ADDIS ABABA UNIVERSITY
SCHOOL OF GRADUATE STUDIES
ADDIS ABABA INSTITUTE OF TECHNOLOGY
SCHOOL OF CHEMICAL AND BIO ENGINEERING

AMMONIUM CHLORIDE PRODUCTION AND OPTIMIZATION OF BRINE AMMONIATION FOR LIME REMOVAL IN LEATHER PROCESSING

By

Michael Moreda Dadi

JUNE 2014
ADDIS ABABA, ETHIOPIA

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A thesis Submitted to the Research and Graduate School of Addis Ababa University, Addis Ababa Institute of Technology, School of Chemical and Bio Engineering in partial fulfillment of the requirements for the attainment of the Degree of Masters of Science in Chemical Engineering under Process Engineering Stream.

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ACRONYMS

ISTM: Indian Society for Testing and Material

ETB: Ethiopian Birr

IUP: International Union of Leather Chemists Physical Testing Methods

IUC: International Union of Leather Chemists Chemical Testing Methods

IULTCS: International Union of Leather Technologist’s and Chemist's Society
SLC: Society of Leather Chemists
CCD: Central Composite Design
SNG: Synthesis Gas
LIDI: Leather Industry Development Institute
ELICO: Ethio - Leather Industry plc
BASF: Baden Anilline and Soda Factory
GTP: Growth and Transformation Plan
EDTA: Ethylene Diamine Tetra Acetic acid
AG: Analytical grade
SG: Specific Gravity
ANOVA: Analysis of Variance
RSM: Response Surface Methodology
IPPC: Integrated Pollution Prevention and Control
ISO: International Standards Organization

ABSTRACT

Leather industry occupies a place of prominence in Ethiopian economy in view of its massive potential for employment, growth and export. The need of import substituting leather processing chemicals from locally available feed stocks is an urgent matter both from economic and environmental point of view. One of the chemicals used in leather processing is ammonium chloride which is a deliming agent in Beam house operation.

In this study, the production of ammonium chloride from proven available urea feed stocks ammonia, carbon dioxide and from the cheapest chlorine source sodium chloride which is readily available in Ethiopia, and its use and efficiency as a deliming chemical as compared to standard ammonium chloride is analyzed.

A modified Solvay process approach was adopted in search of a route to the production of ammonium chloride locally. The method involves brine purification, ammoniated brine formation, carbonation of ammoniated brine, separation of sodium bicarbonate from ammonium chloride containing mother liquor, evaporation of ammonium chloride filtrate, cooling of the evaporated ammonium chloride filtrate to crystallize, centrifugation and drying of ammonium chloride which is collected as a white solid crystal of 98.5 - 99.5 wt.% NH_4Cl. This preparation met the established specification for ammonium chloride of Indian Society for Testing and Materials (ISTM).

The maximum yield of ammonium chloride (92.5%) was produced when the brine ammoniation reaction was carried out at a temperature of 10^0C, ammonium solution to saturated brine molar ratio of 2 and reaction time of 1 hour. Therefore, these values can be considered as optimal for ammonium chloride production using ammonium solution, dry ice and saturated brine in batch reactor. The reaction temperature was varied in the range of 10^0C - 20^0C, ammonium solution to saturated brine molar ratio was varied in the range of 1 – 3; and reaction time was varied in the range of 0.5 - 1.5 hours.

Testing of the optimal product on leather met the IULTCS standards.

1. INTRODUCTION

1.1 Background

The leather industries are one of the highly chemical consuming sectors for its' different unit processes of soaking, liming, unharing, deliming, bating, pickling, tanning and finishing. However, interventions to import substitute these chemicals to recover the hard foreign currency spent and initiations for efficient resource utilization, which results from import substitution, creating job opportunity and waste utilization said to be not well on the move in our country Ethiopia.

According to data from Leather Industry Development Institute and tanneries, 0.3 kg of ammonium chloride is used as a deliming chemical for 20 kg of leather produced. Based on data from Ethiopian custom authority the projected demand for ammonium chloride in 2015G.C is 600tons. In the market the average price of imported ammonium chloride range in ETB from 600 up to 800 per kg. This figure coupled with the expenditures for transport, loading and unloading, amount to make a large proportion of the leather industries budget.

The deliming process serves to remove the lime introduced during the liming process (capillary lime, mechanically deposited or chemically bound lime) and to deplete the skin. Inadequate deliming may give rise to an increase of basicity during chrome tannage and cause wrinkled grain, hardness, loose grain or cracky grain. Furthermore, formation of gypsum may occur in pure sulphate liquors and result in lime stains. Lime tannates may form in vegetable tannage and also cause staining or cracky grain. Inadequate depleting will result in fixation of swelling during tannage and thus results in unelastic, cracky leathers [1, 2].

Ammonium chloride as a deliming chemical for leather manufacture get advantage over other deliming chemicals in that during deliming it forms calcium chloride which is very soluble in water and is washed out of the pelt very readily, has good peptizing and buffering effect [1].

Ammonium chloride can be produced from different varieties of raw materials like ammonia, sodium chloride, carbon dioxide, hydrogen chloride, and ammonium sulphate and ammonium sulphite as long as it can meet the quality specifications in standards. This thesis concerned with ammonium chloride production from raw materials obtain from urea production plant mainly due to the following reasons:

- The major bottleneck in ammonium chloride production is the high cost of feedstock used. Using urea feedstocks, like using a product or recovered ammonia and carbon dioxide from urea production plant, as raw materials provide a means for technology adaptation to alleviate this problem, and moreover, it has extra benefit in recovering vent ammonia and carbon dioxide sequestration as a means for environmental protection.
- Ammonium chloride production using direct neutralization between ammonia and hydrogen chloride is economically not viable due to absence of readily available hydrogen chloride.
- Besides the use of ammonium chloride as a deliming chemical, use of fertilizer grade ammonium chloride as a compound fertilizer lowers the nitrification rate of urea for importance of crop yield.
- Two of the three major raw materials like ammonia and carbon dioxide can be obtained from ammonia synthesis plant which is under construction at Yayu, Iluababora zone of Ethiopia and sodium chloride, which is the cheapest source of chlorine, is readily available in Afar regional state, Afdera for the production of ammonium chloride by adopting the technology of modified Solvay Process.

In Ethiopia currently there are thirty two leather manufacturing industries; Leather making is very complex course including lots of physical and chemical changes. On one hand, the useless parts were removed from raw hide to get pure collagen fiber, and opened up the structure of collagen fiber using deliming chemicals. ‘Opening up’ is the separation of collagen fibers so that the correct chemical penetration and softness is produced in the end product. On the other hand, tanning agent was introduced to strengthen the stability of collagen fiber; and other necessary materials were added to make leather usable [3, 4].

Leather making process demands intensive chemicals usage, import substitute of these vast chemicals are of economic value for developing countries like Ethiopia. Table 1.1 below shows the daily ammonium chloride consumption of some typical tanneries in Ethiopia.

Table 1.1 Ammonium chloride consumption of typical tanneries in Ethiopia [1]

No	Name of Tannery	Daily Production (Pieces)		Daily Production (tone)		Daily ammonium chloride consumption (Kg)
		Skin	Hide	Skin	Hide	
1.	Ethiopia Tannery Share	14500	1300	21.75	33.280	825.45
2.	Dire Tannery	6000	600	9.000	15.360	365.4
3.	Hafde Tannery Plc	9000	500	13.500	12.800	394.5
4.	Wallia Tannery Plc	7000	300	10.500	7.680	272.7
5.	Batu Tannery Plc	3000	700	4.500	2.560	105.9
6.	Modjo Tannery Share Company	5700	200	8.550	5.120	205.05
7.	ELICO	15000	800	22.500	20.480	644.7
8.	Bahir Dar Tannery Plc	3000	100	4.500	2.560	105.9
9	China Africa Tannery	8224	0	12.336	0	185.04
10	Shoa Tannery Plc	6000	500	9.000	12.800	327
Total		77,424	5,000	116.136	112.64	3,431.64

- Daily ammonium chloride consumption is calculated as 1.5% times the weight of skins and hides where the amount was calculated in full usage of ammonium chloride only.
- Source: LIDI and Tanneries.

1.2 Statement of the problem

In Ethiopia currently one of the fastest growing sectors is the leather manufacturing sector which produces finished and semi-finished leather products for local consumption and foreign export. The leather industries have design production capacity range from 7,000 kg leather/day up to 55,000 kg of leather/day [1].

Ammonia and carbon dioxide production takes about 80% of the energy consumed for production of urea, the produced or vent ammonia and carbon dioxide from this urea production plant are resources that can be used for production of value adding products like ammonium chloride [5]. Production of ammonium chloride from these resources by integrating with urea production plant is a practical idea in that efficient resource utilization; creating job opportunity; import substitution and new business development are all included.

Industrial production of ammonium chloride in Ethiopia in this research is intertwined with the large scale intended production of ammonia at Yayu; Iluababora zone of Ethiopia by the year 2014/2015 G.C [6]. The original motivation for producing ammonium chloride was to use it as fertilizer. But it is also used for a wide range of purposes including, deliming agent in tanneries which is the main target of this research.

Deliming chemicals used for leather processing are many where the main classification made between ammonium salt deliming and accelerated carbon dioxide deliming. From the point of view of process, the major problems related with carbon dioxide deliming are formation of hydrogen sulfide gas due to a low operating pH, process can be lengthy on certain pelt types and gas risk is realized if drum pressure valves fail [7].

Ammonium chloride during deliming forms calcium chloride which is very soluble in water and washed out of the pelt very readily; consequently it increases the deliming rate, has better peptizing and buffering capacity. In order to save the hard foreign currency, reduce reliance on imported ammonium chloride and overcome the limitations of carbon dioxide deliming, ammonium sulphate and other organic deliming chemicals like acetic acid and lactic acid, this research focused on production of ammonium chloride from locally available feed stocks by adopting the technology of modified Solvay process.

1.3 Objective of the research

1.3.1 General objective

The main objective of this research is ammonium chloride production, optimization of brine ammoniation process variables, characterization of ammonium chloride and performs deliming experiment on leather processing.

1.3.2 Specific objectives

- Preparation and characterization of saturated brine.
- Ammonium chloride production from saturated brine, ammonium solution and dry ice via laboratory scale modified Solvay process.
- Characterization of Physico - chemical properties of ammonium chloride.
- Investigate the effect and interaction of the three important laboratory scale modified Solvay process parameters; reaction temperature, ammonium solution to saturated brine molar ratio and reaction time, on the yield of ammonium chloride production.
- To determine the optimal operating parameters (temperature, ammonium solution to saturated brine molar ratio and reaction time).
- Conduct an actual experiment on leather by taking the optimal ammonium chloride produced in the laboratory to compare it with the imported one at Leather Industry Development Institute (LIDI) model tannery.
- Ammonium chloride production plant cost estimation and cost analysis.

1.4 Significance of the study

This thesis has great significance and use as one of a bench mark study in terms of import substituting inorganic industrial chemicals from locally available feed stocks by adopting known technologies. It serves as a means of initiations for efficient resource utilization that results in new business development, provides economic and social benefits from employment and generation of income from tax revenue. Moreover, the results of the study will be used as base-line information for further studies.

2. LITERATURE REVIEW

2.1 Introduction

Ammonium chloride is a deliming chemical used in leather manufacturing and produced from major inputs obtained in urea production plant that is intended to start operation by the year 2014/2015 G.C. according to Ethiopian GTP. The plant will produce 300,000 tons of urea/year based on 282,000 tons of ammonia produced by gasification of coal, mined from Yayu, Iluababora zone and 40,000tons/year of carbon dioxide as a byproduct of economic value [6].

Deliming is the removal of the alkali and adjustment of pH for bating which is a further step in purification of the hide prior to tanning. If deliming is not done, and if the limed pelts are treated with chrome tanning liquor; the chrome will be fixed and deposited on the outer surface leaving the interior under tanned. Hence deliming is important and necessary operation [7, 8].

2.2 The Role of deliming (Lime removal)

Hides (large animals) and skins (small animals) from various animal types are processed from raw to finished leather in tanneries. The hides and skins undergo beamhouse operations, which include soaking, liming, deliming, and bating. Tanyard operations include pickling, tanning and basification.

The soaking stage returns the hide/skin back to its initial state (fully hydrated and flexible). The liming stage removes the hair and unwanted components. Deliming removes lime and prepares the hide/skin pH and temperature for bating. Bating removes the interfibrillary proteins and makes the hide/skin soft. Pickling lowers the pH for the correct penetration of the tanning agents. Fixation or basification is the cross-linking of the tanning salts so that a stable leather product is obtained. Adding specific properties through retanning, adding oils in fatliquoring, and adding color through dyeing produces what is known as crust, the dried tanned leather. Beamhouse chemicals are purely preparatory and removed after their use. Liming and deliming are fundamentally linked and their use is vital in obtaining the ‘opening up’ of the hide/skin [3].

Liming also results in the removal of keratin, plumping of hide structure, solubilisation of glycosaminoglycans, and saponification of fats and the chemical alteration of the leather collagen itself. One of the most obvious features of liming is a swollen pelt. The hide/skin swells at high pH values because of electrostatic repulsion and osmotic effects. Swelling of the pelt is at a maximum at pH 12.5. Thereafter it decreases according to the Donnan theory of membrane equilibrium [9].

Osmotic swelling has been described as essentially due to the association of large numbers of cations with ionised collagen (ionisation due to added hydroxyl groups). Lime, upon addition, yields both hydroxyl and calcium ions. The aggregation of divalent calcium ions causes an imbalance in water potential. The initial influx of water is due to the hypertonic nature of water systems associated with collagen, but later, the loss of collagen cohesion (at a pH higher than 11), causes swelling. The divalent nature of lime (calcium hydroxide, $Ca(OH)_2$) as opposed to monovalent caustic soda (NaOH) influences the extent of swelling. It also produces a difference in the ease with which these ions are removed. It has been shown that close linkages are formed between the calcium from lime and the collagen protein. Calcium has a greater solubilising influence on glycosaminoglycans; however more opening up is obtained by calcium [10].

2.2.1 Ammonium chloride deliming

The removal of $Ca(OH)_2$ is done by ammonium salts, either ammonium chloride (NH_4Cl) or ammonium sulfate [$(NH_4)_2SO_4$]. Failure to remove lime results in the formation of lime blast. Lime blast describes the formation of calcium carbonate ($CaCO_3$) when limed material has become exposed to a carbon dioxide-rich atmosphere [11, 12].

The removal of calcium hydroxide involves the addition of deliming acid, which removes the lime by scavenging the hydroxyl ion associated with lime, and thereby lowers the pH [9]. Monitoring of this chemical neutralisation is achieved using pH indicators. The calcium, which is weakly bonded to the collagen, is removed. Calcium chloride is soluble in water and washed out from the pelt readily (in which case the residual calcium determination would be detected) or some other mechanism is involved in its removal like measuring the pH of the pelt before and after deliming or by reading the residual calcium using Varian Atomic Absorption spectrometer (AA). The reaction for deliming with ammonium salts described as:

$$2NH_4Cl(aq) + Ca(OH)_{2(aq)} \rightarrow CaCl_{2(s)} + 2NH_{3(g)} + 2H_2O \qquad (2.1)$$

As can be seen from Equation 2.1, ammonia gas is formed. Some of this becomes volatilized in the headspace of the drum (particularly at a higher pH) and the rest is solubilised. The soluble gas, as well as residual ammonium ions, is a problem in effluents. However a number of methods have been developed for stripping ammonia from wastewaters, and for most modern tanneries, levels of ammonia in effluents are low [13].

2.2.2 Alternatives to ammonium chloride

Alternatives to conventional deliming methods using ammonium salts include magnesium sulfate, esters, magnesium lactate, boric acid, lactic acid, formic acid, acetic acid, mineral acids, and non-swelling organic acids. Magnesium sulfate is a good replacement, but offers two additional problems. Firstly, it contains sulfate, and would still contribute to sulfate containing effluents, and secondly the resulting quality of the pelt after deliming is below standard (particularly with regard to calcium removal). Esters delime the hide by reacting with the alkali in the drum through an acid that is formed by the hydrolysis of the ester .The problem with esters is, however, their price. Boric acid deliming is popular for bookbinding leathers and ostrich processing due to its superficial deliming, but has a high end-pH (pH 9.2), and it contains boron. Superficial deliming can be described as a deliming process that has culminated in a hide/skin cross section, which when tested with a pH indicator shows a high pH in the center and low surface pH. Organic acids: lactic, formic and acetic acid all decrease the pH beyond the required pH if not carefully monitored. Dipolar non-swelling acids, such as sulfophthalic or sulfonic types, are utilised as proprietary ammonia-free chemicals, but also decrease the pH rapidly if not monitored carefully. The non-swelling acids also tend to be very superficial, have slow deliming times but bear good affinity for lime. Proprietary organic acid deliming agents cannot compete with the prices tanneries pay for ammonium salts and they also increase the COD load. Mineral acids can also be used if dosed carefully and used in the presence of a buffering agent. The use of carbon dioxide (CO_2) gas has also been considered as an alternative to ammonium salts as a deliming agent [14, 15, and 16].

2.3 Raw materials for ammonium chloride production

The primary raw materials used in the production of ammonium chloride are ammonia, hydrogen chloride, carbon dioxide and sodium chloride, where sodium chloride may contain magnesium, calcium, sulphate and other impurities depending on the degree of pre-treatment they have received prior to delivery.

Choice of raw materials; ammonia with hydrogen chloride or ammonia with carbon dioxide and sodium chloride in producing ammonium chloride is both a process chemistry decision and an economic decision. With respect to economy, the greatest difference is associated with the availability of feed stocks.

The raw material used for the production of ammonium chloride is desirable with less feed stock cost, and, when production is based on products or byproducts from other processes [17].

2.3.1 Ammonia

Ammonia reaction with water form aqueous ammonia is the most important man- made synthetic chemical critically needed for the existence of human society. The additional food and chemical products required by the continuous increase of world population has been made possible by continuous supply of chemicals to industries and fertilizer to agriculture.

Natural gas or methane currently contributes 77% of the raw materials of the ammonia industries. Steam reforming is found to be the most economical route. The contribution of other gaseous /liquid hydrocarbons reforming process and coal/coke gasification technology in the world to ammonia capacity is about 10% and 13% respectively.

The economics of ammonia production require careful selection of raw materials, process choice and energy management which are necessary to optimize over all plant operation.

The approximate comparison of the investment cost, production cost and energy consumption for the three feed stocks is presented in table 2.1 below [5, 18].

Table 2.1 Investment cost, production cost and energy consumption for different feed stock of ammonia plant

Comparing parameters	Natural gas	Heavy oil	Coal
Investment cost	1.0	1.4	2.4
Production cost	1.0	1.2	1.7
Energy consumption	1.0	1.4	1.8

Based on the above comparison coal has the highest investment, production and energy consumption cost than the remaining feedstocks, however due to the large and proven coal reserves available in Yayu, Iluababora zone of Ethiopia, it became the preferred feedstock for ammonia synthesis locally.

2.3.2 Carbon dioxide

Carbon dioxide in gas, liquid and solid forms has been known for over a century. Although Thilorier produced solid carbon dioxide in 1835 from the liquid material, it was not until 1924 that the solid product which serves as a source of carbon dioxide for inert atmosphere gained industrial importance through its first and still most important use for refrigeration. The production of merchant carbon dioxide in 2006 was about 8.6×10^6t totals for the gaseous, liquid, and solid forms [19].

Although there are many sources of CO_2, the following four are the most important for commercial production:

1. Recovery as a by- product in the production of SNG

2. Recovery from natural wells

3. Recovery from the production of ethanol by fermentation

4. Recovery from synthesis gas in ammonia production

As ammonium chloride production and optimization of brine ammoniation for lime removal in this research based on the feed stock of urea production plant which is under construction inYayu, Iluababora zone of Ethiopia, the carbon dioxide source will be from coal gasification. Gasification is partial oxidation of coal and other carbonaceous feedstock in the presence of oxygen and /or steam, to produce syngas. The coal feed is gasified with a blast, consisting of a mixture of oxygen and process steam. The gasification process is a high temperature non-catalytic process that effectively burns all the carbonaceous feedstock.

Urea synthesis consumes a little over 30% of the carbon dioxide removed from the ammonia production. The remaining carbon dioxide is available for sequestration to produce value adding products like sodium bicarbonate and ammonium chloride [6, 20].

2.3.3 Sodium chloride

Sodium chloride exists naturally in cubic, crystalline form. In its pure state, it is colorless and consists of 60.663 wt% Cl, atomic wt 35.4527, and 39.337 wt% Na, atomic wt 22.989768. Sodium chloride that has been produced commercially can exist as discrete crystals in various size ranges, fine granules of powder, and compressed pellets or blocks. When observed using magnification, all forms of sodium chloride are crystalline.

Depending on gradation and commercial form, salt can be white, gray, reddish, or even brownish. The color can be attributed to impurities present, either occluded or on the surface of the crystals. Large crystals of apparently recrystallized halite found in some salt mines are colorless and transparent, clearly showing the mineral’s characteristic cubic cleavage. Pure sodium chloride is transparent in the near- and mid-infrared (IR) regions. Salt is soluble in polar solvents, insoluble in non-polar types. Sodium chloride (NaCl) contains 60% chloride by weight and its aqueous solution and saturated solution has a pH of 7 and 9 respectively and saturated solution has 1.2 specific gravity with molar concentration of 6M [21, 22].

In producing ammonium chloride using the modified Solvay process saturated brine is the major raw material. Sodium chloride solutions are occasionally available naturally but are more often obtained by solution mining of salt deposits to give raw, near saturated brine containing low concentrations of impurities such as magnesium and calcium salts. Some brine contains significant quantities of sulfates.

Brine purification is required to prevent scaling of processing equipment and contamination of the product. Brine is usually purified by a lime soda treatment where the magnesium is precipitated with Ca $(OH)_2$(milk of lime) and the calcium is precipitated with soda ash. The brine, separated from precipitated impurities, is sent to the ammonia absorbers. Based on a modified Solvay process brine is mixed with ammonia and then exposed to carbon dioxide using different contact techniques. The end result is the conversion of NaCl and CO_2 into a useful solid product namely sodium bicarbonate and ammonium chloride where both used as deacidification and deliming chemicals respectively in the leather manufacturing sector [23, 24].

Since there are many grades of salt available for purchase and purity levels for these grades which varies from a low 95% for some rock salts to a high purity 99.99% for purified evaporated-granulated treated salt from which synthetic brine is produced for laboratory use. It has been necessary to establish standards for particular salt uses (Table 2.2).

Table 2.2 Standard specifications of sodium chloride [25]

Substance	Tolerance Limit (percent by weight)	
	Rock salt	Evaporated salt
Moisture	2.00	0.20
Dry Basis		
Calcium and magnesium(Ca and Mg)	0.60	0.60
Sulphate(SO_4)	1.50	1.00
Water-insoluble impurities(silica,etc.,exclusive of calcium and sulphate)	2.00	0.05
Total impurities	4.00	2.00
Grease ,fat or oil	0.00	0.00

The most common impurities, depending on the origin of the salt, are calcium sulfate, calcium chloride, magnesium chloride or magnesium sulfate, sodium sulfate, and water-insoluble materials consisting of ferric iron compounds, and trace amounts of other elements. Surface moisture is determined by drying, water insoluble matter by weighing, and calcium and magnesium ions by various methods that include called ethylenediaminetetraacetic acid (EDTA) titration, flame photometry, and ion chromatography; however, the plant laboratories mainly utilize EDTA titration due to its simplicity and low cost. Sulfate is typically assayed gravimetrically or by ion chromatography [26, 27].

2.4 Ammonium chloride production technologies

The history of ammonium chloride manufacture is linked to the birth of the soda and synthetic ammonia industries. Consequently this halide had always been a by-product in great supply. Production by direct reaction of ammonia and hydrochloric acid is simple but usually economically unattractive; a process based on metathesis or double decomposition is generally preferred.

Several commercial grades are available: fine crystals of 99 to 100% purity, large crystals, pressed lumps, rods, and granular material.

2.4.1 Double - Decomposition methods - Double-decomposition processes all involve the reaction of sodium chloride, the cheapest chlorine source, with an ammonium salt. The latter may be supplied directly, or generated in situ by the reaction of ammonia and a supplementary ingredient. Ammonium chloride and a sodium salt are formed. The sodium salt is typically less soluble and is separated at lower temperatures; ammonium chloride is recovered from the filtrate by cooling [28, 29].

2.4.1.1 Ammonium sulfate – sodium chloride process

Ammonium sulfate, a readily available by-product, has been much used to make ammonium chloride by a double decomposition reaction with sodium chloride.

$$(\mathrm{NH_4})_2\mathrm{SO4} + 2\mathrm{NaCl} \rightarrow \mathrm{Na_2SO_4} + 2\mathrm{NH_4Cl} \qquad (2.2)$$

The ammonium sulfate and sodium chloride are simultaneously dissolved, preferably in a heel of ammonium chloride solution. The sodium chloride is typically in excess of about 5%. The pasty mixture is kept hot and agitated vigorously. When the mixture is separated by vacuum filtration, the filter and all connections are heated to avoid crust formation. The crystalline sodium sulfate is washed to remove essentially all of the ammonium chloride and the washings recycled to the process. The ammonium chloride filtrate is transferred to acid resistant crystallizing pans, concentrated, and cooled to effect crystallization .The crystalline NH_4Cl is washed with water to remove sulfate and dried to yield a product of high purity. No attempt is made to recover ammonium chloride remaining in solution. The mother liquor remaining after crystallization is reused as a heel.

2.4.1.2 Ammonium sulfite – sodium chloride process

Ammonium chloride has been produced by the reaction of ammonium sulfite, NH_4SO_3, and sodium chloride in a large Canadian plant. Ammonium sulfite is never actually isolated, rather ammonia and sulfur dioxide react in water with sodium chloride.

$$2\mathrm{NaCl} + \mathrm{SO_2} + 2\mathrm{NH_3} + \mathrm{H_2O} \rightarrow \mathrm{Na_2SO_3} + 2\mathrm{NH_4Cl} \qquad (2.3)$$

This process is only practical when the raw materials are readily available and of high purity. The sodium sulfite precipitates first and is removed by centrifugation, washed with water, and dried. The mother liquor containing ammonium chloride is sent to crystallizing tanks and the salt thus formed is washed and dried, giving a product said to analyze well over 99% [30].

2.4.1.3 Ammonia – soda process

Ammonium chloride is made as a by-product of the classic Solvay process, used to manufacture sodium carbonate .The method involves reaction of ammonia, carbon dioxide, and sodium chloride in water.

$$2\mathrm{NH_3} + \mathrm{CO_2} + 2\mathrm{NaCl} + \mathrm{H_2O} \rightarrow \mathrm{Na_2CO_3} + 2\mathrm{NH_4Cl} \qquad (2.4)$$

Ammonium chloride crystallized from the filtrate, separated, washed, and dried. The exact proportion of ammonium chloride recovered depends on the relative demands for sodium carbonate and ammonium chloride. If economic conditions require, part of the ammonia can be recovered and returned to the brine-ammoniation step by distillation of the ammonium chloride solution in the presence of lime. The spent calcium chloride liquor, a final product in manufacture of sodium carbonate by the ammonia–soda process, can also be used to obtain ammonium chloride. This liquor is treated with ammonia and carbon dioxide.

$$\mathrm{CaCl_2 + 2NH_3 + CO_2 + H_2O \rightarrow CaCO_3 + 2NH_4Cl} \qquad (2.5)$$

Calcium carbonate is removed by filtration leaving an ammonium chloride solution.

2.4.1.4 Modified Solvay process

In the Solvay process, ammonia and carbon dioxide are dissolved in aqueous sodium chloride to produce sparingly soluble sodium bicarbonate, which is calcined to sodium carbonate .The ammonia is recovered from the mother liquor by reaction with lime, this reaction also producing calcium chloride .The source of the lime and the carbon dioxide is limestone .The net reaction is the conversion of the feed stocks rock salt and lime stone into sodium carbonate and the byproduct calcium chloride.

Water, carbon dioxide and ammonia are added only to the extent necessary to compensate for plant losses. The feedstock and product dictate the location of a Solvay plant. For this reason, the plants normally function as largely independent units [31].

The modified Solvay process (ammonium chloride- soda ash process) is one of the best examples of integrated industrial production of two substances. It differs from the Solvay process in that ammonium chloride is also precipitated from the mother liquor where sodium chloride and ammonium solution mixed to form ammoniated brine until the solution saturates at 40^0C, the brine ammoniation reaction proceeds while carbon dioxide is added and cooled to precipitate sodium bicarbonate and filter and collect ammonium chloride filtrate.

The reaction steps are;

$$\mathrm{NH_3 + H_2O \leftrightarrow NH_4OH} \qquad (2.6)$$

$$\mathrm{NH_4OH + CO_2 + NaCl \rightarrow NaHCO_3 + NH_4Cl} \qquad (2.7)$$

The net reaction is

$$NH_3 + CO_2 + H_2O + NaCl \rightarrow NH_4Cl + NaHCO_3 \qquad (2.8)$$

The amount of ammonium chloride and sodium bicarbonate produced are almost equal: one mole (53.5g) of NH_4Cl is produced for each mole (84g) of $NaHCO_3$. The modified Solvay process requiring external NH_3 and $CO_{2,}$ in this research the CO_2 obtained from recovery of synthesis gas in ammonia production which must be incorporated in to an integral system of plants [32, 33].

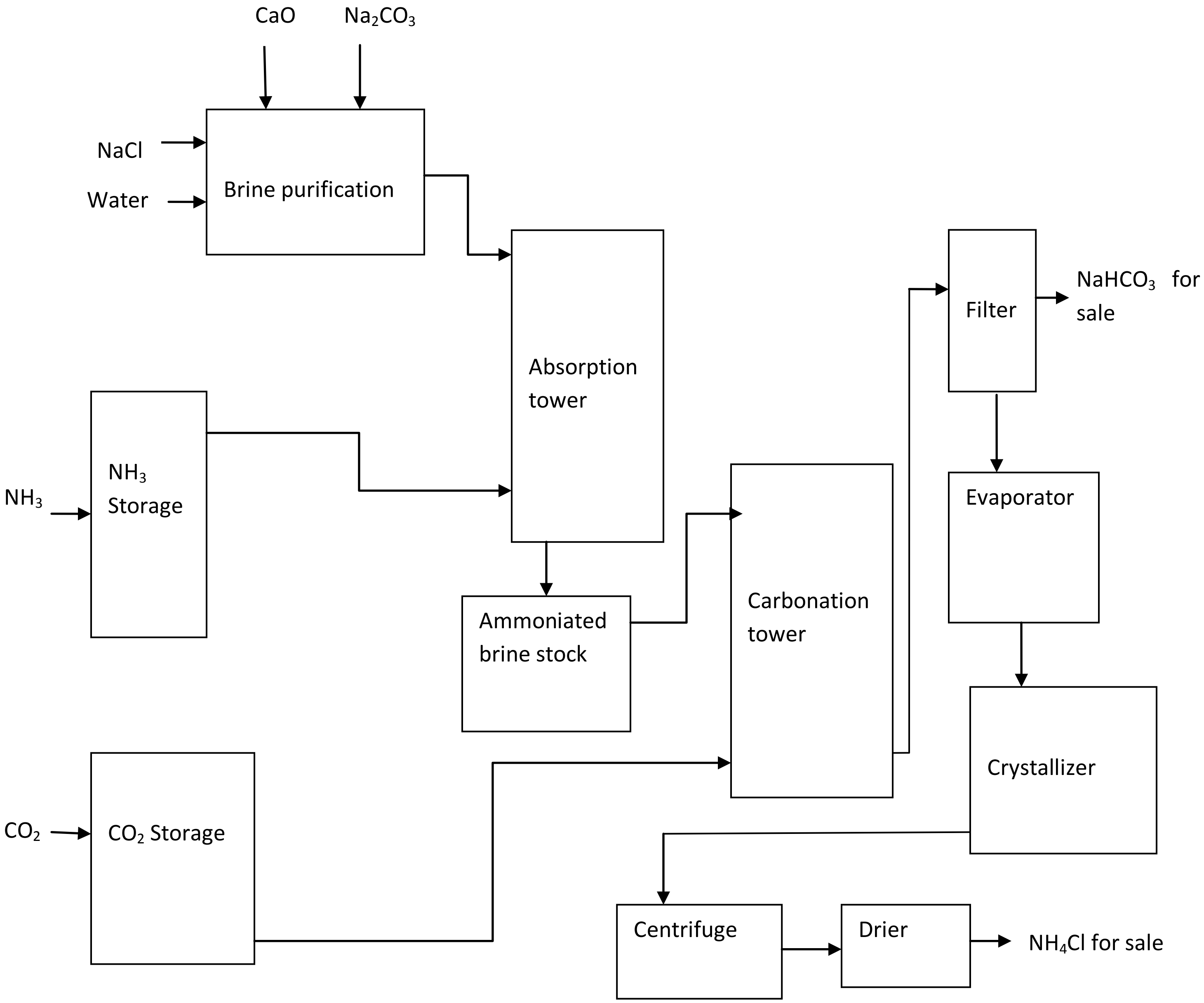

Figure 2.1. Process flow diagram for ammonium chloride production via modified Solvay

Commonly the manufacture of NH_4Cl and $NaHCO_3$ is carried out in a continuously operated recycle process in which the concentrations within the cycle may be adjusted according to whether ammonium chloride or sodium carbonate is the primary product [33].

In this process ammonium chloride is produced as a co-product in equivalent quantities and differs from conventional Solvay process in that it does not recycle ammonia.

Table 2.3 Raw material consumption per ton of co-product

Salt	1.53 tons
Ammonia	335 kgs
Power	250 kwh
Fuel oil	18 litres
Steam(including refrigeration)	5.2 tons

The process has several advantages over the conventional Solvay process in as much as it uses less raw material, has no effluent disposal problem, and both sodium and chloride radical of salt are fully utilized giving valuable ammonium as a byproduct. The ammonium chloride producing process requires, unlike the regular ammonia – soda plant, equipment to process solid salt, and of the ammonium chloride production, crystallizers, filters, dryers, and cooling equipment of corrosion resistant materials. In addition, an ammonia source is required which preferably also supplies carbon dioxide for the bicarbonation [28, 31 and 33].

2.4.2 Direct neutralization of ammonia with hydrochloric acid

Because of the availability of by-product ammonium salts, the double decomposition routes are usually more favorable economically for ammonium chloride manufacture. However, where surplus hydrogen chloride is available, the direct neutralization process has been used.

$$\mathrm{NH_3(g) + HCl(g) \rightarrow NH_4Cl} \qquad \Delta\mathrm{H} = -175.7\mathrm{kJ/mol}\left(-\frac{42\mathrm{Kcal}}{\mathrm{mol}}\right) \tag{2.9}$$

The reaction is very exothermic and the heat generated is used to evaporate a large part of water present when aqueous hydrochloric acid is used. Batch or continuous crystallization is then employed to recover the ammonium chloride [34].

2.5 Parameters Affecting Ammonium chloride Production

In the modified Solvay process there is a reaction between ammoniated brine and carbon dioxide gas or dry ice which was used in the laboratory to produce ammonium chloride and sodium bicarbonate. Reaction between ammoniated brine and carbon dioxide affected by various parameters. The reaction is either incomplete or the yield is reduced to a significant extent if the parameters are not optimized. The important process parameters, which affect the yield of the brine ammoniation process, are discussed below.

2.5.1 Reaction temperature

The rate of the brine ammoniation reaction is strongly influenced by the reaction temperature. Generally, the reaction is carried out close to crystallization temperature of sodium bicarbonate (10 to 20°C) at atmospheric pressure. With further increase in temperature the sodium bicarbonate solubilized and makes the separation less efficient from ammonium chloride containing mother liquor.

The brine ammoniation reaction has been reported to be influenced negatively with increase in temperature, since the absorption of carbon dioxide in aqueous ammonia favored at lower temperature (between 5-25^{0}C) [35].

2.5.2 Reaction time

The conversion rate increases with optimal reaction time. The exothermic reaction between ammoniated brine and carbon dioxide under the condition of ammonium solution to brine molar ratio of 2:1,100 g of dry ice and for reaction temperature of 15^{0}C an approximate ammonium chloride yield of 70% conversion was observed after 30 minute. After 1 hour, the conversions reach up to 80%. For extended reaction time beyond 1 hour the conversion became lower due to impurities present in brine which may compete for ammonia and reduce it’s availability in reaction with carbon dioxide [36].

2.5.3 Ammonium solution to saturated brine molar ratio

The molar ratio of ammonium solution to saturated brine is one of the important factors that affect the conversion efficiency as well as production cost of ammonium chloride. Ammonia dissolves sodium chloride salt and buffers the solution at a basic pH of greater than 9 and hence allows the precipitation of $NaHCO_3$, which is less water-soluble in basic solution than NH_4Cl. Only a small amount of ammonia is needed to raise the pH to above 9; the increase of pH beyond this point is a little slower.

It is important to note that the stoichiometric amount of ammonia required by Reaction (2.8) is one mole. However, in a real process excess ammonia may be needed for the reaction to reach to completion. An experimental evaluation of the effect of excess ammonia on the yield of ammonium chloride at 15°C indicated the yield increased with increasing the $NH_3/NaCl$ ratio, reaching a maximum at 4 [37].

Similar experiments with synthetic brine solution, containing only NaCl in distilled water, in this study and in a previous study (Jibril and Ibrahim, 2001) revealed that the optimum ammonium chloride yield was achieved at a lower molar ratio ($NH_3/NaCl$) of 3. In both cases, the molar ratio is higher than that required stiochiometrically, which may be due to the fact that the reaction was carried out in a semi-batch reactor, where the CO_2 gas leaving the reactor stripped away some of the ammonia from the solution. As for the even higher molar ratio observed for the reject brine ($NH_3/NaCl=4$), it is believed to be due to the presence of other impurities in the brine.

2.5.4 Mixing intensity

According to the study made by P.W.J.Derks and G.F.Versteeg mixing effect is more significant during the slow rate region of the ammoniated brine to dry ice reaction and when the single phase is established, mixing becomes insignificant however 100 up to 200rpm is the optimal rotation speed used to ensure a flat gas-liquid contact area.

2.5.5 Purity of reactants

Impurities present in brine like metal carbonates may compete for ammonia and reduce its availability for reaction with carbon dioxide. Magnesium carbonate ($MgCO_3$), which is commonly present in brine, consumes ammonia to form magnesium hydroxide and ammonium bicarbonate according to the following reaction:

$$NH_3 + MgCO_3 + 2H_2O \rightarrow NH_4HCO_3 + Mg(OH)_2 \qquad (2.10)$$

2.5.6 Solubility of sodium bicarbonate

In aqueous solution NaCl, NH_4HCO_3 and $NaHCO_3$ are present in their ionic format as:

$$NaCl \leftrightarrow Na^+ + Cl^- \qquad (2.11)$$

$$NH_4HCO_3 \leftrightarrow {NH_4}^+ + {HCO_3}^- \qquad (2.12)$$

$$NaHCO_3 \leftrightarrow Na^+ + {HCO_3}^- \qquad (2.13)$$

Increasing the concentration of sodium ion (Na^+), by adding more NaCl into the solution, would force the equilibrium of reaction (2.13) to the left and hence reduce the solubility of $NaHCO_3$, similar argument was made in case of NH_4HCO_3 in terms of affecting the ionic equilibrium of reaction (2.13) because of the common bicarbonate ion present in the two compounds [38].

2.6 Ammonium chloride specifications and properties

The deliming specification defines and sets the quality standards for ammonium chloride. It is based on the standard ISTMA 1113.The ISTM ammonium chloride property specifications with the recommended test methods are given in Table 2.6.

Moisture content is a measure of non-caking performance of ammonium chloride .It is a measure of how easily the ammonium chloride produced can exist as fine crystals, large crystals, pressed lumps, rods, and granular material so that it become easily handled and transported to be applicable for the intended use. The requirement is ≤1.0%wt.

Percentage by weight of ammonium chloride is a measure of the percentage by weight of pure ammonium chloride required to be used as a deliming chemical for leather processing. The requirement is a minimum of 98.5% by weight.

Table 2.4: Standard specifications of ammonium chloride, grade U (Tannery grade): Indian

Property	Unit	Indian	
		ISTM A 1113	Recommended Test method
Density	Kg/m^3	1530 - 1540	ISTM A-1
Moisture content	% by wt, Max	1.0	ISTM A- 3
Ammonium chloride(as NH_4Cl)	% by wt, Min	98.5	ISTM A-4
Iron (as Fe)	% by wt, Max	0.01	ISTM A-5
Sulphates [as$(NH_4)_2SO_4$]	% by wt, Max	0.3	ISTM A-6
Total sulphated residue on sublimation	% by wt, Max	-	ISTM A-7
pH	-	4.5-5.2	ISTM A- 8
Matter insoluble in water	% by wt, Max	0.2	ISTM A-9
Heavy metals including iron(as Pb)	ppm, Max	-	ISTM A- 10
Arsenic (as AS_2O_3)	ppm, Max	-	ISTM A-11

Source: Adopted from Ammonium chloride industries, India 2003

Percentage by weight of iron is a measure of how much iron present in the final product of ammonium chloride and this may be attained by low purity of raw material especially from low purity sodium chloride. The requirement is ≤ 0.01%wt.

Percentage by weight of sulphate as $(NH_4)_2SO_4$ is a measure of the amount of sulphate found in the final product of ammonium chloride that is imparted from calcium sulphate, sodium sulphate and magnesium sulphate which may exist in the raw material sodium chloride. The requirement is ≤ 0.3%wt.

Percentage by weight of matter insoluble in water is a measure of the amount insoluble matters other than iron imparted from the raw material sodium chloride to the product ammonium chloride. The requirement is $\leq$ 0.2%wt.

pH is one of the important properties of ammonium chloride for its use as a deliming agent, pH of ammonium chloride determines the extent to which the pH of the limed pelt lowered from its high alkaline value (pH up to 12.5) during liming to a pH of 7 – 9 after deliming which is the required pH near to the bating and tanning pH range requirements. The requirement is 4.5 up to 5.2.

2.7 Applications of Ammonium chloride

All grades of ammonium chloride are supplied in the form of a fine, white, crystalline powder. Ammonium Chloride Fine White RW, Ammonium Chloride Fine White RWN and Ammonium Chloride Fine White RWS are free-flowing powders which contain an anti-caking agent. Ammonium Chloride Fine White E, Ammonium Chloride Fine White S and Ammonium Chloride Fine White U do not contain any anti-caking agent.

Ammonium Chloride Fine White RWN (Anti-caking agent: stearylamine), free-flowing powder: Applied in powder form, e.g. in the production of dry cell batteries, permitted explosives, in galvanizing and tin plating.

Ammonium Chloride Fine White RW (Anti-caking agent: boron trioxide), free-flowing powder: Applied in solution or slurry form, e.g. in the production of dry cell batteries. Used in cosmetic applications and in the manufacture of detergents and cleaners.

Ammonium Chloride Fine White RWS (Anti-caking agent: calcium phosphate, E 341), free-flowing powder: Flavouring additive for foodstuffs (subject to restrictions).

Ammonium Chloride Fine White U (With no anti-caking agent): Used in photographic applications, in the manufacture of permitted explosives, in the refining of noble metals, as a curing agent for aminoplast resins and in tannery application as a deliming agent.

Ammonium Chloride Fine White S (With no anti-caking agent): Flavouring additive for foodstuffs (subject to restrictions), auxiliary for pharmaceuticals [39].

3. MATERIALS AND METHODS

3.1 Materials and equipments

The major raw materials used during the experiment are analytical grade (AG) Ammonium solution, sodium chloride in the form of brine and dry ice. The ammonium solution (30 wt %) and sodium chloride (99.5% purity) were purchased from Neway chemical trading Plc. and the dry ice (99.9% purity) was purchased from Moha Plc at Addis Ababa.

The equipments used during the experimentations are Glass reactor equipped with mechanical stirrer, chiller, vacuum filter, vacuum evaporator, Centrifuge, drier, Bunsen burner, conical flask, balance, burette and testing drums.

3.2 Experimental Method

3.2.1 Characterization of sodium chloride (physicochemical properties)

3.2.1.1 Moisture content determination

10 g of sodium chloride sample was weighed into a tared moisture dish or weighing bottle and placed in an oven at a temperature of 105°C. 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 sodium chloride was calculated using the formula:

$$\%\text{Moisture content} = \left(\frac{(W_1 - W_2)}{W_1}\right) \times 100 \qquad (3.1)$$

Where W_1= original weight of the sample before drying;

W_2= Weight of the sample after drying.

3.2.1.2 Determination of insoluble matter

Exactly 50 g of the sample was placed in a 400-ml beaker and 250 ml of distilled water was added at room temperature. It was stirred with a glass rod until all the salt was dissolved and filtered through a tared Gooch crucible. The beaker was rinsed three times with 5-7 ml of water to bring all the insoluble on the filter. The residue on the filter was washed six times with 5-7 ml of distilled water each time, or until the filtrate is free from chloride. The residue was dried on an oven for an hour to constant weight at 105°C and finally the weight was taken and compared with the initially recorded weight.

The percentage weight in the sodium chloride was calculated using the formula:

$$\text{Percent insoluble matter (drybasis)} = \left(\frac{W_1}{W_2}\right) \times 100 \qquad (3.2)$$

Where W_1 = Weight of insoluble matter in the filter after drying;

W_2 = Weight of original sample on dry basis.

3.2.2 Saturated brine preparation and characterization

As per the literature information for saturated brine, 6.00 molar concentrations required 350.7g NaCl which dissolves in one liter of distilled water.

3.2.2.1 Determination of pH

The brine solution whose pH is determined is saturated solution of 6M; pH meter was used to measure the pH of saturated brine at 20^0C specified, where the pH meter was washed first by distilled water.

3.2.2.2 Determination of specific gravity

The sample was filled into graduated cylinder (100 ml) and its temperature was recorded. Hydrometer was used to measure the SG of the saturated brine at 20 °C specified. Hence, the density of the saturated brine is determined using the specific gravity.

$$\text{Specific gravity} = \frac{\text{density of brine}}{\text{density of water}} \qquad (3.3)$$

3.2.2.3 Determination of chloride ion ($\mathrm{Cl^-}$) content (Argentometric method)

25ml of filtered brine sample and blank was taken and then 0.2ml (4 drops) of potassium chromate (K_2CrO_4) indicator added. Both brine sample and blank was titrated with 0.0145N $AgNO_3$ until the color changes from yellow to brick red.

Milligram of chloride ion per liter of brine was calculated as:

$$(\mathrm{mgCl^-})^{-\mathrm{L}} = (\mathrm{V_S} - \mathrm{V_B}) \times \mathrm{C} \times 1000 \times \frac{35.45}{\mathrm{L\ of\ sample}} \tag{3.4}$$

Where, $\mathrm{V_S}$ − Volume of silver nitrate consumed for the sample(ml)

$\mathrm{V_B}$ − Volume of silver nitrate consumed for the blank(ml)

C − Concentration of silver nitrate used for the titration(N)

$35.45 =$ equivalent weight of $\mathrm{Cl^-}$

3.2.2.4 Determination of calcium ion ($\mathrm{Ca^{2+}}$) content (EDTA titrimetric method)

100ml of filtered brine sample was taken and 1.5ml of 1N NaOH (buffer) added to increase the pH to 12 to 13. $\mathrm{Ca^{2+}}$ Indicator (calconcarboxilic acid 0.2% in NaCl) was added until color developed, then titrated with 0.0001N EDTA until a blue color was obtained.

Milligram of calcium ion per liter of brine was calculated as:

$$(\mathrm{mgCa^{2+}})^{-\mathrm{L}} = \mathrm{V} \times \mathrm{C} \times 40.08 \times \frac{1000}{\mathrm{L\ of\ sample}} \tag{3.5}$$

Where,

V − Volume of EDTA consumed for the titration(ml)

C − concentration of EDTA

40.08 = formula weight of calcium

3.2.2.5 Determination of magnesium ion ($\mathrm{Mg^{2+}}$) content

Milligram of magnesium ion per liter of brine was calculated as:

$$(\mathrm{mg\ Mg^{2+}})^{-\mathrm{L}} = (\mathrm{V_H} - \mathrm{V_{Ca}}) \times \mathrm{C} \times 1000 \times \frac{24.32}{\mathrm{L\ of\ sample}} \tag{3.6}$$

$$(\text{Total hardness as } (\mathrm{mg\ CaCO_3})^{-\mathrm{L}} - \text{Calcium hardness as } (\mathrm{mg\ CaCO_3})^{-\mathrm{L}}) \times 0.243$$

Where, V_{H} – Volume of EDTA consumed for total hardness

V_{Ca} − Volume of EDTA consumed for calcium

C − Concentration of EDTA

24.32 = formula weight of magnesium

3.2.2.6 Determination of sulphate ion content ($SO_4{}^{2-}$) (gravimetric method with ignition of residue)

50ml of filtered brine sample was taken and diluted to 150ml and 2ml of 37%HCl added, then 5-7ml of 10%(10g/100ml) $BaCl_2.2H_2O$ was added (1ml = 40mg $SO_4{}^{2-}$ precipitate). It was heated at a plate heater by stirring using glass rod, when it became white turbid 1ml of more 37% HCl and 10%$BaCl_2$.$2H_2O$ was added and continued heating until it was boiled. When it started to boil, it was put at water bath for 2 hours.

The boiled solution was filtered, washed with cold and warm water .Crucible dish was taken and burnt in muffle furnace, cooled in a desiccator and weighed it. The filter paper with the residue was burnt at muffle furnace using the already weighed crucible dish at 800^{0}C, cooled at a desiccator and weighed.

Milligram of Sulphate ion per liter of brine was calculated as:

$$\left(\text{mg of } SO_4{}^{2-}\right)^{-L} = \text{mgBaSO}_4 \times 0.4116 \times \frac{1000}{\text{ml of sample}} \tag{3.7}$$

Where,

$$\text{mgBaSO}_4 = \text{Weight of(dish } + \text{residue)in gram} - \text{weight of empty dish in gram}$$

$$0.4116 = \frac{\text{Weight of } SO_4{}^{2-}}{\text{Weight of BaSO}_4} = \frac{96.06}{233.36}$$

3.2.3 Experimental design for ammonium chloride production

In these work the ammonium chloride was prepared using ammonium solution, sodium chloride, and solid carbon dioxide. Experimental design was analyzed and done by the Design-Expert 7.0.0 program.

The experimental design selected for this study is face centered Central Composite Design (CCD) and the response measured is the yield of ammonium chloride. Furthermore, the physicochemical analysis of the ammonium chloride was carried out in AAiT School of Chemical and Bio Engineering laboratory and deliming efficiency in leather processing was carried out in Leather Industry Development Institute (LIDI) model tannery.

Table 3.1 lists the range and levels of the three independent variables studied. The levels of the variables investigated are chosen by considering the operating limits of the ammonium chloride production process conditions.

A two-level-three-factor face centered CCD with two replicate each at the factorial and axial (star) points and three center runs was employed in the optimization study, requiring 31 experiments. The ammonium solution to saturated brine molar ratio, reaction time and reaction temperature were the independent variables selected to optimize the conditions for ammonium chloride production by laboratory scale modified Solvay process. The 31 experiments were carried out and data was statistically analyzed by the Design-Expert program to find the suitable model for the % yield of ammonium chloride as a function of the above three variables.

Table 3.1: Independent variables and levels used in the central composite design for the modified Solvay process chosen for this study

Variable (Factors)	Factor Coding	Unit	Levels		
			-1	0	+1
Reaction Temperature	X_1	^0C	10	15	20
Ammonium solution to saturated brine ratio	X_2	molar	1	2	3
Reaction time	X_3	hour	0.5	1	1.5

Table 3.2 Shows the complete experimental design matrix of face centered CCD for the factorial design (n Factors, each at two-level (minimum and maximum levels with center points)).The order in which the runs were made was randomized to avoid systematic errors.

Table 3.2: Face centered central composite design arrangement (Experimental design matrix)

Run	Coded Factor			Actual Factors		
	X_1	X_2	X_3	Reaction temperature (^0C)	Ammonium solution to saturated brine ratio (molar)	Reaction time (hr)
1	-1	-1	-1	10.00	1.00	0.50
2	0	+1	0	15.00	3.00	1.00
3	0	0	+1	15.00	2.00	1.50
4	-1	+1	+1	10.00	3.00	1.50
5	0	0	0	15.00	2.00	1.00
6	-1	+1	-1	10.00	3.00	0.50
7	-1	0	0	10.00	2.00	1.00
8	-1	+1	+1	10.00	3.00	1.50
9	0	0	+1	15.00	2.00	1.50
10	0	0	0	15.00	2.00	1.00
11	-1	-1	+1	10.00	1.00	1.50

Table 3.2 continued.

12	+1	+1	-1	20.00	3.00	0.50
13	+1	0	0	20.00	2.00	1.00
14	-1	0	0	10.00	2.00	1.00
15	+1	-1	-1	20.00	1.00	0.50
16	-1	-1	+1	10.00	1.00	1.50
17	-1	+1	-1	10.00	3.00	0.50
18	0	0	-1	15.00	2.00	0.50
19	+1	0	0	20.00	2.00	1.00
20	0	-1	0	15.00	1.00	1.00
21	+1	+1	-1	20.00	3.00	0.50
22	-1	-1	-1	10.00	1.00	0.50
23	0	0	0	15.00	2.00	1.00
24	0	0	-1	15.00	2.00	0.50
25	+1	-1	+1	20.00	1.00	1.50
26	+1	-1	+1	20.00	1.00	1.50
27	0	+1	0	15.00	3.00	1.00
28	+1	+1	+1	20.00	3.00	1.50
29	+1	+1	+1	20.00	3.00	1.50
30	0	-1	0	15.00	1.00	1.00
31	+1	-1	-1	20.00	1.00	0.50

3.2.4 Experimental setup

The batch ammoniated brine to dry ice reaction system employed in this work is shown schematically in Figure 3.1; Two liter glass reactor equipped with mechanical stirrer and chiller was used in all experiments. The reactor was connected to chiller which was capable of controlling the temperature to within deviation of 1°C. A mechanical stirrer fitted with stainless steel propeller provided the mixing requirement.

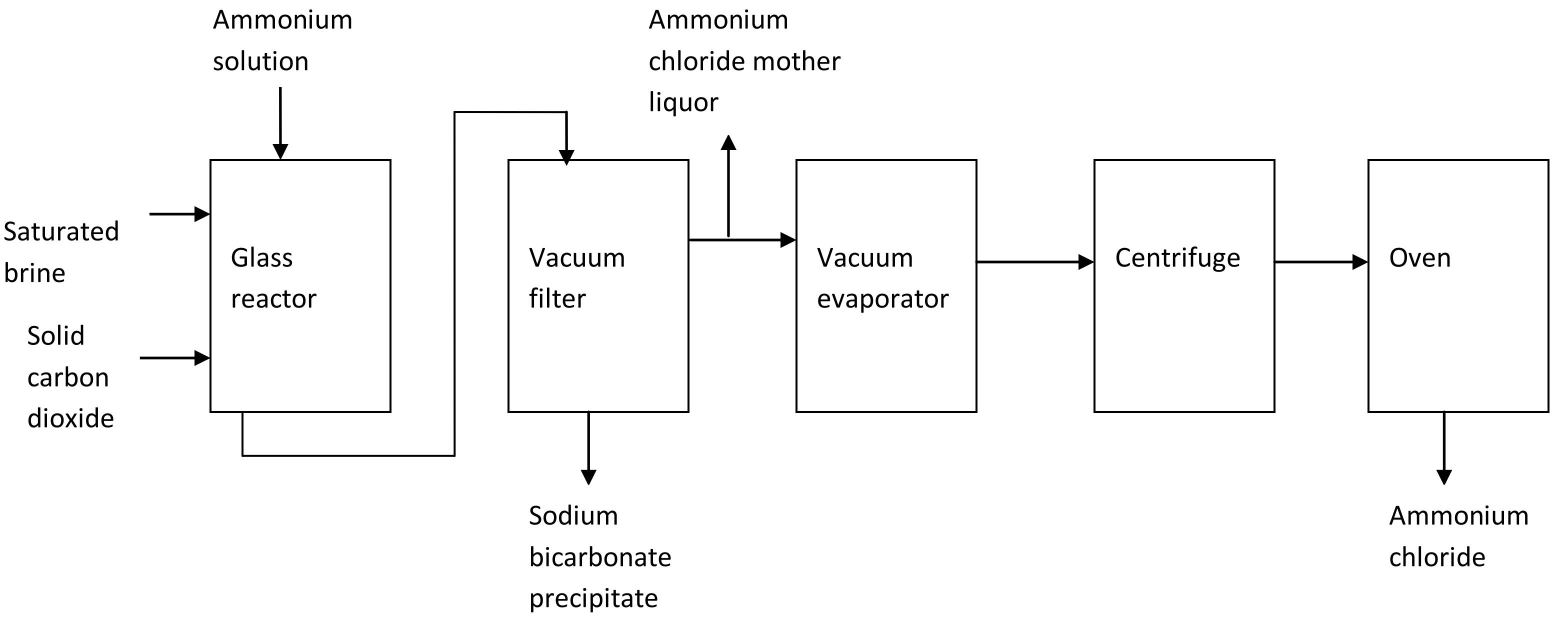

Fig 3.1.Schematic diagram of the experimental set-up for ammonium chloride production through brine ammoniation

3.2.5 Feed material requirement for ammonium chloride production

The following reaction is used to produce ammonium chloride using the modified Solvay process.

$$\mathrm{NaCl(aq) + NH_4OH(aq) + CO_2(s) \rightarrow NH_4Cl(aq) + NaHCO_3(s)} \qquad (3.10)$$

The reaction proceeds through the following two steps:

$$\mathrm{NH_4OH + CO_2 \rightarrow NH_4HCO_3} \qquad (3.11)$$

$$\mathrm{NaCl + NH_4HCO_3 \rightarrow NH_4Cl + NaHCO_3} \qquad (3.12)$$

According to experimental thermodynamic analysis in a semi-batch reactor made by El-Naas, 2010. For its high negativeΔH and ΔG reaction (3.10) is an exothermic reaction that takes place as soon as the carbon dioxide gets in contact with the ammoniated brine. Once ammonium bicarbonate is formed, it reacts with sodium chloride according to reaction (3.12). From the thermodynamic table showing the thermodynamic data of reaction (3.11) and (3.12) in appendix

E, reaction (3.12) is not as spontaneous as reaction (3.11) and it is believed to be the rate limiting step.

For 65g of sodium chloride, 60g of dry ice feed to a batch reactor according to reaction (3.10); the limiting reagent for this reaction was calculated to be sodium chloride which gave the lesser theoretical yield of ammonium chloride (60g NH_4Cl). The calculation of the limiting reactant and the theoretical yield is given in appendix E.

Assuming 100% conversion from the reaction stochiometry, to produce 60g theoretical yield of ammonium chloride per single batch, 186ml of saturated brine and 60g of crushed dry ice required however experimentally this was optimized using different process parameters of reaction temperature, molar ratio of ammonium solution to saturated brine and reaction time.

60g of dry ice and 186ml of saturated brine was used for each run. Hence, the amount of ammonium solution was calculated as follows using the process parameters.
The amount of ammonium solution required when ammonium solution to saturated brine molar ratio 2:1;

$$\frac{\text{mole of Ammonium solution}}{\text{mole of Saturated brine}} = 2 \qquad (3.13)$$

Substituting mass for mole;

$$\frac{\frac{\rho_{\text{ammonium solution}} \times V_{\text{ammonium solution}}}{M_{\text{ammonium solution}}}}{\frac{\rho_{\text{brine}} \times v_{\text{brine}}}{M_{\text{brine}}}} = 2$$

$$\frac{\frac{0.9\text{g/ml} \times v_{\text{ammonium solution}}}{35\text{g/mol}}}{\frac{1.2\text{g/ml} \times 186\text{ml}}{29.81\text{g/mol}}}$$

Solving for $V_{\text{ammonium solution}} = 583\text{ml}$

Similarly, the amount of ammonium solution is calculated for all experiments. The tabulated result for different processes parameter was given in appendix C.

3.2.6 Ammonium chloride production procedure

According to the molar ratio of ammonium solution to saturated brine selected for the specified experimental run, the calculated volume of ammonium solution is added to186 ml of saturated brine containing glass reactor for ammoniated brine preparation, then after 20 minutes of mixing until the solution saturates at 40^0C , 60 g of crushed dry ice was added and reacted for 0.5hr, 1hr and 1.5 hr at a temperature of 10^0C ,15^0C and 20 ^{0}C and molar ratio of ammonium solution to saturated brine 1, 2 and 3 according to the factors selected for each run based on the design matrix. The reaction was timed as soon as mechanical stirrer was turned on.

After the completion of the reaction, sodium bicarbonate precipitate was filtered using vacuum filter; the ammonium chloride filtrate was evaporated in vacuum evaporator at a temperature of 80^oC to remove water and cooled to crystallize and then centrifuged for an hour. The cake which is moist ammonium chloride containing 5 – 7wt. % moisture was collected and dried in an oven at 105^oC for half an hour to a level less than 1wt. % moisture.

The end product, ammonium chloride was obtained as a clear white crystalline solid. These procedures are used for each experiments executed at different parameters using the experimental design matrix.

3.2.7 Methods for ammonium chloride characterization (physico-chemical properties of ammonium chloride)

Standard procedure was used to characterize the Physico-chemical properties of ammonium chloride. The method was given in Table 2.4 and they are discussed as follows.

3.2.7.1 Determination of moisture, ISTM A-3

The sample to be tested was mixed well by shaking the bottle several times and transferred a portion immediately to a wide-mouth bottle and stoppers it. Care was taken that no pieces of cork or sealing wax get mixed with the material and it was also made sure that the prepared sample do not exposed to an atmosphere containing acid or alkaline fumes.

The prepared sample was weighed accurately about 5 g in a weighed shallow porcelain dish and dried for 24 hours in vacuum desiccator over sulphuric acid and reweighed. The dried material was preserved for subsequent test.

The percentage weight of moisture was calculated using the formula:

$$\text{Moisture, percent by weight} = \left(\frac{W_1}{W_2}\right) \times 100 \tag{3.14}$$

Where,

W_1= loss in weight in g on drying, and

W_2= weight in g of the prepared sample taken for the test.

3.2.7.2 Determination of ammonium chloride, ISTM A-4

Fig 3.2 Experimental set up for ammonium chloride determination

The apparatus as assembled is shown in Fig. 3.2. It consists of a flask of 1000ml capacity fitted with a rubber stopper through which passes one end of the connecting tube. The other end of the tube is connected to the condenser by a rubber stopper and the lower end of the condenser is attached by means of rubber tubing to a dip tube which dips into a beaker of 250 ml capacity.

The reagents used for the determination of ammonium chloride were standard sulphuric acid -0.1 N**,** Methyl Red Indicator Solution where 0.15 g of methyl red is dissolved in 500 ml of water, calcium oxide and Standard Sodium Hydroxide Solution 0.1 N.

0.2 g of the dried material was weighed accurately (section 3.2.7.1) and transferred to a beaker and dissolved in about 20 ml of water and the solution was transferred to the distillation flask and about 500 ml of water was added. The apparatus was assembled as shown in Fig 3.2 with the tip of the dip tube dipping in dilute sulphuric acid contained in the beaker to which a few drops of methyl red indicator have been added. 10 g of calcium oxide was added to the distillation flask and distilled at least one third of the total volume of the liquid in the flask to ensure complete distillation. The beaker was lowered until the end of the dip tube is out of the dilute sulphuric acid.

The burner was shut off and when the flask became cool, it was detached from the condenser and the condenser was rinsed thoroughly with water into the beaker. Two or three drops of methyl red indicator was added and titrated with standard sodium hydroxide solution.

A blank test was carried out using all the reagents in the same quantities but without the material.

The ammonium chloride, percent by weight (on dry basis) was calculated using the formula:

$$\text{Ammonium chloride, percent by weight(on dry basis)} = \frac{5.350\ (\mathrm{B}-\mathrm{A})\ \mathrm{N}}{\mathrm{W}} \qquad (3.15)$$

Where,

B = volume in ml of standard sodium hydroxide solution used in the blank determination,
A = volume in ml of standard sodium hydroxide solution used in the test with the material,
N = normality of standard sodium hydroxide solution, and

W = weight in g of the dried material taken for the test.

3.2.7.3 Determination of sulphates [as $(NH_4)_2SO_4$], ISTM A-6

The reagents used for the determination of Sulphates were dilute hydrochloric acid approximately 5 N, barium chloride solution approximately 10% and standard Sulphate solution where 1g of ammonium Sulphate dissolved in water and make up the volume to 1000ml. 10ml of this solution pipetted and again diluted to 100ml. 1ml of the solution contains 0.1mg of Sulphate[as $(NH_4)_2SO_4$].

1g of the material was dissolved in sufficient quantity of water and make up the volume to 100ml. 30ml of this solution transferred to a Nessler tube, and 1ml of dilute hydrochloric acid added. A control test was carried out in another Nessler tube using 3ml of standard Sulphate solution and 1ml of dilute hydrochloric acid. 1ml of barium chloride solution was added to both the tubes and make up the volume to 50ml. The turbidity produced was compared after 5 minutes.

The limit prescribed in table 2.6 shall be taken to be as not having been exceeded if the turbidity produced in the test with the material is not greater than that produced in the control test.

3.2.7.4 Determination of pH, ISTM A-8

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

3.2.7.5 Determination of insoluble matter in water, ISTM A-9

20 g of the material was weighed accurately, dissolved in 150 ml of water and heated on a water-bath for about an hour. A filter paper was taken and washed it well with water, dried to constant weight at 105°C**.**

Any insoluble matter was filtered, washed it with water and dried at 105^0C±2°C to constant weight.

Matter insoluble in water, percent by weight was calculated using the formula:

$$\text{Matter insoluble in water}\,,\text{percent by weight} = \frac{W_1}{W_2} \times 100 \qquad (3.16)$$

Where,

W1 = weight in g of the residue, and

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

3.2.7.6 Determination of specific gravity (Density)

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

$$\text{Then density of ammonium chloride} = \frac{m_{NH_4Cl}}{V_{NH_4Cl}} \quad (3.17)$$

3.2.7.7 Determination of deliming value

According to the definition given by BASF/leather, deliming value is the amount of deliming agent in gram necessary for neutralizing 1g calcium hydroxide.

1.910Kg of ammonium chloride (100%) required for neutralizing 1kg calcium oxide (BASF, 4th edition).

Therefore, the deliming value of ammonium chloride can be calculated as:

$$\text{Deliming value} = 1.910 + (1.910 - \%NH_4Cl \times 1.910) \quad (3.18)$$

3.2.8 Application of ammonium chloride synthesized on leather processing and determination of leather physico - chemical properties

Six goat skins was soaked in a test drum to remove dirt and salt, limed to remove the hair or wool from the skin and to swell and plump the collagen fiber and fibrils, fleshed in a fleshing machine to remove the grease and hypodermic tissue. The skin after fleshing is called pelt.

Four pelts out of the six were splited along the spinal cord and four pieces each was taken in a two separate testing drums for the control deliming agent test (0.5% ammonium chloride (standard), 0.5% sodium bisulphide) and the other drum tested by (0.5% ammonium chloride (synthesized), 0.5% sodium bisulphide) and the remaining two unsplited pelts were tested in the third testing drum by 1% ammonium chloride which was synthesized.

Table 3.3 Chemical dosages for test of ammonium chloride on leather

Testing drum	Weight of the pelt (kg)	Amount of deliming agent used (g)
1	3.75	Control: $0.5\%\ \text{standard ammonium chloride} = 18.75$ $0.5\%\ \text{sodium bisulphide} = 18.75$
2	3.75	Test: $0.5\%\ \text{ammonum chloride(synthesized)} = 18.75$ $0.5\%\ \text{sodium bisulphide} = 18.75$
3	2.6	Test: $1\%\ \text{Ammonium chloride(synthesized)} = 26$

N.B The percentage is based on the weight of the pelt.

Fig 3.3 Pelts after liming and fleshing

The pelts after liming and fleshing was delimed in three testing drums based on the pelt weight as explained in Table 3.2 to remove the lime introduced during liming, reduce the plumping and to reduce the pH near to the bating pH range requirement (pH 7-9). Initially after deliming for 45minutes in a drum, float pH was checked by litmus paper and compared with the float pH of the liming drum.

Fig 3.4 Testing drum

Right after the liming and deliming operations, pH of both the liming and the deliming float was checked using litmus paper to control the extent of pH lowered from the high alkaline pH of liming operation to relatively lower deliming pH. However this result must be supported by standard laboratory analysis as set by IULTCS, therefore samples were taken from the butt portion of each pieces of pelts in the three testing drums and coded. pH test after liming and deliming was carried out to compare the extent of deliming with respect to pH in the pelt.

3.2.8.1 Determination of pH, IUC 11/SLC 13

The pH was determined for pelt samples before and after deliming using IUC 11/SLC 13 standard testing methods.

5g of the prepared pelt samples was transferred into wide-necked flasks; 100ml of water was added at 20^0C, the cap was secured and shaked well by hand for about 30 seconds to wet the leather powder thoroughly. The flask was fitted into the shaker and shaked continuously for 24 hours at 20^0C.The pH value of the aqueous extract was determined using pH meter by washing the electrodes after each determination.

After deliming operation was completed in the testing drums, the subsequent operations of bating, pickling, tanning, retanning, fatliquoring and fixation were carried out in a single drum to know effect of the ammonium chloride synthesized on the Physico- chemical properties of crust leather assuming variables of the subsequent operations constant. Crust leather is higher added value skin and hides already tanned and ready for the finishing stage. The semi-tanned wet-blue leather undergo final tanning to produce crust leather. The distinct feature of this product from the wet-blue leather is that it has visible physical properties such as size, thickness, fullness, looseness of grain and grain damages.

3.2.8.2 Determination of water soluble inorganic matter, IUC 6/SLC 5

The water soluble inorganic matter determination is applied to all types of leather as described in IUC 6 / SLC 5 standard testing method.

2.5g of the sample was weighed to the nearest 0.001g and it was carefully carbonized over a low flame in a crucible which had been previously heated to 750^0C. The fatliquored crust leather was carbonized carefully so that the grease burns very slowly. Then moistened thoroughly with 2N sulphuric acid solution and heated over a low flame until sulphur trioxide fumes are no longer visible. It was heated more vigorously and ignited in the furnace at 750^0C until completely ashed. It was cooled in a desiccator and weighed.

$$\text{water} - \text{soluble inorganic matter, percentage by mass} = 100\frac{\mathrm{M_2}}{\mathrm{M_0}}$$

Where, $\mathrm{M_2}$ the mass of sulphated residue from ignition;

and $\mathrm{M_0}$ is the mass of the origional sample of leather.

3.2.8.3 Determination of shrinkage temperature, ISO 3380:2005

The shrinkage temperature of the wet blue leather was determined using ISO 3380:2005 standard testing method.

A rectangular specimen $50\text{mm} \times 12\text{mm}$ was taken and punched a 3mm hole from each short side on a line parallel to an equidistant from the long sides. The sample was attached to hooks in the shrinkage temperature measuring device which is equipped with thermometer. The water in the device was heated using Bunsen burner at a rate of 2^{o}C/minute. The pointer which indicates the original position of the specimen was observed and noted the temperature at which the specimen has shrunk to such an extent so as to move the pointer half a division from the position corresponding to the maximum length of the specimen. This temperature was taken as the shrinkage temperature and was recorded to the nearest degree.

3.2.8.4 Determination of tensile strength, ISO 3376:2002

The tensile strength of the crust leather was determined using ISO 3376:2002 standard testing method.

The width and the thickness of the specimen were measured to the nearest tenth of a millimeter and the cross sectional area of a specimen was calculated by multiplying its width by its thickness. The tensile strength measuring machine was run until the specimen breaks and take the highest load reached as the breaking load. The tensile strength was calculated by dividing the breaking load by the area of cross-section of the specimen.

$$\text{Tensile strength} = \frac{\text{breaking load}}{\text{cross−sectional area}} \tag{3.19}$$

4. RESULT AND DISCUSSION

4.1 Sodium chloride and saturated brine characterization

4.1.1 Moisture content determination

Table 4.1 Moisture content determination

Run	Sample weight (g)				Average sodium chloride moisture content (%w/w)
	Weight of the sample before drying	Weight of the sample after drying	Difference (before and after drying)	Moisture content (%w/w)	
1	10.010	9.990	0.020	0.199	0.2%
2	10.002	9.980	0.022	0.220	
3	10.006	9.986	0.020	0.199	
4	10.004	9.984	0.020	0.199	
5	10.001	9.981	0.020	0.199	
6	10.005	9.985	0.020	0.199	

The standard moisture content requirement of sodium chloride (Table 2.2) is 0.2wt. % and the average moisture content obtained experimentally as shown in the table above is 0.2wt. % which is acceptable result.

4.1.2 Determination of insoluble matter

Table 4.2 Determination of insoluble matter

Run	Sample weight(g)			Average sodium chloride insoluble matter content(%w/w)
	Weight of the sample before drying	Weight of insoluble matter on the filter after drying	Insoluble matter content on dry basis(%w/w)	
1	50.020	0.008	0.016	0.01%
2	50.001	0.006	0.012	
3	50.012	0.005	0.010	

Table 4.2 Continued.

4	50.003	0.004	0.008
5	50.013	0.004	0.008
6	50.015	0.007	0.014

The standard insoluble matter content requirement of sodium chloride (table 2.2) is 0.05 wt. % and the average insoluble matter content obtained experimentally as shown in the table above is 0.01wt. % which is acceptable result.

4.1.3 Physico- Chemical Properties of saturated brine

The specific gravity, density, pH, chloride ion, calcium ion, magnesium ion and sulphate ion contents of the saturated brine were determined and the results are given in Table 4.3.
The specific gravity and pH of saturated brine was in agreement with the value found in literature [21, 22].

Table 4.3 Physico - chemical properties of saturated brine

Property	Experimental result	unit
Specific gravity	1.2	-
Density	1.2	g/ml
pH	9	-
Chloride ion	181	g/L
Calcium ion	0.12	g/L
Magnesium ion	0.05	g/L
Sulphate ion	2.96	g/L

The ion contents of saturated brine were in agreement with the result reported by IPPC, BAT reference document (approved by European soda ash producers association, 2004) as given in appendix A and the calculation of the experimental result is given in appendix E.

4.2 Analysis on ammonium chloride production

The brine ammoniation reaction was carried out using a 2L capacity glass reactor which is equipped with a stirrer and chiller. The statistical analysis of the Ammonium chloride was discussed below.

4.2.1 Statistical analysis on factors affecting ammonium chloride yield

The central composite design conditions and response, and the statistical analysis of the ANOVA are given in Tables 4.4 and 4.5, respectively. The multiple regression coefficients were obtained by employing a least square technique to predict a quadratic polynomial model for the ammonium chloride yield (Table 4.5). The actual yield of ammonium chloride at different process parameters was calculated and is given in appendix c.

The model was tested for adequacy by analysis of variance. The regression model was found to be highly significant with the correlation coefficients of determination of R-Squared (R^2), adjusted R-Squared and predicted R-Squared having a value of 0.9996, 0.9994 and 0.9991, respectively.

Table 4.4: Experimental and predicted values of ammonium chloride yield

Run	Reaction Temperature (^{0}C)	Molar ratio of ammonium solution to brine	Reaction time (hr)	Experimental Ammonium chloride Yield Value (%)	Predicted Ammonium chloride Yield Value (%)	Residual
1	10.00	1.00	0.50	83	83.11	-0.11
2	15.00	3.00	1.00	69	68.92	0.08
3	15.00	2.00	1.50	88.7	88.79	-0.09
4	10.00	3.00	1.50	80.5	80.41	0.09
5	15.00	2.00	1.00	90.2	89.53	0.67
6	10.00	3.00	0.50	65.2	65.08	0.12
7	10.00	2.00	1.00	92	92.28	-0.28
8	10.00	3.00	1.50	80.3	80.41	-0.11

Table 4.4 Continued.

9	15.00	2.00	1.50	88.5	88.79	-0.29
10	15.00	2.00	1.00	89.8	89.53	0.27
11	10.00	1.00	1.50	88	88.17	-0.17
12	20.00	3.00	0.50	46.3	46.39	-0.09
13	20.00	2.00	1.00	71.8	71.98	-0.18
14	10.00	2.00	1.00	92.5	92.28	0.22
15	20.00	1.00	0.50	76.5	76.65	-0.15
16	10.00	1.00	1.50	88.4	88.17	0.23
17	10.00	3.00	0.50	65	65.08	-0.08
18	15.00	2.00	0.50	86.3	86.32	-0.02
19	20.00	2.00	1.00	71.5	71.98	-0.48
20	15.00	1.00	1.00	87.5	87.94	-0.44
21	20.00	3.00	0.50	46.6	46.39	0.21
22	10.00	1.00	0.50	83.2	83.11	0.09
23	15.00	2.00	1.00	90	89.53	0.47
24	15.00	2.00	0.50	86	86.32	-0.32
25	20.00	1.00	1.50	66.3	66.28	0.02
26	20.00	1.00	1.50	66.4	66.28	0.12
27	15.00	3.00	1.00	68.5	68.92	-0.42
28	20.00	3.00	1.50	45.72	46.26	-0.54
29	20.00	3.00	1.50	47	46.26	0.74
30	15.00	1.00	1.00	88	87.94	0.06
31	20.00	1.00	0.50	77	76.65	0.35

The yield of the brine ammoniation processes was calculated as the ratio of the actual yield to theoretical yield which is calculated as based on the reaction stochiometry assuming complete conversion of the limiting reactant sodium chloride, multiplied by 100. The formula is given as:

$$\text{Yield} = \frac{\text{Amount of product(g) obtained experimentally}}{\text{Amount of product(g) calculated stochiometrically}} \times 100 \qquad (4.1)$$

4.2.1.1 Development of regression model equation

The model equation that correlates the response (% yield of NH_4Cl) to the brine ammoniation process variables in terms of coded value after excluding the insignificant terms was given below. The predicted model for percentage of ammonium chloride yield (R) in terms of the coded factors is given by Eq. 4.3.

$$\begin{aligned}\text{yield of ammonium chloride}(\%) &= +89.53 - 10.15 * \mathrm{A} - 9.51 * \mathrm{B} + 1.24 * \mathrm{C} - 3.06 * \mathrm{A} * \mathrm{B} - 3.86 * \mathrm{A} * \mathrm{C} \\ &+ 2.56 * \mathrm{B} * \mathrm{C} - 7.40 * \mathrm{A}^2 - 11.10 * \mathrm{B}^2 - 1.98\mathrm{C}^2 \qquad (4.2)\end{aligned}$$

Where A = reaction temperature
B = molar ratio of ammonium solution to saturated brine
C = reaction time

4.2.1.2 Model adequacy check

A line of unit slope, i.e. the line of perfect fit with points corresponding to zero error between predicted values and actual values are also shown in Figure 4.1. This plot therefore, shows the performance of the correlation in an obvious way.

The results in Figure 4.1 demonstrated that the regression model equation provided a very accurate description of the experimental data, in which all the points are very close to the line of perfect fit. This result indicates that it was successful in capturing the correlation between the three brine ammoniation process variables to the yield of ammonium chloride.

The adequacy of the model was further checked with analysis of variance (ANOVA) as shown in Table 4.5. Based on a 95% confidence level. 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 likely that any of the factors have a significant effect on the response with the P-value less than 0.05. It is calculated by model mean square divided by residual mean square. Here the model F-value of 5192.39 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.

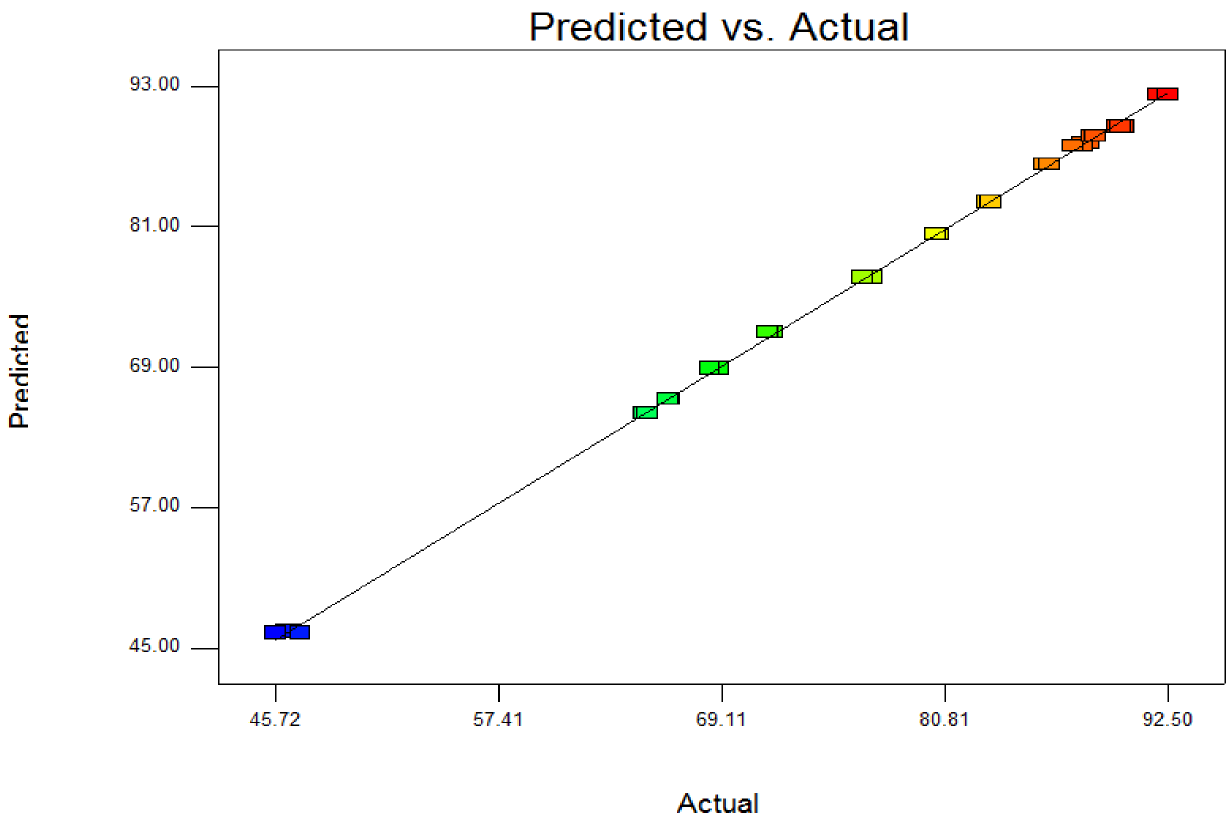

Fig 4.1: Predicted versus actual yield of ammonium chloride

Table 4.5: Analysis of variance (ANOVA) for the regression model equation and coefficients

Source	Sum of Squares	df	Mean Square	F Value	p-value Prob > F	Remark
Model	6420.23	9	713.36	5192.39	< 0.0001	**
A-Reaction Temperature	2060.04	1	2060.04	14994.63	< 0.0001	**
B-ammonium solution to saturated brine ratio	1808.42	1	1808.42	13163.12	< 0.0001	**
C-reaction time	30.55	1	30.55	222.40	<0.0001	*
AB	149.94	1	149.94	1091.38	<0.0001	**
AC	238.55	1	238.55	1736.34	<0.0001	**
BC	105.17	1	105.17	765.47	<0.0001	*
A^2	285.84	1	285.84	2080.59	<0.0001	*
B^2	642.95	1	642.95	4679.91	< 0.0001	*
C^2	20.41	1	20.41	148.57	<0.0001	
Residual	2.89	21	0.14			
Lack of Fit	1.19	5	0.24	2.23	0.1012	not significant
Pure Error	1.70	16	0.11			
Cor Total	6423.11	30				

Where * significant, ** highly significant

The Values of "Prob > F" less than 0.0500 indicate model terms are highly significant. In this case A, B, C, AB, AC, BC, A^2, B^2 and C^2 are significant model terms. Values greater than 0.1000 indicate the model terms are not significant.

This shows that the temperature, ammonium solution to saturated brine molar ratio, interaction between temperature and molar ratio, interaction between molar ratio and time , the interaction between reaction temperature and time and the square of temperature and molar ratio affects the yield much significantly. Thus, from these statistical tests, it was found that the model is adequate for predicting the yield of ammonium chloride within the range of variables studied.

The "Lack of Fit F-value" of 2.23 implies the Lack of Fit is not significant relative to the pure error. There is a 10.12% chance that a “Lack of fit F-value” this large could occur due to noise. Non-significant lack of fit is good because we want the model to fit.

4.2.2 Effect of brine ammoniation process variables

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

4.2.2.1 Effect of individual process variables

Figure 4.2 shows the effect of reaction temperature on the yield of the brine ammoniation reaction. It can be seen that with decreasing reaction temperature, increases the yield. As seen in Figures 4.2, the yields of ammonium chloride were increased significantly.

The increase in the yield of ammonium chloride at lower reaction temperature is due to higher dissolution of ammonia with in brine solution and higher absorption of carbon dioxide gas with in ammoniated brine at lower temperature. As shown from the reaction kinetic analysis done, in appendix D, the reaction rate is strongly influenced by reaction temperature. At optimum reaction conditions, higher rate constant was observed at lower temperature, this will lead to higher rate of reaction and eventually higher ammonium chloride yield.

The brine ammoniation reaction is basically diffusion controlled. Higher reaction temperature does not favor the forward reaction. The loss of ammonia during carbon dioxide absorption in the reactor at higher temperature might cause lower conversion of the reacting mixture that will lead to slower rate of reaction.

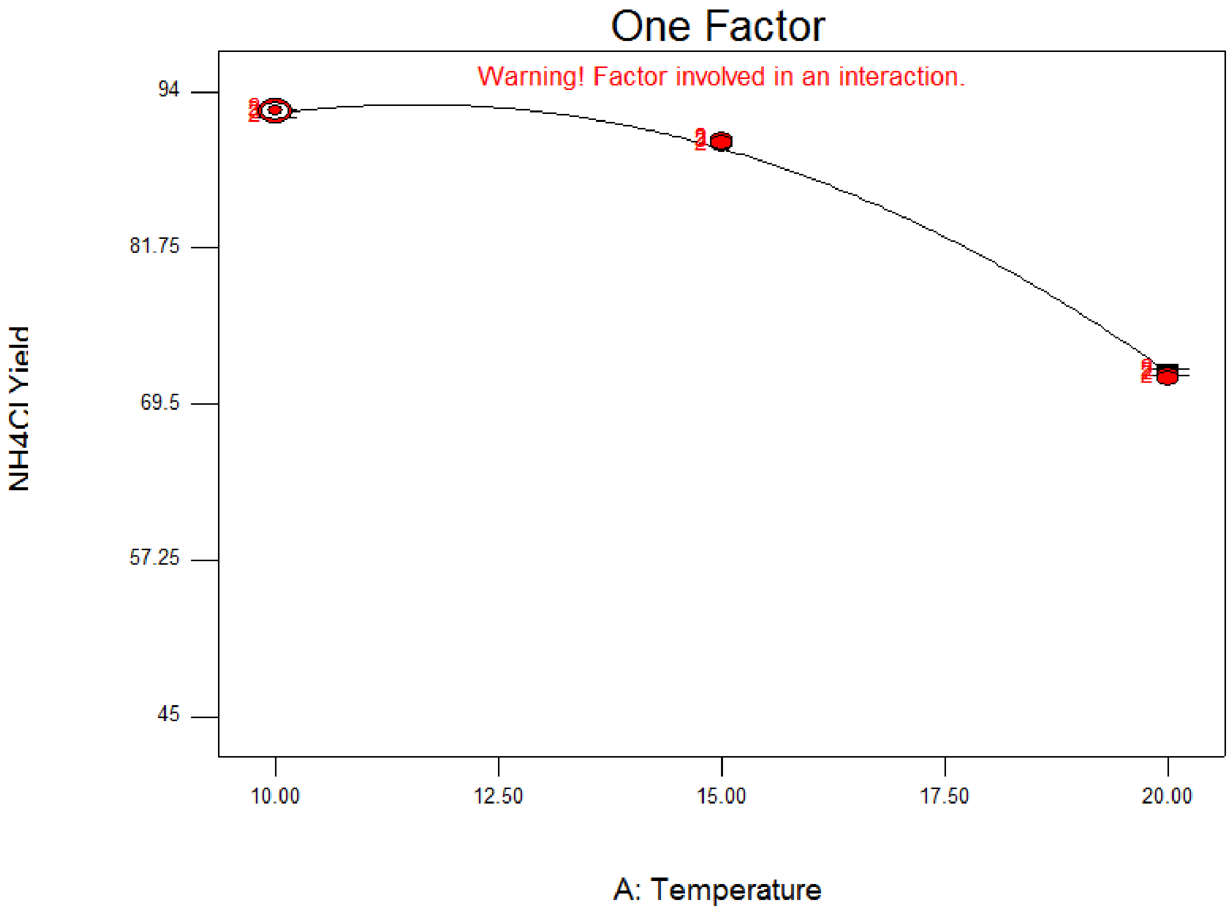

Fig 4.2: Ammonium chloride yield versus reaction temperature at ammonium solution to saturated brine molar ratio of 2 and 1 hr reaction time.

The brine ammoniation reaction consists of a sequence of two consecutive irreversible reactions where the ammoniated brine reacted with carbon dioxide to form ammonium bicarbonate and the ammonium bicarbonate further react with sodium chloride to produce ammonium chloride and sodium bi carbonate.

The ratio of ammonium solution to brine is one of the important factors that affect the conversion of ammoniated brine and carbon dioxide to ammonium chloride. Stiochiometrically, one moles of ammonia is required for each mole of sodium chloride, but in practice, a higher molar ratio is required in order to drive the reaction towards completion and produce more ammonium chloride as main product and sodium bicarbonate as a co-product.

The results obtained in this study are in agreement with this, as shown in Figure. 4.3, where at higher ammonium solution to saturated brine molar ratio, the ammonium chloride yield was increased to maximum. Higher and optimal ratio of ammonium solution to saturated brine used could also compensate for the ammonia loss in the rising carbon dioxide gas during carbonation, Besides that, an increase in the ratio of ammonium solution could also lead to the increase in the purity of the ammonium chloride layer which would also be responsible for the observed increased in ammonium chloride yield.

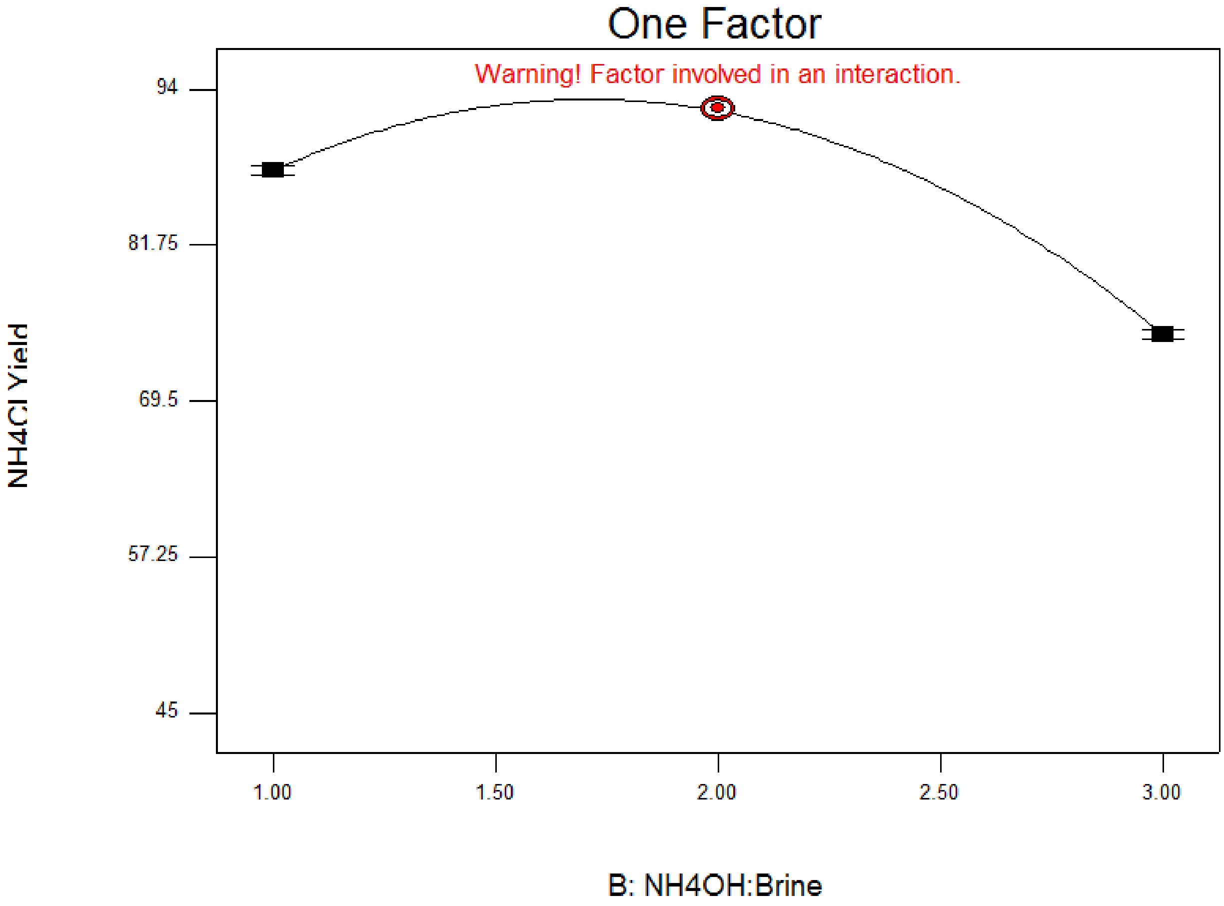

Fig 4.3: Ammonium chloride yield versus ammonium solution to brine ratio at reaction temperature of 10^0C and 1 hr reaction time.

Figure 4.4 below illustrates the effect of reaction time on ammonium chloride yield. When the reaction time was improved from 0.5 hr to 1 hr, the gas liquid contact of ammoniated brine with carbon dioxide was sufficient to react where by increasing ammonium chloride yield.

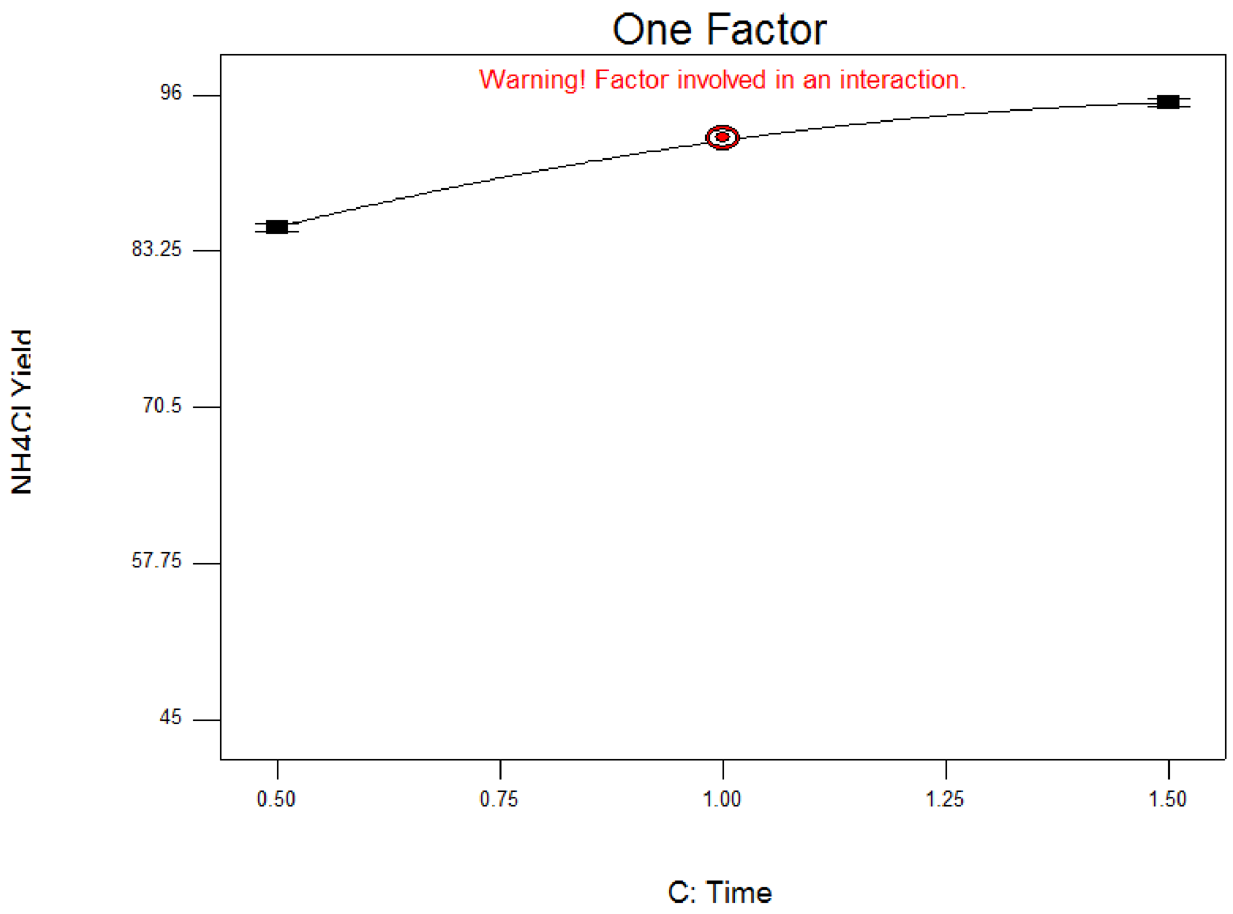

Fig 4.4: Ammonium chloride yield versus reaction time at reaction temperature of 10^0C and ammonium solution to brine ratio of 2.

As shown from Fig. 4.2, 4.3 and 4.4 above the effect of one factor is not sufficient in describing the effects the parameters have on the yield of ammonium chloride. This implies that the interactions between the brine ammoniation reaction parameters were also found significant. This result agrees with the ANOVA output for the regression model equation and coefficients.

4.2.2.2 Effect of Interaction between Process Variables

The process variables were found to have significant interaction effects. Figure 4.5, 4.7 and 4.9 show the interaction between ammonium solution to brine molar ratio and reaction temperature, ammonium solution to brine ratio and reaction time and reaction temperature to reaction time, respectively, on the yield of ammonium chloride.

Generally, a decrease in reaction temperature is found to increase the yield of ammonium chloride in all three cases. This is due to similar explanation given in the previous section.

Another notable observation is that at higher range of reaction temperature, lower reaction time and lower ratio of ammonium solution to brine, always resulted in ammonium chloride yield higher than when using higher ratio of ammonium solution to brine and higher reaction time.

However, at lower range of reaction temperature, totally opposite is observed. Reactions carried out using higher ratio of ammonium solution to brine and optimal reaction time is found to have higher yield as compared to reactions using, lower ratio of ammonium solution to brine and lower reaction time.

The former observation can be easily explained as optimal reaction period will ensure the brine ammoniation reaction goes to completion; excess ammonium solution will drive the reaction forward and lower reaction temperature used will increase the separation efficiency of sodium bicarbonate from ammonium chloride mother liquor which in turn increases the yield.

However, at higher range of reaction temperature, the observations showed that using a combination of both, higher reaction temperature and higher ratio of ammonium solution to brine or higher reaction time used is not beneficial in increasing the yield of ammonium chloride.

This is probably because at these conditions, the higher reaction temperature is already not sufficient to push the reaction forward.

This phenomena is further supported by the fact that reaction temperature is the most significant process variable that affect the yield of the ammonium chloride as indicated by the highest F value in the ANOVA (Table 4.5).
The RSM was used to optimize the conditions of conversion of the reacting mixtures of ammonium solution, saturated brine and solid carbon dioxide for ammonium chloride production and to understand the interaction of the factors affecting ammonium chloride production. Figures

4.5, 4.7 and 4.9 show surface plots between the independent and dependent variables for different fixed parameters.

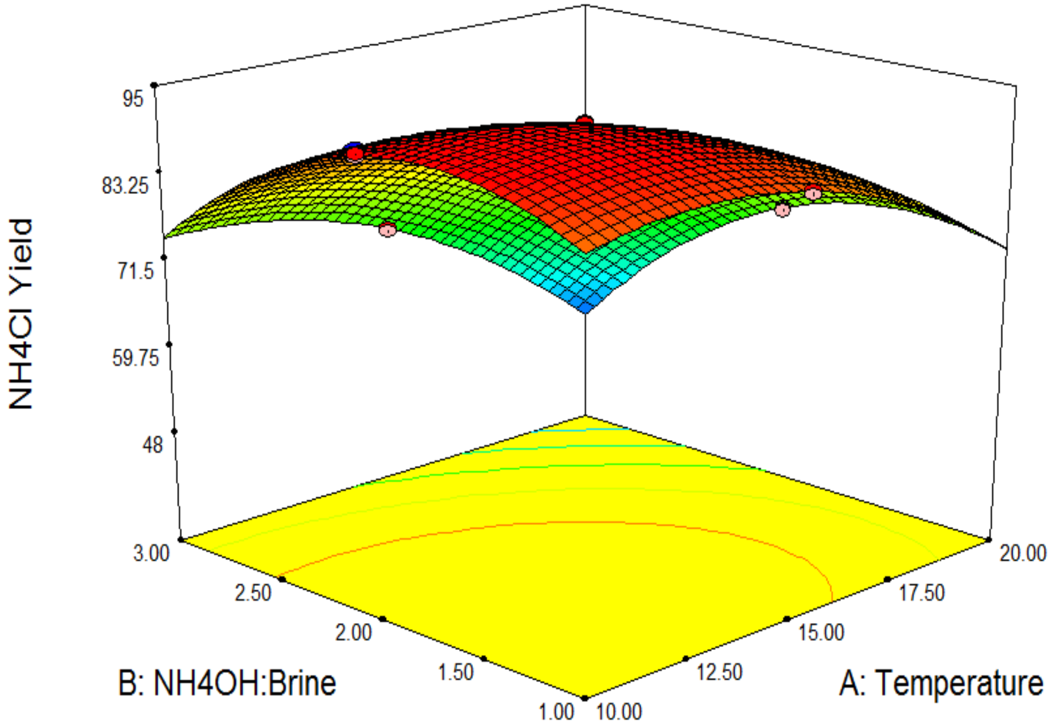

Fig 4.5: Surface plot of the interaction effect of ammonium solution to brine ratio and reaction temperature versus yield when the reaction time is 1 hr.

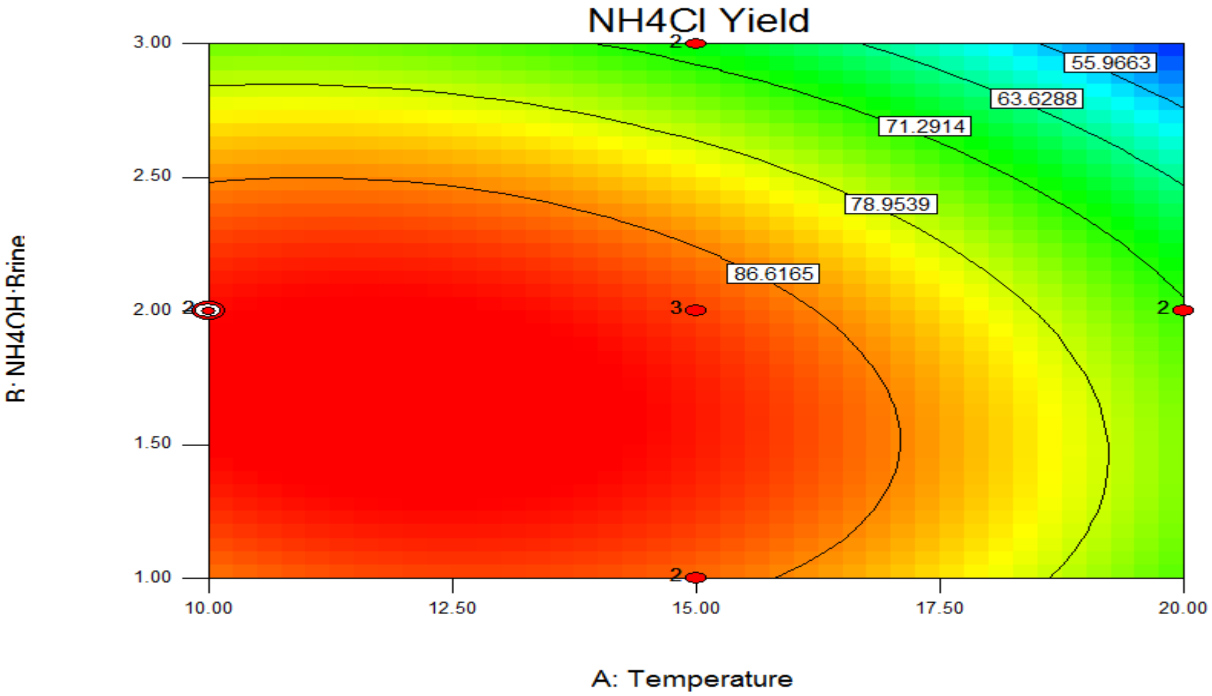

Fig 4.6: Contour plot of the interaction effect of ammonium solution to brine ratio and reaction temperature versus yield when the reaction time is 1 hr.

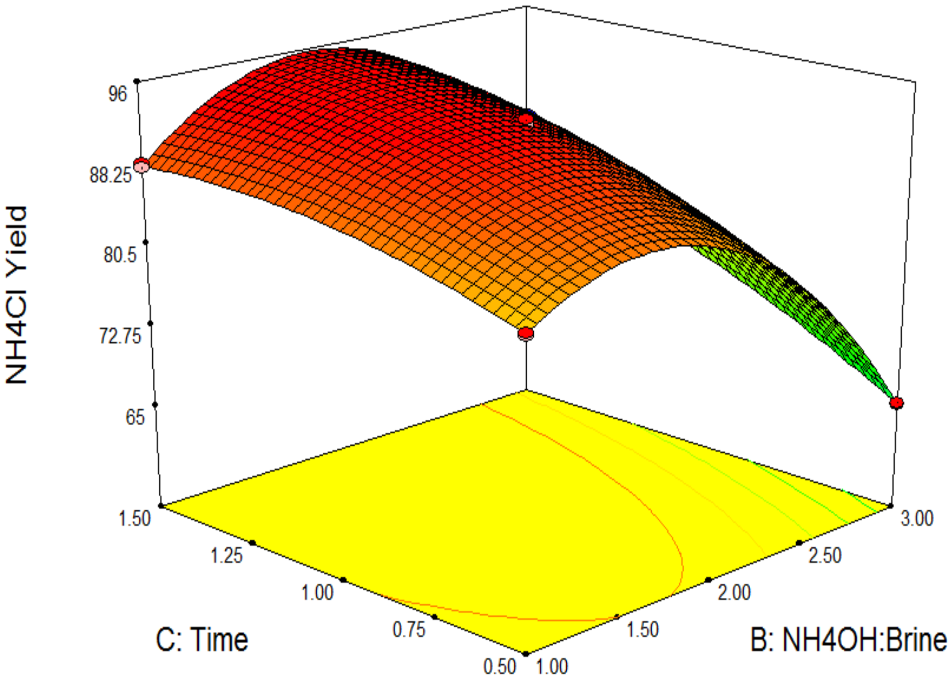

Fig 4.7: Surface plot of the Interaction effect of reaction time and ammonium solution to brine ratio versus yield when the reaction temperature is 10^0C.

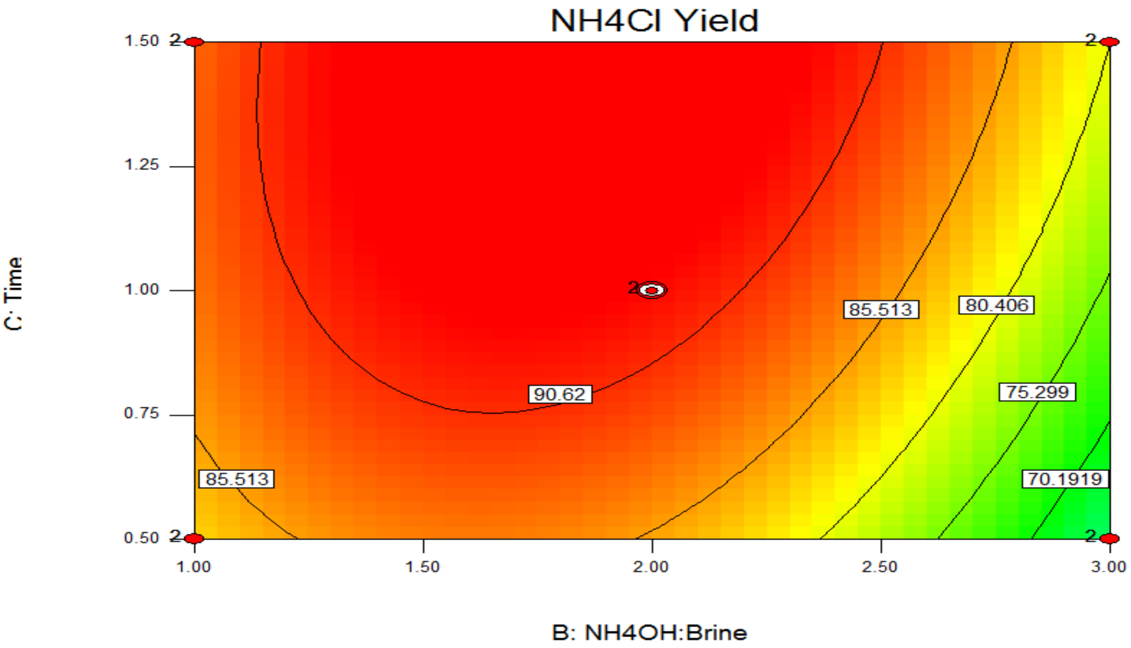

Fig 4.8: Contour plot of the Interaction effect of reaction time and ammonium solution to brine ratio versus yield when the reaction temperature is 10^0C.

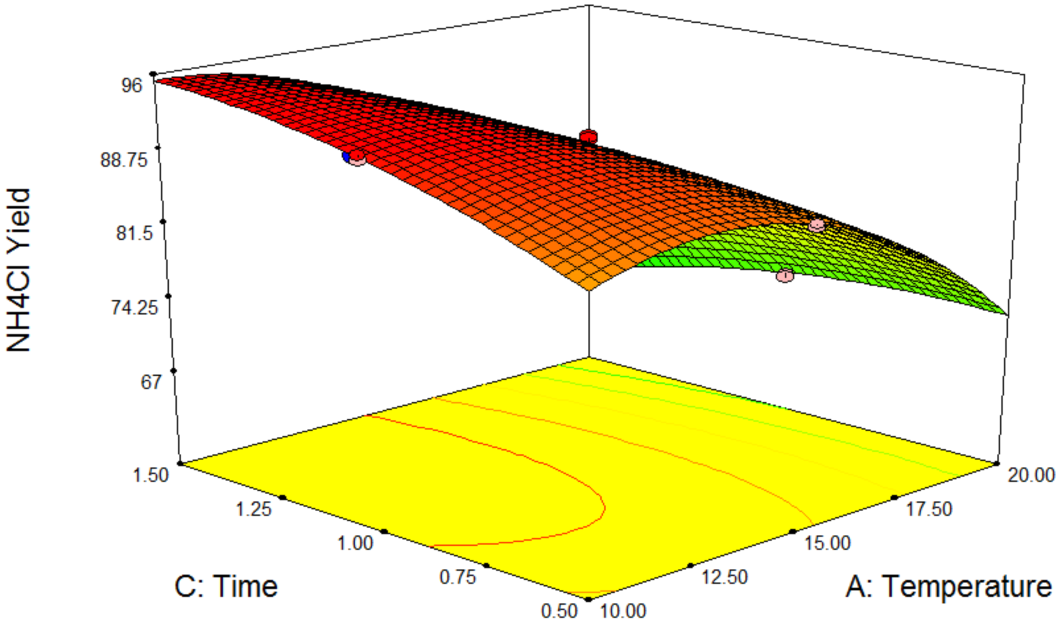

Fig 4.9: Surface plot of the interaction effect of reaction temperature and reaction time versus yield when the molar ratio of ammonium solution to brine is 2.

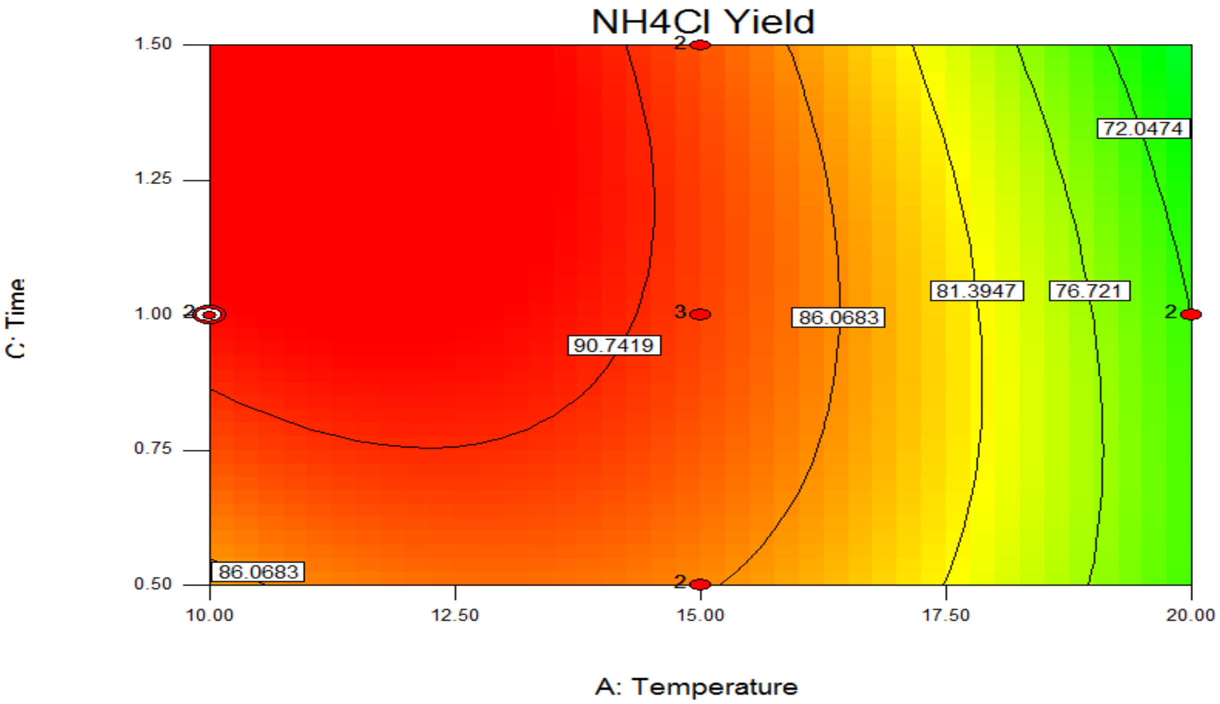

Fig. 4.10: Contour plot of the interaction effect of reaction temperature and reaction time versus yield when the molar ratio of ammonium solution to brine is 2.

Figure 4.7 Show the interaction between ammonium solution to brine ratio and reaction time used, respectively on the yield of ammonium chloride. The drop in ammonium chloride yield at lower ammonium solution to brine ratio with higher reaction time could also due to impurities present in brine like metal carbonates which may compete for ammonia and reduce its availability for reaction with carbon dioxide. Beside to that, at lower ammonium solution to brine ratio, sodium bicarbonate get high solubility and do not precipitate out from the solution consequently minimizes the yield.

From Figure 4.7, the % ammonium chloride amount increased with optimal reaction period at a higher ammonium solution to brine molar ratio. From figure 4.9, the % ammonium chloride amount increased at lower reaction temperature and optimal reaction period. From Figure 4.5, the % ammonium chloride amount decreased with increasing reaction temperature at a higher ammonium solution to brine molar ratio.

4.2.2.3 Optimization of Process Variables

The results above have shown that the three brine ammoniation process variables and the interaction among the variables affect the yield of ammonium chloride. Therefore, the next step is to optimize the process variables in order to obtain the highest yield using the model regression developed.

Using the optimization function in Design Expert, it was predicted that at the following conditions; 10^0C of reaction temperature, ammonium solution to saturated brine molar ratio of 2 and 1hour reaction time, an optimum ammonium chloride yield of 92.28 % can be obtained. In order to verify this prediction, experiments were conducted and the results were comparable with the prediction. It was found that the experimental value of 92.5% yield of ammonium chloride agreed well with the predicted value. Therefore, this study shows that brine ammoniation reaction is a potential reaction process for the production of ammonium chloride from ammonium solution, saturated brine and dry ice via modified Solvay process for lime removal in leather processing.

The optimization result also tells the same result as the ANOVA output. The ANOVA output shows that the brine ammoniation process is highly and significantly affected by the temperature, ammonium solution to saturated brine molar ratio, the interaction between the temperature and ammonium solution to brine molar ratio and the interaction between reaction temperature and reaction time.

4.3 Physico - chemical properties of ammonium chloride

4.3.1 Moisture content

The moisture content of ammonium chloride was performed and observed to be in the range of 0.5-1wt. % at different brine ammoniation process parameters. When we compare the average of the results with the ISTM A-3 for ammonium chloride 1 wt. %, maximum is acceptable. Experimental run results were listed in appendix C.

4.3.2 Ammonium chloride content

Ammonium chloride (as NH_4Cl, percent by weight on dry basis) is a very important property related to the deliming efficiency of ammonium chloride on leather processing. High percentage of ammonium chloride give rise to good deliming value which determines the amount of deliming agent in g necessary for neutralizing 1 g calcium hydroxide. The percentage by weight of ammonium chloride was performed and observed to be in the range of 98.5-99.5 percent at different brine ammoniation process variables. When we compare the average of the results with the ISTM A-4 98.5 wt. % minimum is acceptable.

4.3.3 Sulphates as ammonium Sulphate $(NH_4)_2SO_4$

Qualitative test of Sulphate as ammonium Sulphate in the produced ammonium chloride was performed and observed to be not exceed the limit in ISTM A-6 for ammonium chloride 0.3 wt. % maximum is acceptable. Selected experimental run results were attached in appendix C.

4.3.4 pH determination

The pH of ammonium chloride is also another important property related to the deliming efficiency of ammonium chloride on leather processing. Low value of pH give rise to good deliming value in terms of lowering the pH of the limed pelt in to the bating pH range requirement (pH 7 to 9).

Therefore the ammonium chloride pH must be low to ensure good deliming efficiency and the pH of ammonium chloride was performed and observed to be in the range of 4.5 – 5 at different brine ammoniation process variables. When we compare the results with the ISTM A-8 for ammonium chloride 4.5-5.2 is acceptable. In Table 4.6 the result of ammonium chloride content and pH are given.

The variables studied showed that as ammonium chloride yield increased, the pH decreased. Consequently, the pH, as the other properties, is related with the grade of conversion achieved that is depending on the final yield.

The pH of the ammonium chloride produced at lower temperature is lower than that of the corresponding experiments conducted with the same feed ratio but at higher temperature. This is due to effects of the operating parameters that affect the brine ammoniation reaction.

Table 4.6: Experimental results of ammonium chloride content (wt. % on dry basis), pH of ammonium chloride and empirically determined deliming value of ammonium chloride

Run	Reaction temperature,^{0}C	Molar ratio of ammonium solution to brine	Reaction time, hr	NH_4Cl content, wt.%	pH	Deliming value (g)
1	10.00	1.00	0.50	99	4.5	1.9291
2	15.00	3.00	1.00	98.5	4.75	1.9386
3	15.00	2.00	1.50	99	4.7	1.9291
4	10.00	3.00	1.50	99	4.5	1.9291
5	15.00	2.00	1.00	99.2	4.75	1.9253
6	10.00	3.00	0.50	99	4.5	1.9291
7	10.00	2.00	1.00	99.5	4.5	1.9196
8	10.00	3.00	1.50	99	4.5	1.9291
9	15.00	2.00	1.50	99	4.7	1.9291
10	15.00	2.00	1.00	99.2	4.7	1.9253
11	10.00	1.00	1.50	99	4.5	1.9291
12	20.00	3.00	0.50	98.5	5	1.9386
13	20.00	2.00	1.00	98.5	5	1.9386

Table 4.6 continued.

14	10.00	2.00	1.00	99.5	4.5	1.9196
15	20.00	1.00	0.50	99	5	1.9291
16	10.00	1.00	1.50	99	4.5	1.9291
17	10.00	3.00	0.50	98.5	4.5	1.9386
18	15.00	2.00	0.50	99	4.75	1.9291
19	20.00	2.00	1.00	98.5	5	1.9386
20	15.00	1.00	1.00	99	4.75	1.9291
21	20.00	3.00	0.50	98.5	5	1.9386
22	10.00	1.00	0.50	99	4.5	1.9291
23	15.00	2.00	1.00	99.2	4.75	1.9253
24	15.00	2.00	0.50	99	4.75	1.9291
25	20.00	1.00	1.50	98.5	5	1.9386
26	20.00	1.00	1.50	98.5	5	1.9386
27	15.00	3.00	1.00	98.5	4.7	1.9386
28	20.00	3.00	1.50	98.5	5	1.9386
29	20.00	3.00	1.50	98.5	5	1.9386
30	15.00	1.00	1.00	99	4.7	1.9291
31	20.00	1.00	0.50	99	5	1.9291

Source for deliming value: (BASF, amount of deliming agent required for neutralizing 1 g $Ca(OH)_2$ with respect to wt .% of NH_4Cl)

4.3.5 Matter insoluble in water

The insoluble matter of ammonium chloride produced was performed and observed to be in the range of 0.1-0.2 wt. % at different brine ammoniation process parameters. When we compare the average of the results with the ISTM A-9 for ammonium chloride 0.2 wt. % maximum is acceptable. Selected experimental run results were attached in appendix C.

4.3.6 Specific gravity (Density)

The density of the Ammonium chloride produced was performed and observed to be in the range 1520-1540kg/m^3 at different brine ammoniation process parameters. When we compare the average of the results with the ISTM A-1 for ammonium chloride 1530–1540kg/m^3 is acceptable. The experimental run results and calculation procedure were attached in appendix C and appendix E respectively.

4.3.7 Determination of deliming value

Deliming value is a measure of amount of deliming agent required to neutralize 1 g of calcium hydroxide. As mentioned in the materials and methods part (section 3.2.7.7) the deliming value was determined empirically using equation 3.19 according to the definition given in BASF/leather. The empirical results were listed in the table 4.5 above which served as a bench mark for test of the ammonium chloride on leather processing.

4.4 Application of ammonium chloride synthesized on leather processing and determination of leather physico-chemical properties

4.4.1 Determination of pH

The float pH in the three testing drums was checked using litmus paper to compare the extent of deliming with the two tests (drum 2 and drum 3) to the control deliming test (drum 1).

Table 4.7 Float pH determination by litmus paper

Float (drum) number	pH
1	8.5
2	8.5
3	8

Where the pH of the liming float was 12 as checked using litmus paper. The result implied that the deliming chemicals used in the testing drums 2 and 3 and in the control drum 1 reduced the pH of the limed pelts almost close to a lower pH of 8.5, 8 and 8.5 respectively which is acceptable result with respect to the subsequent operations of bating, pickling and tanning pH range requirements.

To support the above values, standard laboratory test was made in each piece of samples cut from the butt portion of the pelt both before deliming and after deliming. The pH of coded samples was determined and listed as follows:

Table 4.8: pH determination by laboratory analysis for samples before deliming

Coded samples (pelt number)	1	2	3	4	5	6
pH	11.66	11.35	11.21	11.07	11.28	11.41

Table 4.9: pH determination by laboratory analysis for samples after deliming

Coded samples	pH	Coded samples	pH	Coded samples	pH
1^1	7.44	2^1	7.38	3^1	7.55
1^2	7.03	2^2	7.13	3^2	6.84
1^3	7.08	2^3	7.13		
1^4	7.27	2^4	6.84		

M^N: Where M is Drum number and N is sample number

1^n: Left side of the splited pelt samples tested by control deliming agent in test drum number one

2^n: Right side of the splited pelt samples tested by ammonium chloride synthesized in test drum two

3^n: Two unsplited pelt samples in test drum three

As shown in table 4.9 above the results of the pH determination well agreed with the requirement desired for deliming agent in lowering the pH of the limed pelt in table 4.8 with in pH range of 7- 9 which is favorable for enzyme activity in the bating operation. The pH values of sample number four in testing drum 2 and sample number two in testing drum 3 are also acceptable according to some tanners' preference for producing soft leather.

The pelts after deliming was sent to subsequent operations of bating, pickling, tanning and retanning to produce crust leather where there is visible physical properties such as size, thickness, fullness, looseness of grain and grain damages. Therefore assuming other parameters in the bating, pickling, tanning and retanning are constant; the Physico-chemical properties of crust leather determined using the IUP and IUC testing methods to compare the Physico-chemical characteristic of representative crust leather and wet blue samples from the three testing drums. And the results were compared with the values as set by IULTCS (International union of leather technologists and chemists society) reference document.

4.4.2 Determination of water soluble inorganic matter

The water soluble inorganic matter of crust leather was performed and observed to be in the range of 0.15 up to 0.28 Wt.% for the three representative samples taken from the three testing drums. When we compare the average of the results with the IS: 13307 – 1992 for upper goat skin 1wt. % maximum is acceptable.

Table 4.10 Determination of water soluble inorganic matter for crust leather

Testing drum from where samples taken	Water soluble inorganic matter (wt. %)	Average water soluble inorganic matter (wt. %)
1	0.28	0.23
2	0.15	
3	0.25	

4.4.3 Determination of shrinkage temperature

The shrinkage temperature of wet blue leather was performed and observed to be in the range of 100^0C up to 104^0C for three samples taken from testing drum 1, 2 and 3. When we compare the average of the results with the IS: 11230-2003 for upper leather 100^0C minimum is acceptable.

Table 4.11 Determination of shrinkage temperature for wet blue leather

Testing drum from where samples taken	Shrinkage temperature (^{0}C)	Average shrinkage temperature (^{0}C)
1	100	102
2	102	
3	104	

4.4.4 Determination of tensile strength

The tensile strength of the crust leather was performed and observed to be in the range of 27 - 33.6N/mm^2 for three representative crust leather samples in the three testing drums. When we compare the average of the results with the IS: 13307 – 1992 for upper leather 27N/mm^2 minimum is acceptable.

Table 4.12 Determination of tensile strength for crust leather

Testing drum from where samples taken	Tensile strength(N/mm^2)	Average tensile strength(N/mm^2)
1	28	29.5
2	27	
3	33.6	

5. CONCLUSION AND RECOMMENDATION

5.1 Conclusion

In this research, use of brine ammoniation reaction by adopting the technology of modified Solvay process for ammonium chloride production and optimization of brine ammoniation for lime removal has been investigated. Three brine ammoniation parameters affecting the yield of ammonium chloride; reaction temperature, molar ratio of ammonium solution to saturated brine and reaction time has been studied. The outputs of the experiments conducted have been analyzed by employing analysis of physicochemical parameters and testing of the optimal product on leather.

The quality specification of the ammonium chloride synthesized in terms of lime removal in leather processing is comparable with the imported one. A modified Solvay process route for efficient ammonium chloride synthesis from ammonium solution, saturated brine and dry ice is employed, and showed 92.5% yield of ammonium chloride that is better than similar other works of Jibril, B. and A. Ibrahim.2001, and El-Naas, M. H., A. H. Al-Marzouqi, O. Chaalal. 2010., in optimizing the precipitation of sodium bicarbonate by minimizing it's solubility to achieve high conversion.

The result obtained shows that ammonium chloride production by adopting the technology of modified Solvay process using proven available urea feed stocks which are ammonia ,carbon dioxide; and readily available sodium chloride, is a considerable potential in ammonium chloride production for deliming agent in leather processing, mainly because of its high deliming efficiency, good buffering capacity, simplification of separation process from the co product sodium bicarbonate (decrease of production cost).

Based on the experimental results obtained, it is found that all the process variables exhibited significant interaction effect on the yield of ammonium chloride. This shows the capability of design of experiment analysis in successfully capturing these effects. 283K of reaction temperature, ammonium solution to saturated brine molar ratio of 2 and 1 hour reaction time, an optimum ammonium chloride yield of 92.5% was obtained.

Physicochemical properties determined for the ammonium chloride produced meet the ISTM specification, and Physico chemical properties determined for the pelt, wet blue and crust leather samples processed meet IULTCS specifications except pH values of the fourth sample in test drum 2 and the second sample of pelt after deliming in testing drum 3 which are also acceptable results according to some tanners' preference for producing soft leather.

From the result and discussion chapter, it can be concluded that ammonium chloride production locally is both attractive and affordable in technical and financial terms. Moreover, the environmental benefits that can be obtained from investing on ammonium chloride as a deliming agent in leather processing are too significant to disregard in terms of sequestering ammonia and carbon dioxide to produce value adding product. Because it minimizes environmental load, creating job opportunity and most of all reduces reliance on imported ammonium chloride.

It is very clear that chemical industries are up growing in our country Ethiopia, and researches being done based on import substituting industrial chemicals from locally available raw materials are expected to meet the feed stock needs of the chemical industry sector.

5.2 Recommendation

Further research has to be conducted on the analysis of residual calcium of the delimed pelt using Varian Atomic Absorption (AA) Spectrophotometer using a calcium lamp since it will help to know the exact composition of residual calcium before and after deliming.

Investigation and optimization of brine ammoniation reaction for the production of refined food grade sodium bicarbonate and industrial sodium bicarbonate need to be conducted since the food grade sodium bicarbonate used as baking soda and the industrial grade serve as deacidification agent in leather processing.

Moreover, further study is recommended on optimization of ammonium chloride production which meet the quality specification standards for its use as a metal cleaner in soldering, as a flux in thinning and galvanizing, pharmaceutical applications as expectorant and in the manufacture of dry cells.

Additionally, preliminary design of pilot plant, scale- up and product commercialization has to be performed.

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APPENDICES

Appendix A: Typical Composition ranges of raw and purified brine

Table A1: Typical composition ranges of raw and purified brine

Composition [g/l]	Raw brine	Purified brine
Na^+	120 - 125	115 - 125
Cl^-	186 - 192	180 - 190
SO_4^{2-}	2.4 - 10	2.6 - 8.5
Ca^{2+}	0.8 - 1.7	0 - 0.2
Mg^{2+}	0 - 1.5	0 - 0.1
CO_3^{2-}		0.4 - 0.9
OH^-		0 - 0.3

Source: ESAPA – European soda ash producers association, March 2004

Appendix B:

Ammonium chloride and sodium bicarbonate literature characteristics

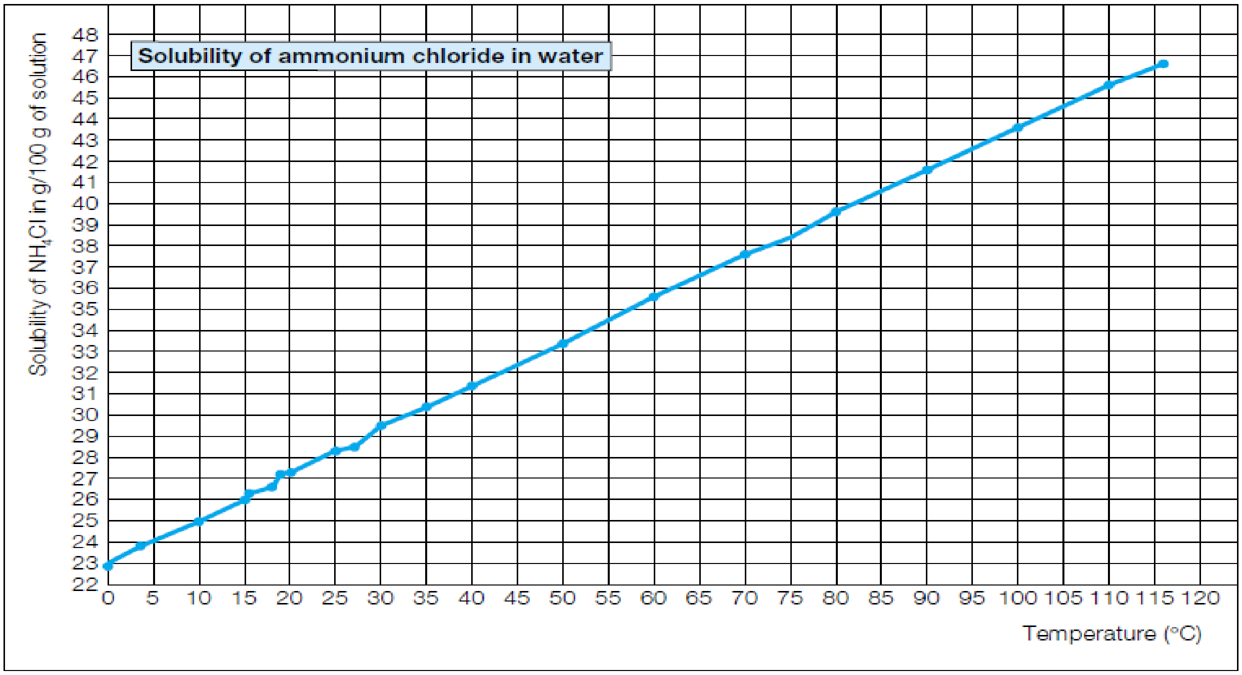

Fig B.1 A. Solubility of ammonium chloride in water

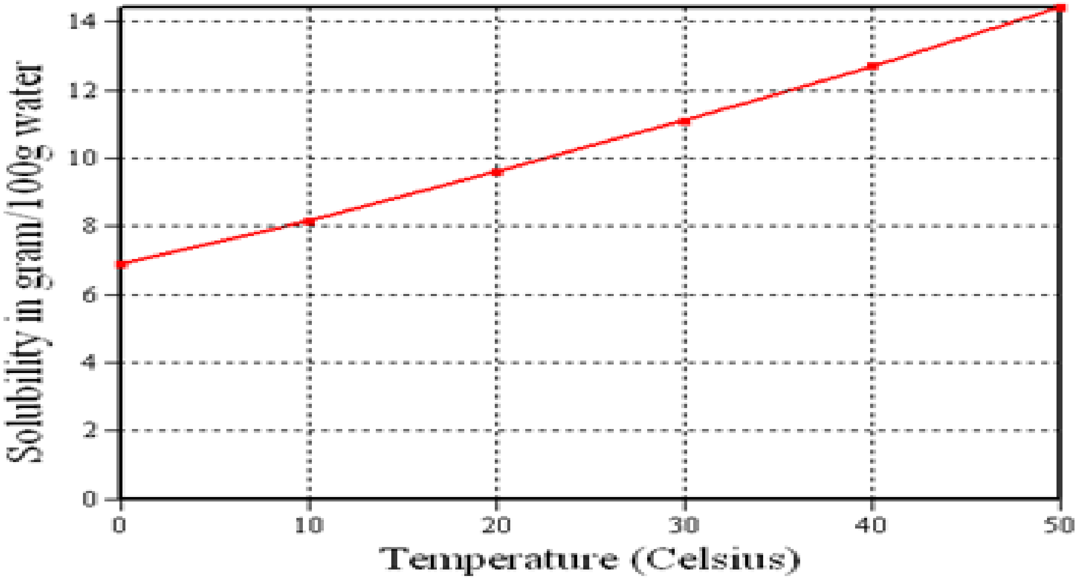

Fig B.1 B. Solubility of sodium bicarbonate in water

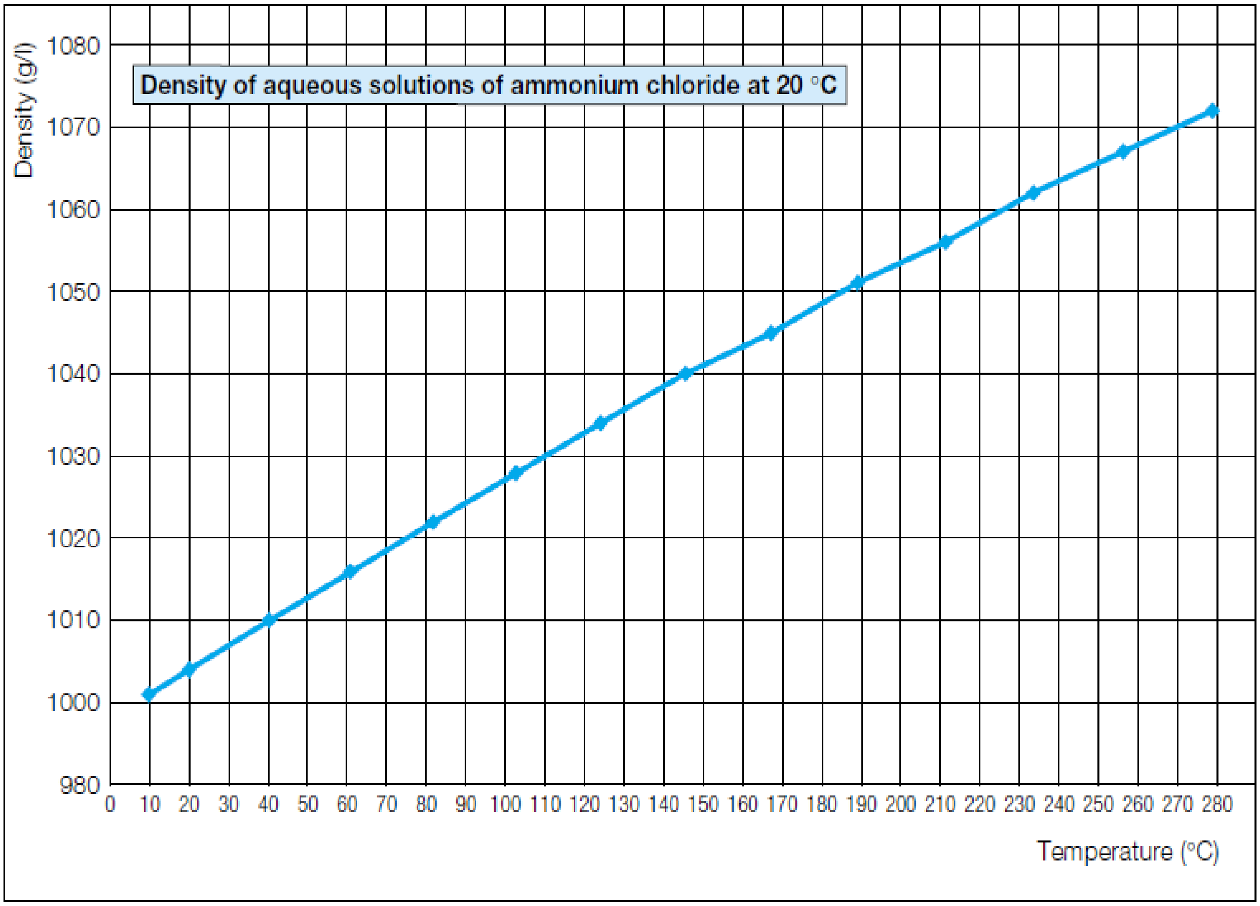

Fig B.2 Density of aqueous solution of ammonium chloride

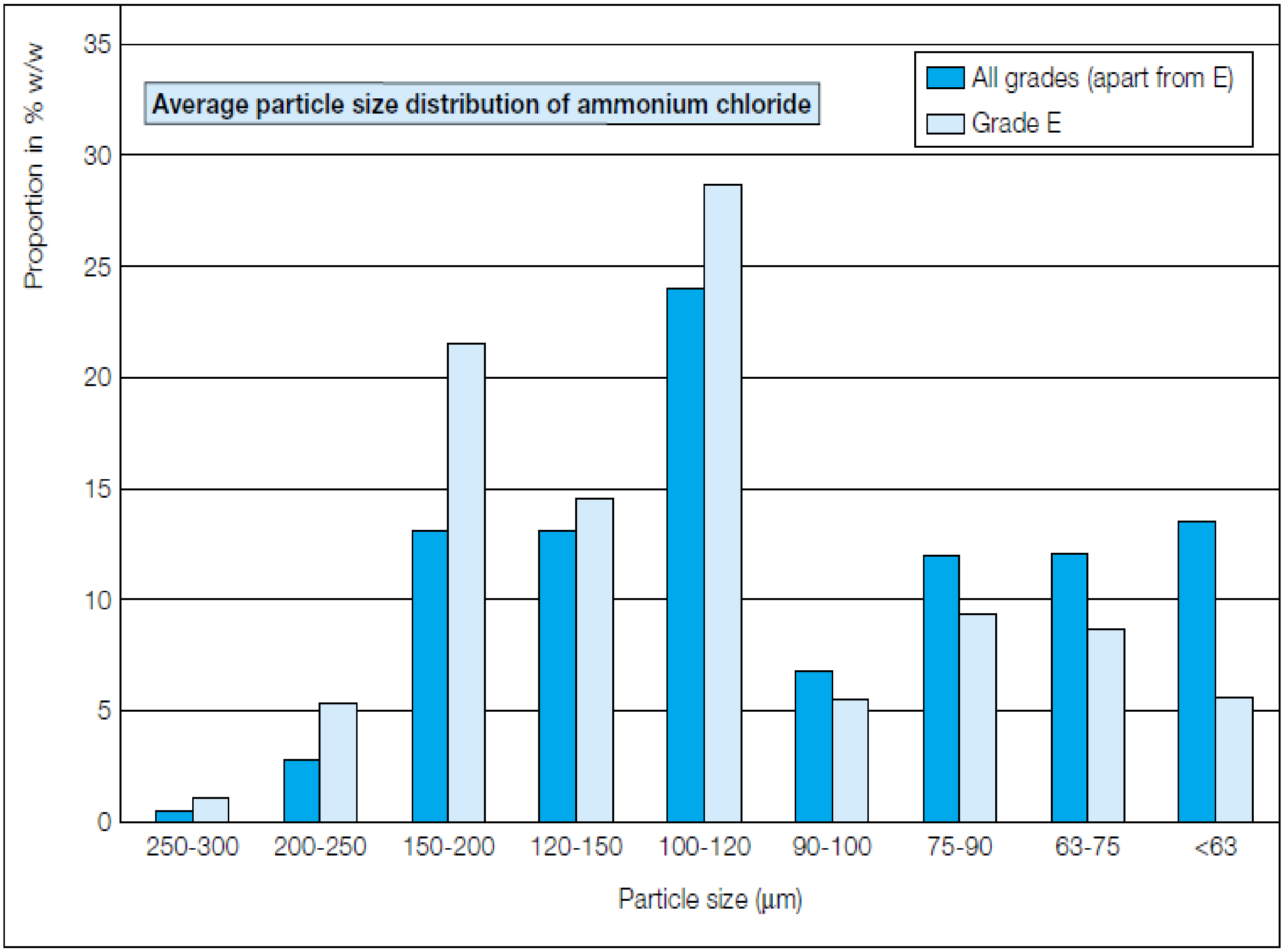

Fig B.3 Average particle size distribution of ammonium chloride (Grade E and all grades apart from E)

Table B1 Ammonium chloride literature characteristics

Grade	Property	Unit	Average content	Specified content
Grade U	NH_4Cl	g/100 g	99	min.98.5
	Ash	g/100 g	0.2	max. 0.25
	NaCl	g/100 g	0.15	max. 0.2
	H_2O	g/100 g	0.03-0.05	max.1
	Fe	mg/ kg	1-2	max.3
Grade RW	NH_4Cl	g/100 g	99.5-99.6	min.99.0
	Ash	g/100 g	0.3-0.5	max.0.7
	NaCl	g/100 g	0.1	max. 0.2
	H_2O	g/100 g	0.03-0.05	max.0.1
	Fe	mg/ kg	1-2	max.3
	Anti-caking agent	g/100 g	0.2-0.4	max.0.5
Grade E	NH_4Cl	g/100 g	99.75	min.99.7
	Ash	g/100 g	0.2	max.0.25
	NaCl	g/100 g	0.15	max.0.2
	H_2O	g/100 g	0.03-0.05	max.0.1
	Fe	mg/ kg	1-2	max.3
Grade RWN	NH_4Cl	g/100 g	99.7	min.99.5
	Ash	g/100 g	0.1-0.2	max.0.25
	NaCl	g/100 g	0.1	max.0.2
	H_2O	g/100 g	0.03-0.05	max.0.1
	Fe	mg/ kg	1-2	max.3
	Anti-caking agent	g/100 g	0.02-0.04	max.0.04
Grade S	NH_4Cl	g/100 g	99.85	min.99.75
	Ash	g/100 g	0.03-0.05	max.0.05
	NaCl	g/100 g	0.02-0.04	max.0.05
	H_2O	g/100 g	0.03-0.05	max.0.1
	Fe	mg/ kg	1-2	max.3
Grade RWS	NH_4Cl	g/100 g	99.3-99.5	min.99.0
	Ash	g/100 g	0.4-0.6	max.0.9
	NaCl	g/100 g	0.15	max.0.2
	H_2O	g/100 g	0.03-0.05	max.0.1
	Fe	mg/ kg	1-2	max.3
	Anti-caking agent	g/100 g	0.4-0.6	max.0.7

Appendix C: Experimental result

Table C1: Experimental process conditions for ammonium chloride production

Factors	Run #1		Run #2		Run #3	
Reaction temperature	10	^{0}C	15	^{0}C	15	^{0}C
NH_4OH:Brine ratio	1	292ml	3	874ml	2	583ml
Time	0.5	hr	1	hr	1.5	hr
	Run #4		Run #5		Run #6	
Reaction temperature	10	^{0}C	15	^{0}C	10	^{0}C
NH_4OH:Brine ratio	3	874ml	2	583ml	3	874ml
Time	1.5	hr	1	hr	0.5	hr
	Run #7		Run #8		Run #9	
Reaction temperature	10	^{0}C	10	^{0}C	15	^{0}C
NH_4OH:Brine ratio	2	583ml	3	874ml	2	583ml
Time	1	hr	1.5	hr	1.5	hr
	Run #10		Run #11		Run #12	
Reaction temperature	15	^{0}C	10	^{0}C	20	^{0}C
NH_4OH:Brine ratio	2	583ml	1	292ml	3	874ml
Time	1	hr	1.5	hr	0.5	hr
	Run #13		Run #14		Run #15	
Reaction temperature	20	^{0}C	10	^{0}C	20	^{0}C
NH_4OH:Brine ratio	2	583ml	2	583ml	1	292ml
Time	1	hr	1	hr	0.5	hr
	Run #16		Run #17		Run #18	
Reaction temperature	10	^{0}C	10	^{0}C	15	^{0}C
NH_4OH:Brine ratio	1	292ml	3	874ml	2	583ml
Time	1.5	hr	0.5	hr	0.5	hr
	Run #19		Run #20		Run #21	
Reaction temperature	20	^{0}C	15	^{0}C	20	^{0}C
NH_4OH:Brine ratio	2	583ml	1	292ml	3	874ml
Time	1	hr	1	hr	0.5	hr
	Run #22		Run #23		Run #24	
Reaction temperature	10	^{0}C	15	^{0}C	15	^{0}C
NH_4OH:Brine ratio	1	292ml	2	583ml	2	583ml
Time	0.5	hr	1	hr	0.5	hr

Table C1 continued

	Run #25		Run #26		Run #27	
Reaction temperature	20	^{0}C	20	^{0}C	15	^{0}C
NH_4OH:Brine ratio	1	292ml	1	292ml	3	874ml
Time	1.5	hr	1.5	hr	1	hr
	Run #28		Run #29		Run #30	
Reaction temperature	20	^{0}C	20	^{0}C	15	^{0}C
NH_4OH:Brine ratio	3	874ml	3	874ml	1	292ml
Time	1.5	hr	1.5	hr	1	hr
	Run #31					
Reaction temperature	20	^{0}C				
NH_4OH:Brine ratio	1	292ml				
Time	0.5	hr				

Table C2: Ammonium chloride composition for different process variables

Run	Reaction temperature (^{0}C)	NH_4OH:Brine (molar)	Reaction time (hr)	Brine input (ml)	Dry ice input (g)	NH_4Cl output (g)
1	10.00	1.00	0.50	186	60	49.8
2	15.00	3.00	1.00	186	60	41.4
3	15.00	2.00	1.50	186	60	53.22
4	10.00	3.00	1.50	186	60	48.3
5	15.00	2.00	1.00	186	60	54.12
6	10.00	3.00	0.50	186	60	39.12
7	10.00	2.00	1.00	186	60	55.2
8	10.00	3.00	1.50	186	60	48.18
9	15.00	2.00	1.50	186	60	53.1
10	15.00	2.00	1.00	186	60	53.88
11	10.00	1.00	1.50	186	60	52.8
12	20.00	3.00	0.50	186	60	27.78
13	20.00	2.00	1.00	186	60	43.08
14	10.00	2.00	1.00	186	60	55.5
15	20.00	1.00	0.50	186	60	45.9

Table C2 continued

16	10.00	1.00	1.50	186	60	53.04
17	10.00	3.00	0.50	186	60	39
18	15.00	2.00	0.50	186	60	51.78
19	20.00	2.00	1.00	186	60	42.9
20	15.00	1.00	1.00	186	60	52.5
21	20.00	3.00	0.50	186	60	27.96
22	10.00	1.00	0.50	186	60	49.92
23	15.00	2.00	1.00	186	60	54
24	15.00	2.00	0.50	186	60	51.6
25	20.00	1.00	1.50	186	60	39.78
26	20.00	1.00	1.50	186	60	39.84
27	15.00	3.00	1.00	186	60	41.1
28	20.00	3.00	1.50	186	60	27.43
29	20.00	3.00	1.50	186	60	28.2
30	15.00	1.00	1.00	186	60	52.8
31	20.00	1.00	0.50	186	60	46.2

Table C3: Ammonium chloride moisture content (wt. %) and density for different processes variables

Run	A	B	C	M1	M2	M3	M4	M5	Mavg	ρ
1	10.00	1.00	0.50	0.8	0.9	0.9	0.7	0.75	0.81	1530
2	15.00	3.00	1.00	1	1	1	1	1	1.00	1530
3	15.00	2.00	1.50	0.7	0.75	0.8	0.9	0.9	0.81	1520
4	10.00	3.00	1.50	0.75	0.85	0.85	0.65	0.72	0.76	1530
5	15.00	2.00	1.00	0.5	0.6	0.6	0.4	0.45	0.50	1520
6	10.00	3.00	0.50	1.1	1	0.86	0.9	1.1	1.00	1540
7	10.00	2.00	1.00	0.6	0.5	0.45	0.4	0.6	0.50	1520
8	10.00	3.00	1.50	0.9	0.9	0.8	0.75	0.7	0.81	1530
9	15.00	2.00	1.50	0.9	1	1	0.8	0.85	0.91	1520
10	15.00	2.00	1.00	0.7	0.4	0.8	0.2	0.5	0.50	1520
11	10.00	1.00	1.50	1	0.9	1.1	0.96	1	1.00	1520
12	20.00	3.00	0.50	1	1.1	0.9	1.1	0.86	1.00	1540
13	20.00	2.00	1.00	0.9	0.7	1.4	0.85	1.3	1.00	1530
14	10.00	2.00	1.00	0.7	0.4	0.8	0.2	0.5	0.50	1520
15	20.00	1.00	0.50	0.8	0.9	0.9	0.7	0.75	0.81	1530
16	10.00	1.00	1.50	0.9	1	1	0.8	0.85	0.91	1520
17	10.00	3.00	0.50	1	1.1	0.9	1.1	0.86	1.00	1540
18	15.00	2.00	0.50	0.8	0.9	1	1	0.85	0.91	1520
19	20.00	2.00	1.00	0.6	0.65	0.7	0.8	0.8	0.71	1530
20	15.00	1.00	1.00	0.9	0.9	1	1	0.85	0.91	1520
21	20.00	3.00	0.50	1	1	1	1	1	1.00	1540
22	10.00	1.00	0.50	0.9	0.9	0.7	0.75	0.8	0.81	1530
23	15.00	2.00	1.00	0.6	0.5	0.45	0.4	0.6	0.50	1520
24	15.00	2.00	0.50	0.8	0.9	1	1	0.85	0.91	1520
25	20.00	1.00	1.50	1	1	1	1	1	1.00	1540
26	20.00	1.00	1.50	1.3	0.9	0.8	1	1	1.00	1540
27	15.00	3.00	1.00	1	1	1	1	1	1.00	1530
28	20.00	3.00	1.50	0.9	1.3	0.8	1	1	1.00	1540
29	20.00	3.00	1.50	0.9	0.7	1.4	0.85	1.3	1.00	1540
30	15.00	1.00	1.00	0.9	1	1	0.8	0.85	0.91	1520
31	20.00	1.00	0.50	0.9	0.9	0.7	0.75	0.8	0.81	1530

M-Moisture content (wt. %), ρ-density (kg/m^3)

Table C4.Ammonium chloride (wt. % on dry basis) for selected experimental run result

Run	B	A	N	W	$NH_4Cl = \frac{5.350\,(B - A)\,N}{W}$
1	41.08	4.07	0.1	0.2	99
5	43.08	6	0.1	0.2	99.2
7	45.19	8	0.1	0.2	99.5
10	43.08	6	0.1	0.2	99.2
11	42.01	5	0.1	0.2	99
12	42.6	5.8	0.1	0.2	98.5
13	42.82	6	0.1	0.2	98.5
15	42.01	5	0.1	0.2	99
18	42.01	5	0.1	0.2	99
20	42.01	5	0.1	0.2	99
25	42.6	5.8	0.1	0.2	98.5
27	42.82	6	0.1	0.2	98.5

B = volume in ml of standard sodium hydroxide solution used in the blank determination,

A = volume in ml of standard sodium hydroxide solution used in the test with the material,

N = normality of standard sodium hydroxide solution, and

W = weight in g of the dried material taken for the test.

Table C5. Sulphate content (wt. %) and matter insoluble in water content of ammonium chloride for selected experimental run result

Run	Turbidity produced Sulphate (wt. %)		Matter insoluble in water (wt. %)
	With the material	With the control test	
1	Less	Greater	0.1
2	Less	Greater	0.2
5	Less	Greater	0.1
6	Less	Greater	0.2
7	Less	Greater	0.1
12	Less	Greater	0.2
13	Less	Greater	0.1
15	Less	Greater	0.1
16	Less	Greater	0.1
18	Less	Greater	0.1
20	Less	Greater	0.1
25	Less	Greater	0.2

Appendix D: Thermodynamic analysis of ammonium chloride production from literature and reaction kinetic analysis

D1: Thermodynamic analysis

As mentioned in the materials and methods part section 3.2.6 (reaction 3.12) is the rate limiting step, the thermodynamic data for reaction (3.11) and (3.12) was adopted from reject brine management which aims at mixing reject brine with ammonia and then exposed to carbon dioxide using different contact techniques to convert NaCl and CO_2 into a useful solid product sodium bicarbonate made in a semi-batch reactor by El-Naas, 2010. The calculated thermodynamic properties for the reaction (3.11) and (3.12) are presented below.

Table D1. Thermodynamic data for reaction (3.11)

Temperature(^{0}C)	ΔH(KJ/mol)	ΔS(KJ/mol.^{0}C)	ΔG(kJ/mol)
0.0	-127.6	-241.6	-61.7
10.0	-129.5	-248.4	-59.2
20.0	-131.5	-255.1	-56.7
30.0	-133.4	-261.5	-54.1
40.0	-135.3	-267.8	-51.5
50.0	-137.2	-273.8	-48.7
60.0	-139.2	-279.7	-46.0
70.0	-141.1	-285.5	-43.2
80.0	-143.1	-291.0	-40.3
90.0	-145.0	-296.5	-37.3

Given its highly negative Δ H and ΔG (Table D1), reaction (3.11) is an exothermic reaction that takes place as soon as the carbon dioxide gets in contact with the ammoniated brine. Once ammonium bicarbonate is formed, it reacts with sodium chloride according to reaction (3.12), as can be seen from the above table reaction (3.12) is not as spontaneous as reaction (3.11) and it is believed to be the rate limiting step.

Table D1A. Thermodynamic data for reaction (3.12)

Temperature(^{0}C)	ΔH(KJ/mol)	ΔS(KJ/mol.^{0}C)	ΔG(kJ/mol)
0.0	-6.3	-11.8	-3.1
10.0	-4.6	-5.5	-3.0
20.0	-2.8	-0.6	-3.0
30.0	-1.1	6.5	-3.1
40.0	0.7	12.2	-3.1
50.0	2.5	17.8	-3.3
60.0	4.2	23.2	-3.5
70.0	6.0	28.5	-3.8
80.0	7.9	33.8	-4.1
90.0	9.7	38.9	-4.4

The thermodynamic analysis indicates that reaction (3.12) is exothermic reaction with a negative heat of reaction up to a temperature of 40^{o}C.Beyond this temperature, the reaction becomes endothermic as shown in Table D1A.This phenomenon was observed experimentally in a semi batch reactor by El-Naas, 2010. The reactor temperature was monitored with time and found to increase up to 41^{o}C, then drop and stabilize at 30^{o}C. Although this sudden change in the heat of reaction may be attributed to the reactor dynamics, a similar finding was reported by Yeh and Bai (1999) who attributed it to variations in the concentration of NH_3 in the solution [40].

D2.Reaction kinetic analysis

For batch reactor of 2L capacity where no material was supplied to or withdrawn from the reactor during the reaction. The amounts of individual components might change due to reaction, but not due to flow in or out of the system. The general mole balance for batch reactor described as:

$$\frac{dn_j}{dt} = \int_0^V r_j \, dV \qquad (D1)$$

Where j=Ammonium chloride

$$r_j = r_{NH_4Cl} = \text{rate of formation of Ammonium chloride}$$

The rate of formation of ammonium chloride is uniform and equal to the system average rate, everywhere in the reaction, and therefore we can take the rate of formation out of the integral.

$$\int_0^V r_j \, dV = r_j \int_0^V dV = r_j V = \frac{\Delta n_j}{\Delta t}$$

Table D2. Kinetic data of representative experimental runs

Experiment #	Time, min	Δnj, mole	Temperature, K	Reaction rate ,(Mmin^{-1})	Rate constant, k (M^{-1}min^{-1})
1	30	0.932	283	1.55E-02	2.53E-03
2	60	0.775	288	6.46E-03	1.04E-03
3	90	0.996	288	5.53E-03	8.87E-04
4	90	0.902	283	5.01E-03	8.16E-04
5	60	1.013	288	8.44E-03	1.35E-03
6	30	0.732	283	1.22E-02	1.99E-03
7	60	1.033	283	8.61E-03	1.40E-03
11	90	0.988	283	5.49E-03	8.94E-04
12	30	0.519	293	8.65E-03	1.37E-03
13	60	0.806	293	6.72E-03	1.07E-03
15	30	0.859	293	1.43E-02	2.27E-03
18	30	0.969	288	1.62E-02	2.59E-03
20	60	0.982	288	8.18E-03	1.31E-03
25	90	0.744	293	4.13E-03	6.56E-04
28	90	0.513	293	2.85E-03	4.53E-04

The rate equation for the limiting reaction 3.12 is as follows:

$$-r_j = kC_AC_B$$

Where A = NaCl;   B = NH_4HCO_3

$$K = \frac{-r_j}{C_AC_B}$$

$$C_A = C_{A,0}(1 - X_A)$$

$$C_B = C_{B,0} - C_{A,0}X_A$$

Implies $K = \frac{r_j}{CA,_O{}^2X_A(1-X_A)}$ (D2)

From the thermodynamic data of reaction 3.12, the standard Gibbs free energy change at

T = 298.15K is $-3\,\frac{kJ}{mol}$.

The standard Gibbs free energy change of the reaction $\Delta G^0 = -RT\ln K$

$$K_{298} = \exp\left(\frac{-\Delta G^0}{RT}\right)$$

$$= \exp\left(\frac{3000}{8.314 \times 298.15}\right)$$

$$= \quad 3.354$$

From the experimental result the optimal yield found at $T = 10^0C$, 2:1 molar ratio and 1 hr reaction time. Using Vant Hoff's equation the equilibrium constant at 10^0C calculated as:

$$\ln\left(\frac{k_2}{k_1}\right) = \frac{-\Delta H^0}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \qquad (D3)$$

Where ΔH^0 was assumed to be constant over small temperature range between T_1 and T_2.

From the thermodynamic Table D1A the standard enthalpy change can be calculated between temperature T = 20^0C and T= 30^0C using interpolation at T=25^0C.

i.e. $\Delta H^0{}_{298.15} = -1.95\text{kJ/mol}$

For k_1=3.354; T_1=298.15K; T_2=283.15K and solve for k_2 using equation D3.

Therefore $\ln\left(\frac{k_2}{3.354}\right) = \frac{1950}{8.314}\left(\frac{1}{283.15} - \frac{1}{298.15}\right)$

k_2 = 3.496

Similarly the equilibrium constant for the limiting reaction 3.12 at T=15^{0}C and 20^{0}C calculated and the results are;

k_{15^0C} = 3.447; k_{20^0C} = 3.40

With the equilibrium constant for the limiting reaction at 10^{0}C, 15^{0}C and 20^{0}C known, the expected maximum conversion of the limiting reactant NaCl calculated as;

$$x_{NaCl} = \frac{k_{eq}}{1 + k_{eq}}$$

At T =10^{0}C K_{eq} = 3.496

$$X_A = \frac{K_{eq}}{1+k_{eq}}$$

$$= \frac{3.496}{1 + 3.496}$$

$$= 0.78$$

Similarly at T =15^{0}C, k_{eq} = 3.447 and $X_{A,\ eq}$ = 0.775

For T = 20^{0}C, k_{eq} = 3.40 and $X_{A,\ eq}$ = 0.772

$C_{A,0}$ is the initial concentration of the limiting reactant sodium chloride, as described in the materials and methods part, section 3.2.6, 186ml of saturate brine was used for all experimental runs ,in 186ml of saturated brine there is 65g of sodium chloride, therefore $C_{A,0} = \frac{m_A/M_A}{V} = \frac{65g/58.45gmol}{0.186L} = 5.98\frac{mol}{L}$

Therefore using equation (D2) the corresponding values of reaction rate constant based on equilibrium conversion for each representative experimental runs calculated and listed in table D2.

The activation energy (E) is additional quantity that is important in understanding the kinetics of any reaction. In order to measure this factor, the Polanyi – Semenov equation can be used to estimate activation energies from the heat of reactions, ΔH_R according to the equation.

$$E = C - \alpha(-\Delta H_R) \qquad \text{(D4)}$$

Where α and C are constants. For exothermic reactions α = -0.25 and C = 48kJ/mol [41].

From thermodynamic Table D1A the heat of reaction ΔH_R at temperature of 10^0C, 15^0C and 20^0C are -4.6kJ/mol,-3.7kJ/mol and -2.8KJ/mol respectively.

Therefore, the corresponding activation energy calculated using equation (D4) as follows:

E at 10^0C

E = 48kJ/mol + 0.25(4.6kJ/mol)

= 49.15kJ/mol

E at 15^0C

E = 48kJ/mol + 0.25(3.7kJ/mol)

= 48.925kJ/mol

E at 20^0C

E = 48kJ/mol + 0.25(2.8kJ/mol)

= 48.7kJ/mol

After examining the experimental data depicted in the Tables D2, important conclusions can be made regarding the chemical kinetics of the equation under investigation ($\mathrm{NaCl} + \mathrm{NH_4HCO_3} \rightarrow \mathrm{NH_4Cl} + \mathrm{NaHCO_3}$). The results demonstrate the general effects that reactant concentration and temperature have on reactions.

In experiments 1, 4, 6, 7, 11; 2, 3, 5, 18, 20 and 12, 13, 15, 25, 28 all factors are held constant with the exception of the concentration of the reactants. These conditions make it possible to observe how changing reactant concentration affects the reaction rate. The data demonstrate that if the concentration of one of the reactants is doubled while the other reactant concentration is held constant, the reaction rate doubles. This is true for both reactants. Thus, it was concluded that each of the reactants have a reaction order of 1.

A general trend can be observed regarding the effects of temperature on reaction rate. The data trend is consistent with the experimental analysis that at optimum reaction conditions, as the temperature of the reaction decreases, the reaction rate will increase.

Appendix E: Calculation part

E1.Experimental data calculation for the determination of saturated brine compositions

Calculation of chloride ion concentration

As mentioned in the materials and methods part (section 3.2.2.3) both brine sample and blank were titrated with the prepared 0.0145N $AgNO_3$ solution until the color changes to brick red, and titration data was recorded as:

$$\mathrm{V_S} - \text{Volume of silver nitrate consumed for the sample(ml)} = 9\text{ml}$$

$$\mathrm{V_B} - \text{Volume of silver nitrate consumed for the blank(ml)} = 0.2\text{ml}$$

$$\mathrm{C} - \text{Concentration of silver nitrate used for the titration(N)} = 0.0145\text{N}$$

$$35.45 \quad = \quad \text{equivalent weight of } \mathrm{Cl^-}$$

Therefore, milligram of chloride ion per liter of brine was calculated as:

$$(\mathrm{mgCl^-})^{-\mathrm{L}} = (\mathrm{V_S} - \mathrm{V_B}) \times \mathrm{C} \times 1000 \times \frac{35.45}{\text{L of sample}}$$

$$= (9 - 0.2) \times 0.0145 \times 1000 \times \frac{35.45}{0.025}$$

$$= 180{,}936.8 \frac{\mathrm{mg}}{\mathrm{L}}$$

$$= 181$$

Calculation of calcium ion concentration

As mentioned in the materials and methods part (section 3.2.2.4) brine sample was titrated with the prepared 0.0001N EDTA solution until the color changes to blue, and titration data was recorded as:

$$\mathrm{V} - \text{Volume of EDTA consumed for the titration(ml)} = 3\text{ml}$$

$$\mathrm{C} - \text{concentration of EDTA(N)} = 0.0001\text{N}$$

$$40.08 = \text{formula weight of calcium}$$

Therefore, milligram of calcium ion per liter of brine was calculated as:

$$(\mathrm{mgCa^{2+}})^{-\mathrm{L}} = \mathrm{V} \times \mathrm{C} \times 40.08 \times \frac{1000}{\mathrm{L\ of\ sample}}$$

$$= 3 \times 0.0001 \times 40.08 \times \frac{1000}{0.1\mathrm{L}}$$

$$= \frac{120.24\mathrm{mg}}{\mathrm{L}}$$

$$= \frac{0.12\mathrm{g}}{\mathrm{L}}$$

Calculation of magnesium ion concentration

The total hardness of the brine sample was made using EDTA titrimetric method to determine milligram of calcium carbonate per liter of brine sample, and the amount of volume of EDTA consumed for the titration was used for the determination of magnesium ion as:

Milligram of magnesium ion per liter of brine was calculated as:

$$(\mathrm{mgMg^{2+}})^{-\mathrm{L}} = (\mathrm{V_H} - \mathrm{V_{Ca}}) \times \mathrm{C} \times 1000 \times \frac{24.32}{\mathrm{L\ of\ dample}}$$

Where, $\mathrm{V_{H}}$_Volume of EDTA consumed for total hardness $= 5\mathrm{ml}$

$\mathrm{V_{Ca}}$ − Volume of EDTA consumed for calcium $= 3\mathrm{ml}$

C − Concentration of EDTA

24.32 = formula weight of magnesium

Therefore milligram of magnesium ion per liter of brine was calculated as:

$$= (5 - 3) \times 0.0001 \times 1000 \times \frac{24.32}{0.1}$$

$$= 48.64 \frac{\mathrm{mg}}{\mathrm{L}}$$

$$= 0.05 \frac{\mathrm{g}}{\mathrm{L}}$$

Calculation of sulphate ion concentration

Milligram of sulphate ion per liter of brine was calculated as:

$$\left(\mathrm{mg\ of\ SO_4{}^{2-}}\right)^{-\mathrm{L}} = \mathrm{mgBaSO_4} \times 0.4116 \times \frac{1000}{\mathrm{L\ of\ sample}}$$

Where,

$$\text{mgBaSO}_4 = \text{Weight of (dish + residue) in gram} - \text{weight of empty dish in gram}$$

$$0.4116 = \frac{\text{weight of SO}_4{}^{2-}}{\text{weight of BaSO}_4} = \frac{96.06}{233.36}$$

$$\text{weight of (dish + residue)} = 39.99\text{g}$$

$$\text{weight of empty dish} = 39.63\text{g}$$

Therefore using the above equation,

$$\left(\text{mg of SO}_4{}^{2-}\right)^{-\text{L}} = \left(\frac{(39.99 - 39.63) \times 0.4116 \times 1000}{0.05}\right)$$

$$= 2{,}963.52\,\frac{\text{mg}}{\text{L}}$$

$$= 2.96\,\frac{\text{g}}{\text{L}}$$

E2: Calculation of limiting reactant and theoretical yield

According to equation 3.10 of materials and method part (section 3.2.6) 65g of sodium chloride in the form of brine and 60g of dry ice reacted.

The theoretical yield of product produced by each reactant was calculated and the reactant which gives the lesser amount of the product was chosen as a limiting reactant:

$$65\text{g NaCl} \times \frac{1\text{ mol NaCl}}{58.45\text{g NaCl}} \times \frac{1\text{ mol NH}_4\text{Cl}}{1\text{ mol NaCl}} \times \frac{53.45\text{gNH}_4\text{Cl}}{1\text{ mol NH}_4\text{Cl}} = 60\text{g NH}_4\text{Cl}$$

$$60\text{g CO}_2 \times \frac{1\text{ mol CO}_2}{44\text{ g CO}_2} \times \frac{1\text{ mol NH}_4\text{Cl}}{1\text{ mol CO}_2} \times \frac{53.45\text{gNH}_4\text{Cl}}{1\text{ mol NH}_4\text{Cl}} = 73\text{g NH}_4\text{Cl}$$

Since NaCl produced lesser product, NaCl is the limiting reagent and $60\text{g NH}_4\text{Cl}$ is the theoretical yield.

E3. Determination of ammonium chloride density using pychnometer

Determination of ammonium chloride density produced in experimental run number 5.

Volume of standard pychnometer = 25ml

Mass of pychnometer = 16g

Mass of pychnometer + unknown mass of ammonium chloride = 21.6g

Mass of pychnometer + mass of ammonium chloride + mass of toluene = 40.147g

N.B Toluene was chosen since NH_4Cl doesn't dissolve in it.

Density of toluene (ρ) = 0.87g/ml at 20^0C

Therefore from the above data:

Mass of toluene = 40.147 – 21.6 = 18.547g

Volume of toluene = $\frac{m_{toluene}}{\rho_{toluene}} = \frac{18.547g}{0.87g/ml} =$ 21.32ml

Volume of NH_4Cl = 25 – 21.32 =3.68ml

Mass of NH_4Cl = (mass of pychnometer + mass of ammonium chloride) – mass of pychnometer

= 21.6 – 16

= 5.6g

Therefore $\rho_{NH_4Cl} = \frac{mass}{volume} = \frac{5.6g}{3.68ml}$

=1.52 g/ml

= 1520 kg/m^3

Similarly the density of ammonium chloride was determined for the remaining experimental runs and listed in table C3.

F. Schematic flow diagram of leather processing

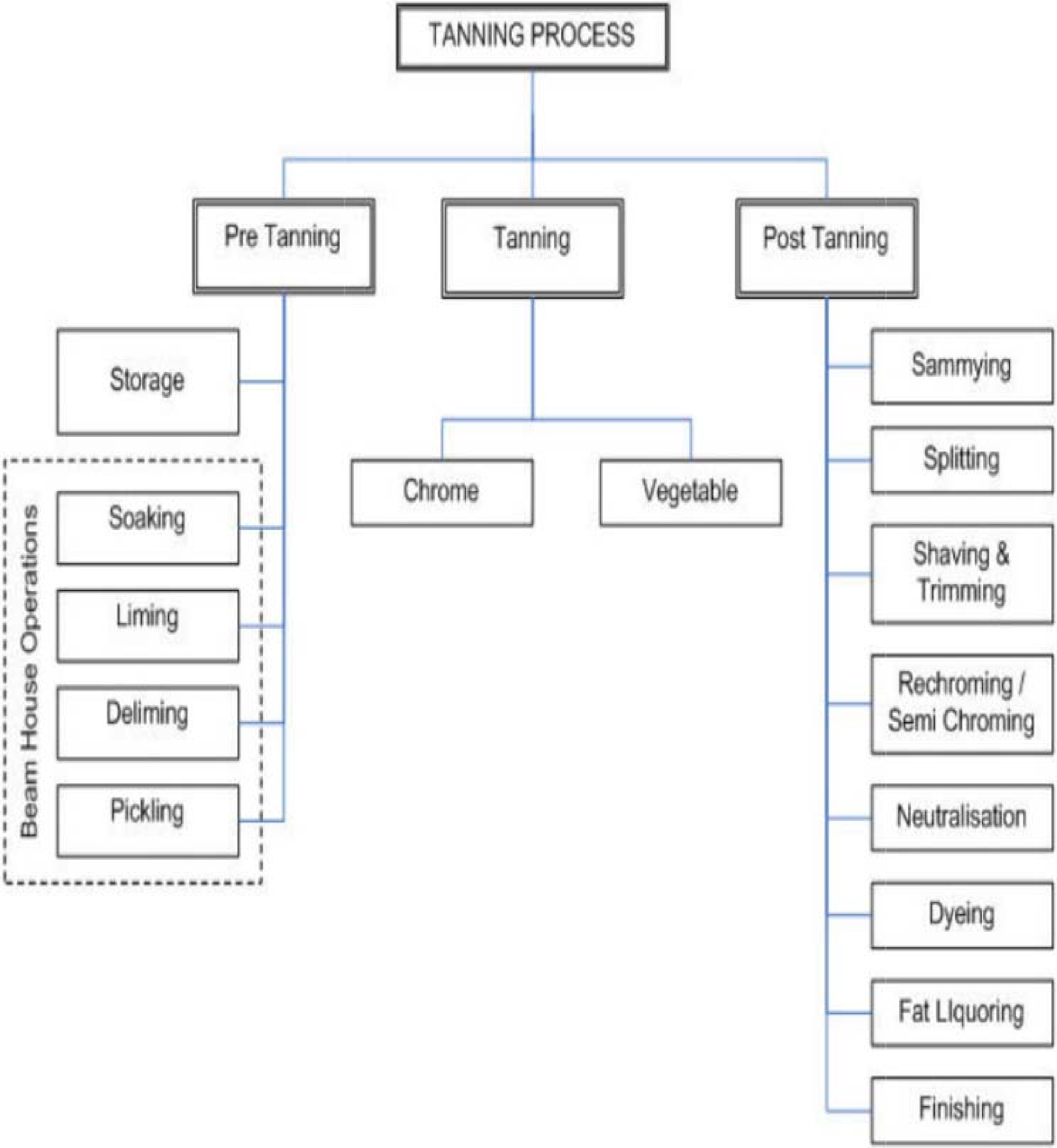

Fig F1.Schematic flow diagram of leather processing

DECLARATION

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

Name: Michael Moreda Dadi

Signature:________________________

Date of Submission: __________________________

This thesis has been submitted for examination with my approval as a university advisor.

Name: Dr.Tassisa Kaba

Signature:_____________________________

Date:____________________________________