CONTENTS:

FERTILIZERS

Fertilizers can be illustrated as follows:

"Those chemical compounds formed by combination of certain mineral nutrients and are required for growth of plants are called as fertilizers."

EXPLANATION:

Natural weathering of mineral in soil provide enough of these elements needed by plants. In a virgin soil supporting a native vegetation, there is no loss of plant food. But the supply of nitrogen, phosphorous, potasium and calcium is insufficient for frequent repitition of same crops and soil become less productive. So the supply of nutrients is

provided in the form of their compounds to make soil reproductive Hence, For this purpose both natural chemical and artificial fertilizers are used

- The natural fertilizers are cowdung, urine or oil cakes etc.
- The chemical or artificial fertilizers include ammonium sulphate, ammonium nitrate, Urea, calcium ammonium nitrate, calcium nitrate, potasium nitrate etc etc.

PROPERTIES OF FERTILIZER:

It should be noted that every compound containing N, Ca, P, k elements are not fertilizer.

But it should contain following properties to be fertilizer:-

i- The elements present in the compound must be easily available to plants.

ii. It must be soluble in H_2O.
iii. It should be stable i.e available to plant for long time.
iv. It should not hygroscopic.
v. It should maintan pH of soil near 7 to 8.
vi. It should not be poisonous for plant.

TYPES OF FERTILIZERS:

Following are most important types of fertilizers:-

i. DIRECT FERTILIZER:

Such fertilizers are direcly absorbed by plants from soil.

EXAMPE:

Nitrates, Super phosphates, ammonium compounds.

ii. INDIRECT FERTILIZER:

Some substances do not act as fertilizes,

but help fertilization indirectly in keeping the soil's pH value suitable for growth.

EXAMPLE:

Lime barnyard etc

iii. COMPLETE FERTILIZER:

Such Fertilizers provide all essential elements required for plant growth.

EXAMPLE:

Fertilizer Guano.

iv. INCOMPLETE FERTILIZER:

They contain only one or two of required elements.

EXAMPLE:

Ammonium phosphate, potasium nitrate etc.

v. MIXED FERTILIZER:

These are formed by mixing appropriate quantities of ammonium salt, superphosphate and potasium salt etc.

They supply more than one essential elements to soil.

⟹ The plants require three elements like nitrogen, phosphorous, potasium for their growth so according to no. of nutrient elements, chemical fertilizers may be

Chemical Fertilizers

Single	Compound
• Single nutrient	• One or two nutrient elements.
• Element	• CAN, NPk, ammonium super phosphate
• Nitrogenous, phosphatic, potasium	

NITROGENOUS FERTILIZER:

These fertilizers are added to soil in order to remove the defeciency of nitrogen in soil hence the fertilizing value is expressed as available quantity of nitrogen.

EXAMPLE:

The most important nitrogenous fertilizers are nitrates of sodium, calcium, potasium, ammonium sulphate, calcium cyanamide, ammonium nitrate & urea.

NEED FOR PLANTS:

These fertilizers are needed for plants because nitrogen deficiency will retard plant growth as well as development the leaves becomes pale yellow so high yield of crop is not possible.

⇒

As we know that all these fertilizers are nitrogenous in nature so they are mostly obtained from synthetic ammonia as well as nitric acid. So overview of imp fertilizers, manufacturing & uses are given below:-

AMMONIA

Ammonia, the most important nitrogen fertilizer in fertilizer industry. Practically, it is the only building block for all Syntheic nitrogen product. About 85% of ammonia production is used for fertilizers, while remaining going to all other uses.

CHARACTERISTICS:

Ammonia has huge no of properties, due to which it is very important fertilizer. Following are most crucial properties of ammonia:

i. It is major raw material for industry and agriculture.

ii. Anhydrous ammonia without further processing is excellent nitrogen fertilizes when properly injected in gaseous form below surface of many soil.

iii. Ammonia is handled in liquified form because it is gas at atmospheric pressure and temperature.

iv. It is cheapest form of fixed nitrogen at point of production, as no further processing is required.

v. The nitrogen contents of anhydrous ammonia are twice than that of most concentrated nitrogen fertilizer. This high nitrogen contents reduces the shipping and handling weight proportionally.

PHYSICAL PROPERTIES:

		"VALUE"
i.	Nitrogen %	88.2%
ii.	Molecular weight	17.03
iii.	Boiling Point	-33.35°C
iv.	Freezing Point	-77.7°C
v.	Solubility in H_2O	42.8 at 0°C
vi.	Specific gravity	0.639 at 0°C
vii.	Critical Temperature	133.0
viii.	Critical Pressure	11,425
ix.	Specific Heat	2097.2 at 0°C

HISTORICAL BACKGROUND:

The historical background of ammonia is given below:

i. Early in twentieth century, the manufacture of Synthetic ammonia first of all succeeded with the development of Haber's process.

ii. During the period 1955 to 1965, world consumption of nitrogen as a fertilizes increased from 8 million tonns to 163 million tons. Till 1990, the consumption was 102 million tons.

iii. Since 1963, there has been a revolution in ammonia-manufacturing technology, which increased their capacity of production.

iv. Now, in these days, the production is increased to a high level as ammonia become most important fertilizer in fertilizes industry.

RAW MATERIAL:

Raw material can be illustrated as follows:-

"Any material (organic or inorganic) which is required for production of specific compound are called raw material."

EXPLANATION:

The cheif raw material in manufacturing of ammonia is nitrogen. Ammonia contain 82% N which is obtained from various sources. These raw material are used throughout the world, to manufacture ammonia and fertilizers synthesized from NH_3. The most important raw materials are :

i. Wood
ii. Lignite
iii. Coal
iv. Hydrogen
v. Coke over gas
vi. Natural Gas
vii. LP Gas
viii. Refinery Gas

ix- Naphtha

x- Fuel oil

xi- Bunker "C"

xii- Crude oil

All raw material described above are used to manufacture NH_3 and are obtained by various sources:

⟹ Some time, air, water and hydrocarbon part and power as well as used as usual material. Coal can replace the hydrocarbon but prcess is more complex and complicated.

SOURCES OF NITROGEN AND HYDROGEN:

Since ammonia contain nitrogen and hydrogen gases, so all ammonia manufacturing process, are based upon synthesis of NH_3 from nitrogen & hydrogen.

Thus, the many processes differen

tiated, among their factors, by method of producing hydrogen and nitrogen for synthesis.

Since they are most important as raw material so obtained by certain (natural) natural process or sometime they are prepared in laboratory for manufacturing purposes.

SOURCE OF HYDROGEN:

The most important sources of hydrogen are given below:-

(i) NATURAL GAS:

In United states, about 95% of hydrogen is obtained by combustion of natural gas. So it is very important source from which hydrogen can be acheived.

(ii) HYDROCARBONS:

Many industries produce hydrogen for ammonia synthesis from hydrocarbons.

Hydrogen is obtained, when the hydrocarbons are washed and then scrubbed the gas with liquid nitrogen to remove methane and CO for hydrogen-nitrogen mixture, to be ready for compression and ammonia Synthesis.

(iii) PETROLEUM PRODUCTS:

With the advent of Platforming of the petroleum products to give unsaturated compounds, for high test gasoline, large volumes of hydrogen off gas have been produced.

"The off gas from platforming operations frequently contains over 90 percent hydrogen."

So, For Synthesis of ammonia, hydrogen can also be obtained from petroleum products.

MANUFACTURING PROCESS:

Today,

hydrogen is manufactured by four principal processes:

1. Steam Reforming
2. Partial combustion of natural gas or oil with pure oxygen
3. Gasification of coal (with *coal), coke with air or oxygen and steam.
4. Recovery of hydrogen from petroleum refinery gases or other cracking operations.
5. Small amount of hydrogen is also manufactured by a process called electrolysis.

SOURCES OF NITROGEN:

Following are most important sources of nitrogen for NH_3 manufacturing process:-

* Mostly, nitrogen can be prepared for ammonia Synthesis.

PREPARATION:

* Mostly, the preparation

of nitrogen can be by separation from air in a standard air plant, or air can be fed to ammonia plant where oxygen is used to combust a portion of hydrocarbon feed, leaving nitrogen for ammonia synthesis.

★ So, the most important source of nitrogen is air in troposphere.

★ Nitrogen is major mineral in soil for plants. So they would be source for ammonia synthesis.

MANUFACTURING PROCESS:

The manufacturing of ammonia take place on industrial scale by a process but four main processes are used given below:

i. Haber's process
ii. Claude's process
iii. Casel's process
iv. American's process

HABER'S PROCESS:

The Haber's process also called Haber Bosch process is nitrogen fixation reaction of nitrogen & hydrogen gases, over an enriched iron or ruthenium catalyst, which is used industrially to produce ammonia.

HISTORY:

- Early in twentieth century, several chemists tried to make ammonia from atmospheric nitrogen.
- Fritz London, a german chemist discovered a process that is still used today.
- Ammonia was first of all manufactured on an industrial scale using Haber process.
- In 1913, during world war the production was shifted from fertilizer to explosive.
- Haber & Basch was awarded

noble prize in 1918 and 1931 for their work.

THEORY OF PROCESS:

The formation of ammonia by Haber's process take place by rex of hydrogen and nitrogen which is an exothermic reaction.

The chemical reaction is given as under:-

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

$$\Delta H = 24 kcal$$

- In above reaction, the N_2 and H_2 are mixed in 1:3 ratio.
- The optimum conditions are a temperature of 500-550°C and at 1000 atmospheric pressure.
- The reaction take place in the presence of catalyst which would be ruthenium catalyst.

REACTION RATE:

The rate of reaction can be expressed by considering following equation :

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

Hence equilibrium constant can be expressed by

$$K_p = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

PROCEDURE:

The manufacturing of ammonia take place by following steps:

(i) COMPRESSORS:

First of all, the synthetic gases are allowed to pass through compressors called as resiprocating or centrifugal compressor. where the H_2 & N_2 are compressed to a pressure of 100 - 1000 atms.

ii) FILTERATION:

Then these gases passed through filter to remove

compression oil.

(iii) COOLING:

The compressed gas mixture is then cooled by two condensers, the first cooled by water and then by ammonia refrigeration.

(iv) AMMONIA CONVERTER:

Then the cooled rex mixture are allowed to enter in a strong chrome vanadium steel pressure vessel called the ammonia converter.

- SIZE: The dimentions of converter is 120-200cm high and 60-90cm in diameter and is provided with a resistance coil which contain an electrically heated filament and also provided with heat interchanger.
- Cold gas mixture passes through inner tube of interchanger, while hot outgoing gas pass through outer tube.

- The converter consist of a contact catalytic chamber which contain catalyst.

PROCESS IN CONVERTER:

The compressed air mixture entes through inner coil of heat interchanger which is situated in middle.

The gases circulate round the catalyst with heating element they get more and more heated when they pass through heat interchanger.

The ammonia & unreacted H_2 & N_2 then enter the outercoil of heat exchanger and after giving their heat, go out from top of converter.

v) Liquification:

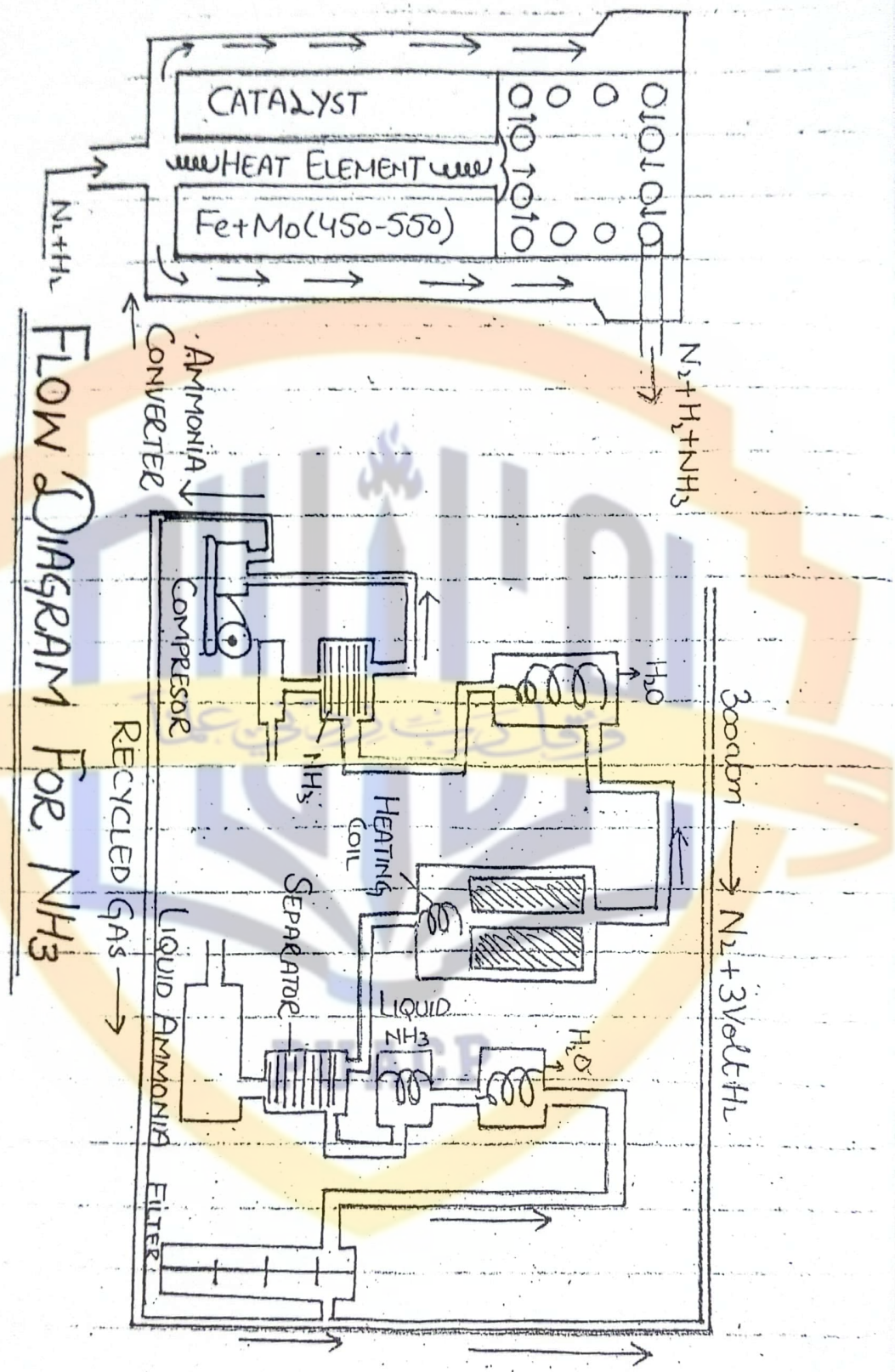
The ammonia after coming out from converter is absorbed in water and then liquified on cooling.

vi) RECYCLATION:

The ammonia gas thus formed is separated, but unreacted gases containg unliquefied ammonia is mixed with pure H_2 and N_2, compressed and then recycled through converter to obtain ammonia. The process is however not stop but continous.

To CONCLUDE:

To conclude, the Haber process is efficient method of manufacturing ammonia. The ammonia produced by this process is almost pure. Now ammonia produced, is of many uses such as in manufacturing of fertilizer and other chemicals. So ammonia is an excellent fertilizer in fertilizing industry.



FLOW DIAGRAM FOR NH3

USES OF AMMONIA:

Ammonia is most important nitrogenous material Most is made synthetically but some continues to be obtained as by-product. It is excellent fertilizer in industry. Following are most important uses of ammonia:

i. Ammonia gas is used disedly as fertilizer in heat treating and pulping process.

ii. Used as explosives.

iii. It is used in manufacturing of nitric acid, nitrates and nitro compounds.

iv. Amines, Amides and miscellaneous organic compounds are derived from ammonia.

v. It is responsible for maximum crop production so it is best fertilizer for effective growth of plants.

vi. It is also building block of many commodities.

vii. It is major constituent for amino acid Thus used in building protein.

FERTILIZERS OF AMMONIA:

Ammonia can be used to form many other fertilizing chemicals which have also many importance in fertilizing industry.

Following are the most important fertilizers of ammonia:

i. Ammonium nitrate
ii. Ammonium Sulphate
iii. Ammonium Chloride
iv. Ammonium Phosphates
v. Urea

AMMONIUM NITRATE:

Ammonium nitrate is most important nitrog-

enous fertilizer because of its high nitrogen content (33%), The simplicity, and cheapness of its manufacture.

PROPERTIES:

The important properties of ammonium nitrate which are of great value in fertilizer industry have been tabulated below:

i. Nitrogen % — 33%
ii. Solubility in H_2O — 118
iii. Melting Point — 170-4
iv. Hygroscopic Point — 594
v. Specific gravity — 1.725

PREPARATION:

Ammonium nitrate is prepared by the chemical rex of NH_3 and nitric acid (made by oxidizing ammonia). The chemical reaction is

$$NH_3 + HNO_3 \longrightarrow NH_4NO_3$$
$$\Delta H = -86.2\ kJ$$

Diagram →

METHOD OF PRODUCTION:

There are three most important methods for production of ammonium nitrate:

i. Crystallisation
ii. Flaking
iii. Prilling

⟹ The latest and most important method is Prilling which was first of all discovered in 1940.

OPERATIONS:

Following are the most important operations used in Prilling for manufacturing of ammonium nitrate:

i. NEUTRALIZATION:

The reaction b/w acid and base to form salt is called neutralization.

The following rex take place in neutalizing tower:

$$HNO_3 + NH_3 \longrightarrow NH_4NO_3 \quad (-26000 \text{ cal/g.mol})$$

That is, heated ammonia Ex

60-70% nitric acid are introduced at the base of neutralizing tower at 3-5 atmospheric pressure, through which neutralized solution is recycled.

ii. EVAPORATION:

Now, the solution obtained from tower contain about 83% NH_4NO_3. This solution is then passed through "HEATER" supplied with steam from neutralizer.

The heated solution is then to a "VACUM EVAPORATOR" where its concentration is increased about 95%.

iii. PRILLING:

The concentrated solution is then passed to a prilling tower, which are quite high upto 185ft.

The solution is sprayed through spray nozles in such a manner that a liquid break up into

drops of uniform and adequete size.
The prills solidify sufficiently when they reach the bottom of tower. They must be handled carefully untill they are dried.

iv. DRYING AND FINISHING:

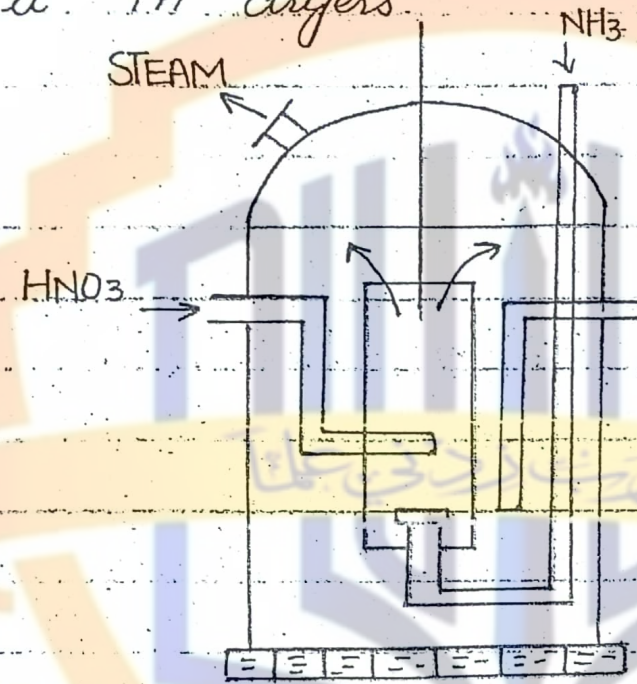
It is very difficult to dry the prills of ammonium nitrate, due to its deliquescent nature. The drying temp must be low to avoid melting.

METHODS FOR DRYING:

Various methods are used for drying however the most important are:

- In one method the material is cooled to below 92°F and remaining moisture is removed in second layer.
- In another method, which is called Short tower Prilling NH_4NO_3 solution concentrated to about 99.5% rather than 95% is prilled

in a short tower, making use of fact that strong solution soldifies faster. The last traces of water may be removed by a process of evaporation and then removing it in dryers.



Industralization of installation for Ammonium Nitrate Production

USES:

Followings are most important uses of ammonium nitrate:-

i. They are used as military explosives.

ii- It is decomposed to give nitrous oxide at 200-260°C That is

$NH_4NO_3 \xrightarrow{200-260°C} N_2O + 2H_2O$

(Laughing gas)

iii- A mixture of lime stone and ammonium nitrate is known as Nitro Chalk in fertilizing industry.

iv- It is used as excellent fertilizer for plants.

ii- AMMONIUM SULPHATE:

Ammonium Sulphate generally represented by $(NH_4)_2SO_4$ is an excellent nitrogen-Sulphur fertilizes with good physical properties

Ammonium sulphate contain about 21% nitrogen It can be obtained as a by-product or may be made Synthetically-

PHYSICAL PROPERTIES:

Some of the cheif physical properties of

ammonium sulphate are as given below:

i. Nitrogen % 21
ii. Solubility in H_2O at 32F° 70.6
iii. Melting Point 513°C
iv. Sp. gravity 1.769
v. Density 50

PREPARATION:

Now a day, Synthetic $(NH_4)_2SO_4$ can be made by Gypsum represented by $CaSO_4.2H_2O$ That is

$$(NH_4)_2CO_3 + CaSO_4.2H_2O \longrightarrow \downarrow CaCO_3 + (NH_4)_2SO_4 + 2H_2O$$

This method of production is used in India at Sindri.

PROCESS:

In this process, the propes proportion of finally ground gypsum is added to aqous soln. of ammonium carbonate in large tanks where calcium carbonate is

precipitated out. CO_2 and NH_3 are passed until whole of the $CaCO_3$ are precipitated out. The resulting $CaCO_3$ is removed by FILTERATION and $(NH_4)_2SO_4$ solution is evaporated and crystallized in vacum.

ANOTHER METHOD:

Ammonium Sulphate $(NH_4)_2SO_4$, can also be prepared by another method by which ammonia (obtained by Haber's process) react with Sulphuric acid. That is ammonia from coke oven is absorbed in Sulphuric acid.

The chemical reaction b/w NH_3 and H_2SO_4 is given below:

$$NH_3 + H_2SO_4 \longrightarrow (NH_4)_2SO_4$$

ADVANTAGE:

One of the major advantage of this process is that the production of ammonium sulphate

is about 2.3×10^6 t/year with about 20 percent from ammonia.

USE OF AMMONIUM SULPHATE:

One of the best use of $(NH_4)_2SO_4$ is that it act as fertilizer for plants.

ACTION AS FERTILIZER:

Ammonium Sulphate react with lime present in soil to form ammonium hydroxide. This NH_4OH is oxidized by air with help of nitrosifying bacteria and converted into nitrous aiid or nitrites. The nitrous aiid and nitrites undergo oxidation by bacterial action & form nitric aiid and nitrates.

The bases present in soil react with nitric aiid to give potasium and calcium nitrate etc. Most of plants take nitrogen

in form of nitrates.

Thus, ammonium sulphate would be source of providing nitrogen to plants in form of nitrates.

iii. AMMONIUM CHLORIDE:

Ammonium chloride generally have formula NH_4Cl, contains 26% nitrogen in nature.

It is obtained as coproduct in manufacture of soda ash by Solvay's process.

It can also be obtained on large scale by direct neutralization of hydrochloric acid.

iv. AMMONIUM PHOSPHATES:

There are three possible ammonium ortha phosphates, only two of which are manufactured on any scale:

a) Mono-ammonium phosphate

b) di-ammonium phosphate

a) MONO AMMONIUM PHOSPHATE:

It is also called MAP. It is obtained by action of Sulphuric acid with a mixture of calcium phosphate & ammonium sulphate like

$$Ca_3(PO_4)_2 + (NH_4)_2SO_4 + 2H_2SO_4 \longrightarrow 2NH_4H_2PO_4 + CaSO_4\downarrow$$

Mono ammonium phosphate

This is formed along with slurry of $CaSO_4$. The phosphate is separated from slurry and then crystallised to obtained fine crystals of mono ammonium phosphate which contain 12% nitrogen and 50% P_2O_5.

b) DI AMMONIUM PHOSPHATE:

The di-ammonium phosphate is obtained by a continous process where

anhydrous NH_3 gas and pure phosphoric acid are passed into saturated mother liquor containing mono ammonium phosphate.

"The temperature is about 60-70°C and pH at about 6.0"

The heat of reaction vapourises water from liquor and crystals of pure diammonium phosphate are obtained, these are centrifused, washed and at last dried.

USES:

Both mono and di-ammonium phosphates are excellent fertilizers and source of nitrogen and phosphorous for plants for their growth and nourishment.

IRAM NASIR
ROLL No 170
2010 - 2012

UREA

Urea is the most convenient form for fixed nitrogen. It is highest in nutrient concentration because in pure form, it contain 45-47% nitrogen.

CHARACTERISTICS:

Urea is most widely used fertilizes in industry because it contain a huge no. of properties which are given below:

i. It is easy to produce as prills or granules and easily transported in bulk or bags with no explosive hazard.

ii. It readily dissolve in water.

iii. It leaves no salt residue after use on crops and can be used as foliar feeding.

iv. It is hygroscopic in nature.
v. Urea is not flammable, but with melt and decompose to give (urea) NH_3.

PHYSICAL PROPERTIES:

Urea has formula NH_2CONH_2, have most crucial properties, the most physical properties are given below:

i.	Nitrogen percentage	45%
ii.	Melting Point	132.7°C
iii.	Hygroscopic Point	72%
iv.	Bulk density	42-45
v.	Solubility in water	119
vi.	Particle Size	95%
vii.	Specific gravity	1.335

HISTORICAL BACKGROUND:

Following is the historical background of urea:

i. Urea came into prominence as fertilizer industry in 1950's.

ii. It was first of all synthesized by Wohler in 1828 from ammonia and cyanic acid.

iii. In 1980's, the production rate of urea was increased to 7percent.

iv. The annual production of urea in US reaches to about 6.4×10^6 tonns in 1982.

v. In 1988, production was estimated to have exceeded 155 billion lb.

vi. Now a days the production of urea on industrial scale is reaching to top as most important fertilizer in industry is urea.

RAW MATERIAL:

Raw material can be defined as follows:

"The principle components used in manufacturing

of some compounds and play important part in their properties are called raw material."

EXPLANATION:

Raw materials are expansion gas obtained in the process of manufacturing NH_3, used in 100-125% excess over the stiometric amount. When using 100% CO_2 and pure ammonia, the urea yield under optimum conditions is 60-70% and molten mass obtained by dehydration of urea (ammonium carbamate) contains 35% urea.

The chief raw materials in manufacturing of urea are:

i. AMMONIA (NH_3):

It is most important raw material in urea manufacturing, as it is most imp constituent in urea. In some process, the urea is manufactured in ammonia

plant.

ii. CARBON DIOXIDE (CO_2):

It is crucial raw material as urea is made in ammonia production plant in which CO_2 is produced as byproduct, thus this CO_2 is used as raw material in manufacturing process.

iii. FLUE GAS:

It is used as an alternative of CO_2 in urea manufacturing, when ammonia plant become insufficient for producing urea. This happens when ammonia plant which uses source of hydrogen other than synthetic gas, such as by-product refinery gas or coke oven gas, have disadvantage of not being able to produce urea.

iv. AMMONIUM CARBAMATE:

It is an intermediate which on heating produce urea. Thus decomposition of ammonia carbamate yield urea.

v. RAW TEMPERATURE:

The raw temperature required for production of urea is 180°C

vi- RAW PRRESURE:

The raw pressure for manufactusing of urea would be 14MPa

MANUFACTURING OF UREA:

Generally, urea is manufactured by various ways. However, the most important methods for production of urea are given below:-

i- BY HYDROLYSIS OF CYANAMIDE:

Urea can be manufactured by hydrolysis of cyanamide like

$$CNNH_2 + H_2O \longrightarrow Co(NH_2)_2$$

ii- By HEATING AMMONIUM CARBONATE:

The fertilizing urea can also be produced by heating ammonium carbonate

$$(NH_4)_2CO_3 \xrightarrow[\Delta]{33-53\ atm} (NH_2)_2CO$$

urea

iii. BY SULPHUR:

Urea can also be produced by sulphur dissolved in methanol in presence of NH_3 and CO at 100°C and 20atm with H_2S liberating along with urea.

$$NH_3 + CO + S \xrightarrow{methanol} (NH_2)_2CO + H_2S$$

iv. FROM AMMONIA:

By action of ammonia with CO_2 under pressure, the ammonium carbamate is formed which on heating yield urea:

$$CO_2 + 2NH_3 \xrightarrow[180\,^\circ C]{14MPa} NH_2COONH_2$$

$\Delta H = -155\ MJ/kg.mol$

$$NH_2COONH_2 \xrightleftharpoons{\Delta} CO(NH_2)_2 + H_2O$$

$\Delta H = +42\ MJ/kg.mol$

NOTE:

In industry, urea synthesis is carried out without catalyst at 180-200atm and 180-200°C. High temperature can't be employed because they

increase corrosion of apparatus.
100% excess NH_3 is used.

-: MANUFACTURING PROCEDURE :-

The manufacturing procedure is based upon the process like "Carbamate Solution Recycle" which involve following steps:

1. AMMONIA PUMPING:

First of all, ammonia is pumped into reactor which are vertical vessels lined with stainless steel and protected from corrosion by a film of oxide. The film is maintained by continous pass of air into reactor. The temperature of reactor is about 380°F. Note that, ammonia enter into reactor by "Piston type pumps."

2. INTRODUCTION OF CO_2:

The carbon dioxide is introduced from

ammonia plant by passing from desorber into urea plant.

iii. DECOMPOSITION OF CARBAMATE:

Solution from reactor is passed through valve which reduces pressure from about 2500-3000 psig to 200 psig, then it enter high pressure decomposer which is heated by using steam. Excess of ammonia and CO_2 (evolved as result of partial decomposition of carbamate) escape from solution.

ABSORBER:

The gases are introduced into absorber, where they are scrubbed with carbamate solution from later stage. The newly formed carbamate solution contain unreacted CO_2 as carbamate. This solution is recycled back into reactor. Excess of NH_3 liberating from absorber is condensed and pumped back as liquid NH_3.

DECOMPOSER:

In first stage, solution is taken to low Pressure decomposer, where remaining carbamate is decomposed due to heat and boiled out of solution.

⟹ The gases evolved, are scrubbed with water in low pressure absorber. The carbamate solution is taken as scrubbing agent in first absorber.

iv. CONCENTRATION:

The concentration of urea is carried out in vacuum evaporator. The urea is concentrated to 99% in this stage.

v. PRILLING:

The concentrated solution is changed into globules by spraying from top of prilling tower and heated by hot air. In this way, the drying of prills is not needed.

"SINDRI METHOD"

Urea is also

manufactured at Sindri in India, by introducing pure liquid NH_3 and liq. CO_2 in an autoclave whose temp. is 180°C with Pressure 180kg/cm^3.

In this manner, 37-40% urea is manufactured unreacted NH_3 and CO_2 are converted into ammonium carbonate.

$$CO_2 + NH_3 + H_2O \longrightarrow (NH_4)_2CO_3$$

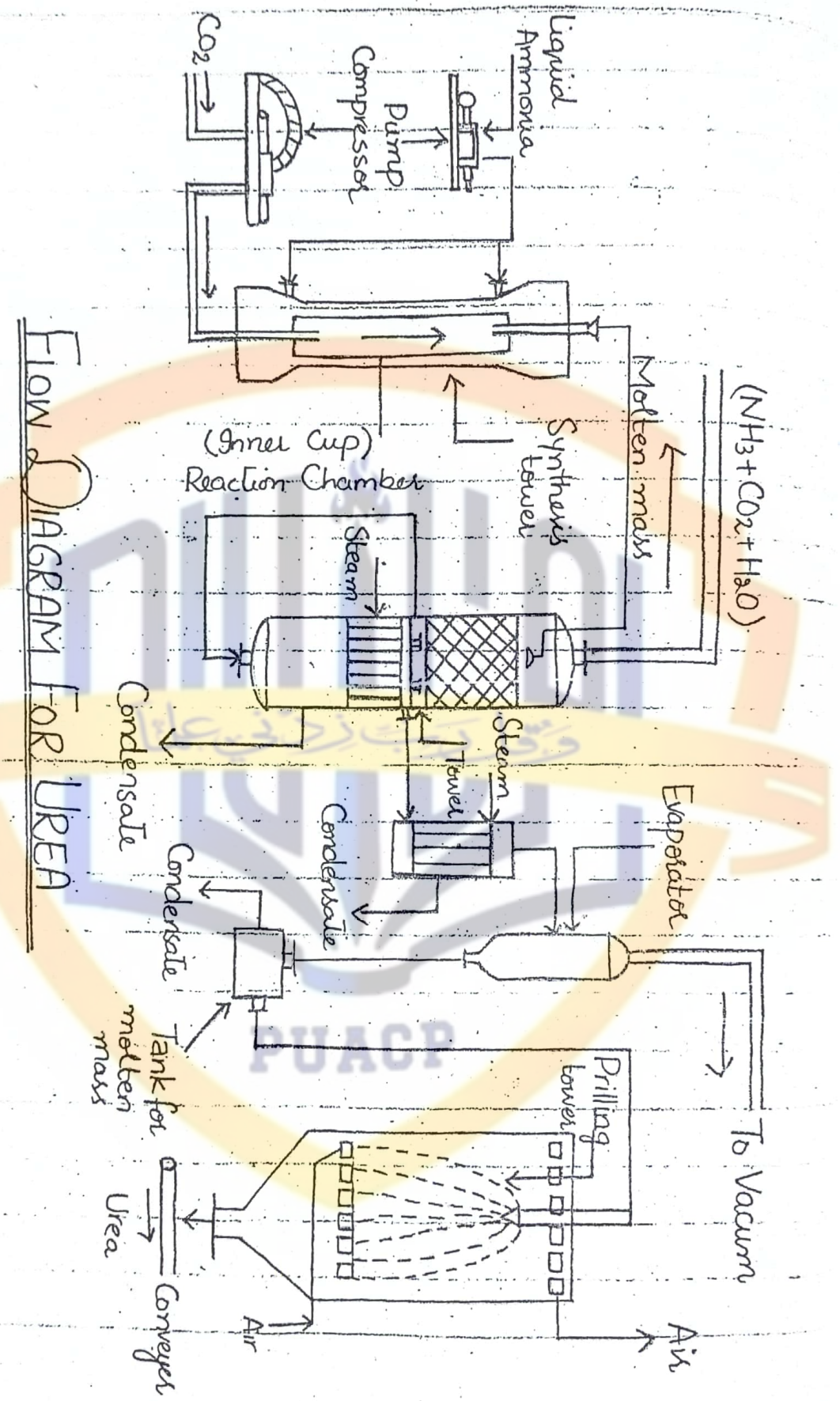
it is further allowed to react with dil HNO_3 to give ammonium nitrate and CO_2

$$(NH_4)_2CO_3 + HNO_3 \longrightarrow 2NH_4NO_3 + CO_2 + H_2O$$

The CO_2 formed is recycle. Urea solution is concentrated to 78% and finally to 97%. At last, the concentrated solution is crystallised into globules.

To CONCLUDE:

To conclude, both processes are very usefull in urea manufacturing. As they produce 96-97% urea used as fertilizer.



FLOW DIAGRAM FOR UREA

USES OF UREA:

The annual production of urea is very large, 6.4×10^6 t at $150 to $160 per metric ton in 1982. This Scale shows its importance. Following are most important uses of urea:

i. The principle use for urea is as fertilizer, with over 80% of all production being consumed for this.

ii. Urea is used as solid fertilizer and also in solution in combination with ammonia and ammonium nitrate.

iii. Urea is used as foliar feeding.

iv. It is used as softener for cellulose, cellophane and wood So used as an ingredient in softening chemicals.

v. Used as protein supplement for ruminent animals.

vi. Used for melamine production.

vii. Used as ingredient for manufacturing of resin, plastics, adhesives, coating,

and textile antishrink agents.

viii. It is intermediate in manufacturing of ammonium Sulphamate, Sulphamic acid and pthalocyanins.

:- ASSIMILAITION IN SOIL :-

ASSIMILATION:-

Assimilation can be defined as follows:

"The process of Splitting of particular compound into Smaller compounds (urea → NH_3 + CO_2) which spread into soil and consumed by plants for growth & nourishment is called assimilation."

EXPLANATION:

Assimilation of urea is natural phenomenon as it is present in soil it completely assimilate in soil

by reacting with other compound necessary for increasing fertility of soil and replenish defeciency of these nutrients in soil and thus increases growth of plant.

DECOMPOSITION OF UREA:

Urea comes in contact with soil (either as artifially made fertilizer or natural fertilizer coming from animal excretion, garbage etc) splits up into following compounds :

$$NH_2CONH_2 \rightleftharpoons NH_3 + CO_2$$

The NH_3 undergo many processes react with many compound present already in soil, thus increases fertility of soil. It also helps to maintain nitrogen cycle.

1. Oxidation of NH_3 :

The ammonia undergo oxidation with

help of nitrifying bacteria like nitrosomonas and form nitrous acid and nitrites like

$NH_3 + 1/2O_2 \longrightarrow HNO_2 +$ nitrites

The nitrous acid and nitrites undergo oxidation to form as nitric acid and nitrates like

$HNO_2 + NO_2^- \longrightarrow HNO_3 + NO_3^-$

These nitrites, nitrates are consumed by plants to increase growth of plants, increases fertility of soil

2- Ammonia react with bases already present in soil to form ammonium hydroxide which is excellent nitrogenous fertilizer

$NH_3 +$ Bases $\longrightarrow NH_4OH$

It undergo oxidation to form nitrous acid, nitric acid, nitrites or nitrates etc which also increases crop productivity with good nutrient concentration

3.

Ammonia comes from urea react with HNO_3, H_2SO_4 to form ammonium nitrate and ammonium Sulphate which also act as fertilizer.

$$NH_3 + HNO_3 \longrightarrow NH_4NO_3$$

$$NH_3 + H_2SO_4 \longrightarrow (NH_4)_2SO_4$$

4.

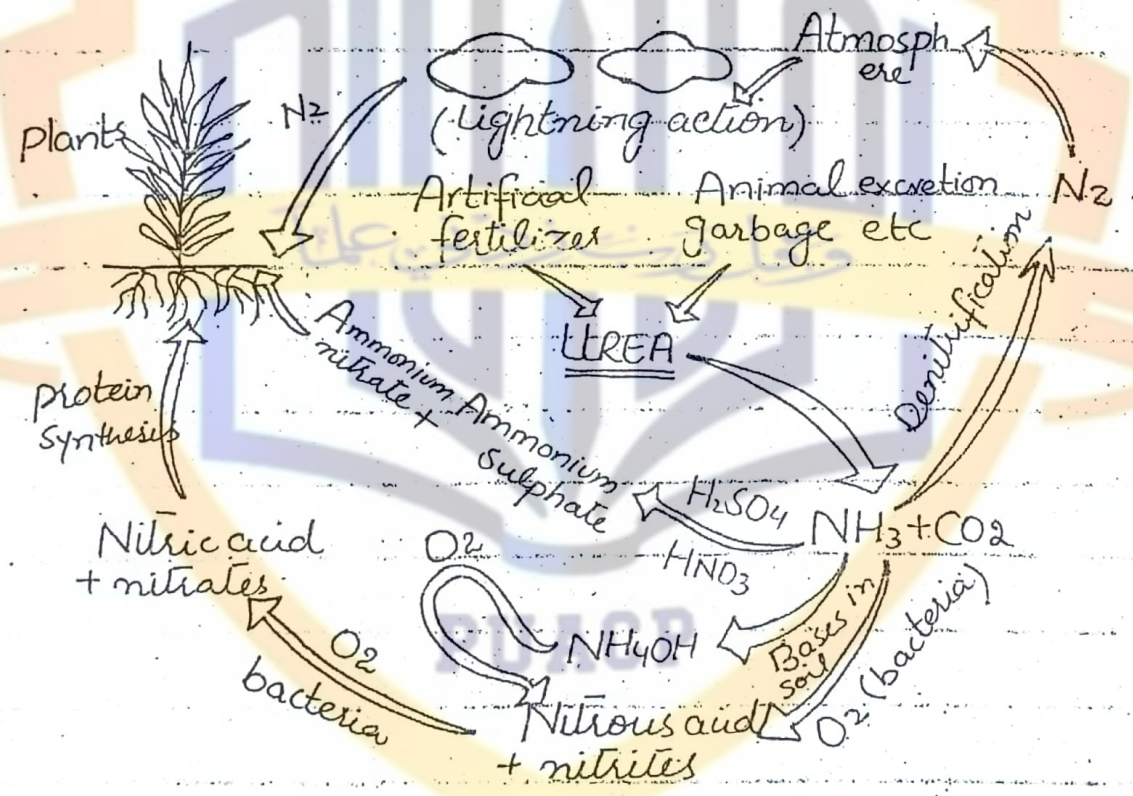
When urea assimilate into soil, the NH_3 undergo denitrification by bacteria and fungi to obtain oxygen and release nitrogen in atmosphere which come back to soil and thus it also (urea) helps to maintain nitrogen cycle (ecosystem).

To Conclude:

To conclude, assimilation of urea is very important phenomenon as it completely assimilate in soil,

and thus increases fertility of soil, increases growth of plant and thus increases crop production to an extent, it also helps to improve nitrogen cycle and thus maintain ecosystem.

DIAGRAMATIC REPRESENTATION OF ASSIMILATION OF UREA:



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SESSION 2010-12

CALCIUM FERTILIZERS

1. Definition

Those fertilizers that contain the high proportion of calcium are called calcium fertilizers.

Types of calcium fertilizers

There are four important types of calcium fertilizers.

i. Calcium cyanamide
ii. Calcium ammonium nitrate fertilizer
iii. Calcium super phosphate
iv. Triple super phosphate.

i. CALCIUM CYANAMIDE

It is the most important calcium fertilizer that will increase the fertility of soil on large scale. It also makes the soil perfect for the proper existence and growth of plants.

MANUFACTURING OF CALCIUM CYNAMIDE

Raw material

Raw material that is essential for the manufacturing of calcium cynamide is I lime II Coke III. Nitrogen.

Procedure

It is manufactured by combining lime and coke in the electric furnace to form calcium carbide. The charge containing calcium carbide is introduced in the electric furnace and nitrogen gas is allowed to pass from the bottom of the furnace. The reaction is started by passing an electric current through a thin carbon rod in the centre. The important reactions are

I $CaO + 3C \xrightarrow{2000^\circ C} CaC_2 + CO$

II $CaC_2 + N_2 \longrightarrow CaCN_2 + C \quad \Delta H = -72.7 Kcals$

The positions shown in the furnace are made of card board. As a result of the passage of current, heat is produced and then all the card board is carbonised leaving openings.

through which nitrogen gas can be circulate freely.

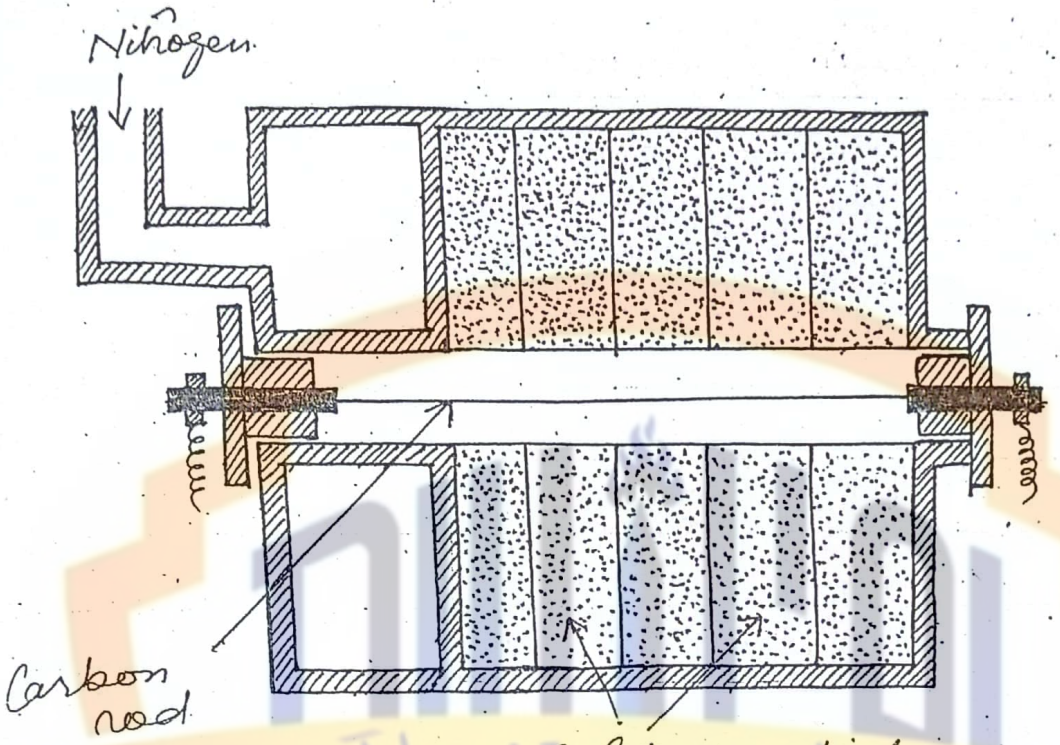

Fig :- Manufacture of calcium cyanamide

The reaction is complete after about 25-30 hours. The heat of reaction helps in maintaining the temp at about 1000°c. At last calcium carbide is prepared.

Uses

1. Production of nitrolim

Calcium cyanamide is used in the production of nitrolim.

Calcium cyanamide react with

carbon or mixed with carbon then the resulting product is called nitrolim which is an important nitrogenous fertilizer.

II- Production of urea

Calcium cyanamide will undergo hydrolysis to form urea that is also the main source of nitrogen for plants in soil.

$$CaCN_2 + 3H_2O \longrightarrow Ca(OH)_2 + NH_2CONH_2$$

III- Production of NH_3

Urea that formed by the hydrolysis of calcium cyanamide, upon hydrolysis give ammonia.

$$NH_2CONH_2 + H_2O \longrightarrow CO_2 + 2NH_3$$

II CALCIUM AMMONIUM NITRATE

It is also an important calcium fertilizer that play important role in increasing the fertility of soil.

MANUFACTURING PROCESS

Raw material

Lime stone, conc. HNO_3, NH_3.

Procedure

Its manufacturing process

involves reaction of limestone with cone. HNO_3, addition of ammonia to neutralise excess of acid, evaporation of the resulting solution, and prilling or flaking the melt. The resulting product is a double salt $5Ca(NO_3)_2 \cdot NH_4NO_3$ called calcium ammonium nitrate and is more useful than the single salt calcium nitrate

CHEMICAL REACTIONS

Ammonium nitrate is first prepared by the reaction of ammonia as describe earlier

$$NH_3 + HNO_3 \longrightarrow NH_4NO_3$$

Ammonium nitrate so obtained contains some unreacted nitric acid which is neutralised by adding calcium carbonate. On cooling grains of calcium ammonium nitrate separate out.

$$NH_3 + HNO_3 \longrightarrow NH_4NO_3$$

$$CaCO_3 + 2HNO_3 \longrightarrow Ca(NO_3)_2 + CO_2 + H_2O$$

$$CaCO_3 + NH_3 + 3HNO_3 \longrightarrow Ca(NO_3)_2 \cdot NH_4NO_3 + CO_2 + H_2O.$$

The granules of calcium ammonium nitrate are finally coated with thin layer of soap stone powder, which acts as a protective coating and prevents the absorption of moisture during storage

and transportation. CO_2 is obtained as a by-product.

III CALCIUM SUPER PHOSPHATE

Calcium super phosphate is the third type of calcium fertilizer. Phosphate present in the plants in soluble form due to the agency of acids present already in the soil. It is estimated that the rock phosphate transformed quickly into the soluble phosphate, which is then applied to the soil and easily taken up by the plants.

Super Phosphate

Definition

Artificially prepared mixture of monocalcium phosphate $Ca(H_2PO_4)_2$ is known as superphosphate.

MANUFACTURING OF SUPERPHOSPHATE

Raw material

Phosphate rock, conc. H_2SO_4, Water.

Procedure

The procedure of manufacture of super-phosphate is divided into four main steps.

1. Grinding of phosphate rock.
2. Mixing with acid

III Curing and drying of original slurry by completion of reaction

IV Excavation, milling and bagging of the finished product.

I Grinding of phosphate rock:

It is the first step of preparation of calcium superphosphate in which phosphate rock is grind with the help of special grinders. After grinding the powdered rock is stored for short ~~sooselime~~ in ground phosphate rock storage tank.

II Mixing with acid:

The ground phosphate rock is fed by a weigh feeder into a double conical mixer, where it is thoroughly mixed with metered quantities of sulfuric acid.

The sulfuric acid is diluted with water in the cone to a concentration of 51° Be', the heat of dilution serves to heat the H_2SO_4 to proper reaction temp and the excess heat is dissipated.

The rate of addition of acid and water concentration may be varied to control product moisture. The acid and water are fed into the cone mixer tangentially to.

provide the necessary mixing with the phosphate rock.

The important reaction between phosphate rock, water and sulfuric acid is describe as follows.

$$Ca_3(PO_4)_2 + 2H_2SO_4 + 4H_2O \longrightarrow Ca(H_2PO_4)_2 + 2(CaSO_4 \cdot 2H_2O)$$

Phosphate rock. — Mono calcium Phosphate — Gypsum

After the completion of reaction, the fresh super phosphate drops onto the den conveyor, which has a very low travel speed to allow about 1 hour for solidifying before reaching the disintegrator.

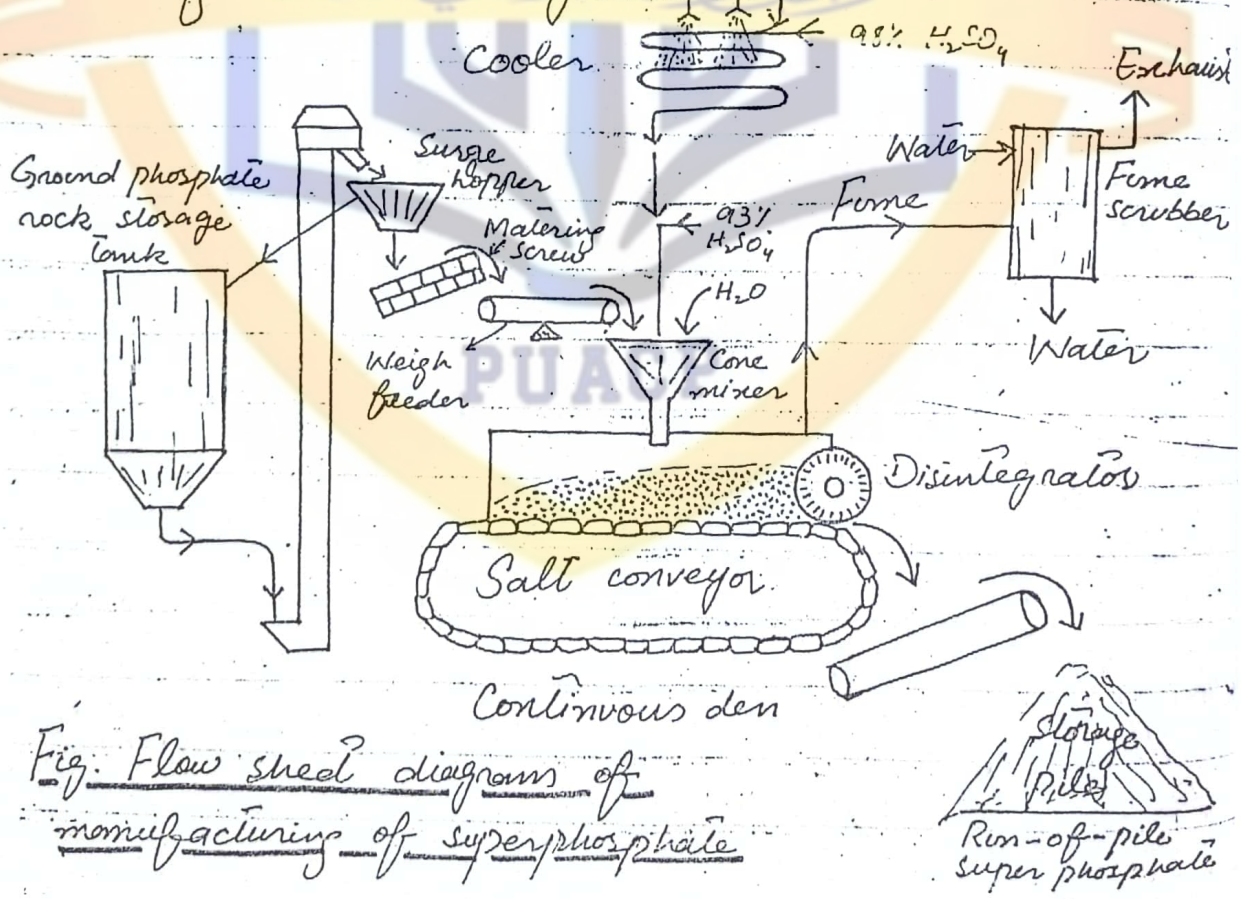

Fig. Flow sheet diagram of manufacturing of superphosphate

The disintegrator slices the solid mass of crude product so that it may be conveyed to pile storage for curing

III Curing

Curing is also called the step of completion of chemical reaction which takes about 4 to 6 weeks to reach a P_2O_5 availability acceptable for the plants food.

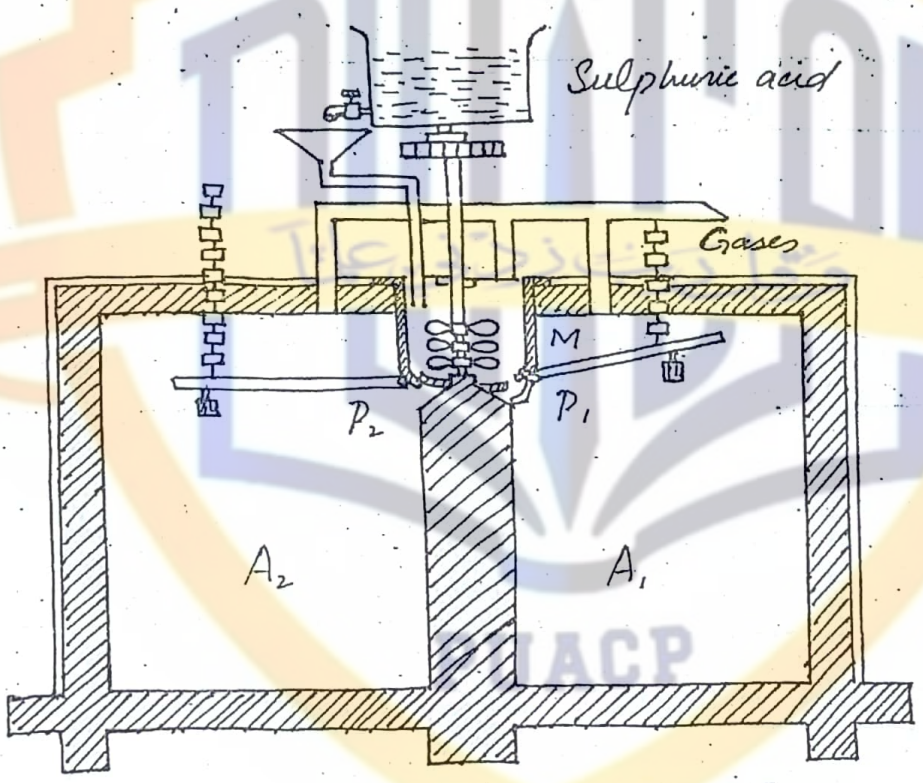

Fig:- Manufacture of Superphosphate

IV Excavation, milling and bagging

The final product that is calcium superphosphate at last excavate. After excavation,

milling and bagging is done and calcium super-phosphate ready for sale.

④ TRIPLE SUPER PHOSPHATE

Triple super phosphate is a much more concentrate fertilizer than ordinary superphosphate, containing from 45 to 46% of available P_2O_5 or nearly three times of the amount in regular superphosphate.

MANUFACTURING PROCESS

Raw material

i. 78% phosphoric acid (containing 52-54% P_2O_5)

ii. Calcium phosphate or phosphate rock (containing about 32.5-33% P_2O_5 contents)

Procedure

Triple super phosphate is prepared when pulverized phosphate rock is mixed with phosphoric acid in a two-stage reactor.

The resultant slurry is sprayed into the granulator. The product obtained from the granulator is dried, screened. Reaction that occure between phosphoric acid and phosphate rock during the manufacturing of superphosphate is

$$Ca_3(PO_4)_6 + 4H_3PO_4 \longrightarrow 3Ca(H_2PO_4)_2$$

After screening the oversized material crushed and cooled again.

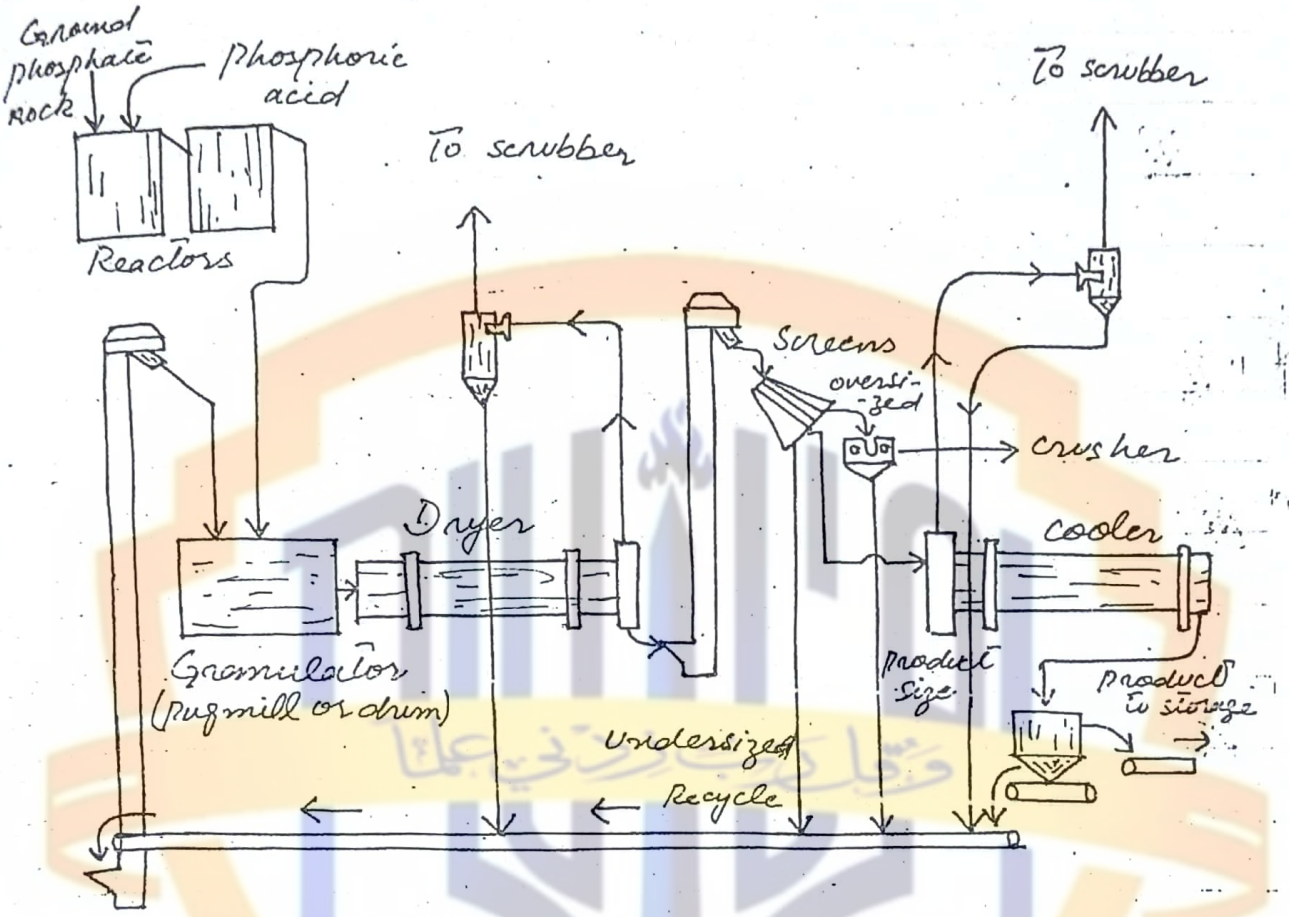

Fig:- Flow sheet diagrame of manufacturing process of Triple Super Phosphate.

The final product is conveyed to bulk storage where the material is cured 4 to 6 weeks during which time a further reaction of acid and rock occures which increases the availability of P_2O_5 as plants food. The exhaust gases are scrubbed with H_2O to remove unwanted materials.

ROLE OF CALCIUM FERTILIZER IN PLANTS

Some important roles of calcium fertilizers in plants are describe as following

I Calcium is used in the synthesis of new cell walls, particularly in middle lamella separating newly divided cells.

II Plant membranes require calcium for their normal functioning.

III It is considered that calcium acts as a second messenger for a number of plant reponses to both environmental and harmonal signals.

IV Calcium may bind to calmodulin, a protein found in cytosol, to form calcium-calmodulin complex that is considered to be involved in regulation of many metabolic processes.

DEFICIENCY SYMPTOMS

The deficiency symptoms are more prominent in young tissues or in growing plants. These symptoms are describe as following

I Necrosis

Necrosis develop in plants due to deficiency of calcium in which leaves develop small spots of dead tissues called ~~nect~~ ~~nacta~~ nacrotic spots.

ii Chlorosis

Necrosis is followed by chlorosis and downward hooking of young leaves. The young leaves appear to be deformed.

iii Poor root system

The root system of calcium deficient plant is brownish, short and highly branched.

POTASH FERTILIZERS

Definition

Those fertilizers that contains the high proportion of potassium element in them are called potash fertilizers.

Potash fertilizers are very important for the proper growth of plants as it is they are able to regulate osmotic potential of plant cells. It is also able to act as enzyme activator that are involved in both respiration and photosynthesis.

Types of potash fertilizers

There are four important types of potash fertilizers that are commonly

used.

I Potassium sulfate
II Potassium hydroxide
III Potassium carbonate
IV Potassium nitrate

(I) POTASSIUM SULFATE

History

Prior to 1939, The German potash industry was the chief source of potassium sulfate for the American chemical and fertilizer industries. Although considerable industries were started (work) in different countries of the whole world for the preparation of potassium sulfate.

MANUFACTURING OF POTASSIUM SULFATE

Raw material

Raw materials are

I KCl II H_2SO_4 III $Na_2CO_3 \cdot 2Na_2SO_4$ (Burkeite)

Procedure - I

In first process of manufacturing of potassium sulfate, Potassium chloride and sulphuric acid react together and

form a salt-cake

$$2KCl + H_2SO_4 \longrightarrow K_2SO_4 + 2HCl$$

This salt-cake is potassium sulfate which on further process changes to pure potassium sulfate.

Procedure -ii)

In the second method of preparation of potassium sulfate potassium chloride react with burkeite ($Na_2CO_3 \cdot 2Na_2SO_4$) / such as

$$4KCl + Na_2CO_3 \cdot 2Na_2SO_4 \longrightarrow 2K_2SO_4 + 4NaCl + CO_2 \uparrow$$

During the reaction sodium chloride is formed as a by-product along with the removal of CO_2 gas.

Uses

Some important uses of potassium fertilizers are

i) Potassium sulfate is preferred for the tobacco crops for their proper growth and survival usually in south eastern countries

ii) Potassium sulfate is also used for the good productivity of citrus crop of southern California.

iv POTASSIUM HYDROXIDE

Potassium hydroxide is also an essential plant fertilizer that make the soil able for the proper growth and survival of plants.

MANUFACTURING OF POTASSIUM HYDROXIDE

Raw material

Raw materials essential for the manufacturing of potassium hydroxide are

i KCl ii NaOH iii Electrolytic cell

Procedure

Potassium hydroxide is made by the electrolysis of KCl and NaOH the reaction is describe as following

$$KCl + NaOH \xrightarrow{Electrolysis} KOH + NaCl.$$

After electrolysis potassium hydroxide is prepared along with sodium chloride that is a by-product of this reaction.

Sodium chloride will be removed from potassium hydroxide and pure KOH is used as a fertilizer.

Uses

Some important uses of potassium hydroxide are

I KOH contain potassium that is used for the removal of mottling in plants.
Mottling is a process of formation of patches on the green leaves that develop due to the formation of dead tissues.

II Potassium is also useful for those plants that have small size and their growth become stunted. It is able to increase the size of plant as well as OH^- ions combine together and increases the water contents of soil.

III If KOH sprayed on those plants that are suseptible to fengal attack. Then potassium will completely destroy fungus and make the plants healthy.

(iii) POTASSIUM CARBONATE

It is the third type of potash fertilizers is potassium carbonate. It provide the large amount of CO_2 to plants and thus will increases the rate of photosynthesis

in plants through which plants can prepare their own food that is very impor- tant for their growth and survival.

MANUFACTURING OF POTASSIUM CARBONATE

Raw material

The essential raw materials that are used in the manufacturing of potassium carbonate are.

Caustic potash (KOH), Carbon dioxide CO_2.

Procedure

Potassium carbonate is made by reacting caustic potash with carbon dioxide The reaction is describe as following.

$$2KOH + CO_2 \longrightarrow K_2CO_3 + H_2O$$

Potassium carbonate will formed by the reaction of potassium hydroxide with carbon dioxide along with a by-product that is in the form of water.

Uses

Some important uses of potassium carbonate are describe as follows.

i- Used in the form of fertilizer

ii- Used in the manufacturing of potash/hard glass

(iii)- Used for making pottery, smalts and soaps.
(iv)- Used for finishing leather.
(v)- Used as absorbent for acid gases (CO_2 and H_2S)

(2) POTASSIUM NITRATE

The fourth type of potassium ~~nitrate~~ fertilizers is potassium nitrate that is very much essential fertilizer in soil as it provide potassium as well as nitrate to plants that is very important for proper growth of plants.

MANUFACTURING OF POTASSIUM NITRATE

Raw material

Raw material used for the production of potassium nitrate is $NaNO_3$, KCl, Water (H_2O), HNO_3

Procedure -1

The first procedure explains that potassium nitrate is usually made by double

decomposition between $NaNO_3$ and KCl.

A strong hot solution of $NaNO_3$ is made and solid KCl is dumped into the kettle. Upon heating, the KCl crystals changes to NaCl crystals, and hot potassium nitrate solution is run through the NaCl crystals at the bottom of the kettle.

$$NaNO_3 + KCl \longrightarrow NaCl + KNO_3 \quad \Delta H = +13.2\ KJ$$

A little water is added to prevent further decomposition of NaCl as the solution is cooled. Then at last a good yield of potassium nitrate results.

Procedure - II

The second method of preparation of potassium nitrate involves the reaction of potassium chloride with nitric acid.

Chemical equation

$$2KCl + 2HNO_3 + \tfrac{1}{2}O_2 \longrightarrow 2KNO_3 + Cl_2 + H_2O$$

Mechanism

Step-I :- $3KCl + 4HNO_3 \xrightarrow{100^\circ C} 3KNO_3 + NOCl + Cl_2 + 2H_2O$

Step-II :- $NOCl + 2HNO_3 \longrightarrow 3NO_2 + \tfrac{1}{2}Cl_2 + H_2O$

Step-III :- $2NO_2 + H_2 + \tfrac{1}{2}O_2 \longrightarrow 2HNO_3$

Step - i

The mechanism of this reaction explains that KCl when react with HNO_3 then KNO_3 is produced along with NOCl, Cl_2 and H_2O.

A shift in the composition of the nitric acid - water azeotrope from about 70% HNO_3 to over 80% HNO_3 in the presence of KNO_3 at high concentration.

Step - ii

In step-ii the capability of oxidizing nitrosyl chloride to Cl_2 and NO_2 with nitric acid in the 70 - 80% concentration range at temperature and pressure that are practical for operation.

Step - iii

While in third step HNO_3 is again synthesized again react with KCl as in the first step and the process will continue.

تو رحیم ہے تو کریم ہے میری لغزشوں پہ نظر نہ کر
میری خوخطا تیری خوعطا نہ یہ مجھ میں کم، نہ وہ تجھ میں کم

Uses

Some important uses of potassium nitrate are describe as follows

I- It is used as fertilizer.

II- Used in pyrotechnic mixture.

III- Used as heat-transfer medium for heat treating steel.

IV- It is also used as food/in foods.

V It is also the major source of potassium and nitrogen for tobacco that are adversely affected by chloride in the soil. In this way used for proper plant growth.

ROLE OF POTASSIUM FERTILIZERS IN PLANTS

Some important roles of potassium fertilizers in plants are describe as following

I- potassium play an important role in regulation of osmotic potential of plant cells.

II- potassium act as enzyme activator that are involved in the

processes of respiration and photo-synthesis

iii - potassium that is obtained from different potash fertilizers is also special for the activation of enzymes that are required for the synthesis of proteins and starch.

DEFICIENCY SYMPTOMS

Some important deficiency symptoms that adversely affect the plants growth are describe as

i Melting of Leaves

First observable deficiency symptom is melting or marginal chlorosis which then develops into necrosis (formation of dead tissues) that occures primarily at the leaf tips and margins and between veins.

ii Stunted growth

The stems of potassium deficient plants may be slender weak and have short internodes. This type of condition is called stunted growth

iii Lodging

In corn, the roots become susceptible to fungal attack due to shortage of potassium and results in lodging (plant easily bent to the ground)

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