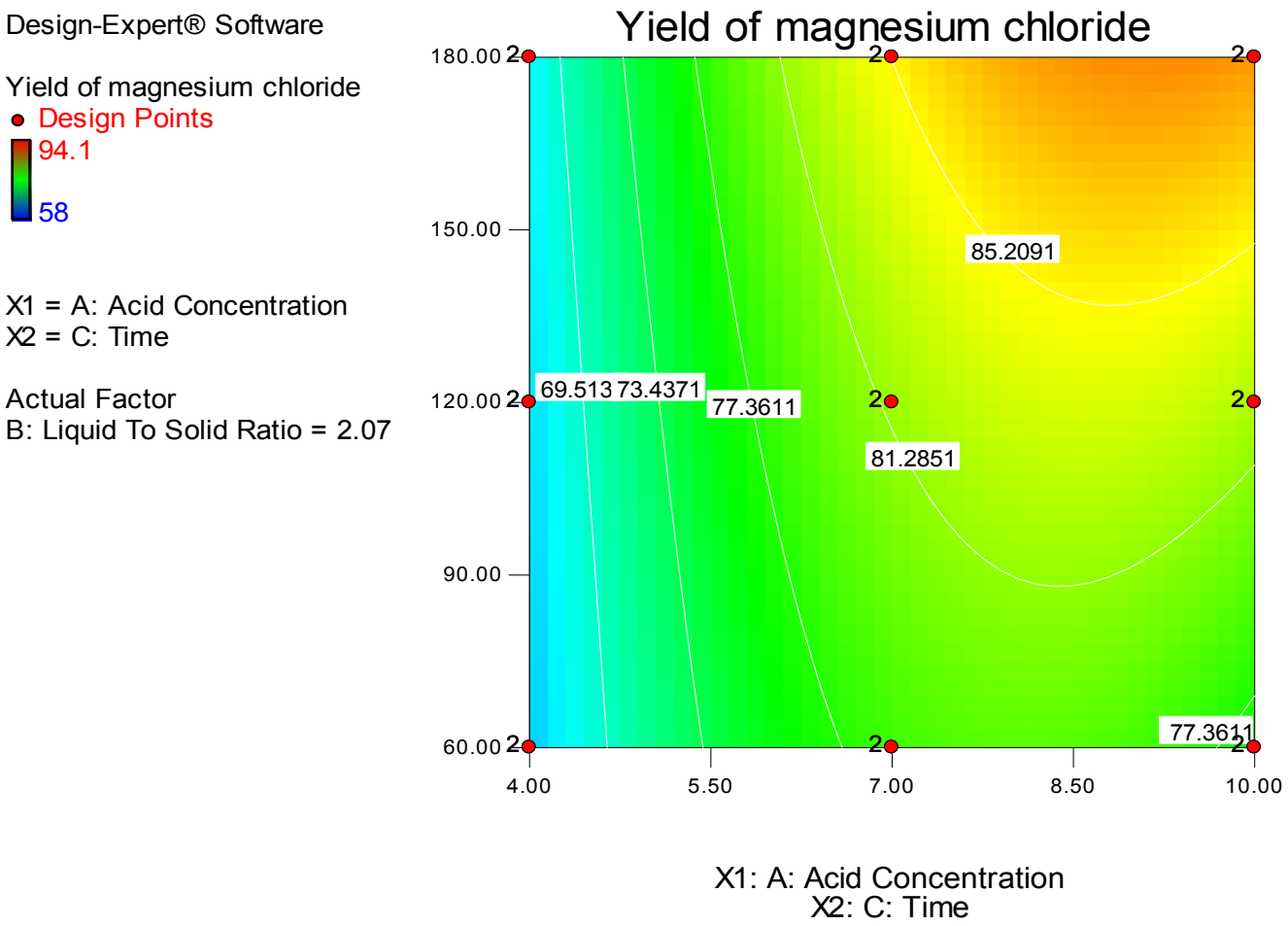
■ C- 60.000
▲ C+ 180.000

X1 = A: Acid Concentration
X2 = C: Time

Actual Factor
B: Liquid To Solid Ratio = 2.07



c)



d)

Fig.4.5 the effect of acid concentration and time on magnesium chloride yield at liquid to solid ratio 2.07 ml/g. **c** interaction plot and **d** contour plot.

Design-Expert® Software

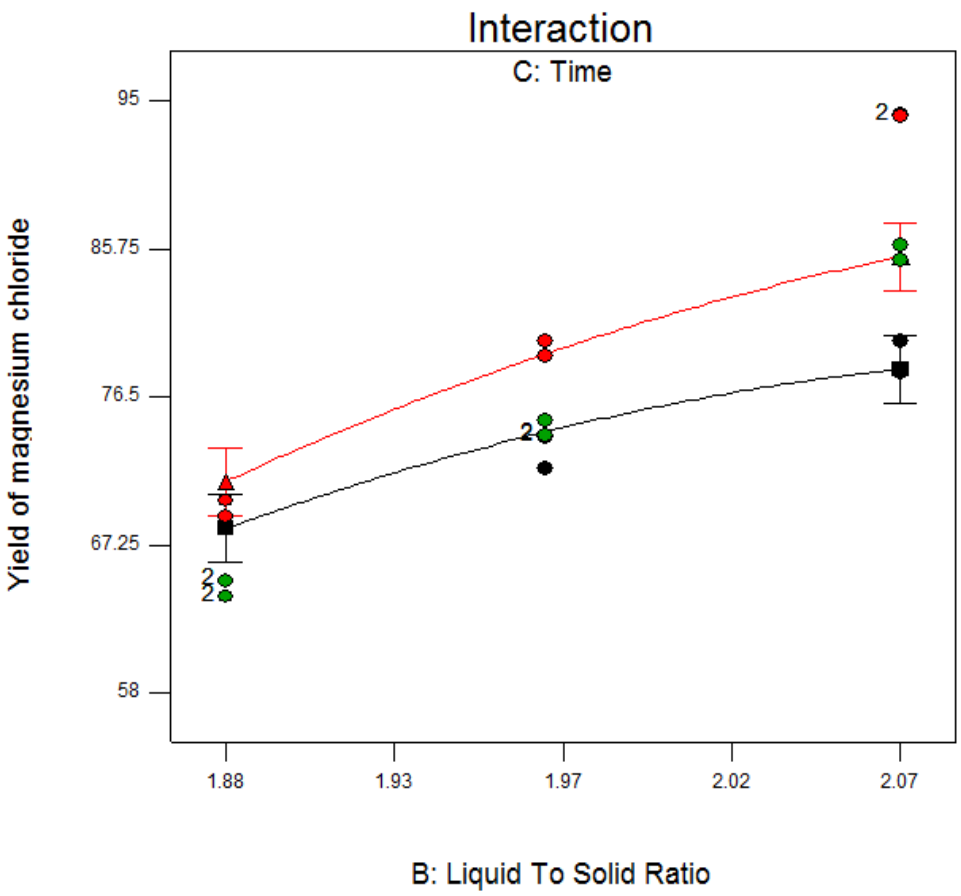
Yield of magnesium chloride

● Design Points

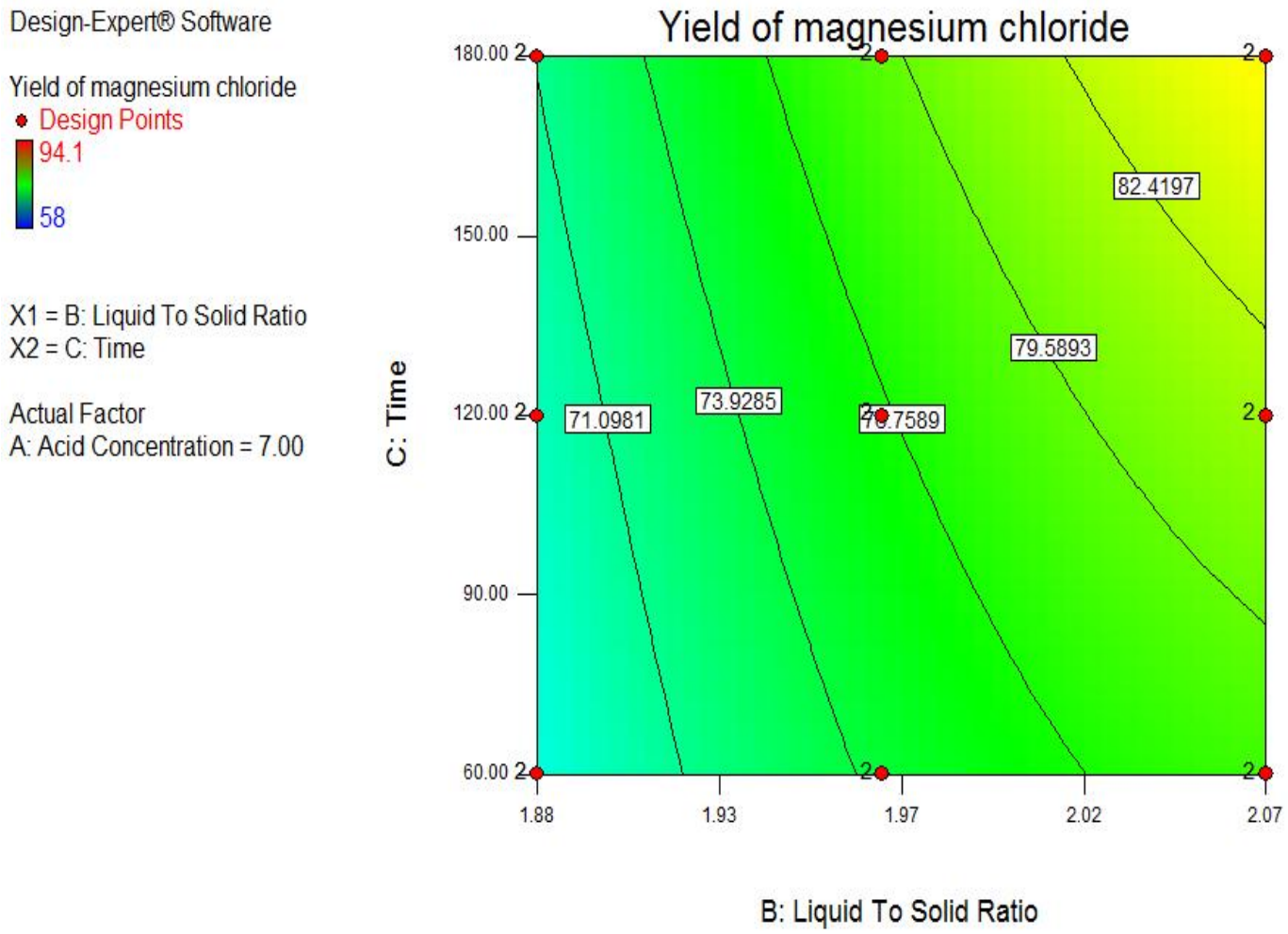
■ C- 60.000
▲ C+ 180.000

X1 = B: Liquid To Solid Ratio
X2 = C: Time

Actual Factor
A: Acid Concentration = 7.00



e)



f)

Fig. 4.6.The effect liquid to solid ratio and time on yield of magnesium chloride at acid concentration 7 M. **e**, interaction plot and **f,** contour plot.

The above figure interaction and contour plots show that the interaction effects between the test variables are have significant effect on the process.

Figure 4.4 show that the interaction between acid concentration and liquid to solid ratio at time at 180 min on the response. The results in figure shows the positive effect of the hydrochloric acid concentration on yield of magnesium chloride until acid concentration reached to 7M on the dissolution of magnesium carbonate but, as acid concentration increases it was started to decrease. It was conclude that, the amount of dissolved magnesium carbonate decreased when the acid concentration exceeds the optimum point at which the yield of magnesium chloride was 7M. since the appearance rate of the product increased as the product approached to the saturation value on the surface of the solid particle and it forms a difficultly soluble solid film

layer around the particle. Therefore, at higher acid concentration, solid particle formed is difficult soluble at solid film layer around the particle and caused a drop in the yield [6].

Figure 4.5, **c** interaction and **d** contour plots shows that the interaction effects between time and acid concentration. The % yield of magnesium chloride amount was increased with increasing time at moderate acid concentration. In all cases the yield was increased as reaction time increased. The above figure 4.6, **e** interaction and **f** contour plots shows that the interaction effects between Liquid to solid ratio and reaction time. It shows that, the % magnesium chloride amount increased with increasing liquid to solid ratio at a higher reaction time..

4.5. Optimization of Process Variables

Our interest is to maximize the yield of magnesium chloride content from raw magnesite as much as possible so that the possible to minimize acid concentration, reaction time and liquid to sold ratio. The results above have shown that the three factors influential process variables affect the production of magnesium chloride from magnesite. The next step is to optimize the process variables in order to obtain the highest yield of magnesium chloride using the model regression developed.

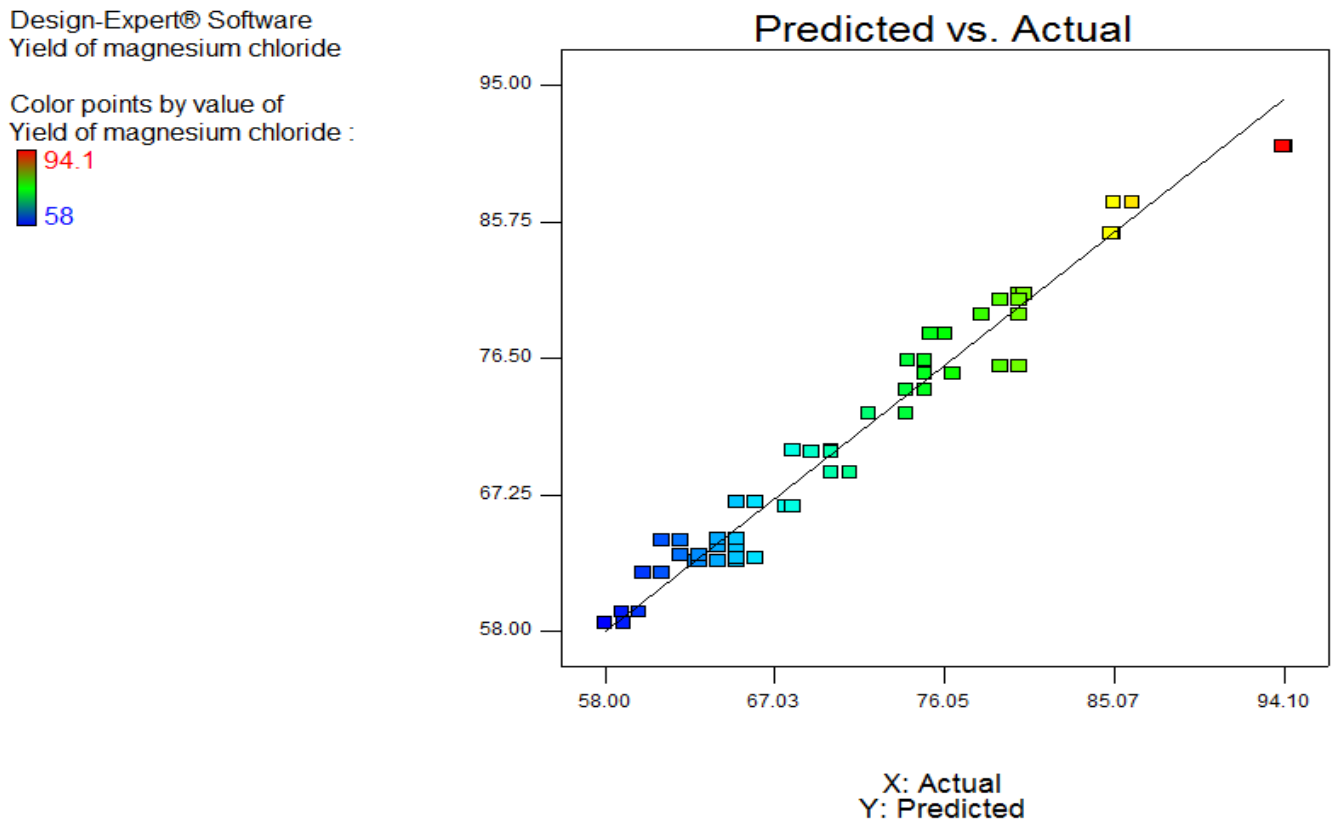


Fig. 4.7 actual versus predict for yield of magnesium chloride.

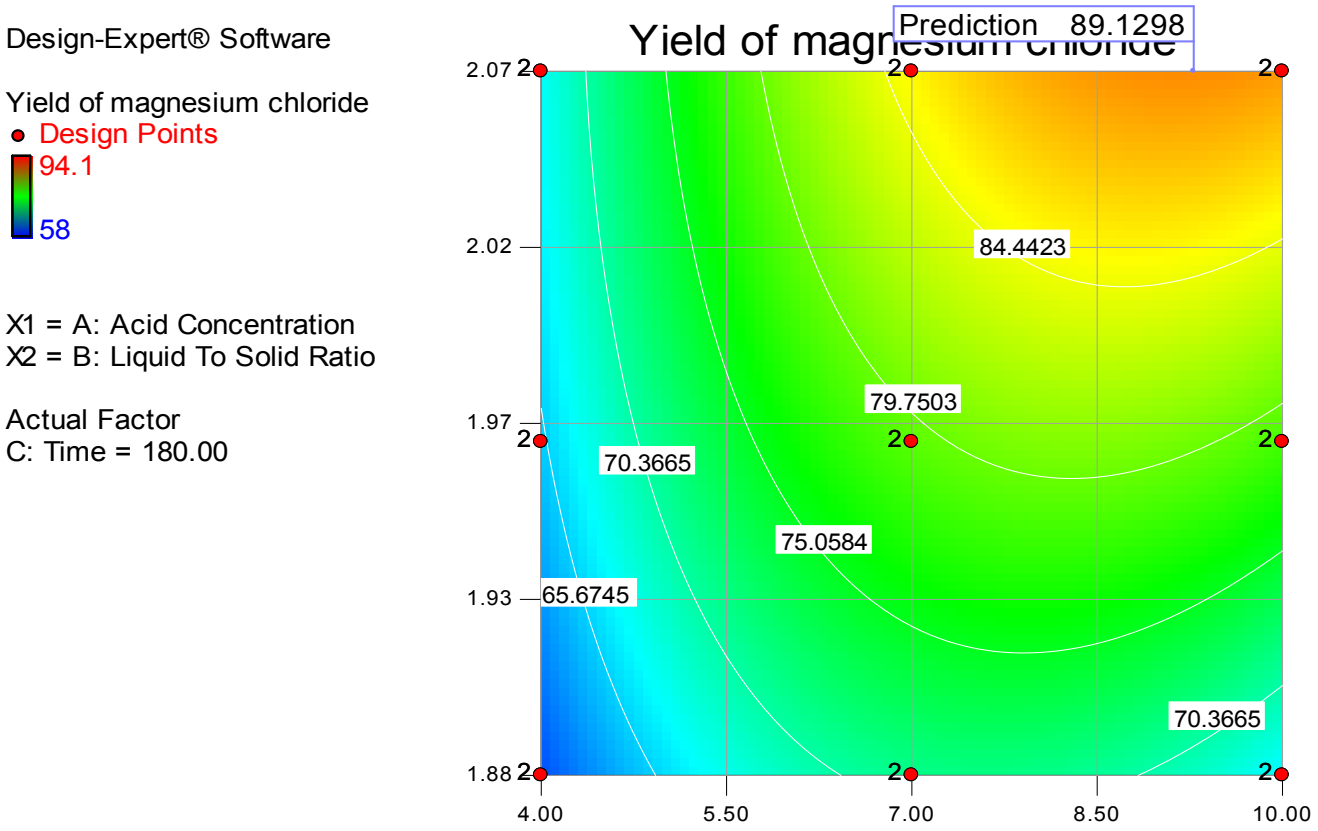


Fig. 4.8 experimental value versus predicted

As shown from fig.4.7 and 4.8, experimental value versus predicted using the optimization function in Design Expert software package, it was predicted that at conditions; 7M acid concentration, 2.07ml/g liquid to solid ratio and 180 min reaction time for dissolution of magnesium carbonate in HCl results in the optimum (maximum) percent of magnesium chloride which is 89.1348%. In order to verify this prediction, with experimental value, experiments were conducted and the result of 94.1% magnesium chloride was obtained which is approximately agree with the predicted value difference 0.049652. Therefore, it shows that, the maximum yield of magnesium chloride is obtained at higher reaction time (180 min), moderate acid concentration 7M and liquid to solid ratio (2.07ml/g) ratio. Similar results was reported by [6].

5. ECONOMIC EVALUATION

5.1. Material and Energy Balance

Material balances are fundamental to the control of processing, particularly in the control of yields of the products. The first material balances are determined in the exploratory stages of a new process, improved during pilot plant experiments when the process is being planned and tested, checked out when the plant is commissioned and then refined and maintained as a control instrument as production continues. When any changes occur in the process the material balances need to be determined again. The increasing cost of energy has caused the industries to examine means of reducing energy consumption in processing. Energy balances are used in the examination of the various stages of a process, over the whole process and even extending over the total production system from the raw material to the finished product. The energy balance determinations are also made to determine the energy requirements of the process, the heating, cooling and power required. In this plant operation it is thought that an energy balance (energy audit) on the plant will show the pattern of energy usage and suggest areas for conservation and savings. Material and energy balance for the production of magnesium chloride is carried out based up on the generated laboratory data and by considering the assumptions, that the plant has a capacity of 10000 ton per year and the plant will operates for 300 days in a year and 8 working hours per day with three shifts and six batch per day. To facilitate the calculations, the literature data, experimental data and Stoichiometry relation were used. Then the calculation was performed for each unit operations based on the assumptions and generated data. Batch reactor process was used for production of magnesium chloride and beaker was used as tank reactor for laboratory scale. A batch reactor (BR) is sometimes used for investigation of the kinetics of a chemical reaction in the laboratory, and also for larger scale (commercial) operations in which a number of different products are made by different reactions on an intermittent basis.

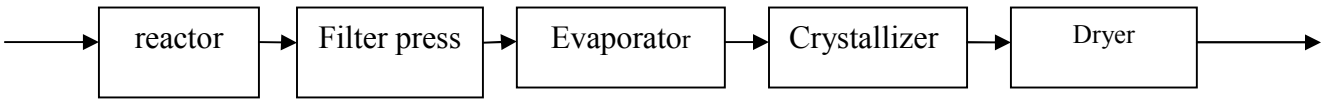


Fig 5.1. Process flow diagram for magnesium chloride production

5.1.1. Material balances

A). General mass balances

I) **The general mole balance equation**

The variable r_j shall represent the rate of formation of species j per unit volume

Alternatively phrased, r_A has units of moles per unit volume per unit time (i.e. concentration per time).

The rate of reaction is defined as $-r_A$ such that it is a positive number for a reactant being consumed

The rate equation is a function of the properties of the reacting materials and reaction conditions (not the type of reactor)

• The general mole balance is given as the following for species A:

$$F_{AO} - F_A + G_A = \frac{dN_A}{dt} \text{----------(5.1)}$$

Where, F_{AO} is the input molar flow rate, F_A is the output molar flow rate, G_A is the generation, and the differential term is the accumulation (all units moles/time)

Reaction

$$MgCO_3 + 2HCl \longrightarrow MgCl_{2\,(aq)} + H_2O + CO_2$$

$$A + 2B \longrightarrow C + D + E$$

Assumptions for batch reactor

Assumption 1. All reactants enter at the same time

Assumption 2. The system variables are uniform throughout the system volume, then the generation term is given by

$$G_A = r_A V \text{----------(5.2)}$$

Where V is the system volume

Assumption 3. No material has charged to the reactor and withdraw when the reaction is occurring ($F_{AO} = F_A = 0$), so the equation is reduced to,

$$\frac{dN_A}{dt} = \int r_A \, dV \text{----------(5.3)}$$

Assumption 4. Reaction mixture is perfectly mixed so that r_A is independent of the position ,

$$\frac{dN_A}{dt} = r_A V \text{----------(5.4)}$$

II) **Rate law**

The rate law is given as follows:

$$-r_A = k_A C_A \text{----------(5.5)}$$

III) **Stoichiometry**

In defining conversion, we choose one of the reactants as the basis of calculation and then relate the other species involved in the reaction to this basis.

In this case magnesium carbonate was selected as limiting reactant

Conversion (of substance A) is defined as:

$$X_A = \frac{\text{mass of A consumed}}{\text{mass of A feed}} \quad \text{or} \quad \frac{\text{moles of A reacted}}{\text{moles of A feed}} = \frac{N_{AO} - N_A}{N_{AO}} \text{--(5.6)}$$

The number of moles of A in the reactor after a conversion X_A has been achieved is

$$X_A = \frac{C_{AO} - C_A}{C_{AO}} = 1 - \frac{C_A V}{C_{AO} V_O} \text{----------(5.7)}$$

$$N_A = N_{A0}(1 - X_A) \text{----------(5.8)}$$

$$C_A = C_{AO}(1 - X_A) \text{----------(5.9)}$$

IV) **Combined equation**

By differentiating the above expression with respect to t and plugging into the expression for the batch reactor, (for a constant-volume batch reactor), $\frac{dC_A}{dt} = r_A$

$$-r_A = N_{AO}/v \int_0^x \frac{dX_A}{dt} = kC_{AO}(1 - X_A) = \frac{1 dN_A}{V dt} \text{--------(5.10)}$$

Determination of initial and final moles

From reaction between $MgCO_3$ (94.43%) and HCl (35%), the initial mass of 30 g magnesium carbonate reacted with 25.97 g of HCl.

If this ratio is represented by weight to volume ratio between solid(weight) and liquid (volume) the ratio is 20% w/v). 30 g of $MgCO_3$ reacted with 62.18 ml of HCl and the volume of the solution was 150 ml. to determine weight by volume relation 30 g is in the solution and for 100 ml let Yg then,

$Y = \frac{30\ g * 100\ ml}{150\ ml}$ = 20 g .Which means; 20% w/v

To determine the moles of $MgCO_3$ consumed and final present in the reaction (unreacted), unreacted mass of the sample must be determined first. From the components present in the product.

CaO	=	3.99 %
SiO_2	=	0.62 %
Al_2O_3	=	0.05 %
Sulphate	=	0.03 %
Total	=	4.69 %
Yield	=	94.1%

Unreacted sample $= 100\ \% - (4.69\% + 94.1\ \%) = 1.21\%$

1.21 % was unreacted magnesium carbonate. Therefore the initial, final and consumed moles of the sample can be determined as follows.

- Initial mole of magnesium carbonate to the reactor

30 g (94.43%) of magnesium carbonate fed to the reactor. Then,

30 g*94.43% = 28.32 g of magnesium carbonate initially feed to the reactor.

By dividing by 28.32 g for molecular mass of magnesium carbonate, initial mole was obtained.

$(mole)_{Initial} = \frac{30\ g * 0.9443}{84.314 \frac{g}{mol}}$ = 0.336 mole of magnesium carbonate.

- Final mole of magnesium carbonate(unreacted)

The final mole of magnesium carbonate can calculated from un reacted percent of magnesium carbonate by determining the mass of unreacted sample.

Unreacted percent of the final sample: 1.21

Final mole of magnesium carbonate = percent of unreacted *initial mass feed to the reactor

$(MgCO_3)_{Final,\ unreacted}$ = 0.0121*30 g*94.43 = 0.343 g. Therefore 0.344 g of magnesium carbonate was unreacted.

Unreacted mole $= \frac{0.344\ g}{84.314\ g/mol}$ = 0.0043 mole of magnesium carbonate.

- Consumed mole of magnesium carbonate

Consumed mole of magnesium carbonate can determined by subtracting final mole of magnesium carbonate unreacted from initial mole of magnesium carbonate feed to the reactor.

$(MgCO_3)_{Consumed}$ = 30 g (94.43%) - $(MgCO_3)_{Final,\ unreacted}$

= 30*94.43% -0.343 = 27.89 g consumed

$(\text{Mole})_{\text{Consumed}} = \frac{27.89\ \text{g}}{84.314\ \text{g/mol}} = 0.33$ mole

Rate of reaction and rate constant determination

From the above combined eq. (5.12) the rate of reaction is given by:

$$r_A = \frac{1dN_A}{Vdt} = \frac{dC_A}{dt} = \int_0^x \frac{dX_A}{dt} = kC_{AO}(1 - X_A)$$

From eq.(5.2) rate interms of A and B, $r_A = k\, C_A C_B$ ----------(5.11)

In each cases A and B reaction order is fist order according [8]. from eq.(5.11),

$C_A = C_{AO}(1 - X_A)$ and $C_B = C_{AO}(\Theta_B - X_A/2)$

Where, $\Theta_B = C_{BO}/C_{AO}$ then by inserting into the above equation for both C_A and C_B,

$$r_A = kC_{AO}(1 - X_A)C_{AO}(\Theta_B - X_A/2)\text{----------(5.12)}$$

But, $r_A = C_{AO}\int_0^x \frac{dX_A}{dt} = kC_{AO}(1 - X_A)C_{AO}(\Theta_B - X_A/2)$

By rearranging $\int_0^x \frac{dX_A}{(1-X_A)(\Theta_B - X_A)} = kC_{AO}dt$----------(5.13)

From Elements of Chemical Reaction engineering (Fogler) appendix A and [2].

$\int_0^x \frac{dX_A}{(1-X_A)(\Theta_B - X_A)} = \frac{\ln((\Theta_B - X_A/\Theta_B(1-X_A))}{(\Theta_B - 1)}$ ----------(5.14)

$$kC_{AO}dt = \int_0^x \frac{dX_A}{(1-X_A)(\Theta_B - X_A)} = \frac{\ln((\Theta_B - X_A/\Theta_B(1-X_A))}{(\Theta_B - 1)}\text{---------(5.15)}$$

To determine concentration of magnesium carbonate final present as unreacted, by dividing the number of moles of unreacted to the volume of the solution.

Concentration is given as:

Concentration, C_{Ai} = (numbe rof moles(N_{Ai}))/(Volume of the solution (L)) ----------(5.16)

Initial mole , N_{AO} = 0.336 mole

Volume of the solution = 150 ml = 0.015 L

concentration, C_{AO} from eq (5.13) = 2.24 mol/L

concentration, C_{BO} from eq(5.13) = 2.37 mol/L

conversion, X_A from eq (5.8) = 0.97.8 mol/mol (w/w)

change of time, Δt from experiment = 3h

Θ_B under eq (5.13) = 1.058

According to eq(5.16) rate constant and eq(5.14) rate of reaction values were calculated.

Rate constant, k = 0.1434 L/mol.h

Rate of reaction, $-r_A$ = 11.1 mol/Lh

a) Volume of the reactor

Assume the type of the reactor is cylindrical shape.

The volume of the reactor can be determined from relation between the rate of the reaction and volume of the reactor.

From eq(5.5) the rate is given by $r_A V = \frac{dN_A}{dt}$, the volume of the reactor is ,

$$V_r = \frac{dN_A}{r_A dt} \text{----------(5.16)}$$

Where, V_r is volume of the reactor.

Then from the calculated values of r_A and N_A and from eq(5.18), the volume of the reactor is, V_r = 7065 L

Let assume safety factor is 0.9 to protect over flow of the materials.

The volume of the reactor is V_r = 7850 L = 7.85 m^3

b) Diameter and Height of the tank determination

From relation $V_r = \frac{D^2 \pi H}{4}$, let H to D ratio is (H/D = 2.7, source: Perry's Chemical Engineering Seventh edition), then H = 2.7D the diameter is based on materials contained in the system (volume).

$V_r = \frac{1.5 * D^3 \pi}{4}$, and D = $\sqrt[3]{\frac{\pi * 4 * V_r}{1.5}}$ = 1.5 m

Height of the tank from relation H/D = 2.7, H = 2.7D = 4.05 m

B). Material Balance on some unit operations based the above information

By scale upping from laboratory to industry and from the above information's the following material balance was done on some unit operations

Based on the above assumptions and information based on general mole balance.

- General assumption for the proposed production capacity:
  - Production capacity = 10,000 ton/year.
  - Working days = 300d/year.
  - Working hours = 24h/day.

- Shift of operation per day = 3
- Six batch per day

The plant will start operation at 80% of its rated capacity in the first year. It will then build up its production capacity to 85%/ 90%, 95% and 100% in the next time respectively.

Because, the low production level at the initial stage is to develop substantial market outlets for the product. Machinery operators will also get enough time to develop the required skills and experience. 94% cannot be directly used as optimization number since the efficiency of production cannot achieve due to process loss, equipments faller and etc.

1. **Raw material**

Magnesite (magnesium carbonate) (solid lumps) $MgCO_3$ source from mining of magnesite

b. Hydrochloric acid(35%) solution in water(liquid state), by product of chloroalkali plant

2. **Process description**:-

a) Hydrochloric is charged into a acid proof brick lined tank.

b) magnesium carbonate is then charged slowly into the tank over certain time

c) the whole tank content is kept for reaction for 3 hrs till all the acid is consumed and reaction completed

d) the Ph of the reaction mass is adjusted to 7.5 to 8 using magnesium hydroxide

e) the reacted mass is then transferred the settling tank

f) the settled reaction solution is then siphoned into the other tank (collection tank)

g) the unreacted solid from settling tank is again recycled to the reaction tank

h) the clear reacted solution in the collection tank is then filtered through filter press for polishing the solution

i) the filtered magnesium chloride solution is then send to the evaporation vessel where the water evaporated and the solid magnesium chloride recovered and it is dried in the dryer

j) the magnesium chloride is then pulverized to the desired size and packed

3**. Pollution abatement**

Unreacted solids are recycled so there is no solid waste production. The reaction produce carbon dioxide which is scrubbed into the lime / ammonia solution so gases are taken care of and the product is non toxic.

4. Reaction

	1 $MgCO_3$ + 2HCl ⟶	$MgCl_2$ +	CO_2 +	H_2O
Molecur weight (g/mol)	84.314 36.5	95.21	44	18
Balanced	84.314 2*36.5	95.21	44	18
Purity (100%) for 1 ton	0.88 0.77	1		

Product of $MgCl_2$

Based on Stoichiometry relation, one mole of magnesium carbonate reacted with two moles of hydrochloric acid to produce one mole of magnesium chloride. And 31.77g of $MgCO_3$ (94.43%) reacted with 71.43 g HCl (35%), volume to weight ratio, 2.07 ml/g or 20% w/v to produce theoretically 33.92 g of $MgCl_2$. But, actually 31.87 g was produced. By scale upping if the production capacity will be 10000 ton per year, the need of raw materials shown below.

a) Magnesium Carbonate

Molecular weight of 100% pure magnesium carbonate = 84g/mol

For 94.4% MgCO3 = 84/0.944 = 89 g/mol

$MgCO_3$ required to produce 10000 tonne of magnesium chloride(Mw = 95g/mol) annually,

$MgCO_3$ = (10000*89g/mol)/95g/mol = 9368.4 tonne required annually.

b) Hydrochloric acid

Molecular weight of 100% pure hydrochloric acid = 2*36.5g/mol 73g/mol (2 from chemical reaction above).

For HCl (35%) = 208.57g/mol

HCl required for 10000 magnesium chloride annual production,

amount of HCl = (10000 tonne *208.57g/mol)/95g/mol = 21954.7 tonne annually.

Based on molar ratio /stiochiometric relation the following table shows raw materials required and product.

Table 5.1 amounts of material required and produced per batch, day and year

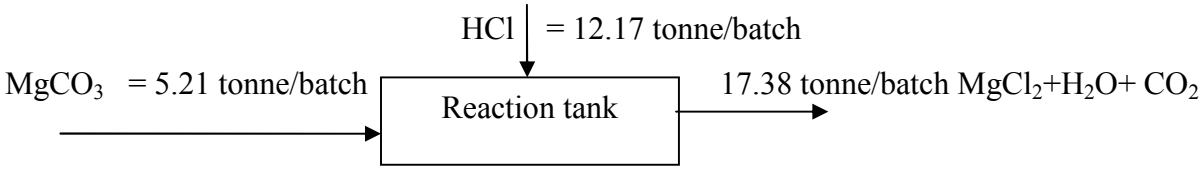
Materials	Units	Annual capacity	Per day	Per batch
$MgCO_3$ (94.4%)	Tonne	9368.4	31.26	5.21
HCl (35%)	Tonne	21954.7	73.02	12.17

1. Reaction stage:-

For optimum magnesium chloride yield magnesium carbonate to hydrochloric acid 1:2 mole or 2.07 ml/g ratio for1 mole of magnesium chloride 4.92 ton/batch magnesium carbonate and 4.26 ton/batch hydrochloric acid is used

$MgCO_3$:- 0.9443*5.21 ton/batch = 4.92 tonne/batch , pure $MgCO_3$

HCl:- 12.17*0.35= 4.26 ton/batch, pure HCl



Amount of water = 2.156 tonne

Amount of Corbondioxide =2.75 tonne

Amount of water Mass of Corbondioxide and water based on stochiometetry and material balance.

To determine mass of Corbondioxide:-

$(5.56 \text{ tonne } MgCl_2)/(95{,}21 \text{ g/mol } MgCl_2) = (Y \text{ tonne})/(44 \text{g/mol})$

$Y = (5.56 \text{ tonne } MgCl_2)/(95{,}21 \text{ g/mol } MgCl_2) * 44 \text{ g/mol}$

$Y = 2.75$ tonne of CO_2

Based on laboratory result, unreacted and consumed magnesium carbonate was determined under filter press.

2. **Collector tank stage**

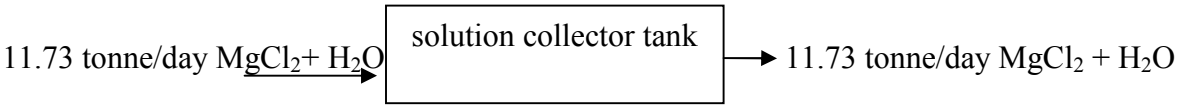
After material reacted together with each other, the product must be collected to another tank for the next unit operation. The collector tank collect the product and material transferred to filter press. No reaction is carried out in collector tank it is used as storage of material.

The reaction produce carbon dioxide which is scrubbed into the lime / ammonia solution at reaction stage so gas doesn't exist for the next stage.

$MgCl_2 + H_2O$ = 9.18 tonne per day -2.57 tonne CO_2 = 6.61 tonne/batch ($MgCl_2 + H_2O$)

Corbondioxide can be removed(scrubbed) as mentioned under process description

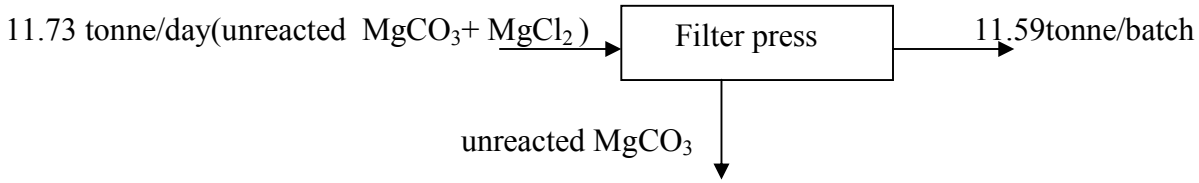
The same procedure was applied for magnesium carbonate and HCl.



3. **Filtration Stage (Filter press)**

The separation of solids from a suspension in a liquid by means of a porous medium or screen which retains the solids and allows the liquid to pass is termed filtration. In general, the pores of the medium are larger than the particles which are to be removed, and the filter works efficiently only after an initial deposit has been trapped in the medium. In the laboratory, filtration is often carried out using a form of Buchner funnel, and the liquid is sucked through the thin layer of particles using a source of vacuum. In even simpler cases the suspension is poured into a conical funnel fitted with a filter paper. In the industrial equivalent, difficulties are encountered in the mechanical handling of much larger quantities of suspension and solids. A thicker layer of solids has to form , in order to achieve a high rate of passage of liquid through the solids and in order to achieve a high rate of passage of liquid through the solids, higher pressures are needed, and a far greater area has to be provided. The most suitable filter for any given operation is the one which will fulfill the requirements at minimum overall cost. Based on this reality filter press is selected compared to the others.

According to laboratory result, 1.21% of total material after the reaction was remain as residue (unreacted solid + some impurities) using the filter paper. Therefore it can apply for filter press system.



unreacted $MgCO_3$ = 01.21% total material feed to the filter

= 11.73*1.21/100 = 0.14 tonne/batch

consumed magnesium carbonate is given as:

= (initial amount to feed the reactor − unreacted magnesium carbonate)

$$= 4.92 - 0.14 = 4.84 \frac{\text{tonne}}{\text{batch}}$$

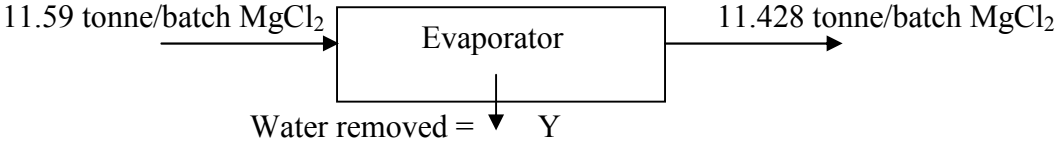
From5.21 (94.43%) of magnesium carbonate 4.84 tonne was consumed.

The residue can be recycled from filter press again to the reaction tank to the reaction tank to maximize the yield of product to complete the reaction based on recycled material and its profitability.

4. **Evaporation stage**

After the filtration process is carried out the solution is transferred to the evaporation stage to remove unwanted amount of water from the solution. But completely evaporation can be remove all the water and therefore care must be taken. Because complete evaporation reduce percentage of required and crystallization can proceed after evaporation. Evaporation can be used for aqua's of magnesium chloride and crystallization can used to produce solid with crystal of water.

Based on laboratory works from the magnesium chloride about 16.2% (w/w) of water was removed in the evaporator as evaporator disk plate heated used as evaporator. The target to concentrate magnesium chloride in the solution to 46 % w/w



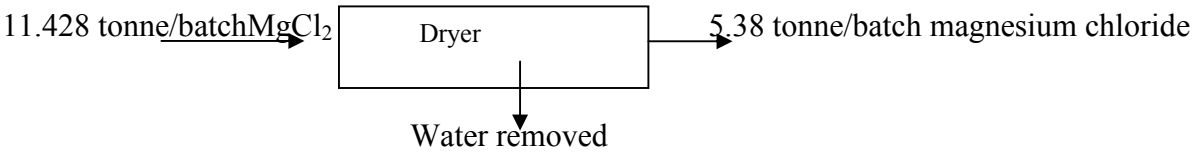
Percentage of water removed = (11.59 - 11.428)/(11.59)*1 = 16.2%

To change from percent to ton, Y =16.2% *11.59 tonne= 1.84 tonne

Therefore from total 6.53 tonne of material, 16.2% of water was removed which was agreed with lab.

5. **Dryer stage**

The next stage to evaporation to obtain desired dry solid in dryer from evaporation stage clear liquid solution can be obtained but for transportation in solid form is also advantages. In the dryer (oven as dryer) about 52.9 % (w/w) is removed as water and from the sample and according to laboratory checked 44.1% (w/w) of magnesium chloride was obtained.



mass of $MgCl_2$ hydrate (before heating) = 11.428 tonne

mass of salt (after heating) = 5.38 tonne

mass lost (water of hydration) 6.1 tonne

moles of $MgCl_2$ = 5.38*1000 Kg/(95.2Kg/Kmol) = 56.51 Kmol

moles of H_2O = 6.1 *1000 Kg/(18Kg/Kmol) = 338.9Kmol

$$\frac{\text{Moles } HO_2}{\text{Moles } MgCl_2} = \frac{338.9\text{Kmol}}{56.51\ \text{Kmol}} = 5.99997 \sim 6$$

There are 6 moles of water for each mole of $MgCl_2$. Therefore the formula for the hydrate is $MgCl_2.6H_2O$

5.1.2. Energy balance

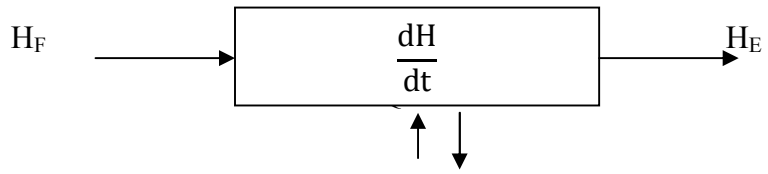
In certain circumstances, it may be desirable to maintain nearly isothermal conditions, even if the reaction is significantly exothermic or endothermic. In the absence of any attempt to control T, it may become too high for product stability or too low for reaction rate. If control of T is required, a cooling or heating coil or jacket can be added to the reactor to balance the energy generated or consumed by the reaction. The reaction temperature (T,) was adjusted to control the rate of heat transfer ($\dot{Q}$) and reaction to achieve (nearly) isothermal conditions'

For producing an optimum amount of magnesium chloride yield the temperature inside the reactor should be maintained at70^0C. This temperature is used to be achieve the maximum rate of reaction. so that the temperature inside the reactor was adjusted to the required (70^0C) value after charging the needed magnesium carbonate and hydrochloric acid at reference temperature. The reference (surrounding) temperature (25^0C).

The statement of conservation of energy of the system takes the form,

{Rate of accumulation of energy} = {rate of energy In} - {rate of energy Out} + {rate of energy generation} -------(5.17)

For any open model system



Using the above diagram the energy balance for the above model open system is

$$H_F - H_E + Q = \frac{dH}{dt} \quad \text{---------- ----------} \quad (5.18)$$

Where

H_F – inflow of enthalpy

H_E – outflow of enthalpy

Q – rate of heat supply from the surrounding or withdrawn from the system

$$Q = UA(T_S - T) \text{ ----------(5.19)}$$

dH – Change of enthalpy

Substituting for Q into the above equation, the model equation be comes,

$$H_F - H_E + UA(T_S - T) = \frac{dH}{dt} \text{ ----------(5.20)}$$

where

U-Overall heat transfer coefficient

T_S-Surrounding (cooling, heating) temperature

A- Effective area for heat transfer

T- The temperature of the reaction mixture

In a batch process ,t he enthalpy change should be expressed into two elements:

1) The enthalpy change with time due to the change in composition. In another word, the energy change due to the heat of the reaction

$$\Delta H_R(rV)dt \text{ ----------(5.21)}$$

2) The enthalpy change due to the change of temperature

$$m_T C_P dT \text{ ----------(5.22)}$$

hence

$$dH = m_T C_P dT + \Delta H_R(rV)dt \text{ ----------(5.23)}$$

Where : m_T is the total mass of the reaction mixture; C_P is the specific heat for the composition of the mixture.

The system or process that was applied for magnesium chloride production/reaction of magnesium carbonate with HCl was batch reaction process. Therefore in a batch process, there is no in- and out-flow of materials during the reaction , then the energy balance equation yields

$$m_T C_P \frac{dT}{dt} = \Delta H_R(-r_A V) + UA(T_S - T) \text{ ---------- (5.24)}$$

Equation (5.29) is the general form of equation used for batch reaction process and which applies for magnesium chloride production.

The relationship between $\dot{Q}$ and X_A can be determined by combining the material and energy balances equations.

In the energy balance, for isothermal operation of the reaction for eq(5.2) and eq (5.29), $\frac{dT}{dt} = 0$, so that equation (5.29) becomes, for the required rate of heat transfer:

$$\dot{Q} = UA(T_S - T), = (-\Delta H)(-r_A)V \text{ (isothermal operation) -------(5.25)}$$

From the material balance in terms of X_A, equation 5.12 becomes

$$-r_A = = \frac{N_{AO}dX}{Vdt}$$

Eliminating $(-r_A)$ from equation (5.30) with equation (5.12) we have

$$\dot{Q} = UA(T_S - T) = (\Delta H_r)N_{AO}(\frac{dX}{dt})\text{----------(5.26)}$$

Where,T and T_S are reaction temperature and surrounding temperature respectively.

As discussed in under moles (material balance) and at the introduction of energy balance assumptions for batch reaction based on the literature, isothermal reactor was used.

Therefore for isothermal reaction the left term on the eq (5.29) is reduced to zero. Because the temperature was adjusted to 70^0C.

1) Reactor

Assumptions

Phases : liquid- solid

Operating model : batch

Reactor type : cylindrical glass bricks, to protect reaction of HCl with metal reactor.

Flow type : agitated (stir)

Calculation Procedures

1^{first} .the reaction volume,V_r was calculated from eq(5.18) under material balance

V_r = 7065 L

2^{nd} . the reactor volume,V_R was determined using relation V_R = f(V_r) the reactor volume is greater than the reaction volume because of an allowance for headspace (safety factor = 0.9) .

V_R = 7085 L

3^{third}. Determination of diameter of the reactor based on reactor volume

From relation $V_R = \pi r^2 H = \frac{\pi D^2 H}{4}$ ----------(5.27)

where H is height of reactor

Assume that H to D ratio is (H/D = 2.7)), Bayrak et al, Ozdemir et al.Then H = 2.7D the diameter is based on materials contained in the system (volume)

$V_R = \frac{2.7\pi D^3}{4}$ and $D = \sqrt[3]{\frac{4VR}{2.7*3.14}}$ = 1.495 m ~ 1.5 m

4^{th}. Height of the reactor determination

From relation under eq(5.30) volume and diameter of reactor, the height of the reactor can be determined.

From relation diameter to height ratio or $V_R = \frac{\pi D^2 H}{4}$,

$H = \frac{4VR}{\pi * D^2}$ and H = 4.001 m ~ 4.0 m

5th . after calculating the reactor volume determination of heat transfer surface area (A).

From relation $V_R = \pi r^2 H = \frac{\pi D^2 H}{4}$, as assumed in the introduction the reactor is cylindrical type.

$$\pi r^2 = \frac{\pi D^2}{4} = A\ (m^2)$$ ----------(5.28)

From eq(5.32), heat transfer surface area A = 1.88 m^2

6th. determination of heat transfer rate due to heat supply from the surrounding or withdrawn from the system($\dot{Q}$) from eq (5.30)

$\dot{Q} = UA(T_S - T), = (-\Delta H)(-r_A)V$, cause the system is isothermal as mentioned at the beginning.

Rate of reaction from eq (5.16), volume of reactor from eq(5.18) and heat of reaction from eq (3.5 and 4.11)

Rate of reaction, r_A = 11.1mol/Lh

Volume of reactor,V_R = 7.085 m^3

Heat of reaction, ΔH = -50.4kJ/mol calculated from standard heat of reaction.

$$Q = \frac{50.4\ kJ}{mol} * \frac{11.1\ mol}{h\ L} * 7085\ L = \frac{3963632.4\ kJ}{1h} * \frac{1\ h}{3600\ s} = 110.10\ kJ/s$$

= -110.10 kW (exothermic reaction)

The overall heat transfer coefficient can be determined from eq (5.30)

$Q = UA(T_S - T)$ where T_S and T are surrounding and reaction temperature respectively.

$U = \frac{Q}{A(T_S - T)}$, ($T_S = 25^0C$) and U =13.04 kW/m^2 ^{0}C

5th. determination power (P) required for the mixer

Mixer power = P*V_r, p= f(application)----------(5.29)

Where, V_r is volume of the reaction and P for reaction with heat transfer the power, P vary from 1.5 to 5hp/1000gal, the average is 3.25hp/1000gal(640w/m^3), (source Ref.16).

To determine the power required by the mixer, the volume of the reaction is required and calculated from eq (5.18)

Mixer power = P*V_r, p $\frac{3.25\ hp}{1000\ gal} * 1846.96\ gal$ = 6.00 hp

$= 6.00 \text{ hp} * \frac{0.745 \text{ kW}}{1 \text{hp}} = 4.47 \text{ kW}$ is required.

2) **Filtration unit**

The solution is filtrated on a by filtration process By creating a vacuum under the belt, liquid is separated from the solid crystals. From the collector system, two liquid -solid mixtures are being produced.. The solid liquid mixture has to be separated into a solid and a liquid. This can easily be done by filtration. However, some mother liquor is bonded to the solid crystals, causing contaminations in the products. In this case washing of the crystals solid can the influence on the product purity.

The solution entered the belt filter at room temperature . The belt filter is an open system, which is in direct contact with the surrounding air at approximately 20°C. This high temper- ture is sucked through the layer by the vacuum pump causing lots of heat transfer. The mixed solution with the impurity was separated and the impurity was left on the filter, depending on the amount of solid present.

From the left of the belt filter, By filtration of this solution 1.21% was unreacted magnesium carbonate appeared to be solid.

3) **Evaporation unit**

After the filtration process is carried out the solution is transferred to the evaporation stage to remove unwanted amount of water from the solution to obtain clear solution.

Boilers built in a central thermal in the caustic soda processing plant in Zeway is available to supply the steam required to concentrate the solution.

Assumptions and data [2].

The solution containing 6.53 ton of $MgCl_2 + H_2O$ is sent to the evaporator .In evaporator temp around 150 to 155 ^{0}C & pressure 2.1 kg/cm^2 is maintained.

source: caustic soda plant feasibility study) and the others from lab. Results and literatures

(T_{Steam} = 150 ^{0}C and $C_{ondensate}$ = 79^{0}C), Datum = 273 K

Steam is available at temperature = 150^{0}C

From steam table @ which the steam temperature (T =150^{0}C)

The total enthalpy = 2558.6 kJ/kg

Evaporation takes place at maintained pressure = 21.1 kN/m^2.

The feed to the evaporator is at T_F = 294K

The condensate leaves the heating space T =352.7 K.

The overall coefficient of heat transfer is 3 kW/m^2 deg K,

The feed to the evaporator is at 294 K and the condensate leaves the heating space at 352.7K.

Assuming that the steam is saturated at 150^0C, then from the Steam Tables in the

Appendix F, at which the total enthalpy = 2558.6 kJ/kg.

At 21. kN/m^2, water boils at 335 K and, in the absence of data on the boiling point elevation, this will be taken as the temperature of evaporation, assuming an aqueous solution.

The total enthalpy of steam at 335 K is 2459 kJ/kg.

Water =4.18kJ/Kg ^{0}C =

Magnesium chloride = 75.3 ca/mol.^{0}C*4.2 J/1cal *1Kmol/95.21Kg = 3.32 KJ/^{0}CsKg

Specific heat capacity of the solution can be determined from heat of the reaction mixtures.

From 4.18kJ/Kg^{0}C*0.16 + 3.32 kJ/Kg^{0}C *0.84 = 3.46kJ/ Kg ^{0}C

Thus the feed, containing 6.53 tonne of the solution to be heated from 294 to 335 K) at which the temperature of evaporation takes place.

The water to be b evaporated = 16.2% from laboratory result

Feed = 6.53 tonne/batch = 0.60 Kg/s

Product = 5.49 tonne /batch = 0.51 Kg/s

Evaporation = 16.2 % * 6.53 = 1.04 tonne/batch = 0.096 Kg/s

Using a datum of 273 K:

Heat entering with the feed = (0.6Kg/s*3.97 kJ/^{0}C)(294 − 273)^{0}C = 115.02 kW

Heat leaving with the product = (0.51 *3.46)(335 − 273)^{0}C = 109.4 kW

Heat leaving with the evaporated water = (0.096 *2459)^{0}C = 249.02 kW

Thus:

Heat transferred from the steam = (249.02 + 109.4) − 115.02 = 246.06Kw

The enthalpy of the condensed steam leaving at 352.7 K = 4.18(352.7 − 273) = 333.2 kJ/kg

The heat transferred from 1 kg steam = (2558 − 333.2) = 225.8 kJ/kg

and hence: Steam required = (246.35/225.8) = 1.16 kg/s

As the preheating of the solution and the sub-cooling of the condensate represent but a small proportion of the heat load, the temperature driving force may be taken as the difference between the temperatures of the condensing steam and the evaporating water, or:

$$\Delta T = (423 - 335) = 78 \text{ deg K}$$

To determine the heat transfer surface area(A), of the evaporator, the above information can be used.

Thus heat transfer area for the evaporator= Q/(U* ΔT)----------5.30

Heat transfer area, A = 246.35/(3*78) = 1.5m^2

Minimum heat transfer surface area, result minimum cost of the materials.

4) Energy balance for dryer

Dryer is used to remove water or moisture from material feed to the dryer to make a solid

The drying of materials is often the final operation in a manufacturing process, carried out immediately prior to packaging or dispatch. Drying refers to the final removal of water, or another solute, and the operation often follows evaporation, filtration, . In some cases, drying is an essential part of the manufacturing process.

Assuming from liquid to solid drying is carried out for the following reasons:

(a) To reduce the cost of transport.

(b) To make a material more suitable for handling

(c) To provide definite properties, such as, for example, maintaining the free-flowing nature of salt.

(d) To remove moisture which may otherwise lead to corrosion.

The dryer was used to dry the sample by 105^{0}C from 20 ^{0}C

ΔT temperature difference between T- T_S

T = temperature of the dryer (^{0}C)

Ts = surrounding temperature (^{0}C)

Where m =mass of the sample (g)

Cp = specific heat of the sample (kJ/g^{0}C)

From material balance material feed to the dryer = 5.49 ton

Water removed from material = 2.1% feed or 0.113 ton

The rate of energy required is given as follows:

Q = m Cp ΔT = [(5490 Kg*75.3 cal/mol ^{0}C*4.2 J/1cal* 1Kmol/95.21Kg] *(105-21)^{0}C

=152454 KJ/batch = 50818KJ/h.

Therefore the energy required for one batch of the product was as calculated for the dryer.

5.2. Cost Analysis

Cost estimation is a specialized subject and a profession in its own right. The design engineer, however, needs to be able to make quick, rough, cost estimates to decide between alternative designs and for project evaluation. Chemical plants are built to make a profit, and an estimate of the investment required and the cost of production are needed before the profitability of a project can be assessed.

The cost of the purchased equipment is used as the basis of the factorial method of cost estimation and must be determined as accurately as possible. It should preferably be based on recent prices paid for similar equipment.

The evaluation determines whether one should undertake the project, abandon it, continue with it (but with further research) or take it to the pilot plant stage. The economic evaluation used to determine if the project is economically and financially feasible or not. A project economically feasible when it is more profitable than other competing project, and financially feasible when management can raise the capital for its implementation.

Assumption

Calculating mass and energy flows

Determining the size of some unit operations

Estimating the production cost

Forecast the product sales price

Estimating profitability and etc.

The ultimate purpose for developing such a detailed process design and cost estimate is to determine the economics of production

Preliminary Equipment Design

Following completion of the mass and energy balances, preliminary equipment designs can be undertaken.

a) Storage tank for hydrochloric acid

The storage tank selected for HCl is bricks lined tank because HCl can react with reactor made from metals. Therefore to protect this problem bricks lined tank is used.

Storage tanks are sized depended on daily requirement; they can store and the assumption that the plant works for 3 shifts and 8 hour with 5% safety factor for the volume. For the tank it should be given 30 days allowance for storage and 80%for design safety.

Amount of HCl = 1day*18hr/24hr*12.2tonne/day=9.15 tonne/*1000 kg/tonne =9150kg

Volume of tank = 9150kg /1180 kg/m^3 =7.7m^3 and for the 5% safety factor;

Volume of tank=7.75m^3+0.05*7.75m^3= 8.1 m^3/day*30day = 243.9 m^3 for 30 days

b) Volume of the reactor

The volume of the reactor was calculated from eq. (5.18) under material and energy balance.

It was 7.85m for batch based on the raw materials feed to the reactor

Volume of reaction(V_r) = 7.085 m^3

Volume of reactor(V_R) =7.87 m^3

c) Collector tank of the solution

The collector tank can be used to store the solution comes from the reaction and to store material for the next filtration.

Filtration can be carried out by taking the stored solution from the collector tank.

Amount of materials or solution to the collector tank = 6.61 tonne*1000Kg/tonne = 6610Kg/batch*3 h/batch= 19830Kg

Volume of tank = 19830kg /1489 kg/m^3 = 13.32m^3 and for the 10% safety factor;

Volume of tank=13.32m^3+0.1*16.24m^3= 14.65 m^3 for one day

d). Filtration equipment

For laboratory the filter paper as filter press and conical flask were used as storage

Volume of conical flask = 250 ml = 1/3*3.14*r^2*h

Diameter of filter paper 90 mm

Time of filtration = 10 min 600s

Material feed to the filter = 6610 Kg/batch

Density of the mixture = 1504Kg/m^3

Volume the solution =total mass per density of mixture

V= 6610 Kg/1504Kg/m^3 =4.4 m^3

To determine volume of the filter press assume head allowance 5%and The volume of filter press can be determined as follows:

$V_{filter.p}$ =4.4m^3 +0.05*4.4m^3 =4.62m^3

Area of the filter press

From relation area, $= A = \pi r^2$ and diameter of the filter 0.9m, radius of the filter r,

R=d/2 =0.45 , Area, $A = \pi r^2$ =2.1m^2

e) Storage tank for the solution after filtration

Mass of the solution after filtration = 6530 Kg and density of the solution 1500 Kg/m^3

volume of the storage tank = mass/ density =4.34 m^3

$$= \frac{4.34m^3}{1\ batch=3h)} * \frac{6\ batch\ (1day)}{1day} = 26.04m^3$$

f) Evaporator

Material stored in the storage tank can be transferred to the evaporator

Material to the evaporator = 6530 Kg

Assume the volume of evaporator the same as storage tank, but assume safety facto or head allowance 6% .

$(evaporator)_{Volume} = 4.34m^3 + 0.06 * 4.34m^3 = 4.6m^3$

Assume from material and energy balance cylindrical type and the surface area of the evaporator is $V = Ah = \pi r^2 h$ and let height of the evaporator ~ 3.0 m then

Diameter of the evaporator, D = 1.3 m , Surface area of the evaporator, A = 1.5m^2

h) Dryer

Assumption used under material and energy balance can used to determine the area of the dryer or heater. From standard the surface area of the tray dryer is from 0. 3 to1m^2 therefore let's take the average area of the range. Surface area, A =0.65m^2

i) Storage tank for the product

Assume the tank with fixed coned roofs. Because the materials stored will not be harmed by water, weather, or atmospheric pollution

The volume of the fixed cone tank is given by Perrys Chemical Engineering Hand Book seven edition. volume of fixed cone tank storage is $V = 0.215H^2(3R-H),(H/D= 6\ -10)$

Where ,V is volume of the tank, H is height of the tank and R is radius of the tank

The total capacity f the plant per year will be 10000 tonne.

The total storage tank volume= 10000 tonne*1000Kg/tonne by density magnesium chloride

$V = 10^7/Kg1560Kg/m^3 = 640\ m^3$ volume of the material.

5.3. Estimation of Total Capital Investment

a) Purchased Equipment Cost estimation

Purchased cost for some basic plant equipments are estimated from the empirical relations www.mhhe.com/engcs/chemical/peters/data/ce.html and www.Matche/Equipcost/index.com.

Materials of construction were based on glass lined for HCl and reactor, and for the others based on carbon steel except for dryer stainless.

Table 5.2 Estimation of purchased equipments cost

Equipments	Amounts	Capacity or size	Unit cost ($)	Total Cost ($)
Process equipments				
Reactor	1	1847 gal	65000	65000
Grinding mill	1	0.46Kg/s	98435	98435
Filter	1	2.1 m^2	26800	26800
Pump	5	0.1m	7400	37000
Evaporator	1	15 m^2	8481	8481
Heater	1	0.68	9400	9400
Dryer	1	1.85 m^2	9900	9900
Conveyer	3	-	600.0	1800
Storage tanks				
HC l storage	1	4498 gal	51500	51500
Solution storage	1	1145 gal	10900	10900
Collector tank	1	3430 gal	19000	19000
Product storage	1	56376 gal	78000	78000
Transportation cost = 10% Total cost				40730.6
Total				407306
Total in($)				448036.6
Total in ETB				8960732

Source **:**www.mhhe.com/engcs/chemical/peters/data/ce.html and www.matche.com

b) Estimation of Fixed Capital Investment

Direct and Indirect cost: both the direct and indirect cost the plant determination is based the ratio solid-fluid processing plant for individual components. Because in the production of magnesium chloride both solid-liquid process exist. These both cost estimation is performed according to Peters & Timmerhaus (1991) as shown in table 5.3.

Table 5.3 Estimation of Fixed Capital Investment

	Components	Factors	Cost in Birr
1. Direct cost	Purchase equipment cost(PEC)	PEC	8960732
	Equipment erection	0.25PEC	2201488.93
	Instrument and control	0.25 PEC	2201488.93
	Electricity	0.2 PEC	1761191.144
	Piping, installation	0.1PEC	896073.2
	Building	0.2PEC	1761191.144
	Total Direct Cost		17611911.44
2. Indirect cost	Contractors fee	0.06DC	1056714.6864
	Engineering and supervision	0.05DC	880595.572
	Contingency	0.05 FCI	1028906.4
	Total Indirect Cost		18640817.84
3.Fixed Capital Investment	FCI =Direct Cost +Indirect Cost		20578128.1
4.Working Capital (WC)		0.15TCI	3086719.215
5.Total Capital Investment		FCI+WC	23664847.315

The total capital investment for the production of magnesium chloride is estimated by summing up the fixed capital investment (FCI) and working capital. The working capital is taken as 15% of the total capital investment (0.15TCI) which is commonly used (Peters & Timmerhaus, 1991). and the table 5.3 was filled based on this relation

FCI = 19549221.69+ Contingency, Contingency= 0.05FIC

= 19549221.69birr +0.05FIC

FCI-0.05FIC = 19549221.69Birr

=0.95FCI =19549221.69Birr

FCI = 19549221.69/0.95 = 20578128.1Birr

Contingency= 0.05FIC = 1028906.4Birr

WC = 0.15TCI = 3086719.215Birr

FCI+WC= 23664847.315Birr.Based on this relations the above table was filled.

5.3.1. Estimation of Total Production Cost

The total production costs for the production of magnesium chloride are estimated by summing up the manufacturing cost and general expenses. The Manufacturing costs can be calculated by

adding direct production cost, fixed charge and plant overhead cost and the General expenses also calculated by summing up the distribution and administration expenses, research and development etc.

Raw materials: The cost of each raw material per year is estimated by multiplying the raw material required per day by 300 working days per year and 24 working hours per day, and then multiplying by raw material unit price..

Raw Materials Cost

a) $MgCO_3$

- Unit cost of magnesium carbonate =250 Birr/ton,
- Unit cost of transportation = 2 Birr/ Km

Source: Feasibility study for Rehabilitation and renovation caustic soda share company.

Annually 9386 tonne*250 Birr/ton =2346500 Birr

- Transportation cost

Distance = 600Km

Total cost =annual quantity(tonne) *distance(Km) *Birr/Km

= 9368.4tonne* 600Km*2 Birr/Km= 11241600 Birr

Total cost of magnesium carbonate = annual cost + transportation cost=1358800 Birr/Year

b) HCl

Unit cost (Birr/ton) = 9,213 Birr/ton

From 10000 tonne of Caustic soda annually, 6803.18 tonne HCl (100%) or HCl(35%) 19437.65 tonne produced for 21079.09 tonne of Magnesium chloride production. Therefore for annual capacity of 10000 tonne of magnesium chloride, HCl (100%) 3227.45tonne and HCl (35%) 9221.29 tonne required.

Annual cost of HCl = 9221.29 tonne*9,213 Birr/ton = 8495073 Birr

Total cost of raw materials = 1358800 Birr +8495073 Birr = 9854173 Birr.

Table 5.6: Estimation of total production cost

	Components	Factors	Cost (Birr)
1.Manufacturing cost	A. Direct production cost		
	Raw material cost	Calculated	9854173
	Operating labor	15%TPC	5724461.08
	Direct supervision	15%TPC	5724461.08
	Utilities	10%TPC	3816307.39
	Maintenance and repair	10%FCI	2057812.81
	Laboratory charges	15%TPC	5724461.8
	Direct production cost		121588677.16
	B. Fixed charges		
	Depreciation	10%FCI	2057812.1
	Capital charge	1%FCI	205781.28
	Insurance	0.4%FCI	823125.12
	Total		3086719.22
	C. Plant over head	20%TPC	4115625.62
	A+B+C		128791021.99
2.Generaexpenses	Administration	6%TPC	2289784.4358
	R and D	3%TPC	1144892.2179
	Distribution and sell cost	5%TPC	1908153.6965

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

=98541173+89%TPC+21.4%FCI

= 98541173+89%TPC + 20.4%*20578128.1

=4197938.1324 +89%TPC

TPC-0.89TPC = 4197938.1324Birr

TPC = 5891516.3Birr/0.16 =38163073.93Birr

The above table 5.3was filled based on TPC after TPC was calculated

5.4. Profitability Measurements

The basic aim of a profitability analysis is to give a measure of the attractiveness of the project for comparison to other possible courses of action.

a**. Net income** (total income per year)

Current price of magnesium chloride imported = 7,819 Birr/ton (Source: Ethiopian Revenue and Custom Authority).

By assuming, based on feasibility study for Rehabilitation and renovation caustic soda share company, Selling price of magnesium chloride = 7,446Birr/ton

Annual revenue = annual production rate * selling price

= 10000 tonne/year *7,446Birr/ton

= 74460000Birr/ year

Total production cost = 38163073.93Birr/year

Gross annual profit = Annual revenue- Total production cost

Gross annual profit = 74460000Birr/ year -38163073.93Birr/year

= 36296926.07Birr/year

Assume income tax on gross profit =30%

= 36296926.07Birr*0.3

= 10889077.821 Birr

Net income = Gross annual profit-income tax

= 36296926.07Birr -10889077.821 Birr

= 25407848.249 Birr

b. Percent of Profit

percent of profit = net income/TPC*100%

=(25407848.249 Birr/ 38163073.93Birr)*100% =66.6%

c. Cash flow

Assumption it was assumed the plant would cease production after seven years of operation and at that time. The working capital would be sold at its estimated value and the plant equipment would have no salvage value and money was borrowed. The discounted rate of return or DCFR of the project and values at individual years, considering the plant capacity starting with 80% capacity at the first year, 85% capacity in the second year 90% third year and with 100% capacity starting from halve of three years project life.

Table 5.7: Projected cash flow of the plant value "000 Birr"

Year	0	1	2	3	4	5	6	7
Capacity utilization	-	80	85	90	100	100	100	100
I. Cash inflow	-	20326.2	21596.6	22867.0	25407	25407	25407	25407
Income birr	-	20326.2	21596.6	22867.0	25407	25407	25407	25407
Salvage value	-	-	-	-	-	-	-	-
II. Cash out flow	23664.8	8156.38	17042.1	18044.6	20049	20049	20049	20049
Investment	23664.8	-	-	-	-	-	-	-
Utilities	-	3053.04	3243.9	3434.67	3816.3	3816.3	3816.3	3816.3
RM and others		7883.28	8375.98	8868.69	9854.1	9854.1	9854.1	9854.1
Plant overhead	-	3292.48	3498.26	3704.04	4115.6	4115.6	4115.6	4115.6
Depreciation		1646.24	1749.13	1852.02	2057.8	2057.8	2057.8	2057.8
Interest (15%)	-	-	-	-	-	-	-	-
Capital charge	-	164.624	174.913	185.202	205.78	205.78	205.78	205.78
Gross profit=I-II	-	12169.8	4554.5	4822.4	5358	5358	5358	5358
Net profit	-	12169.8	4554.5	4822.4	5358	5358	5358	5358
Discount factor at (12%)	1	0.893	0.797	0.712	0.636	0.567	0.506	0.452
Present value (PV)		10867.6	3629.93	3433.54	3407.9	3037.9	2711.1	2421.8

Discount factor (DCF) = $(1 + r)^{-n}$

Present Value(PV) = yearly gross profit *discount factor

Assuming 12% opportunity cost of capital(discounted rate) for new plant according to Peters & Timmerhaus (1991).

d. **Payback Period**

Depending on the income statement, other indicators of profitability which show the viability of the project has been calculated as follows:

Year	0	1	2	3	4	5
Cumulative cash flow	- 23664.8	-12797.2	-9167.27	-5733.73	-2325.83	712.07
Yearly cash flow	-	10867.6	3629.93	3433.54	3407.9	3037.9

Payback period = 4 years + 2325.83 /3037.9 = 4.76 year

The above result shows that, the plant initial investment cost will be fully recovered within 4.76 operation year. Therefore, implementing of plant for magnesium chloride production is financially feasible after 5 years.

e. Net Present Value (NPV), by addition of all PVs, including the initial investment outlay, which is negative because it is a cash outflow)

NPV=$\sum_0^7$ PV (Cach flow) = (- 23664.8+29509.77)* 10^3 Birr

= 5844.97 *10^3 =5844970Birr

f. Net Present Value Ratio (NPVR)

$$(\text{NPVR}) = \frac{\sum \text{NPV OF NCFS}}{\text{NPVI}}$$

$$= \frac{29509.77}{23664.8} = 1.25$$

Based on the preliminary economic evaluation, the suggested project has payback period of 4.76 years and project will start generating profit in the 4.76 year of operation.

Since the net present value is positive and the net present value ratio is greater than 1 the project is acceptable and viable for implementation. Moreover, the payback period of less than five years, apparently minimizes any risk in regaining/recouping the initial investment.

6. CONCLUSION AND RECOMMENDATION

6.1. Conclusion

Magnesium chloride was produced from local raw material magnesium carbonate by reacting with hydrochloric acid which fulfilled the objective of the study.

The reaction of magnesite in aqueous hydrochloric acid solution was studied in a batch reactor. According to the result obtained from composition analysis, magnesite has composition of: 46.77% MgO, 0.78% SiO_2, 3.03% CaO, 0% Fe_2O_3, 0.2% Al_2O_3, 49.12%L.O.I and 94.4% $MgCO_3$.

The experimental parameters were, acid concentration, liquid to solid ratio, reaction time and parameters taken as constants were reaction temperature, mixing speed and particle size. The effects of reaction parameters were determined by using Design Expert 7.0.0 soft ware, with three levels; three factors. In order to determine the effect of the hydrochloric acid concentration, liquid to solid ratio and reaction time on the production of magnesium chloride, the experiments were carried out in the range of 4 to 10 M acid concentrations, 1.88, to 2.07ml/g liquid to solid ratio and 60 to 180 min reaction time. For hydrochloric acid concentration from 4 to 7M, the positive effect was observed on the dissolution of magnesium carbonate to give the maximum yield of magnesium chloride. However, further increase of acid concentration resulted in reduction of magnesium chloride yield. Since the amount of dissolved magnesium carbonate decreased when the acid concentration exceeded the optimum point, the appearance rate of the product increased as the product approached to the saturation value on the surface of the solid and it forms a difficultly soluble the solid. For liquid to solid ratio on the yield of magnesium chloride, the yield of production was increased by increasing liquid to solid ratio. In other words, according to the results, the yield decreased as the solid to liquid ratio increased. This might be explained by the fact that the amount of reagent is not sufficient to leach magnesium from magnesium carbonate when the amounts of solid in the liquid is high. For reaction time, the maximum the yield of magnesium chloride was obtained at180 min.

Therefore, the maximum yield of magnesium chloride (94%w/w) was attained at 7M acid concentration, 2.07ml/g liquid to solid ratio and 180min reaction time. In contrast, the minimum yield of magnesium chloride (58%) was attained at 4M acid concentration, 1.88ml/g liquid to solid ratio and 60min reaction time.

According to the results of the product analysis, the sample contained compositions of; 0.62%SiO_2,0.05%Al_2O_3, mimm3.99%CaO, 0.03%SO_3 and 0%Fe_2O_3 in product. The imported composition of magnesium chloride hexahydrate is 99% to 100% with $MgCl_2$ 46%w/w. But the content of magnesium chloride hexahydrate (94% with 44%$MgCl_{2)}$ found to be less, the difference is due to the impurities present in the raw material.

6.2. Recommendation

1. The ultimate utilization of the $MgCl_2$ is in the manufacture of magnesium boards by mixing it with magnesium oxide and other fillers. Currently, both public and private organizations are making magnesium board partition walls for low cost housing construction using imported $MgCl_2$.

The effect of the presence of $CaCl_2$ in the $MgCl_2$ made from local magnesite has to be investigated further by manufacturing magnesium boards from local $MgCl_2$.

2. It has been proven that local magnesite can be utilized for producing $MgCl_2$ at laboratory scale. Upscaling study or pilot testing need to be conducted, say at the Zeway Caustic Soda Factory, in order to ascertaining the reaction parameters of magnesite with hydrochloric acid.

3. An attempt has to be made at the Kenticha magnesite mining site for hand picking the mineral with the higher content of magnesium carbonate in order to reduce impurities at source.

4. The hitherto hindrance to establish a chlor-alkali plant in Ethiopia was the lack of market outlet for the chlorine gas and its derivatives. Thanks to the booming construction industry and the growing demand for $MgCl_2$, the Zway Caustic Soda Plant can embark on the process of its converting its technology to a chlor-alkali process instead of the defunct lime-soda process which has proven to be ineffective cost wise.

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8. APPENDIXES

8.1. Appendix A: Physico Chemical Properties of Magnesium Carbonate

The anhydrous salt consists of white trigonal crystals; refractive index 1.717; density 2.958 g/cm^3; decomposes at 350°C; practically insoluble in water (106 mg/L at room temperature); K_{sp} $1.0x10^{-5}$; low to moderate solubility under partial pressure of CO_2 (3.5 and 5.9 g $MgCO_3$/100g saturated solution at CO_2 pressure 2 and 10 atm, respectively); insoluble in acetone and ammonia; dissolves in acids.The di and trihydrates, $MgCO_3 \cdot 2H_2O$ and $MgCO_3 \cdot 3H_2O$ are colorless crystals having triclinic and monoclinic structures, respectively; the refractive index 1.458 and 1.412, respectively; and their densities are 2.825 and 1.837 g/cm^3. The pentahydrate, $MgCO_3 \cdot 5H_2O$, occurring naturally as the mineral lansfordite is a white crystalline solid; monoclinic crystals; refractive index 1.456; density 1.73g/cm^3; decomposes in air; slightly soluble in water (0.375 g/100 mL at 20°C). All three basic carbonates, artinite, hydromagnestite and dypingite, are white crystalline substances of monoclinic crystal structures; refractive index 1.488, 1.523 and 1.508, respectively; the index of refraction for the basic carbonate octahydrate is 1.515; the densities are 2.02 and 2.16 g/cm^3 for artinite and hydromagnesite; the basic carbonates are all practically insoluble in water.

Table:A1 Thermochemical Properties of magnesium carbonate

Thermochemical Properties	
$\Delta H f°$ ($MgCO_3$)	–261.9 kcal/mol
$\Delta G f°$ ($MgCO_3$)	–241.9 kcal/mol
$\Delta G f°$ ($MgCO_3 \cdot 3H_2O$)	–412.6 kcal/mol
$\Delta G f°$ ($MgCO_3 \cdot 5H_2O$)	–525.7 kcal/mol
S° ($MgCO_3$)	15.7 cal/degree mol
C_p ($MgCO_3$)	18.05 cal/degree mol

source: [2]

8.2. Appendix B: Physicochemical Properties Of Magnesium Chloride

Magnesium chloride hexahydrate is a white crystalline solid and is deliquescent. It decomposes on heating to give magnesium oxide. When heated in a current of dry hydrogen chloride gas it gives anhydrous salt. A saturated solution of this salt when mixed with magnesium oxide, sets to a hard mass with the formula $MgCl_2.5MgO.xH_2O$. The hard mass is known as magnesia cement or Sorel cement.

$MgCl_2 . 6H_2O \xrightarrow{heat} MgO + 5H_2O + 2HCl$

Anhydrous salt consists of white lustrous hexagonal crystals; refractive index 1.675; density 2.32 g/cm^3; melts at 714°C; decomposes at a lower temperature of 300°C when heated slowly, releasing chlorine; vaporizes at 1,412°C; highly soluble in water. Hexahydrate constitutes colorless monoclinic crystals; deliquescent; refractive index 1.495; density 1.569 g/cm^3; decomposes on heating at 116°C; highly soluble in water (157 g/100mL at 20°C); solubility increased on heating; soluble in alcohol.

$MgCl_2$ crystallizes in the cadmium chloride motif, which features octahedral Mg. A variety of hydrates are known with the formula $MgCl_2(H_2O)_x$, and each loses water with increasing temperature: x = 12 (−16.4 °C), 8 (−3.4 °C), 6 (116.7 °C), 4 (181 °C), 2 (ca. 300 °C) [27]. In the hexahydrate, the Mg^{2+} remains octahedral, but is coordinated to six water legends [29].

Table: B1 physicochemical properties of magnesium chloride

Properties	Anhydrous,	Hexahydrate,
Chemical formula	$MgCl_2$	$MgCl_2 . 6H_2O$
Molar mass	95.211 g/mol	203.31 g/mol
Appearance	white or colourless crystalline solid	
Density	2.32g/cm^3	1.569 g/cm^3
Melting point	714 °C(1,317 °F987 K)	117 °C (243 °F; 390 K)
Boiling point	300 °C (572 °F; 573 K)	1,412 °C(2,574 °F;1,685 K)
Solubility in water	54.3 g/100 mL (20 °C)	72.6 g/100 mL (100 °C)
Thermochemical Properties		
Specific heat capacity	71.09 J/mol K	75.30 cal/degree mol
Entropy(ΔS°)	21.42 cal/degree mol	89.88 J/mol *K
Enthalpy formation($\Delta_f H^\circ$)	-641.1 kJ/mol	–597.28 kcal/mol
Gibbs free energy($\Delta_f G^\circ$)	-591.6 kJ/mol	–505.49 kcal/mol

source: [14]

8.3. Appendix C: Calculation of Magnesium Carbonate %w/w

The maximum amount of $MgCO_3$ that could possibly be present in the sample was calculated according to stechiometric ratio relations.

The magnesite sample (triplicates) 0.25 g was dissolved in 50 ml amounts of hydrochloric acid (con. 0.5 M). The metal carbonate reacted with the acid to give the water soluble chlorides. An excess amount of acid that is somewhat in excess of the maximum stechiometric amount needed to dissolve the maximum possible amount of $MgCO_3$,was added to the sample. It was allowed to react with a sample and the solution was heated using bussen burner and gently boiled over five (5 min) minute to speed up the reaction. The residue carbon dioxide liberated can interfere with the subsequent determination and is therefore expelled by boiling the solution. The solution was cooled to room temperature and two drop of phenolphthalein indicator was added to the solution and the excess hydrochloric acid was then titrated with standardized sodium hydroxide (con. 0.5 M) solution to neutralize un reacted /excess HCl. The volume of NaOH consumed was represented in the following table. The end point was detected by colour change. The experiments were repeated three time times to obtain the same result. The experiment was repeated again at laboratory of Mugher Cement Factor due to insufficient of different laboratory chemicals to determine all composition in the sample.

The maximum amount of $MgCO_3$ that could possibly be present in the sample was calculated according to stechiometric ratio relations.

No. titration	Mass of sample (g)	Volume of HCl (0.5 M)	Volume f NaOH (0.5 M)
1	0.25	50 ml	38.6 ml
2	0.25	50 ml	39.5 ml
3	0.25	50 ml	38.4 ml
Average	0.25	50 ml	38.8 ml

The percentage composition of magnesium carbonate was determinate according to the following formula:$MgCO_3(w/w\%) = \frac{\text{mass of } MgCO_3 \text{ after titration}}{\text{mass of the sample}} * 100\%$

Calculations

The equation for the reaction between magnesium carbonate and hydrochloric acid is given below. $MgCO_3 + 2HCl \rightarrow MgCl_2\,(aq) + H_2O + CO_2$

1.Determination the number of moles of HCl in 50 cm^3 of 0.500mol./dm^3 hydrochloric acid.

Mol HCl = 50/1000*0.500 = 0.025mol HCl was added originally.

2. Determination the number of moles of NaOH used to neutralise the unreacted HCl.

Mol NaOH = 38.8/1000*0.500 = 0.0194 mol NaOH.

Mol of HCl that reacted with the sample = 0.025 - 0.0194 = 0.0056 mol HCl reacted with sample.

4. Determination of the number of moles and the mass of $MgCO_3$ in the sample, and hence deduce the percentage by mass of $MgCO_3$ in the sample.

First write a balanced equation for the reaction HCl with $MgCO_3$:

$MgCO_3 + 2HCl \rightarrow MgCl_2 + CO2 + H_2O$

From this balanced equation:

1mol $MgCO_3$ react with 2 mol HCl

Then from balanced equation : there must have been 0.00.0056/2 = 0.0028 mol $MgCO_3$ in the original sample.

Molar mass $MgCO_3$ = 84.3141 g/mol

Mass of $MgCO_3$ = 0.0028*84.3141 = 0.2363 g $MgCO_3$ in the original sample.

Mass of original sample = 0.25. This contains 0.236 g $MgCO_3$

5 . Mass percentage of magnesium carbonate

% MgCO3 = 0.236/0.25*100 = 94.4% $MgCO_3$ in sample.

The result indicated that the original sample with mass 0.25g is impure $MgCO_3$.

A calculated mass of $MgCO_3$ (which has to be less than 0.25g) the sample is 5.6% impurities, which did not react with HCl.

8.4. Appendix D: Magnesium chloride composition analysis

In order to determine the quality/composition of the magnesium chloride, chemical analysis was undertaken using a wet chemical analysis method. Complexometric method using EDTA and gravimetric analysis were used for complete chemical analysis

a) **Sample Preparation**

- 0.5 g sample was weighted into a 100 ml volumetric flask
- 4ml of concentrated HCl was added to the sample, the flask was filled to mark and mixed.
- 10 ml the sample was Pipetted into a 250 ml Erlenmeyer flask
- 80 ml of DI water was added to the solution in a 250 ml Erlenmeyer flask
- 10 g of Ammonium Chloride was added to the sample and stirred to dissolve.
- 10ml of 10% Hydroxylamine Hydrochloride solution was pipetted to the sample.
- 40 ml of concentrated Ammonium Hydroxide was added to the sample and stirred.
- 4 drops of Eriochrome Black T indicator (ASTM E50) was added to solution and stirred.

- Titration was carried out according to Method c

b) EDTA standardization

The Standardized EDTA solution was prepared according to ASTM E449 using standard $MgCl_2$ solution having a $MgCl_2$ content of 0.00714 g / ml.

$MgCl_2$ was prepared by weighting 15.241 g of $MgCl_2.6\ H_2O$ in a 1000 ml volumetric flask and dilute to the mark.

c)Test Method (Titration)

- 50ml of the prepared sample was taken into 250ml conical flask
- Set up a 50 ml burette with 0.1 M EDTA solution (prepared and standardized according to method **b**).
- the sample was Titrated to a black endpoint from the starting color of red.
- the volume of EDTA added to the solution from buret (consumed) was recorded.
- procedure were repeated until concord result was recorded

$$\%\ MgCl_2 = \frac{\text{Volume of EDTA consumed} * C_{EDTA} * MgCl_{2\ equivalent}}{\text{sample weight}} * 100 \quad \text{eq(3.10)}$$

Table appendix D, amount of Magnesium Chloride in Magnesium Chloride Hexahydrate

No.	Volume of EDTA consumed	Colour change	$\%MgCl_2$
1	46.9	Red to black (dark)	44.18
2	46.63	Red to black (dark)	43.92
3	46.62	Red to black (dark)	43.9
Average	46.87		44.0

8.5. Appendix E: Table contains Equipments and Chemicals used for complete chemical analysis at Mugher Cement Factory based on Complexometric and gravimetric analysis methods

Equipments	**Chemicals**
Burret	Distilled water
Pippet	20% Potassium hydroxide (KOH)
Beak gass rod	Tri-ethanol amine
Iron (metal)stand	PH = 10 buffer
Volumetric flask	PH = 4.3 buffer
Funnel	Hydrogen-sodium potassium tartarate
Filter paper	KB indicator
Analytical balance	CMP indicator
Desiccator	1+1 HCl
Crucible	Ammonia (1+1 NH_3)
Platinum crucible	Sulfosulsalic acid
Muffle furnace	PAN indicator
Tonge	0.015 EDTA
Stove	0.015 copper sulphate ($CuSO_4$)
Hot plate	Barium chloride ($BaCl_2$)
Washing glass (washer)	Sodium carbonate (Na_2CO_3)
Forcep	Ammonium chloride NH_4Cl)
Ph indicator	Nitric acid (HNO_3)