-9-
The Cement Industry

9.1 Introduction

The cement industry represents an extremely important sector worldwide. The world production of cement has exceeded 4100 million tons per year (2018). The main producer is China with more than 2400 million tons.

In Egypt, the cement industry is a major industrial sector, one of the main reasons being that Egypt has one of the highest per capita productions in the world. In 2011, the annual production was about 48 million tons. This figure has since been raised to about 83 Mt (December 2018) while the local consumption did not exceed 56 Mt.

Exportation of cement has steadily increased over the past decade. The export figure slumped from 6 Mt in 2006 (Cement + clinker) to less than 0.5 Mt in 2016, the main importers being Brazil, Spain, Jamaica and some Arab countries.

At the moment there are 18 operating cement companies with 42 producing lines, which are geographically diversified in location across Egypt. Out of the 42 lines, 18 are owned by the private sector, while the others are mainly owned by international companies.

9.2 Economics of cement production

The fixed capital of a cement production line is characterized by the "Specific Investment Cost" which represents the ratio between the total capital investment and the annual production in tons per year. This figure ranges from \$140 to 180 per ton per year. For example, the total fixed of a unit producing 1.5×10^6 tons per year will range from 210 to 270 million USD.

In Egypt, the percent Return on Investment (ROI) of cement production plants used to exceed 250% making it an extremely lucrative investment. However, in the later years, the fuel cost, the high interest rate on bank loans and the decrease in demand have contributed to reduce the ROI to much lower figures, including negative values in some cases.

9.3 Constitution of Ordinary Portland Cement (OPC)
9.3.1 Definition

Ordinary Portland cement (OPC) is defined as being *the product obtained by pulverizing clinker consisting essentially of calcium silicates, to which no addition has been made after calcination other than water and gypsum.*

9.3.2 Raw materials

Raw materials for OPC production are essentially, clay and limestone with regulating doses of silica and a source of iron (usually oxides). The major contributor to the raw meal is limestone, the percentage of which is about 78%, followed by clay which accounts for about 18% of the mix. There are certain conditions that have to be met for any of these raw materials to be of use. For example, their total percent alkali oxides (Na_2O and K_2O) should not exceed 2%. This will limit the maximum percent of alkalis in the product cement to 0.6%. Table (9.1) shows a typical oxide analysis of a raw mix.

Table 9.1: Oxide analysis of a raw mix

Oxide	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	TiO_2	Mn_2O_3	P_2O_5	LOI
%	14.3	3.6	2.0	42.0	1.8	0.63	0.22	0.17	0.10	0.06	35.1

Loss on ignition (LOI) is essentially due to the loss of carbon dioxide from limestone and chemical water from clays.

9.3.3 Clinker components

The reactions occurring in the rotary kiln used for firing the raw mix produce four main compounds:

- Tricalcium silicate (Alite) $3CaO.SiO_2 (C_3S)$
- Dicalcium silicate (Belite) $2CaO.SiO_2 (C_2S)$
- Tricalcium aluminate (Aluminate) $3CaO.Al_2O_3 (C_3A)$
- Tetra calcium alumino ferrite (Ferrite) $4CaO.Al_2O_3.Fe_2O_3 (C_4AF)$

Each of these compounds has a specific function as cement is mixed with water.

- Tricalcium silicate is responsible for early strength of cement.
- Dicalcium silicate is responsible for acquired strength after long time periods.
- Tricalcium aluminate is responsible for initial setting and heat evolution upon adding water.
- Tetra calcium alumino ferrite plays a minor role similar to aluminate.

A typical cement clinker will consist of these compounds as well as free CaO and MgO in minor amounts. Table (9.2) shows the usual limits of different oxides present in cement.

Table 9.2: Typical oxide levels in cement

Oxide	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	Alkalis	SO_3*
%	60-67	17-25	3-8	0.5-6	0.1-4	0.2-1.2	1-3

* SO_3 is present as gypsum added to clinker to retard setting.

Whenever the percent oxides are known, it is possible to estimate the clinker composition from the **Bogue** formulas:

$$\% \ C_3S = 4.07 \ CaO - 7.6 \ SiO_2 - 6.72 \ Al_2O_3 - 1.43 \ Fe_2O_3 \qquad (9.1)$$

$$\% \ C_2S = -3.07 \ CaO + 8.6 \ SiO_2 + 5.07 \ Al_2O_3 + 2.08 \ Fe_2O_3 \qquad (9.2)$$

$$\% \ C_3A = 2.65 \ Al_2O_3 - 1.69 \ Fe_2O_3 \qquad (9.3)$$

$$\% \ C_4AF = 3.04 \ Fe_2O_3 \qquad (9.4)$$

For example, a typical clinker would consist of about 13% C_3A, 60% C_3S, 18% C_2S and 9% C_4AF

9.3.4 Cement indices

In order that cement fulfills its function properly, the clinker composition should abide by certain indices. Two common indices are:

(a) The silica ratio (SR)

$$S.I. = \frac{SiO_2}{Al_2O_3 + Fe_2O_3}$$ (9.5)

In clinker, its range should be: $1.8 - 3.6$

(b) The Lime saturation factor (LSF)

$$L.S.F. = \frac{CaO}{2.8\, SiO_2 + 1.18\, Al_2O_3 + 0.65\, Fe_2O_3}$$ (9.6)

This index is a measure of the lime content of clinker with respect to other oxides. Its value ranges from $0.7 - 1$. If its value exceeds 1, then the final cement will contain free lime (CaO), which can cause trouble on use.

9.4 Manufacture of OPC

9.4.1 Introduction

For several decades, cement was produced using the **wet process**. In this process, the raw mix was prepared in slurry form before admittance to the firing kiln. Nowadays more than 90% of cement production is made through the **dry process** which excludes the use of water in production. In Egypt, to date, there remain two production lines using the wet process, while more than 97% of cement is produced the other way. In certain cases, when clay raw materials are extremely plastic, their high water content makes it uneconomical to dry them. In that case, a semi – dry process can be used, such as the **Lepol** process, devised by the Polysius Company.

In the following section the wet process is briefly discussed, for sake of comparison with the much more widespread dry process.

9.4.2 The wet process for cement manufacture

In this process, raw materials are separately crushed, then mixed with water and ground in ball mills. The slurry, containing about $35 - 40\%$ water is mixed into large tanks, called **correcting tanks**, where samples are regularly taken for analysis. It is then transported through an elevator to the raw mix silo. From this silo, it is delivered to the **rotary kiln** where reactions take place to finally form small nodules of diameter $\sim 10^0 - 10^1$ mm (**clinker**). The final hot clinker leaves the kiln at a temperature exceeding 1400ºC, to be then rapidly cooled by cold air. The cooled clinker is then mixed with gypsum (a setting retarder) and finely ground in ball mills. The fine cement powder is then pneumatically lifted in storage silos.

Wet kilns are very long (reaching 200 m in length) since part of the kiln is devoted for dehydrating the slurry. Also, the specific heat consumption is very high, exceeding 6000 kJ/kg clinker. Heat economy can be improved by using hot air from the clinker cooler (600 – 800ºC), after de-dusting in a filter, as secondary air for combustion in the kiln. Finally, the flue gases from the kiln entrain a large amount of dust that is collected using an electrostatic precipitator, and recycled to the kiln. One main limitation of long wet kilns is their limited productivity that does not exceed 3000 tpd clinker.

9.4.3 The dry process for cement manufacture
(a) Description

As the name implies, the dry process does not make use of any water. The crushed raw materials are stored and after proper proportioning, stacked in a confined area from where

they are delivered to the grinding section. The finely ground raw mix is transferred to the raw meal silo. This latter is specially designed so as to have continuous air swirling to avoid any segregation. The raw mix is then admitted to a heat exchange system known as **suspended preheaters**. This consists of several vertically mounted cyclones where the hot flue gases leaving the kiln (at about 1100ºC) flow in almost countercurrent manner against the descending raw mix. This latter reaches a temperature of about 850ºC at the kiln entrance and the flue gases are cooled down to about 350ºC. This causes partial calcination of limestone and clay into the preheater and hence decreases the specific heat consumption of the process.

The hot mix is then admitted to the rotary kiln where clinker is formed. Cooling of hot clinker takes place against cold air. This is used, after de-dusting, as secondary air for combustion in the kiln. The cold clinker, after gypsum addition, is then finely ground. The fine cement is then stored into silos prior to packaging or simply delivering to cement trucks.

Electrostatic precipitators or bag filters are commonly used to rid flue gases emanating from the suspended calciners from flue dust. This dust is then recycled to the raw mix silo. Figure (9.1) shows a flowsheet for this process.

(b) Main features of the dry process
(b.1) Cyclone preheaters

Originally, the number of cyclones in the raw mix preheating section, was one or two. This reduced the specific heat consumption to 4000 kJ/kg clinker, and the exit flue gases temperature was about 450ºC. Later, four cyclones were used, reducing the specific heat consumption to 3500 kJ/kg clinker and the exit gases temperature to 350ºC. Recently, up to six cyclones have been used further reducing the specific heat consumption to less than 3000 kJ/kg clinker and the exit gases temperature down to less than 300ºC.

The use of such devices has also made it possible to increase the productivity of existing kilns to reach values reaching 10000 tpd clinker. In case of erecting new units, the use of suspended preheaters has allowed for the use of short kilns, their length rarely exceeding 100 m.

Figure (9.2) shows a four stage suspended preheaters arrangement. The flow of solids and gases proceeds as follows:

The dry homogeneous raw mix is discharged from the raw mix silo to a charging bin (1), then discharged to the multicyclone (3) in its gas duct, where it is entrained with gases emerging from cyclone (4). The heated mix then moves to cyclone (4) where it is entrained with gases emerging from cyclone (5). The hot mix settling in cyclone (4) is then carried out to cyclone (5) by hot gases escaping from cyclone (6). Kiln gases (7) carry material settling in cyclone (5) to cyclone (6). Solids settling in cyclone (6) are then admitted to the kiln. As previously mentioned, the hot raw mix temperature at kiln entrance reaches 850ºC, and about 35% of limestone in the charge is calcined. The total contact time between gases and solids in this arrangement is $\sim 10^1$ s.

Fig (9.3) shows a live picture taken for a cement plant possessing four production units.
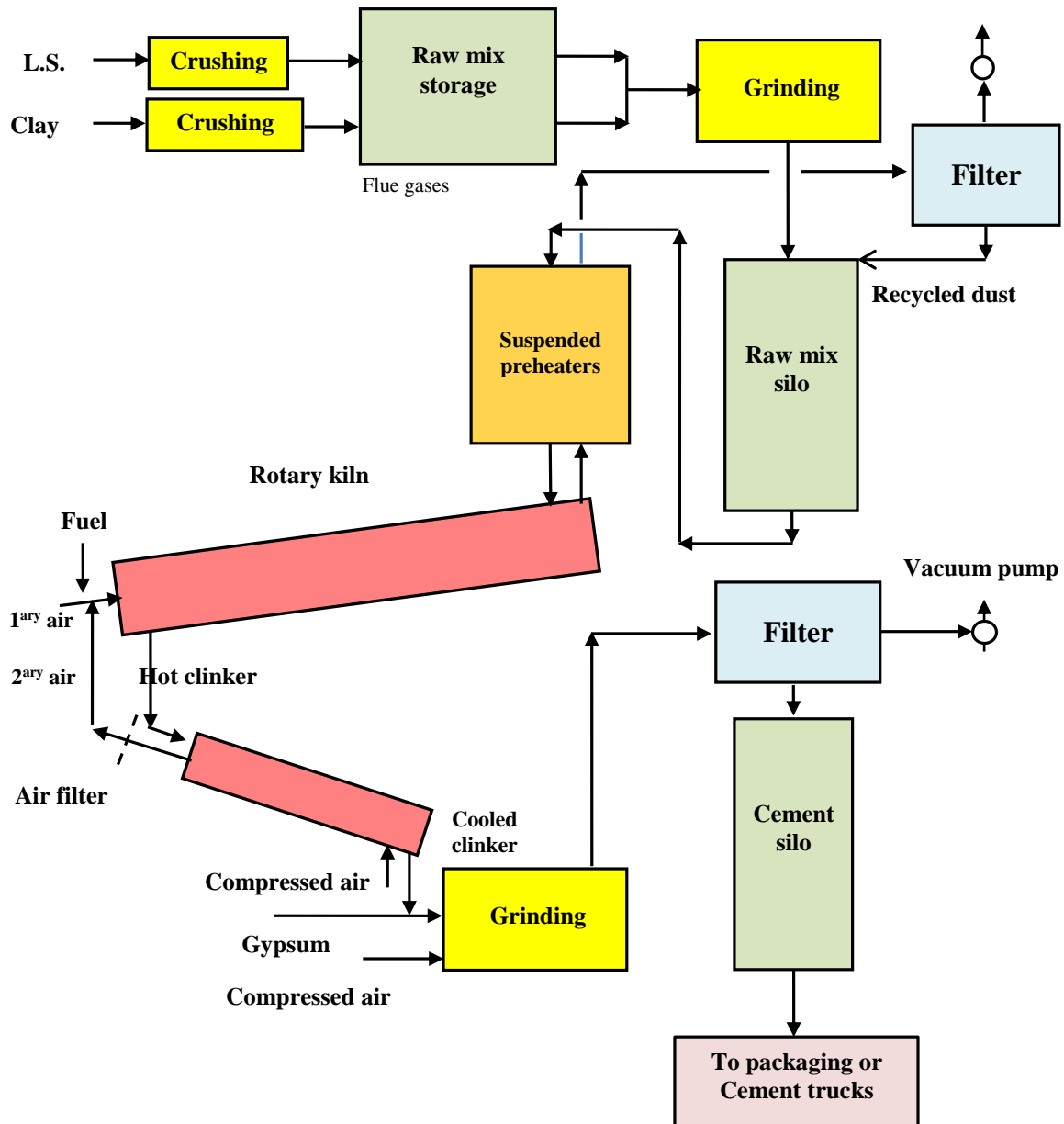
Vacuum pump

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L.S. → **Crushing** → **Raw mix storage** → **Grinding** → **Filter**

Clay → **Crushing**

Flue gases

Suspended preheaters

Raw mix silo

Recycled dust

Rotary kiln

Fuel

1ᵃʳʸ air

2ᵃʳʸ air

Hot clinker

Air filter

Cooled clinker

Compressed air

Grinding

Gypsum

Compressed air

Vacuum pump

Filter

Cement silo

To packaging or Cement trucks

Fig 9.1 Production of OPC by the dry process
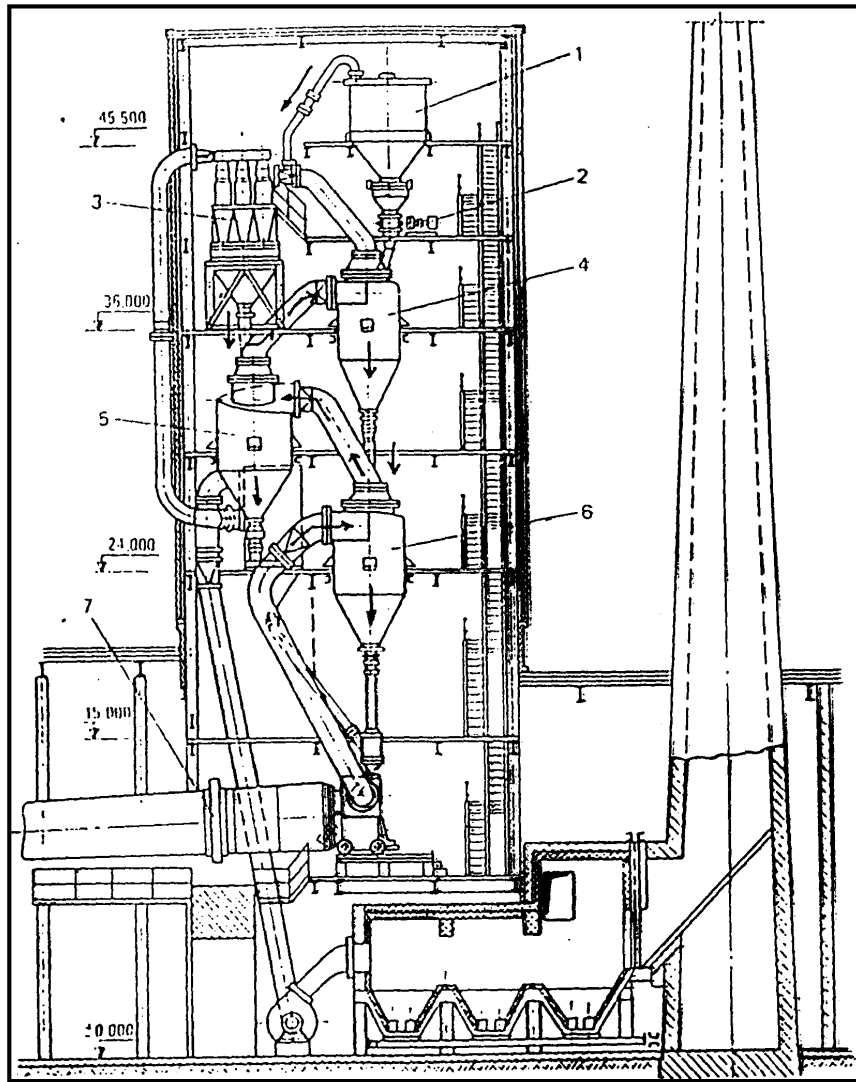
Fig 9.2 Four stages suspended cyclones preheater

Fig 9.3 Typical view of a cement factory

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(b.2) Total precalcination

Further fuel economy can be achieved by adding an external furnace known as **calciner** beneath the lowest cyclone in which fuel can be burnt to give hot flue gases that are routed to the cyclones system. This causes total calcination of the raw mix (> 95 %). Hot air for running this external furnace is supplied form the clinker cooler and is known as **tertiary air**. This usually requires the use of a special type of cooler (grate cooler). Figure (9.4) shows a common arrangement for total precalcination.
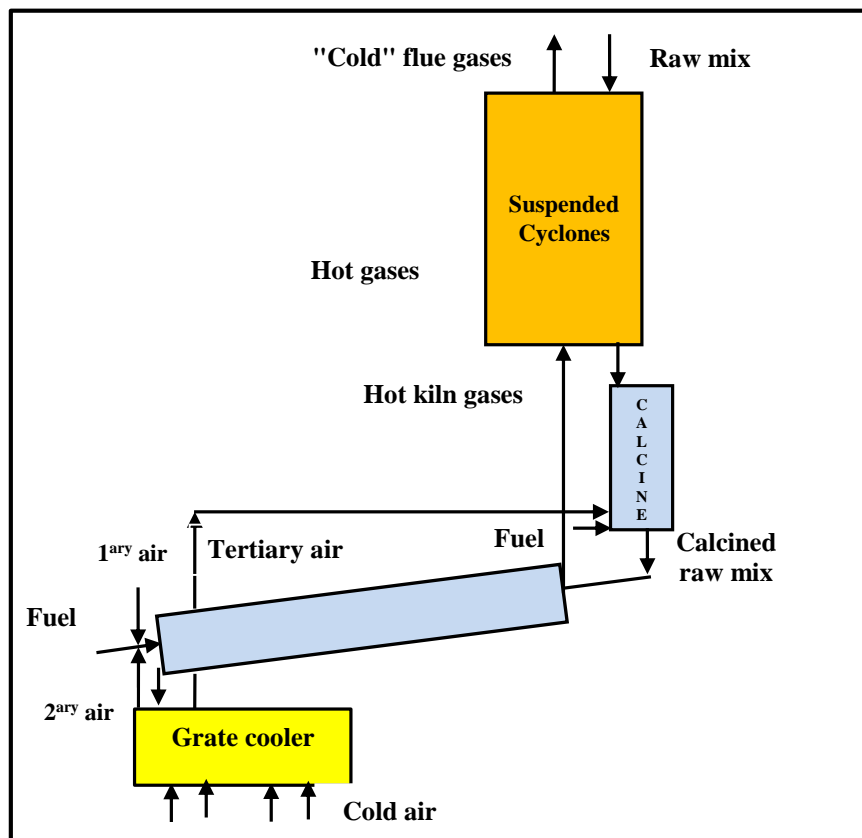
Fig 9.4 Total precalcination arrangement

(b.3) The rotary kiln

- **Reactions and phase transformations occurring in the kiln:**

The operations and processes taking place inside the kiln are shown in Table (9.3). These mainly consist of physical and chemical dehydration and calcination, solid state reactions and melting.

Table 9.3: **Reactions and phase transformations inside the kiln**

Temp. ºC	Transformation or reaction	Heat effect
80 – 120	Loss of physical water	Endothermic
400 – 800	Loss of chemical water	Endothermic
> 500	Structural changes in silicates	Exothermic
600 – 900	Dissociation of calcium carbonate	Endothermic
> 900	Formation of belite, aluminate and ferrite	Exothermic
> 1250	Beginning of melting	Endothermic
	Formation of alite	Exothermic
>1300	Further melting and clinker formation	Exothermic

- **Design features of the kiln:**

     The rotary kiln consists of a long cylinder of length reaching 100 m. in the dry process. Its diameter to length ratio is about 1:11**.** It is inclined on the horizontal at 1 to 3º and rotates about its axis at 1 – 3 rpm. Revolution is made possible by means of a girth gear roughly located at the middle of the kiln body. The kiln is internally lined with refractory bricks. On the cold end, fireclay refractories are used while at the hot end, magnesite bricks are preferred, because of the basic nature of the clinker. Usually, molten clinker solidifies on the internal surface of the refractory lining in this zone and provides an excellent refractory coat. Next to the refractory layer, on its cold end, is an insulating refractory bricks layer. The external cover of the kiln is made of welded steel sheets. Steel bandings or rings are fitted on the outside surface of the kiln to facilitate its rolling on idle rollers.

     The lower end of the kiln projects into a stationary brick flue where a central burner is fitted. Hot clinker leaves the kiln in this section. On the other hand, its upper end is fixed to a stationary cylindrical block where the raw mix enters the kiln. Figure (9.5) shows a simplified sketch.

- **Kiln seals:**

     Special flexible joints are necessary at both ends of the kiln to fix stationary chambers to the rotating body of the kiln. Figure (9.6) shows one type of joints. This consists of a ring made out of a soft metallic material like copper that is pressed on the stationary surface by means of spring bolts located on the moving part. As this ring abrades, the bolts will be pushed by spring action to maintain pressure. Recently, sliding graphite blocks are used, similar in action to balls in ball bearings.

     To avoid escape of gases from the kiln, these are moved by applying vacuum, so that the kiln is under slight negative pressure. This may cause air to be sucked into the kiln if special precautions are not taken. This **false air** will decrease the temperature inside the kiln and can impair its function. That is why seals are placed at bandings and at the gear to avoid such phenomenon.
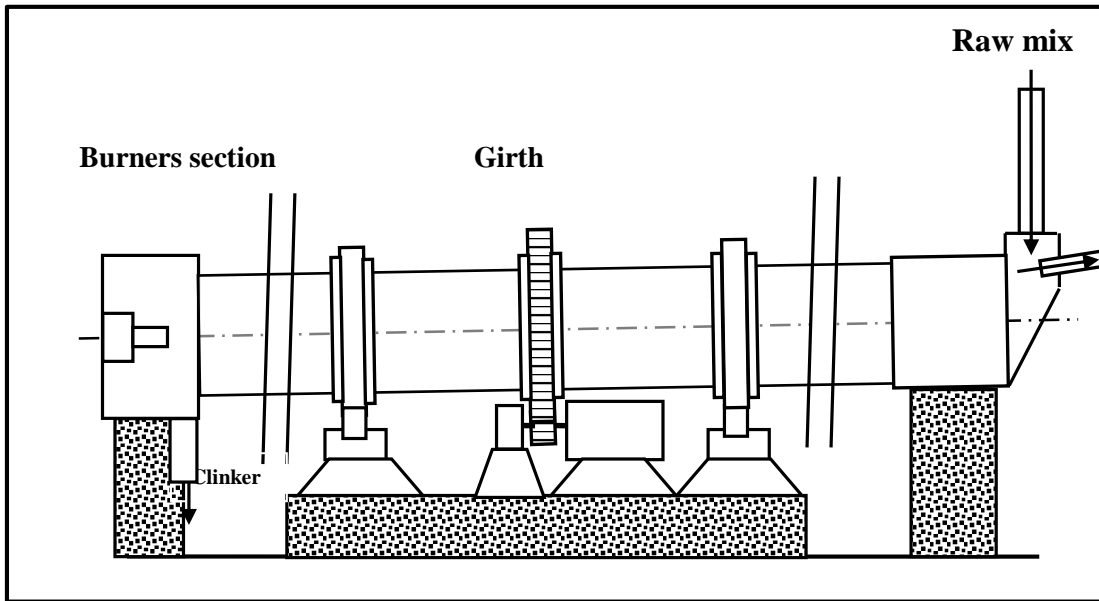
Fig 9.5 Rotary kiln for cement burning

- **Heat transfer in the kiln:**

Heat is essentially transmitted by radiation from the flame to the solids and the walls. Hot flue gases also radiate to solids and walls. Only a small fraction of heat is transferred by convection from gases. Heat is mainly lost by flue gases and to a lesser extent by conduction from the walls.
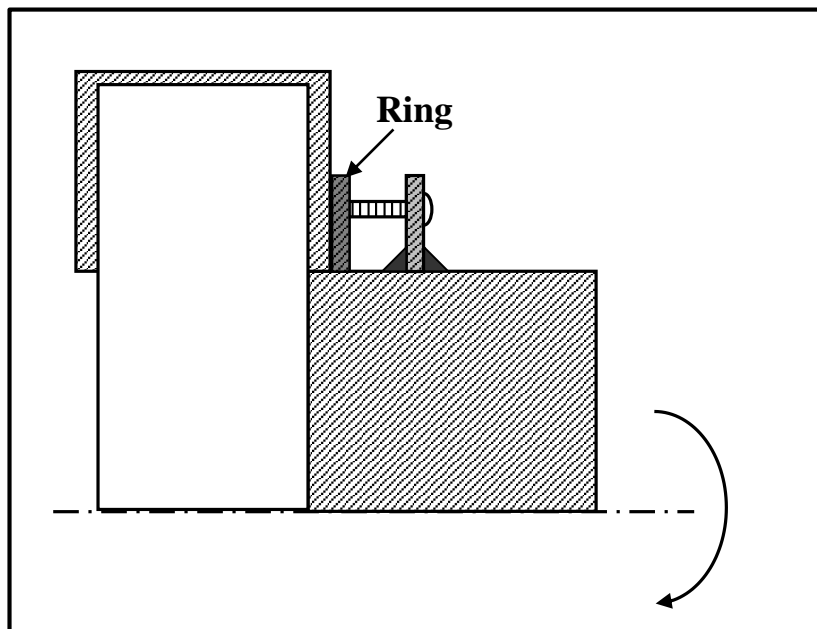

Fig 9.6 Typical rotary gas seal

- **Power required to drive the kiln**

The total power required to drive a rotary kiln takes into consideration several factors: the rotating speed, the total weight of the kiln and the weight of charge. The following empirical equation can be used to estimate the power to a reasonable degree of accuracy (in hp)

$$P = N(4.75\,d.m + 0.1925\,D.M + 0.33M) \times 10^{-5}\ \text{hp} \tag{9.7}$$

Where,
N is the rpm
d is the internal diameter, ft
D is the outside diameter, ft
M is the mass of kiln, lb
m is the mass of charge, lb

The mass of charge can be obtained by multiplying the mass rate of raw mix by the residence time. This latter can be obtained from the following formula:

$$t = \frac{1.77L.f}{\theta.d.N} \tag{9.8}$$

Where,
t is the residence time, min.
L is the kiln length, ft (or m)
θ is the angle of slope of kiln
d is the internal diameter, ft (or m)
f is the percent filling ratio f

The value of f usually ranges from 7 to 15%.

Typical residence periods range from 20 – 120 min., while typical power figures range from 100 – 600 hp.

Example 9.1
A rotary kiln 120m in length has an internal diameter = 10m and slopes to the horizontal at an angle = 3°. It rotates ate 1.2rpm. If the average filling ratio = 12%, estimate the residence time of solids in the kiln.

Solution:

Applying equation (9.8):

$$t = \frac{1.77 \times 120 \times 12}{3 \times 10 \times 1.2} = \textbf{71 min}$$

To calculate the mass of the kiln, first, we calculate the mass of the cylinder of length L, internal diameter d and outer diameter D. The figure shows that the inner diameter extends between the hot faces of the internal refractory lining. This refractory layer is followed by an external insulating refractory layer then the steel cover of the kiln. Since all these layers are much thinner than the kiln diameter, their volume can be calculated by the approximate formula: $V = 2\pi rxL$, where, x is the thickness of the layer and L the kiln length.

Let x_1, x_2 and x_3 be the thicknesses of the inner refractory layer, the insulating refractory layer and the steel cover respectively. Also, let the densities of these three materials be ρ_1, ρ_2 and ρ_3 respectively. Figure (9.7) shows that:

$x_1 = r_2 - r_1$

$x_2 = r_3 - r_2$

$x_3 = r_4 - r_3$

Where, $d = 2r_1$ and $D = 2r_4$

Fig 9.7 Kiln layers
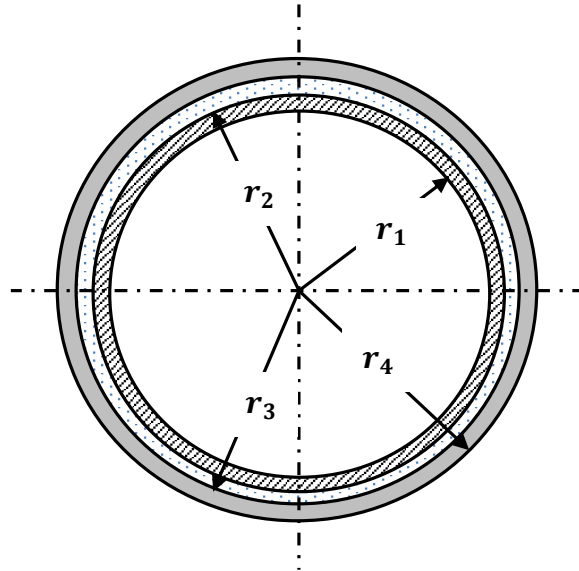
The mass of the three layers can be approximated by:

$$m_1 = 2\pi r_1 L x_1 \rho_1 \qquad\qquad m_2 = 2\pi r_2 L x_2 \rho_2 \qquad\qquad m_3 = 2\pi r_3 L x_3 \rho_3$$

Therefore the mass of empty cylinder will be:

$$M = 2\pi r_1 L x_1 \rho_1 + 2\pi r_2 L x_2 \rho_2 + 2\pi r_3 L x_3 \rho_3 \tag{9.9}$$

Since the kiln body also contains gears and rings, the actual mass is obtained by multiplying the above equation by a factor of about 1.2.

Example 9.1
Raw mix is fed to a rotary kiln at the rate of 250t.h⁻¹. The kiln has the following dimensions:
Inside diameter = 5m, thickness of refractory layer = 230 mm, thickness of insulating layer
= 230 mm, shell thickness = 0.5", length = 54 m. It rotates at 1 rpm and slopes at 3° to the
horizontal. Assume the filling ratio = 8%. Calculate the following:
(a) The maximum mass of charge inside the kiln.
(b) The mass of empty kiln.
(c) The required power to drive the kiln.
Densities of layers: Refractory = 2800 kg.m⁻³, Insulating refractory = 800 kg.m⁻³, steel shell
= 7800 kg.m⁻³.
Solution:
(a) From equation (9.8), the time of passage of solids through the kiln is:

$$t = \frac{1.77 \times 54 \times 8}{3 \times 5 \times 1} = 51 \text{ min} \equiv 0.85 \text{ h}$$

The solid flow rate is 250t.h^{-1}

Hence the maximum mass of charge $m = 250 \times 0.85 \approx$ **213 t.**

(b) The inner radii and thicknesses of different layers are as follows:

Refractory layer inner radius: $r_1 = 0.5 \times 5 = 2.5$ m, $x_1 = 0.23$ m

Insulating layer inner radius: $r_2 = 2.5 + 0.23 = 2.73$ m, $x_2 = 0.23$ m

Steel shell inner radius: $r_3 = 2.73 + 0.23 = 2.96$ m, $x_3 = 0.0127$ m

The mass of empty cylinder is therefore (Equation 9.9):

$(2\pi \times 2.5 \times 2800 \times 0.23 + 2\pi \times 2.83 \times 800 \times 0.23 + 2\pi \times 3.06 \times 7800 \times 0.0127) \times 54 \approx 816200$ kg

The global mass of the empty kiln is therefore estimated at

$M = 1.2 \times 816200 \approx 979400$ kg $\equiv$ **980 t.**

(c) $M = 980000$ kg $\equiv 2158600$ lb

$m = 213000$ kg $\equiv 471400$ lb

$d = 5\text{m} \equiv 16.4\text{ft}$

$D = 2 \times (2.5 + 0.23 + 0.23 + 0.0127) = 5.95$ m $\equiv 19.5\text{ft}$

Substituting in equation (9.7), one gets:

$P = 1 \times (4.75 \times 16.4 \times 471400 + 0.1925 \times 19.5 \times 2158600 + 0.33 \times 2158600) \times 10^{-5} = 455$ hp

Hence $P = $ **455 hp**

(b.4) Circulation phenomena

If the clay ore used in production is rich in alkalis, these will be mainly present in the form of chlorides. If liquid fuel oil is used for combustion, sulfur oxides will be released in flue gases. These will convert part of these chlorides to sulfates. Alkali salts are extremely volatile at the high temperatures prevailing inside the kiln. They tend to condense inside the cyclone preheaters and are recirculated to the kiln with the incoming raw mix, causing what is known as the **alkali cycle**. If their amount is appreciable they may clog cyclone openings as they condense causing disruption of operation. Such phenomenon is particularly observed when clay quarries lie in maritime regions.

Such cycle can be interrupted by changing the raw material source, using a sulfur free fuel (such as NG), or installing an **alkali by-pass system.** Although this latter solution is costly and is associated with a lot of operational and ecological problems, it remains the only alternative whenever the source of raw materials cannot be varied.

This consists in purging part of the gases at the temperature of vaporization of alkalis (900 – 1000ºC). This stream is then rapidly cooled by air (or water) and the entrained condensed dust collected by means of an electro static precipitator or more likely by bag filters. (Figure 9.8)

This dust contains a large amount of alkali salts (> 6%) and accumulates in large amounts beneath the precipitators and cannot obviously be recycled to the kiln. An average kiln can produce as much as 300 tpd by-pass dust. Although several solutions have been proposed for its use, none of them, to date, can cope with the huge amounts produced. This dust is simply dumped in desert areas.
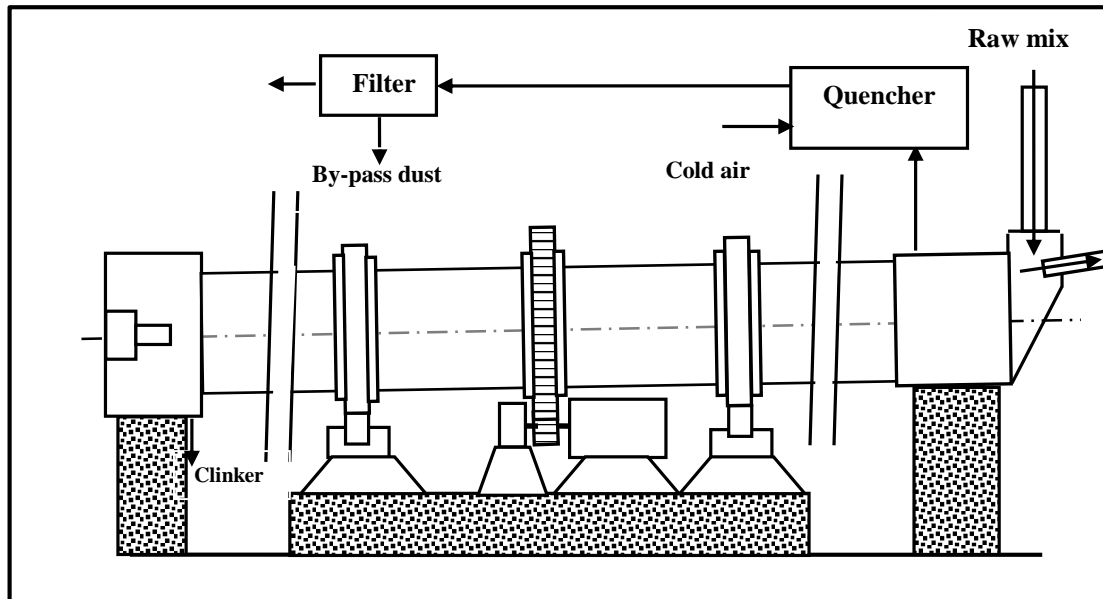
Fig 9.8 Alkali by-pass system

(b.5) Rings formation

As material slides and tumbles slowly through a heated rotary kiln, a thin layer of dust invariably forms on its inner lateral surface. Some zones of the kiln may be particularly prone to particle accumulation in such a way that the combination of particular thermal and flow conditions results in the formation of cylindrical deposits of solid crystalline structures referred to as **rings**. As such rings grow thicker they form a dam in the kiln free space, hindering the flow of material and flue gasses through the kiln. In particular, rings that are formed close to the burner are known to be caused by the direct impingement of the burner flame on the lateral surface of the kiln causing local overheating. These are the most common and most troublesome type of rings as they are impossible to remove while the kiln is in operation. In severe cases, ring dams grow rapidly and cause the unscheduled shutdown of the kiln. This in turns causes very important production and turnover losses. (Figure 9.9)

To avoid excessive ring formation, it is necessary to reduce local overheating associated with excessive liquid phase formation. This can be achieved by altering the air to fuel ratio by decreasing the amount of secondary air. This reduces peaks in temperature which in turns limits the amount of liquid phase formed.

(b.5) Clinker coolers

As clinker leaves the rotary kiln, it has to be rapidly cooled. The main reason for rapid cooling is that C_2S is present in clinker in the variety β C_2S. If left to cool slowly, this will transform to the allotropic γ form. This transition is accompanied with a large volume change causing shuttering of clinker nodules, a phenomenon known as **dusting of cement**.

There are several types of clinker coolers, the three main types are discussed in what follows:

Fig 9.9 Ring formation in cement kiln

- **The rotary cooler:** This is the oldest type of coolers. It resembles in its features a rotary kiln, although of smaller size and higher inclination. Its use is usually restricted to low capacity furnaces (< 500 tpd), although recently it has been adapted to larger capacities reaching 4500 tpd. Despite its simple design and low energy consumption, it suffers from the following disadvantages: It produces clinker at a relatively high temperature ($\approx 150^{\circ}$C) and inlet clinker often forms build-ups in the inlet chute.

- **The planetary cooler:** This type of coolers can be used for large capacities, and has been particularly used with wet process kilns. It consists of several drums fixed on the periphery of the rotating kiln, parallel to its axis. This block is mounted on the housing of the kiln at its hot end (Figure 9.10). Hot clinker leaves the kiln to the drums, where it flows against a countercurrent blast of cold air. When it reaches the end of the drum, it will have cooled down to less than 200°C. The drums have diameters in the 1 m. range and their length reaches 6 m. Hot air emerging from the cooler is at about 700°C. Its main advantage is that it does not require a special drive as it rotates with the kiln. However, its design is intricate and the cooled clinker leaves at a relatively high temperature.

- **The grate cooler:** This type has become the most widespread used in the production of cement by the dry process with total precalcination, since it offers the possibility of getting tertiary air necessary for this process. It consists of a reciprocating grate with drive system enclosed in a casing with kiln hoods. Beneath the grate are located air ducts with fans that circulate air across the clinker moving on the grate. As the clinker is about to be discharged from the cooler, it is occasionally crushed. (Figure 9.11 and 9.12)
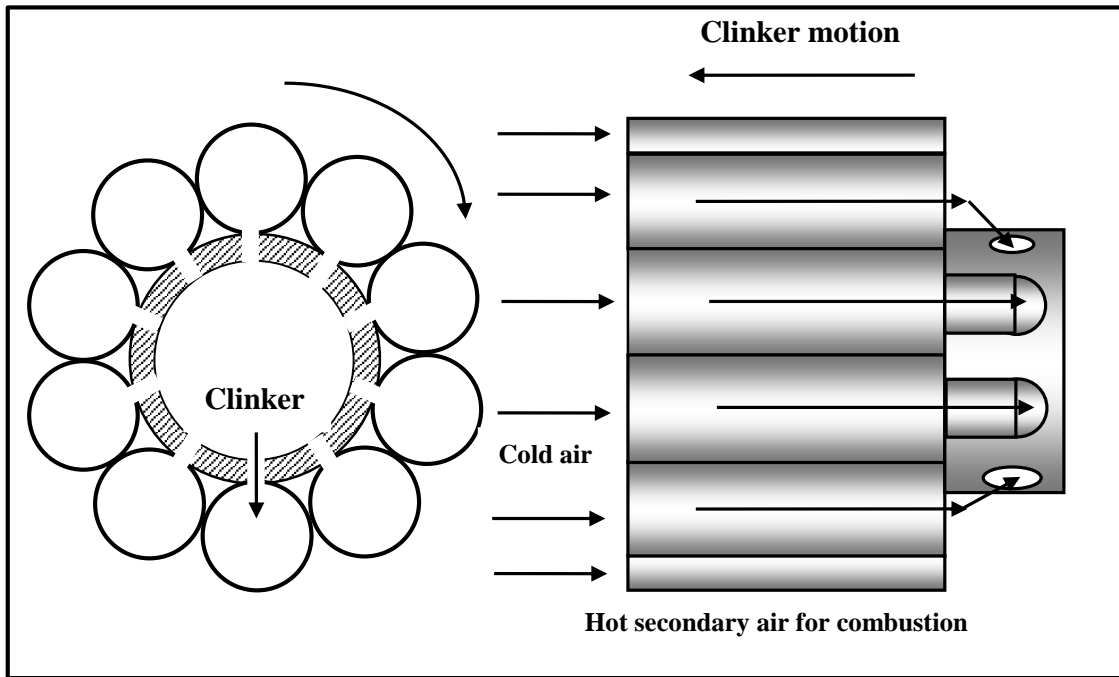
Fig 9.10 A planetary cooler

Clinker moves along the cooler by the reciprocating action of grate plates and a vertical partition along the cooler allows for obtaining two or more hot air streams. In modern designs, the outlet air temperature in the first section, used as secondary air, reaches 1000ºC. It may account for 90% of air required for combustion in the kiln. Air from the middle section leaving at about 450ºC may be used for drying raw materials. In addition, tertiary air at temperatures from 800 to 1000ºC can be extracted from the kiln hood to be used in the total precalcination furnace. Special provision has to be made if tertiary air is to be obtained.
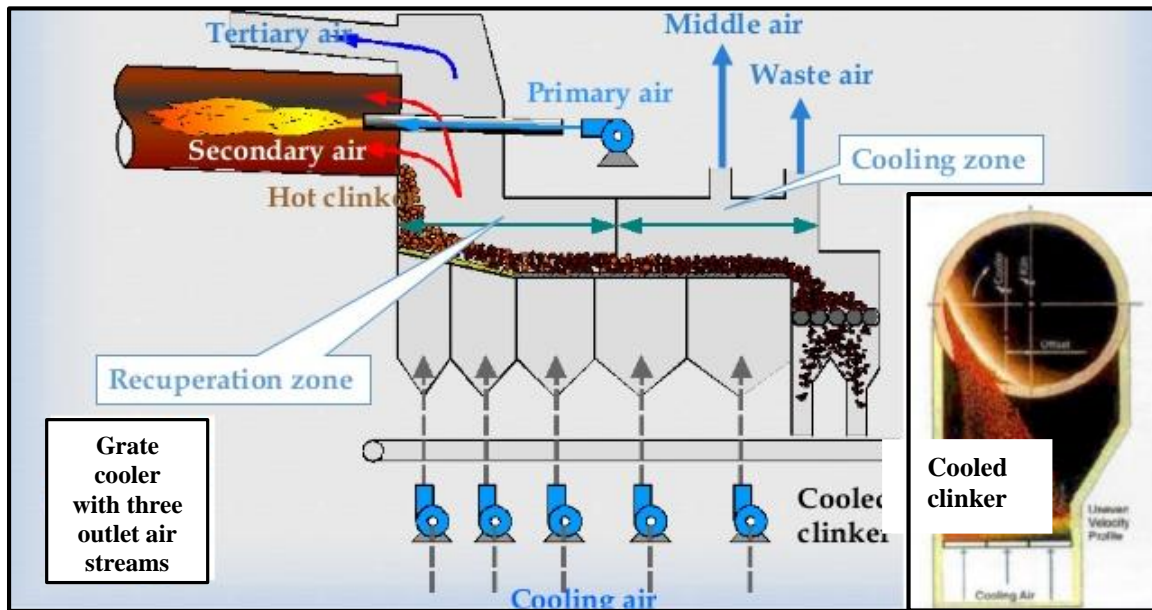

Fig 9.11 Grate cooler entrance

Fig 9.12 Grate cooler operation

(b.6) Gas cleaning

Flue gases from the kiln or from an eventual by-pass system are commonly cleaned using electrostatic precipitators (EP). These can rid the gases from particles as fine as 0.01 μm. They rely on the following principle: If a high voltage is set up between two conductors, then the atoms of ambient gas will be ionized. If this latter contains dust particles, then they will be charged and can subsequently be collected by earthed electrodes.

In cement industry, the commonly used type consists of vertical wires (or rods) placed between collecting plates. High intensity current is made to flow through these plates and the charged dust particles are collected at the plates. The rods act as cathodes while the plates are positively charged. These are regularly shaken or hammered to get rid of adhering particles. The retention time of gases into the precipitator is a few seconds, and the applied voltage is in the range 10^5 V. Collection efficiencies as high as 99.9% are not uncommon. This is necessary to abide by standard norms of dust concentrations in the cleaned gas stream (< 50 mg/Nm^3). The collection efficiency increases with a decrease in gas temperature and an increase in its humidity. Fig (9.13) shows a typical electrodes arrangement as well as a photo of a typical such precipitator.

One common problem encountered is the fact that CO can combine with air to form an explosive mixture if its concentration in the flue gas stream exceeds 1%. That is why, it is necessary to install a rigid control system that cuts off power whenever the CO level becomes critical.
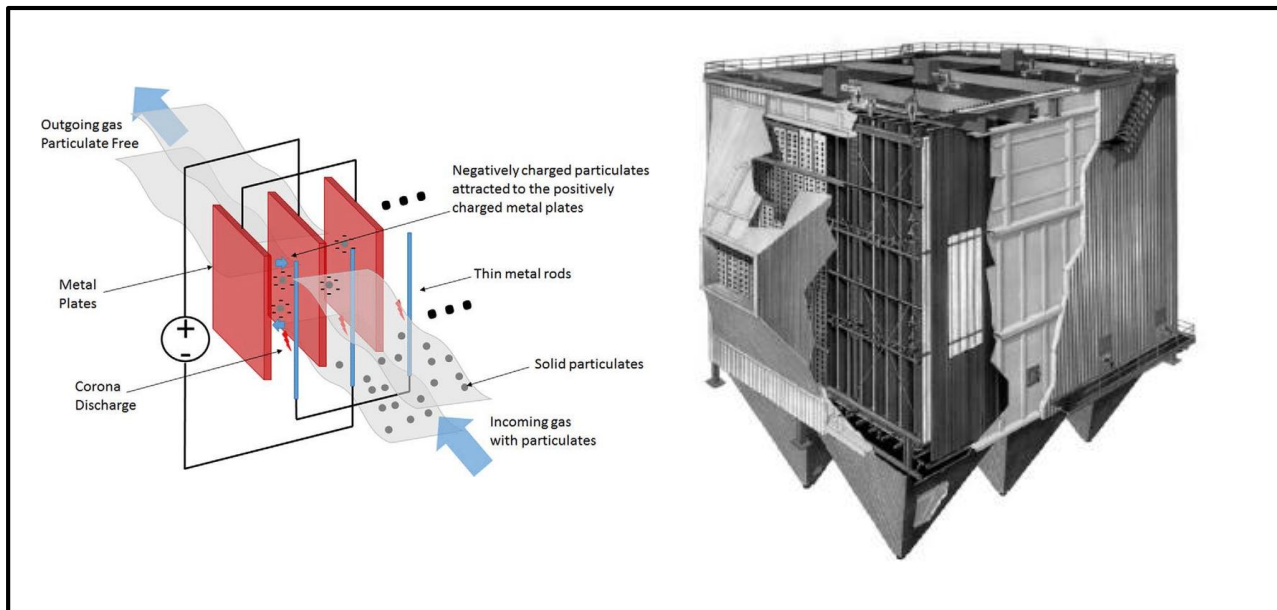
Fig 9.13 Electrodes arrangement in electrostatic precipitator

9.4.4   Some trends in cement manufacture

Although some of the trends discussed were devised a few decades ago, they have gained increased importance in recent years.

(a) Decreasing CO_2 emissions

One simple method of decreasing such greenhouse gas emissions is simply to surround the factory area by a green periphery consisting of a forest of trees and other vegetation.

(b) Blending part of the by-pass dust with product cement

Part of the by-pass dust can be blended with cement without a ltering its properties. A main condition is that the chloride content of the final blend should not exceed 0.1%. This way, depending on the chloride content of clay raw material, up to half the by-pass load can be used, resulting in improved economic and ecological aspects.

(c) Using vertical roll mills (VRM) for grinding

A vertical grinding mill (VRM) consists of a rotating grinding table on which several rollers (up to 6) grind the raw material. A special system (not shown in figure) allows for the partly ground material to be entrained by a stream of air to a separator. In this latter, coarse particles move towards the periphery of the cone and fell onto the table to be ground once more (Figure 9.14). Fine particles are entrained by the air stream to an outlet opening.

Over the last three decades, VRM has increasingly replaced conventional ball mills in grinding raw materials. A main advantage is that classification does not require a separate unit, but readily occurs in the mill. Its use in clinker grinding is less frequent. The decision to use either VRM or ball mills mainly depends on economic considerations.

VRM has been conventionally used to grind raw materials offering the possibility to use one such equipment instead of a series of tube mills. Another advantage over conventional tube mills is the lower ground floor space it occupies. However, cement manufacturers have

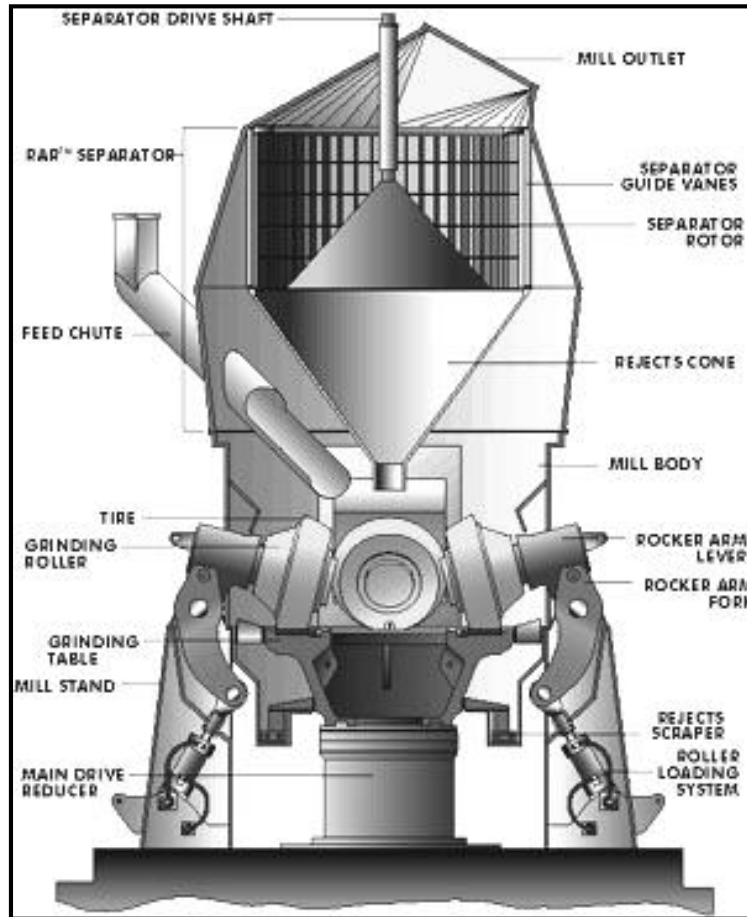been reluctant to use VRM for clinker grinding because of the flaky nature of ground product.

Fig 9.14 Vertical Roller Mill VRM

This shortcoming has been overcome by introducing vertical mills (OK mills) with a curved grinding table profile that produces ground clinker particles in shapes close to spherical. Figure (9.15) shows a typical such mill and the rollers – curved table arrangement.

Fig 9.15 Curved Table OK mill

(e) The use of alternate fuels

Classical fuels used in cement kilns are coal, fuel oil, diesel oil and NG. In the last two decades, combustible waste materials (Refuse derived fuels, RDF) have been used as alternate fuels in cement kilns. Their use represents two main advantages: Safely disposing of more or less hazardous waste and decreasing fuel consumption. The use of any waste derived fuel is limited by the presence of undesirable elements such as S or Cl, possible radioactivity and low calorific value. Table (9.4) lists some waste fuels together with their calorific value.

Table 9.4 Some alternate fuels used in cement kilns

Fuel source	Type of WDF	C.V. kJ/kg
Municipal WDF	Domestic refuse	9000
	Mixed plastics	19000– 42000
	Waste tires or rubber	27000– 38000
	Dried sewage sludge	7400
Agricultural WDF	Rice husks	11000– 16000
	Saw dust	10000- 13000
	Bagasse	9000
Industrial WDF	Waste oil (refinery)	30000- 40000
	Paper pulp	15000
	Corn kernels	11000– 15000

(f) The use of bag filters

Owing to the increased cost of electric energy, cement manufacturers are more and more inclined to replace electrostatic precipitators by bag filters.

Conventional bag filters consist of an arrangement of vertical bags where dusty air (or gases) is allowed to pass through the woven fabrics which filter the air. Actually, dust removal is rather performed by the coat of dust deposited on the fabric rather than by the fabric itself. Figure (9.16) shows a typical arrangement of vertical bags in a rectangular housing. Commonly, dusty air is circulated on the outer periphery of the bags, thereby depositing the dust on the outer surface of the bags.

Cleaning of the bags is done periodically by closing the incoming air valve to a set of bags and either mechanically shaking these bags or introducing compressed clean air in a reverse direction to make the dust particles drop in the collecting funnel. In that case, cleaning is done by passing clean air inside the bags thus expelling the dust to the bottom funnel.

The bags are usually made from cotton, Nylon, Dacron, Polyethylene for normal operation, and from fiberglass for high temperature uses.
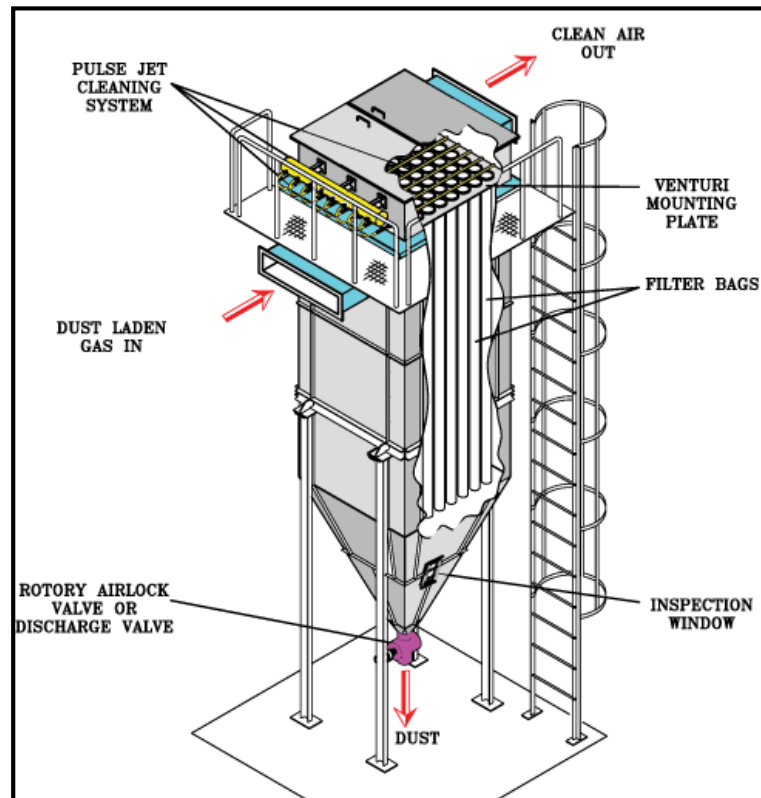
Fig 9.16 Bag house arrangement

(g) The use of coal as fuel

Due to shortages in fuel oil and natural gas, emphasis has been put on using coal as a substitute for these fuels. Coal is normally imported then transported as lumps to the premises of the factory. This has to be stored in special sheds in a slightly compressed form. Next, coal is pneumatically transported to a VRM unit to be finely ground and simultaneously pneumatically conveyed to a bag filter house. Circulating air is substituted by CO_2 to avoid CO formation during grinding and pneumatic conveying. Finely ground coal is then stored to be fed to the furnace for burning. It is customary to use a multichannel burner that can accommodate several types of fuel.

However the use of coal faces several challenges:

a) Poor storage conditions can result in self ignition of coal. Such hazards can be minimized by installing water sprinklers that cool down the stored mass besides installing a carbon monoxide detector in feeding and storage zones.

b) Egypt has no appreciable coal reserves so that coal has to be imported.

c) The grinding unit will generate a small amount of fine dust that escapes bag filtration. Its amount and concentration must not exceed the values fixed by environmental authorities.

d) The carbon dioxide level in flue gases will increase upon using coal as fuel instead of natural gas. Provisions have to be taken to regulate such emissions.

e) Specific heat consumption of the rotary kiln has been shown to increase on suing coal as fuel. One recommendation is that it should not exceed 4000 kJ/kg clinker.

f) In the event of using petcoke instead of charcoal as fuel, grinding has to be carried out in tube mills rather than VRM. This is since the reduction in size of petcoke takes place by impact and compressive forces and not by attrition.

9.4.5 Environmental impact of cement manufacture

The main environmental issues associated with cement production are consumption of raw materials and energy use as well as emissions to air. Waste water discharge is usually limited to surface run off and cooling water only and causes no substantial contribution to water pollution.

The storage and handling of fuels is a potential source of contamination of soil and groundwater. Additionally, the environment can be affected by noise and odors.

The key polluting substances emitted to air are dust (Particulate matter PM), carbon oxides nitrogen oxides (NO_x) and sulfur dioxide (SO_2). Carbon oxides, dioxins and dibenzofurans, total organic carbon, metals, hydrogen chloride and hydrogen fluoride are emitted as well. The type and quantity of air pollution depend on different parameters, e.g. inputs (the raw materials and fuels used) and the type of process applied. Table (9.5) summarizes the environmental aspects related to cement manufacture.

Table (9.5): Environmental effects in cement manufacture

| #	Step	Type of emission
1	Quarrying of raw materials	PM
2	Crushing of raw materials	PM, noise
3	Grinding of raw materials	PM, noise
4	Suspended preheaters	PM, gases
5	Calciner	PM, gases, heat
6	Rotary kiln	PM, gases, heat
7	Clinker cooler	PM, gases
8	Grinding of clinker and gypsum	PM, noise
9	Packaging	PM

9.5 Hydration of cement

9.5.1 Mechanism of hydration

As water is added to cement, a paste is formed that develops consistency and strength. This is due to the formation of hydrates out of the main clinker constituents. First, C_3A hydrates forming cubic hexahydrate crystals. The reaction is very rapid and full hydration takes place in a few hours.

$$C_3A + 6\ H_2O = C_3A.6H_2O \hspace{4cm} (CAH)$$

Then, C_3S and C_2S follow at lower rates, although the rate at which the latter hydrates is much lower than the former. Both yield a hydrate of formula: $C_3S_2. 3H_2O$.

$$2\ C_3S + 6\ H_2O = C_3S_2.3H_2O + 3Ca(OH)_2$$

$$2\ C_2S + 4\ H_2O = C_3S_2. 3H_2O + Ca(OH)_2$$
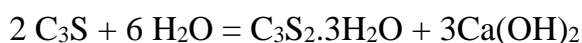
Also, C_4AF hydrates to give $C_3A. 6H_2O$ and a calcium ferrite hydrate. If any free lime or magnesia is present, then the corresponding hydroxides will be formed.

While C_3A hydrates in a few hours, C_3S will take about seven days to totally hydrate. C_2S, on the other hand, will not complete its hydration before several months. The rate at which these reactions occur follows the order: $C_3A > C_4AF > C_3S > C_2S$

Hydration is also accompanied by exothermic heat release, being mainly due to the hydration of C_3A.

9.5.2 Development of strength

Although C_3A is the first compound to hydrate, the crystals formed are weak and do not influence the strength of the paste. On the other hand, $C_3S_2.3H_2O$ crystals are the main contributors to strength. Since C_3S is faster to hydrate than C_2S it is considered to be the compound that is mainly responsible for strength development or **hardening** particularly during the first few weeks following hydration. As C_2S is much slower to hydrate it will not seriously contribute to strength before a few months. At the age of one year their contribution to strength is comparable. Fig (9.17) shows the effect of time on the developed strength of each hydrate. It shows that, after about one year, the strengths reached by the hydration of C_3S and C_2S are comparable.
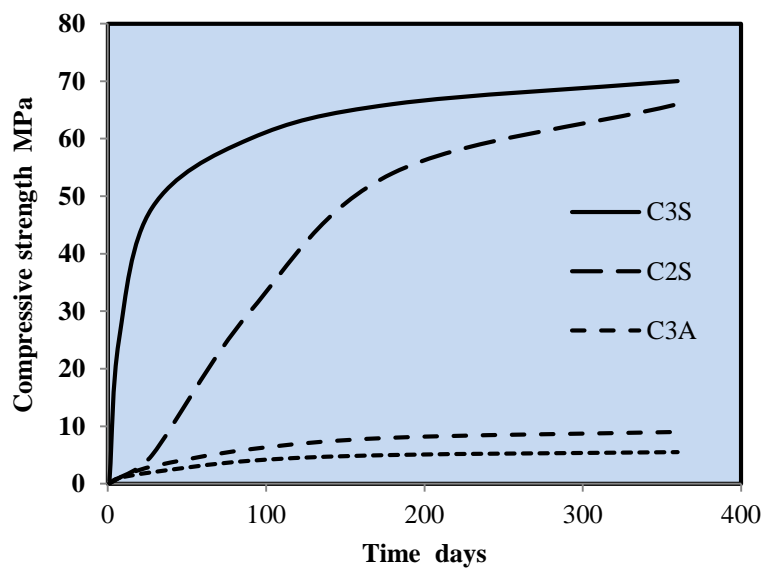

Fig 9.17 Development of strength in clinker components

9.5.3 The role of gypsum in cement manufacture

If ground clinker is directly treated with water, then C_3A present will readily react and setting will occur in a few minutes before any proper molding can be done, a phenomenon known as **flash setting**. If gypsum is added in a few percentages ($\approx 5\%$), then C_3A will selectively react with $CaSO_4$ to form calcium sulfo-aluminate, otherwise known as **Ettringite**: $C_3A.3CaSO_4.32H_2O$. This gives enough time for C_3S to begin hydration.

If too much gypsum is added, then setting will be seriously delayed. On the other hand, if clinker is not cold enough, then, on grinding with gypsum, it may convert to the hemihydrate through the reaction:

$$CaSO_4.2H_2O = CaSO_4.\tfrac{1}{2}H_2O + {}^3/_2H_2O$$

On adding water, the hemihydrate will rapidly set to the original dehydrate and an apparently hard mass will be obtained, a phenomenon known as **false setting**. That is why it is common to water spraying the clinker ball mills on their outer surface to prevent overheating of gypsum. The use of grate coolers is beneficial in this respect as the produced cooled clinker normally has its temperature lower than 100^oC.

A recent trend consists in heating gypsum to a relatively high temperature (about 200ºC) to convert it to the inert anhydrite ($CaSO_4$) before grinding with clinker. Since this compound does not possess any hydration properties, the clinker temperature is irrelevant. Whether it is more convenient to use this technique or to cool the mills is an economic matter.

9.6 Properties of Portland Cement

9.6.1 Setting and hardening (ASTM C191 - 13)

By setting is meant the acquirement by a cement paste of a solid – like consistency, while hardening means the ability of set cement to with-stand external stresses.

An important parameter to start with is the **water of consistency**. This is the amount of water needed to form a workable plastic mass. It is determined using a standard apparatus known as the **Vicat needle**. This is shown in Figure (9.18) and consists of a standard needle that is fixed to a vertical rod, both capable of motion along a stand.

Water of consistency is calculated as the amount of water to be added to 100 g. of cement so that the needle penetrates 5 mm from the bottom in a freshly prepared paste.
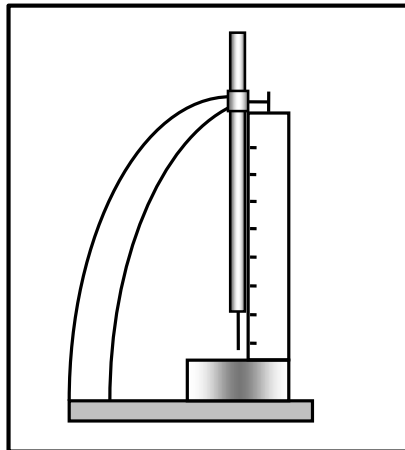

Fig 9.18 The Vicat needle

Initial setting is the time taken for the needle to penetrate 5 mm from the bottom in a paste prepared with by mixing cement with its water of consistency, while final setting is reached when the needle just leaves an impression on the surface of the hard paste, while the circular edge representing the tip of the rod does not. Initial setting time should not be less than 30 min., while final setting should occur in less than 10 hrs.

Hardening is associated with strength development and is discussed in the next section.

9.6.2 Strength (ASTM C109–16a)

Standard compressive strength tests are usually performed on 2" cubes filled with cement mortar after 1 day, 3 days, 7 days and 28 days. This last test is of particular importance although it is sometimes not performed for lack of time. Cement pastes reach 70 to 80% of its final strength after 28 days. OPC mortars should have a compressive strength of at least 32.5 MPa after 28 days.

9.6.3 Soundness (Constancy of volume) (IS 4031-Part 3–1988)

If free CaO or free MgO is present in the final product, then they will hydrate producing the corresponding hydroxides. This process is accompanied with an increase in volume that may cause cracks to develop in the hardened mass. A simple test, known as the Le Chatelier fork test is used to assess the possibility of excessive volume expansion. In this test, cement is mixed with 78% of water of consistency to form a paste. This is confined in a horizontal brass ring of standard dimensions to which are fixed two flat slabs of standard length. The paste is left for 24 hours in water at 27ºC and the clearance between the tips of the slabs measured then boiled for one hour and the clearance measured. A difference in the two readings of more than 10 mm denotes the presence of excess free lime (Figure 9.19).
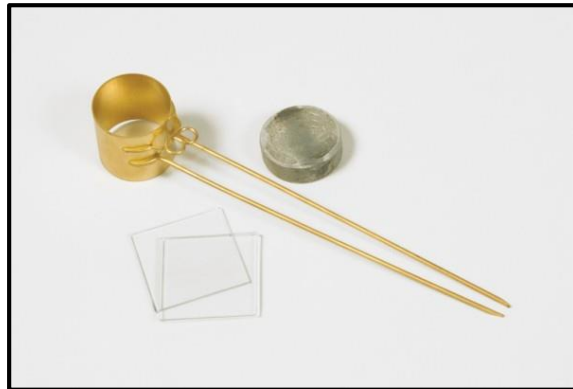

Fig 9.19 Le Chatelier fork test

9.6.4 Chemical Composition (ASTM C114–15)

This is generally related to the type of cement. However, there are certain general requirements: The Loss on ignition should not exceed 5%, the percent of solids insoluble in HCl should not exceed 5%, the sulfate and chloride content should not exceed 3.5% and 0.15% respectively.

9.6.5 Heat of Hydration (ASTM C186–15a)

This test is of particular importance if the cement is to be of low heat release type. It should not exceed 270 J/g. after 7 days.

9.6.6 Fineness (ASTM: C 204–16)

This test is used to evaluate the specific surface area to ensure its fulfilling some minimum value. This is particularly true in case of rapid hardening cement which should have a larger specific surface than OPC. The specific surface is determined by a test known as the Blaine test, which makes use of the pressure drop accompanying the flow of air through a porous cement bed. The specific surface of OPC usually exceeds 2500 cm^2/g. This figure increases to more than 3500 cm^2/g in case of rapid hardening types.

9.7 Types of Portland Cements (E.S.S. 4756 – 1 / 2007)

The above standard has replaced previous classifications and is in harmony with EN 197-1 standard.

Cement types are generally divided according to their constitution: OPC (CEM I) is by far the most important with its various applications. Other types include mixed cements

with iron slag (CEM II/S), with silica fume (CEM II/A-D), with pozzolanic cement (a natural cement of volcanic origin) (CEM II/P and Q), with burnt clay (CEM II/T), with limestone (CEM II/L), with fly ash (CEM II/V) as well as other mixed types with different ratios of the above additions.

Mixed cements containing silica fume and fly ash exhibit high strength and can be used for structural purposes. On the other hand, slag and pozzolanic cements can be cautiously used for the same purpose. Limestone and burnt clay cements will generally exhibit lower strength and should only be used for masonry and non – structural works.

Eventually, any other types required that were described by the previous standards (Such as rapid hardening cement, low heat cement, etc.) have to be delivered according to the specifications required by the end user.

9.8 Corrosion of concrete

9.8.1 Deterioration of concrete in aggressive environment

Concrete usually consists of a mixture of cement, sand and gravel to which is added water to effect setting and subsequent hardening of cement. It is common to have 300 to 350 kg cement per cubic meter concrete. While concrete is usually evaluated according to structural criteria (Like strength), deterioration due to chemical attack is often overlooked. In the following is given a brief outlook about the causes and mechanisms of concrete corrosion.

(a) Leaching corrosion

As previously stated, the hydration of calcium silicates produces calcium hydroxide. Actually, the pores of concrete are filled with a saturated solution of $Ca(OH)_2$. If water is allowed to seep through a concrete structure, it will dilute that solution forcing it to diffuse across the concrete body to external walls. Once the caustic solution reaches external walls, carbonation takes place due to its interaction with atmospheric CO_2:

$Ca(OH)_2 + CO_2 = CaCO_3$ (white precipitate) $+ H_2O$
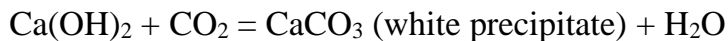
This white precipitate shows as patches on the external walls (Figure 9.20).
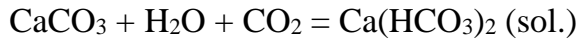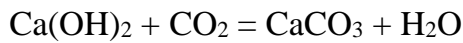

Fig 9.20 White patches on external walls

This type of corrosion is not harmful from a structural point of view although it causes cracking and peeling of the wall paint.

(b) Carbonate corrosion

In presence of CO_2, the previous mechanism is accelerated owing its reaction with $Ca(OH)_2$ first producing calcium carbonate, followed by formation of water soluble calcium bicarbonate which rapidly diffuses to the external wall:

$Ca(OH)_2 + CO_2 = CaCO_3 + H_2O$

$CaCO_3 + H_2O + CO_2 = Ca(HCO_3)_2$ (sol.)

Upon reaching the external wall and under the influence of warming sun, bicarbonate decomposes to the carbonate producing white patches. This is particularly common in industrial areas and crowded downtown regions where the CO_2 level is more elevated than in rural areas.

(c) Sulfate (sea water) corrosion

Concrete structures exposed to sea water deteriorate very rapidly as their surface shutters into white flakes traditionally known as the **white death of concrete**. We recall that after enough time a concrete structure will be composed of calcium aluminate hexahydrate ($C_3A.6H_2O$), the hydrate $C_3S_2. 3H_2O$ and $Ca(OH)_2$.
Sea water contains about 7% magnesium ions, mostly in the form of sulfates. As sea water is allowed to seep through a concrete structure, double exchange takes place between $MgSO_4$ and $Ca(OH)_2$ to yield $CaSO_4$. This in turns attacks the hexahydrate to form **ettringite**:

$3CaSO_4 + C_3A.6H_2O + 26 H_2O = C_3A. 3CaSO_4.32H_2O$

The formation of ettringite is accompanied with a large expansion in crystals causing an overall expansion in concrete body that can reach 1%. This causes rapid crack formation accompanied with shuttering of concrete in the form of white layers. (Figure 9.21)

Fig 9.21 Deterioration of concrete in sea water

In order for a concrete structure to resist sea water attack, dense concrete of low porosity should be used (By increasing the content of cement per cubic meter concrete). Also, a special type of cement known as **sulfate resistant (or sea water) cement** should be used.
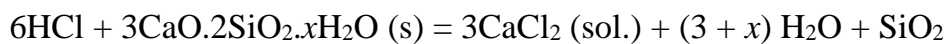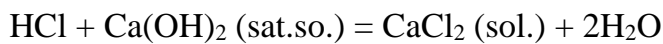
The raw mix of that particular cement is designed so as to minimize the extent of sulfate attack by decreasing both C_3A and $Ca(OH)_2$ levels. This is done by decreasing the LSF (section 9.3.4) thereby decreasing the calcium oxide level which in turns decreases the levels of C_3A and C_3S produced in clinker. The reason behind decreasing C_3S is that it

produces large amounts of $Ca(OH)_2$ on hydrating compared to C_2S (section 9.5.1). The use of such cement has however several drawbacks: the lower level of C_3A will retard setting and the decrease in C_3S formation will result in a lower rate of strength development. Also, a decrease in $Ca(OH)_2$ concentration will decrease the resistance of concrete to corrosion of steel reinforcement as will be seen later.

(d) Acid corrosion

In general, plain concrete does not show good resistance to acids. In fact, no hydraulic cement concrete, regardless of its composition, will hold up for long if exposed to a solution with a pH of 3 or lower. Occasionally, some weak acids can be tolerated, particularly if the exposure is occasional.

Hydrochloric acid and nitric acid are the most aggressive acids in that respect since on reacting with calcium hydroxide and silicate hydrates they produce soluble salts that leach out the attacked face. This uncovers more exposed areas and ends up with total collapse of the concrete member.

$HCl + Ca(OH)_2$ (sat.so.) $= CaCl_2$ (sol.) $+ 2H_2O$

$6HCl + 3CaO.2SiO_2.xH_2O$ (s) $= 3CaCl_2$ (sol.) $+ (3 + x) H_2O + SiO_2$

The attack of sulfuric acid causes a similar effect although initially at lower rate because of the low solubility of calcium sulfate formed. However, once this salt has formed in reasonable amount, formation of ettringite will follow causing shuttering of the concrete faces. Also, acid rain dissolving SO_x and NO_x in industrial areas penetrates the concrete mass and slowly causes its deterioration. Likewise, certain bacteria convert sewage into sulfuric acid causing a similar effect.

9.8.2 Corrosion of reinforced concrete

Concrete offers a normal protection of steel bars (rebars) against corrosion since, in principle, it shields them from atmospheric attack. However, owing to the presence of pores, atmospheric oxygen and water vapor will diffuse into the concrete mass. Because of the presence of saturated $Ca(OH)_2$ in pores, the pH of the concrete mass is about 13. This highly alkaline medium causes the following anodic and cathodic reactions to occur:

$Fe = Fe^{2+} + 2e^-$

$\frac{1}{2} O_2 + H_2O + 2e^- = 2OH^-$
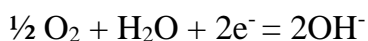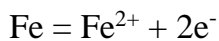
The net reaction will be the production of $Fe(OH)_2$ which forms a passive layer surrounding the steel bars. Figure (9.22) shows that state of affairs.
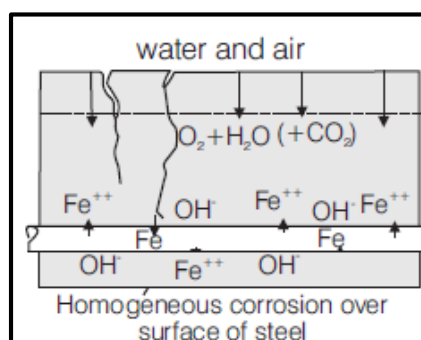

Fig 9.22 Formation of passive layer

When the chloride ions concentration increases within the concrete mass, a mechanism resulting in decreasing the pH of the medium occurs. There is more than one explanation for that mechanism although the most probable is that Cl^- ions compete with OH^- ions in reacting with Fe^{2+} ions, thus breaking down the protective layer. As the pH drops, galvanic corrosion takes place as Fe^{2+} and Fe^{3+} ions go into solution. The e.m.f. of the galvanic reaction increases resulting in continuous loss of iron metal. Figure (9.23) illustrates a corroded bundle of rebars in a concrete ceiling. The maximum allowable concentration of Cl^- ions in cement is fixed at 0.15% although it is common to have lower levels in commercialized cement.

Fig 9.23 Corroded steel bars

The dissolution of iron metal is not the only problem associated with corrosion of steel bars. This is since among the products of corrosion is a complex oxide-hydroxide mixture ($Fe_2O_3.xH_2O$, Fe_3O_4, $FeOOH$) better known as **rust**. Its formation is accompanied with an appreciable increase in volume (exceeding 300%!) that generates stresses in the concrete mass resulting in the formation of cracks.

Reinforced concrete corrosion can be minimized by the following provisions:

- Having at least a 200 mm cover of concrete over the nearest bar.
- Increasing the cement to water ratio in concrete making so as to decrease the level of porosity. This results in less plastic mixes that cause problems in concrete placing. Polymeric superplasticizers are now available on the market, which allows using less mixing water.
- Steel bars can be coated with an epoxy resin or cheaper bitumen to delay possible attack. An ideal solution would be to use chromium rich stainless steel alloys. However this alternative is limited by economic considerations.
- Mixing siliceous additives during the preparation of concrete that react with part of the $Ca(OH)_2$ present in pores forming silicate hydrates that contribute to increasing the strength while at the same time reducing the porosity as these salts crystallize into the pores.

Suggested additional reading

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