

CEMENT INDUSTRY

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1- An Introduction:

*General Information about the Cement Industry:

Cement is a basic material for building and civil engineering construction. In Europe, the use of cement and concrete (a mixture of cement, aggregates (gravel and sand), and water) in large civic works can be traced back to antiquity. Portland cement, the most widely used cement in concrete construction, was patented in 1824. The output from the cement industry is directly related to the state of the construction business in general and therefore tracks the overall economic situation closely.

* Hydraulic and Non-Hydraulic Cement:

Cement used in construction can be characterized as being either hydraulic or non-hydraulic, depending upon the ability of the cement to set in the presence of water. Non-hydraulic cement will not set in wet conditions or underwater; rather, it sets as it dries and reacts with carbon dioxide in the air. It can be attacked by some aggressive chemicals after setting.



Hydraulic cement (e.g., Portland cement) set and become adhesive due to a chemical reaction between the dry ingredients and water. The chemical reaction results in mineral hydrates that are not very water-soluble and so are quite durable in water and safe from chemical attack. This allows setting in wet condition or underwater and further protects the hardened material from chemical attack. The chemical process for hydraulic cement found by ancient Romans used volcanic ash.

2-Raw materials for cement manufacture:

The first step in the manufacture of cement is to combine a variety of raw ingredients so that the resulting cement will have the desired chemical composition. These ingredients are ground into small particles to make them more reactive, blended together, and then the resulting raw mix is fed into a cement kiln which heats them to extremely high temperatures.

Since the final composition and properties of cement are specified within rather strict bounds, it might be supposed that the requirements for the raw mix would be similarly strict. While it is important to have the correct proportions of calcium, silicon, aluminum, and iron, the overall chemical composition and structure of the individual raw ingredients can vary considerably. The reason for this is that at the very high temperatures in the kiln, many chemical components in the raw ingredients are burned off and replaced with oxygen from the air.

Table1: some of the many possible raw ingredients that can be used to provide each of the main cement elements.

Calcium: Limestone, Marl, Calcite, Aragonite, Shale Fly ash, Sea Shells, Cement kiln dust.

Silicon: Clay, Marl, Sand, Shale, Fly ash, Rice hull ash, Slag.

Aluminum: Clay, Shale, Fly ash.

Iron: Clay, Iron ore, Shale, Blast furnace dust.

The cement industry is considered of strategic industries. It is so simple with the industry compared to major industries, and depend on the availability of the necessary raw materials for it.

The basic mixture of the cement industry consists of:

* Chalk * limestone * Clay * Calcium carbonate * Silicon oxide * Aluminum oxide * Iron oxide.

3-Description of Raw Materials of Cement:

***Chalk:**

Chalk is a fine-grained white limestone. On average, it consists of 97.5 – 98.5% calcium carbonate. Clay and quartz are the most common impurities. Most chalk is a soft, friable rock that does not require explosives in mining.

Chalk as a form of carbonate rocks containing high calcium carbonate can be used in many industrial applications such as

*Chalk can be used as a building stone, and chalk rubble is often used in road construction.

*When heated, chalk becomes lime, which has a great many industrial applications.

***Limestone:**

Pure limestone is among the most important non-metallic raw material used for industrial and agricultural purposes. Sedimentary limestone deposits can be extensive, covering hundreds of square miles, and can be relatively uniform in thickness and quality. Therefore, limestone quarries can be large and long-lived, mining limestone layers that can be hundreds of feet thick over areas of several square miles.

Many quarries produce multiple products, and crushed rocks that are not pure enough for certain uses may still be suitable as road aggregate. Marble quarries can also be very large. However, these rocks that were once regularly layered have been metamorphosed into irregularly shaped bodies that are more difficult and costly to mine.

In the white cement industry, pure limestone should have CaO >52%. The insistent need for pure limestone deposit are due to the increasing prices of cement and the development of construction industries, so the investment opportunity will be increased in this industry.

***Clay:** Kaolin is white, soft, plastic clay mainly composed of the fine-grained platy mineral kaolinite; a white hydrous aluminum silicate, containing 23.5% alumina, 46.5% silica. It is used in the manufacturing of white-ware ceramics and infilling and coating of paper. It is also used as filler in paints, rubber, plastics, and many other productions.

4-Raw Materials Processing

Portland cement is by far the most common type of cement in general use around the world. This cement is made by heating limestone (calcium carbonate) with other materials (such as clay) to 1450 °C in a kiln, in a process known as calcination, whereby a molecule of carbon dioxide is liberated from the calcium carbonate to form calcium oxide, or quicklime, which is then blended with the other materials that have been included in the mix to form calcium silicates and other cementitious compounds.

The resulting hard substance, called 'clinker', is then ground with a small amount of gypsum into a powder to make 'Ordinary Portland Cement', the most commonly used type of cement (often referred to as OPC). Portland cement is a basic ingredient of concrete, mortar, and most non-specialty grout. The most common use of Portland cement is in the production of concrete. Concrete is a composite material consisting of aggregate (gravel and sand), cement, and water. As a construction material, concrete can be cast in almost any shape desired, and once hardened, can become a structural (loadbearing) element. Portland cement may be gray or white,**Figure 1**

***Setting and curing:**

Cement starts to set when mixed with water which causes a series of hydration chemical reactions. The constituents slowly hydrate and the mineral hydrates solidify; the interlocking of the hydrates gives cement its strength. Contrary to popular perceptions, hydraulic cement does not set by drying out; proper curing requires maintaining the appropriate moisture content during the curing process.

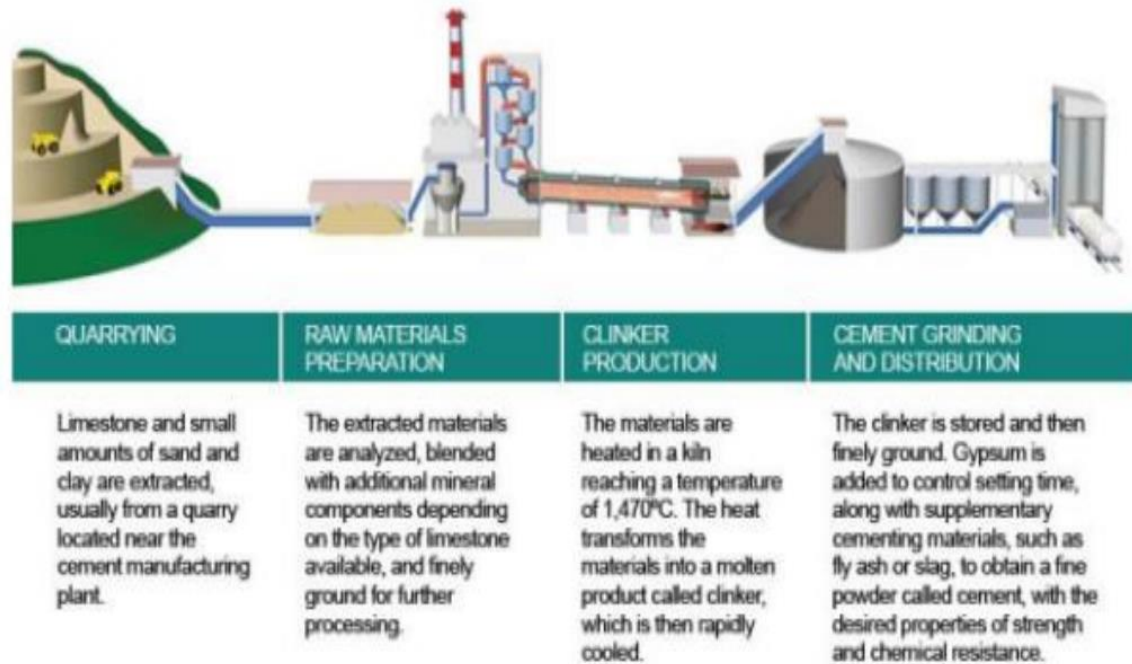


Figure 1

5-Cement manufacturing process:

a-The quarry:-

Cement plants are usually located closely either to active spots in the market or to areas with sufficient quantities of raw materials. The aim is to keep transportation costs low. The basic constituents for cement (**limestone and clay**) are taken from quarries in these areas. Basically, cement is produced in two steps: first, clinker is produced from raw materials. In the second step, cement is produced from cement clinker. The first step can be a dry, wet, semi-dry, or semi-wet process according to the state of the raw material.

b-Making clinker:

The raw materials are delivered in bulk, crushed and homogenized into a mixture which is fed into a rotary kiln. This is an enormous rotating pipe of 60 to 90 m long and up to 6 m in diameter. This huge kiln is heated by a 2000°C flame inside of it. The kiln is slightly inclined to allow for the materials to slowly reach the other end, where it is quickly cooled to 100-200°. Four basic oxides in the correct proportions make cement clinker: calcium oxide (65%), silicon oxide (20%), alumina oxide (10%) and iron oxide (5%). These elements mixed homogeneously (**called “raw meal” or slurry**) will combine when heated by the flame at a temperature of approximately 1450°C. New compounds are formed: silicates, aluminates and ferrites of calcium. Hydraulic hardening of cement is due to the hydration of these compounds. The final product of this phase is called **“clinker”**. These solid grains (pellets) are then stored in huge silos.

6-Process Description:

To make clinker there are three processes:
a-Wet process: (grinding and mixing of the raw materials in the existence of water)This process is done by cylindrical type kiln the length of it = 40 times of the shell's inner diameter it is used to help dry the slurry see figure 2&3.
b- Semi-dry process: It is example of dry process, and use a Lepol kiln: in the lepol kiln the pellets are dried and preheated once by the movable grate.

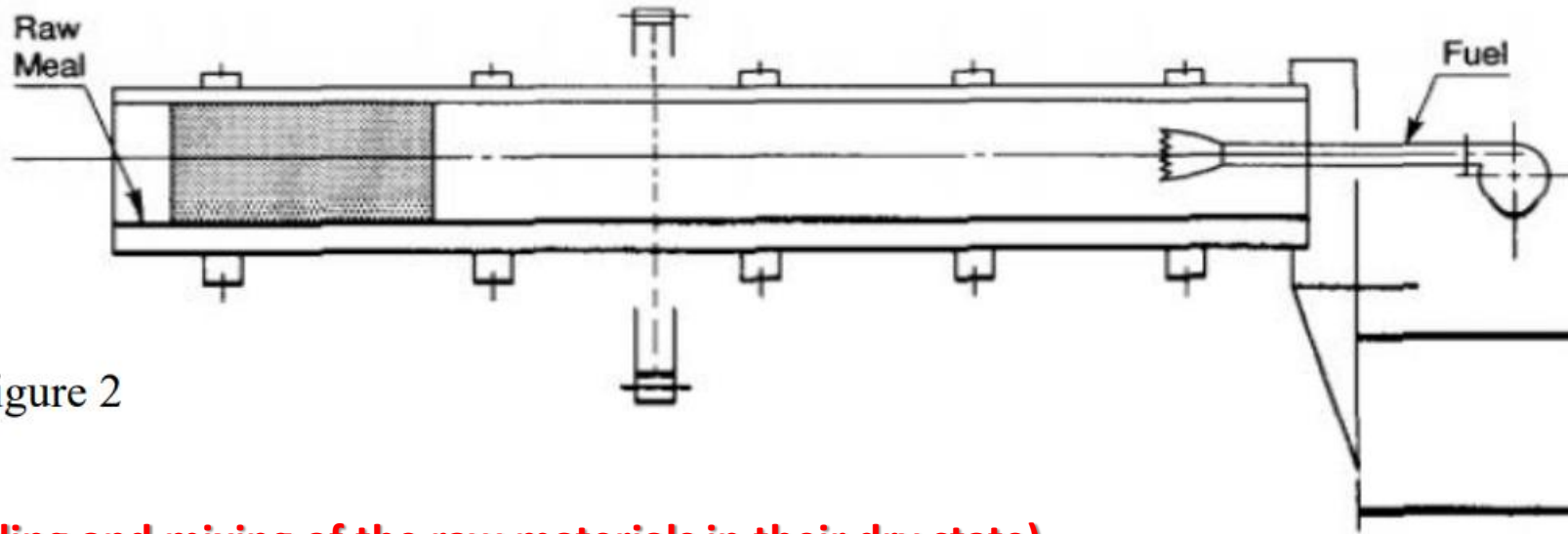


Figure 2

c- Dry process: (grinding and mixing of the raw materials in their dry state)

The Cement Roasting Machine is the device to heat and dry materials. The Materials in the coaxial type roasting machine are roasted through retracing and raising between the helical lobe and the intermittent spiral plate. The sleeve structure of the machine can several fold shorten the length of the dryer, hereby the radiating surface and heat consumption are significantly reduced, while the increased heat exchange surface greatly enhances the thermal efficiency. As to the materials that could not contact smoke, the multi drum cement roasting machine is equipped with inside smokestacks and ring-like smokestacks, and each smoke tube linked through the radial flue, consequently, reaching the effect of high efficiency and energy saving see **Figure 4**.

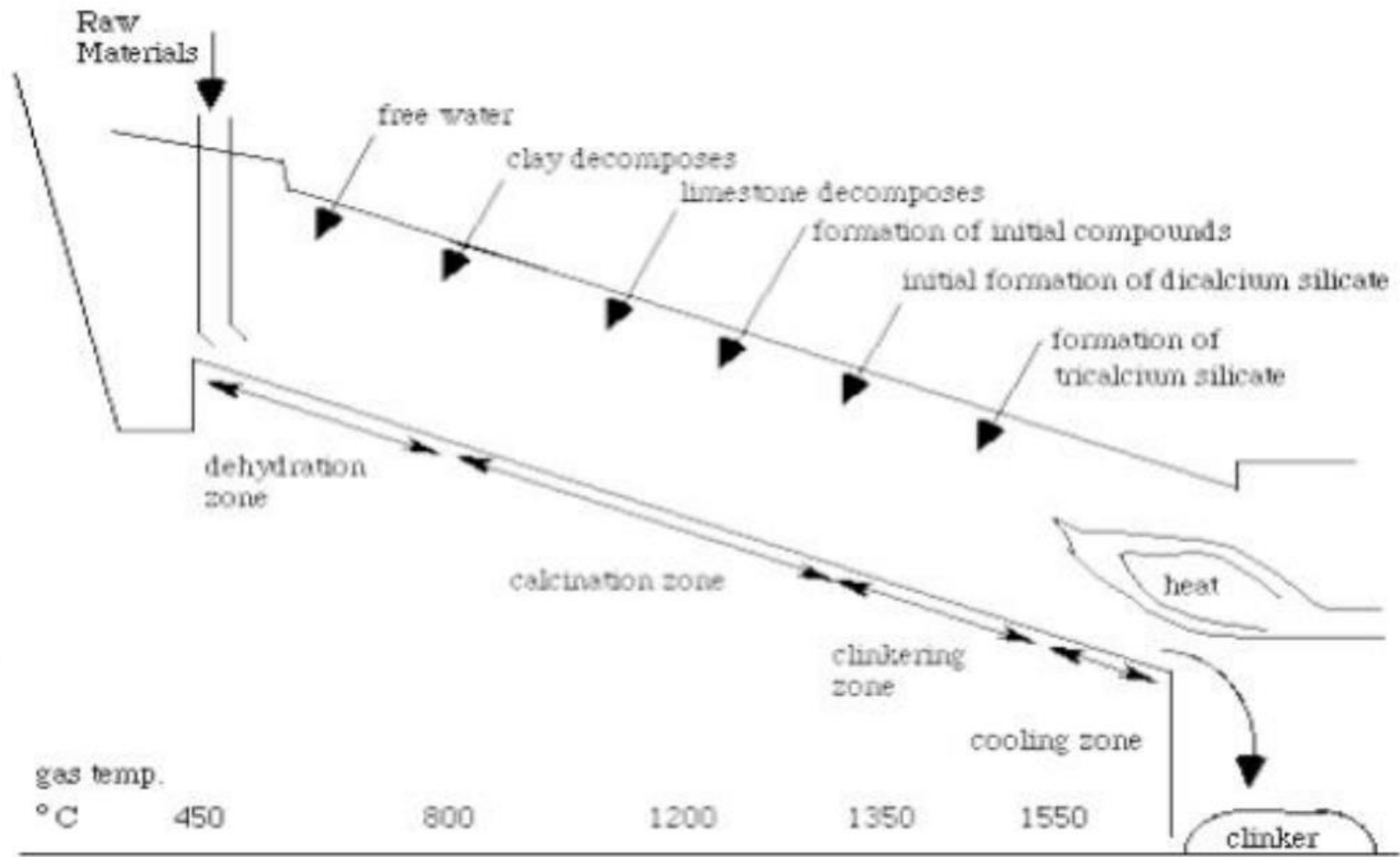


Figure 3

Production of Cement by the Dry Process

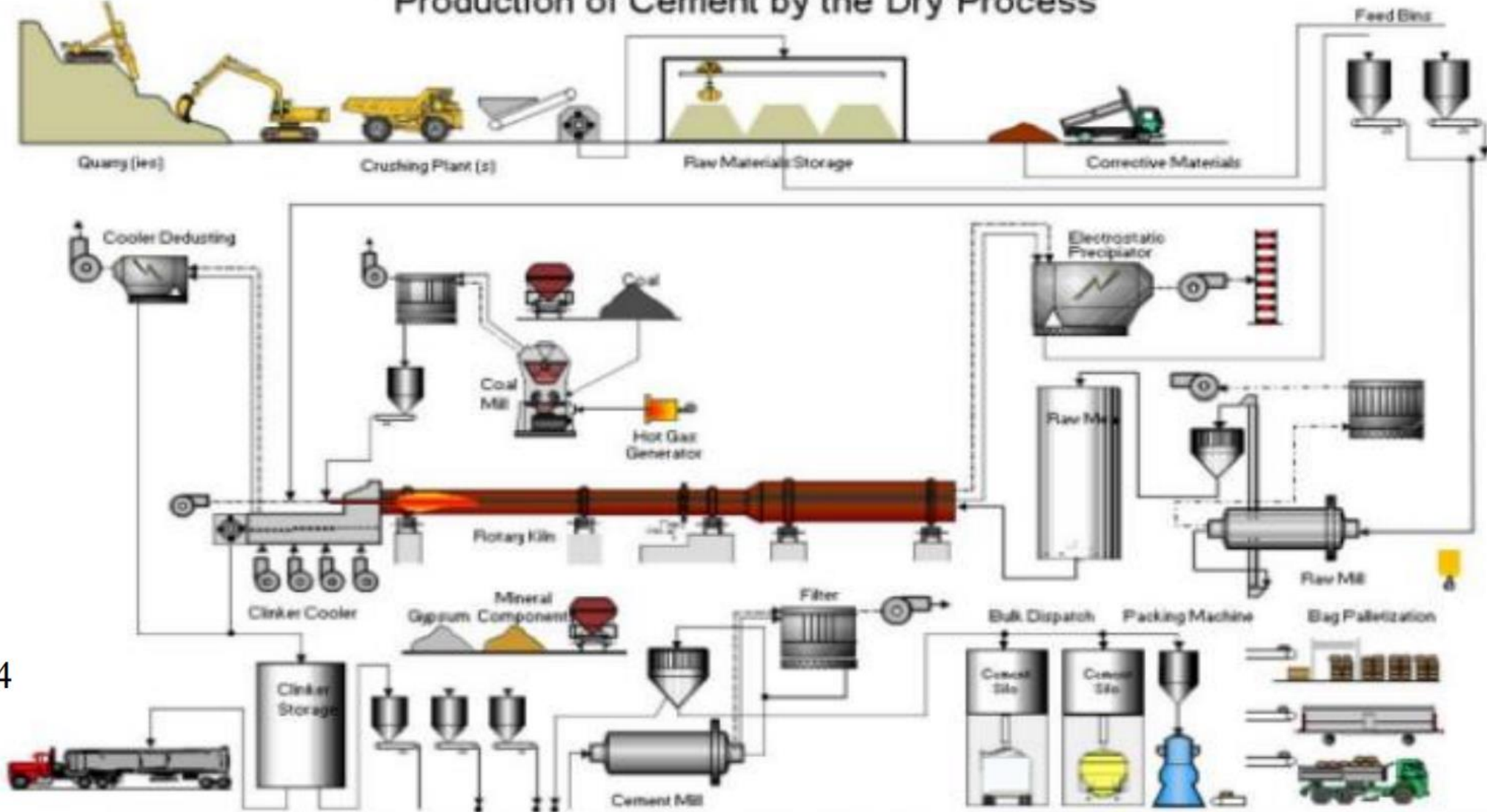


Figure 4

In this case, there are three types of kilns to use:

- * long kiln, the short kiln with the boiler, the SP kiln, and the NSP (new suspension preheater)
- * the long kiln is used in the Near and Middle East, it is used because rain falls less. It can be seen that the wet process is rapidly replaced by the dry process, the cause is energy conservation.

d- Finish process:

The second phase is handled in a cement grinding mill, which may be located in a different place in the clinker plant. Gypsum (calcium sulfates) and possibly additional cementations (such as blast furnace slag, coal fly ash, natural pozzolana, etc.) or inert materials (limestone) are added to the clinker. All constituents are ground leading to a fine and homogenous powder. The cement is then stored in silos before being dispatched either in bulk or bagged.

Usual Composition Limits of Portland Cement:

CaO 60-67% , SiO₂ 17-25% , Al₂O₃ 3-8% , Fe₂O₃ 0.5-6% , MgO 0.5-4% , Alkalis (as Na₂O) 0.3-1.2% , SO₃ 2.0-3.5% .

Typical compound composition in ordinary Portland cement:

C₃S 54% , C₂S 17% , C₃A 11% , C₄AF 9% .

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7-Chemical composition of Portland cement:

* Major compounds of cement:

- Tricalcium silicate $3\text{CaO}\cdot\text{SiO}_2$ – (C3S)
- Dicalcium silicate $2\text{CaO}\cdot\text{SiO}_2$ – (C2S)
- Tricalcium aluminate $3\text{CaO}\cdot\text{Al}_2\text{O}_3$ – (C3A)
- Tetracalcium aluminoferrite $4\text{CaO}\cdot\text{Al}_2\text{O}_3$.

Fe_2O_3 – (C4AF) CaO – C , SiO_2 – S , Al_2O_3 – A , Fe_2O_3 – F , H_2O – H

* **Minor compounds:**

In addition to the main compounds mentioned above, **there exist minor compounds, such as MgO , TiO_2 , Mn_2O_3 , K_2O and Na_2O .** Two of the minor compounds are of particular interest: K_2O and Na_2O , known as the alkalis (about 0.4-1.3% by weight of cement). They have been found to react with the reactive silica found in some aggregates, the products of the reaction causing increase in volume leading to disintegration of the concrete. The increase in the alkalis percentage has been observed to affect the setting time and the rate of the gain of strength of cement.

SO_3 comes from the gypsum added (2-6% by weight) during grinding of the clinker, and from the impurities in the raw materials, also from the fuel used through firing process. Iraqi specification no. 5 limited max. SO_3 by 2.5% when $\text{C}_3\text{A} \leq 7\%$, and by 3% when $\text{C}_3\text{A} > 7\%$.

MgO , present in the cement by 1-4%, which comes from the magnesia compounds present in the raw materials. Iraqi specification no. 5 limited max. MgO by 5%, to control the expansion resulted from the hydration of this compound in the hardened concrete. When the magnesia is in amorphous form, it has no harmful effect on the concrete.

Other minor compounds such as TiO_2 , Mn_2O_3 , P_2O_5 , represent $< 1\%$, and they have little importance.

Loss on Ignition (L.O.I):

It is the loss of the cement sample weight when it expose to the red temperature (at 1000 C). It shows the extent of carbonation and hydration of free lime and free magnesia due to the exposure of cement to the atmosphere. Also, part of the loss in weight comes from losing water from the gypsum composition. The maximum loss on ignition permitted by Iraqi specification no. 5 is 4% by weight.

Insoluble residue:

It is that part of cement sample that is insoluble in HCl. It comes from the unreacted silica, to form soluble cement compounds diluting in this acid, largely arising from impurities in gypsum. The maximum insoluble residue permitted by Iraqi specification no. 5 is 1.5% by weight.

Hydration of cement:

It is the reaction (series of chemical reactions) of cement with water to form the binding material. In other words, in the presence of water, the silicates (C3S and C2S) and aluminates (C3A and C4AF) form products of hydration which in time produce a firm and hard mass – the hydrated cement paste.

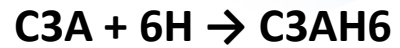
Tricalcium aluminate hydrate (C3A)and the action of gypsum:

The reaction of gypsum with C3A continues until one of them exhausted, while C3S continue in hydration.

If C3A exhausted before gypsum:

The surplus gypsum → expand → become an agent assist the disruption and deterioration of cement paste.

If gypsum exhausted before C3A ,the remaining C3A begins in hydration:



C3AH6

is stable –cubical crystals- with high sulfate resistance.

What happens when gypsum is added to cement?

When cement is mixed with water, it becomes hard over a period of time. This is called the setting of cement. Gypsum is often added to Portland cement to prevent early hardening, allowing a longer working time. Gypsum slows down the setting of cement so that cement is adequately hardened.

Important Questions:

1- How can we improve the quality of cement?

كيف يمكننا تحسين جودة الاسمنت؟

2-What is known as clinker in the cement industry?

ما هو الشيء المعروف باسم الكلنكر في صناعة السمنت؟

3-Why fly ash is used in the cement industry?

لماذا يستخدم الرماد المتطاير في صناعة الاسمنت؟

4-What are the properties of good quality cement?

ما هي خصائص الأسمنت عالي الجودة؟

5-Explain the cement industry steps in sequence (only the names)?

وضح خطوات صناعة السمنت
بالتسلسل (فقط الاسماء)؟

6-What is the role of silica in cement production?

ما هو دور السيليكا في انتاج الاسمنت؟

7-What is the role of alumina in cement production?

ما هو دور الالومينا في انتاج الاسمنت؟

8-What is the role of lime in cement production ?

ما هو دور الجير في انتاج الاسمنت؟

9-What is the role of iron oxide in cement production ?

ما هو دور أكسيد الحديد في انتاج الأسمنت؟

10-What is the effect of alkalis in the cement production ?

ما هو تأثير القلويات في انتاج السمنت؟

11-What environmental problems are associated with the manufacture of cement?

ما هي المشاكل البيئية المرتبطة
بصناعة الاسمنت؟

12-Why is gypsum added during cement production?

لماذا يضاف الجبس اثناء انتاج الاسمنت؟