

Chapter 15

COMMON CHEMICAL INDUSTRIES IN PAKISTAN

INTRODUCTION

At the time of independence in 1947, Pakistan had no industrial base. For the past 55 years, the Pakistan has undergone a structural change from a agrarian economy to a semi-chemical industrial state. Pakistan is now making many household products like, soap, detergents, glasses, plastics, fibers, paint, varnish etc. Heavy industry like iron, cement, fertilizer, paper, and textile are also on the road to development.

The natural resources are being exhausted with growing population and increase in the standard of living all over the world. To meet this situation, the scientists and technologists are busy in the development of the substitute materials from cheaper and reversible sources, e.g., the natural fibers like cotton, silk, wool cannot meet the clothing requirements of the world; therefore, scientists have developed the artificial fibers.

Similarly, crop yield has been increased by the development of fertilizers, pesticides and herbicides to meet the world food requirements. All these materials require their chemical preparation on industrial scales. In fact the magnitude of chemical industry of country is a measure of its economic development and progress. Different chemical industries such as fertilizer, cement and paper are developing very fast in Pakistan.

FERTILIZERS

Early History:

Agriculture is the oldest industry known to man. The use of manure as fertilizer dates back to the beginning of agriculture, since 5000 B.C. The Chinese used animal **manure as fertilizer**. *“A manure is an organic material used to fertilize land and it usually consists of faeces and urine of domestic livestock.”*

What are Fertilizers?

“Fertilizers are the substances added to the soil to make up the deficiency of essential elements like nitrogen, phosphorus and potassium (NPK) required for the proper growth of plants”. Fertilizers increase the natural fertility of the soil and replenish the chemical elements taken up from soil by the previous crops.

ELEMENTS ESSENTIAL FOR PLANT GROWTH

Elements essential for the plant growth are divided into two classes; macro-nutrients and Micro-nutrients.

Macro-nutrient:

“The nutrients which are required in large amount for the growth of plants are called macronutrients.”

Nitrogen, phosphorus and potassium are primary plant nutrient and required in greater amount for the growth of plants. These are generally required in quantities ranging from 5 kg to 200 kg per acre.

Micro-nutrients:

“The nutrients which are required in a very small amount for the growth of plant, are called micro-nutrients.” These include boron, copper, iron, manganese, zinc, molybdenum and chlorine. Only minute amount of these elements are needed for healthy plant growth and it may be dangerous to add too much quantity because they are poisonous in larger quantities. These are generally required in quantities ranging from 6 grams to 200 grams per acre.

REQUIREMENTS OF A GOOD FERTILIZER

A good fertilizer must have the following qualities in it.

- (i) The nutrient elements present in it, must be readily available to the plant.
- (ii) It must be fairly soluble in water so that it thoroughly mixes with the soil.
- (iii) It should not be injurious to plant.
- (iv) It should be cheap.
- (v) It must be stable so that it is available for longer time to the growing plant.
- (vi) It should not alter the pH of the soil.
- (vii) By rain or water, it should be converted into a form, which the plant can assimilate easily.
- (viii) It should provide all the nutrients necessary for the growth of a plant.

CLASSIFICATION OF FERTILIZERS

Fertilizers are classified according to the nature of the elements like nitrogen, phosphorus and potassium which they provide to the soil. This classification gives the following types of fertilizers.

- (i) Nitrogenous fertilizers
- (ii) Phosphatic fertilizers
- (iii) potassium fertilizers

(i) Nitrogenous Fertilizers:

These fertilizers supply nitrogen to the plants or soil. Nitrogen is required during the early stage of plant growth for the developments of stem and leaves. It is the main constituent of protein, imparts green colour to the leaves and enhance the yield and quality of the plants. Some of the examples of nitrogen fertilizers are:- ammonium sulphate, calcium ammonium nitrate, basic calcium nitrate, calcium cyanamide, ammonia, ammonium nitrate, ammonium phosphate, ammonium chloride and urea.

(1) Ammonia (NH₃) as Fertilizer:

Ammonia is prepared by the direct combination of H₂ and N₂ at 200 atmospheric pressure, 450°C in the presence of Fe or Al₂O₃ as catalyst.



Ammonia is used in liquid state while other nitrogen fertilizers are solid. Ammonia contains 82% nitrogen in it and it is injected, 6 inches under the surface of the soil, to avoid it from seeping out.

All nitrogen fertilizers make the soil acidic, except potassium nitrate KNO₃, sodium nitrate NaNO₃ and Calcium nitrate Ca(NO₃)₂. Acidity of the soil can be controlled by adding lime (CaO) at the regular intervals of time.

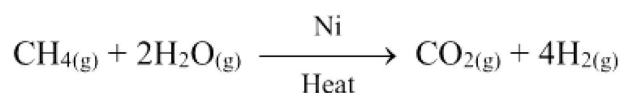
(2) Urea NH₂CONH₂ (Aminomethanamide):

*“Urea is a high quality nitrogenous fertilizer. It contain about 46% of **nitrogen** and its the most concentrated solid nitrogen fertilizer.”* This is most widely used nitrogen fertilizer in Pakistan.

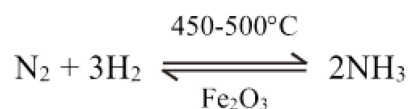
Manufacturing Process:

Following steps are involved in the manufacture of urea:

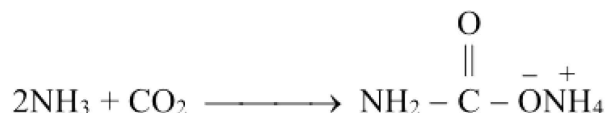
- (i) Preparation of hydrogen by passing a mixture of natural gas and steam over heated nickel.



- (ii) Synthesis of ammonia by combining hydrogen with nitrogen of air.



- (iii) Synthesis of ammonium carbamate by reacting liquid ammonia with carbon dioxide.



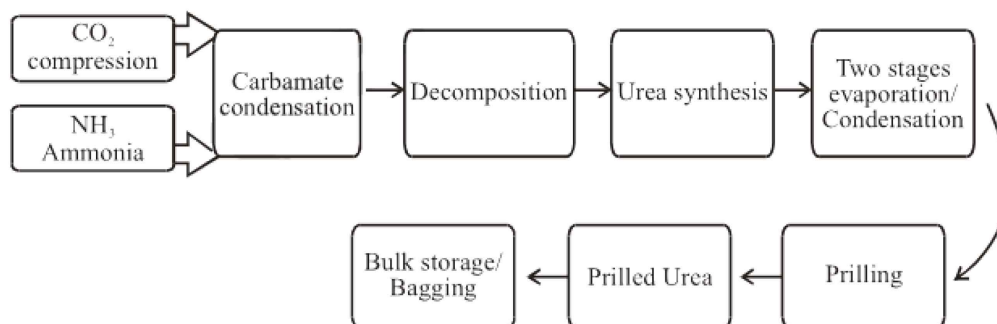
- (iv) **Ammonia Carbon Dioxide Ammonia Carbamate:** Dehydration of ammonium carbamate to produce urea solution.



Ammonium Carbamate

Urea

- (v) **Concentration of Urea Solution:** The urea solution is concentrated in an evaporation section where water is evaporated by heating with steam under vacuum in two evaporation stages where by 99.7% urea melt is obtained. It is pumped to prilling tower.
- (vi) **Prilling:** The molten urea is sprayed at the prilling tower by means of prilling bucket where it is cooled by the air rising upward. Molten droplets solidify into the form of prills. Urea prills thus produced are either sent to the bagging section or to the bulk storage.



Flow sheet diagram for manufacture of urea

(3) Ammonium Nitrate:

It is manufactured by the neutralization reaction between ammonia and nitric acid as given below.



After neutralization, the water is evaporated. The solid ammonium nitrate is melted and then sprayed down from a tall tower. The falling droplets are dried by an upward current of air. The fertilizer solidifies as tiny, hard pellets called prills. Prills of fertilizers are free of dust, easy to handle and easy to spread on the field. Ammonium nitrate contains 33–33.5% nitrogen.

It is a useful fertilizer for many crops except paddy rice because the microbial bacteria in flooded fields decomposes it to nitrogen gas. It is also used in combination with limestone. It is hygroscopic in nature.

(ii) Phosphatic Fertilizers:

These fertilizers provide phosphorus to the plants or soil. Phosphorus is required to **stimulate early growth of plants** and to accelerate the **seed and fruit formation** during the later stage of growth. It also increases the **resistance** of plants against diseases.

The various phosphatic fertilizers have different composition, due to which they have different solubility. The two most important water soluble fertilizers are super phosphate (calcium super phosphate) $\text{Ca}(\text{H}_2\text{PO}_4)_2$ and triple phosphate (diammonium-phosphate) $(\text{NH}_4)_2\text{HPO}_4$.

Diammonium Phosphate $(\text{NH}_4)_2\text{HPO}_4$:

This compound is prepared by continuous process. In this process, anhydrous ammonia gas is reacted with phosphoric acid at 60–70°C and pH 5.8 to 6.



It is an exothermic reaction. The heat of reaction vaporizes water from the liquor and the crystals of diammonium phosphate are taken out, centrifuged, washed and dried. It contains 16% nitrogen and 48% P_2O_5 . This product contains about 75% plant nutrients and is deemed suitable for use either alone or in mixture with other fertilizers.

(iii) Potassium Fertilizer:

These fertilizers provide potassium to the plant or soil.

- (1) Potassium is required for the formation of starch, sugar and the fibrous material of the plant.
- (2) They increase resistance to diseases and make the plants strong by helping in healthy root development.
- (3) They also help in ripening of seeds, fruits and cereals.
- (4) Potassium fertilizers are especially useful for tobacco, coffee, potato and corn.

(1) Potassium nitrate (KNO_3) :

On industrial scale, it is prepared by the double decomposition reaction between potassium chloride and sodium nitrate.



A concentrated hot solution of sodium nitrate is prepared and solid potassium chloride is added into it. On heating, the potassium chloride crystals change into sodium chloride crystals, **and the hot potassium nitrate is run through the sodium chloride crystals at the bottom of the kettle.** A little water is added to prevent further deposition of sodium chloride as the solution is cooled, which result into a good yield of pale yellow solid potassium nitrate. It contains 13% nitrogen and 44% potash.

FERTILIZER INDUSTRY IN PAKISTAN

Pakistan is an agricultural country. Due to repeated cultivation of crops and to increase the potential of land, fertilizers are gaining importance. Urea is the most important fertilizer used in Pakistan.

Government of Pakistan is trying to increase the production of fertilizers and reduce the gap between demand and supply. At present, there are 14 fertilizers plants working in private as well as public sector. The total production of urea fertilizer in Pakistan is 56,30,100 metric tonnes per annum.

CEMENT

Cement is very important building material which is used for the construction of houses, roads, dams, and bridges.

Origin of name “Portland Cement”:

In 1824 an English mason Josheph Aspdin introduced cement. He prepared cement by strong heating of the mixture of clay and limestone. When it was mixed with water it changes to a hard mass like stone. The cement had resemblance with the famous building stone obtained from the island of “Portland” near England. Hence the name “Portland Cement” was given to cement.

Definition:

“Cement is the material obtained by burning mixture of calcarious (lime bearing) and argillaceous (clay) material at sufficiently high temperature to produce clinkers. These clinkers are mixed and ground with gypsum to form a fine powder called cement or Portland cement”.

Average Composition of Good Cement:

Cement is a mixture of so many compounds and each compound has its own properties. The final properties of cement depends upon the variation in composition, heating rate, maximum heating temperature and fineness of the powder.

Average composition of a good cement is given below:

Table – Average composition of good cement

No.	Compound	%age
(1)	Lime (CaO)	62
(2)	Silica (SiO ₂)	22
(3)	Alumina (Al ₂ O ₃)	7.5
(4)	Magnesia (MgO)	2.5
(5)	Iron oxide (Fe ₂ O ₃)	2.5
(6)	Sulphur tri-oxide (SO ₃)	1.5
(7)	Sodium oxide (Na ₂ O)	1.0
(8)	Potassium oxide (K ₂ O)	1.0

The essential constituents are lime (obtained from limestone) silica and alumina (present in clay)

Raw Materials:

The important raw materials used for the manufacture of cement are:

- (i) **Calcarious material** (limestone, marble, chalks, marine shell) as source of CaO.
- (ii) **Argillaceous material** (clay, shale, slate, blast furnace slag). They provide acidic components such as aluminates and silicates.
- (iii) **Gypsum.**

MANUFACTURING PROCESS

The manufacturing process of cement involves either a dry process or a wet process. The choice of dry or wet process, depends on the followings factors.

- (i) Physical condition of the raw materials.
- (ii) Local climatic conditions of the factory.
- (iii) The price of the fuel.

In Pakistan most of the factories use wet process for the production of cement. Dry process needs excessive fine grinding and it is more suited for the hard material. Wet process, on the other hand, is free from dust, grinding is easier and the composition of the cement can easily be controlled.

Wet Process:

In this process grinding is done in the presence of water. There are five stages in the manufacture of Portland cement.

- (i) Crushing and grinding of the raw material.
- (ii) Mixing the material in correct proportion.

- (iii) Heating the prepared mixture in a rotary kiln.
- (iv) Grinding the heated product known as clinker.
- (v) Mixing and grinding of cement clinker with gypsum.

(i) Crushing and Grinding of Raw Material:

Soft raw materials are first crushed into a suitable size, often in two stages, and then ground in the presence of water, usually in rotating cylindrical ball or tube mills containing a charge of steel balls.

(ii) Mixing of the Raw Material:

The powdered limestone is then mixed with the clay paste in proper proportion (**limestone 75%, clay 25%**); the mixture is finely ground and made homogeneous by means of compressed air mixing arrangement. The resulting material is known as **slurry or filler cake**. The slurry, which contains 35 to 45% water, is sometimes filtered to reduce the water contents to **20% to 30%** and the filler cakes are stored in storage bins, this reduces the fuel consumption for heating stage.

(iii) Heating the Slurry in a Rotary Kiln:

Raw meal or slurry prepared as above is introduced into the rotary kiln with the help of a conveyer. The rotary kiln consists of a large cylinder, 8 to 15 feet in diameter and 300-500 feet in length. It is made of steel and is lined inside with firebricks. The kiln rotates on its axis at the rate of rotation is 1-2 revolution per minute and horizontally it is inclined a few degree. As the kiln rotates, the charge slowly moves downward due to the rotary motion.

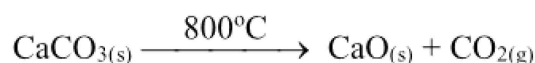
Now the charge is heated by burning coal, oil or natural gas. In the rotary kiln the charge passes through the different zones of temperature where different reaction take place. The charge takes 2-3 hours to complete the journey in the kiln.

(a) Drying or Preheating Zone:

In this zone, the temperature is kept at 500°C, where by the moisture is removed and thy clay is broken into Al_2O_3 , SiO_2 , and Fe_2O_3 .

(b) Decomposition Zone (Moderate Temperature Zone):

Here the temperature goes upto 800°C. In this zone the limestone (CaCO_3) decomposes into lime (CaO) and CO_2 .

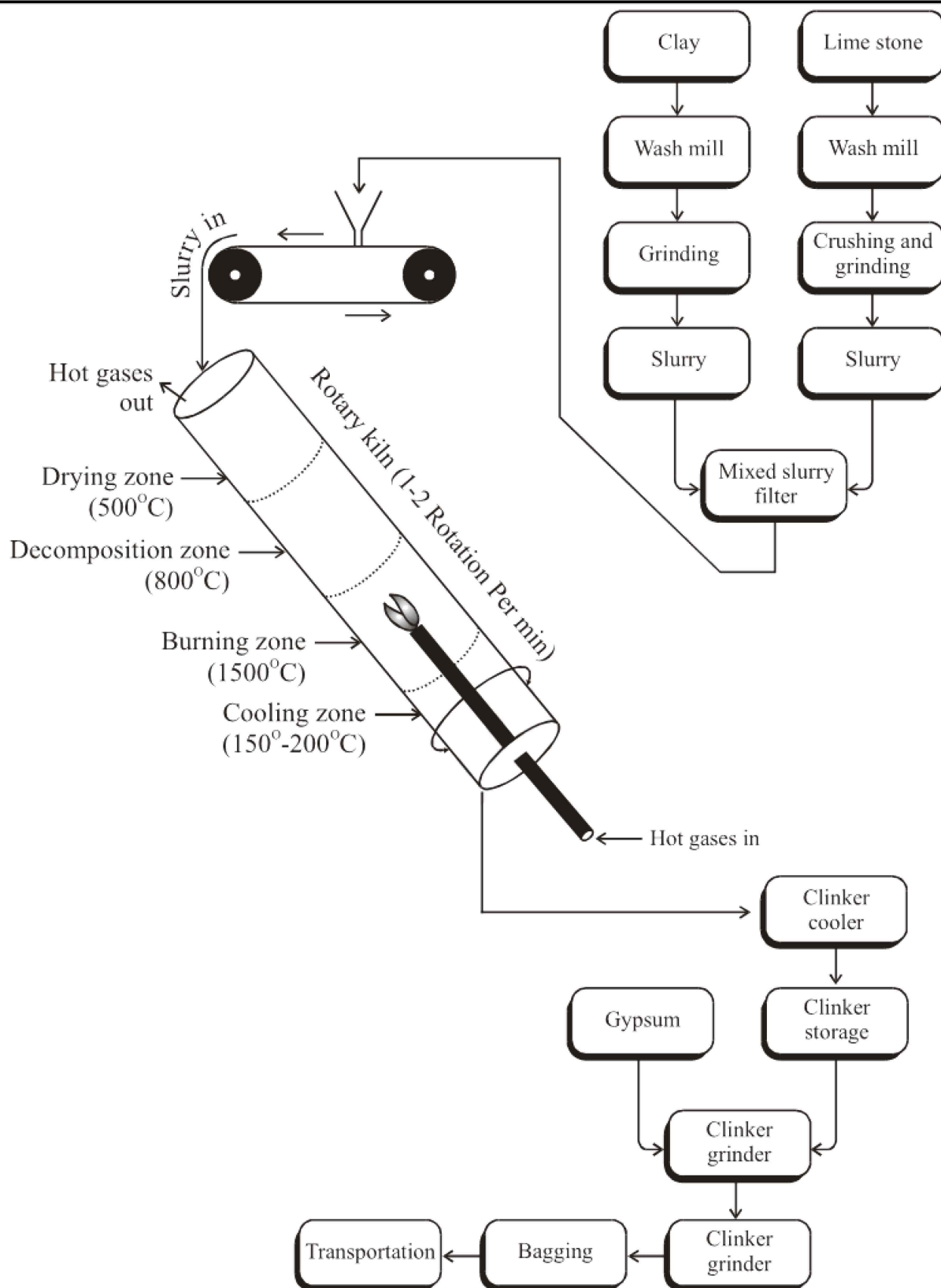


(c) Burning Zone (Maximum Temperature Zone):

In this zone, the temperature goes up to 1500°C and the oxides, e.g. CaO , SiO_2 , Al_2O_3 and Fe_2O_3 combine together and form calcium silicate, calcium aluminate and calcium ferrite.

(d) Cooling Zone:

This is the last stage in the kiln where the charge is cooled up to 150-200°C.



(vi) Clinker Formation:

The resulting product obtained from the kiln is known as cement clinker. This has the appearance of greenish black or grey coloured balls varying in size from small nuts to peas.

(v) Grinding the Clinker:

The cement clinkers are then air-cooled. The required amount of gypsum (2-5%) is first ground to a fine powder and then mixed with clinkers.

At this stage, finished cement is pumped pneumatically to storage silos from where it is drawn for packing in paper bags or for dispatch in bulk containers.

SETTING OF CEMENT

"Cement combines with water and the resulting mass becomes hard and very resistant to pressure. This process is known as setting of cement."

Setting process is based upon hydration followed by the crystallization. Following changes take place when cement is mixed with water.

(a) Reactions taking place in first 24 hours:

A short time after the cement is mixed with water, tri-calcium aluminate absorbs water (hydration) and forms a colloidal gel of the composition, $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$.

This gel starts crystallizing slowly, reacts with gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) to form the crystals of calcium sulpho-aluminate ($3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$).

(b) Reaction taken place between 1 to 7 days:

Tri-Calcium silicate ($3\text{CaO} \cdot \text{SiO}_2$) and tri-calcium aluminate ($3\text{CaO} \cdot \text{Al}_2\text{O}_3$) get hydrolyzed to produce calcium hydroxide and aluminium hydroxide. The calcium hydroxide, thus formed, starts changing into needle-shaped crystals, which get studded in the colloidal gel and impart strength to it. Aluminium hydroxide, on the other, fills the interstices resulting in hardening the mass. The gel formed starts losing water partly by evaporation and sets to a hard mass.

CEMENT INDUSTRY IN PAKISTAN

At the time of independence in 1947, there were four cement plants in West Pakistan, producing about 330,000 tons of cement every year. However, in 1954 the production of cement went up to 660,000 tons. In 1956 two more cement factories were set up at Daud Khel and Hyderabad, but even then the production of cement was not enough to meet the increasing demand of the construction industry in the country.

For a developing country like Pakistan there is always an increasing need of cement for development projects. Efforts were thus made to build more factories. At

present there are about 22 cement factories in privates as well as in public sectors, which are manufacturing cement both by dry and wet processes. The total production of these 22 cement plants is 9,578,802 metric tons/annum.

PAPER INDUSTRY

Early History:

The word “Paper” is derived from the reed plant “Papyrus”. This reed plant grew abundantly along the Marshy Delta of River Nile in Egypt around 3000 B.C. The Chinese invented good processes for paper manufactured from bamboo at about 105 A.D. Ts'ai Lun of China, who was official attached to the imperial court of China, invented paper in 105 A.D. He prepared a sheet of paper, using the bark of mulberry tree that was treated with lime and mixed with bamboo and other fibers to get desired properties.

Definition:

“The sheet material made up to a network of natural cellulose fibers which has been deposited from an aqueous suspension is called paper.”

The product or paper has a network interlocking of fibers of cellulose. Some additives are also added to improve the qualities of paper.

Raw Materials:

The main raw materials used in the production of pulp and paper in Pakistan is of two types, that is non-woody and woody raw materials.

Non-woody Raw Materials				Woody Raw Materials	
(i)	Wheat straw	(vi)	Bamboo	(i)	Poplar (hard wood)
(ii)	Corn straw	(vii)	Cotton stalk	(ii)	Eucalyptus (Hard wood)
(iii)	Rice straw	(viii)	Cotton linter	(iii)	Dourglas fir (soft wood)
(iv)	Bagasse	(ix)	Kahi		
(v)	Rag	(x)	Grasses		

Pulping Method:

The following are the three principal methods of chemical pulping and are used for the production of paper making pulps.

- (1) Kraft process (Alkaline)
- (2) Sulphite Process (Acidic)
- (3) Neutral Sulphite Semi Chemical process (NSSC)

The neutral sulphite semi chemical process has come to occupy the dominant position because of the advantages in chemical recovery and pulp strength. In this chapter we will discuss only the neutral sulphite semi-chemical process which is mostly used in pulp and paper industry in Pakistan.

NEUTRAL SULPHITE SEMI-CHEMICAL PROCESS (NSSC)

This process utilizes sodium sulphite cooking liquor which is buffered with sodium carbonate or NaOH to neutralize the organic acid liberated from the raw materials.

The non-woody raw materials which are used in this process; are wheat straw, rice straw, bagasse, cotton linters and rags. Wheat straw may be used alone or combined with other materials in different proportion. The essential steps in the process are as follows.

- | | |
|----------------------------------|--------------------|
| (1) Cutting of the raw materials | (2) Dry cleaning |
| (3) Wet Cleaning | (4) Screening |
| (5) Digestion | (6) Blow tank |
| (7) Pulp washing | (8) Bleaching |
| (9) Machine chest | (10) Paper Machine |
| (11) Drying | |

(1) Cutting of Raw Material:

The non-woody raw materials come in the precut state and are processed as such. But in the case of wood based raw materials, big logs are debarked and cut into small chips before further processing.

(2) Dry Cleaning:

Wheat straw is collected from the stock and is then sent for dry cleaning. For this purpose air is blown into the raw material, which removes unwanted particles.

(3) Wet Cleaning:

Dry wheat straw is then subjected to wet cleaning, which not only removes the remaining dust particles, but the soluble materials also get dissolved in water.

(4) Screening:

In most pulp and paper processes some type of stock screening operation is required to remove the over sized troublesome and unwanted particles. **Magnetic separator** removes iron pieces like nails and bolts, etc. stones and other oversized pieces are removed by **centri-cleaners**. The major types of stock screens are vibratory, gravity, and centrifugal. The material is then sent to wet silo.

(5) Digestion:

From wet silo, the material is sent to digester. The digester is usually 30 feet in length and 7 feet in diameter, it is made of steel and wrought iron. This is main unit of the process. The digestion process can be either batch or continuous. In our country batch process is mostly used.

As the raw material enters into the digester, steam is introduced at the bottom and a liquor containing sodium sulphite is injected simultaneously to cover the raw material. Sodium sulphite used is buffered with sodium carbonate or sodium hydroxide to maintain its pH 7-9

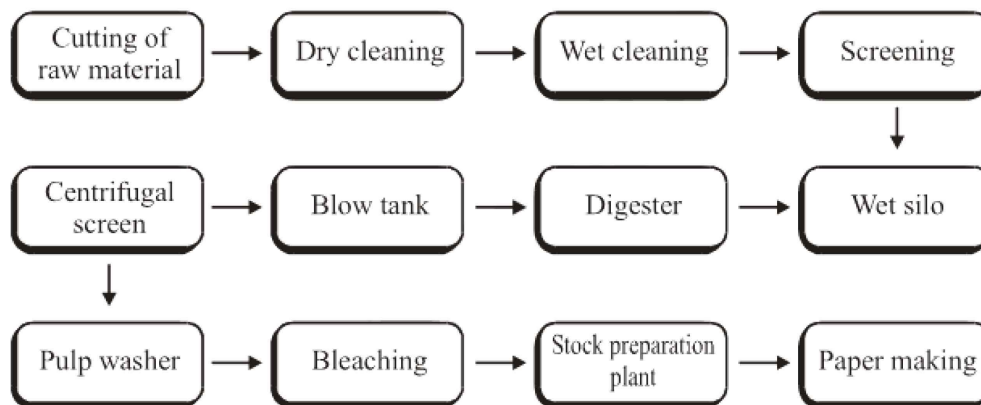
The digester is closed carefully. It revolves at 2.5 R.P.M and a temperature of **160–180°C** is maintained. The digester **takes 45 minutes** to attain the desired temperature after which it gets switched off automatically and pressure is released.

(6) Blow Tank:

The cooked material from the digester is blown into a blow tank and then pumped to a centrifugal screen for the separation of cooked from uncooked materials.

(7) Pulp Wash:

The cooked material from the blow tank is washed thoroughly with water using 80-mesh sieve to remove the black liquor that would contaminate the pulp during subsequent processing steps. The pulp is washed with required amount of water to remove soluble lignin and coloured compounds. Lignin is an aromatic polymer and causes paper to become brittle. Pulp is then thickened and finally stored in high-density storage tower.



Flow sheet diagram for neutral sulphite semi-chemical process

(8) Bleaching:

The pulps obtained from chemical pulping are brown in colour and are unsuitable for printing and writing papers which require a bright white pulp. The colour of these pulps is mainly due to residual lignin. These pulps are then sent to bleaching unit.

In Pakistan bleaching is done with chlorine dioxide (ClO_2) or **sodium hypochlorite** (NaClO). After washing, the unbleached pulp is sent to the chlorinator where chlorine at 4 – 5 bar pressure is injected from chlorine tank. The chlorine reacts with unbleached pulp at about 45°C for 45 – 60 minutes to give good result. The residual chlorine reacts with water which acts as antichlor. The correct dosage is very important and enough chlorine is needed to achieve the required brightness. After chlorination, pulp is washed with hot water at 60°C and is then sent to the storage.

(9) Stock Preparation Plant:

There are three important stages in the treatment of the pulp before delivering it to the paper making machine.

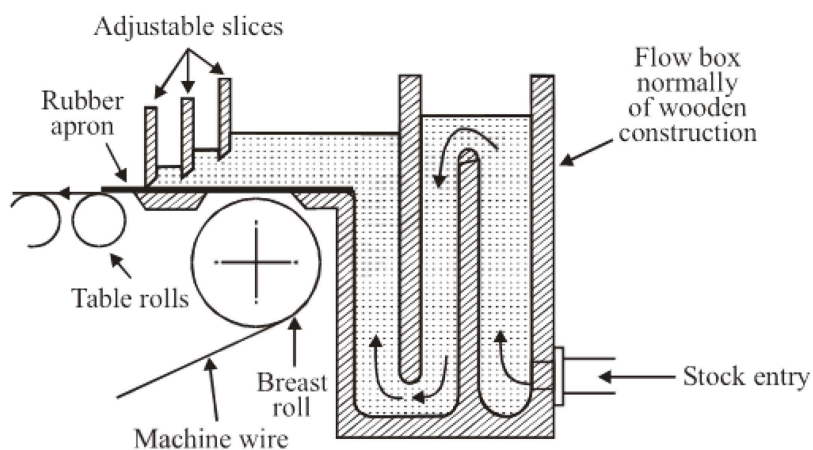
- (i) Pulp is dispersed in water and slurry is obtained.
- (ii) Mechanical refining and beating of fibres develop appropriate physical and mechanical properties of the product being made.
- (iii) Addition of chemical additives and addition of recycled fibres from the waste paper plant. All papers except the absorbent paper like tissue, toweling and filter paper, require some fillers or additives to give a smooth surface. Common additives of paper are talc, titanium oxide (TiO_2), precipitated calcium carbonate, silico-aluminates, starch, alum, etc.

(10) Paper Making Machine:

Commonly Fourdrinier machine is used for paper making. Its detail is given below:

(i) Flow spreader:

The flow spreader takes the pulp and distribute it evenly across the machine from back to front.



Slow speed flow box and apron slice

(ii) Head Box:

The pressurized box discharges a uniform jet of pulp suspension on a fabric or screen. Some special devices work for the removal of water. The pulp remains on the screen and water is drained off. The water which is removed through the screen is called white water or back water.

(iii) Fourdrinier Table:

The paper endless, moving Fourdrinier fabric forms the fiber into a continuous matted web while the Fourdrinier table drains the water by suction forces.

(iv) Press Section:

The paper sheet is conveyed through a series of roll presses where additional water is removed and the web structure is consolidated.

(v) Dryer Section:

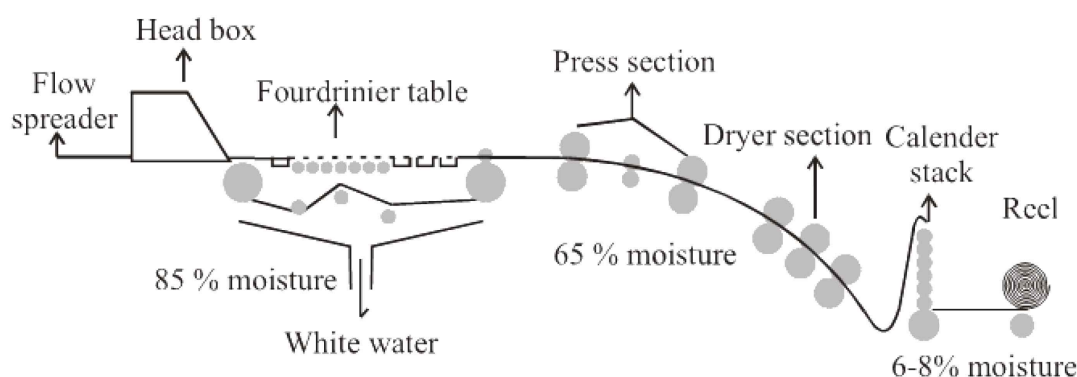
Wet sheet of paper so formed is dried in the dryer section of the machine with the help of rotary drum. Water is separated from the fiber either by gravity, by suction or by pressing.

(vi) Calender Stock:

The sheet is calendered or ironed through a series of roll nips to reduce thickness and smooth the surface. It makes a non-porous surface of the paper.

(vii) Reel:

The dried paper is wound in the form of a reel having final moisture of about 6-8%.

**PAPER INDUSTRY IN PAKISTAN**

Paper plays such an important role in the present day economic development that its consumption is taken as an index of a country's progress and prosperity. There was no pulp and paper industry in Pakistan at the time of independence in 1947. The country consumed about 25000 tons of pulp and paper products per year and all of these were imported from abroad at a cost of 25 million rupees. The start of the paper industry in our country was very slow because of various reasons amongst the major ones being the non-availability of suitable fibrous raw material.

Due to high prices of paper in Pakistan, its per head consumption is among the lowest in the world. Paper consumption in Pakistan is around **5 kg per person per year**.

To make our country self-sufficient in this important commodity, we must utilize every source of raw material like non-woody and woody. Fortunately, Pakistan has enough source of non-woody material, which in future can meet the requirements of our pulp and paper industry. The efforts are being made to install more pulp and paper industries in the country.

At present, there are 30 pulp and paper industries in Pakistan.