Chapter # 15
Common Chemical Industries In Pakistan

Cement

Definition

Cement is the material obtained by heating an intimate mixture of calcarious and argillaceous materials at sufficiently high temperature to produce clinkers. These clinkers are then ground to a fine powder.

History

It is an important building material. In 1824, it was introduced by an English Mason Joseph Aspdin.

He found, when a strongly heated mixture of limestone and clay was mixed with water and allowed to stand, it hardened to a stone like mass, which resembled Portland rock, which is a famous building stone of England.

Thus name Portland cement is given to the mixture of lime (obtained from lime stone), silica, iron oxide and alumina.

Composition

An average composition of Portland cement is given below.

Lime (CaO)	*62%*	*Iron oxide (Fe_2O_3)*	*2.5%*
Silica (SiO_2)	*22%*	*Sulpher trioxide (SO_3)*	*1.5%*
Alumina (Al_2O_3)	*7.5%*	*Sodium oxide (Na_2O)*	*1%*
Magnesia (MgO)	*2.5%*	*Potassium oxide (K_2O)*	*1%*

Essential constituents are lime (obtained from lime stone) silica and alumina (present in clay).

Raw Materials

Raw materials used in cement manufacture are

1. *Calcarious Material*

It is used as limestone, marble, chalks and marine shell. These provide CaO.

2. *Argillaceous Material*

It is introduced as clay, shale, state and blast furnance slag. These provide components such as aluminates and silicates.

3. *Gypsum*

Addition of gypsum decreases the selling time of cement.

A normal batch for cement manufacture consists of about 75% limestone 20-25% clay and 3-4% gypsum.

In Pakistan, sui gas is used in most of cement kilns.

Manufacture

Cement is manufactured either by dry process or wet process.

- *Dry process cheaper, but needs excessive fine grinding. This process is more suited for hard material.*
- *Wet process is free from dust, grinding is easier and composition of the cement can easily be controlled.*

The choice of wet or dry process depends upon

- *Physical condition of the raw material*
- *Local climatic conditions of the factory*
- *Price of fuel*

WET PROCESS

In this grinding is done in water.

It involves following steps

1. *Crushing and grinding of the raw material.*
2. *Mixing the material in correct proportion.*
3. *Heating the slurry in rotary kiln.*
4. *Clinker Formation*
5. *Grinding of cement clinker with gypsum.*

1. CRUSHING AND GRINDING

Soft raw material is first crushed into a suitable size, often in two stages. It is then ground in the presence of water. Grinding is done in rotating cylindrical ball or tube mills containing a charge of steel ball.

2. MIXING OF RAW MATERIAL

Powder lime stone is mixed with clay in proper proportion (limestone 75%, clay 25%). Mixer is finely ground and made homogeneous by compressed air. Thus a paste is obtained called slurry.

Slurry contain 35 to 45% water. It is sometimes filtered to reduce water content to 20 to 30%, and the filler cakes are stored in storage bins. This reduces the fuel consumption for heating stage.

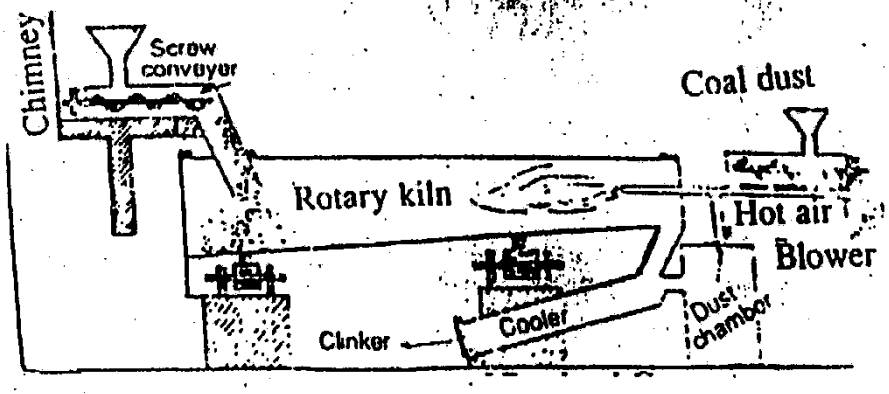
3. HEATING THE SLURRY IN A ROTARY KILN

Rotary kiln

It consists of a large cylinder. It is 8 to 15 feet in diameter and 300-500 feet in length. It is made of steel. It is lined inside with firebricks.

The kiln rotate on its axis at a rate of 1- 2 turn per minute. It is rotated horizontally and inclined a few degree.

With the rotation of kiln, charge slowly moves downward.



Process

Charge or slurry is introduced into kiln by a conveyer. Charge is heated by burning coal, oil or natural gas.

In rotary kiln, charge passes through three different temperature zones where different reactions take place. Charge takes 2-3 hours to pass through a kiln.

(i) *Drying Or Pre-Heating Zone (Minimum Temperature Zone)*

In this zone T is about 500°C. Here moisture is removed and clay is broken into Al_2O_3, SiO_2 and Fe_2O_3.

(ii) *Decomposition Zone (Moderatate Temperature Zone)*

Here temperature goes upto 800°C. Here limestone decomposes into lime and CO_2.

$$CaCO_3 \longrightarrow CaO + CO_2$$

(iii) *Burning Zone*

In this zone, temperature goes upto 1500°C. Here most of the reactions of cement formation take place. CaO, SiO_2, Al_2O_3 and Fe_2O_3 combine together and form tricalcium silicate, tricalciumaluminate and calcium ferrite etc.

$$3CaO + Al_2O_3 \longrightarrow 3CaO.Al_2O_3 \text{ (tricalcium aluminate)}$$
$$3CaO + SiO_2 \longrightarrow 3CaOSiO_3 \text{ (tricalcium silicate)}$$
$$4CaO+Al_2O_3+Fe_2O_3 \longrightarrow 4CaO.Al_2O_3.Fe_2O_3 \text{ (tetracalcium alumino ferrite)}$$

(iv) *Cooling Zone*

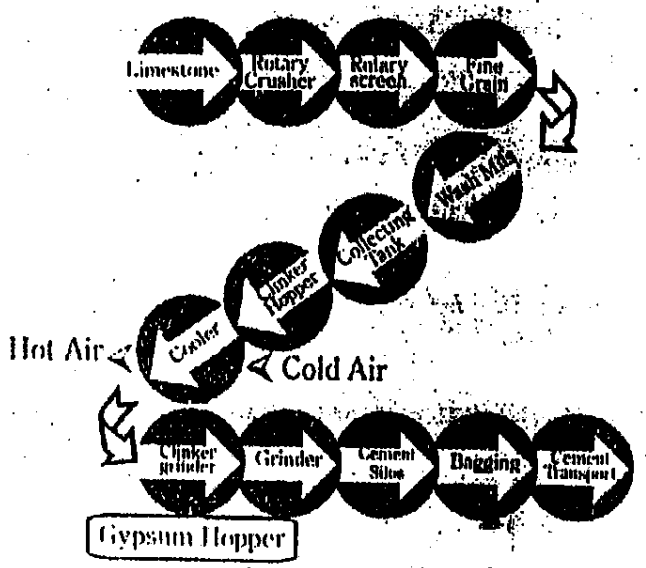
In this last zone, charge is cooled to 150°C to 200°C

4. Clinker Formation

The resulting product obtained from kiln is known as cement clinkers. It is greenish black or grey coloured balls, varying in size from small nuts to peas.

5. Grinding the Clinkers with Gypsum

Cement clinkers are air-cooled, about 5% gypsum is ground to fine powder. It is then mixed with clinkers and again ground. Finally finished cement is pumped pneumatically to storage silos from where it is drawn for packing. It is packed in paper bags or for dispatch in bulk containers.



SETTING OF CEMENT

When cement is mixed with water, and allowed to stand, it is hardened. This is called setting of cement.

Setting of cement involves hydration and hydrolysis processes

Reaction Taking Place In First 24 Hours

After mixing with water, tri-calcium aluminate absorbs water (hydration) and forms a colloidal gel of composition $3CaO.Al_2O_3.6H_2O$.

$$3CaO.Al_2O_3 + 6H_2O \longrightarrow 3CaO.Al_2O_3.6H_2O$$

This gel crystallizes slowly and reacts with gypsum ($CaSO_4.2H_2O$) to form crystals of calcium sulphoaluminate ($3CaO.Al_2O_3.3CaSO_4.2H_2O$)

$$3CaO.Al_2O_3 + CaSO_4.2H_2O \longrightarrow 3CaO.Al_2O_3.3CaSO_4.2H_2O$$

Reactions Taking Place Between 1 To 7 Days

Tri-calcium silicate and tri-calcium aluminate hydrolyze to produce crystals of $Ca(OH)_2$ and $Al(OH)_3$

$$3CaO.SiO_2 + H_2O \longrightarrow Ca(OH)_2 + 2CaO.SiO_2$$
$$3CaO.Al_2O_3 + 6H_2O \longrightarrow 3Ca(OH)_2 + 6Al(OH)_3$$

Needle shaped crystals of $Ca(OH)_2$ get studded in the colloidal gel and impart strength to it.

$Al(OH)_3$ fills the interstices resulting in hardening the mass. The gel starts loosing water partly by evaporation and sets to a hard mass.

CEMENT INDUSTRY IN PAKISTAN

In 1947, there were four cement plants in West Pakistan. These produced 330,000 tons of coments per year. In 1954, production of cement went upto 000,000 tons per year. In 1956 two more cement factories were set up at Daud Khel and Hydrabad. But still production of cement was less than needed.

For developing countries like Pakistan, there is always need for cement for new projects. At present 22 factories are working in Pakistan both in private and public sector. These are using both dry and wet processes. Currently annual production of cement is 0,578,802 metric tons/annum.

Fertilizers

These are substances which are added to soil to make up the deficiency of essential elements like nitrogen, phosphorous and postassium (NPK) required for the proper growth of plants.

These increases the fertility of soil and replenish the elements taken up from soil by previous crops.

History

Agriculture is one of the early industry known. From the very beginning, fertilizers were used to increase the fertility of soil. Chinees used manure since 500 B.C.

A manure is an organic material used to fertilize land. It is usually consists of faeaces and urine of domestic livestock.

Elements essential for plant Growth

Nutrient elements needed for the normal growth of plants can be classified as micronutrient and macronutrient

Micro-Nutrients

The nutrients required in very small amount for growth of plants are called micro-nutrients.

These include Boron, Copper, Iron, Manganese, Zinc, Molybdenum and Chlorine.

These are required in minute quantities. These are dangerous in large amount. Their requirement varies form 6 g. to 200 g. per acre

Macro-Nutrients

The nutrients required in a large amount for growth of plants are called macro-nutrients.

These include Nitrogen, Phosphorous, Potassium, Calcium, Magnesium, Sulpher, Carbon, Hydrogen and Oxygen.

Nitrogen , Phosphorous and Potassium are of prime importance while Sulpher, Magnesium and Calcium are of secondary importance.

Their requirement varies from 5Kg to 200Kg per acre.

Requirement of a Fertilizer

All compounds of a given element can not be used as fertilizer. The required element should be present in water-soluble compound. Thus plants can easily take it up. Further this compound should be stable both in soil and storage. It should not be deliquescent. It should not harden to stony mass. It should be cheap.

Essential conditions of a good fertilizer.

1. Nutrient elements of fertilizer should be readily available to plants.
2. It must be soluble in water so that it mixes with soil
3. It should not be injurious to plants
4. It should be cheap
5. It must be stable so that it is available to growing plants for longer time.
6. It should not change the pH of soil
7. Rain or water should convert it in such form so that plants can easily use it.

CLASSIFICATION OF FERTILIZERS

Fertilizers are classified according to the nature of elements present in them. Following are important fertilizers

A. Nitrogenous fertilizers
B. Phosphatic fertilizers
C. Potassium fertilizers

A. NITROGENOUS FERTILIZERS

These supply nitrogen to the soil.
Important nitrogenous fertilizers are

Ammonium Nitrate	Calcium Ammonium Nitrate	Basic Calcium Nitrate
Calcium Cyanamide	Ammonium Nitrate	Ammonium Phoaphate
Ammonium Chloride	Urea	Ammonia.

Except ammonia all the fertilizers are used in solid form. All nitrogeneous fertilizers make the soil acidic except calcium nitrate, sodium nitrate and potassium nitrate. Acidity of the soil can be controlled by regular liming (adding lime) of soil.

Importance Of Nitrogen

- Nitrogen is essential during early state for the development of leaves and stem.
- It is the main constituent of protein.
- It gives green colour to the leaves
- It increases the yield and quality of plants.

1. AMMONIA AS FERTILIZER

It is used in liquid state. It contains 82% nitrogen. It is injected six inches below the surface of soil to avoid it from seeping out.

2. UREA

It is high quality nitrogenous fertilizer. It is most widely used in Pakistan. It contains 46% nitrogen.

Manufacture

Manufacture of urea involves following steps

(i) Preparation Of Hydrogen
(ii) Preparation Of Ammonia By Haber's Process
(iii) Preparation Of Ammonium Carbamate
(iv) Preparation Of Urea
(v) Concentration Of Urea
(vi) Prilling

(i) Preparation Of Hydrogen

Hydrogen is obtained from natural gas by passing its mixture with steam over heated Ni.

$$CH_4 + 2H_2O \longrightarrow CO_2 + 4H_2$$

(ii) Preparation Of Ammonia By Haber's Process

Ammonia is prepared by Haber's process. In this process N_2 from air and H_2 are reacted in the ratio of 1:3 in reaction chamber in the presence of catalyst.

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

(iii) Preparation Of Ammonium Carbamate

Gaseous CO_2 is mixed with gaseous NH_3 in the ratio 1:2 in a reactor. This reaction produces ammonium carbamate

$$CO_2 + 2NH_3 \longrightarrow H_2N-\overset{\overset{O}{\|}}{C}-O-NH_4$$

(iv) Preparation Of Urea

Ammonium carbamate on dehydration gives urea

$$H_2N-\overset{\overset{O}{\|}}{C}-O.NH_4 \longrightarrow H_2N-\overset{\overset{O}{\|}}{C}-NH_2 + H_2O$$

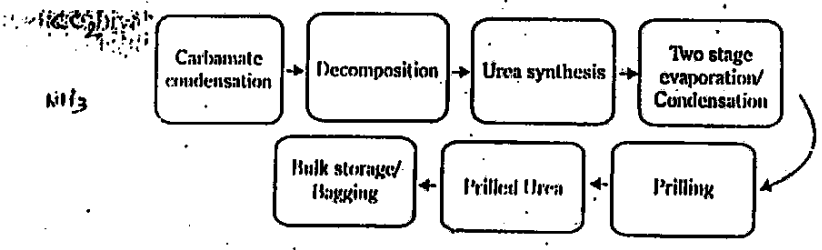
(v) Concentration Of Urea Solution

Urea solution obtained is concentrated in an evaporator. Here water is removed by passing steam under vacuum in two evaporation stages. Thus 99.7% urea melt is obtained. It is then pumped to prilling tower.

(vi) Prilling

Molten urea is sprayed at the prilling tower by means of prilling bucket. It is cooled by air rising upward. Molten droplets of urea solidify to prills. Prills of fertilizers are free of dust, easy to handle and easy to spread on the field.

Urea prills are then bagged or stored



3. AMMONIUM NITRATE

It contains 33 – 33.5% nitrogen. It is hygroscopic.

It is obtained by neutralizing nitric acid with ammonia.

$$NH_3 + HNO_3 \longrightarrow NH_4NO_3$$

After neutralization, water is evaporated. Solid ammonium nitrate is melted.

Molten ammonium nitrate is sprayed at the prilling tower by means of prilling bucket. It is cooled by air rising upward. Molten droplets of ammonium solidify to prills. Prills of fertilizers are free of dust, easy to handle and easy to spread on the field.

It is used as fertilizer for many crops except paddy rice. It is because bacteria in flooded fields convert it to nitrogen gas. It is also used along with lime.

B. PHOSPHATIC FERTILIZERS

These provides phosphorous to the soil

Phosphorous fertilizers have different composition. Thus they have different solubilities in soil. Two important water-soluble fertilizers are

Calcium Super Phosphate or Super Phosphate $Ca(H_2PO_4)_2$

Diammonium Phosphate or Triple Super Phosphate $(NH_4)_2HPO_4$

Importance Of Phosphorous

- *It is required to stimulate early growth.*
- *It also accelerates seed and fruit formation during later stages of growth.*
- *It also increases resistant to diseases.*

DIAMMONIUM PHOSPHATE [$(NH_4)_2HPO_4$]

It contains 16% nitrogen and 48% P_2O_5.

This high purity compound is prepared by a continuous process. In this process anhydrous ammonia gas is reacted with phosphoric acid at 60 – 70°C

$$2NH_3 + H_3PO_4 \longrightarrow (NH_4)_2HPO_4 + heat$$

It is an exothermic reaction. Heat evolved evaporates water from liquor. From this crystals of diammonium phosphate are obtained. These crystals are centrifuged, washed and dried. This product contains 75% plant nutrients. It is suitable to use alone or with other fertilizers.

C. POTASSIUM FERTILIZERS

These fertilizers provide potassium to the soil. These are especially used for tobacco, coffee, potato and corn.

Importance of Potassium

- *It is required for formation of starch, sugar and the fibrous material of the plant.*
- *It increases resistant to diseases.*
- *It makes plant strong by helping in healthy root system.*
- *It also help in ripening of seeds, fruits and cereals.*

POTASSIUM NITRATE (KNO_3)

It contains 13% nitrogen and 44% potash.

In industry, it is prepared by double decomposition reaction b/w KCl and $NaNO_3$.

$$NaNO_3 + KCl \longrightarrow NaCl + KNO_3$$

Process

A hot solution of $NaNO_3$ *is prepared. Solid KCl is added to it. On heating, crystals of KCl changes into NaCl crystals. Hot potassium nitrate solution moves through the crystals at the bottom of kettle. Solution is cooled. Small amount of water is added to prevent further deposition of NaCl during cooling. This give pale yellow solid* KNO_3.

PAPER INDUSTRY

DEFINITION

It is a sheet material made up of a network of natural cellulosic fibers, which have been deposited from an aqueous suspension. The product obtained is a network of interlocking fibers.

HISTORY

Word paper is derived from the name of reedy plant Papyrus. This plant grew along the marshy delta of the River Nile in Egypt around 3000 B.C.

Modern paper was invented by Ts' ai Lun of China. In 105 A.D., he was an official of the Imperial Court of China. He prepared a sheet of paper using the bark of mulberry tree. It was treated with lime and mixed with bamboo and other fibres to give the paper.

MANUFACTURING

RAW MATERIAL

Two types of raw materials are used. Non-woody and woody.

Nonwoody raw materials		Woody raw materials	
(i)	Wheat straw	(i)	Poplar
(ii)	Corn straw	(ii)	Eucalyptus
(iii)	Rice straw	(iii)	Fur
(iv)	Bagasse		
(v)	Rag		
(vi)	Bamboo		
(vii)	Cotton stalk		
(viii)	Cotton linter		
(ix)	Kahi		
(x)	Grasses		

PULPING METHODS

Following three methods are generally used

1. *Kraft process (Alkaline)*
2. *Sulphite process (Acidic)*
3. *Neutral sulphite semi chemical process (NSSC)*

Neutral sulphite semi chemical process is better due to easy chemical recovery and pulp strength. It is the most widely used process in Pakistan.

NEUTRAL SULPHITE SEMI CHEMICAL PROCESS

It uses sodium sulphite cooking liquor. It is buffered with sodium carbonate or NaOH to neutralize organic acid liberated from raw materials.

Non-woody raw materials are wheat straw, rice straw, bagasse, cotton linters and rags. Wheat straw may be used alone or combined with other materials in different proportions.

This process is done in following steps

1. *Cutting of the Raw material*
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

i) Cutting Of Raw Materials

Non-woody raw materials come in the precut state. These are used as such. Big logs of woody raw material are cut into small chips.

ii) Dry Cleaning

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

iii) Wet Cleaning

Wet cleaning removes the remaining dust particles. It also removes soluble materials.

iv) Screening

Screening is required to remove over sized and unwanted particles.
Magnetic separator removes iron pieces like nails and bolts, etc.
Centri-cleaners remove stones and other oversized pieces.
Major types of stock screens are vibratory, gravity and centrifugal.
The material is then sent to wet silo.

v) Digestion

From wet silo, the material is sent to digester.

The digester is 30 feet in length and 7 feet in diameter. It is made of steel and wrought iron. This is the main unit of the process.

Digestion process can be either batch or continuous.

In Pakistan batch process is mostly used.

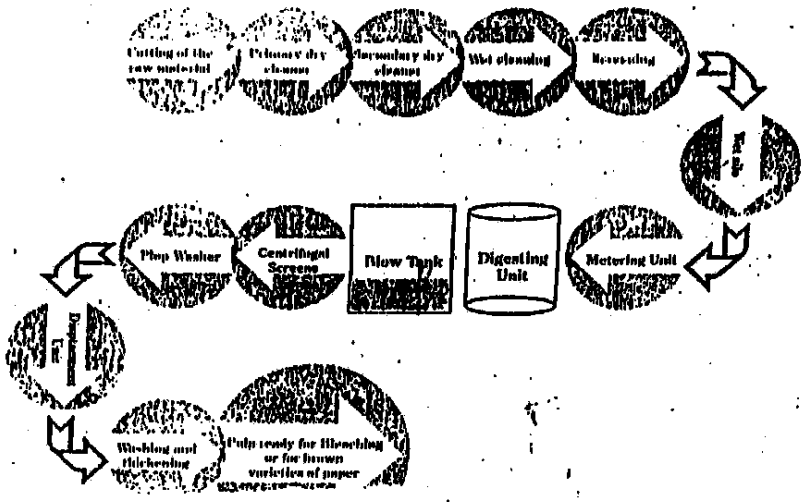
Raw material is fed into the digester. Steam is introduced at the bottom. Sodium sulphite liquor is injected simultaneously to cover the raw material. Sodium sulphite used is buffered with sodium carbonate or sodium hydroxide to maintain its pH 7-9. The digester is closed carefully. It is revolved at 2.5 R.P.M. It is maintained at a temperature of 160-180°C. The digester takes 45 minutes to attain the desired temperature. After this it gets switched off automatically and pressure is released.

vi) Blow Tank

From digester cooked material is blown into a blow tank. It is then pumped to a centrifugal screen to separate cooked material from uncooked materials.

vii) Pulp Washing

The cooked material form the blow tank is washed thoroughly with water using 80-mesh sieve. This removes black liquor. The pulp is washed with required amount of water to remove soluble lignin and coloured compounds. Lignin is an aromatic polymer. It makes paper brittle. It is then thickened and stored in high-density storage tower.



viii) *Bleaching*

The pulp so obtained is brown in colour. It is unsuitable for printing and writing papers. For this purpose bright white pulp is required. Colour of these pulps is mainly due to residual lignin. These pulps are then bleached.

In Pakistan, bleaching is done with chlorine or sodium hypochlorite.

Chlorine reacts very rapidly with pulp. The correct dosage is very important. Enough chlorine is needed to get required brightness. After chlorination, pulp is washed with hot water at 60°C. It is then sent to the storage.

ix) *Drying*

Pulp is dried with hot air supply. Now it is ready for manufacturing of paper.

x) *Stock Preparation Plant*

Following three steps are done.

- *Dispersion of the pulp as a slurry in water.*
- *Mechanical refining or beating of the fibers. It gives required physical and mechanical properties to the product.*
- *Addition of chemical additives and recycled fibers from the waste paper plant.*

x) *Paper Making Machine*

A basic Fourdrinier type machine is used for paper making.

It has following components

a) *Flow spreader*

It takes the pulp and distributes it evenly across the machine from back to front.

b) *Head box*

The pressurized head box discharges a uniform jet of pulp suspension on a fabric where special suction devices work for the removal of water.

c) *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.

d) Press section

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

e) Dryer section

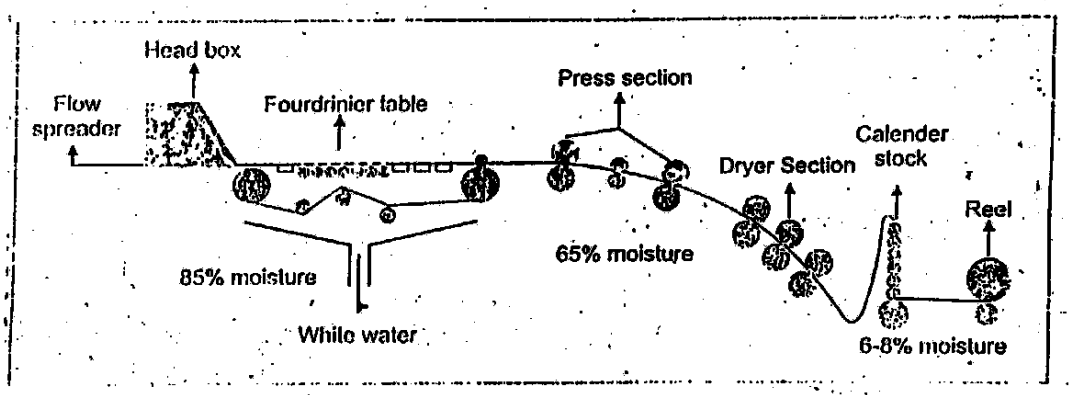
Wet sheet of paper so formed is dried in the dryer section of the machine with the help of rotary drum. Water is separated from the fibre either by gravity, by suction or by pressing.

f) Calender stack

The sheet is calendered through a series of roll nips to reduce thickness and smooth the surface.

g) Real

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. Its consumption indicates 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. 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. The major reason was 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. Pakistan has enough source of non-woody material. The efforts are being made to install more pulp and paper industries in the country.

At present there are more than 30 pulp and paper industries in private as well as in public sectors. These are manufacturing pulp and paperboard.