A STUDY OF PROCESS PARAMETERS FOR PRODUCING AMMONIUM SULFATE UTILIZING BY-PRODUCT GYPSUM

A Thesis
Submitted to the Department of Chemical Engineering in partial fulfilment of the requirements for the degree of Master of Science in Engineering (Chemical)

By

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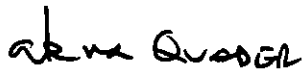BUET, Dhaka
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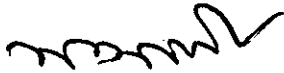
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<u>CERTIFICATION OF THESIS WORK</u>

We, the undersigned, certify that **Md. Ruhul Amin,** candidate for the degree of **Master of Science in Engineering (Chemical),** has presented his thesis on the subject **"A Study of Process Parameters for Producing Ammonium Sulfate Utilizing By-Product Gypsum".** The thesis is acceptable in form and content, and that the student demonstrated a satisfactory knowledge of the field covered by this thesis in the oral examination held on the 25th April, 1999.
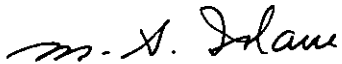

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Abstract

This work deals with the study of the process parameters such as reactant concentrations, reaction time and reaction temperature for the production of ammonium sulfate utilizing by-product gypsum of TSP Complex, Chittagong for obtaining the optimum conditions for commercial application.

A liquid phase reaction was carried out using excess ammonia and carbon dioxide. Keeping the possible parameters constant, reaction time was changed and it was seen that with the increase in reaction time conversion increases. With the increase of excess ammonia, conversion increases and at 50% excess ammonia (3.0 mole ammonia and 1.25 mole carbon-dioxide per mole of calcium sulfate fed) maximum conversion of 88.41% was achieved. Reaction temperature was $38^{o}C$ and the reaction was completed within 11 hours.

ACKNOWLEDGEMENT

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CHAPTER – ONE

INTRODUCTION

The manufacture of triple superphosphate (TSP) by the TSP complex at Chittagong requires phosphoric acid. The wet process is used for making phosphoric acid by reacting rock phosphate with sulphuric acid and gypsum is produced as a by-product.

The TSP complex produces about 250,000 tons of by-product gypsum annually against 152,000 tons of fertilizer grade TSP. While planning the complex, utilization or disposal of this huge quantity of gypsum was not taken into consideration. Disposal of this gypsum is a serious problem. It cannot be dumped into the sea as it will endanger marine environment and aquatic life. Moreover, disposing gypsum on land requires a large area but there is no vacant land close to the site to be used for such purpose.

This work was undertaken to study the process involving the reaction between gypsum and ammonium carbonate for the production of ammonium sulfate which can be used as a fertilizer. Other notable applications of ammonium sulfate include: fireproofing and fire-fighting mixtures, tanning and fermentation etc. The main advantages of ammonium sulfate as a fertilizer are its low hygroscopicity, good physical properties, chemical stability, good agronomic and effectiveness. It is a good source of sulfur as well as nitrogen. Its reaction in the soil is strongly acid forming which is an advantage on alkaline soils and for some crops such as tea.

While studying the process for the industrial production of ammonium sulfate on small scale utilizing the reaction between by-product gypsum and ammonium carbonate, the following issues were looked into:

i)   minimization of the consumption of the reactants,

ii)   optimization of the reaction parameters such as reactant concentrations, temperature and time, and

iii)   recovery of the excess reactants.

CHAPTER – TWO

LITERATURE REVIEW

2.1 Historical Background

The idea of manufacturing ammonium sulfate by the reaction between calcium sulfate and ammonium carbonate was first used at a plant in Austria in 1809 [17]. This early ammonium sulfate process was not successful enough to be used commercially, and it was more than 100 years before a viable commercial process was developed by Badische Anilin and Soda Fabrik in Germany [17]. Two plants were built and operated in Germany during World War I [1].

This production method is still used in parts of the world where sulfuric acid is expensive and where a supply of calcium sulfate is available, such as in England, France, Germany, and India.

2.2 Characteristics of Ammonium Sulfate

Commercial ammonium sulfate may vary in color from a white through yellow to a gray salt, but it is usually white. Occasionally various tints of brown, blue, yellow, or gray may be present. These tints are due to impurities such as ferric ferrocyanide and arsenious sulfide, or to traces of tar or its derivatives.

The by-product ammonium sulfate now found in the market contains practically no free acid. The better grades have a free sulfuric acid content of less than 0.15 per cent. Some of the commercial grades might slightly exceed this figure, but the free acid content is seldom over 0.5 per cent. This was not always the case in the past. At one time free acid adhering to the crystals of ammonium sulfate caused rotting of shipping bags and the formation of lumps and hard cakes. This condition has been overcome by more thorough washing of the salt and in some cases by neutralizing the free acid with

ammonia. It has been shown that large crystals are to be preferred to small ones as the tendency to cake is thus reduced.

Pure ammonium sulfate contains 21.2 per cent nitrogen and 27.5 per cent sulfur. The commercial product is sold for fertilizer under a guaranteed analysis of 20 per cent nitrogen. In addition it contains about 24 per cent of sulfur. It is a fine crystalline salt, almost moisture-free and requires no grinding before use. It does not absorb moisture if it is stored in a reasonably dry place. At ordinary temperatures the solubility of ammonium sulfate in water is practically equal to that of sodium nitrate. Tidmore and Williamson [27] and many other investigators have shown that the nitrogen of ammonium sulfate may be retained by the soil for a limited length of time, in an exchangeable form which does not leach as readily as the nitrogen of sodium nitrate.

2.3 Mixing Superphosphate with Ammonium Sulfate

When ammonium sulfate is added to a fertilizer mixture containing superphosphate, and the mixture is allowed to stand for a time, the mixture is likely to become hard owing to a chemical reaction that may take place between the ammonium sulfate and the monocalcium phosphate, as follows:

$$(NH_4)_2SO_4 + CaH_4(PO_4)_2.H_2O + H_2O = CaSO_4.2H_2O + 2NH_4H_2PO_4$$
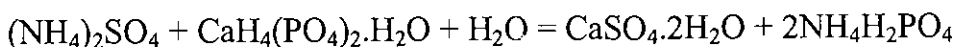
For this reason, when ammonium sulfate is used in the preparation of complete fertilizers containing superphosphate, sufficient time must be allowed for the curing or completion of this chemical reaction. Once the mixture has been cured, there is no secondary caking from this cause. The gypsum which is formed in the reaction has 2 molecules of water of crystallization; and as only 1 molecule is supplied by the monocalcium phosphate, the other molecule of water is taken from the free moisture in the mixture. This moisture absorption is very advantageous in preparing a dry fertilizer mixture. The addition of woody or fibrous organic material or of 40 to 50 pounds of pulverized Cynamide per ton to the mixture prior to curing, also reduces the extent of caking.

Ammonium sulfate is not compatible with alkali materials such as lime, basic slag and calcium nitrate. The mixtures of these materials may result in a loss of some of the nitrogen of ammonium sulfate to the atmosphere. Ammonium sulfate may be mixed, however, with urea if it is used immediately after mixing.

2.4 Influence of Ammonium Sulfate on Soil Acidity, Toxicity and Structure

Ammonium sulfate, like other ammoniacal fertilizer materials, is physiologically acidic and, as shown by Barnette and Hester [4] and Pierre [21], produces, when added to soil, an increase in the hydrogen-ion concentration of the soil solution. When the acidity of the soil is greatly increased, many beneficial soil processes are interfered with. The rate of nitrification in particular is decreased, for nitrification does not proceed extensively in the soil when the pH of the soil solution is below 5.5. That the increase in soil acidity resulting from the use of ammonium sulfate can easily be corrected through the use of lime or other basic materials was earlier shown by Hall and Gimmingham [10].

Studies have shown also that the continuous use of ammonium sulfate without lime may result in the production in the soil of compounds that are toxic to crops [6]. The free acid produced when ammonium sulfate is added to the soil in humid regions probably first reacts with the calcium and magnesium compounds of the soil if such are present. When these compounds are absent, it reacts with the iron, aluminum, and manganese compounds of the soil. The iron, aluminum, and manganese compounds which are thus rendered soluble appear to be responsible for a large portion of the toxic effects so often noted where ammonium sulfate and other ammoniacals have been applied to the same soil for a number of years. If a quantity of time sufficient to neutralize the acidity produced by ammonium sulfate is present in the soil to which the ammonium sulfate is applied, the toxic iron, aluminum, and manganese compounds will not be formed.

The application of ammonium sulfate has been known also to produce chlorine toxicity in crops when applied with chlorine-carrying fertilizer materials.

2.5 Influence of Ammonium Sulfate on Lime Requirement of Soil

According to White and Holber [28], 40-year results secured from the Jordan plots, located on a limestone soil at the Pennsylvania Experiment Station, showed that the increase in the lime requirement of plots receiving ammonium sulfate above that of the lime requirement of plots receiving sodium nitrate was equal to about 67 pounds of calcium carbonate for each 100 pounds of ammonium sulfate applied. Hartwell and Damon [11], of the Rhode Island Experiment Station, concluded that the theoretical requirement of about 7 pounds of calcium carbonate to 1 pound of nitrogen supplied as ammonium sulfate should be the basis of liming to maintain land fertilized with ammonium sulfte at the same reaction as if receiving sodium nitrate.

Allison and Cooke [3] found that for every 100 pounds of ammonium sulfate applied to a soil an increase in soil acidity occurred equivalent to that which could be neutralized by 143 pounds of calcium carbonate. Theoretically, this is about what might be expected. In general, for most acid soils the proper addition of lime appears to be about 1.5 to 2.0 tons of ground limestone per ton of ammonium sulfate applied. Mary agronomists now recommend that a sufficient amount of limestone be mixed with the ammonium sulfate to make a physiologically neutral mixture before the ammonium sulfate is applied [3]. Such a practice is unnecessary if the pH of the soil is being maintained at an optimum value by liming.

2.6 Application of Ammonium Sulfate

Ammonium sulfate may be put under the crop or applied as a top or side dressing. Ammonium sulfate usually is applied to crops in about the same manner and in about the same amounts, on an equivalent nitrogen basis, as sodium nitrate. Seventy five

pounds of ammonium sulfate is equivalent to about 100 pounds of sodium nitrate. From 100 to 500 pounds of ammonium sulfate per acre is the most common application. Recently some very good results have been reported from plowing under ammonium sulfate when the land is broken, and rice growers of California have successfully applied ammonium sulfate by airplane [6].

2.7 Loss of Ammonia Following Application of Ammonium Sulfate

Following an application, the ammonia of ammonium sulfate is readily fixed by the colloidal complex of acid soils. Like all ammoniacal compounds, the nitrogen of ammonium sulfate is resistant to leaching and this may under some conditions be more suitable than nitrates for use at planting time. It appears, however, that alkaline soils of low ion-exchange capacity cannot absorb and hold ammonia. Jewett [12] found that considerable quantities of ammonia were lost in drainage water following an application of ammonium sulfate to the alkaline soils.

2.8 Influence of Ammonium Sulfate on Growth of Various Crops

Preferably, unless lime is applied, ammonium sulfate should not be applied to most humid soils continuously for a long term of years as the only source of nitrogen, nor should it be applied in quantities to nonacid-tolerant crops [6]. This principle holds true for most of the ammoniacal fertilizers. On the other hand, ammonium sulfate may be applied longer with satisfactory results to soils upon which are to be grown cranberries, blueberries, watermelons, and rhododendrons, or other plants that thrive well on acid soils. In some areas potato growers favor ammonium sulfate because by maintaining an acid condition of the soil as it aids in controlling potato scab.

2.9 Nitrification of Ammonium Sulfate

For many years it was generally thought by agriculturists, but without conclusive supporting evidence, that all field crops use nitrates exclusively as their source of nitrogen, and that all non-nitrate nitrogenous fertilizers must be converted into the nitrate form before they could be assimilated by plants [6]. Later, however, it was abundantly shown that ammonia was absorbed and utilized by many plants. In fact, some nitrogen in ammoniacal form was shown to be necessary for optimum growth of potatoes, buckwheat, and other crops, especially during their seedling stage of development. That seedlings absorb ammonia as such, and often in quantities greater than they absorb nitrates, was shown by Shive [25], of the New Jersey Experiment Station. Shive found that as seedlings become older the absorption ratio of nitrogen as ammonia to nitrogen as nitrate becomes smaller until finally it is less than unity. In general, it might be said that if the reaction of the soil solution is slightly acidic, neutral, or alkaline, young plants will absorb ammoniacal nitrogen rapidly and by preference. In fact, it has been pointed out by Pierre and Bower [21] that a relatively high pH value of the soil is most favorable for the absorption of ammonium ions by plants.

It has been established fairly conclusively that for crops such as those tolerant to acid soil conditions the ammoniacal form of nitrogen is effective. It also appears that the ammoniacal form would be superior for most crops if the masking effect of the resulting acidity could be overcome. According to Russell [22] plants which are relatively rich in carbohydrates, such as barley, maize, and pumpkins, readily utilize ammonia, whereas peas which contain less carbohydrate, utilize ammonia only when calcium carbonate is present. Plants that grow well under conditions of poor soil aeration and in soils that are low in soluble potassium, sodium, and calcium appear to tolerate part or all of their nitrogen in the ammoniacal form. Bear [5] has suggested that the absorption of ammonium (NH_4) rather than nitrate (NO_3) nitrogen by plants may lower the intake of mineral cations and increase that of the mineral anions. Stewart, Thomas, and Horner [26], showed that pineapples are able to utilize all their

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nitrogen in the form of ammoniacal compounds; and Kelly [14] demonstrated that rice grown on submerged soils absorbs nitrogen in the ammoniacal form and that this nutrient should be applied to rice as an ammonium salt. Kelly states that when nitrates are applied to rice on submerged soils, they are partly reduced to nitrites, and that if nitrites accumulate in the soil to any considerable extent, injury to the rice is likely to result. This last observation was confirmed by Kapp [13]. Allison [2] concluded that higher plants may utilize more ammoniacal nitrogen than is generally supposed.

2.10 Recent Developments in the Production of Ammonium Sulfate

In 1923 synthetic ammonium sulfate came into the world market in large quantities from Germany for plant nitrogen fixation application [6]. It is now manufactured in large quantities in Germany and in many other countries. The method of manufacture followed is known as the gypsum process. By this method ammonia water is conducted into a tank containing pulverized gypsum suspended in water. At the same time carbon dioxide is bubbled through the mixture under 5 atmospheric pressure. Ammonium carbonate is formed first, which in turn reacts with the calcium sulfate to form ammonium sulfate. The ammonium sulfate remains in solution and is recovered by evaporation after the resultant calcium carbonate has been filtered off.

In 1950 Klempt [15] investigated the possibility of converting NH_3 in crude coke-oven gas into $(NH_4)_2SO_4$ with gypsum as the SO_4 – donor. The reaction proceeds according to the equation:

$$2NH_3 + CO_2 + H_2O + CaSO_4 = CaCO_3 + (NH_4)_2SO_4$$

Contrary to the conversion of NH_3 into $(NH_4)_2SO_4$ with H_2SO_4, the reaction with gypsum is reversible. Laboratory scale experiments were carried where H_2S – free NH_3 gas mixed with CO_2 and water vapor being bubbled through a slurry of $CaSO_4$ and water. The most suitable condition for the reaction was a temperature between 35 and $40^\circ C$ and a 4-10% excess of CO_2 (0.52 – 0.55 mole CO_2 per mole NH_3). An 85% yield
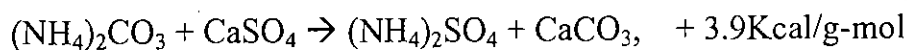
of $(NH_4)SO_4$ was obtained. It is, therefore, possible to convert gaseous NH_3 as well as concentrated NH_4OH, both H_2S – free, with $CaSO_4$ into $(NH_4)_2SO_4$.

Sam P. Robinson [24] reported that $(NH_4)_2SO_4$ and $CaCO_3$ are produced by the reaction of an aqueous slurry of $CaSO_4$ with an aqueous solution of $(NH_4)_2CO_3$ in a series of reaction zone in the presence of a small amount of NH_4HCO_3. The reactors are of progressively larger size and are supplied with progressively decreasing amounts of agitation. The reactants and sufficient NH_4HCO_3 to maintain the pH between 6 and 8 are introduced into the first reactor, and sufficient NH_3 is added to the mixture as it passes through the subsequent reactors to increase the pH to 9-10 in the last one. The residence time of the reactants in the reactors is progressively increased, with a total time of 42-115 min, and the temperature is progressively decreased from 40-45°C down to 36-40°C. The products are recovered from the mixture leaving the last reactor to obtain a $CaSO_4$ conversion up to 99% by weigh. Readily filterable $CaCO_3$ having an average particle diameter of 5-10 µ may thus be produced.

In 1955 Jan Pluim [18] found that in order to bring about the double decomposition of $CaSO_4$ and $(NH_4)_2CO_3$, at first one of the double salts, $CaSO_4.(NH_4)_2.H_2O$ or $2CaSO_4.(NH_4)_2SO_4$, is prepared by treating Calcium sulfate (gypsum, hemihydrate, or anhydrite) with solutions of $(NH_4)_2SO_4$, the concentration of which is at least 35% by weight in the case of the first mentioned double salt, this then being in equilibrium with $CaSO_4.2H_2O$. The double salt is separated from the solution of $(NH_4)_2SO_4$, and the solution is then treated with NH_3 and CO_2 to form a solution of $(NH_4)_2CO_3$ containing so much $(NH_4)_2SO_4$, that reaction of this solution with the double salt causes separation of solid $(NH_4)_2SO_4$ in a quantity at least equivalent with the quantity of $CaSO_4$ in the double salt.

In 1962 Roland Syers [23] investigated that a mixture of $(NH_4)_2CO_3$ with $CaSO_4$ – $\frac{1}{2}H_2O$ is allowed to stand 4-5 days, during which time the reaction occurs at ambient temperature. The product is dried and heated to décompose. The residual $(NH_4)_2CO_3$ and the product sieved are sold as a fertilizer.

The reactions of calcium sulfate with ammonium carbonate are:

$$NH_3 + H_2O \rightarrow NH_4OH, \quad + 8.3 \text{ Kcal/g-mol}$$

$$2NH_4OH + CO_2 \rightarrow (NH_4)_2CO_3 + H_2O, \quad + 22 \text{ Kcal/g-mol}$$

$$(NH_4)_2CO_3 + CaSO_4 \rightarrow (NH_4)_2SO_4 + CaCO_3, \quad + 3.9 \text{Kcal/g-mol}$$

Aqueous ammonium sulfate solutions are obtained from these reactions and these are processed to recover crystalline product [17]. When a saturated solution of a crystallizable salt such as ammonium sulfate is cooled or supercooled, it is metastable just before solid crystal nuclei form. After nuclei are formed the solution is labile or unstable and crystals will grow from each nucleus if additional metastable liquid is supplied. Metastable conditions are affected by pH, temperature, impurities, crystals surface area, and agitation. Uniformly sized crystals are produced in a crystallizer when the supply of metastable liquid feed is kept constant and when the number of new nuclei formed is equal to the number of crystals removed. Production rates are normally held constant, therefore, the average crystal size is a function of the nucleation rate.

Various improvements have been made in processes and equipment over the years with the objective of improving the size, size distribution, and shape of the recovered crystalline ammonium sulfate to make it easier to handle, store and use. There are also granulation processes available for increasing the ammonium sulfate particle size when crystal growth is restricted because of equipment limitations or the presence of crystal growth inhibitors.

In one granulation process the fine ammonium sulfate solid, containing 2 to 3% moisture, is passed through a set of rotating compacting rolls which compress the feed into a continuous sheet about 1/8 inch thick. This material is dried to a moisture content of about 0.1% and is then passed through serrated steel granulator rolls where the dried compacted material is reduced in size [29]. The flat irregular-shaped particles are screened and the undersized particles are recyled to the process. The oversized granules are broken into smaller particles and then recycled to the process.

In another process a mixture of fine solid ammonium sulfate particles and small moist crystals of ammonium sulfate are passed through a blunger [7]. This equipment consists of a long tube with a shaft running through the middle to which are attached a number of paddles. When the shaft is rotated, the paddles mix the small moist crystals and the dry recycle material, causing them to stick together to form granules because of the tackiness of the saturated mother liquor present. The moist granules emerging from the blunger are dried in a rotary drier. When the moisture is removed, the particles in each individual granule are cemented together by crystallization of the ammonium sulfate that was present in the mother liquor phase. The dried granules are screened, and the undersize and oversize materials are reprocessed.

Particle size can also be increased by moistening fine particles of ammonium sulfate in a drum granulator with liquids such as a lignosulfonate solution or ammonium phosphate solution and drying the resulting granules [16, 30]. Also, a mixture of fine ammonium sulfate and fly ash can be moistened with a solution of ammonium sulfate followed by pelleting and drying.

Another method [8] describes that ammonia and carbon dioxide are passed into the suspension of ground gypsum ($CaSO_4.2H_2O$ or anhydride ($CaSO_4$ containing twice its weight of water forming first ammonium carbonate, which then reacts with the calcium sulfate (gypsum) forming calcium carbonate and ammonium sulfate which remains in solution [8]. At the end of the reaction (6 to 9 hr), the 25 per cent ammonium sulfate solution is filtered to remove the insoluble calcium carbonate. The clear solution is concentrated in evaporators to crystallize out the ammonium sulfate. The crystals are centrifuged and may be further dried in a rotary dryer. The mother liquor is returned to the reactor for subsequent batches.

In one Indian plant (Sindri), ammonia gas is absorbed in water and carbonated at a pressure of about 2.1 kg/cm^2g in two series-connected aluminum towers. The elevated pressure allows a higher cooling-water temperature to be employed than if atmospheric pressure were used. Carbon dioxide is introduced at the base of the primary tower,

which is packed with 5-cm stoneware rings wetted with a solution of ammonium hydroxide and recycling ammonium carbonate. Final absorption takes place in the secondary tower, and reaction heat is removed by recirculating liquor through water-cooled heat exchangers in closed circuit with each tower. The preferred liquor strength corresponds to approximately 170 gm of ammonia and 225 gm of carbon dioxide per liter. Stainless steel is used for the wetted parts of pumps and liquor piping is made of aluminum.

In a more recent Indian plant (Fertilizers and Chemicals Ltd., Travancore), jet absorbers are used to prepare both the ammonia solution and the ammonium carbonate liquor in conjunction with a carbonating tower. Cooling is undertaken by recycling liquor through water-cooled heat exchangers and the heat of reaction thereby vaporizes the liquid anhydrous ammonia used in the process. When the desired strength has been reached, the solution is sent to storage and subsequent reaction.

When natural gypsum or anhydrite is used, it is crushed and ground before reaction. In one case, the preferred final size is about 90% through 120-mesh although, under certain circumstances, there are indications that a coarser grade is permissible.

Reaction can be undertaken either in a series of wooden vessels or mild-steel tanks fitted with steam coils and agitators, and the reaction train is usually designed to give a total retention time of 4-6 hours. The slurry produced is filtered and the calcium carbonate cake washed and dewatered on a two-stage drum-filter installation. Final clarification by pressure filtration or settling is sometimes employed to ensure maximum purity of product, followed by neutralization with sulfuric acid and heating to about 110°C to remove excess ammonia prior to concentration and crystallization. Evaporation is undertaken in continuous multiple-effect evaporator crystallizers. Crystals of the required size range are separated and washed in a centrifuge. The crystals are then dried in a rotary drier at 120°-130°C and sent to storage [7].

CHAPTER – THREE

STATEMENT OF THE OBJECTIVES

The followings were the objectives to develop a process for the industrial production of ammonium sulfate on small scale utilizing the reaction between byproduct gypsum and ammonium carbonate:

    i)   minimization of consumption of the reactants;

    ii)   optimization of the reaction parameters such as reactant concentrations, temperature and time; and

    iii)   recovery of the excess reactants.

In order to achieve these objectives, a number of experiments were carried out in glass wares using small samples to appraise the production process. This was followed by experimentation using a stirred stainless steel reactor.

Reactants were: gypsum from the TSP complex at Chittagong; commercial grade ammonium hydroxide and carbon dioxide in gas cylinders from British Oxygen Company (BOC), Bangladesh Ltd.

CHAPTER – FOUR

EXPERIMENTAL SET-UP AND PROCEDURE

4.1 Experimental Equipment

This work dealing with the production of ammonium sulfate was carried out in two stages. In order to appraise the production of ammonium sulfate, preliminary experiments were carried out using glass wares.

On the basis of the experience gained, different equipment were constructed and the experimental arrangements are shown in Figures 4.1.1, 4.1.2 and 4.1.3 and the photograph of those are shown in Figures 4.1.4 and 4.1.5. The experimental set-up consists of a reactor, an evaporator, a condenser and an absorber.

REACTOR

A stainless steel cylindrical jacketed reactor (Figure 4.1.3) of 18 litre capacity (inside dia 20.3 cm, length 40.6 cm) with a motorized flat-blade stirrer was used. The reactor was jacketed for maintaining the desired operating temperature by flowing cooling water through the jacket. The reactor was baffled for proper mixing of the reactants. The reactor was provided with a sampling and a temperature ports at the top and the CO_2 distributor was located at bottom of the reactor.

EVAPORATOR

A steam heated jacketed cylindrical type evaporator was used to evaporate the solution obtained from the reactor. The inside dia of the evaporator was 15.3 cm and the length was 38.1 cm. A thermometer was placed at the top of the evaporator outlet to measure the temperature of the vapor.
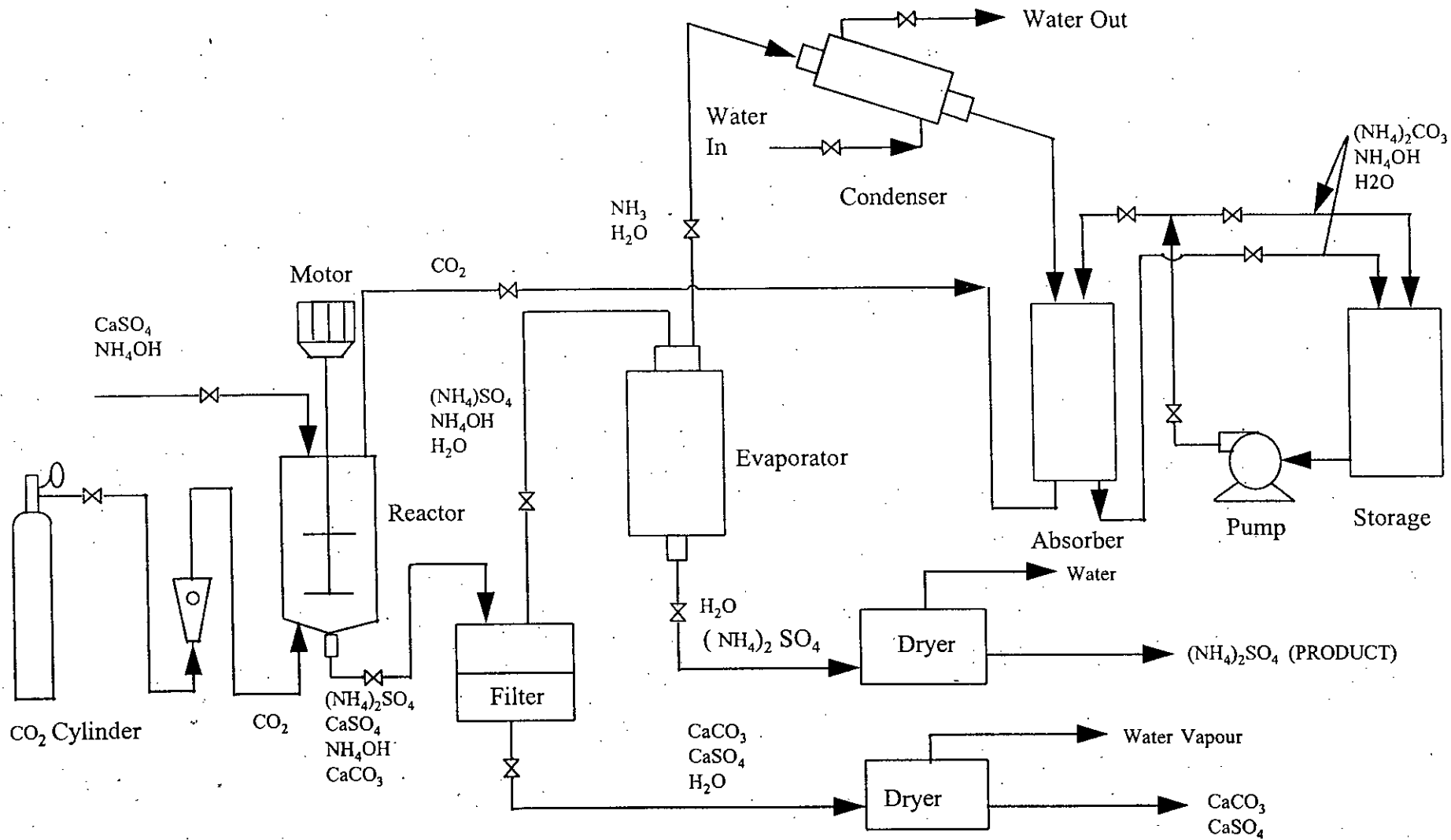
Fig.4.1.1 Experimental Process Flow Diagram

CaSO$_4$.1/2H$_2$O(Solid)
NH$_4$OH(Liquid)

NH$_3$
H$_2$O

Condenser

(NH$_4$)$_2$CO$_3$
NH$_4$OH
H$_2$O

CO$_2$

Reactor

CO$_2$ (Gas)

(NH$_4$)$_2$SO$_4$
NH$_4$OH
H$_2$O

Evaporator

Filter

(NH$_4$)$_2$SO$_4$
NH$_4$OH
CaSO$_4$
CaCO$_3$
H$_2$O

(NH$_4$)$_2$SO$_4$
H$_2$O

H$_2$O

Dryer

Absorber

(NH$_4$)$_2$SO$_4$ (Solid)

Pump   Storage

CaCO$_3$
CaSO$_4$
H$_2$O

H$_2$O

Dryer

CaCO$_3$(Solid)
CaSO$_4$ (Solid)
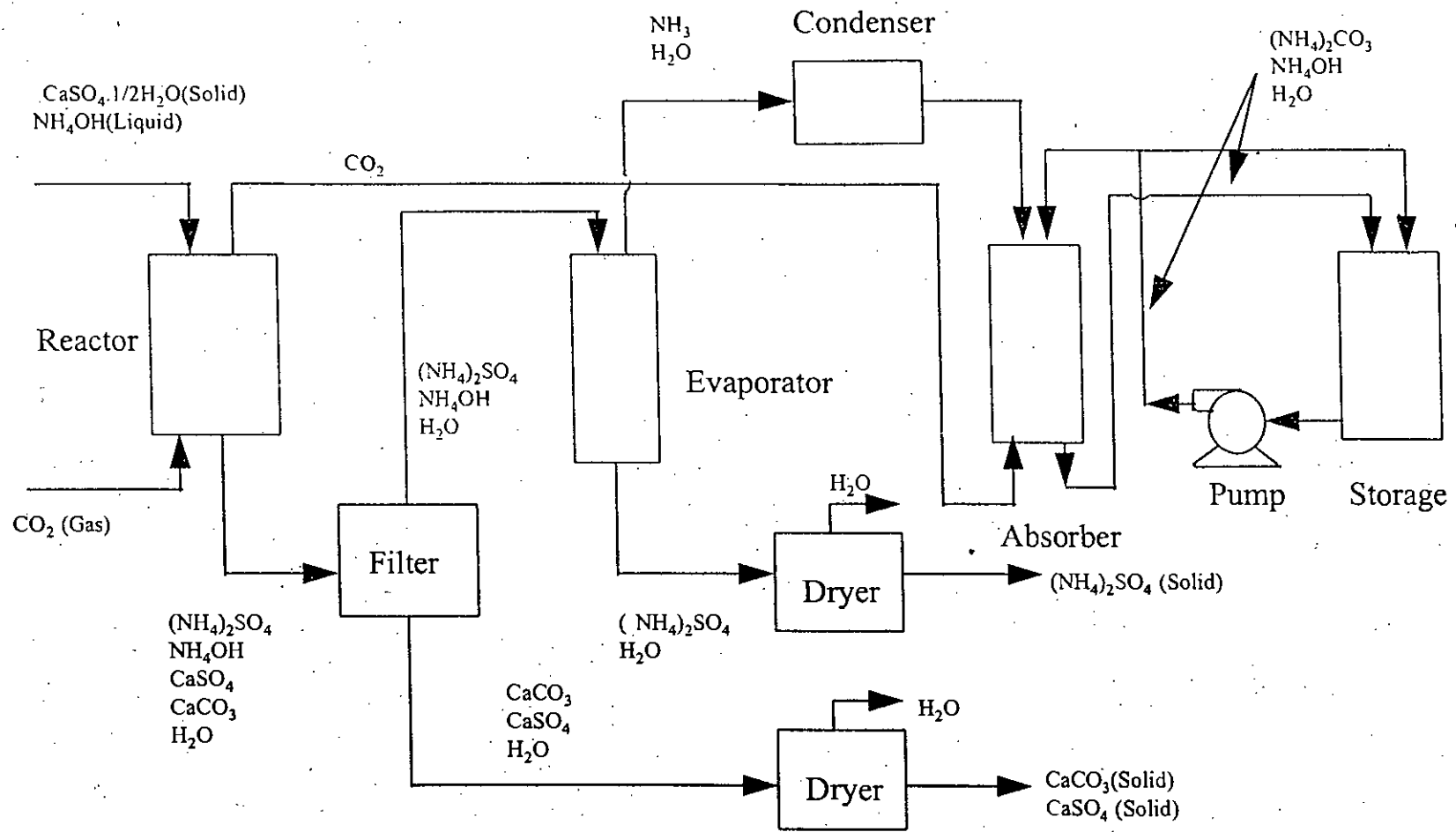
Fig.4.1.2 Block Diagram of Experimental Set-up

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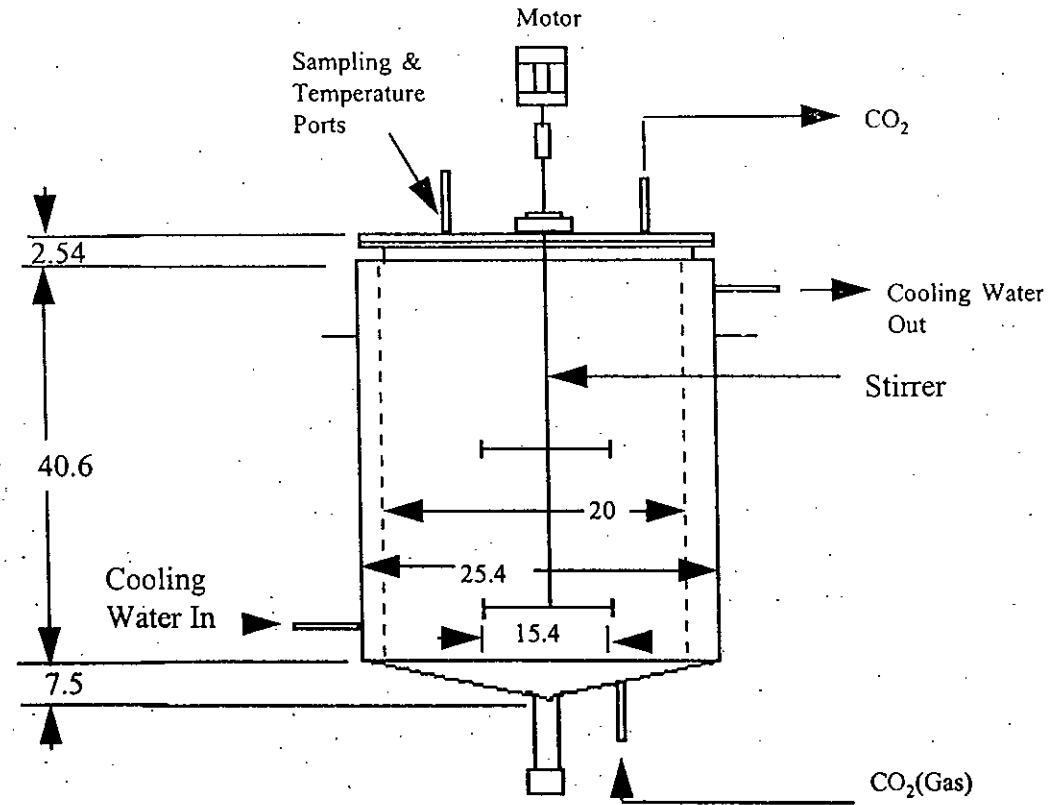
Fig.4.1.3 Diagram of the Reactor .(All the dimensions are in cm. Not to scale.)
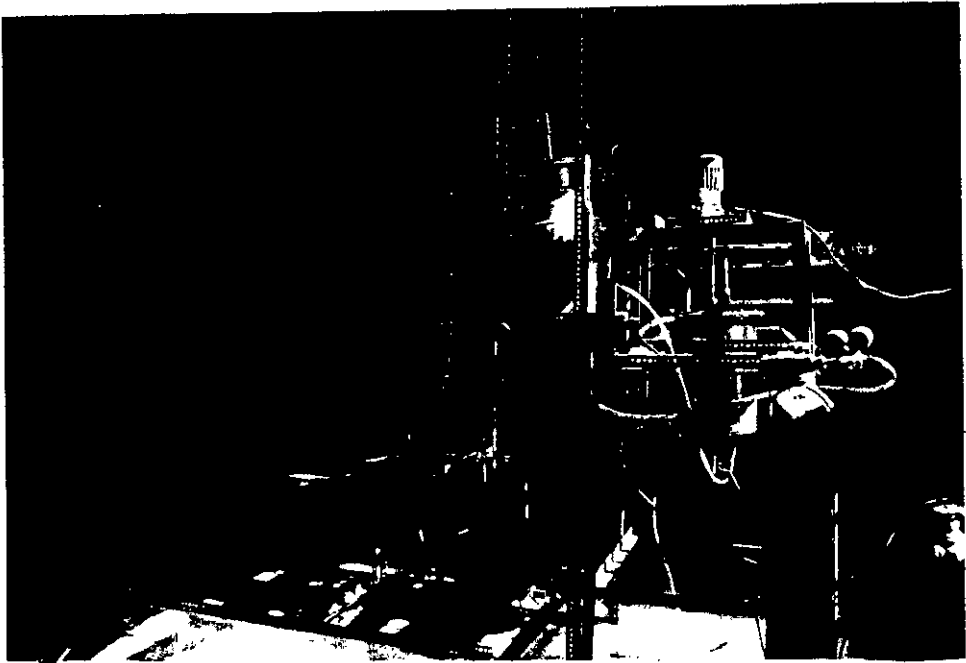
Figure 4.1.4: Photograph of the experimental set-up.
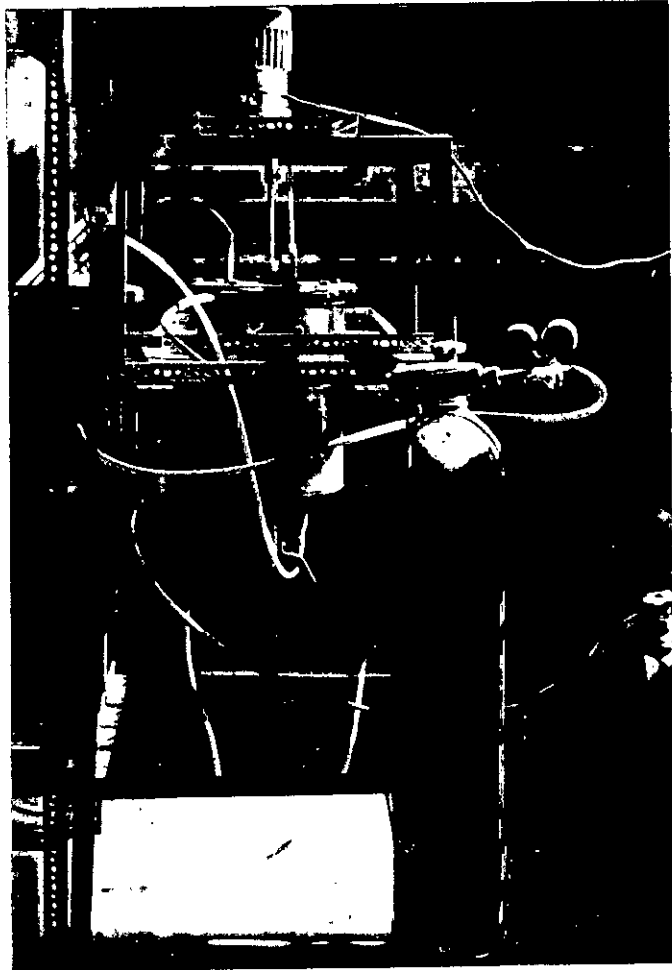
Figure 4.1.5: Photograph of the reactor.

CONDENSER

A 121.1 cm long double pipe condenser (ID of inner pipe 2.54 cm and ID of outer pipe 5.08 cm) was used to condense the vapors from the evaporator. Inner pipe was made up of stainless steel and the outer pipe was of mild steel. Cooling water was circulated through the outer pipe.

ABSORBER

A glass made absorption column was used to absorb the excess carbon-dioxide from the reactor and the excess ammonia from the evaporator. The inside dia of the column was 5 cm and length was 121.2 cm and glass beads were used as packing materials. A plastic pump was used to circulate the absorbing solution from the top of the column.

4.2 Experimental Procedure

The following steps were involved in the preparation of ammonia sulfate throughout the work:

- i)   Cleaning, drying and determination of moisture content of gypsum
- ii) Determination of NH_3 concentration of NH_4OH solution
- iii) Reaction of gypsum suspension in ammonia water with CO_2 gas
- iv) Filtration
- v)   Evaporation
- vi) Absorption of excess NH_3
- vii) Crystallization
- viii) Drying of $(NH_4)_2SO_4$ and $CaCO_3$
- ix) Testing the product.

The procedures for the above mentioned steps are described below:

4.2.1 Cleaning, drying and determination of moisture content of gypsum

The byproduct gypsum obtained from the TSP complex at Chittangong, was screened. It was then dried first in the air and it was further dried at 105°C. Final drying was stopped when two successive weights of the sample became constant.

4.2.2 Determination of NH_3 content in NH_4OH solution

Reagents: Standard Hydrochloric Acid – 1N

Standard Sodium Hydroxide Solution - 1N

Methyl Orange Indicator Solution.

Procedure: A glass-stoppered weighing bottle containing 10 ml of water was weighed and 2.0 to 3.0 gm of the sample was added to it. Measuring 50 ml of 1N hydrochloric acid in a beaker, the weighing bottle with the sample in it was put in the beaker. Sufficient water was added to completely cover the weighing bottle and the excess of acid is titrated with 1N sodium hydroxide using methyl orange indicator.

NH_3 content in solution was calculated by the following formula:

$$wt\% NH_3 = \frac{1.703(50 N_1 - VN_2)N_1}{W}$$

where, V = volume in milliliters of sodium hydroxide consumed by excess of acid

N_1 = normality of HCl

N_2 = normality of NaOH and

W = weight in grams of the material taken for the test.

4.2.3 Reaction of gypsum with NH_3 and CO_2

Ammoniacal liquor and finely ground gypsum were first charged into the reactor. Carbon dioxide gas was bubbled thereafter into the mixture at atmospheric pressure while the total reacting mass was agitated with the agitator. The reaction temperature was kept constant at about 35 to 40°C by circulating cooling water through the jacket of the reactor. Flowrate of carbon-dioxide and amount of excess ammonia were varied with each run. Ammonium carbonate is formed first, which in turn reacts with calcium sulfate to form ammonium sulfate. After every one hour interval, 10 ml sample was taken from the reactor and was filtered using filter paper and the clear solution was dried at 105°C to obtain dried ammonium sulfate and the reaction was stopped when two successive weights of dry ammonium sulfate became constant.

4.2.4 Filtration

At the end of the reaction (10 to 11 hr.), the 20-25 per cent ammonium sulphate solution was filtered first over a cloth and then over a filter paper to remove the insoluble calcium carbonate.

4.2.5 Evaporation

The clear solution was concentrated in the steam heated evaporator crystallize out the ammonium sulfate. The solubility of ammonia sulfate in water is 70.6 g per 100 ml at 0°C and 103.8 g per 100 ml at 100°C.

4.2.6 NH_3 Absorption

The vapor from the evaporator was condensed in the double pipe condenser to recover ammonia. The condensed ammonia was returned to the absorber while excess NH_3 was absorbed by water and stored in the reservoir.

4.2.7 Drying of $(NH_4)_2SO_4$ and $CaCO_3$

The ammonium sulfate crystallized out from the evaporator was dried first in air and then in an oven at $105^\circ C$ to produce dry ammonium sulfate product. $CaCO_3$ filtered out from the solution was dried first in the sun and then dried in an oven at $105^\circ C$ to produce dry $CaCO_3$ by-product.

4.2.8 Testing of the product

The product ammonium sulfate was tested by Natural Gas Fertilizer Factory Ltd., Fenchuganj and calcium carbonate was tested by Chhatak Cement Company Ltd., Sunamganj.

CHAPTER – FIVE

EXPERIMENTAL RESULTS

5.1 Physical Properties of Raw Materials

Gypsum used in this work was obtained from the TSP complex at Chittagong. Moisture content of gypsum was 13% and relevant data are shown in Table A.1. (Appendix). Commercial grade ammonium hydroxide was used, ammonia content of which was 17%, Table A.2 (Appendix). Carbon dioxide in cylinders used was obtained from British Oxygen Company (BOC), Bangladesh Ltd.

5.2 Experiments for Estimating Parameters

After every one hour interval, 10 ml sample was taken from the reactor and was filtered over filter paper and the clear solution was dried at 105°C to obtain dried ammonium sulfate and the data are tabulated in Table A.3 (Appendix) and plotted, Fig. 5.1.

Excess carbon dioxide from the reactor was absorbed by ammoniacal solution in the absorption column. The solution was circulated from top of the column and carbon dioxide was bubbled through the solution from bottom of the column. Carbon dioxide reacted with ammoniacal solution to form ammonium carbonate.

At the end of each run, 10 ml solution taken from the absorber was weighed. 5 ml 1N hydrochloric acid was added to it. The following reaction was then taken place:

$$(NH_4)_2CO_3 + 2HCl \rightarrow 2NH_4Cl + CO_2\uparrow + H_2O$$
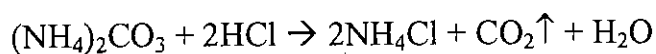
Carbon dioxide was evolved from the solution in bubble form and the amount of carbon dioxide evolved was estimated from the weight loss of the sample and is shown in Table A.4 (Appendix).

Table 5.1: Observed Data

Run No.	Reactants, Kg			% Excess NH₃	% Excess CO₂	Residence Time (hr)	Reaction Temp. °C	Products, Kg	
	Gypsum	NH_4OH	Rotameter reading					$(NH_4)_2SO_4$	$CaCO_3$
1	2.01	1.119	8.5	Stoich*	Stoich*	11	35	1.07	0.9678
2	4.4	2.69	18	10	20	10	39	2.378	1.97
3	5.37	3.587	21	20	25	10	35	3.08	2.7
4	6.35	4.947	29	40	20	10	35	3.99	2.80
5	5.86	4.89	28	50	25	11	38	3.329	2.61
6	4.88	4.34	23	60	20	10	32	3.136	2.3
7	5.86	5.54	28	70	25	11	33	3.04	2.75
8	3.89	3.77	18	75	20	11	35	2.01	2.1

* Stoichiometric

Table 5.2: Calculated Data

Run No.	Reactants, mol			Products		% NH₃ Loss	% CO₂ Loss	% Conversion
	$CaSO_4$	NH_3	CO_2	$(NH_4)_2SO_4$ (mol)	$CaCO_3$, (mol)			
1	8.88	17.76	8.89	6.65	6.78	17	13	74.88
2	19.42	42.724	23.3	15.48	15.98	15	14	79.71
3	23.74	56.976	29.67	19.6	19.6	16	15	82.56
4	28.06	78.568	33.67	24.6	25.1	15	12	87.67
5	25.9	77.70	32.375	22.9	23.2	14	15	88.41
6	21.58	69.056	25.89	18.9	19.4	16	14	87.58
7	25.9	88.06	32.375	21.9	22.1	18	11	84.55
8	17.26	60.41	20.712	14.3	14.8	17	13	82.85
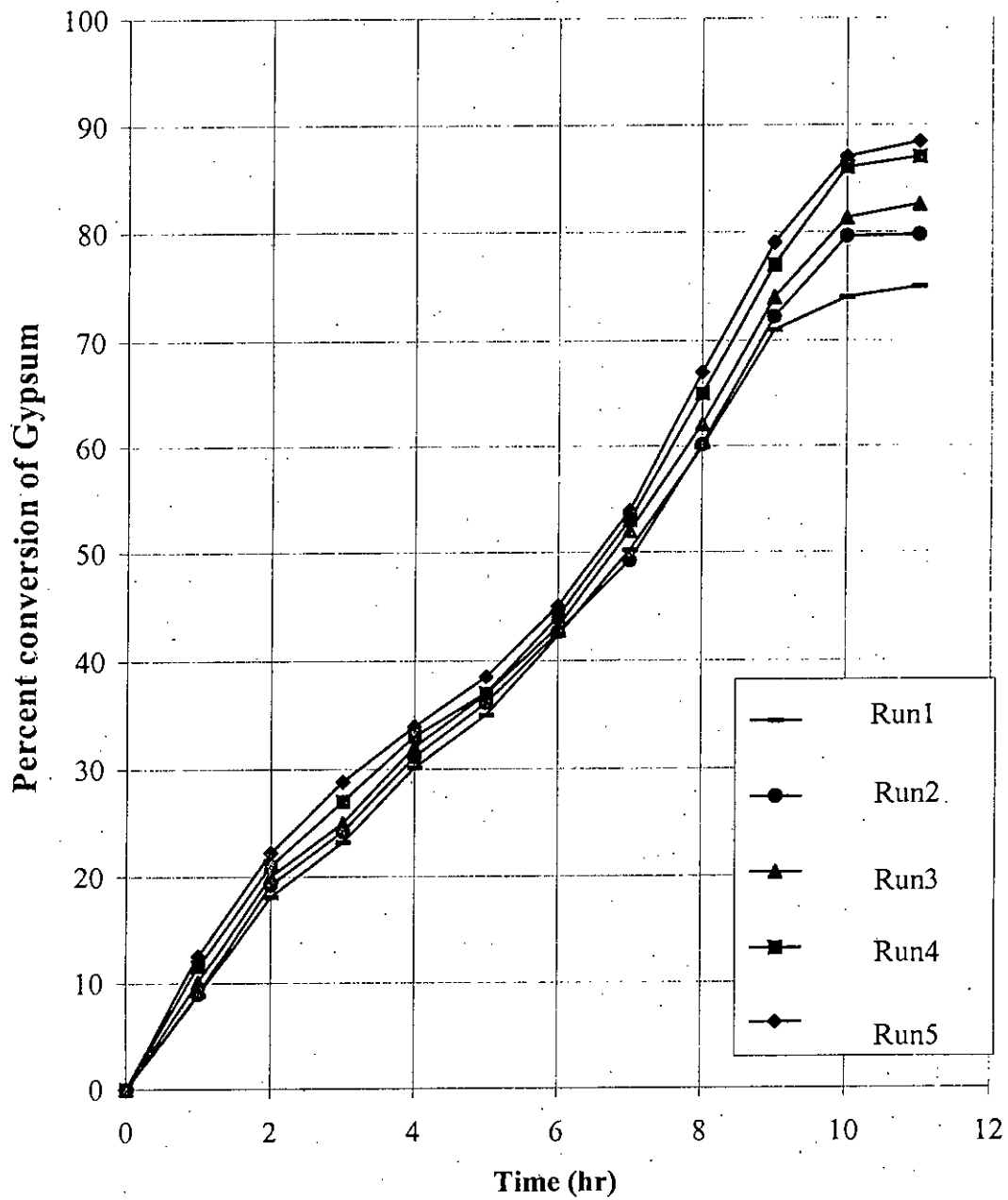
Fig.5.1 Percent conversion of Gypsum vs. Time

Optimum use of reactants and reaction time was determined by maximizing the recovery of ammonia and carbon dioxide and the experimental data are listed in Table 5.1 and Table 5.2.

The product ammonium sulfate samples were analyzed at Natural Gas Fertilizer Factory, Ltd., Fenchuganj and is shown in Table A.5 (Appendix). The by-product calcium carbonate samples were analyzed at Chhatak Cement Co. Ltd., Sunamgonj and is shown in Table A.6 (Appendix).

CHAPTER – SIX

DISCUSSIONS

The parameters which affect the conversion of gypsum to ammonium sulfate are reaction time, reaction temperature, system pressure, amount of inerts or impurities present in the reactants, nature of impurities, solution pH, and amount of excess ammonia, etc. The reaction was carried out at atmospheric pressure and a temperature of 38°C was found to be the optimum reaction temperature.

The heat of reaction was removed by circulating cooling water around the reactor. The heat of reaction can also be removed by evaporating water added to the system for temperature-control purposes.

Ammonium sulfate liquors are quite corrosive, and wetted parts of equipment were made of stainless steel of Type 304. In this work all the equipment used were made of Type 304 stainless steel.

Under certain conditions, this process of making ammonium sulfate has several advantages, for example, countries without indigenous sulfur supplies but having byproduct sources of gypsum like Bangladesh, can produce ammonium sulfate without purchasing sulfur from abroad. In addition, the byproduct calcium carbonate can be used for cement production or other purposes, such as for agricultural lime or in calcium ammonium nitrate manufacture. One disadvantage is the large amount of energy (steam) required to recover solid ammonium sulfate from the relatively dilute solution. In this work ammonium sulfate solution was concentrated in an evaporator by condensing steam. It was first dried in the sun and then in an oven at 105°C. The whole drying process was time consuming.

The reaction mixture was filtered to separate calcium carbonate and unreacted calcium sulfate from the ammonium sulfate solution. After first time filtration, ammonium sulfate and smell of ammonia were present in the cake. For this reason, the cake was

washed with water and all the ammonium sulfate solution can be removed from the cake by repeated washing with water. But the increase of washing causes the increase of filtration time and also increases the subsequent evaporation load causing energy loss tremendously. This is one of the major disadvantages of this process. In this work the cake was washed twice. Therefore all the ammonium sulfate could not be removed from the solution and the conversion reported is slightly less from the actual value. The addition of certain carboxylic or sulfonic acid salts is reported of facilitate removal of very fine precipitate in the filtration step [17]. But such salts were not used in this work.

Laboratory scale experiments carried by Klempt [15] showed that the most suitable condition for the reaction was a temperature between 35 and 40°C. An 85% yield of $(NH_4)_2SO_4$ was obtained. It was reported [17] that the conversion of gypsum and saturated ammonium carbonate solution is 95% after 5 hours if the gypsum is ground fine enough for at least 95% of it pass through a 120-mesh screen and if the reaction temperature is kept at 70°C. Therefore, the reaction temperature has a prominent effect on the conversion of gypsum and ammonium carbonate solution. In this work, the reaction temperature was kept within 35-40°C by circulating cooling water around the reactor, and a conversion of 88.5% was achieved. But at high temperature ammonium carbonate decomposes. Therefore, the reaction is to be carried out at about 40°C.

Experiments showed that the lower value of reaction time was 9.0 hr. and the upper value was 11 hr. The results obtained can be generalized as following, with the increase of reaction time, the percent conversion increases and the later becomes constant after a certain time and the reaction time of 10 hours was found to be the optimum for practical applications.

It was found that ammonia loss was 14-16% and that of carbon dioxide was 11-14%. These losses, however, can be minimized by improving the system by incorporating recovery units, controllers and detectors.

The impurities present in gypsum such as phosphoric acid, rock phosphate, oxides of iron, chloride, fluoride etc. affect the conversion by consuming ammonia and carbon dioxide changed. It is desirable to use ammonia more than the theoretical amount to precipitate iron impurities [17].

Use of the stoichiometric amount of reactants showed that the conversion was only 76.92%. With the increase of excess ammonia, percent conversion increased slightly and at 50% excess ammonia the conversion was 88.5%. The optimum reactant concentrations were 3.0 mole ammonia and 1.25 mole CO_2 per mole of $CaSO_4$ fed.

CHAPTER – SEVEN

CONCLUSIONS

The following conclusions are drawn from this work dealing with the optimization of the process parameters for the commercial production of ammonium sulfate on small scale by utilizing byproduct gypsum of TSP complex :

i) The reaction can be carried out at atmospheric pressure.

ii) Reaction temperature will be 38°C.

iii) Reactants concentration will be 3.0 mole ammonia and 1.25 mole carbon dioxide per mole of calcium sulfate fed.

iv) Minimization of the use of reactants can be obtained by absorbing the excess NH_3 and CO_2 in an absorber and recycling the same.

v) Reaction time would be in the range of 10-11 hours for maximum yiled.

CHAPTER – EIGHT

RECOMMENDATIONS FOR FUTURE WORK

The following works may be carried out in future dealing with the production process of ammonium sulfate:

i) Recycling of the reactants to achieve stoichiometric level of consumption of reactants.

ii) Recovery of NH_3 and CO_2 to be achieved upto 95% plus.

iii) Investigation on how the side products of reactions affect the production parameters and how much of these side products can be tolerated in recycle process for maximizing the use of reactants for obtaining a commercial grade ammonium sulfate.

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APPENDIX A

Table A.1 Moisture Content of Gypsum

Amount of Gypsum, gm	Drying Temperature, °C	Weight of dry Gypsum, gm	% Moisture, content	% Average Moisture content
50	105	43.34	13.31	13.315
60	105	52.008	13.32	

Table A.2 Ammonia Content in Ammonium Hydroxide Solution

Sample wt, gm.	Normality of		Volume of NaOH consumed by excess acid, ml	Wt% NH$_3$ = $\dfrac{1.703(50N_1 - VN_2)N_1}{W}$	Average wt% NH$_3$ in NH$_4$OH solution
	HCl (N$_1$)	NaOH (N$_2$)			
2.0	1N	1N	30.15	16.91	
2.5	1N	1N	25.03	17.01	17.0
3.0	1N	1N	19.86	17.11	

Table A.3 Percent Conversion of Calcium Sulfate vs. Time

Run No.	Percent Conversion of Calcium Sulfate after every one hour interval										
	1	2	3	4	5	6	7	8	9	10	11
1	-	18.1	23.2	30.1	35.0	42.3	50.2	59.9	71.0	74.2	75.4
2	9.8	19.2	24.2	31.1	36.1	42.8	49.2	60.1	72.2	79.6	79.7
3	10.1	20.1	25.2	32.1	36.9	43.1	52.0	62.1	74.2	81.9	82.5
4	11.6	21.1	27.5	33.1	37.2	43.8	53.1	65.2	77.3	86.2	87.6
5	12.6	22.2	28.8	33.9	38.5	44.5	53.5	65.6	78.2	87.1	88.4
6	10.5	22.1	26.5	32.9	35.5	41.1	52.2	64.9	77.2	86.3	87.5
7	9.9	20.1	23.2	29.6	34.1	40.9	51.9	63.6	74.6	83.2	84.5
8	8.7	19.2	22.1	26.7	32.1	39.2	50.0	61.2	73.2	81.6	82.8

Table A.4 CO_2 content in Absorbing Solution (Expt. No. 5)

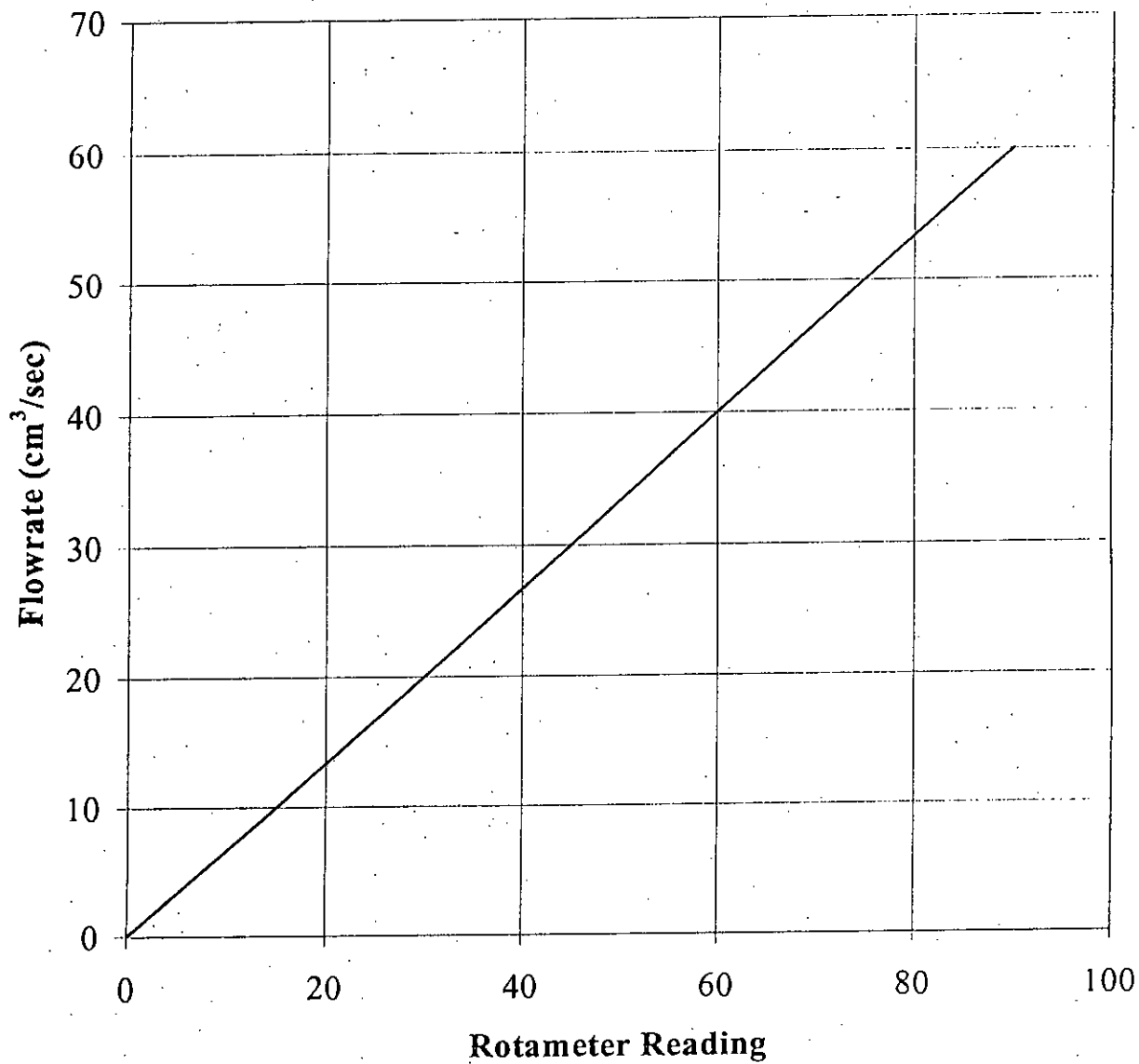| Wt. Of 10 ml sample, gm.	Wt of 5 ml 1N HCl, gm	Wt. Of sample after CO_2 evolution, gm.	Wt loss, gm.	CO_2 absorbed g/ml	Average CO_2 absorbed g/ml
11.10	5.9	11.0628	0.0372	0.00335	0.003345
11.099	5.89	11.0619	0.037	0.00334	

Fig.A.1 Rotameter Calibration Curve

Table A.5 The Physical and Chemical Analysis of Precipitated Calcium Carbonate Samples (Chhatak Cement Co. Ltd.)

Sample No.	Physical Properties			Chemical Analysis (Dry Basis)							$CaCO_3$ in the sample
	Visual color	State/ Size	Moisture content	SiO_2 (%)	R_2O_3 (Al_2O_3 + F_2O_3) %	SO_3 %	Loss on Ignition (%)	Total CaO (%)	MgO (%)	Total (%)	
1	White	Powder	0.18	1.10	0.70	12.0	36.87	48.51	-	99.97	70.64
2	White	Powder	1.85	0.80	0.60	14.0	31.54	42.00	-	99.73	74.0
3	White	Powder	1.65	1.12	0.80	13.0	34.90	46.81	-	98.93	77.0
4	Whitish	Powder	14.38	0.90	0.28	8.08	37.01	48.79	-	99.44	83.1
5	Whitish	Powder	18.31	0.86	0.66	7.2	35.88	42.66	0.27	98.76	84.2
6	White	Lump	1.83	0.40	0.22	9.3	37.55	49.73	-	99.87	83.1
7	White	Granular Powder	4.92	0.68	0.44	11.0	37.29	49.02	-	99.33	80.2
8	White	Granular Powder	5.90	2.00	0.04	12.15	34.50	46.27	-	99.05	78.3

Table A.6 Analysis Report of Ammonium Sulfate Samples (NGFF)

Sample No.	Total Nitrogen %	Moisture %	Acidity as H_2SO_4 %	Physical Appearance
1	19.15	9.11	0.023	White, Crystalline
2	19.30	5.56	0.083	White, Crystalline
3	19.11	6.73	0.02	Dirty white
4	18.80	8.17	0.033	Dirty white
5	20.39	5.53	Nil	Dirty white, Crystalline
6	18.78	8.74	0.12	White Powder
7	20.68	2.46	0.05	White, Crystalline
8	20.40	2.67	Nil	Dirty, Fine Crystalline

APPENDIX B

SAMPLE CALCULATION
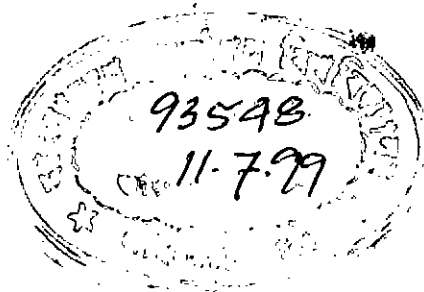
Experiment No. 1:

From the analysis of Gypsum by TSP complex, Chittagong, it was found that SO_3 content of Gypsum sample = 40.63% w/w

$$\text{Wt \% } CaSO_4 \text{ in Gypsum} = \frac{40.63 \times 136}{80} = 69.071\%$$

Moreover, Gypsum contains 13% moisture.

$$(CaSO_4)_{IN} = \frac{2.01 \times 0.87 \times 0.69071 \times 1000}{136} = 8.88 \, mol$$

Rotameter reading = 8.5

$\quad\quad CO_2$ flowrate = 5.02 cc/s $\quad$ (from rotameter calibration curve)

$$\text{Total volume of } CO_2 \text{ fed after 11 hr.} = \frac{5.02 \times 11 \times 3600}{22400} = 8.88 \, mol$$

$(NH_4)_2SO_4$ produced = 1.07 kg containing 9.11% moisture and 19.15% N_2 (from plant analysis).

In pure ammonium sulphate, N_2 content is $28/132 = .2121$

$$(NH_4)_2SO_4 \text{ produced} = \frac{1.07 \times 0.9089 \times 0.1915}{132 \times 0.2121} \times 1000 = 6.65 \, mol$$

$(CaSO_4)$reacted = $(NH_4)_2SO_4$ produced = 6.65 mol

$$\% \text{ Conversion} = \frac{(CaSO_4) \, reacted}{(CaSO)_{IN}} \times 100\% = \frac{6.65}{8.88} \times 100\% = 74.88\%$$

After eight hour interval, $(NH_4)_2SO_4$ produced was 5.32 mol.

$$\% \text{ Conversion of } CaSO_4 \; \frac{5.32 \, mol \, (NH_4)_2 SO_4 \, produced}{8.88 \, mol \, CaSO_4 \, fed} \times 100\% = 59.9\%$$

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