CEMENT

Introduction, Classification, Raw Materials, Gypsum, Manufacture of Portland Cement (Both Wet and Dry Process),

Chemical Composition of Cement,

Chemical Constitution of Cement,

Setting and Hardening of Cement,

Special Cements: Aluminous Cement, High Early Strength Cement, White Portland Cement, Water Proof Cement,

Physical Requirements of Cement.

Introduction of Concrete and RCC

History of Cement

- Egyptians - Calcined gypsum
- Greeks and Romans - Lime made by heating limestone and added sand to make mortar, with coarser stones for concrete.
- Romans - Cement which set under water, for the construction of harbours. It was made by adding crushed volcanic ash to lime (Pozzolana cement), named after the village of Pozzuoli near Mount Vesuvius.
- Britain - Crushed brick or tile was used

Portland Cement

- Smeaton, building the third Eddystone lighthouse (1759) off the coast of Cornwall in Southwestern England.
- A mix of lime, clay and crushed slag from iron-making produced a mortar which hardened under water.
- In 1824 Joseph Aspdin made "Portland Cement"
- Present day cement - firing finely-ground clay and limestone until the limestone was calcined.
- Portland Cement because the concrete made from it looked like Portland stone, a widely-used building stone in England.

Cements

- Inorganic cements are materials that exhibit characteristic properties of setting and hardening, when mixed with water to make a paste.
- This makes them capable of joining bricks, stones, tiles etc.
- Inorganic cements are divided into two parts:
- Hydraulic cementing materials – These are capable of setting and hardening under water
- Non- Hydraulic cementing materials – These are capable of setting and hardening in air and cannot be used under water.

Principal Constituents of Cement

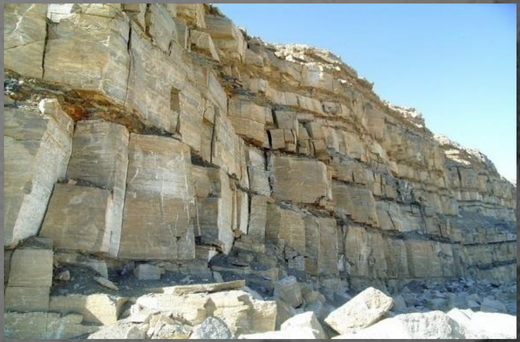
Lime stone

Calcerious Materials: These contain compound of Calcium, like lime stone, chalk, cement rock, marine shells and waste calcium carbonate from industries.

silica

Argillaceous Materials: These supplies Silica, Aluminium and Iron oxide, like clay, shale, blast-furnace slag, ashes and cement rock.

Gypsum ($CaSO_4.2H_2O$)



gypsum

Functions of Ingredients

- Lime: The principal constituent of cement. Proper proportion is essential as excess lime reduces the strength of cement because it makes the cement to expand and disintegrate, whereas lesser amount makes it quick-setting.
- Silica: It imparts strength.
- Alumina: Same as lime.
- Calcium sulphate: It helps to retard the setting action of cement.
- Iron oxide: It provides colour, strength and hardness.
- Sulphur trioxide : When present in small amount, it imparts soundness to cement. (soundness: stability of the volume change in the process of setting and hardening)
- Alkalis : If present in excess, cause the cement efflorescent (chalky white residue over surface)

Manufacture of Portland Cement

Step 1 - Quarrying

- Raw material - 80% limestone (which is rich in $CaCO_3$) and 20% clay or shale (a source of silica, alumina and Fe_2O_3).
- These are quarried and stored separately.
- Limestone - Karnataka 28% , Andhra Pradesh (20%), Rajasthan (12%)
- The **largest limestone** mine is in Gujarat, near Dwarka.

<u>Step 2</u> - Raw material preparation

- Cement raw materials are received with an initial moisture content varying from 1 to more than 50 percent.
- Three main processes currently used: <u>the dry process, the wet process and the Semi-dry process</u>.

<u>*The dry process*</u>

- The quarried clay and limestone are crushed separately until nothing bigger than a tennis ball remains.
- Samples of both rocks are then sent off to the laboratory for mineral analysis.

- If necessary, minerals are then added to either the clay or the limestone to ensure that the correct amounts of aluminium, iron etc. are present.
- The clay and limestone are then fed together into a mill where the rock is ground until more than 85% of the material is less than 90μm in diameter.
- This dry mix is stored in storage bins called silos.

The wet process

- The argillaceous material (clay) is mixed with water and pulverised.
- Crushed lime is then added and the whole mixture further ground.
- The slurry is then tested to ensure that it contains the correct balance of minerals.
- This slurry contains about 38-40% water.

Semi-dry process

- The raw materials are initially ground dry and then mixed with 10-14% water.

Average composition

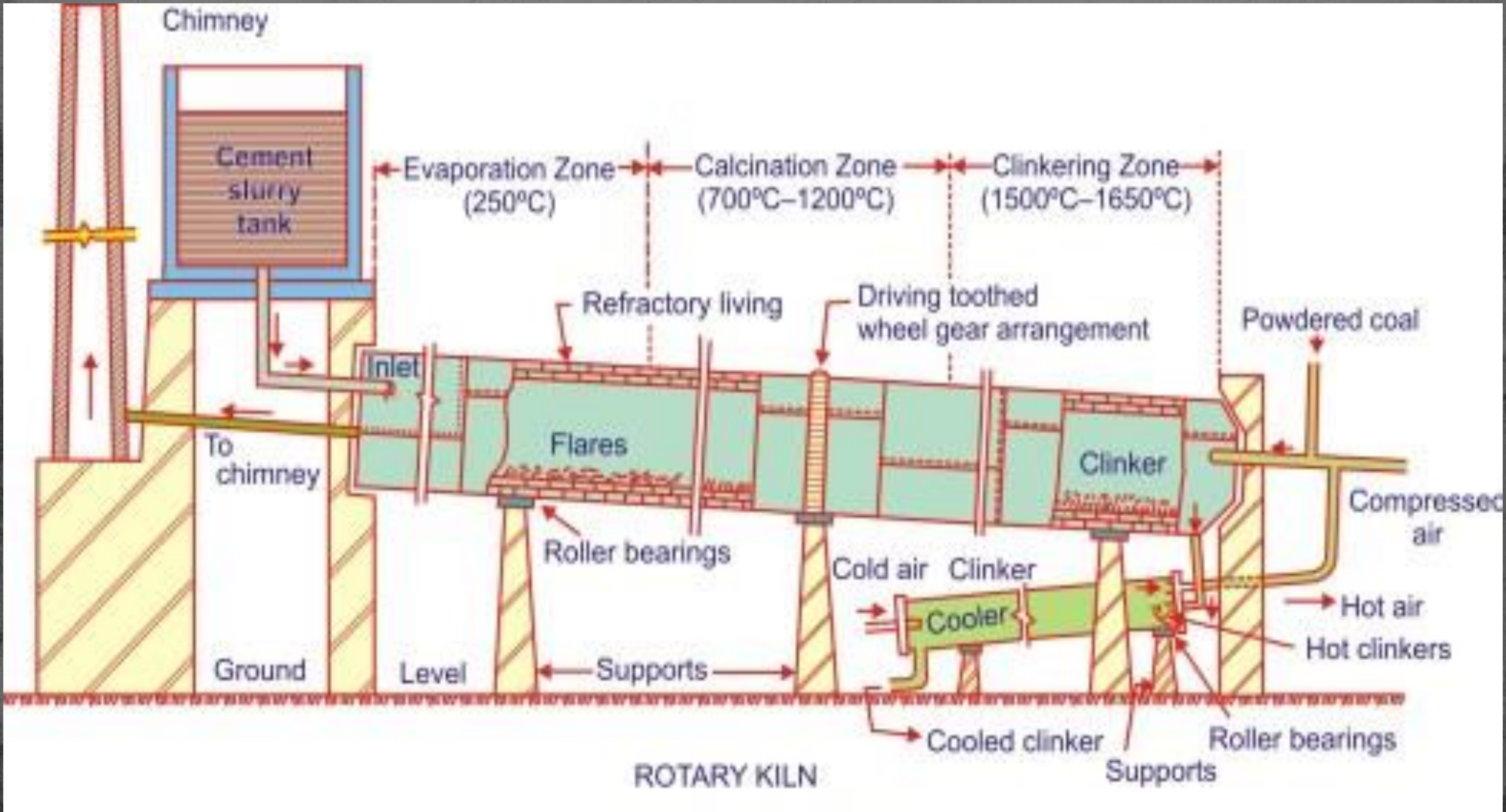
Component	Percentage range by mass
Lime (CaO)	60-69
Silica (SiO_2)	17-25
Alumina (Al_2O_3)	3-8
Iron Oxide (Fe_2O_3)	2-4
Magnesium Oxide (MgO)	1-5
Sulphur Trioxide (SO_3)	1-3
Alkali Oxides ($Na_2O + K_2O$)	0.3-1.5

Comparison between Wet and Dry process

Dry Process	Wet Process
1. The cost of grinding is more. 2. Shorter kiln is sufficient. 3. Fuel consumption is less. 4. It is adopted when the raw materials are hard. 5. It is adopted when the climate is dry. 6. Process is slow. 7. Cement produced is of inferior quality.	1. The cost of grinding is less. 2. Longer kiln is needed. 3. Fuel consumption is more in order to remove water. 4. It is adopted when the raw materials are softer. 5. It is adopted when the climate is humid. 6. Process is comparatively faster. 7. Cement produced is of superior quality.

Step 3 – Clinkering using Rotary Kiln

- Characteristic step in the manufacture of Portland cement.



- The kiln shell is made of steel,
- long horizontal cylinder lined with refractory bricks,
- 90-120 m (300-400ft) long, 2.5-3.0 m (10 ft) in diameter and inclined at an angle (3 - 4 degrees).
- The shell is supported on 3 rollers on concrete and weighs in at over 1100 Tonnes.
- The kiln is heated by injecting pulverized coal with air into the kiln at a rate of 9 - 12 Tonnes per hour.
- Rotated slowly about its longitudinal axis (1-3 rpm)

Sequential Events

1. Evaporation of free water
2. Evolution of combined water in the argillaceous components
3. Calcination of the calcium carbonate ($CaCO_3$) to calcium oxide (CaO)
4. Reaction of CaO with silica to form dicalcium silicate
5. Reaction of CaO with the aluminum and iron-bearing constituents to form the liquid phase
6. Formation of the clinker nodules
7. Evaporation of volatile constituents (e. g., sodium, potassium, chlorides, and sulfates)
8. Reaction of excess CaO with dicalcium silicate to form tricalcium silicate.

Stages: as a function of location and temperature of the materials in the rotary kiln

- Evaporation of uncombined water from raw materials, as material temperature increases to 100°C
- Dehydration, as the material temperature increases from 100°C to approximately 430°C to form oxides of silicon, aluminum, and iron
- Calcination, during which carbon dioxide (CO_2) is evolved, between 900°C and 982°C, to form CaO
- Reaction, of the oxides in the burning zone of the rotary kiln, to form cement clinker at temperatures of approximately 1510°C.

The reaction processes

Zone 1: Drying Zone

- Temperature is about 400°C. Here most of the water is driven out by hot gases.

Zone 2: Pre-heating Zone 400-700°C.

- Here clay and magnesium carbonate decomposes.

Zone 3: Calcining Zone 700-1000 °C.

- Here limestone decomposes to give quicklime and carbon dioxide (it escapes out).
- $CaCO_3 \rightarrow CaO + CO_2$
- The material forms small lumps called nodules.

Zone 4: Burning and Clinkering zone: 1500-1700°C,

- Lime and clay react with each other forming aluminates and silicates.

- $2CaO + SiO_2 \rightarrow 2CaO{\cdot}SiO_2$
  (C$_2$S) (Dicalcium silicate)
- $2CaO{\cdot}SiO_2 + CaO \rightarrow 3CaO{\cdot}SiO_2$
- (C$_3$S) (Tricalcium silicate)
- $3CaO + Al_2O_3 \rightarrow 3CaO{\cdot}Al_2O_3$
- (C$_3$A) (Tricalcium aluminate)
- $3CaO{\cdot}Al_2O_3 + CaO + Fe_2O_3 \rightarrow 4CaO{\cdot}Al_2O_3{\cdot}Fe_2O_3$
- (C$_4$AF) (Tetracalcium Aluminoferrite)
- The aluminates and silicates of calcium then fuse together to form small (0.5-1 cm diameter) hard, grayish stones, called clinkers.
- These clinkers are very hot (~ 1000^{o}C).

CaO written as C
SiO_2 as S
Al_2O_3 as A
Fe_2O_3 as F

The cooler

Immediately following the kiln is a large cooler designed to drop the temperature of the clinker from 1000°C to 150°C.

This is achieved by forcing air through a bed of clinker via perforated plates in the base of the cooler.

The plates within the cooler slide back and forth, shuffling the clinker down the cooler to the discharge point and transport to a storage area.

Step 4: Cement milling

- Clinker is mixed with gypsum ($CaSO_4 \cdot 2H_2O$)(2-3%), which is added as a **Set Retarder**, and ground for approximately 30 minutes in large tube mills.
- The cement flows from the inlet to the outlet of the mill (a rotating chamber), being first ground with 60 mm then 30 mm diameter steel balls.
- Then finally packing in usually 50Kg bags.

Gypsum

- Hydrated Calcium sulphate $CaSO_4.2H_2O$
- 79.1% $CaSO_4$ and 20.9% water
- Plaster of Paris ($CaSO_4.1/2H_2O$)
- Produced by heating pure gypsum around 120-160 ^oC .
- Has property of expanding slightly while setting
- Used for making moulds, surgical bandages, tiles, plastering boards and walls
- Not much strength so can not take load
- Has water so set down slowly and that is why can be moulded easily.

Setting and Hardening of cement

- Setting: Stiffening of the original plastic mass due to initial gel formation.
- Hardening: Development of strength due to crystallization
- The Setting and Hardening of cement are mainly due to hydration and hydrolysis reactions taking place when different compounds present in the cement interact with water.

Step-wise Setting and Hardening of cement

$3CaO.Al_2O_3 + 6H_2O \rightarrow 3CaO.Al_2O_3.6H_2O + 880$ KJ/Kg

Tricalcium aluminate hydrated calcium aluminate

$4CaO.Al_2O_3.Fe_2O_3 + 7H_2O \rightarrow 3CaO.Al_2O_3.6H_2O + CaO.Fe_2O_3.H_2O +$

Tetracalcium aluminoferrite Crystals Gels 420 KJ/kg

$2[2CaO.SiO_2] + 4H_2O \rightarrow 3CaO.2SiO_2.3H_2O + Ca(OH)_2 + 250$ KJ/Kg

Dicalcium silicate Tobermonite gel

$2[3CaO.SiO_2] + 6H_2O \rightarrow 3CaO.2SiO_2.3H_2O + 3Ca(OH)_2 + 500$ KJ/Kg

Tricalcium silicate Tobermonite gel

Characteristics of Constituents

Tricalcium silicate (C_3S) – It has medium rate of hydration and develops high ultimate strength quite rapidly, which is also highest among all. Its hydration begins within 24 hrs and gets completed in 7 days.

The heat of hydration is 500 kJ/kg.

Dicalcium silicate (C_2S) - It has low early-strength but develops ultimate-strength slightly less than C_3S. Its hydration begins within 7 days and gets completed in 28 days.

It hydrates very slowly. It is also responsible for ultimate strength. The heat of hydration is 250 kJ/kg.

Tricalcium aluminate (C_3A) - It hydrates very fast and does not contribute much to the strength of cement, since it's early- strength and ultimate- strength are poorest among all the constituents.

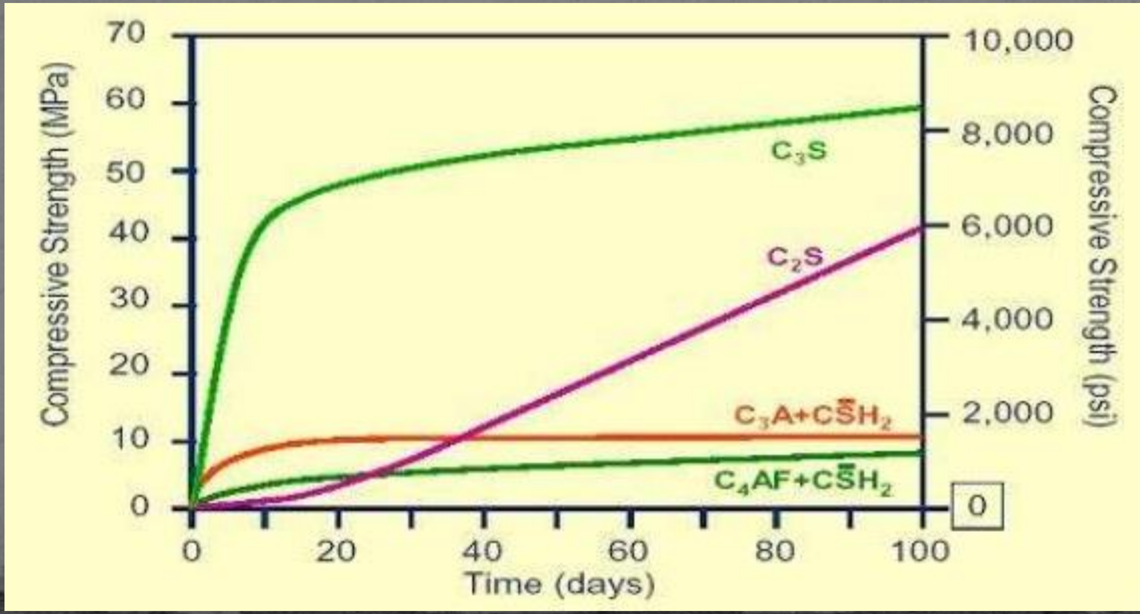
The heat of hydration is 880 kJ/kg.

Tetracalcium aluminoferrite (C_4AF) - It hydrates very fast and does not contribute much to the strength of cement, since it's early- strength and ultimate- strength are poor.

The heat of hydration is 420 kJ/kg.

Chemical Constitution of Portland Cement

Name of Compound	Chemical Formula	Abbreviation Used	Average %	Setting Time
Tricalcium silicate	$3CaO.SiO_2$	C_3S	45	7 days
Dicalcium silicate	$2CaO.SiO_2$	C_2S	25	28 days
Tricalcium aluminate	$3CaO.Al_2O_3$	C_3A	1	1 days
Tetracalcium aluminoferrite	$4CaO.Al_2O_3.Fe_2O_3$	C_4AF	9	1 days
Calcium sulphate	$CaSO_4$		5	
Calcium oxide	CaO		2	
Magnesium oxide	MgO		4	



Role of Gypsum

- For ordinary Portland cement it remains between 3 to 4% and in case of Quick setting cement it can be reduced up to 2.5%.
- When cement is mixed with water, the paste becomes quite rigid within a short time which is known as **initial set or flash set**. This is due to C_3A which hydrates very rapidly
- Gypsum retards the dissolution of C_3A by interacting with it and forming insoluble complex sulfo aluminate which does not have quick hydrating property.

$$3CaO.Al_2O_3 + xH_2O + yCaSO_4.2H_2O \rightarrow 3CaO.Al_2O_3.yCaSO_4.xH_2O$$

Tricalcium aluminate   Gypsum   Insoluble calcium sulfo aluminate

Effects of Gypsum on Cement

- Gypsum prevents Flash Setting of cement during manufacturing.
- It retards the setting time of cement.
- Allows a longer working time for mixing, transporting and placing.
- When water is mixed to cement Aluminates and sulfates get react and evolve some heat but gypsum acts as coolant and brings down the heat of hydration.
- Gypsum cements possess considerably greater strength and hardness when compared to non gypsum cement.
- Water required in gypsum based cement for hydration process is less.

Aluminous/High-Alumina Cement (HAC)

- Made by fusing together a mixture of a calcium-bearing material (normally limestone) and an aluminium-bearing material (normally bauxite) in a rotary kiln at 1500-1600 ^{o}C.
- Compossition: CaO: 35-40%, Al_2O_3: 35-55%, FeO + Fe_2O_3 : 5-15%, SiO_2: 5-10%
- Main constituent –Monocalcium aluminate (CA) and Tricalcium pentaluminate (C_3A_5)
- Setting time similar to Portland cement but rate of hardening is very rapid.
- Full strength attained in 24 hours.

Advantages:

1. Retains its strength at high temperature also.
2. Superior chemical resistance to sea water and sulphate bearing ground water
3. Resistant to dilute acid solutions and hydrogen sulphide solutions (industries)
4. Rapid evolution of heat so good in very cold conditions

But it could be disadvantage also, thus layer should be spread thinly (3 cm approx.)

High early-strength (H.E.S.) Cements

High lime to silica ratio (5:2 in Portland cement).

Has higher proportion of tricalciumsilicate thus, harden more quickly and with greater evolution of heat.

Gypsum is not added.

Cement is grinded more finely.

These have only 5 minutes initial and 30 minutes final setting times.

White Portland Cement

- Similar to ordinary Portland cement except for its high degree of whiteness.
- Amount of chromium, manganese and iron is minimized as far as possible. Cr_2O_3 is kept below 0.003%, Mn_2O_3 is kept below 0.03%, and Fe_2O_3 is kept below 0.35% in the clinker.
- It is used in combination with white aggregates to produce white concrete for prestige construction projects and decorative work.

Water-Proof Cement

Obtained by adding water-proofing substances like calcium stearate, aluminium stearate and gypsum with tannic acid, to Portland cement during grinding.

Its function are: to make concrete impervious to water under pressure and to resist the absorption of water.

Chemically inactive substances added are calcium and aluminium soaps, resins, vegetable oils, waxes, coal-tar residues and bitumen. These act as pore-blocking agents.

Barium and Strontium Cements

These are obtained by replacing calcium with barium or strontium.

These are resistant to penetration by radioactivity. Thus they are used in concrete shields for atomic piles.

Concrete

- Concrete is a construction material composed of cement, fine aggregates (sand) and coarse aggregates mixed with water which hardens with time.
- Admixtures are added to modify the cure rate or properties of the material. e.g recycled materials like fly ash, blast furnace slag, silica fume or chemicals.
- Accelerators, air-entraining agents, corrosion inhibitor, plasticizers, etc.

- Curing of Concrete:
- 1. To create gels and crystals
- 2. To develop strength
- 3. To take away heat of hydration
- 4. To prevent cracking
- The process of maintaining a satisfactory moisture content and favourable temperature in concrete during the period immediately following placement, so that hydration of the cement may continue, until the desired properties are developed to a sufficient degree to meet the requirement of the service.

Reinforced Cement Concrete/ RCC

RCC is concrete that contains steel bars, called reinforcement bars.

Concrete is very strong in compression, easy to produce at site, and inexpensive, and steel is very strong in tension.

To make reinforced concrete, one first makes a mould, called *formwork*, that will contain the liquid concrete and give it the form and shape we need.

Then places in the steel reinforcement bars, and ties them in place using wire.

The tied steel is called a *reinforcement cage*, because it is shaped like one.

Pour in the liquid concrete into the formwork till exactly the right level is reached.



- Advantages:
- 1. Easier to make and cast into desired shapes, to bear all types of loads.
- 2. Possesses greater rigidity, moisture and fire-resistance
- 3. Distribute smaller cracks to prevent bigger cracks appearing
- 4. negligible maintenance cost