CERAMICS

Introduction

Ceramics includes all articles which are essentially silicates. But those articles which are made of clay are mainly known as ceramics. They are therefore also known as clay products. They were known also as pottery products. From the prehistoric age clay had been one of the chief agencies by the help of which mankind was able to develop art and architecture, as well as make houses and utensils. Clay bears the history of man's scientific and cultural development. It carries the imprint of the fine culture of ancient age. Even at the present time ceramics remain important in many spheres of life. Buildings, roads, bridges, furnaces, electrical insulators, house hold goods, table and kitchenwares, decorative works, artistic things, scientific apparatus and many others are dependent on ceramics for their existence.

Raw materials

Both glazed and unglazed clay products are manufactured. The glazed product is obtained by applying glaze on the unglazed body (either after firing or before firing). Hence in all cases the unglazed product has to be made. The chief raw materials for the unglazed products are the following :

(1) **Primary white clay or China clay** : Pure China clay has the composition $Al_2O_3, 2SiO_2, 2H_2O$. On heating this becomes dehydrated at 600°C. On further heating it is converted into mullite ($3Al_2O_3, 2SiO_2$). Then as the temperature rises the remaining SiO_2 changes to cristoballite. Under certain conditions corundum is formed at high temperature. The pure clay softens at 1550°C. The softening temperature diminishes with the

TABLE 12

COMPOSITION OF WHITE CLAY

Constituents	Primary Kaolin or China clay (%)	Secondary Kaolin or Ball Clay (%)
SiO_2	44.2	53.3
Al_2O_3	39.8	28.2
Fe_2O_3	0.4	0.5
CaO	0.1	0.4
MgO	0.3	0.5
$K_2O + Na_2O$	0.8+0.1	0.5+0.4
TiO_2	0.1	1.7
H_2O	14.00	14.00

increase of fluxing constituents such as Na_2O, K_2O, CaO, MgO, FeO & Fe_2O_3 etc.

(2) **Secondary white clay or ball-clay** : Even white clay both primary and secondary contain small quantities of fluxing material.

The fluxing impurities in common clay are much higher. The common clay has the following average composition:

TABLE 13

COMPOSITION OF COMMON CLAY

SiO_2	66.67 p.c.
Al_2O_3	18.27 ,,
Fe_2O_3	3.11 ,,
CaO	1.18 ,,
MgO	1.09 ,,
Na_2O+K_2O	4.22 ,,
TiO_2	0.85 ,,
H_2O	4.03 ,,

The softening temp. of the common clay is about 1000°C.

(3) *Flint* : Sand stone in concretionary form. It is almost pure SiO_2 containing some $CaCO_3$. It is powdered before use.

(4) Cornish stone, or China stone or potash feldspar. Its average composition is :

TABLE 14

COMPOSITION OF CHINA STONE

K_2O	6 p.c.
CaO	1 p.c.
Al_2O_3	18 p.c.
SiO_2	75 p.c.

(5)	Marble	$CaCO_3$
	Whiting	$CaCO_3$
(6)	Quartz	SiO_2

Raw materials for Glaze

(1) *Frit* : Frit is a sort of powdered glass. The glass is made from the batch materials consisting of :

TABLE 15

Cornish stone	30 parts
China clay	5 parts
Flint	15 parts
Whiting	20 parts

(1) Borax—30 parts. (2) China stone, (3) White lead, (4) Porcelain grog (in case of porcelain), (5) Quartz, (6) Marble, and (7) Kaolin.

Materials for Crude Glaze

Either sodium chloride or PbO or white lead or Borax.

These are classified as follows :

(1) *Unglazed earthen-ware* : Ordinary hollow wares usually red or yellow made from common clay. This can be scratched by iron. Porous hard, and fired at 900°C. Colour red or yellow.

(2) *Terra-cota or baked earth i.e. solid clay products* : Bricks, tiles, and terra-cota blocks, all being manufactured from common clay. Colour is usually red. These are porous hard, and softens at about 1000°C. These can be scratched by iron.

(3) *Glazed pottery products* : Some pottery hollow wares and decorative articles are glazed with crude glaze.

On glazing with salt, sodium aluminium silicate is formed on the surface, by reaction of NaCl with clay. HCl is simultaneously given out. PbO or white lead produces lead aluminium silicate on the surface. Borax produces sodium aluminium boro silicate on the surface.

(4) Glazed fine earthenware or engobed fine earthen ware or semiporcelain.

TABLE 16

Composition of the body	(%)	Frit	(%)	Glaze	(%)
Ball Clay	46	Borax	30	Frit	50
China clay	23	Flint	15	China stone	25
Flint	21	Feldspar or		White lead	25
Cornish stone	10	Cornish stone	30		
		CaCO₃	20		
		China clay	5		

Glazing temp. is lower than the firing temperature of the unglazed body, which is 1200°C.

The glaze can be scratched with steel.

China clay increases whiteness and resistance to sudden change of temperature.

(5) Hard porcelain.

TABLE 17

COMPOSITION FOR THE BISCUIT

	Severes (%)	Berlin (%)	Chinese (%)
Kaolin			47
Potash Feldspar	38	77	15
Quartz	38	23	38
	24	—	

TABLE 18

COMPOSITION OF GLAZE OF HARD PORCELAIN

	Per cent
Ground hard porcelain grog	25
Quartz	42
Chalk or Marble	33

The biscuit is made at 950°C after putting the glaze, the glazed biscuit is fired at 1200°C—1400°C. The glaze and biscuit soften simultaneously and forms a single surface. Hard porcelain is unique in this respect. The glaze cannot be scratched with steel.

TABLE 19

COMPOSITION OF GLAZE FOR ROYAL BERLIN

Potash Feldspar	8 parts
Quartz	57 ,,
Kaolin	28 ,,
Marble	7 ,,

(6) China ware or English China or Bone China

TABLE 20

COMPOSITION OF THE BODY

China clay or Kaolin	20 to 30 p.c.
Bone ash	27 to 40 ,,
China stone	20 to 32 ,,

TABLE 21

COMPOSITION OF THE GLAZE

First frit is made from the following batch materials :

China clay	12 parts
Quartz of Flint	15 ,,
Cornish stone	20 ,,
Chalk or Whiting	18 ,,
Borax	35 ,,

After making the frit the glaze is then made from the following batch materials :

TABLE 22

Firt	65 parts
Cornish stone	11 ,,
Flint	11 ,,
White lead	13 ,,

The biscuit is fired at 1250°C. Temperature of glaze firing is below 1100°C.

Hard porcelain is non-porous completely vitrified.

China ware is semi-vitrified and the glaze is less hard than that of hard porcelain.

Stone Ware

This is a kind of porcelain. This kind of porcelain is not always white, because the ingredients contain Fe_2O_3 and other impurities. The stone ware is used for making sewer pipes and conduit pipes. The stone ware is glazed with salt.

Chemical stone ware : It is used for making jars suitable for storing acids. The quality of the body and that of the glaze is better than those of stone ware. Porcelain and English China are used for varieties of purpose :

(1) For making dinner wares and tea sets.
(2) For making chemical apparatus such as basins and crucibles.
(3) For making electrical insulators, floor and wall tiles.
(4) For making high class sanitary goods, vases and other decorative articles.

Use of Semi-porcelain : Cheaper table wares, tea cups and saucers, vases, decorative articles, toys, cheap sanitary goods,etc. are made of it.

Ceramics also include porcelain enamel and certain refractories, which will be described under separate chapters.

Theory underlying the Manufacture of Ceramics

In making white wares (porcelain and semiporcelain) powdered potash feldspar and flint or quartz are mixed with white clay (china clay and ball clay), of these ingredients feldspar is a fluxing material and flint or quartz is a refractory. Thus it is evident that a successful white clay ware in order that it may not shrink on drying or crack on firing, and also does not become much porous, has to be made with white clay mixed with certain fluxing materials and some refractories.

The compositions of the porcelain or semi-porcelain biscuits mentioned above are only a few of the wide varieties applied to produce different varieties of white wares. In these clay mixtures one or more of the fluxing materials such as soda ash, borax, potash, feldspar and cryolite together with one or more refractory materials such as alumina, magnesia, chromite (FeO. Cr_2O_3), TiO_2, ZrO_2, CaO and $CaCO_3$, are present. The impurities in comparatively smaller quantities are added. The presence of impurities depresses the transformation temperatures, of mullite, cristoballite, and corundum in the SiO_2—Al_2O_3 (Clay) system. They also help to form a glassy substance which acts as a binder of the refractories (mullite, cristoballite, corundum and added refractories). In case of ordinary unglazed earthen

ware obtained from common clay, as the firing is done at about 900°C, the body contains anhydrous kaolin, and other impurities forming little or no glass. So the body is very porous. Heavy clay products such as common bricks, tiles, etc. obtained from common clay which are fired at about 1000°C form a superficial layer of small amounts of alkali and calcium silicates on the body consisting of anhydrous Kaolin mixed with impurities. The amount of glassy substance being small these are also porous. Superficial vitrification causes the formation of glassy substance. Thus it is found that in all classes of ceramics, the different grades of strength are all due to small or large chemical and physical change of the clay. Hence the rationale of the manufacture of clay products depend upon the study and understanding of clay.

Clay is a colloidal gel which shrinks and becomes hard on being dehydrated. This colloidal gel has a very important and useful property, viz. plasticity. The plasticity depends upon three factors, viz. colloidal nature, extent of hydration and particle size. The use of clay as the basic material for ceramic industry depends upon this plasticity, which imparts two essential qualities to clay, viz.

(i) Deformability i.e. the capacity to be shaped, (ii) Tenacity i.e. the capacity for resisting tearing force (especially when hard).

Although plasticity is a very useful property of clay highly plastic, clay is unsuitable for making clay products, because articles made of such clay, on drying undergo large shrinkage causing loss of shape and cracking when fired. Such clay articles also become highly porous. This excessive shrinkage and tendency to crack are prevented by adding some proportions of non-plastic ingredient such as ground flint and some fluxing materials such as feldspar. Other materials such as highly fired porcelain or grog ; chalk powder, magnesite powder, finely powdered mica, alumina, zirconium silicate and oxide, berylium oxide etc. are the materials for addition to the clay mixture (white clay, flint and feldspar) according to the purpose for which the mixture will be used. One or more ingredients in the above list in small quantities are added.

Manufacture of Ceramics White Warest

(1) Preparation of clay mixture.

(2) Ageing of clay mixture.

(3) Deairing of clay mixture.

(4) Shaping of articles by pressing, or slip casting or jiggering.

(5) Drying and trimming of articles.

(6) Putting on glaze on blanks in case of single firing process.

(7) (Fig. 29) Firing to producing unglazed ceramic bodies or biscuits or bispues or to produce glazed products in tunnel or updraft kilns.

(8) Putting glaze on biscuits. In case of decorated articles biscuits are decorated and then glaze is put (underglaze). In case of overglaze articles decorations are put on glaze and then fired.

(9) Firing the biscuits with glaze on.

(1) The mixture of china clay and ball clay after being weighed are taken in a blunger and stirred well with water to form a creamy liquid known as clay slip. The slip which flows easily, is then allowed to flow from the blunger over a vibrating screen to remove foreign materials. Next the slip is treated in a magnetic separator to remove
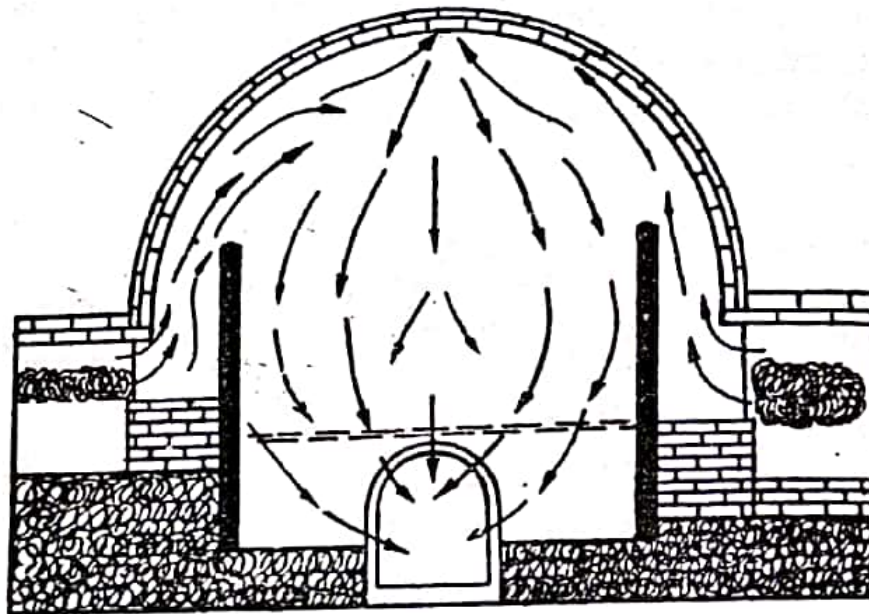

Fig. 29. Downdrost Furnace

bits of iron. The purified and uniformly blended clay mixture is then mixed with requisite quantities of ground flint and feldspar (and other additions where necessary) to make an uniform clay mixture.

(2) Ageing—The final slip is filter-pressed. The residual cake contains 10-30% water. The cakes are then dumped in a dump storage for some days. This improves the plasticity of the clay mixture, because uniform hydration accompanied by gelation takes place. Plasticity also improves due to diminution of particle size on account of bacterial action.

(3) The aged cakes are deaired in a pug mill by slicing with knives and putting under vacuum.

(4) Shaping is done by varieties of methods. (a) Electrical insulators are shaped by hot-pressing the deaired clay mixture in moulds. (b) Complicated shapes such as some pieces of dinner ware and similar other articles are obtained by slip-casting. The aged and deaired clay mixture is mixed with 35 p.c. water together with 0.1 p.c. Na_2SiO_3 and 0.1 p.c. Na_2CO_3 (on the weight of dry clay mixture). The slurry thus formed gives the casting slip. The sodium salts are added in order to increase the fluidity of the slip. The slip casting is done in plaster of Paris moulds, which are filled with the slip. After allowing the slip to stand for some time a

layer of clay (lining) is deposited on the inside surface of the mould by absorption of water. After this the excess slip is poured off. The time which elapses before pouring off the excess slip varies from 10 to 30 minutes depending upon the wall-thickness of the shaped article. Shape of articles by slip-casting is obtained as a lining in the mould. After pouring off the excess the mould with the lining is allowed to dry in a warm place for 20-45 minutes. After this period of drying the shaped articles shrink and separate from the mould. When solid articles are shaped by slip-casting, instead of pouring off the excess slip, the mould is filled several times with the slip to make up for the loss of water by absorption.

(c) Simple articles such as cups, plates etc. are shaped on potters' wheel or jigger.

(5) The shaped articles after air drying are trimmed and then dried in hot-air drivers under exactly controlled conditions.

(6) Finally dried articles are known as blanks. In a few cases glaze is put on the blanks before firing. But in most cases blanks are fired to produce bisques or biscuits. In these cases glazed products are obtained by putting glaze on cold biscuits and then firing. The firing is done either in a tunnel furnace or an updraft kiln. At the present time high class porcelain is also made in electric furnaces. Usual maximum temperature is 1400°C, but in some cases temperature rises upto 1500°C. The tunnel furnace consists of a tunnel made of fire-bricks. The length varies from 300 to 500 ft., width from 5 ft. to 8 ft. and height from 5 ft. to 8 ft. The tunnel is fitted with special steel rails on which cars made of special steels move from one end to the other being either pushed by a hydraulic ram or pulled by a chain. The rate of movement varies from 3 ft. to 8 ft. per hour. The tunnel is divided into preheating zone, firing zone and cooling zone. The firing zone is fitted with fire-boxes in which oil or coal or producer gas is used as fuel. Cold air is circulated from the exit end towards the firing zone over the hot articles which move from the firing zone towards the exit. Thus as the hot articles move through the cooling zone they are annealed. The hot air as it reaches the firing zone is piped to the preheating zone and is used to preheat the incoming articles. In this way the articles are preheated before entering into the firing zone. Articles dried by hot air are placed in saggers made of fire-clay. The saggers are suitable boxes fitted with shelves in which articles may be placed in piles without touching one another. This is more important during glaze firing. The saggers are piled in the cars.

The updraft kiln is a domeshaped circular structure made of bricks and lined with refractory bricks. The kiln is fitted with fire-boxes in which solid fuel is usually used. Gaseous fuels are

also used in such kilns. The saggers with the blanks are piled on the floor. The temperature reaches maximum gradually, and kept at the maximum for some time. Then the fired articles are allowed to cool gradually. In this way the fired articles become annealed.

(7) *Glazing* : The glazing ingredients are finely powdered, and mixed in requisite proportions. The mixture is next mixed with proper quantity of water to make the slip of necessary consistancy. The slip is then applied either to the dry blanks or more frequently to the biscuits by dipping, or pouring, or spraying or brushing very carefully. Except in case of hard porcelain firing temperature for producing biscuits is higher than that applied to produce glazed ware. Glaze is a sort of glass, which is applied on the surface to cover the pores which are present almost in all class of ceramics excepting hard porcelain. These pores are present in large numbers in common clay products which are obtained at lower temperature, they are also present in smaller number in white wares which are produced at comparatively higher temperature. Only in hard porcelain which is produced at about 1400°C, pores are closed up due to vitrification. The glazing material in hard porcelain fuse on the biscuit to become one with the surface of the biscuit.

Decoration : There are two kinds of decorations—underglaze and overglaze. Decorations are first painted with the slip made of inorganic oxides (used in case of coloured glass, such as oxides of cobalt, chromium, manganese etc.) and then fired. In case of underglaze the decoration is put on biscuits, and then after drying the decoration glaze is applied, and then fired. In case of overglaze, the decoration is put on the glaze, and then fired. In large scale productions decorations are applied by means of transfer paper (decalcomania paper).

Certain glazes are opaque due to the presence of an opacifier such as SnO_2.

Enamel Porcelain

A coating of coloured and opaque glass fused on gold, silver and brass surfaces formed the ancient art of enamelling. In the nineteenth century this art of enamelling metals was developed into an useful industry. At the present time the enamelled metals—cast-iron, steel or aluminium—articles are being extensively used for various purposes. Enamelled iron cooking and other utensils as well as sanitary goods were principally in former use. Now the field of application of enamelled metal wares has been extended. Enamelled signs, building equipments, chutes in coal mines, enamelled aluminium industrial equipments are in use.

The enamels used to coat the metal surfaces are known as porcelain enamels. The different enamels differ in the proportions of the ingredients and those

of colouring agents, although the nature of different ingredients does not much vary. All porcelain enamels are opaque, they are either white or coloured. This enamel which is an opaque glass, is fused on the metal surface. Both the enamel and the metal are so chosen as to possess the same coefficient of expansion. In such cases the enamel does not easily peel off the metal surface. The materials for making an enamel are divided into two classes, viz. the frit and the mill charge. The frit is a friable glass made by fusion of appropriate batch materials, previous to mixing with the mill charge.

The mill charge consists of clay and an opacifier like SnO_2 or TiO_2. The clay has a dual role. It acts as a floating agent as well as the body forming agent. The clay makes the enamel a porcelain like substance. In the enamel the refractory particles of Al_2O_3, $2SiO_2$, are held in the matrix of the solidified glass. As the frit is a glass, it has to be previously made at a temperature much higher than that at which the enamel is fused on the metal. The latter temp. is 1400°-1500°F. In case of enamelling aluminium this temperature is still lower.

Manufacture of enamelled iron wares :

(1) For this purpose cast-iron or mild-steel articles are first made and this are then annealed. Outside and inside surfaces of these articles are cleaned. Cast-iron articles are sandblasted and steel articles are pickled by 8 p.c. sulphuric acid.

(2) For making the enamel at first, frit is made from glass forming materials such as sand, soda ash, feldspar, calcium fluoride, borax etc. When melted the ingredients react to form a glass consisting of sodium, potassium, calcium borosilicate. For regulating the co-efficient of expansion many changes have to be made in the composition of the frit.

A composition of a typical frit is given below :

TABLE 23

$KAlSi_2O_6$	29.5 p.c.
$Na_2B_4O_7$	22.00 ,,
$AlF_3,3NaF$	13.5 ,,
Na_2CO_3	3.5 ,,
$NaNO_3$	3.5 ,,
Sb_2O_3	3.00 ,,
ZnO	3.00 ,,
SiO_2	19.00 ,,

The weighed material are ground, weighed and mixed in requisite proportions. The batch materials are next melted in a fireclay pot, set in a furnace, at about 1370°C for one to three hours. The molten glass is then poured in cold water, when innumerable particles of friable glass are formed by

quenching. These particles are then mixed with requisite quantities of clay, opacifier, and colouring matter. To 100 parts of frit 6 parts of clay and 5 parts of SnO_2 are added, the amount of colouring matter depends upon the tint. These ingredients along with water are ground in a porcelain-ball mill (below 200 mesh size). After grinding the slurry is screened in a vibrating 200 mesh screen. The slip thus formed is then allowed to age.

(3) Next a thin coating of enamelling materials is applied on all the surfaces of the metal article by either dipping, or pouring, or spraying process. When excess slip drains away, a wet coating of the enamel forming materials is formed on the metal surface. After the wet coating has been dried, the slip coated articles are fired.

(4) For firing the slip-coated articles are placed in the furnace, after avoiding mutual touching. The furnace used is either an intermittent muffle kiln, or a tunnel furnace. Temperature maintained is 1400° to 1500°F (760 to 815°C).

A thin glassy coating is thus formed. A second coating is usually applied by wet or dry process. In the wet process the surface with single coating is again slip coated, dried and refired. In the dry process a ground mixture of frit, clay, opacifier and colouring matter is dusted uniformly on the still hot first coating. After applying the dust the article is refired. Colouring agents similar to those used in making coloured glass are used. Refrigerators, dairy equipments, canning and food processing equipments are some of the various new fields of application of enamelled wares.

EXERCISE

1. Define with illustration the following : (a) Pottery products, (b) Semiporcelain, (c) Porcelain, (d) Glaze, (e) Frit, and (f) Enamel.

2. Describe the making of an ordinary tea-set. Ellucidiate the raw materials used, and also the method overglaze and underglaze paintings.

3. Describe the different clays, and other raw materials used for making glazed white earthen ware, and finished porcelain articles such as electrical insulators, dinner sets, and laboratory equipments.

4. Name the different ceramic products. What is stone ware ? Discuss the theories underlying the production of ceramic bodies.

5. Write notes on : (a) Tunnel kiln, (b) Updraft kiln, (c) Porcelain enamel, (d) Distinction between different ceramic products, (e) Composition of porcelain, and (f) Composition of enamel.

6. Discuss the industrial importance of enamels. Describe in detail the process of making enamel wares.

CEMENT

A CEMENT is a substance which sets to a hard mass in presence of water. Egyptians, Greeks and Romans used volcanic stuff, such as *puzzuolanic* cement a volcanic tufa obtained near Puzzuoli in Italy. These natural cements are nothing but mixture of burnt silicates and lime. The acidic siliceous matter combine with $Ca(OH)_2$ during the setting of the natural cement. At the present time lime concrete and laying of bricks are made with the help of a mixture of lime and ground burnt bricks (known as 'Surki'). A cement of far more quick setting and of much greater strength is now-a-days artificially made. This cement is called portland cement. The portland cement was first made by an English brick-layer named Joseph Aspdin in 1824. The name was derived from the Portland stone found in Portland island near England, because Mr. Aspdin thought that the cemented material resembled the Portland stone in appearance. The portland cement is a mixture of the following compounds :

Tricalcium aluminate, $(CaO)_3$, Al_2O_3
Tricalcium silicate, $(CaO)_3$, SiO_2
Dicalcium silicate, $(CaO)_2$, SiO_2
Tetracalcium alumino ferrate, $(CaO)_4$, Al_2O_3, Fe_2O_3

Small amount of MgO, derived from raw materials, is also present. Some cement contains Gypsum or plaster of Paris which is added in small quantities (to increase plasticity). The Portland cement is defined as the finely ground clinker obtained by heating together a mixture of limestone and clay to the point of incipient fusion (the iron oxide is present in clay or marl or cement rock used). The raw materials should be so proportioned as to produce a cement in which the ratio of the amount of CaO (less the amount combined with SO_3) to the amount of $2.8\ SiO_2+1.2\ Al_2O_3 +0.65\ Fe_2O_3$; should not be more than 1.02, and not less than 0.66.

The formula is $$\frac{CaO}{2.8\ SiO_2+1.2\ Al_2O_3+0.65\ Fe_2O_3}$$

The regular portland cement contains medium amount of CaO. High early strength cement contains high proportion of $(CaO)_3SiO_2$. It is made from raw materials containing high lime to silica ratio. Low heat portland cement contains high proportion of tetracalcium alumino ferrate and dicalcium silicate. A concrete of better chemical resistance contains higher proportion of $(CaO)_4Al_2O_3,Fe_2O_3$.

Manufacturing Process

(a) The raw materials used are limestone and clay which supply all the four principal ingredients, viz. CaO, Al_2O_3, SiO_2 and Fe_2O_3. To supply the CaO sometime chalk is used, where cement rock and marl which are (mixtures of calcium carbonate and clay) are available, they may be used with proper additions of calcium carbonate or clay. Where precipitated calcium carbonate is available on a large scale, such as obtained during the formation of ammonium sulphate from synthetic ammonia, gypsum and CO_2, it may be used to supply CaO. The calcium carbonate from the Sindri (India) Synthetic Ammonia Factory is utilised by the A.C.C. Company nearby to make cement. As alkali content in the cement must be as low as possible, and as other impurities should be eliminated, the cement rock, marl, and clay are often beneficated or treated to remove such impurities. The raw materials (after proper treatment, where necessary) mixed in finely state of subdivision in proper proportion is fed into kiln, where the mixture reacts at high temperature to form cliker of cement. There are two processes, wet and dry processes for making the mixture and also for feeding the kiln. In the wet process a mixture of raw materials with about forty p.c. of water is made into thick slurry which is then fed into the kiln. (Fig. 30) In the dry process, the dry mixture containing not more
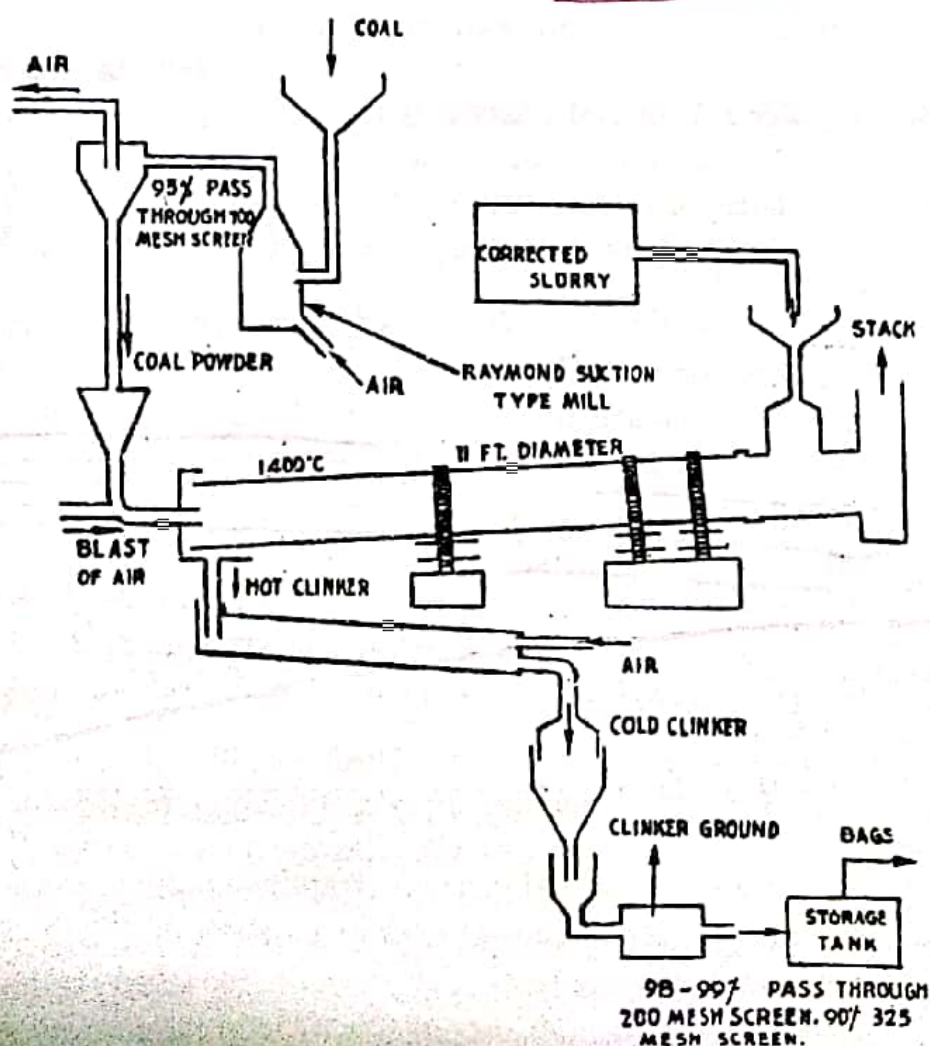

Fig. 30. Plant for Cement manufacture.

than 2 p.c. of water or briquettes formed from the dry mixture, are fed in the kiln. In the wet process the clay slurry is made in a wash-mill, where the clay is mixed with water and agitated by special device. The hard bigger particles are removed as the slurry passes out of the wash mill through a sieve. Where chalk is used, the powder chalk is made into a slurry in wash mill. Two slurries are then mixed in a ball-mill in proper proportion for further grinding. The mixture from the ball-mill is stored in the correct-ing tank where after analysis the proportion of clay and calcium carbonate is adjusted. Where limestone is used, the limestone is first crushed in one inch size pebbles then fed in the ball mill along with the clay slurry in proper proportion. The ground mixture from ball-mill is further ground in tube-mill and then stored in the correcting tank where after analysis additions are made to adjust the proportion. The proportions are adjusted according to the formula mentioned previously.

Dry process is adopted where hard clay such as shale and limestone, cement rock and marl are usually used. The raw materials are separately crushed and ground (when clay and chalk are used, the raw materials are ground after drying). The ground meterials are then analysed and mixed in mixers, in proper proportions. The dry mixture is briquetted (when necessary) by making a stiff paste in a pug mill, and cutting the paste into briquettes which are dried by hot air.

The slurry (mixture) or the dry mixture is fed into a hopper continuously at the upper end of a rotary kiln for making the clinker. The rotary kiln is a long steel cylinder inclined to the horizontal. The inclination is $\frac{1}{2}$" to $\frac{3}{4}$" to a foot. The cylinder is made of rivetted steel plates. The cylinder is 200 ft. to 350 ft. long, longest furnace in use is 450 ft. long. The diameter varies from 7 ft. to $12\frac{1}{2}$ ft. The upper end tapers where it enters into the flue. The lower end is broader. The lower end is provided with a fire-proof hood, to which is attached a short rotating cylinder inclined in the opposite direction for the passing out of the hot clinkers and for cooling them. Upper 40 ft. is bare inside, middle portion is lined with 7" thick firebrick lining, the lower firing zone is lined with a firebrick (9" thick) made of fireclay consisting of equal proportions of Al_2O_3 and SiO_2, or the lining is made of a concrete made of cement clinker pebbles ($\frac{1}{2}$" diam.) and cement (2 parts of clinker and 1 to $1\frac{1}{2}$ parts of cement). It is usual to give a protective coating of clinker on the lining when starting the kiln. Ordi-nary bricks may be used to line the upper portion instead of keeping it bare. The cylinder is slowly rotated by a girth gear situated near its middle and a train of reducing gears. The output varies from 1000 tons to 3000 tons. The lower end is the firing end, where 100 mesh coal powder is blown in with air, the hot air obtained by cooling the clinker also is introduced in the kiln. The temperature at the firing zone is 1400°C and the gas which leaves through the flue is of 600°C. 80 lbs. to 160 lbs. of fuel are necessary per barrel of cement. After introduction of the wet charge, the charge becomes dry (by means of the hot gas flowing upwards) as it travels down-

wards. Then the $CaCO_3$ decomposes at about 1000°C near the middle zone, and as the material enters the high temperature zone, the CaO, SiO_2, Al_2O_3 and Fe_2O_3 react to form the different constituents of cement men-. tioned previously. These undergo incipient fusion and form clinkers. These clinkers then pass out through the lower end into the rotary cooler. As the hot clinkers travel downwards air enters from the opposite direction, thus cooling the clinkers. The cold clinkers delivered from the lower end of the cooler are crushed and finely ground. The clinkers are very finely ground—the ground clinker is screened. 98 to 99 p.c. passes through 325 mesh screen. The cement is bagged and stored in silos 80 ft. high and 35 ft. in diam.

Setting of Cement

At first $(CaO)_3 Al_2O_3$ hydrates to form CaO, Al_2O_3, $12H_2O + 2Ca(OH)_2$ then $(CaO)_3 SiO_2$ hydrates to form CaO, SiO_2, $2H_2O + 2Ca(OH)_2$, then $(CaO)_2 SiO_2$ hydrates to form CaO, SiO_2, $2H_2O$, $+Ca(OH)_2$ then $(CaO)_4$, Al_2O_3, Fe_2O_3 hydrates. At first the hydrated salts form a colloidal gel coating on the anhydrous grains. The gel contains much free water which is gradually withdrawn by the anhydrous core. In this way the core becomes hydrated and the surface becomes hard due to drying. At this stage cracking appears if sufficient water is not available, due to overdrying, of the surface. The process continues for 10 to 20 days.

Then the hydrates and $Ca(OH)_2$ crystallise. The crystals interlace with one another and with sand grains, to form an impervious continuous hard mass.

EXERCISE

1. Define: (a) Puzzuolanic cement and (b) Portland cement. Distinguish between the two cements.

2. What are the criteria of the portland cement raw materials? What do you mean by wet process and dry process in cement manufacture ? How is portland cement manufactured ?

3. Describe the rotary kiln used in cement manufacture. Discuss the composition of portland cement. Discuss the setting of portland cement.

FERTILISERS

Introduction

Plants supply mankind the staple foodstuffs and other necessities of life. From plants the cattle get their fodder, and other animals directly or indirectly live on plants. Thus all animal food including milk are obtained from plants. The plants so essential for our life require some food for their nourishment. These food materials build up the body of the plant which contains carbohydrates, proteins, lignin, and other organic matter. Carbon, oxygen and hydrogen are supplied by CO_2 and water. The nitrogen is supplied by nitrates, which are ultimately produced in the soil. Some plants may also sustain themselves by ammonia. Plants also require phosphates and potassium salts for their growth. All these plant food are supplied by nature. CO_2 and some moisture are taken from the air, most of the water and nitrogenous, phosphatic and potassium compounds in aqueous solution are drawn from the soil by the roots of the plants. Oxygenation of the roots and other parts of the plants are also essential for plant metabolism. The food materials derived from the soil are known as fertilisers or manures. Each year these fertilisers are depleted from the soil and they are to be replenished every year. Application of fertilisers to the soil increase the fertility of the soil, hence plant products have to be sustained on normal level by replenishing the fertilisers, and can be increased above the normal level by applying larger amount of fertilisers. At the present time this increment of food production has become essential owing to enormous growth of population. Ordinarily the nitrogenous fertilisers are replenished by the nitric acid produced by lightning, and by the organic manure—the cattle excreta, the plant and animal decomposition products, etc. The phosphatic fertilisers are replenished from animal bones, farm yard manure, and plant and animal decomposition products. Potassium fertilisers are replenished by wood ash, and plant decomposition products.

But the natural fertilisers described above are limited in amount, moreover much of them are withdrawn from their use as fertilisers, being used as fuel in the countryside (in India). Hence it has become necessary to add artificial fertilisers along with farm yard manure to the soil in order to maintain and increase the fertility of the soil.

Fixation of Nitrogen

Plants require nitrogen for their growth, but this nitrogen cannot be assimilated by plants from the atmosphere. For assimilation of nitrogen by plants, it is necessary that the atmospheric nitrogen be converted into assimilable nitrogenous compounds and must be presented to the plants

in the assimilable form in aqueous solution in the soil. The conversion of the atmospheric nitrogen into compounds assimilable by plants is known as fixation of nitrogen (Fixed into the soil). Every year vast amount of nitrates are formed from atmospheric nitrogen through the agency of lightning. When lightning (30,000 volts) passes through air, nitric oxide is formed by the endothermic reaction between nitrogen and oxygen. Because the duration of lightning is very small, nitric oxide survives decomposition. This nitric oxide is next oxidised to nitrogen peroxide by atmospheric oxygen. This latter oxide when washed with rain water comes down, nitric acid is introduced into the soil. This nitric acid reacting with $CaCO_3$, K_2CO_3 $(NH_4)_2CO_3$ are converted into $Ca(NO_3)_2$, KNO_3 and NH_4NO_3. Thus atmospheric nitrogen becomes fixed into the soil as nitrates, the most efficient plant food. Annually 100 million tons of nitric acid are produced by lightning (but a large proportion of it falling on the seas, oceans, deserts, mountains and hills are lost to agriculture).

Nitrogen Cycle

The nitrates formed by lightning are assimilated by plants. Proteins of the human body and the animal bodies are derived from the plants. Hence part of the fixed nitrogen is taken up by plants and animals. Some plants (leguminous) have the power to convert nitrogen of the air into assimilable compounds with the help of certain bacteria. Now part of the animal and plant protein get into the soil and after decomposition the proteins are ultimately transformed into ammonia and then to nitrates. These nitrates are again transformed into plant and animal proteins. Thus a part of fixed atmospheric nitrogen goes round in nature again and again in the fixed condition and the rest of the fixed nitrogen goes back to air by decomposition of protein matter during burning and by action of denitrifying bacteria. Going round of fixed atmospheric nitrogen (suitable for plant food) as well as the decomposition of fixed nitrogen compounds and their reformation are known as nitrogen cycle (Fig. 12).

Nitrogen cycle is nature's 2nd device for the fixation of nitrogen. Now natural fixation of nitrogen has been found insufficient for the continual demand for increase of food materials and other necessities of life due to the vast increase in the world population. Hence to keep pace with increasing demand of fertilisers, it has been necessary to produce artificial fertilisers. The nitrogenous artificial fertilisers are made synthetically (starting from atmospheric nitrogen). Hence these processes are known by the name of artificial fixation of nitrogen. Artificial phosphatic fertilisers consist of soluble phosphates made from rock and bone phosphate. Artificial potassium fertilisers are obtained by extracting potassium salts, such as KNO_3, KCl, K_2CO_3.

The nitrogenous fertilisers usually used are (1) $(NH_4)_2SO_4$ containing 20 p.c. N_2, (2) Double Salt mixture of $(NH_4)_2SO_4$ and NH_4NO_3 containing 26 p.c. of N_2, (3) NH_4NO_3 containing 35 p.c. N_2, (4) Urea containing 44 p.c. N_2, (5)
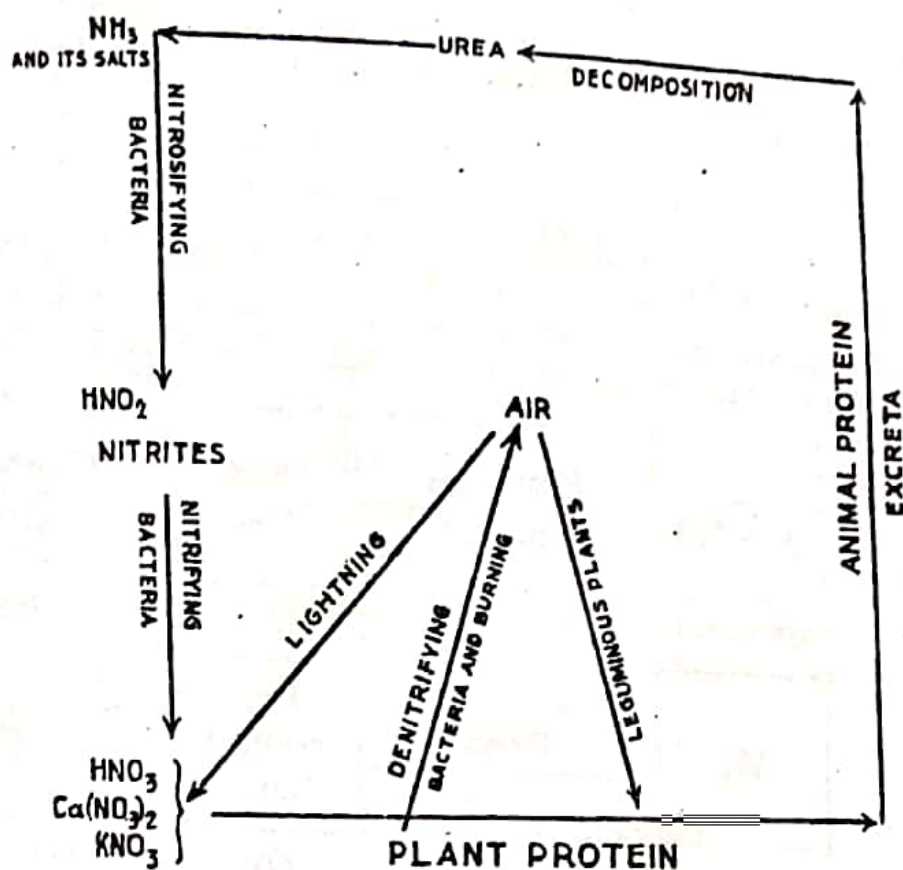
Fig. 12.   Nitrogen Cycle

$NaNO_3$ in the form of Chilian nitrate. This is also manufactured by the action of synthetic nitric acid on Na_2CO_3, it contains 16% N_2. It is best used in combination with cattle manure. (6) Calcium ammonium nitrate, produced by mixing ground limestone, ground dolomite stone or $CaCO_3$ with NH_4NO_3, to make the latter safe. It contains 15.5% of N_2. Nitrochalk (I.C.I.), Cal-Nitre A.N.L., are prepared in a similar way but contain 20.5% N_2, 9% $CaO+7\%$ MgO. It is one of the most important nitrogenous fertilisers which is to be produced in large quantities in India.[1] It has been proved in field experiments that continuous use of ammonium sulphate reduces the fertility of the soil when the soil is low lime or acid soil. When the pH of the soil falls below 6, the rate of nitrification is slowed down. Moreover beneficial ions of iron, manganese and aluminium are removed at low pH. Hence $(NH_4)_2SO_4$ should always be used with proper quantity of lime, the quantity of which depends upon the lime content of the soil.

Other artificial fertilisers used in India are superphosphate of lime, triple phosphate, bonemeal, rock phosphate, ammonium phosphate, ammoniated superphosphate and nitrophosphate, basic slag and dicalcium phosphate.

KCl, K_2SO_4 and KNO_3.

Superphosphate : It contains 14.5 to 20% water soluble P_2O_5, 25 to 30% CaO, 28 to 30% SO_4. A typical sample contains 50% gypsum, 26.6% mono-

[1] Another important nitrogenous fertiliser is calcium cynamide or nitrolim.

calcium phosphate, 4.6% di and tri calcium phosphate, 7% SiO_2, 4% Fe & Al sulphates and 1.5% CaF_2.

Concentrated superphosphate or *triple phosphate* : It contains as much as 45 to 50% water soluble P_2O_5 and 17 to 20% lime produced by the action of rock phosphate on H_3PO_4 obtained by the wet process by H_2SO_4.

Advantage : Low grade phosphate rock can be utilised, and cost of transport is diminished.

When produced from concentrated phosphoric acid produced by electrical method, the product is dry and granular. Basic slag from Indian steel factories contain low P_2O_5 content, in one factory the P_2O_5 content was 7.5% of which 80% was soluble in 2% citric acid. Therefore crop response is much greater.

Advantages of Organic Manure

(1) Helps to prevent erosion. (2) Helps bacterial growth. But the organic manure cannot be increased to the desired extent, moreover due to the want of fuel in countryside most of the cattle manure is burnt as fuel. Hence judicious combination of organic manure with artificial fertiliser is best. In Italy and Japan the yield of rice has been considerably increased by combining organic manure with artificial fertiliser. In Italy 10-50 tons of farm yard manure per acre is applied to the field before plantation, and 700 lbs. of mixture of ammonium sulphate, superphosphate and potassium chloride.

In India it has been found that combination of organic manure and inorganic fertilisers give better yield of paddy in alluvial and laterite soils than in red soils.

Mixed Fertiliser

They are made by mixing nitrogenous, phosphatic and potasssium fertilisers in required proportions. The mixture is then mixed with inert matter like sand or soil known as fillers. The fillers act as make-weights for the fertilisers. Sometimes organic manure, such as green manure or farmyard manure is used as fillers.

Uses in India

For paddy in Madras, 4000-6000 lbs. of green manure, 100-150 lbs. of superphosphate and bone-meal, and 100 lbs. of sulphate of ammonia per acre.

In U.P. for sugar cane 90 lbs. of N_2 as farm yard manure and green manure per acre together with 15 to 20 lbs. N_2 as castorcube, plus 100 lbs. of N_2 as ammonium sulphate.

In North Bihar for sugar cane 10 mds. of cake plus 2 mds. of ammonium sulphate per acre.

In Bombay for sugar cane 600-750 lbs. of ammonium sulphate, 4 to 5 thousand lbs. of cake and 250 lbs. of superphosphate per acre.

Manufacture of Nitrogenous Fertilisers

(1) Ammonium sulphate is manufactured by first manufacturing synthetic ammonia by Bosch-Haber process or by Haber process. The ammonia is allowed to react with sulphuric acid or simultaneously with gypsum powder and CO_2.

(2) Double salt is made by mixing $(NH_4)_2SO_4$ and NH_4NO_3, the latter is made from synthetic nitric acid (made by Ostwald's process), and ammonia.

(3) Urea from synthetic ammonia and CO_2.

(4) CaNCN—from CaC_2 and atmospheric nitrogen.

(5) $NaNO_3$.

(6) Calcium ammonium nitrate, i.e. NH_4NO_3 stabilised by ground lime stone.

All the above fertilisers except CaNCN are made from synthetic ammonia or nitric acid produced by catalytic oxidation of synthetic ammonia. Hence artificial fixation of nitrogen is done in two ways, viz. (a) by forming synthetic ammonia, and (b) by forming CaNCN.

Manufacture of Calcium Cyanamide or Nitrolim   (Fig. 13)

Calcium cyanamide is a derivative of cyanamide, $N \equiv C-NH_2$, which has been formed by replacing the OH of cyanic acid, $N \equiv C-OH$ by NH_2 Hence calcium cyanamide is $N \equiv C-N = Ca$.

The nitrolim of commerce is a grey powder containing 60 p.c. CaNCN mixed with graphite, and lime (the unchanged CaC_2 is ultimately converted into lime). It is made by the action of nitrogen on crushed calcium carbide at 982°C.
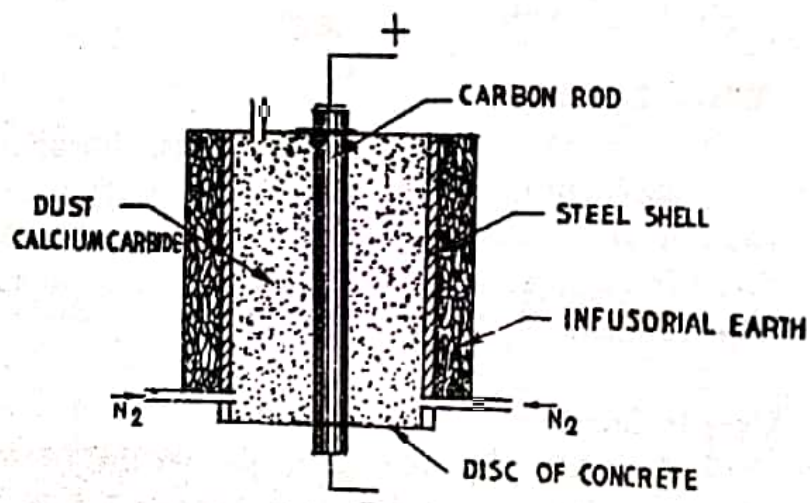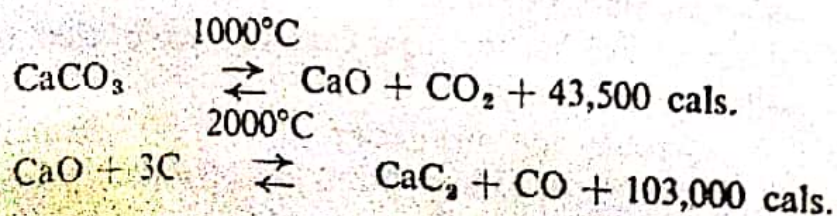

Fig. 13. Furnace for making Nitrolim

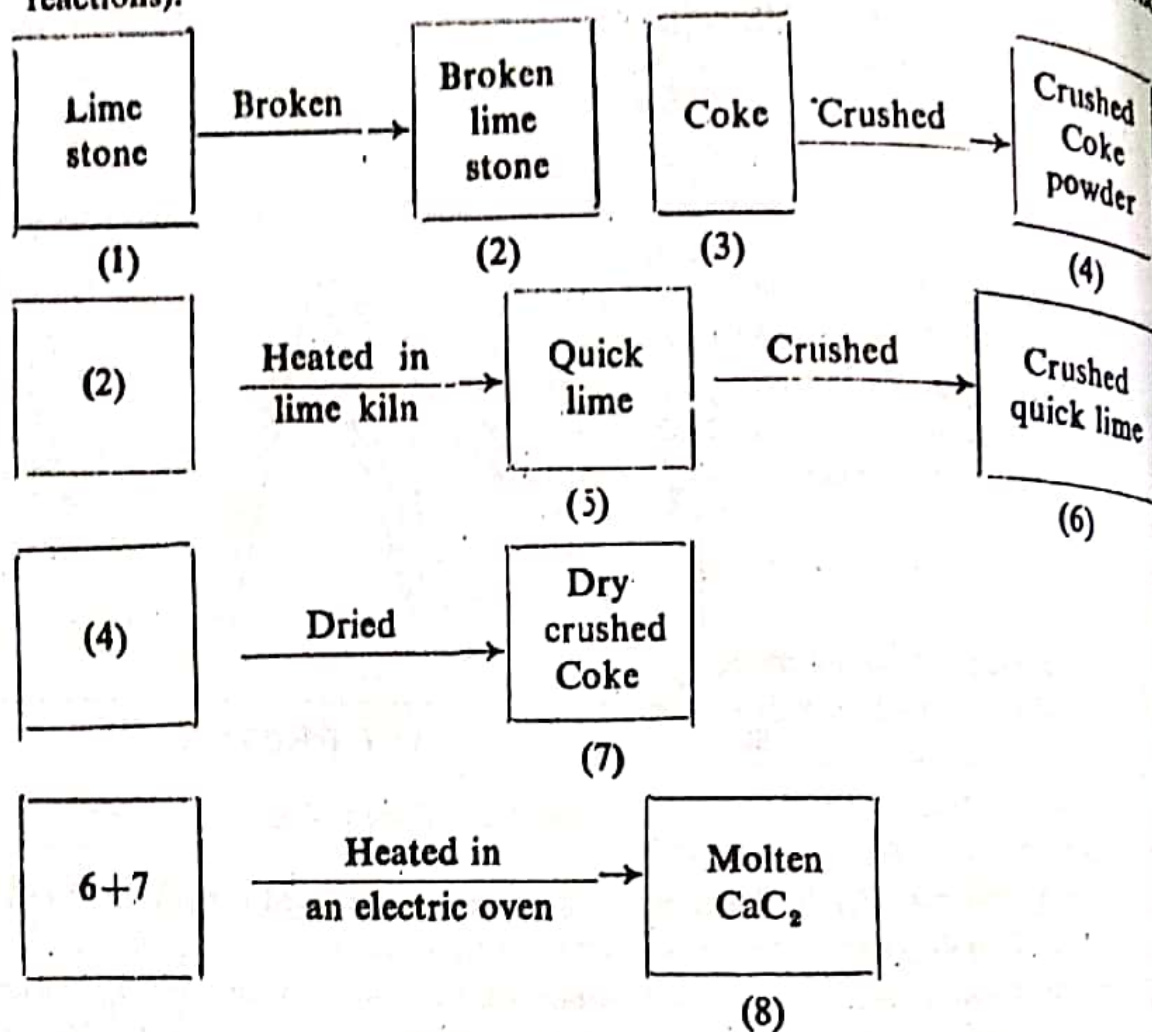The reactions involved in the production of raw materials and calcium cyanamide are :

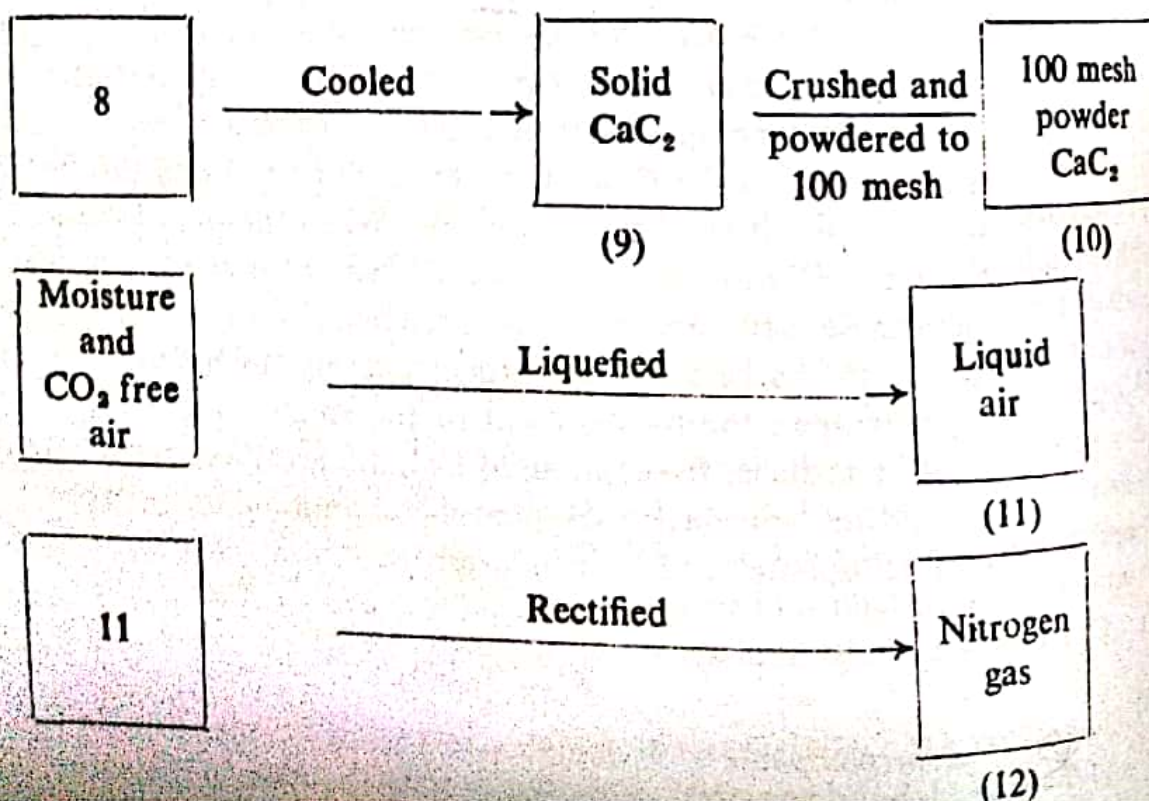$$CaCO_3 \underset{2000°C}{\overset{1000°C}{\rightleftarrows}} CaO + CO_2 + 43,500 \text{ cals.}$$

$$CaO + 3C \rightleftarrows CaC_2 + CO + 103,000 \text{ cals.}$$

$$CaC_2 + N_2 \underset{982°C}{\overset{}{\rightleftarrows}} CaNCN + C - 68,000 \text{ cals.}$$

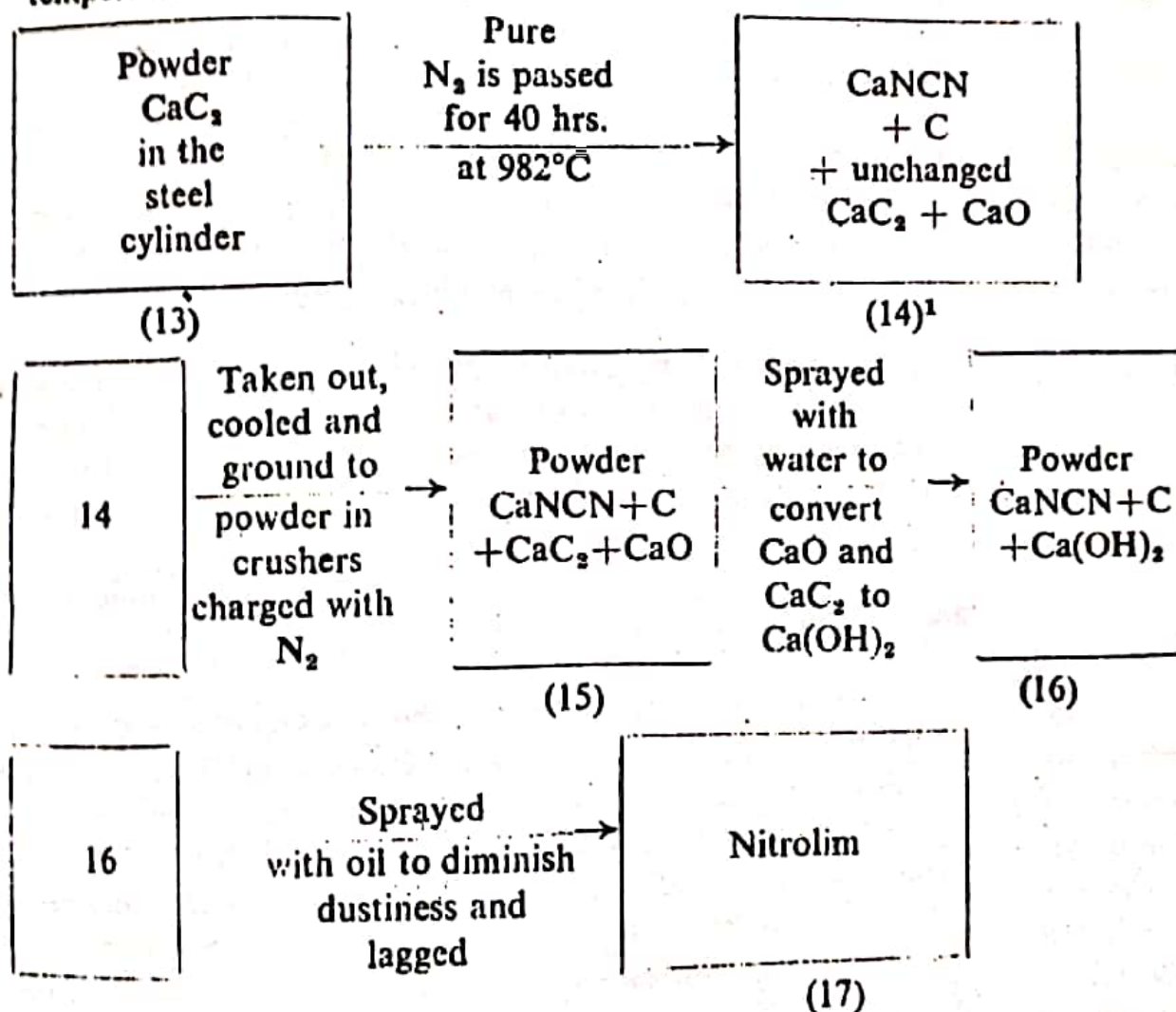(minus cals. indicate exothermic reaction and plus cals. endothermic reactions).

Lime stone	Broken →	Broken lime stone	Coke	Crushed →	Crushed Coke powder
(1)		(2)	(3)		(4)

(2)	Heated in lime kiln →	Quick lime	Crushed →	Crushed quick lime
		(5)		(6)

(4)	Dried →	Dry crushed Coke
		(7)

6+7	Heated in an electric oven →	Molten CaC₂
		(8)

40 p.c. dry coke powder (excess) is mixed with 60 p.c. powder CaO.

8	Cooled →	Solid CaC₂	Crushed and powdered to 100 mesh	100 mesh powder CaC₂
		(9)		(10)

Moisture and CO₂ free air	Liquefied →	Liquid air
		(11)

11	Rectified →	Nitrogen gas
		(12)

Powder CaC_2 is taken in a closed steel cylinder with a bottom of concrete disc. A carbon rod acting as the heating element is fitted vertically in the middle of the cylinder. The outer surface of the steel shell is lagged with infusorial earth. Above the bottom, there are inlet pipes for the en'ry of nitrogen, on the top there is an outlet pipe.

The reaction is an exothermic one. The optimum temperature is 982°C. The reaction is started by passing electricity through the carbon rod in the middle (as described above). The heat developed in the above resistant furnace starts the reaction between CaC_2 and N_2, and the temperature gradually rises to 982°C or near about 1000°C. Then the electricity is cut off, and the temperature is maintained by the heat of reaction.

Powder CaC_2 in the steel cylinder	Pure N_2 is passed for 40 hrs. at 982°C	CaNCN + C + unchanged CaC_2 + CaO
(13)		(14)[1]

14	Taken out, cooled and ground to powder in crushers charged with N_2	Powder CaNCN+C +CaC_2+CaO	Sprayed with water to convert CaO and CaC_2 to $Ca(OH)_2$	Powder CaNCN+C +$Ca(OH)_2$
		(15)		(16)

16	Sprayed with oil to diminish dustiness and lagged	Nitrolim
		(17)

Manufacture of Ammonia by Synthetic Process (Fig. No. 14)

Ammonia is synthesised by allowing one volume of nitrogen to react with 3 volumes of hydrogen both under pressure heated at an optimum temperature in presence of a catalyst. The process was developed by Fritz Haber and Carl Bosch (German Chemists) and is known as Bosch-Haber process. In this process hydrogen is taken from water gas, and nitrogen from producer gas. Later on the raw materials were obtained from other sources and ammonia was synthesised from them. The synthesis of ammonia is done by

[1]At the end of the reaction nitrogen goes out unabsorbed.

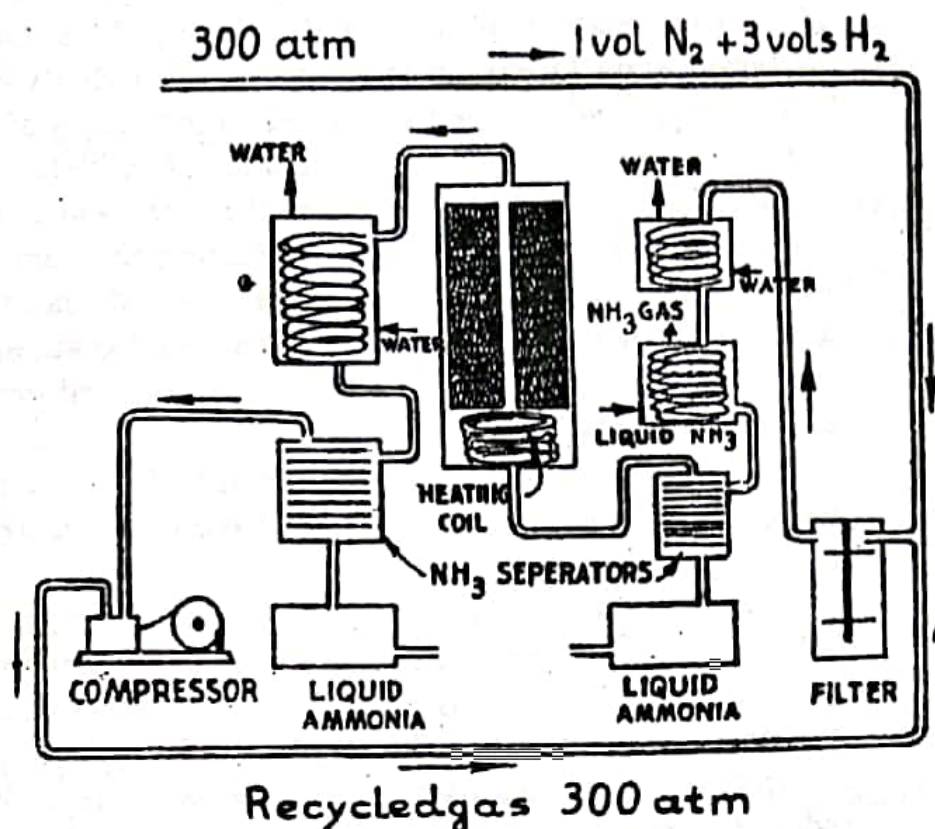Haber process. In these cases nitrogen is obtained by rectification of liquid

Fig. 14. Haber's Process for making Ammonia.

air and hydrogen is prepared by (*i*) Steam hydrocarbon process or (*ii*) Electrolytic process. In India nitrogenous fertilisers are manufactured by the different units of Fertiliser Corporation of India Ltd. In the Sindri Unit in Bihar both Bosch-Haber process and Haber process are followed. In the latter process hydrogen is obtained by steam hydrocarbon process (the hydrocarbon is CH_4 of coke oven gas), the nitrogen is supplied from liquid air. In Langal (in the Punjab) Unit, hydrogen is obtained by electrolysis of water, and nitrogen from liquid air. In Rourkella hydrogen is obtained by steam hydrocarbon (CH_4) process, CH_4 being obtained from coke oven gas, and nitrogen from liquid air. Production of nitrogenous fertilisers in Sindri Unit :

In 1957-58—332031 tons of $(NH_4)_2SO_4$

In 1963—Urea was being produced at a rate of 70 tons per day, and 400 tons of double salt [NH_4NO_3 and $(NH_4)_2SO_4$] per day.[1]

Theory : Synthetically ammonia is formed by the reaction:

$$N_2 + 3H_2 \rightleftarrows 2NH_3 - 24{,}000 \text{ cals.}$$
1 vol. 3 vol. $\rightleftarrows$ 2 vol.
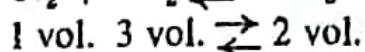
(— 24,000 cals. indicate evolution of 24,000 cals. of heat).

[1]The total production of nitrogenous fertiliser in 1964-65 is 26 lakh tons. The target is ten million tons.
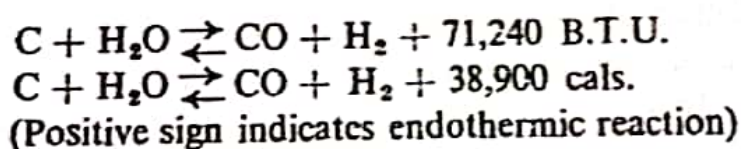
As the reaction is exothermic an optimum temperature of 550°C is maintained. Optimum temperature is the minimum temp. for maximum amount of product (See hydrogenation of oils for discussion). It is 550°C in actual practice described here. This is according to Le Chatelier's Principle. According to the same principle where the number of molecules of the reactant gases in a gaseous reversible reaction are greater than those of the products ; the equilibrium is shifted to the right by the increment of pressure. Hence in this case the increment of pressure will increase the amount of ammonia in the equilibrium mixture (containing ammonia and unconverted N_2 & H_2). In actual practice the synthesis is carried out at 200 atmos. pr. in Haber process with 8 p.c. conversion at 550°C, and in a modified process at 300 atmos. pr. at 550°C with 19 p.c. conversion.

The catalyst used is specially prepared iron promoted with potassium oxide (1 p.c.) and aluminium oxide (3 p.c.). The catalyst is prepared by the following process :

Pure iron is burnt in oxygen to form Fe_3O_4. Fe_3O_4 is fused in an electric furnace lined with Fe_3O_4. The fused oxide is mixed with the above promoters, and the solidified oxide is crushed to desired particle size. The promoted iron oxide is then placed in the converter where on the passage of N_2 and H_2, the iron oxide is reduced to iron, (the promoters are not reduced). The reduced iron mixed with promoters serves as the catalyst.

Modified Bosch-Haber Process

(1) Water gas (from which hydrogen is obtained) is prepared by passing steam through heated coke(1,400°—1,000°C) (see Gaseous Fuels). The water gas is cooled and then purified by passing through lime and iron oxide coated wood shavings.

$$C + H_2O \rightleftarrows CO + H_2 + 71,240 \text{ B.T.U.}$$
$$C + H_2O \rightleftarrows CO + H_2 + 38,900 \text{ cals.}$$

(Positive sign indicates endothermic reaction)

(2) Producer gas is prepared by passing air through heated coke or coal bed (1000°-1400°C). The CO_2 formed initially passing through the hot bed of the fuel is reduced to carbon monoxide, the nitrogen of the air remains mixed with CO. The gas is cooled and purified. In both the cases sensible heat of the gases is utilised by raising steam in waste heat boiler.

$$C + \tfrac{1}{2}O_2 \rightleftarrows CO - 28,900 \text{ cals.}$$
$$\text{or} - 52,000 \text{ B.T.U.}$$
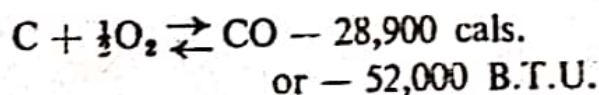
(3) Water gas and producer gas are mixed together in proper proportions so that after removal of carbon monoxide, the proportion of nitrogen and hydrogen by volume becomes one is to three (1 : 3).

(4) The cold mixed gas is mixed with excess of steam and after passing through the heat exchanger, the hot gas is passed through horizontal converters containing a catalyst consisting of iron oxide promoted with

Cr_2O_3 and CeO_2. Steam catalytically reacts with carbon monoxide to form carbon dioxide and hydrogen. This reaction is exothermic hence the temp. is maintained at an optimum temp. 450°C (by the heat of reaction).

$$CO + H_2 + H_2O \rightleftharpoons CO_2 + 2H_2 - 98,000 \text{ cals.}$$
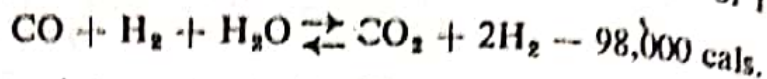
(5) The hot mixture of CO_2, H_2, N_2, and CO is cooled by passing through the heat exchanger mentioned in (4) and then in a tower. The cooled gas is stored.

(6) The CO_2 is removed by either of two methods :

(a) By compressing the mixed gas to 25 to 30 atmos. pressure and then absorbing CO_2 in water under pressure. In this case the unconverted carbon monoxide is removed by ammoniacal cuprous formate solution.

(b) By dissolving the CO_2 in an absorber tower where an aqueous solution of monoethanol amine ($NH_2C_2H_4OH$) is showered down to meet the ascending gas. The carbon monoxide and other hydrocarbon gases (present in small quantities in water and producer gases) are completely removed by repeating the operation of passing through iron oxide shift converter and absorption in monoethanol amine solution.

6(a). The gas compressed to 25 atmos. ascends up a pressure bubble-cap tower down which falls cold water under same pressure. The absorbed CO_2 is removed by releasing the pressure as the compressed water is used in a turbine. The gas contains 2 p.c. carbon monoxide and nitrogen and hydrogen in the proportion of 1 vol. to 3 vols.

6(b). The CO_2 is removed from the monoethanol amine solution by boiling and stripping with steam. The CO_2 is utilised.

(7) The gas from 6(a) after removal of CO_2, is compressed to 200 atmos. pressure, cooled, and treated in a pressure tower with ammoniacal solution of cuprous formate (HCOOCu). The resultant gas mixture is a mixture of H_2 and N_2 (3 vol. : 1 vol.). The cuprous formate solution is freed from carbon monoxide (releasing the pressure and heating) and recycled.

(8) The pure $N_2 + H_2$ mixture at 200 atmos. pr. is further compressed to 300 atmos. pr. mixed with recycling gas at the same pressure and passed through oil filters (glass capillaries remove the oil introduced (in the gas) from the compressor). The compressed gas mixture is then cooled by cold water followed by refrigeration by liquid ammonia. The recycling gas in the mixed gas contained some ammonia. This ammonia is liquefied by pressure and refrigeration, hence before allowing the gas mixture to enter into the converter, the liquid ammonia is separated.

(9) The gas mixture then passes into the converter. The converter is made of Ni, V, Cr steel (dimension of a typical converter is 7 ft. high, and 21 inches diam.). The cap is held by bolts of nickel steel. It is seamless and the wall is 3" thick. It is a 3 ton converter, the Sindri converter's

bigger, it is a ten ton converter. The converter is fitted with a double coil acting as heat interchanger through the inner tube of which cold gas mixture passes, and through the outer tube of which passes the hot outgoing gas mixture. At the base of the coil there is a resistance coil for electrical heating. In the converter there is the contact catalyst chamber (containing the granular catalyst). This consists of three concentric tubes.
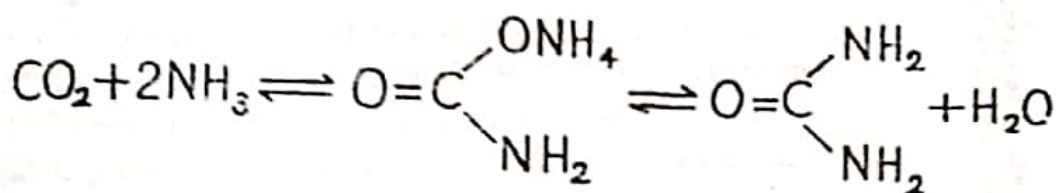
The compressed gas enters through the inner coil of the heat interchanger (which is situated in the middle surrounded by the first contact chamber). After passing through the interchanger the gas is heated by the resistance coil (electrically) and then goes up the first catalyst chamber, and then down through the 2nd, and lastly up through the last. It then enters the outer coil of the central heat exchanger, gives up the heat to the incoming gas, and then goes out of the converter from the top.

(10) The mixed outgoing gas containing 19 p.c. ammonia and rest N_2 and H_2 (1 vol. : 3 vol.), going out of the converter is cooled by cold water in a condenser. Major portion of ammonia liquefies. The liquid ammonia is separated, and the unconverted gas mixture containing some unliquefied ammonia is compressed to 300 atm. pr. and then mixed with fresh compressed gas mixture and recycled as described in (8) above. A part of the recycled gas is rejected from time to time to prevent the accumulation of argon and methane. The temp. in the contact chamber is 550°C.
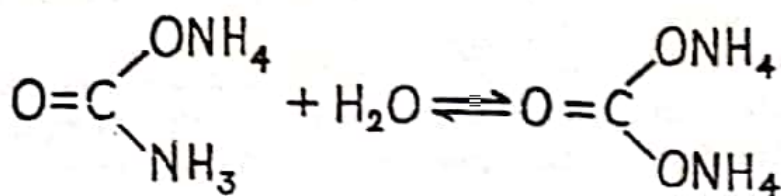
Manufacture of Urea (by synthetic process)

Theory : Urea is synthetically made by the action of ammonia and carbon dioxide under high pressure and a temp. of 200°C to 210°C. It is an exothermic reaction, the heat of reaction is 7900 cals., critical temperature of ammonia is 132.5°C and critical pr. 112.3 atmos., critical temp. of CO_2 is 31.1°C and critical pr. is 72.85 atmos. At ordinary pressure CO_2 and NH_3 react very slowly in absence of water, if water is present $(NH_4)_2CO_3$ instead of ammonium carbamate is formed. But under high pressure ammonium carbamate is formed. The ammonium carbamate liquefies at the optimum temperature maintained. As the optimum temperature is higher than the critical temperatures of both constituent gases, the gases do not liquefy, but they remain in equilibrium with the liquid ammonium carbamate. The liquid phase in equilibrium with the gaseous phase is ultimately made up of aqueous solution of ammonium carbamate and urea. The ammonium carbamate is decomposed into urea and water, which remains in equilibrium with ammonium carbamate and therefore with CO_2 and NH_3. If the equilibrium is not kept shifted towards the right, the water may react with ammonium carbamate to form ammonium carbonate which diminishes the amount of urea in the equilibrium mixture. The reaction thus proceeds in the liquid phase at a high pressure and temperature. In order to keep the equilibrium shifted towards the right an excess of ammonia gas is used. The reactant gases (CO_2 : NH_3 :: 1 : 3 or 4 molecules) are passed into the reactor (silver lined special steel)

and a pressure of 378 atmos. is maintained. The temperature is partially maintained by the heat of reaction at 200°C to 210°C, and the rest is supplied by external heat.
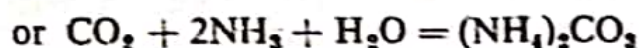
$$CO_2 + 2NH_3 \rightleftharpoons O=C\underset{NH_2}{\overset{ONH_4}{\Big\langle}} \rightleftharpoons O=C\underset{NH_2}{\overset{NH_2}{\Big\langle}} + H_2O$$

Ammonium carbamate   Urea

$$O=C\underset{NH_3}{\overset{ONH_4}{\Big\langle}} + H_2O \rightleftharpoons O=C\underset{ONH_4}{\overset{ONH_4}{\Big\langle}}$$

Ammonium carbonate

or $CO_2 + 2NH_3 + H_2O = (NH_4)_2CO_3$

After several hours the equilibrium is attained with 80 p.c. conversion. Urea remains in aqueous solution. The resultant charge is passed into another vessel and steam is introduced at the bottom which takes up the unconverted ammonia and carbon dioxide. The $NH_3 + CO_2$ come out from the top and recycled.

The urea solution is concentrated to 97 p.c. in vacuum evaporator. The 97 p.c. solution is converted into globules by spraying from the top of a 70 ft. tower and heated by hot air.

In Sindri excess of NH_3 is not used. A 30 ft. vertical steel cylinder lined with stainless steel is used. Liquid ammonia 99 p.c. pure and gaseous CO_2 97 p.c. pure are introduced in the autoclave. Pressure is 180 kg/cm², temperature is 180°C. The conversion is low—37 p.c. urea is formed.
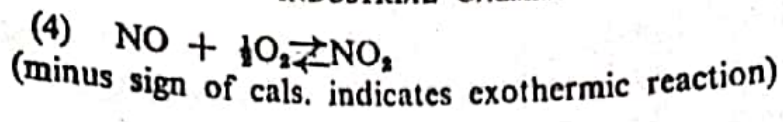
Ammonia and carbon dioxide gases separated from urea solution is onverted into ammonium carbonate. The latter with dilute nitric acid cprepared in the factory) is converted into ammonium nitrate (to be made (into double salt) and CO_2. The CO_2 is recycled. Urea solution is concentrated to 78 p.c. solution, and then to 97 p.c. solution and then to globules.

Manufacture of Nitric Acid

Ostwald's Process

Ammonia is catalytically oxidised (Fig. 15) by air to nitric oxide which reacting with oxygen of air gives NO_2. The latter gas with water gives nitric acid solution.

(1) $4NH_3 + 5O_2 \rightleftharpoons 4NO + 6H_2O - 216.000$ cals.
(2) $2NO + O_2 \rightleftharpoons 2NO_2 - 27,100$ cals.
(3) $3NO_2 + H_2O \rightleftharpoons 2HNO_3 + NO - 32,000$ cals.

(4) $NO + \tfrac{1}{2}O_2 \rightleftharpoons NO_2$

(minus sign of cals. indicates exothermic reaction)

Theory

(a) Excess of air should be taken, because oxygen will be necessary to convert NO into NO_2 in the (2) and (4) reactions.

(b) The time of contact of the gas mixture passing through the catalyst gauze should be very low (actually .0014 sec.), otherwise NO will be decomposed into N_2 and O_2 by the hot catalyst.

(c) The optimum temp. for the first reaction is 750°C at normal pressure, and 920°C at 100 psi.

In the 2nd, 3rd and 4th reactions cooling is necessary.

(d) Although increase of pressure shifts the equilibrium to a small extent in the first reaction towards the left, yet there is some advantage gained by pressure increase even in the first reaction. By increasing the pressure the space velocity (the volume of exit gas at N.T.P. which passes over one cubic foot of catalyst per sec.) increases, hence larger volume of gas is converted by the same volume of catalyst. Thus a smaller proportion of catalyst becomes necessary. For the other reactions increase of pressure shifts the equilibrium to the right, hence larger amount of nitric acid is formed at high pressure. The pressure applied is 100 psi.

(e) The mixture of air and ammonia should contain not more than 9.5 to 10.5 p.c. by volume of ammonia, when reaction takes place under pressure ; otherwise explosion will take place.

(f) Catalyst used is made up of 20 layers of 10 p.c. Rh and 90 p.c. Pt. 80 mesh gauze (wire diam. ·003"). The total wt. of the gauze is 105 ounces (this wt. is critical).

Fig. 15. Converter for Ostwald's Process of oxidation of Ammonia

Process : The catalyst gauze pad is fitted on a horizontal grid (of nickel chromium steel) of hexagonal shape (16" diam.). This is surmounted by a vertical dome fitted with an inlet pipe. Below the grid is fitted the exit cylinder with an outlet pipe. There is an electrical arrangement for starting the reaction after which the reaction continues at 920°C by the heat of the highly exothermic reaction.
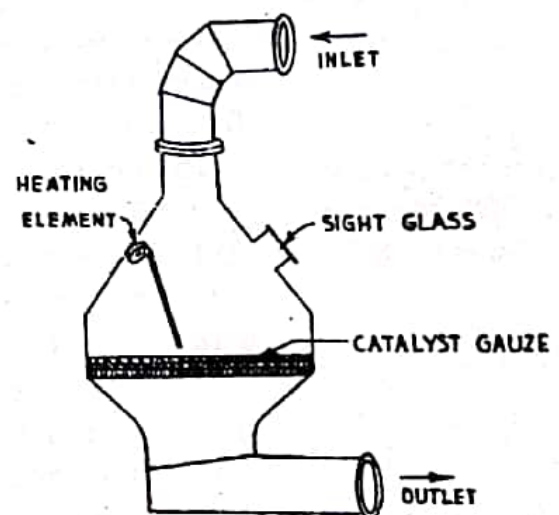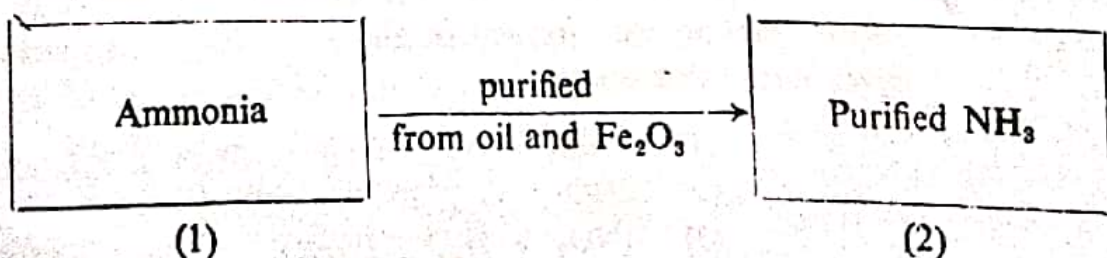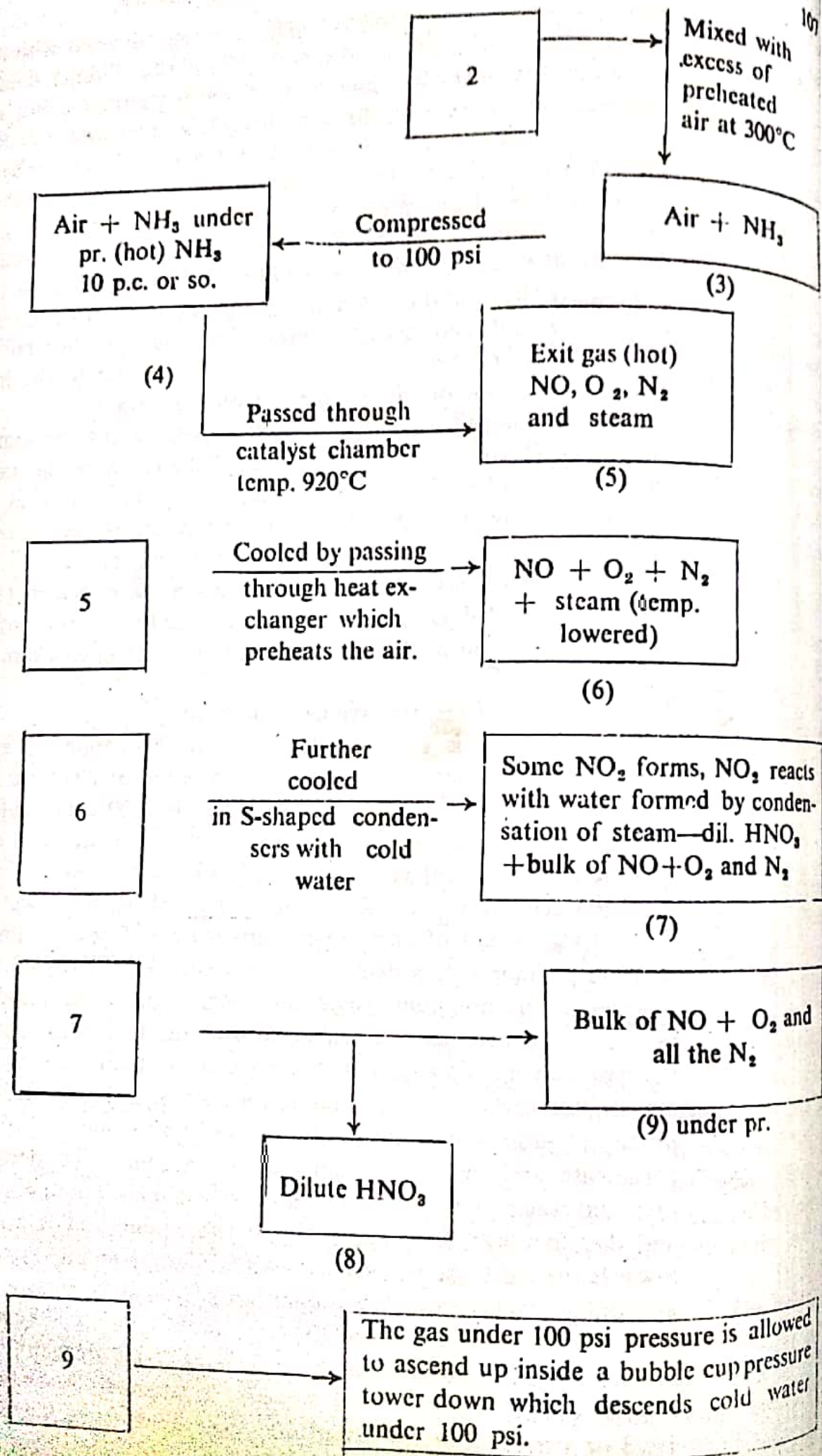
Ammonia	purified from oil and Fe_2O_3	Purified NH_3
(1)		(2)

| | 2 | → | Mixed with excess of preheated air at 300°C (10) |

| Air + NH₃ under pr. (hot) NH₃ 10 p.c. or so. | ← Compressed to 100 psi | Air + NH₃ (3) |

$$Air + NH_3 \text{ under pr. (hot) } NH_3 \; 10 \text{ p.c. or so.}$$

(4)

Passed through catalyst chamber temp. 920°C → Exit gas (hot) NO, O_2, N_2 and steam (5)

| 5 | Cooled by passing through heat exchanger which preheats the air. | → | NO + O_2 + N_2 + steam (temp. lowered) (6) |

| 6 | Further cooled in S-shaped condensers with cold water | → | Some NO_2 forms, NO_2 reacts with water formed by condensation of steam—dil. HNO_3 +bulk of NO+O_2 and N_2 (7) |

| 7 | | → | Bulk of NO + O_2 and all the N_2 (9) under pr. |

Dilute HNO_3 (8)

| 9 | → | The gas under 100 psi pressure is allowed to ascend up inside a bubble cup pressure tower down which descends cold water under 100 psi. |

Dilute HNO_3 (8) under pr. is fed through the side of the tower. The bubble cap tower is a 35 ft. high and 5.25 ft. diam. 40 plates tower. Sufficient space is kept between adjacent plates so that the NO of reaction (4) may get sufficient time for oxidation. To absorb the heat of oxidation and heat of formation of HNO_3 each plate is cooled by cooling coils with circulating cold water. Fourteen p.c. of the total compressed air necessary for oxidation in the tower is supplied from outside at the base.

Conversion is 91 to 94 p.c.

HNO_3 obtained is 61 to 62 p.c.

Superphosphate

Superphosphate is the soluble phosphate of calcium. Of the three clacium phosphates, viz. tri, di and mono, the first two are insoluble and only monocalcium phosphate is soluble.

Tricalcium phosphate, $Ca_3(PO_4)_2$
Dicalcium phosphate, $Ca_2H_2(PO_4)_2$
Monocalcium phosphate, $CaH_4(PO_4)_2$

difference between superphosphate and rock phosphate

Phosphatic manure can be taken up by the plants in the soluble form. When tricalcium phosphate in the form of bone-meal or rock phosphate powder (main source of P_2O_5) is applied to the soil, the $Ca_3(PO_4)_2$ is slowly transformed into the $CaH_4(PO_4)_2$ in the soil (through the agency of acids in the soil) and then the soluble phosphate is taken up by the plants. To avoid this slow process of transformation, rock phosphate is transformed quickly into the soluble phosphate which is then applied to the soil. This artificially prepared monocalcium phosphate is known as superphosphate.

Commercial superphosphate is a mixture of monocalcium phosphate and crystalline calcium sulphate—$CaSO_4$, $2H_2O$. It contains 16 p.c. P_2O_5.

Manufacture of Superphosphate
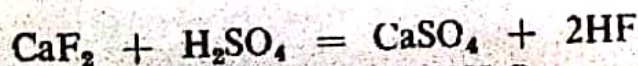
(a) Raw material is rock phosphate :

(i) Phosphorite,   (ii) Chlorapatite and   (iii) Fluorapatite. The formulae are (i) $Ca_3(PO_4)_2$; (ii) $3Ca_3(PO_4)_2$, $CaCl_2$; (iii) $3Ca_3(PO_4)_2$, CaF_2.

Reaction : Powder rock phosphate is treated with requisite amount of 62 to 70 p.c. sulphuric acid at the ordinary temperature.

$$Ca_3(PO_4)_2 + 2H_2SO_4 = CaH_4(PO_4)_2 + 2CaSO_4$$
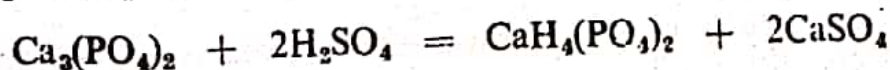
When apatites are used the following reactions also take place.

$$CaF_2 + H_2SO_4 = CaSO_4 + 2HF$$
$$SiO_2 + 4HF = SiF_4 + 2H_2O$$
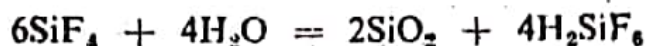$$SiF_4 + 2HF = H_2SiF_6$$

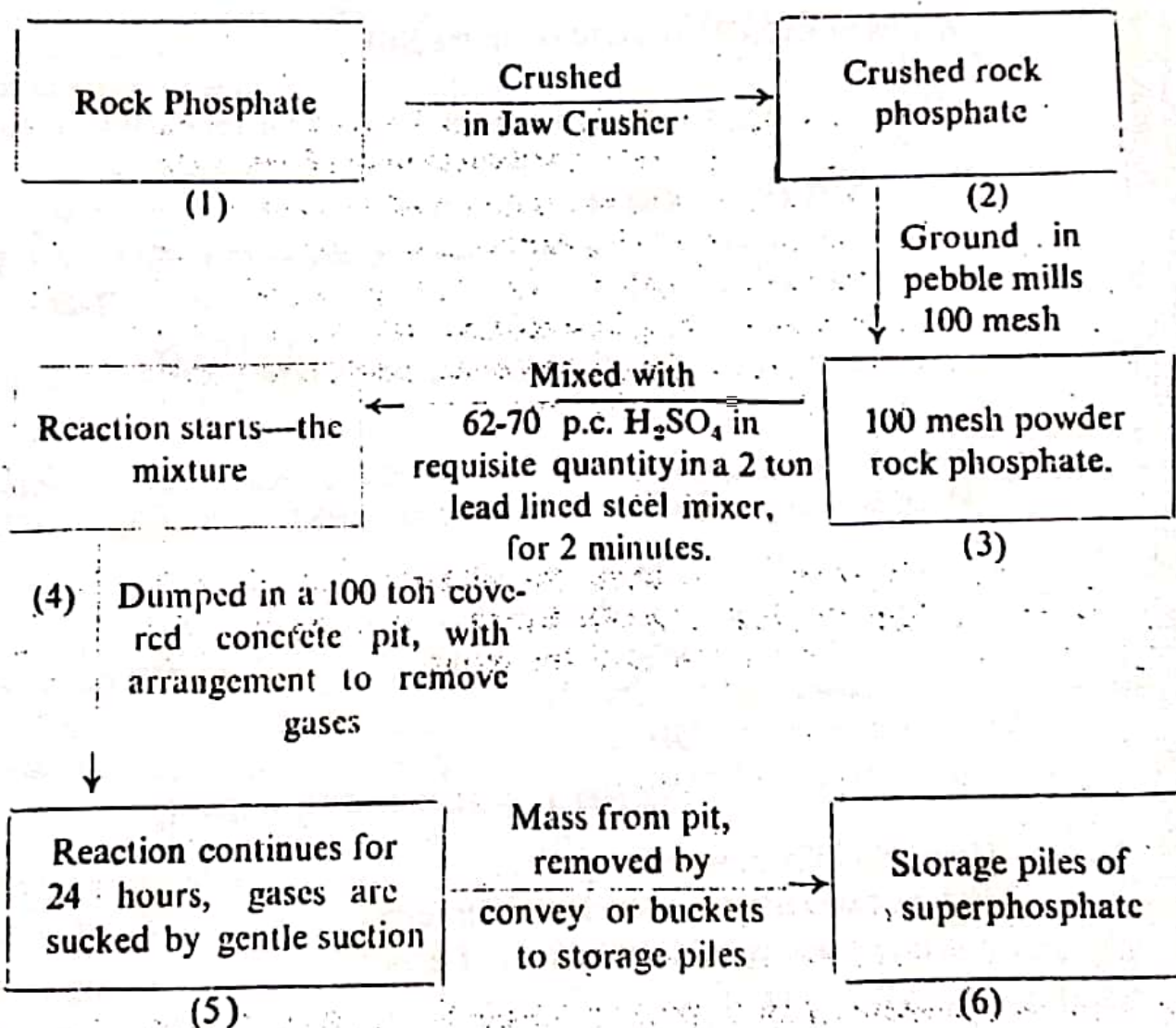Amongst the rock phosphates fluorapatite is the most abundant. Hence

a valuable by product i.e. HF is obtained in large quantities. In Bengal the superphosphate factory at Rishra is arranging to manufacture cryolite with this HF.

$$CaCl_2 + H_2SO_4 = CaSO_4 + 2HCl$$
$$CaCO_3 + H_2SO_4 = CO_2 + CaSO_4$$
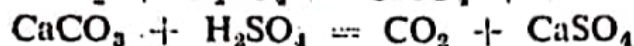
SiF_4 when passed through water gives H_2SiF_6.

$$6SiF_4 + 4H_2O = 2SiO_2 + 4H_2SiF_6$$

H_2SiF_6 is converted into Na_2SiF_6 (insecticide) and $MgSiF_6$ (Portland cement preservative).

Rock Phosphate (1)	→ Crushed in Jaw Crusher →	Crushed rock phosphate (2)

Ground in pebble mills 100 mesh

Reaction starts—the mixture (4)	← Mixed with 62-70 p.c. H_2SO_4 in requisite quantity in a 2 ton lead lined steel mixer, for 2 minutes.	100 mesh powder rock phosphate. (3)

(4) Dumped in a 100 ton cove-red concrete pit, with arrangement to remove gases

Reaction continues for 24 hours, gases are sucked by gentle suction (5)	Mass from pit, removed by convey or buckets to storage piles →	Storage piles of superphosphate (6)

6

is cured for 8 to 10 weeks. Further reaction takes place. The residual H_2SO_4 is then adjusted by adding lime, and mixing. The superphosphate is then bagged.
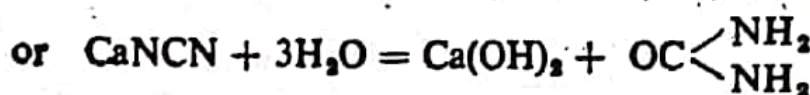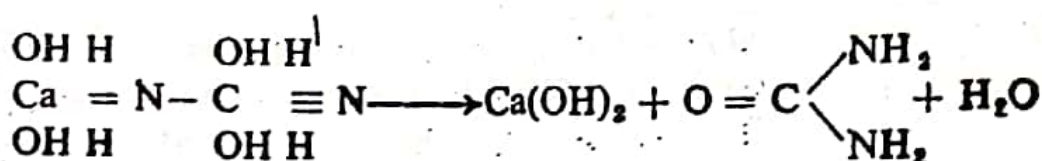
Tripple phosphate : In order to save transport cost a superphosphate consisting of almost pure $CaH_4(PO_4)_2$ is now manufactured. This superphosphate is known as tripple phosphate. The tripple phosphate contains 45 to 50 p.c. P_2O_5 (water soluble). At first syrupy phosphoric acid (62 p.c.) is manufactured by the action of H_2SO_4 on $Ca_3(PO_4)_2$.

Ground rock phosphate is then mixed with requisite quantity of 62 p.c. H_3PO_4 in a 2 ton mixer (previously described) and agitated for several hours, (because the rate of action is much slower) at ordinary temperature. The charge from the mixer containing 20 p.c. water is transferred to a storage building where it is allowed to age for 30 to 40 days, when the reaction becomes complete. During aging some amount of water evaporates, after the aging period the tripple phosphate is dried by hot flue gases (moisture content of a few p.c. remains). The dried tripple phosphate is screened by vibrating screens, and then is made ready for sale.
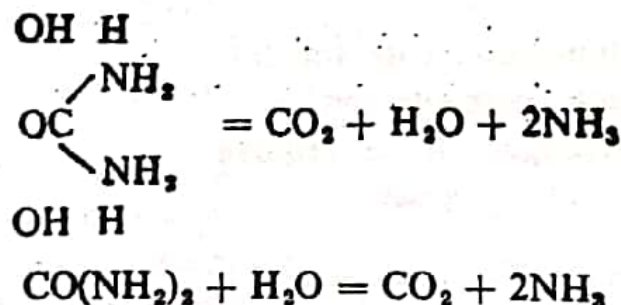
$$Ca_3(PO_4)_2 + 4H_3PO_4 = 3CaH_4(PO_4)_2$$

Action of CaNCN as Fertiliser in the Soil

Finely ground nitrolim when applied to the soil, is hydrolysed to $Ca(OH)_2$ and urea ; the hydrolytic action is catalysed by soil catalysts (microorganisms).

$$\begin{array}{l} OH\ H \qquad OH\ H \\ Ca = N-C \equiv N \longrightarrow Ca(OH)_2 + O = C\big\langle\begin{smallmatrix}NH_2\\NH_2\end{smallmatrix} + H_2O \\ OH\ H \qquad OH\ H \end{array}$$

or $CaNCN + 3H_2O = Ca(OH)_2 + OC\big\langle\begin{smallmatrix}NH_2\\NH_2\end{smallmatrix}$

The urea is then hydrolysed with the help of urease (enzyme) into ammonia which is then oxidised to nitric acid (converted to nitrates).

$$\begin{array}{l} OH\ H \\ OC\big\langle\begin{smallmatrix}NH_2\\NH_2\end{smallmatrix} = CO_2 + H_2O + 2NH_3 \\ OH\ H \end{array}$$

$$CO(NH_2)_2 + H_2O = CO_2 + 2NH_3$$

Urea contains more nitrogen than in any other nitrogenous fertiliser, It is 44 p.c. It is marketed as such or as urammon containing 42 p.c. urea nitrogen. It is also used as UAZ a mixture of urea and ammonia.

Manufacture of Ammonium Sulphate

Ammonium sulphate is manufactured either by the action of 1.7 p.c. sp. gr. H_2SO_4 on gaseous ammonia or by passing simultaneously CO_2 and NH_3 through water containing suspended powder gypsum. In the former case lead lined cast iron vat is used, and the reaction takes place at 60°C.

$$2NH_4OH + H_2SO_4 = (NH_4)_2SO_4 + 2H_2O$$
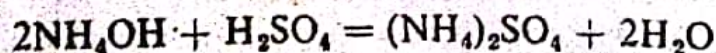
The ammonia gas is passed through the acid, the acid concentration is continually maintained by adding sulphuric acid continuously. The crystals

of ammonium sulphate are withdrawn from the bottom continuously by an air injector.

In the latter case, the reaction takes place at the ordinary temperature.

$$CO_2 + 2NH_3 + H_2O = (NH_4)_2CO_3$$
$$(NH_4)_2CO_3 + CaSO_4 = (NH_4)_2SO_4 + CaCO_3$$
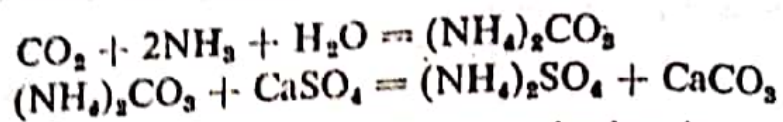
The $CaCO_3$ is precipitated gradually by agitation in a tank. CO_2 and NH_3 are passed until all the gypsum is converted into calcium carbonate. The $CaCO_3$ is settled and the supernatant ammonium sulphate solution is filtered. The settled $CaCO_3$ is filtered pressed to remove the solution. The $(NH_4)_2SO_4$ solution is then crystallised.

Action of $(NH_4)_2SO_4$ as a Fertiliser

Ammonium sulphate reacts with lime of the soil to form ammonium hydroxide. The latter is oxidised by air with the help of nitrosifying bacteria into nitrous acid which is converted into nitrities. The nitrous acid and the nitrites are oxidised by air with the help of nitrifying bacteria, to nitric acid and nitrates. The nitric acid is converted into $Ca(NO_3)_2$ and KNO_3 by the action of bases present in the soil. Most of the plants take up nitrogen in the form of soluble nitrates. Some plants of course can take up nitrogen in the form of ammonia and its salts (in solution).

EXERCISE

1. Explain the term fixation of nitrogen and nitrogen cycle. Name the different artificial nitrogenous fertilisers with formulae. Explain how they are transformed into the form assimilable by the plants.

2. How are the following manufactured ?
   (a) Synthetic ammonia.
   (b) Nitric acid by Ostwald's process
   (c) Superphosphate.
   (d) Tripple phosphate.
   (e) Double salt.
   (f) Nitrolim. (g) Urea from ammonia.

3. Discuss the theories underlying the large scale production of the following :
   (a) Ammonia by Bosch-Haber process.
   (b) Nitric acid by Ostwald's process.
   (c) Nitrolim.
   (d) Urea from ammonia.

4. Write notes on :
   (a) Composition of nitrolim.
   (b) Mixed fertilisers.
   (c) Comparison of rock phosphate and superphosphate as fertiliser.
   (d) Fertilisers