CEMENT AND LIME

Chemical Process Technology

CHE F419

INDIAN CEMENT INDUSTRY

- India, being the second largest cement producer in the world after China with a total capacity of 210 Million Tones (MT)[*based on USGS Mineral Program Cement Report, Jan 2012].
- The cement industry in India is dominated by around 20 companies, which account for almost 70% of the total cement production in India.
- Following are the list of top 10 cement companies in India:

- ACC Limited
- Ambuja Cements Limited
- UltraTech Cement Limited
- India Cement Limited
- Shree Cement Limited
- Rain Cement Limited
- Prism Cement Limited
- Madras Cement Limite
- Birla Cement Limited
- JK Cement Limited

CEMENT

Cement : It is the generic name for powdered materials which initially have plastic flow when mixed with water or other liquid, but forms a solid structure in several hours with varying degree of strength and bonding properties which continues to improve with age.

Constituents of cement

Chemical formula	**Type**	**Code**	**Property**
$2CaO.SiO_2$ $3CaO.SiO_2$	Silicate	C_2S C_3S	Provides strength High heat of hydration
$3CaO.Al_2O_3$ $4CaO.Al_2O_3.Fe_2O_3$	Aluminate	C_3A C_4AF	Superior resistance to sea and sulfate water
$Ca(OH)_2$	Hydroxide	-	Low strength

TYPES OF CEMENT

Depending on the type of constituent the cement can be classified as –

1. **Portland –** Major having silicates, eg. C_2S; C_3S
2. **High alumina –** Major having aluminates , C_3A, C_4AF
3. **Hydraulic hydrated lime** – Hydroxide, $Ca(OH)_2$

Also cement is characterized on various other factors such as: strength, heat evolution, rate of setting.

- **Rapid-hardening cement** is used in precast concrete, pipes and tiles. It is finer ground so that it hydrates more quickly and has more gypsum than other cements.
- **Moderate-heat cement** is used for the construction of hydro-electric dams, as the heat produced by ordinary cement creates uneven expansion and hence cracking when such a large volume of concrete is used.

Methods of Production

- Most common type is **Portland cement.**

- The method of production of cement from lime rock can be done in two steps-

1. Cement rock beneficiation- Mostly based on use of the local limestone rock with high silica and iron content.
2. Portland cement production- chemical reactions limestone and other constituents.

PORTLAND CEMENT PROCESS

Raw material –

Limestone (70-80% rich in $CaCO_3$)

Clay (15-20% , a source of silica, alumina and Fe_2O_3)

Other : gypsum, coal, water.

Chemical reaction –

$CaCO_3 \rightarrow CaO + CO_2$ (1000 °C)

$CaO + Al_2O_3 + SiO_2 \rightarrow$ Mixtures of C_3S , C_2S, C_3A

Process Type-

- Dry Process: uses more energy in grinding but less in the kiln
- Wet Process has lower overheads than the dry process

Limestone Beneficiation

If available limestone has too high a silica and iron content and undesired constituent, these are removed by ore dressing or beneficiation methods.

Grinding → Classification → Flotation → Thickening

[1] Raw material preparation

Dry Process: Quarried clay and limestone are crushed separately and then fed together into a mill where the rock is ground until more than 85% of the material is less than 90μm in diameter.

Wet process: The clay is mixed to a paste in a washmill - a tank in which the clay is pulverised in the presence of water. Crushed lime is then added and the whole mixture to further ground.

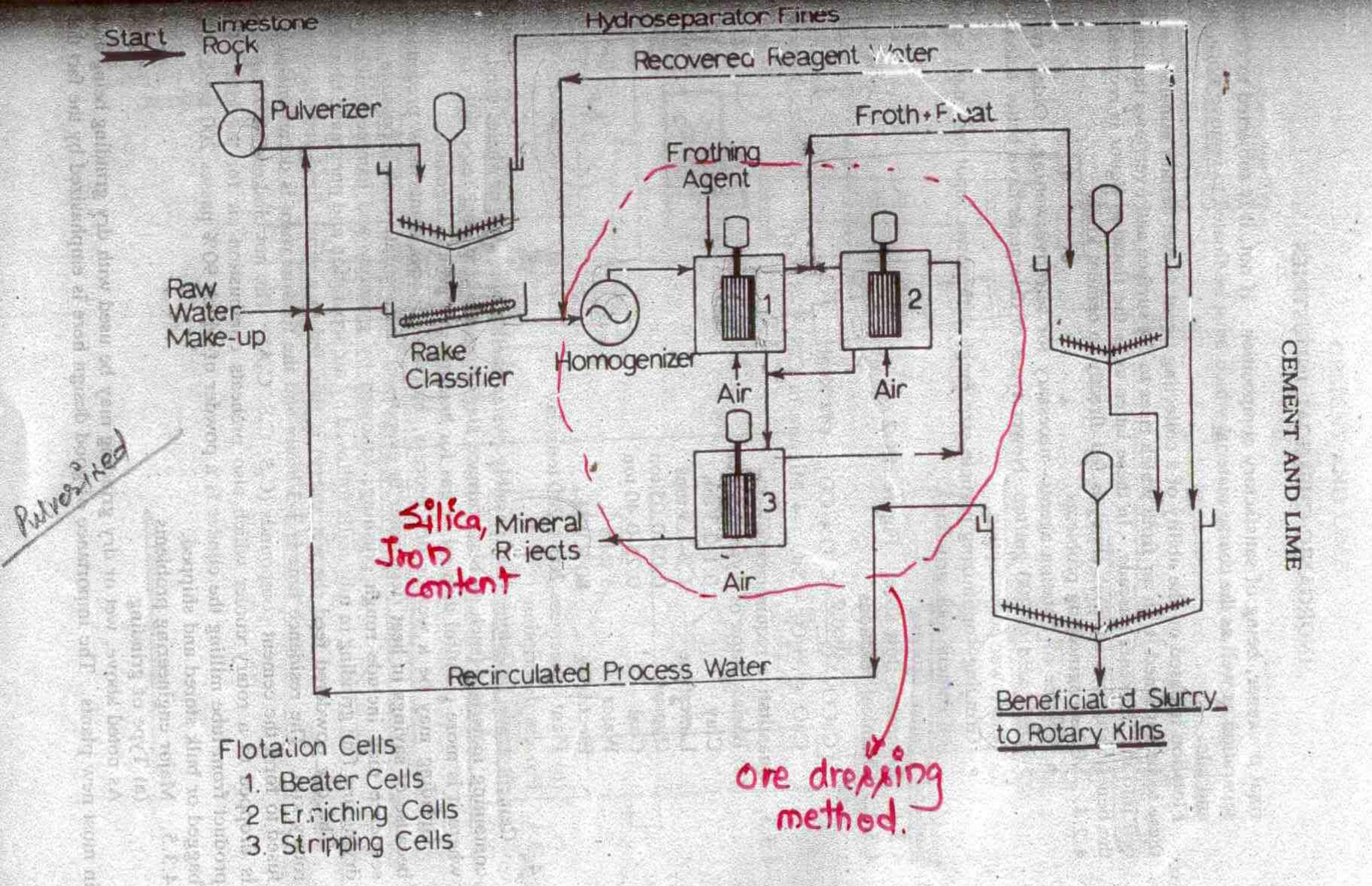


Fig. IIK-1. Limestone beneficiation.

RAKE CLASSIFIERS

RAKE CLASSIFIER

- A rake classifier uses a set of rakes which moves in an eccentric motion causing it to dip into the settled material and to move up an inclined ramp for a short distance. The rakes are then withdrawn, and return to the starting-point, where the cycle is repeated; the settled material is slowly moved up the incline to the oversize discharge point.

  In a duplex type, one set of rakes moves up the incline, while the other set returns. Simplex and quadruple machines are also made in which there are one or four raking assemblies. The undersize material remains in suspension in the pool of fluid at the bottom of the rake assemble. The pulp in this pool overflows a weir to become the fine fraction.

  Rake classifiers are basically used for closed circuit grinding, washing dewatering and desliming; particularly where clean dry sands are important. The extra residence time of pulp in a rake classifer can sometimes be beneficial in the cyanidation of gold ores where up to 75 percent of dissolution may take place during grinding.

[2] Clinkering

- The finely ground material is dried, heated (to enable the sintering reactions to take place) and then cooled down again. While it is being heated various chemical reactions take place to form the major mineral constituents of Portland cement.
- The powder from the dry process doesn't contain much moisture, so can be dried in a preheater.
- The slurry from the wet process contains too much moisture to be successfully dried in a preheater tower. Instead, the slurry is fed directly into the kiln where it is formed into dry balls by the heat and rotation of the kiln.
- Because of this extra role of the kiln, wet process kilns are generally longer (100 m) than dry process kilns (60 m long).
- The kilns used in both processes are inclined on a shallow angle and lined with heat-resistant bricks.

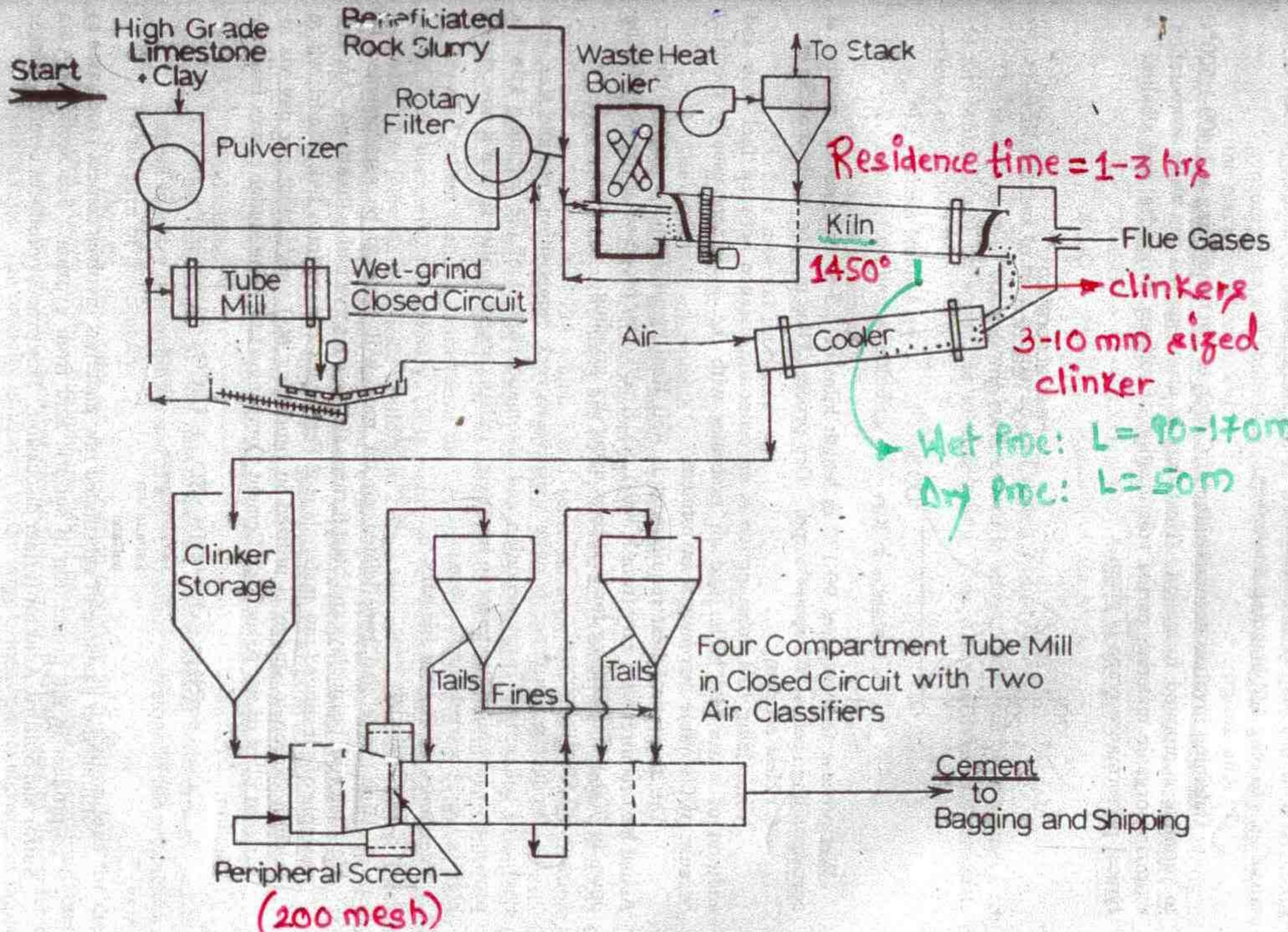


Fig. IIK-2. Portland cement manufacture.

KILN

The kiln is heated by injecting pulverized coal dust into the discharge end where it spontaneously ignites due to the very high temperatures.

Zone 1: 0 - 35 min, 150-800 - °C

Dehydration in wet process (in dry process preheating removes water)

Zone 2: 35 - 40 min, 900 - 1300°C

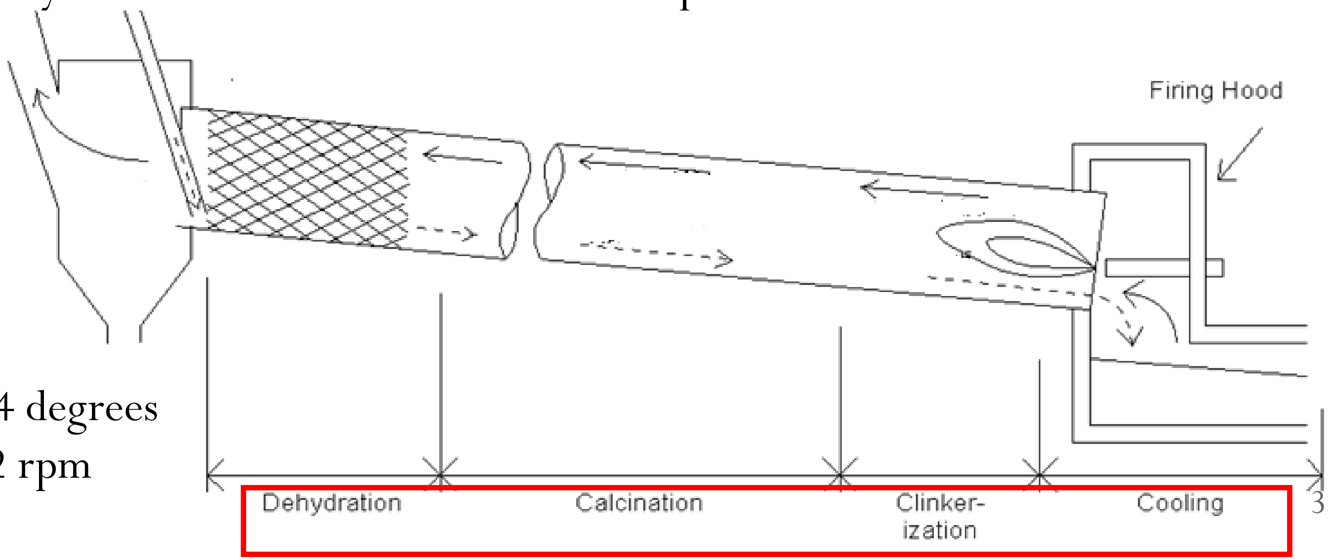
Decarbonation. Formation of $3CaO \bullet Al_2O_3$, Melting of fluxing compounds Al_2O_3 and Fe_2O_3. Exothermic reactions and the formation of secondary silicate phases

Zone 3: 40 - 50 min, 1300 - 1450 - 1300°C

Sintering and reaction within the melt to form ternary silicates and tetracalcium aluminoferrates:

Zone 4: 50 - 60 min, 1300 - 1000°C

Cooling and crystallization of the various mineral phases formed in the kiln.



Inclination :3 -4 degrees

Rotation :1.2-2 rpm

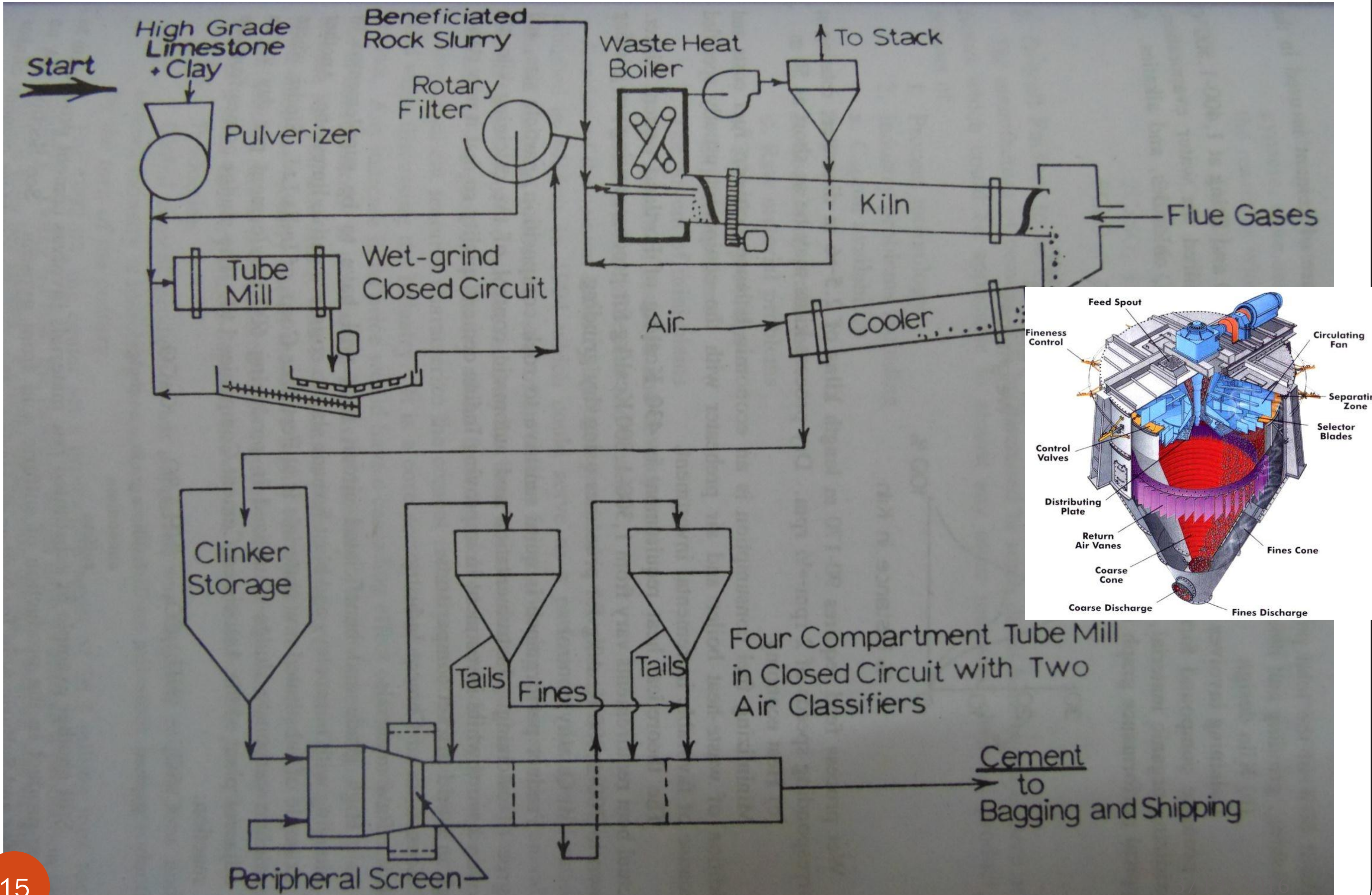
[3] Cooling

Immediately following the kiln is a large cooler designed to drop the temperature of the clinker (as the fused material is now called) 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.

[4] Cement Milling

To produce the final product the clinker is mixed with gypsum ($CaSO_4 \cdot 2H_2O$), 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. The first grinding breaks up the material and the second grinds it to a fine powder.

Process Flow sheet



Major Engineering Problems

- **Type of grinding**
  - Wet or dry grinding (dry grinding being used in most new plants).
  - Emphasis on good design as 80% of total power consumed in crushing, grinding and blending.
- **Kiln Design**
  - Calcining, concreting requires heat for water evaporation, oxidizing organic material, volatilization.
  - Wet process requires 90-170 m length kiln, dry process kilns may be as short as 50 m.
- **Heat Economy**
  - Balance between fuel cost and addition of waste heat boiler and air preheater.
  - Heat requirement for wet grinding process1,300-1800 Kcal/kg and 700-1000 for dry grinding process.

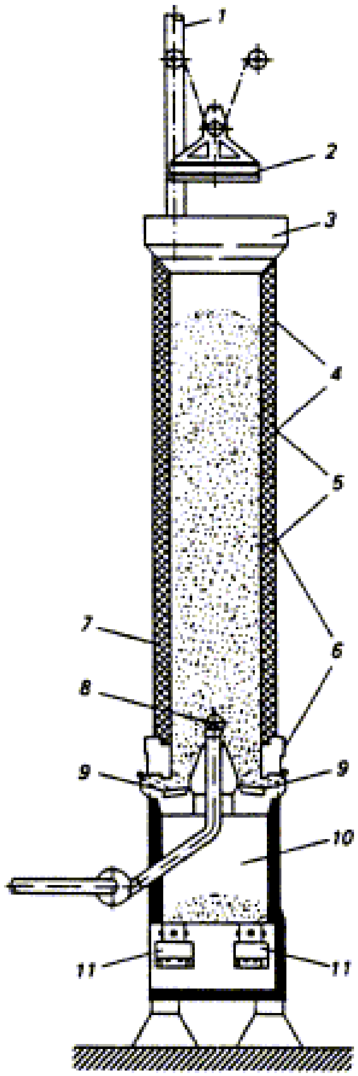
- **Quality Control**
  - Product performance is sensitive to rock composition, particle size, and degree of calcining.
  - Instrumentation and control of kiln has proven quality improve.

- **Economics of Cement Industry**
  - In view of ecological and economic aspects, nowadays, Portland cement components are increasingly substituted by e.g. blast-furnace slags, puzzolana, fly ashes or lime stone powders.
  - $CaCO_3$ from fertilizer (as sludge) can be used
  - Thus, the cement can be optimally tailored to the requirements on the construction site. And, there is more to it than that: Carbon dioxide emissions are reduced, too.

Introduction

- Used in the pyro processing stage of manufacture of Portland & types of hydraulic cement.
- Main energy-consumption and greenhouse-gas emission stage.
- Improvement of kiln efficiency has been the central concern of cement manufacturing technology.
- Types of Cement Kilns
  - Shaft Kilns – Briefly used from 1970. Still in use in low-tech plants.
  - Rotary Kilns – Currently in use. Accounts for 95% of global production.

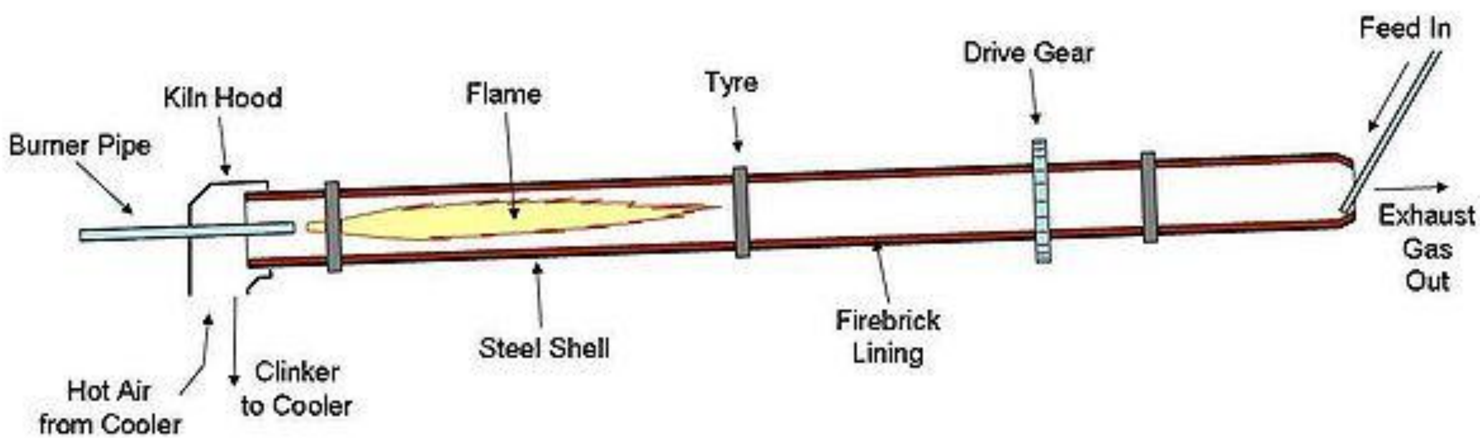
The Shaft Kiln



1. Exhaust gas
2. Charging bucket with raw material and fuel
3.Gas seal bell
4. *Preheating zone*
5. *Calcining zone*
6. *Cooling zone*
7. Kiln lining
8. Combustion air inlet
9. Lime discharge
10. Intermediate hopper
11. Discharge channels

The Rotary Kiln

- Consists of a steel tube, lined with firebrick.
- Tube slopes at (1-4°) and slowly rotates on its axis between 30 and 250 rev/h.
- Rawmix is fed from the upper end. The lower end of the tube has a large concentric flame.

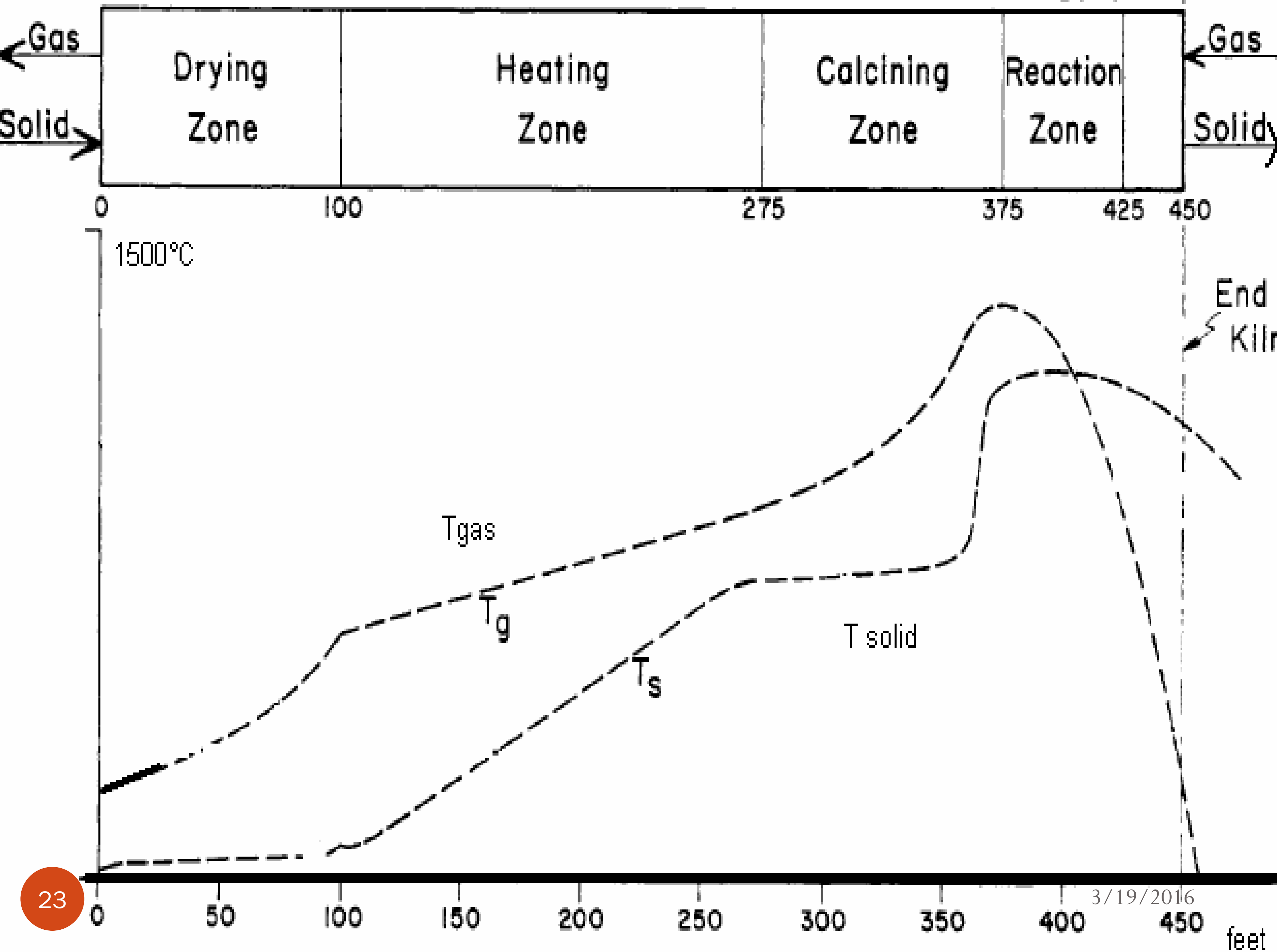


Methods of Rawmix Preparation

- Two different methods of rawmix preparation are used:
  - Dry Process
    - Mineral components are dry-ground to a form a powder.
  - Wet Process
    - Water is added to the mineral components to produce a slurry with 40-50% water content.
- Comparison:
  - Dry process saves on extra fuel needed for water evaporation.
  - In dry process, no kiln length is used up in drying rawmix.
  - It is difficult to keep the dry powdered rawmix in kiln due to fast flowing combustion gases, hence spray water is used.
  - Granulation is more difficult in dry process.

Different zones and temperature profile

- Successive chemical reactions take place as the temperature of the raw mix rises:
- 70 to 110 °C - Free water is evaporated.
- 400 to 600 °C - clay-like minerals are decomposed into their constituent oxides; principally SiO_2 and Al_2O_3. Dolomite ($CaMg(CO_3)_2$) decomposes to calcium carbonate, MgO and CO_2.
- 650 to 900 °C - calcium carbonate reacts with SiO_2 to form belite(Ca_2SiO_4).
- 900 to 1050 °C - the remaining calcium carbonate decomposes to calcium oxide and CO_2.
- 1300 to 1450 °C - partial (20–30%) melting takes place, and belite reacts with calcium oxide to form alite ($Ca_3O \cdot SiO_4$).



Gas
Solid
Drying
Zone
Heating
Zone
Calcining
Zone
Reaction
Zone
Gas
Solid
0
100
275
375
425
450
1500°C
End
Kiln
Tgas
Tg
Ts
T solid
0
50
100
150
200
250
300
350
400
450
feet

LIME

LIME refers to Limestone ($CaCO_3$) and it's derivative burnt/quick lime (CaO) and slaked/hydrated lime ($Ca(OH)_2$).

Physical properties –

CaO (Quick lime)		Ca(OH)$_2$ (Slaked lime)	
Mol. Wt	56.08	Mol. Wt	74.10
M.P	2570 °C	Density	2.2 g /cm^3
B.P	2850 °C	Decomposes to CaO at 580°C	
Density	3.32 g / cm^3		
Soluble in water and acids		Slightly soluble in water,	

- **Uses:** Burnt and hydrated lime are used in many industries to neutralize acid waste, and are used as causticisers in the pulp and paper industry and as flux in the steel industry.

LIME

Methods of production –

- Quick lime
  - Calcining limestone to yield quicklime
- Slaked Lime
  - Hydration of quicklime

- Write the reactions, temperature, (exo/endothermic)
- Based on above information and process discussed for cement production, draw a conceptual block diagram (combined) for Quick and Slaked Lime.

Method of production

Quick lime

- Calcining limestone to yield quicklime

$$CaCO_3\,(s) \rightarrow CaO\,(s) + CO_2\,(g) \quad \Delta H = +44\ \text{kcal}$$

- High quality limestone (>95% $CaCO_3$) is calcined in a continuous process using rotary or vertical kilns at (1000-1100°C), volatilizing off the carbon dioxide to leave the calcium oxide:

Slaked Lime

- Hydration of quicklime

$$CaO(s) + H_2O\,(l \text{ or } V) \rightarrow Ca(OH)_2$$

- It is produced by reacting burnt lime with water in a continuous hydrator. During this process large amounts of heat are given off. The resultant micron-sized particles are then classified by air separators which reject coarse particles.

The basic processes in the production of lime are:

Quick Lime

(1) Quarrying raw limestone

(2) Preparing limestone for the kilns by crushing and sizing

- Jaw or gyratory crushers for hard rock
- Hammer or roll mills for soft rock
- Size of feed depends on calciner type.

(3) Calcining limestone

Type	Particle size	
Vertical Shaft	10-20 cm	Efficient for small production
Rotary Kiln	0.5-5 cm	Large production, better control

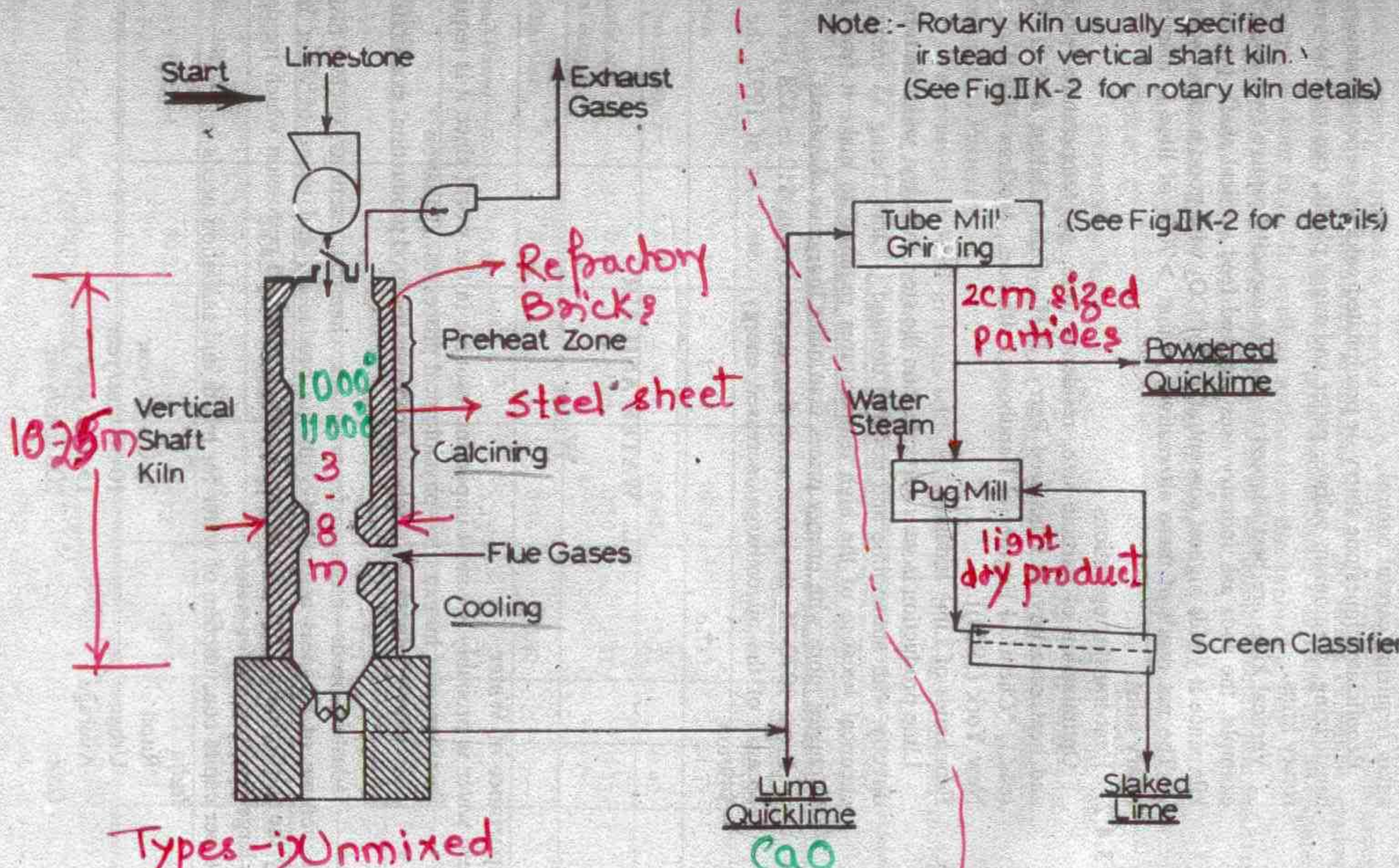
Operation is of two type : Unmixed and mixed

(4) Cooling in conveyor and the lime is either packaged as Lump lime or crushed and screened to yield pulverized lime.

Hydrated Lime

(5) Processing the lime further by hydration

- Quicklime lumps are crushed to 2 cm or less then added along with water or steam to a vertical cylindrical pug mill.
- Product from complete reaction is light, dry slaked lime which is classified by screen or air separators to remove any unreactive lime.

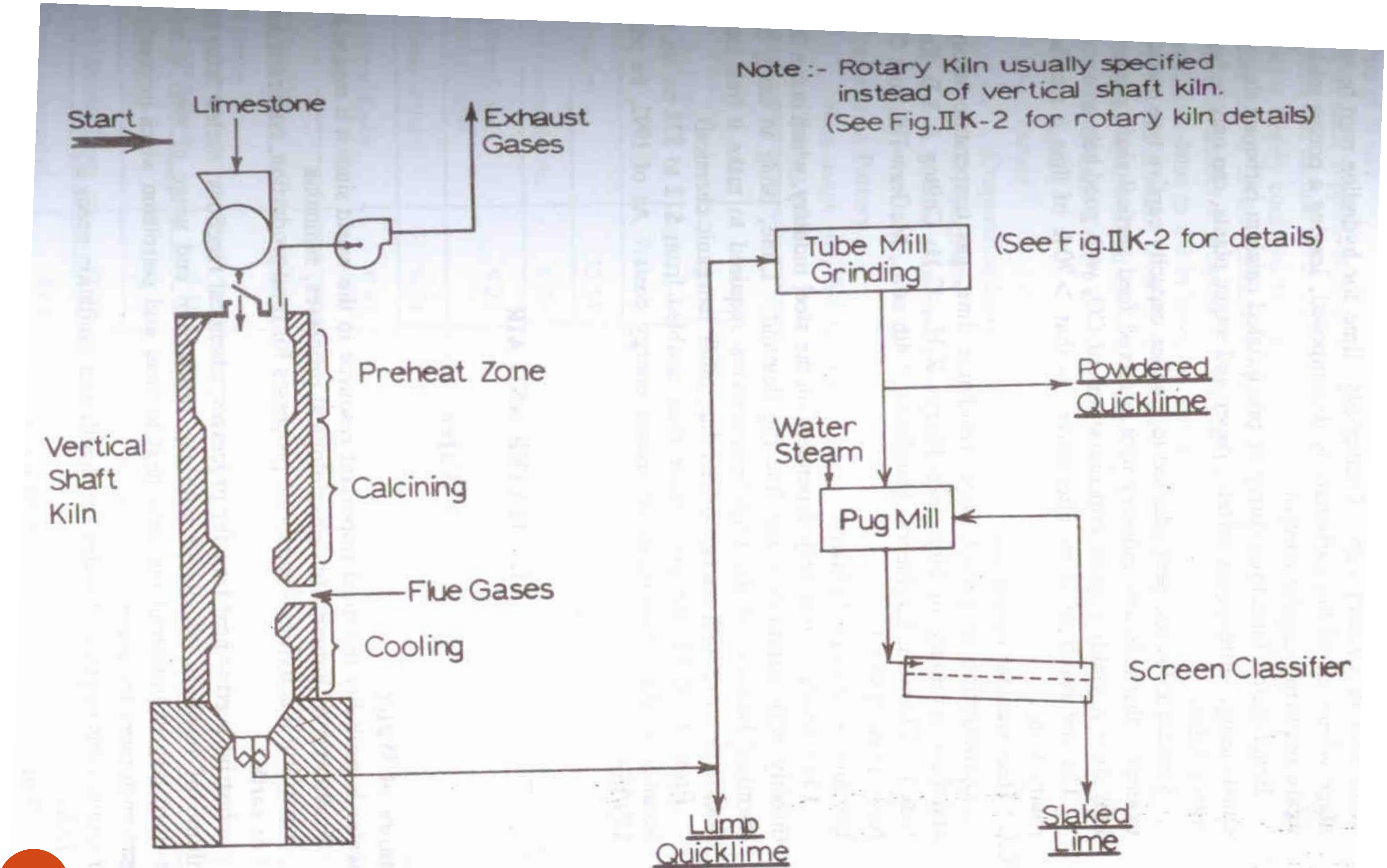


Types - i) Unmixed
ii) Mixed

Fig. IIK-3. Lime manufacture.

$CaCO_3$ decomposes at 898°C

Flow-sheet for CaO and $Ca(OH)_2$



Major Engineering problems

1. Choice of kiln
   - Vertical Kilns: Suitable for smaller capacity type operations; yield highest CO_2 concentrations and good heat economy, higher fuel effciency.
   - Rotary Kilns: Favored for large production rates, easy control over temperature and residence time, Beneficiated limestone slurry or precipitated calcium carbonate sludge cal also be handled.
2. Heat transfer operation
   - Optimization of particle size, residence time, gas temperature, velocity profile and heat economy in kilns.
3. Economics of lime industry
   - Very dependent on steel industry as lime use as slag removal (silica impurity) from iron.
   - Energy intensive, as high temperature is required to make it from limestone.

LIME KILN

- A lime kiln is used to produce quicklime through the calcination of limestone (calcium carbonate).

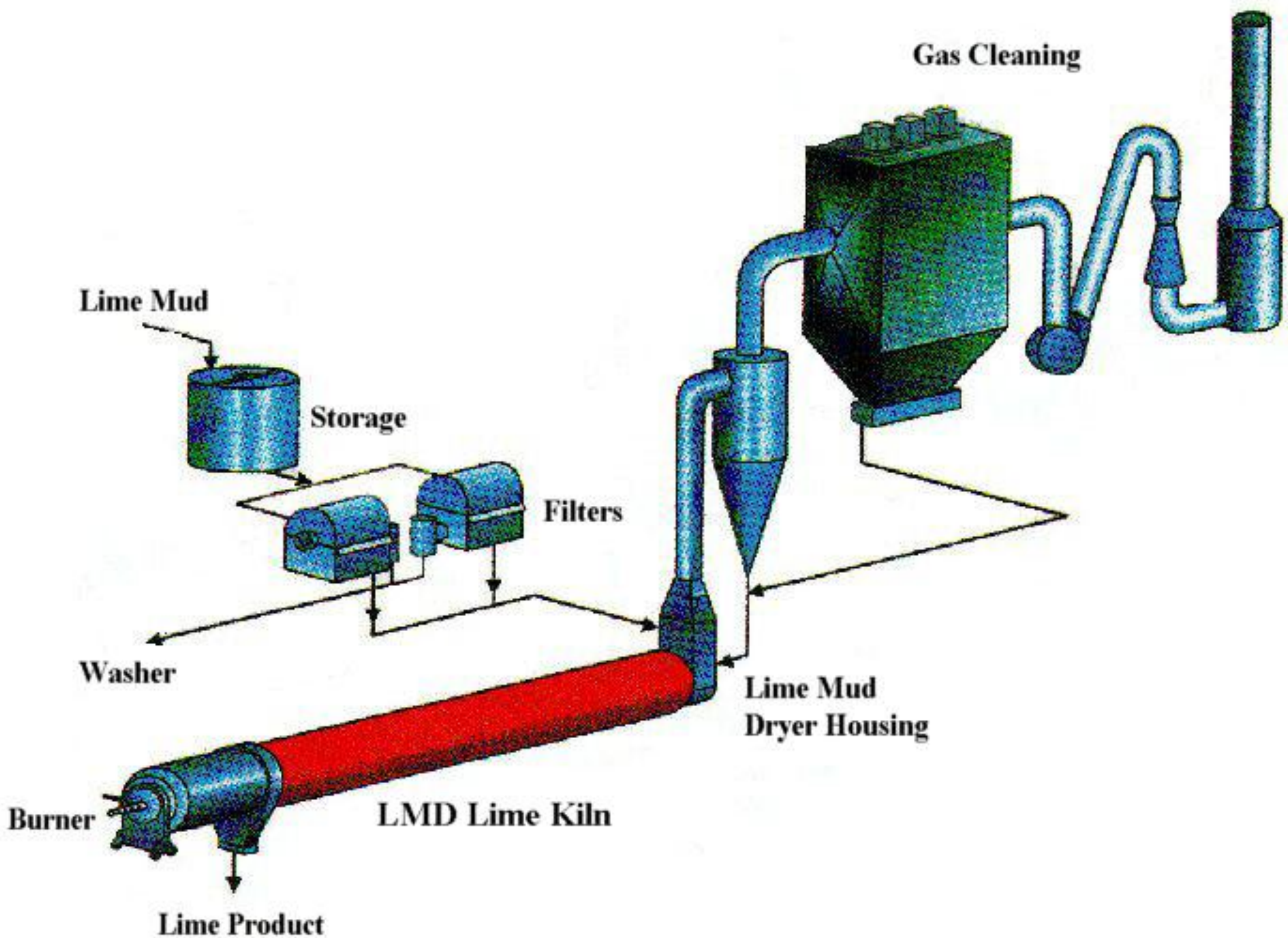
- The chemical equation for this reaction is

$$CaCO_3 + heat \rightarrow CaO + CO_2$$

a temperature around 1000°C is usually used to make the reaction proceed quickly.

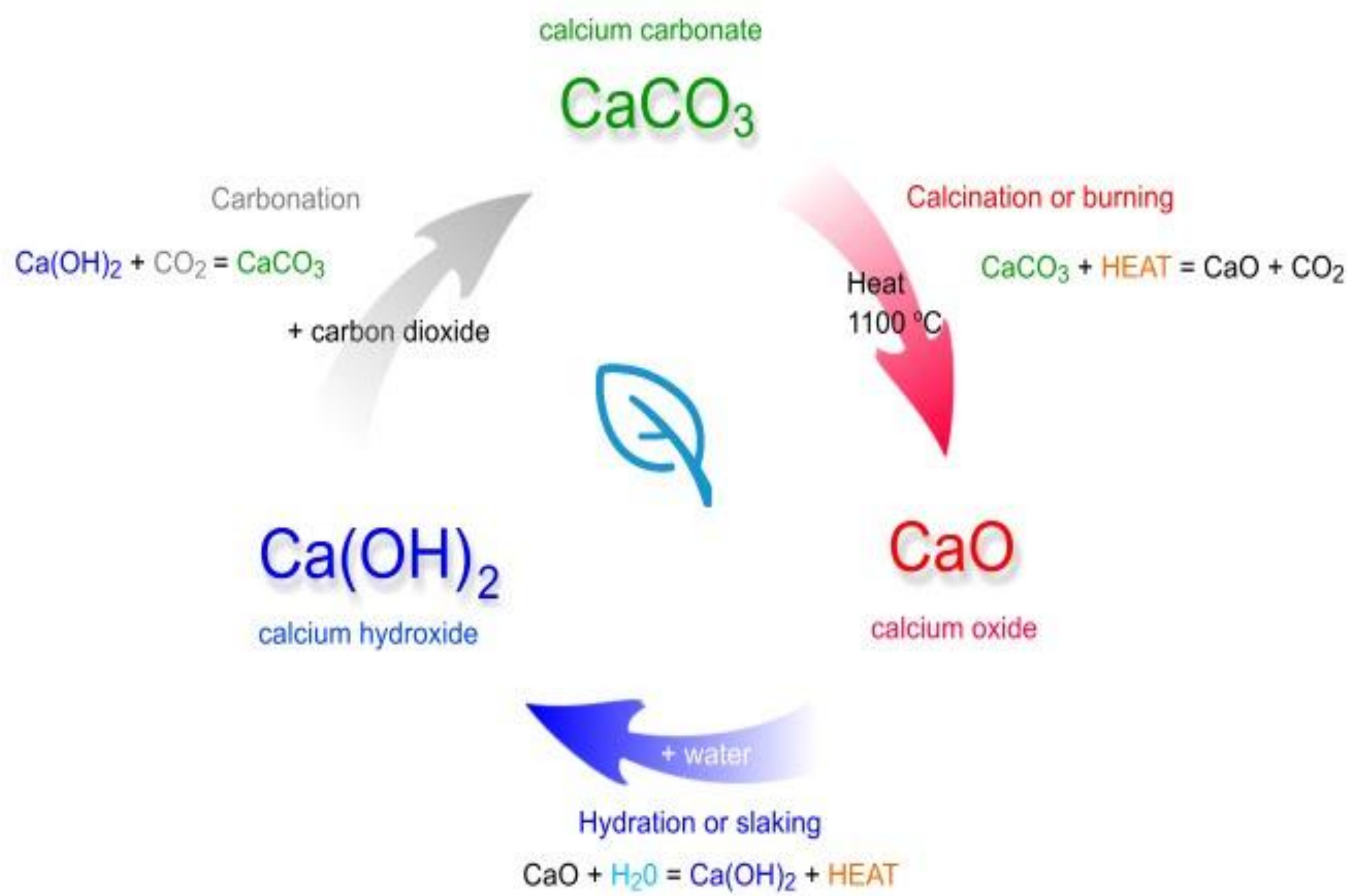
GAS CLEANING

- All kiln designs produce exhaust gas that carries an appreciable amount of dust.
- Lime dust is particularly corrosive. Equipment is installed to trap this dust, typically in the form of electrostatic precipitators or bag filters.
- The dust usually contains a high concentration of elements such as alkali metals, halogens and sulphur.


Gas Cleaning
Lime Mud
Storage
Filters
Washer
Lime Mud
Dryer Housing
Burner
LMD Lime Kiln
Lime Product

Carbon dioxide emission

- The lime industry is a significant carbon dioxide emitter.
- The manufacture of one tonne of calcium oxide involves decomposing calcium carbonate, with the formation of 785 kg of CO_2
- Additionally, if the heat supplied to form the lime (3.75 MJ/kg in an efficient kiln) is obtained by burning fossil fuel it will release CO_2: in the case of coal fuel 295 kg/t; in the case of natural gas fuel 206 kg/t.
- Thus, total emission may be around 1 tonne of CO_2 for every tonne of lime even in efficient industrial plants, but is typically 1.3 t/t.


calcium carbonate
CaCO3
Carbonation
Ca(OH)2 + CO2 = CaCO3
+ carbon dioxide
Calcination or burning
CaCO3 + HEAT = CaO + CO2
Heat
1100 °C
Ca(OH)2
calcium hydroxide
CaO
calcium oxide
+ water
Hydration or slaking
CaO + H20 = Ca(OH)2 + HEAT

EMISSION CONTROL

- Carbon dioxide scrubber
  - A **carbon dioxide scrubber** is a device which absorbs carbon dioxide (CO_2).
  - Carbon dioxide scrubbers are also used in controlled atmosphere (CA) storage.

Technologies

- **Sodium hydroxide**
- **Amine scrubbing**
- **Minerals and zeolites**
- **Lithium hydroxide**
- **Activated carbon**

Sodium hydroxide

- First, CO_2 is absorbed by an alkaline NaOH solution to produce dissolved sodium carbonate.
- The absorption reaction is a gas liquid reaction, strongly exothermic.

$$2NaOH(aq) + CO_2(g) \rightarrow Na_2CO_3(aq) + H_2O(l)$$

$$Na_2CO_3(aq) + Ca(OH)_2(s) \rightarrow\text{->}\ 2NaOH(aq) + CaCO_3(s)$$

$$[\Delta H° = -5.3\ kJ/mol]$$

- Subsequently, the calcium carbonate precipitate is filtered from solution and thermally decomposed to produce gaseous CO_2.
- The calcination reaction is the only endothermic reaction in the process.

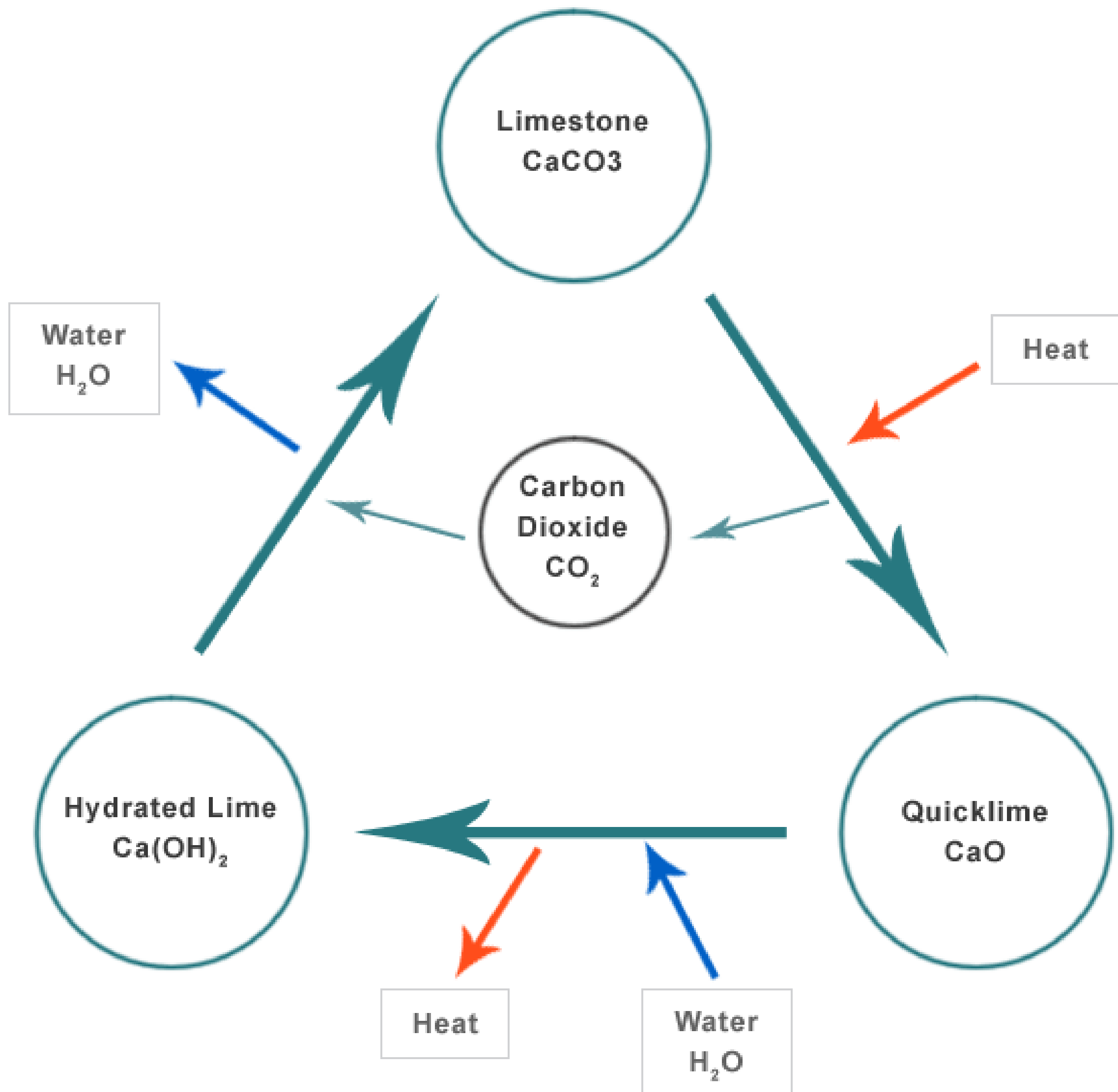
$$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$$

$\Delta H° = + 179.2$ kJ/mol

- Hydration of the lime (CaO) completes the cycle.

$$CaO(s) + H_2O(l) \rightarrow Ca(OH)_2(s)$$

$\Delta H° = -64.5$ kJ/mol


Limestone
CaCO3
Heat
Quicklime
CaO
Water
H2O
Heat
Hydrated Lime
Ca(OH)2
Water
H2O
Carbon
Dioxide
CO2

Amine scrubbing

- Virtually the only technology being seriously evaluated involves the use of various amines, e.g. monoethanolamine.
- Cold solutions of these organic compounds bind CO_2, but the binding is reversed at higher temperatures:

$$\mathbf{CO_2 + 2HOCH_2CH_2NH_2 \longleftrightarrow HOCH_2CH_2NH_3^{+} HOCH_2CH_2NH(CO_2^{-})}$$

- This technology has only been lightly implemented because of capital costs of installing the facility and the operating costs of utilizing it.

Activated carbon

- Air with high carbon dioxide content, can be blown through beds of activated carbon and the carbon dioxide will adsorb onto the activated carbon.
- Once the bed is saturated it must then be "regenerated" by blowing low carbon dioxide air, such as ambient air, through the bed.
- This will release the carbon dioxide from the bed, and it can then be used to scrub again, leaving the net amount of carbon dioxide in the air the same as when the process was started.