Local Chemical Industries:

Cement Production

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CEMENT

Reference: Shreve's Book Ch. 10, pp. 171-186

Definition

- Cement is a crystalline compound of calcium silicates and other calcium compounds having hydraulic properties" (Macfadyen, 2006).

- Cements are considered hydraulic because of their ability to set and harden under or with excess water through the hydration of the cement's chemical compounds or minerals.

History

- Lime and clay have been used as cementing material on constructions through many centuries.

- Romans are commonly given the credit for the development of hydraulic cement, the most significant incorporation of the Roman's was the use of pozzolan-lime cement by mixing volcanic ash with lime.

- In 1824 Joseph Aspdin from England invented the Portland cement

Types of Cements

1. **Pozzolan cement**

   Called Roman. It is made by mixing volcanic ash with lime.

   Pozzolan (material which is not cementitious in it self but which becomes so upon admixture with lime).

   Natural pozzolans (volcanic tuff)

   Artificial pozzolan(fly ash)

Types of Cements

2. Portland cement

Artificial cement. Made by the mixing clinker with gypsum.

Types of Cements

3. Masonry cements

Portland cement where other materials have been added primarily to impart plasticity.

(calcium stearate, petroleum and high-colloidal clays)

- plasticity, also known as plastic deformation, is the ability of a solid material to undergo permanent deformation, a non-reversible change of shape in response to applied forces.

Types of Cements

4. High Alumina cement (Calcium Aluminate Cement)

Is obtained by melting mixture of bauxite and lime and grinding with the clinker.

Used for refractory applications (such as cementing furnace bricks) and certain applications where rapid hardening is required. It is more expensive than portland.

Types of Cements

5. Special or corrosion resistance cement :

Used for fabrication and corrosion proof linings for chemical equipment such as brick-lined reactors, storage tanks, absorption towers.

Types of Cements

6. Controlled cement

Prevents shrinking and cracking upon setting. Combining 10 to 20% calcium sulfoaluminate (from bauxite, gypsum and limestone) with portland cement.

Clinker

- Clinker consisting essentially of hydraulic calcium silicates, usually containing one or more of the forms of calcium sulfate as an additives .
- **Clinker compounds**

Formula	Name	Abbreviation
$2\,CaO.SiO_2$	Dicalcium Silicate	C_2S
$3CaO.SiO_2$	Tricalcium Silicate	C_3S
$3CaO.Al_2O_3$	Tricalcium Aluminate	C_3A
$4CaO.Al_2O_3\,.\,Fe_2O_3$	Tetracalcium Aluminoferrite	C_4AF

Types of Portland Cement

1. Ordinary Portland Cement (OPC)

Is the most widely used type of cement which is suitable for all general concrete construction.

- Other types of this cement White (contains less or no ferric oxide or manganese, the substances that give conventional cement its gray color).

Types of Portland Cement

2. Moderate –heat- of hydrating and sulfate resisting Portland cement

used where moderate heat of hydration is required, or for concrete construction exposed to moderate sulfate action.

Types of Portland Cement

3. High-early-Strength (HES)

Quick setting cement (attains high strength in early days, it is used in concrete where formworks are removed at an early stage.

contains higher lime to silica ratio, finer particles, and higher proportion of tricalcium silicate (C_3S) than type I → quicker hardening and faster evolution of heat, used for roads for faster put into service.

Types of Portland Cement

4. Low Heat Cement

Prepared by maintaining the percentage of tricalcium aluminate below 6% by increasing the proportion of C_2S. This makes the concrete to produce low heat of hydration and thus is used in mass concrete construction like gravity dams, as the low heat of hydration prevents the cracking of concrete due to heat.

Types of Portland Cement

5. Sulphate Resisting Cement

used to reduce the risk of sulphate attack on concrete and thus is used in construction of foundations where soil has high sulphate content. This cement has lower content of C_3A and higher content of C_4AF.

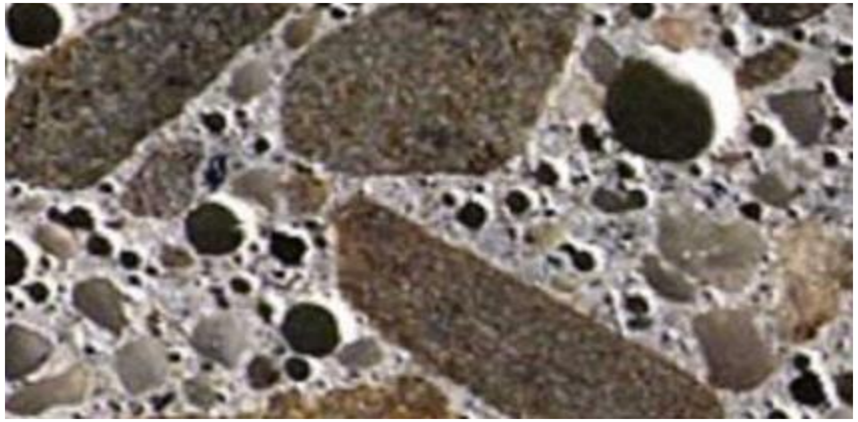
used in construction exposed to severe sulphate action by water and soil in places like canals linings, culverts, retaining walls, siphons etc.

Types of Portland Cement

6. Air Entraining Cement

Air entraining cement is produced by adding air entraining agents such as resins, glues, sodium salts of sulphates etc. during the grinding of clinker.

This type of cement is especially suited to improve the workability with smaller water cement ratio and to improve frost resistance of concrete.



Abbreviations Used in Cement Industry

$CaO = C$	$MgO = M$	$CO_2 = \bar{C}$
$SiO_2 = S$	$SO_3 = \bar{S}$	$H_2O = H$
$Al_2O_3 = A$	$Na_2O = N$	
$Fe_2O_3 = F$	$K_2O = K$	

$$\mathbf{Ca_3SiO_5 = 3CaO.SiO_2 = C_3S}$$

Portland Cement Manufacturing

Preparation of Raw materials

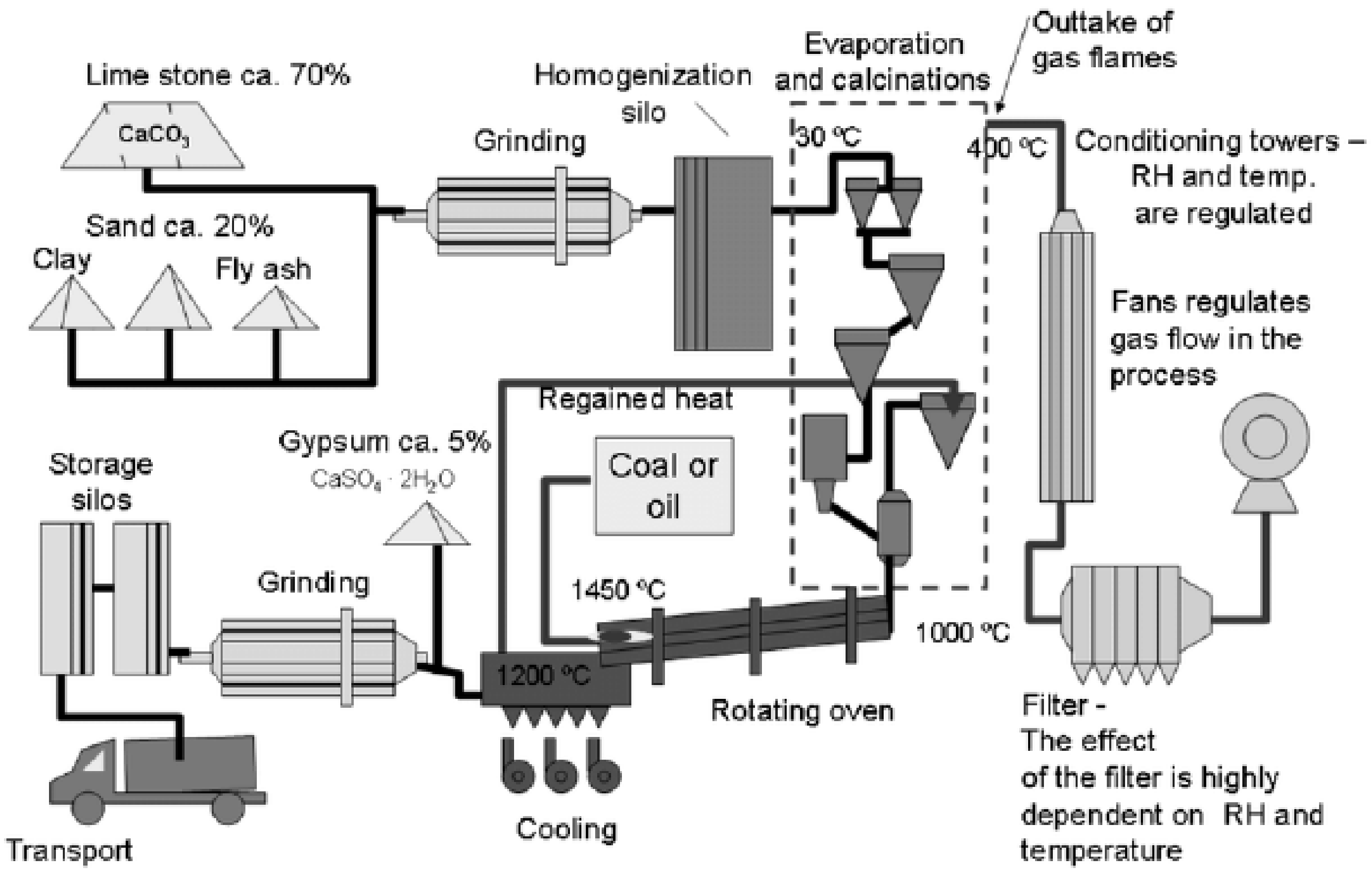
- **Grinding & Mixing**

Burning in a Kiln

- **Forming Cement Clinker**

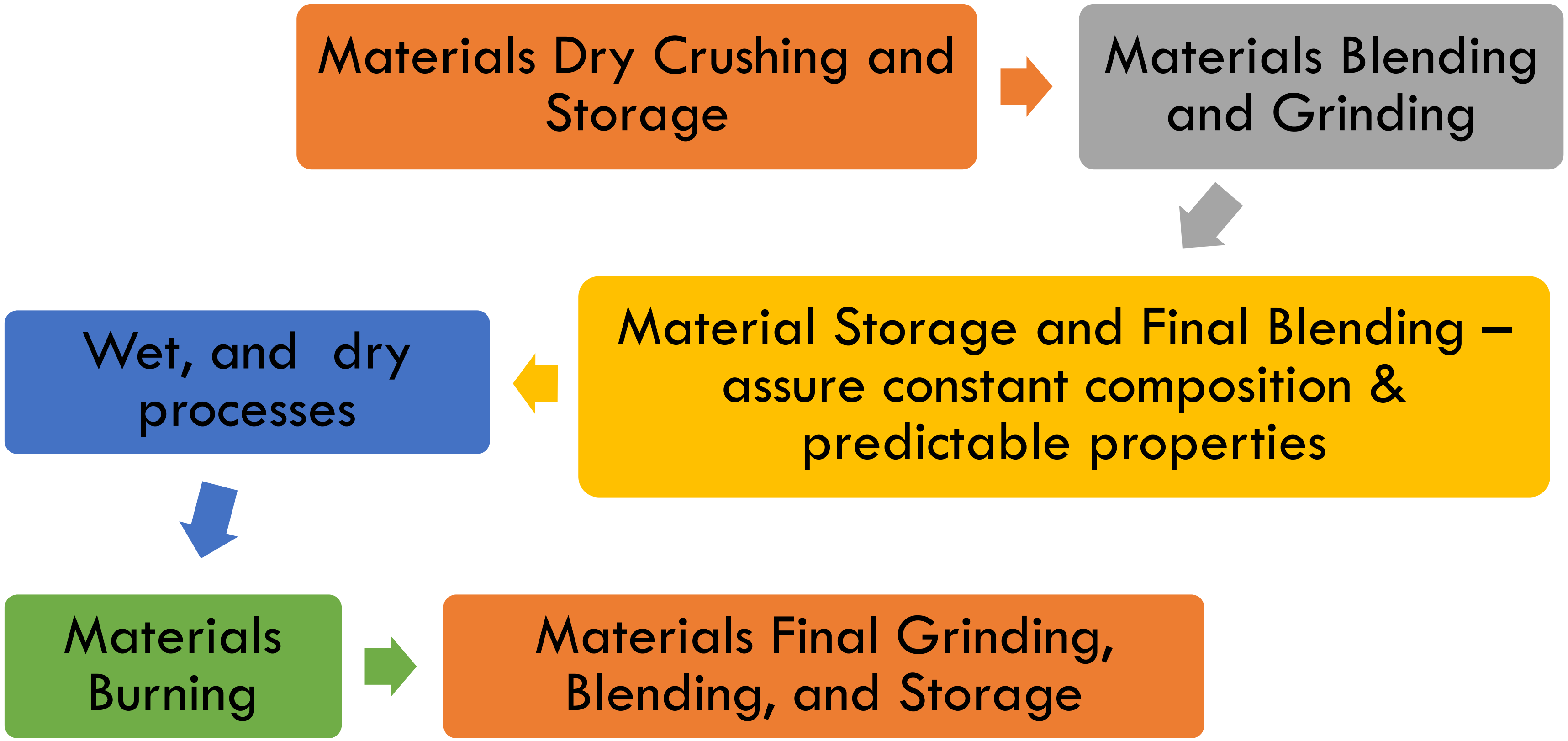
Final Processing

Quality Control



1: Simplified schematic flow chart of the dry process of manufacturing of Portland cement (after (Johannesson, 2012)).

Portland Cement Manufacturing



Raw Materials

Two Types of Materials

- Calcareous — Rich in Calcium
  - Limestone
  - Chalk
- Argillaceous — Rich in Silica
  - Clay

Gypsum (4 to 5%) is added to regulate the setting time of the cement.

Raw Materials

- Limestone (calcium carbonate) is a common source of calcium oxide.
- Iron-bearing aluminosilicates are the most common source of silica.
- Aluminum and iron oxides act as fluxing agents i.e. lower fusion temperature of part of the raw mix to a practical firing temperature

Clinker Formation and Compounds

Raw materials

(limestone, clays, additives)

→

High temperature clinker formation reactions in a kiln

- Water evaporation
- CO_2 evolution
- Reaction between lime & clay

↓

Clinker

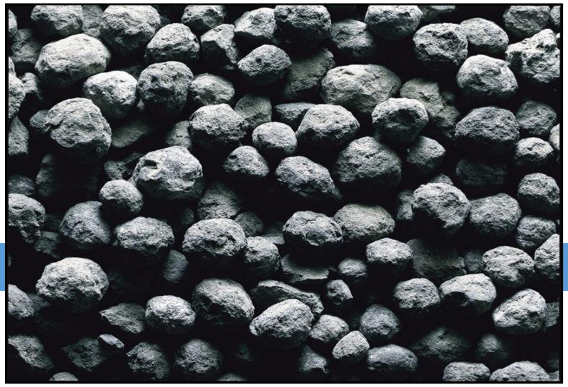
The main reactions in clinker formation are as follows:

1. $CaCO_3 \rightarrow CaO + CO_2$
2. $2CaO + SiO_2 \rightarrow C_2S$ $(2CaO*SiO_2)$
3. $3CaO + Al_2O_3 \rightarrow C_3A$ $(3CaO*Al_2O_3)$
4. $4CaO + Al_2O_3 + Fe_2O_3 \rightarrow C_4AF$ $(4CaO*Al_2O_3*Fe_2O_3)$
5. $CaO + C_2S \rightarrow C_3S$ $(3CaO*SiO_2)$

Burning Process

- Sintering (become a coherent mass with no melting)
- Fusion (complete melting)
- Clinkering – only about ¼ of the charge is in the liquid state

Clinker



- Hard black or greenish black granular masses that are from 3 to 20 mm in size.
- Clinker is pulverized and finely ground in tube ball mills, and automatically packaged.
- During fine grinding, the following may be added:
  - Gypsum, plaster, and calcium lignosulfonate
  - Air-entraining, dispersing, and waterproofing agents

Clinker

Clinker

Gypsum

- Gypsum absorbs water and prevents setting of C_3A during shipment

Mining, Transporting and Crushing

- **Limestone and clay.**

- Limestone and clay are mined from the quarry by blasting explosives.

- Transported from the mining area to the process plant.

- Fed into a primary hopper to the primary crusher (Jaw Crusher).

- The crushed material pieces are discharged to the vibrating screen.

- The muddy material particles are removed by the vibratory screen action and is conveyed and rejected with the help of belt conveyor.

Mining, Transporting and Crushing

- The belt conveyor conveys the mud free material to the Intermediate hopper.

-The material from the Intermediate hopper is fed into the belt conveyor and is fed to the Secondary Crusher for further size reduction.

- The crushed material is discharged to the belt conveyor and the same is conveyed to the loading bunker.

-A lot of dust particles are also produced while crushing and discharging limestone.

- To prevent the dust pollution, bag filters are employed in the discharge points of the Primary and Secondary crushers.

Mining, Transporting and Crushing

- The collected dust particles are retrieved with the help of a compressed air purging.
- Electronic sequential timer panel and solenoid valves are used for air purging to be done in a sequential manner.

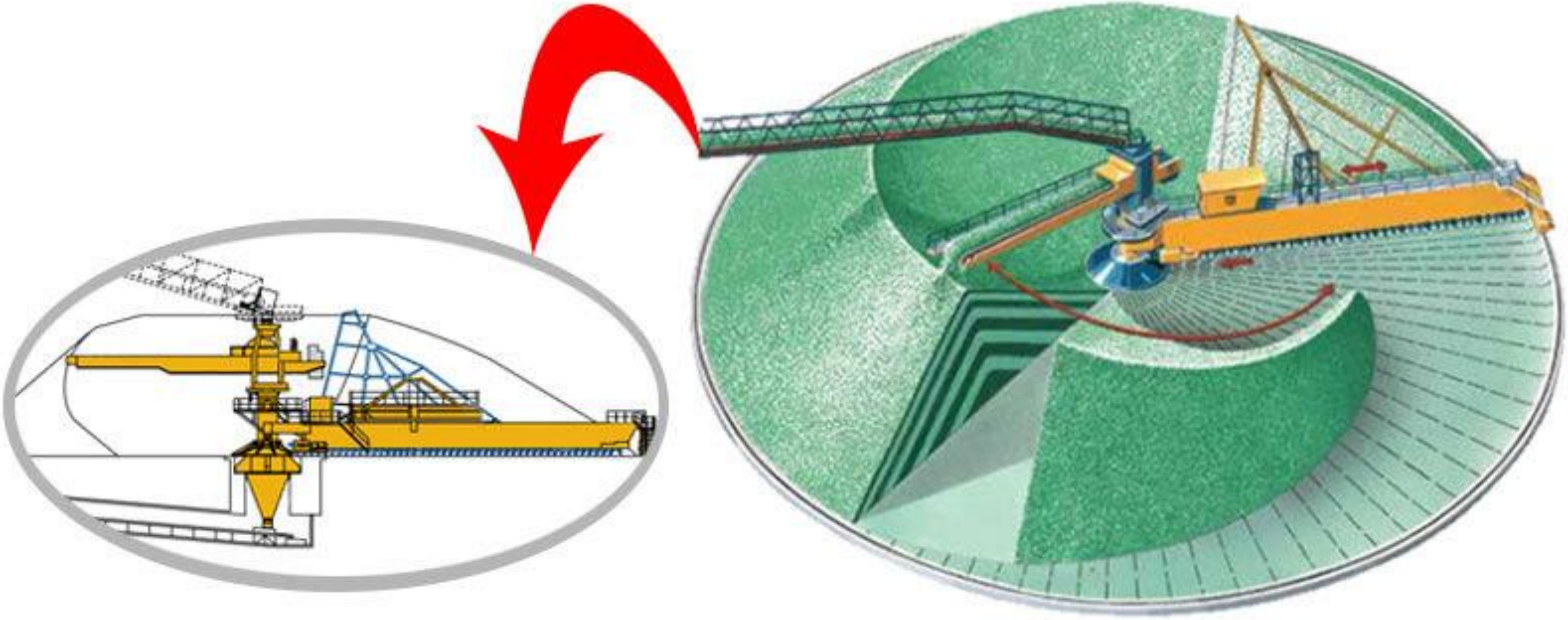
Jaw Crusher

Bag Filter

Stacker and Reclaimer Pre-homogenisation

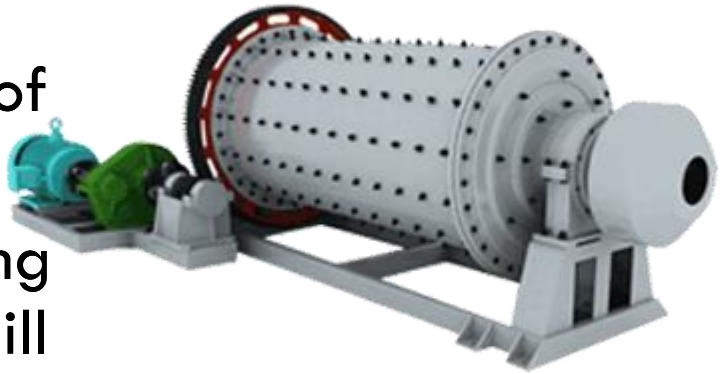
- https://www.youtube.com/watch?v=mzXB_7m1Ang
- The property of the mined limestone may vary day by day so the limestone is stocked in the stocker in a circular manner, layer by layer every day.
- Limestone from the unloading hopper is extracted and conveyed to the stacker with the help of a vibrating feeder and belt conveyors.
- This material is dropped on the table feeder at the top of stacker and then to the Boom conveyor.
- The stacker and the boom conveyor are capable to move 360 degree.

Stacker and Reclaimer



Raw Material Grinding and Storage

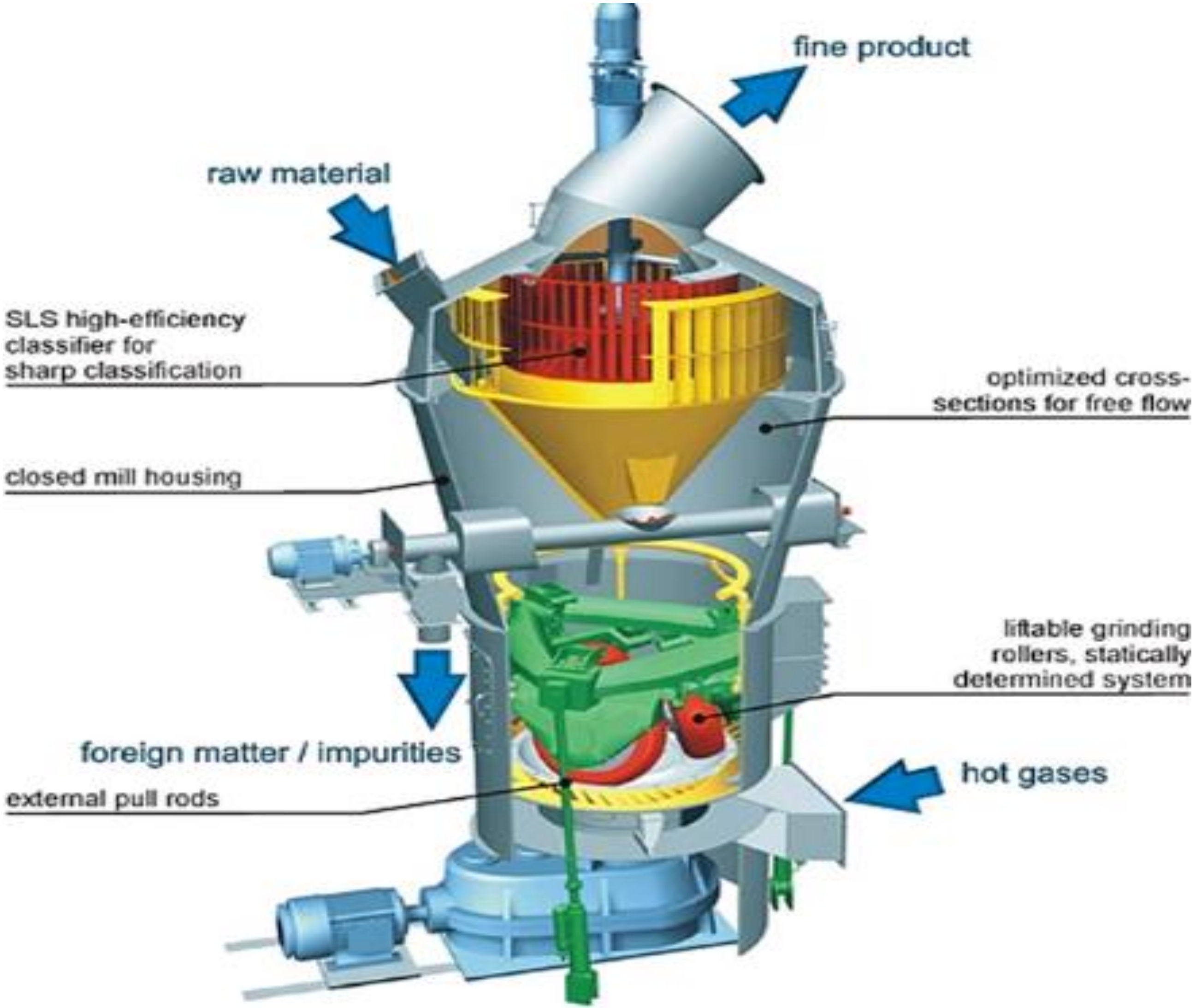
- Material from the limestone and additive hoppers are fed to respective weigh feeders which weigh and feed the material as per the set ratio and quantity.
- Then fed to the raw mill inlet with the help of belt conveyors.
- Two types of Raw Mills are used for grinding raw material (ball mill and vertical roller mill (VRM)).
- The ball mill combines the drying, grinding and separation processes into just one unit.



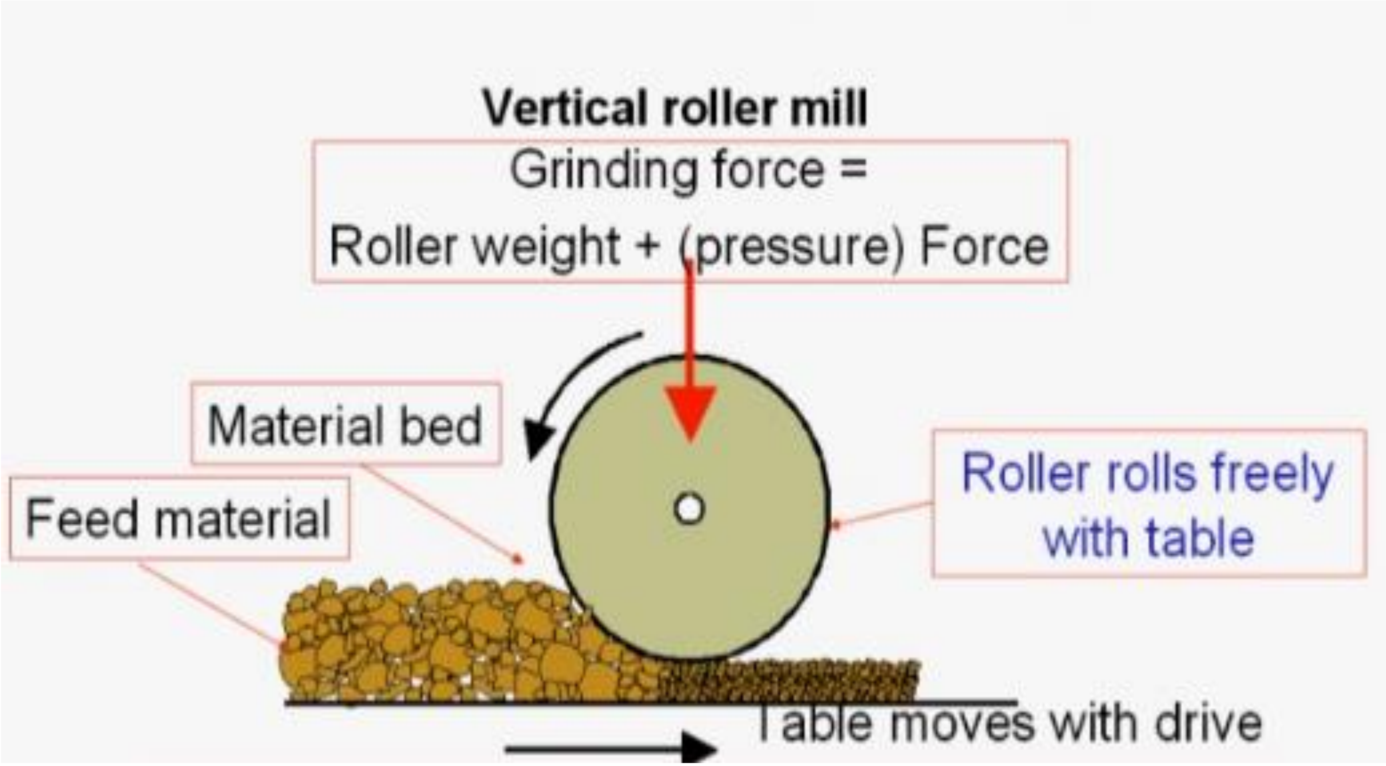
Raw Material Grinding and Storage

- In VRM, raw material from the feed mouth fells into the center of millstone, which moved to the edge of mill under the action of centrifugal force and is ground by roller (coarse powder returns to be grinded until reaching to qualified granularity).
- Qualified fine powder comes out mill with airflow, and becomes products after collection of dust collecting device.
- VRM operates at a low noise level, therefore, outdoor installation is feasible.

Vertical Roller Mill (VRM)



Vertical Roller Mill (VRM)



Raw Material Grinding and Storage

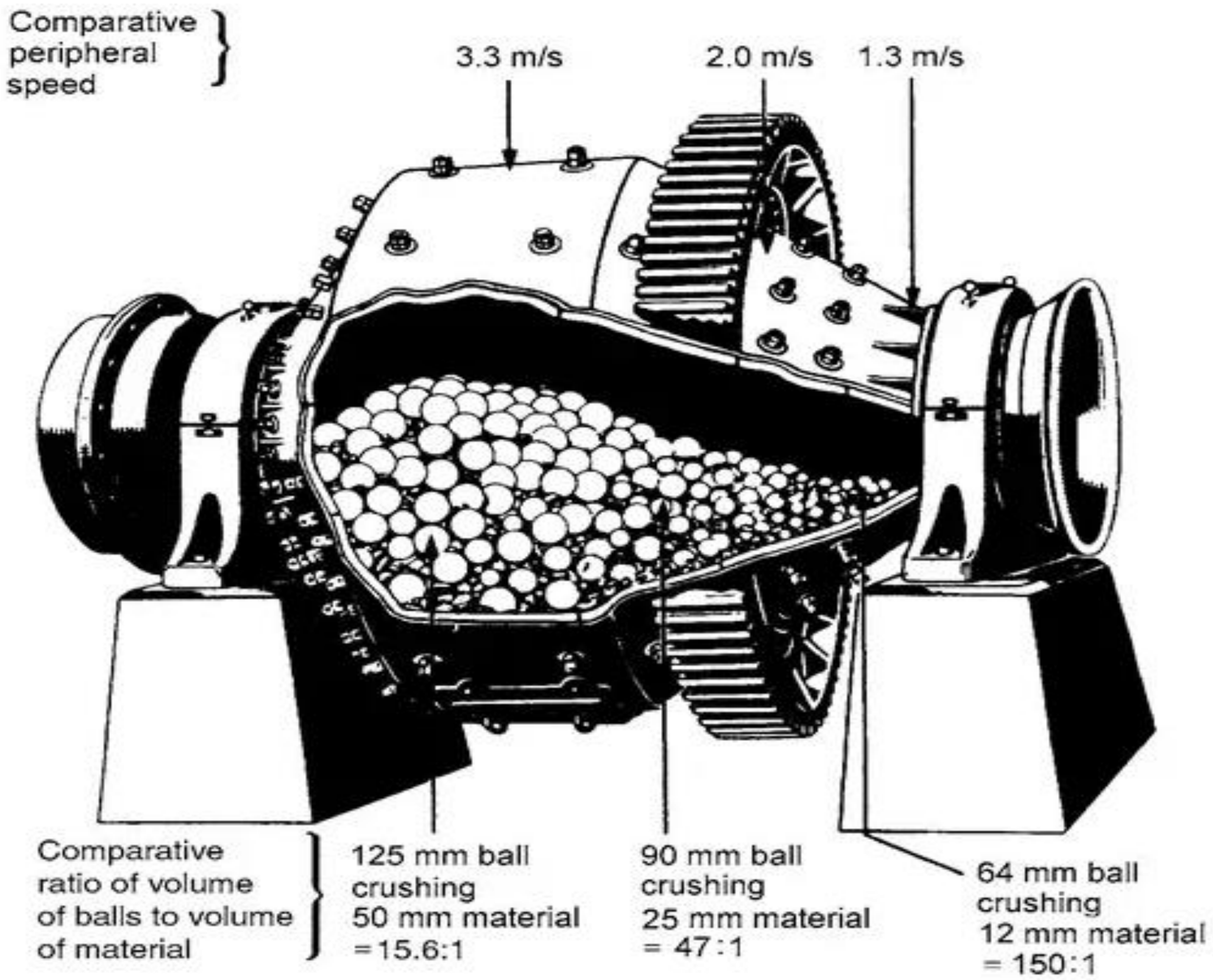
- The Ball mill consists of three chambers, one drying chambers and two grinding chambers.
- Hot gas vent out from Kiln is used in raw mill to drive out the moisture present in the raw material.
- The dried material is gradually transferred to the grinding chamber. In the grinding chamber the material is grinded with the help of grinding media balls.
- The powdered Material is discharged and conveyed to the Air Separator with the help of Air slides and bucket elevators.

Raw Material Grinding and Storage

- The Air Separator separates the powdered material into fine and coarse particles.
- The fine particles are conveyed to blending silos with the help of Air slides and belt elevators.
- The coarse particles are again fed to the other end of the mill for further grinding.
- An exhaust fan (vent fan) is used to control the material and hot gas flow inside the mill.
- A grit separator and a cyclone are employed in the suction line vent fan to collect the dust particles.

Ball Mill

Ball Mill

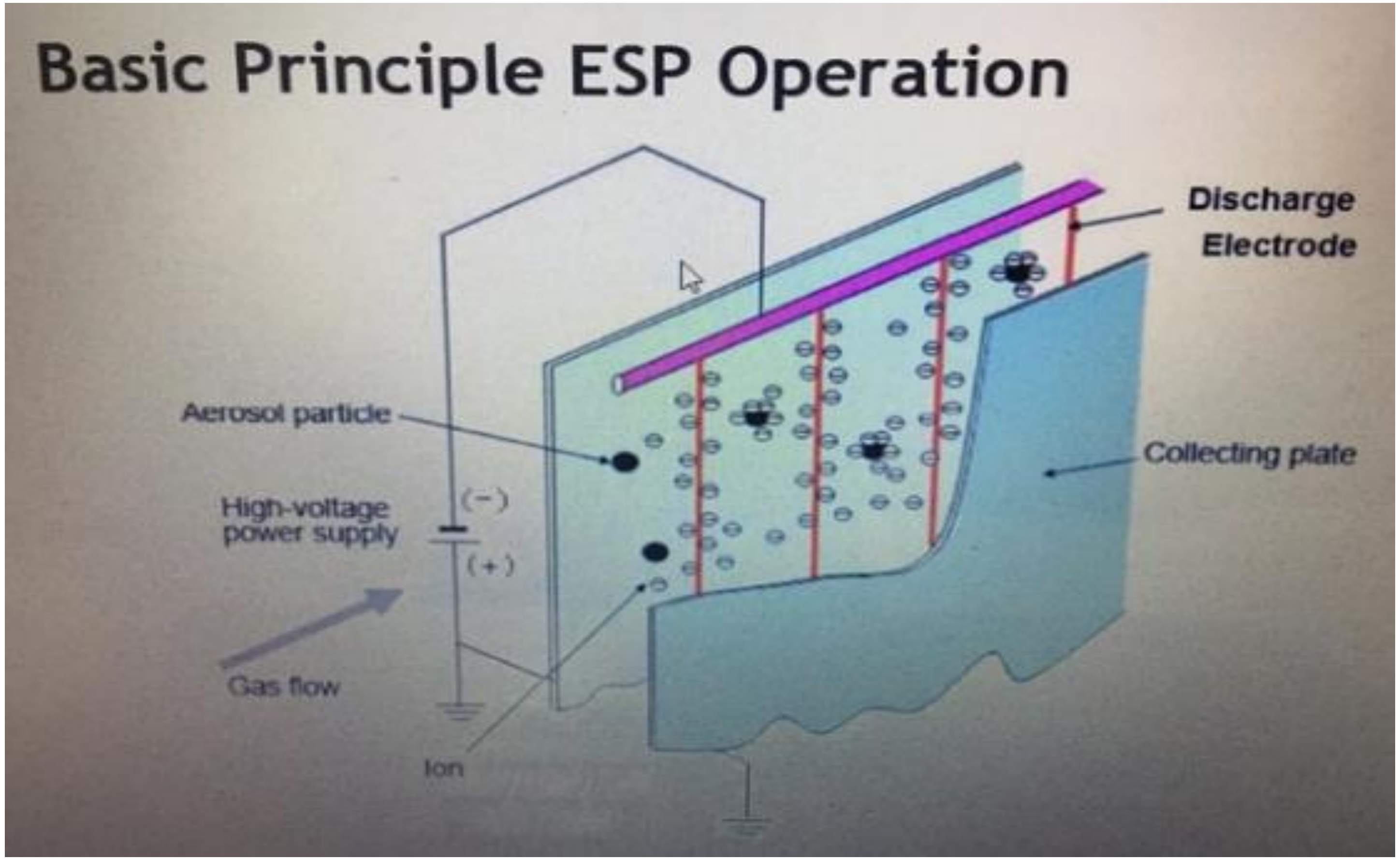

Comparative peripheral speed
3.3 m/s
2.0 m/s
1.3 m/s
Comparative ratio of volume of balls to volume of material
125 mm ball crushing 50 mm material =15.6:1
90 mm ball crushing 25 mm material = 47:1
64 mm ball crushing 12 mm material = 150:1

Raw Material Grinding and Storage

- The collected dust is fed back to the process. The outlet gas of the vent fan is fed to electro static precipitator (ESP).
- The outlet gas from the fan contains large amount of fine particles of raw material, Inside the ESP, electrodes of positive and negative potentials are arranged by applying high voltage direct current.
- The strong electrical fields in the ESP ionize the gas passing through it.
- The positive ionized particles are attracted and collected in the negative ionized electrodes and the negative air is vented out to the atmosphere.
- The collected fine powder is retrieved with the help of rapping mechanism and the same is fed to the process.

Electro Static Precipitator

Electro Static Precipitator



Blending and Storage

- After filling the powdered materials from raw mill to a certain level in the blending silos, this materials is blended for 2 to 3 hours with compressed air.
- After blending, the material sample is collected and analyzed in the laboratory. If the composition of the filled material is not appropriate, the required quantity of corrected material is again filled to the blending silo after changing the ratio to the raw mill.
- Again the material is blended for 2 to 3 hours and the sample is analyses in the laboratory.
- After correcting the composition, the material is dropped to the

  bottom part of the silo. The bottom part of the silo is called storage silo.

Kiln Feed Section

- The material from the storage silo is extracted, and the same is fed to the weighing hopper by using air slides and bucket elevators.
- The material flow to the weighing hopper is controlled with a variable speed rotary feeder.
- If the set quantity of material is filled in the hopper, the rotary feeder stops feeding.
- The balance material is fed to the overflow hopper and back to the process.
- The material from the weighing hopper is fed to the electronic weigh feeder and the same is conveyed to the preheater

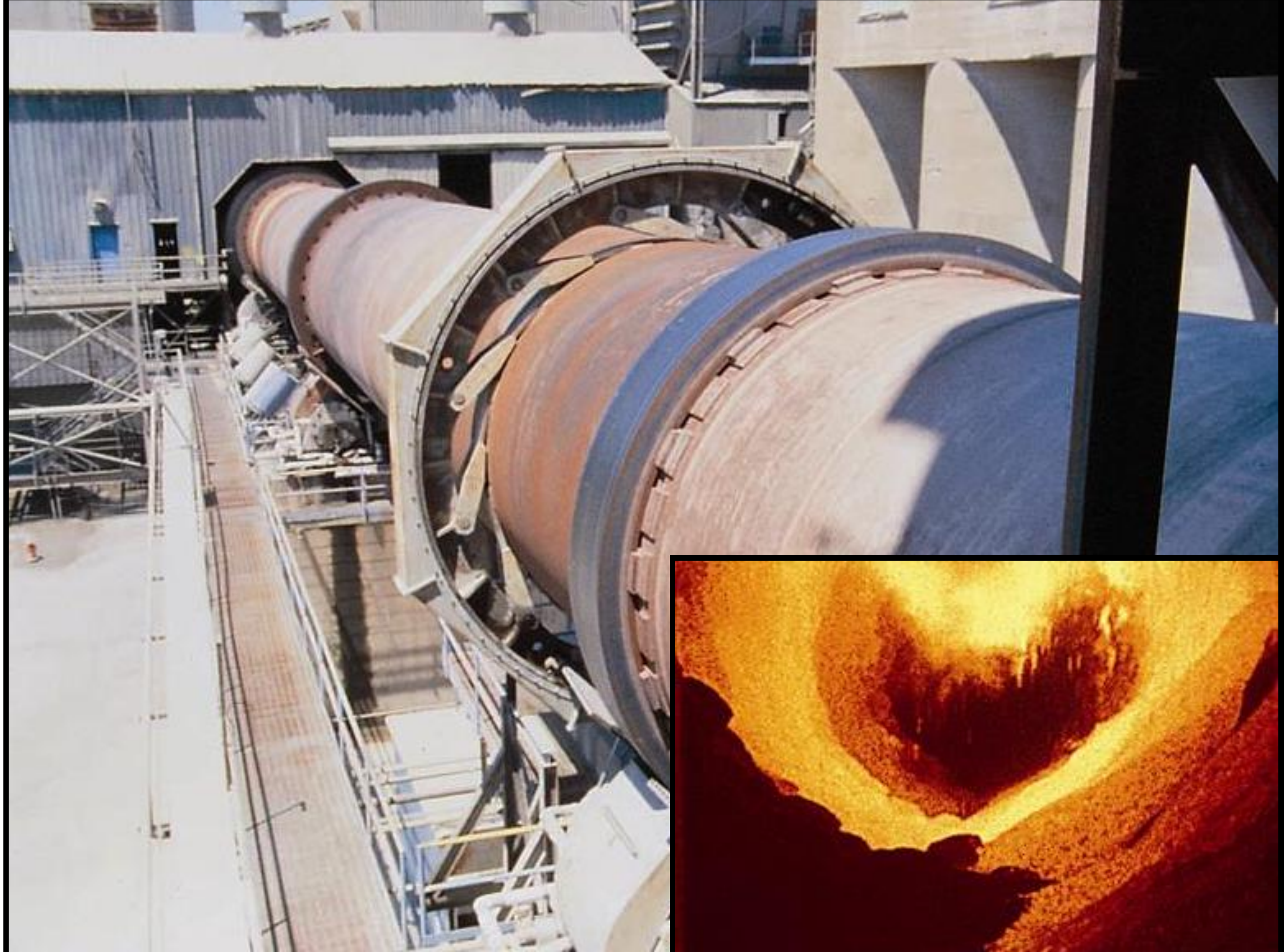
  top with the help of air slides and belt bucket elevators or pneumatic pumps.

Kiln

- Long steel (a hollow cylinder).
- Lined with refractory brick (high-alumina and high-magnesia bricks)
- Slightly inclined, so that material fed in at the upper end travel slowly through to the lower firing end, taking from 1 to 3 hours.
- Rotating at 60 to 200 rev/h (½ – 2 rpm)
- Typically 2.5 – 6 m in diameter and 120 – 180 m long

Kiln

Kiln



Reactions during Clinker Formation in Kiln

- Evaporation of free water (endothermic): 100 °C
- Evolution of combined water from clay (endothermic): 500°C and above
- Calcination: 600 to 1100 °C
  - Clay decomposes (600 °C)
  - Limestone decomposes (700 °C) → CO_2 driven off, calcination of carbon dioxide (CO_2) to form (CaO) (endothermic)

    Limestone → Lime + Carbon Dioxide
  - This oxide reacts with silica, alumina and iron oxide to form initial compounds (1000 °C) (exothermic)

$$\text{Clay (Silica \& Alumina)} + \text{Lime} \xrightarrow[\text{kiln burning zone}]{\text{solid state}} \text{Calcium Aluminate}$$

Reactions during Clinker Formation in Kiln

  - Initial formation of C_2S (1200 °C), formation of calcium aluminates and Ferrites
  - Formation of melt (flux compounds melt)(liquid formation) (1350 °C) (endothermic)
- Clinkering – charge temperature is 1400 to 1600°C: Formation of C_3S
- Cooling: The discharge end of the Kiln is connected to the Air cooler, rate of cooling significantly affects the reactivity of the final cement.

Exit Gas from Kiln

- The Kiln is heated by pulverized coal which imparts the thermal energy for this entire process.
- Some part of the exit hot gas from the preheater is diverted back to the raw mill for drying the raw material.
- The balance part of the hot gas is venting out to the atmosphere.
- This gas contains lot of fine material and has a temperature around 400°C.

Exit Gas from Kiln

- To prevent the dust pollution, an ESP or bag house is employed. After cooling, the hot and dusty gas in Gas Conditioning Tower (GCT) is allowed to pass through the ESP or bag house to collect the dust particles.

Clinker Cooler

- The hot clinker from the Kiln is cooled with the help of atmospheric air in the cooler.
- Inside the cooler, fixed and movable rows of plate with holes are arranged.
- The movements of the cooler plates are carried out by two variable speed DC drives.
- The atmospheric air is blows(by a fan) through the holes of the cooler plates, and cools the hot clinker accumulated over the plates.

Clinker Cooler

- The movements of the cooler plates pushes material to the discharge end.

- The cooled clinker is discharged to the Deep Bucket Conveyor (DBC) after breaking (if big size is present) with the help of clinker breaker.

- The DBC conveyed the cooled clinker to the clinker stockpile.

Clinker Cooler

- Part of the air, used to cool the clinker is used as secondary air for burning the coal inside the Kiln.

- Another part of the air is used to dry coal in the coal mill.

Clinker Cooler

Clinker Cooler

Cement Grinding and Storage

- Clinker from the stockpile is extracted and stored in the clinker hopper near the cement mill.
- Gypsum is extracted from the stockyards and is stored in the hoppers.
- The respective material of required ratio and quantity is fed into the mill from the hoppers using electronic weigh feeders and belt conveyors.
- This material is ground inside the cement mill using the grinding media balls.
- The ground powder is discharged through the mill outlet and is fed to the belt elevator.

Cement Grinding and Storage

- A variable speed separator and recirculating fan is used to separate the coarse and fine material.
- The fine powder is conveyed to cement silos by using air slides and belt elevators/pneumatic pumps whereas the coarse material is again fed to the cement mill inlet for further grinding.
- Fine powder (cement) and stored in storage bins, cement silos, or bagged.
- Cement is packed in 50 kg bags and should be stored on pallets in a dry place.

Cement Silos

- The **cement silo** allows the product to be stored in bulk, keeping costs to a minimum.

- Storage **silos** are cylindrical structures, typically (3 to 27 m) in diameter and (10 to 90 m).

- In most **silos**, gravity causes grain to flow from the top of the **silo** and out through an opening at the bottom near the center.

Cement Silo

Types of Processes

Wet Process

Dry Process

- In both processes closed-circuit grinding is preferred than open-circuit grinding in preparing raw material.
- Why wet process is replaced by dry process, especially for new plants?

Wet Process

- Wet process could be selected as manufacturing technology is when raw materials have natural high moisture content.
- The amount of moisture in mineral sometimes can be even more than 12% as in case of chalk.
- The fuel and power consumption is higher than dry process.

Wet Process

- Raw materials are homogenized by crushing, grinding and blending .
- The mix is turned into form of slurry by adding 30 – 40% of water.
- It is then heated to about 1500 °C in horizontal revolving kilns.
- Natural gas, petroleum or coal are used for burning. High fuel requirement make it uneconomical compared to dry process.

Wet process is obsolete

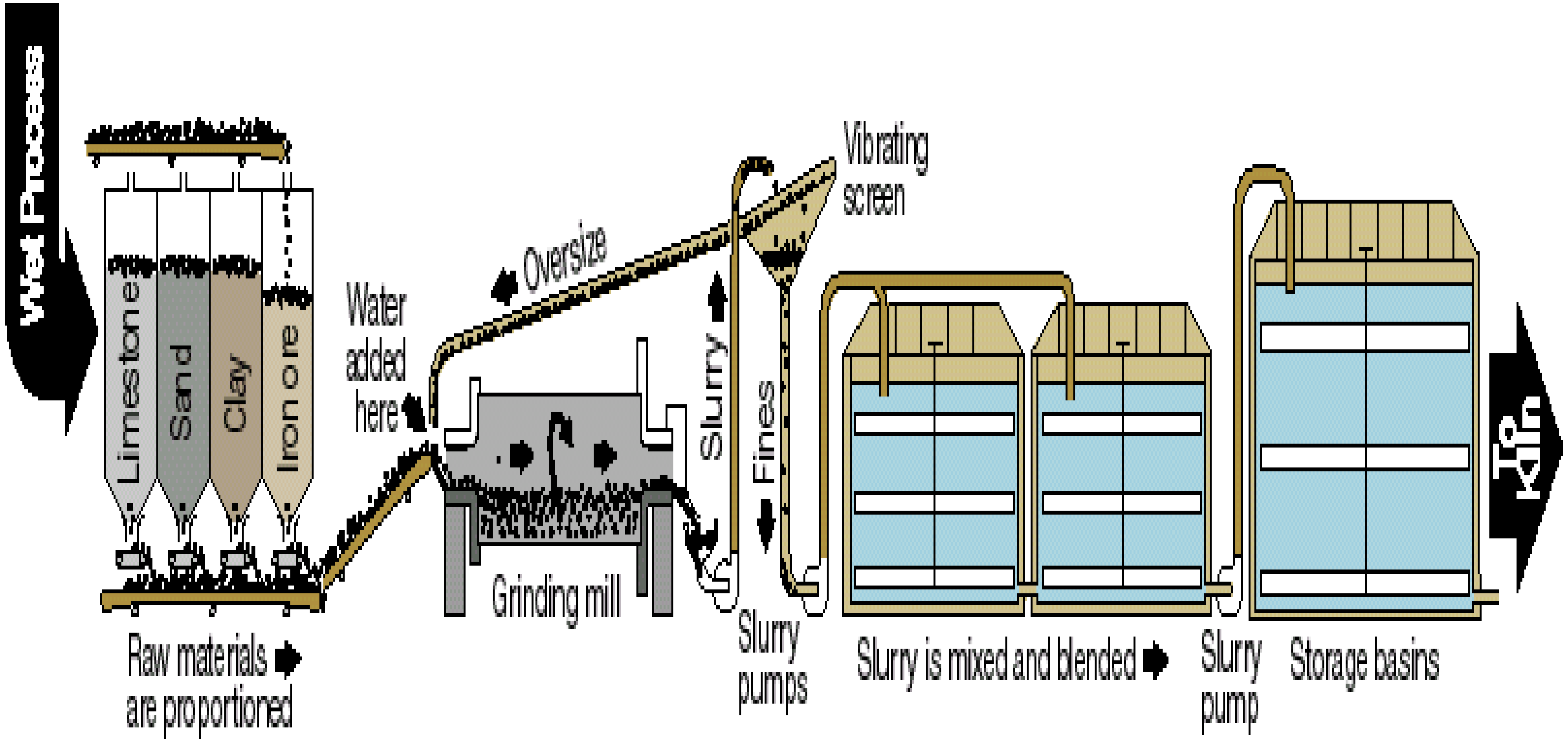
Dry Process

- Raw materials are homogenized by crushing, grinding and blending.

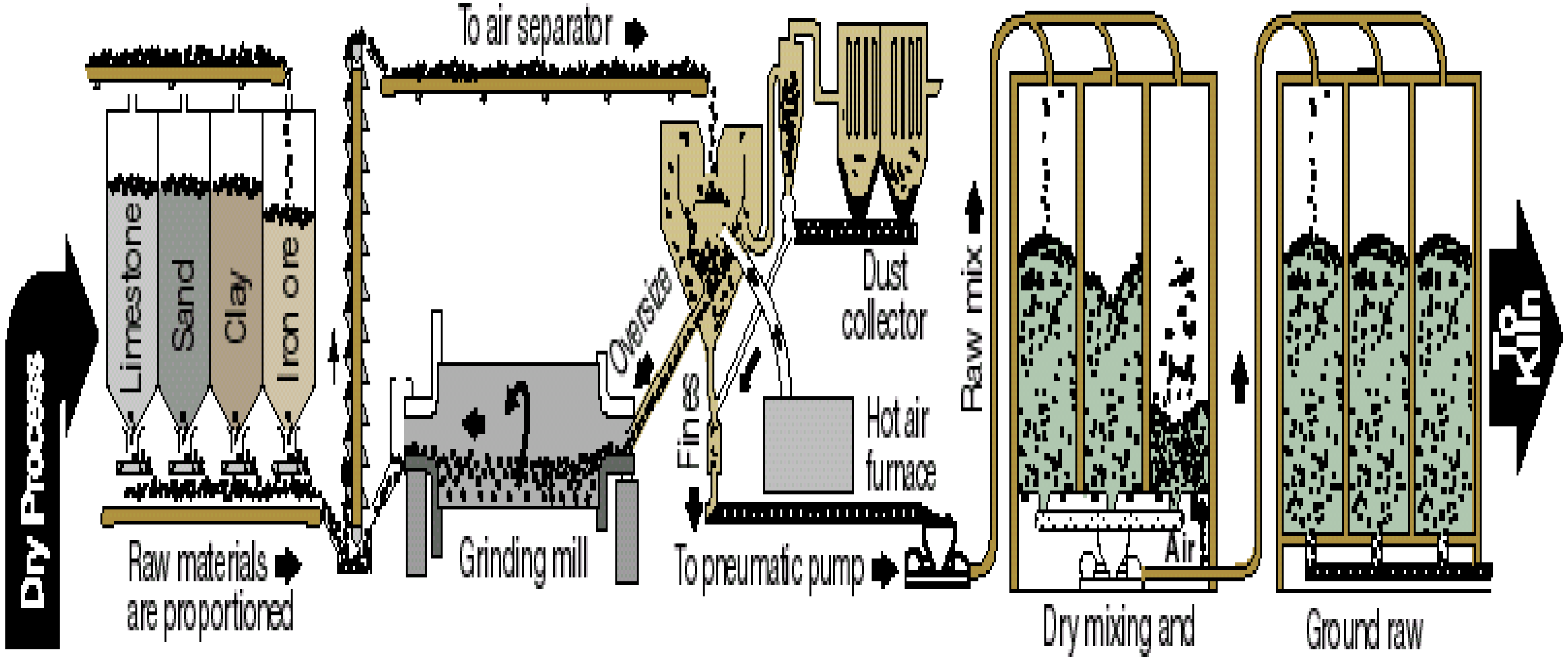
- Mixture is fed into kiln and burned in a dry state.

- This process provides considerable savings in fuel consumption and water usage but the process is dustier compared to wet process that is more efficient than grinding.

Wet process


Wet Process
Limestone
Sand
Clay
Iron ore
Raw materials are proportioned
Water added here
Oversize
Grinding mill
Slurry
Fines
Vibrating screen
Slurry pumps
Slurry is mixed and blended
Slurry pump
Storage basins
To kiln

Dry process



OR

Portland Cement Manufacturing

Preparation of Raw materials

- Grinding & Mixing

Burning in a Kiln

- Forming Cement Clinker

Final Processing

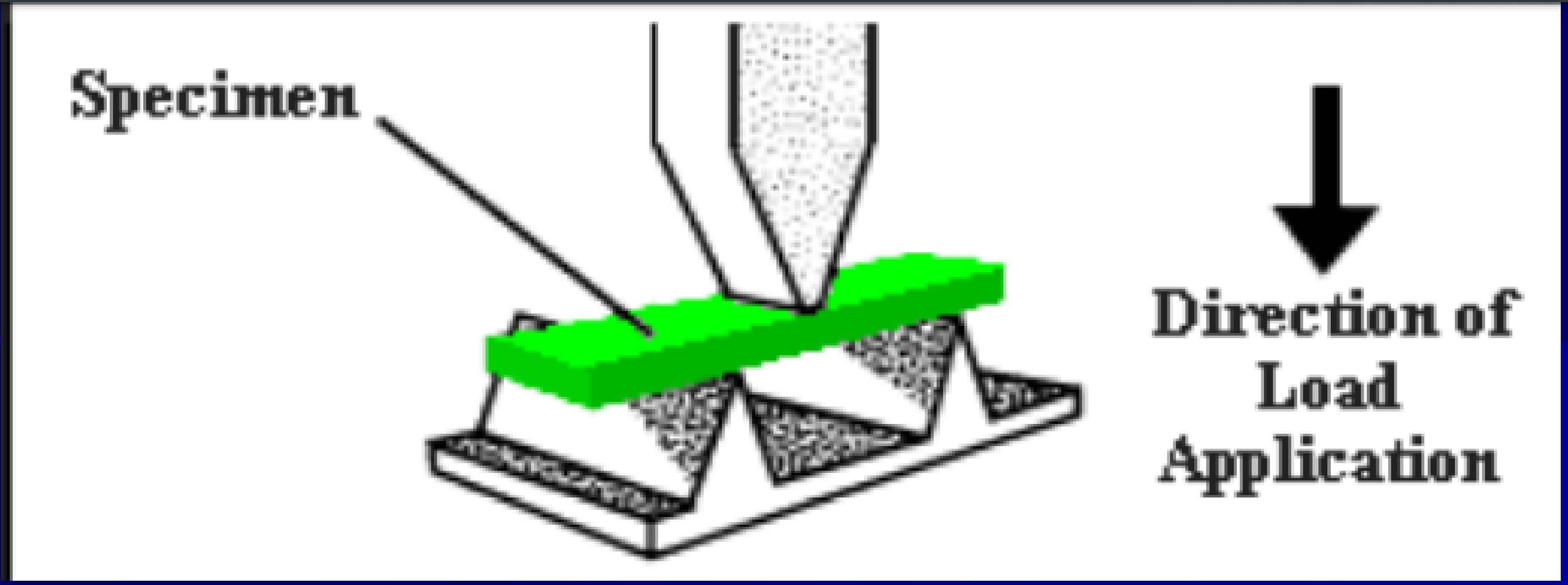
Quality Control

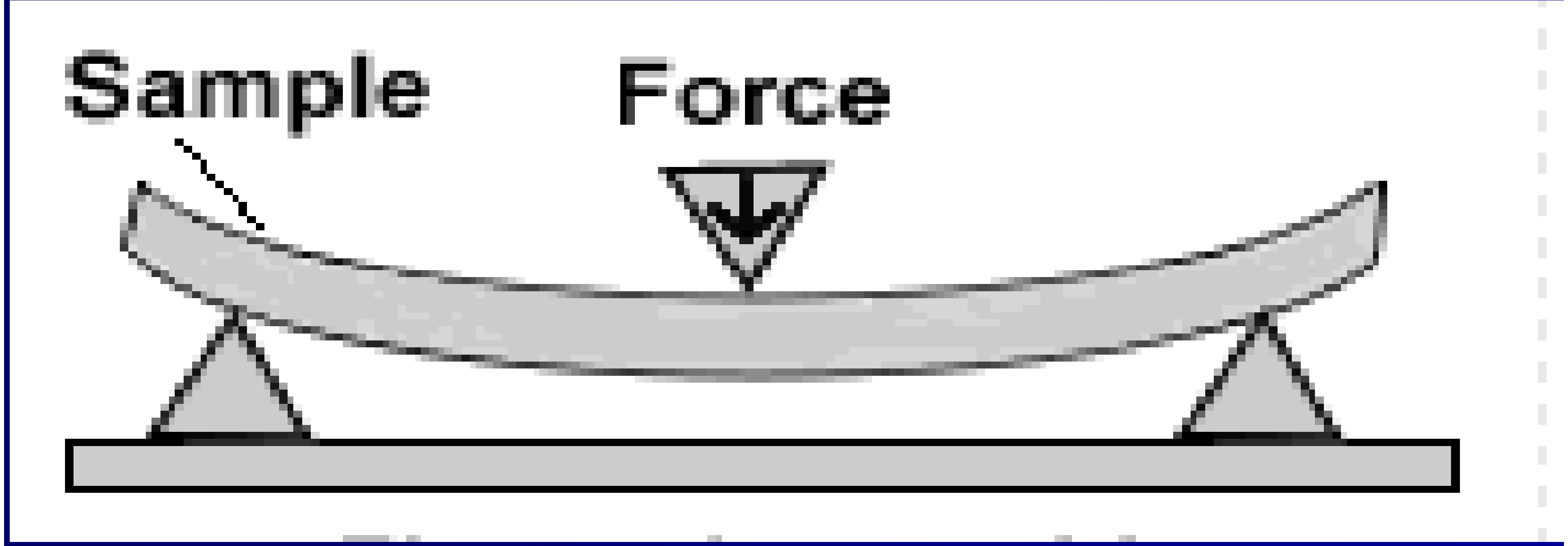
Physical properties of cement

Physical properties of cement

- **Compressive Strength**

  - Compressive strength of cement is tested by 50 mm cubes made by using standard sand and cured in a prescribed way.
  - Tested under a compression testing machine. The strength of cement varies with time, therefore in general it is reported as 3 day, 7 day or 28 day strength.


Specimen
Direction of Load Application


Sample
Force

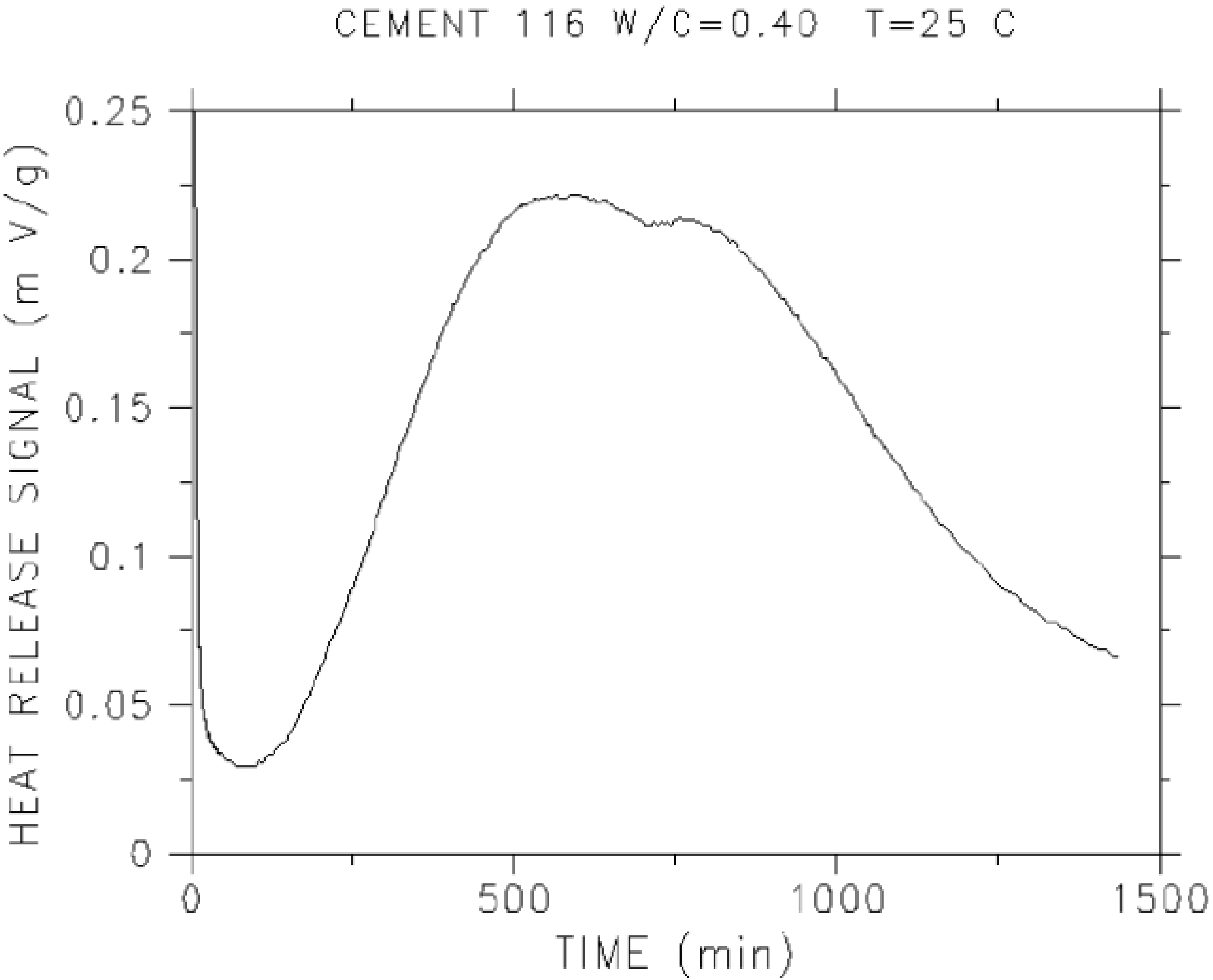
Physical properties of cement

- **Heat of Hydration**

- The heat generated during the reaction of cement and water is known as heat of hydration.

- The factors affecting heat of hydration are C_3A, C_2S. water-cement ratio. Fineness of cement and curing temperature.

- Conduction calorimeter is used to test heat of hydration.


CEMENT 116 W/C=0.40 T=25 C
HEAT RELEASE SIGNAL (m V/g)
0.25
0.2
0.15
0.1
0.05
0
0
500
1000
1500
TIME (min)

Physical properties of cement

- **Loss on Ignition**

- A cement sample of known weight is heated between 900-1000 C (1650-1830 F) until a constant weight is obtained.
- The weight loss of the sample due to heating is then determined.
- A high loss on ignition (more than 3%) indicates prehydration and carbonation, which may be due to inappropriate storage.

Physical properties of cement

- **Fineness ,or particle size**

- Particle size affects rate of hydration which is responsible for the strength gain.
- The smaller the particle size, the greater the surface area to volume ratio which means more area available for water –cement reaction per unit volume approximately 95%of cement particles are smaller then 45 micron with the average particle size about 15 micron.
- Fineness can be tested by turbidity meter test, 45 micrometer sieve and electronic particle size analyzer.

Physical properties of cement

- **Soundness**

- Soundness refers to the ability of a hardened cement paste to retain its volume after setting.
- lack of soundness is observed in the cement samples containing excessive amount of hard burnt free lime or magnesia.
- Autoclave expansion test is used to determine soundness of cement.

Physical properties of cement

- **Consistency**

- Consistency of cement paste refers to its ability to flow.
- Normal consistency pastes are required to be prepared for testing cement specimens
- A paste is said to have a normal consistency when the plunger of apparatus penetrates it by **10+1 mm**
- The corresponding water cement ratio is reported .

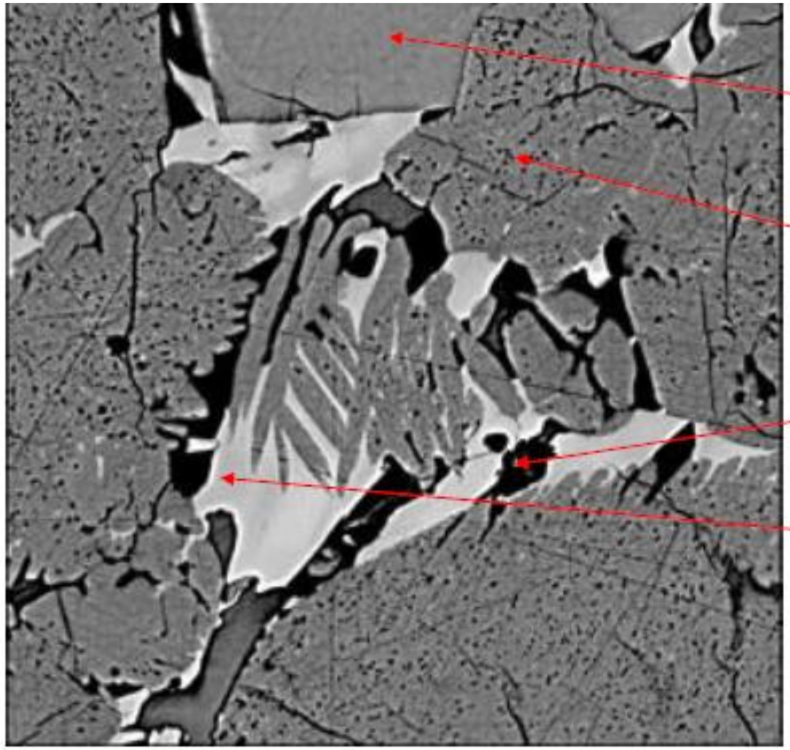
Physical properties of cement

- **Setting Time**
  - **Initial setting time** is the time that elapsed from the instance of adding water until the pastes ceases to behave as fluid or plastic.
  - It is measured as the time elapsed between the moments when water is added to the cement to the time when the square needle penetrates a depth of 33 to 35 mm from the top of the mould.
  - The initial Setting Time **should not be less than 30 minutes for Ordinary Portland Cement.**

Physical properties of cement

- **Setting Time**
  - **The time at which cement completely loses its plasticity and became hard** is a final setting time of cement.
  - The time taken by cement to gain its entire strength is a Final setting time of cement. For Ordinary Portland Cement, The Final Setting Time is 600 minutes (10hrs).

Microscopic Images of Clinker



Alite impure form of C_3S

Belite C_2S with SiO_2 and CaO

Ferrite

Aluminate

QC: Analysis of Portland Cement (%)

	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	Alkali Oxides	SO_3
	Regular Cement						
Minimum	61.17	18.58	3.86	1.53	0.60	0.66	0.82
Maximum	66.92	23.26	7.44	6.18	5.24	2.9	2.26
Average	63.85	21.08	5.79	2.86	2.47	1.4	1.73
	High-Early-Strength: High C_3S						
Minimum	62.7	18.0	4.1	1.7	-	-	2.2
Maximum	67.5	22.9	7.5	4.2	-	-	2.7
Average	64.6	19.9	6.0	2.6	-	-	2.3
	Low-Heat-of-Hardening: Lower C_3S and C_3A, Higher C_2S and C_4AF						
Minimum	59.3	21.9	3.3	1.9	-	-	1.6
Maximum	61.5	26.4	5.4	5.7	-	-	1.9
Average	60.2	23.8	4.9	4.9	-	-	1.7

Chemical analysis of cement

- SiO_2, Al_2O_3, Fe_2O_3, CaO, MgO, SO_3, K_2O, Na_2O, TiO_2, P_2O_5, Mn_2O_3, SrO, Cl and Br using X-ray fluorescence (XRF).

Environmental impact

- **Environmental impact caused by emissions into the air**

- Atoms dirt (damage to the respiratory tract)
- Sulfur Oxides (acid rain)
- NOx (can combine with hemoglobin cells to limit the ability of blood to carry oxygen)
- Carbon dioxide (greenhouse gases that cause global warming)

Environmental impact

- **Environmental impact resulting from the liquid waste**

- oils and lubricants resulting from garages and workshops

Environmental impact

- **Environmental impact resulting from the disposal of solid waste**

- Atoms dirt minute of crushing and milling operations

(lead to serious risks to the population surrounding environment in case of high proportion of these pollutants in the air)