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Modélisation de la chimie du clinker et de l'ingénierie du processus de fabrication du ciment : Etat de l'art

[Modeling of cement clinker chemistry and engineering of cement manufacturing process : State of the art]

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ABSTRACT: The purpose of this article is to review the aspects related to cement chemistry, more particularly to the process of clinkerization in the cement rotary kiln. The article also discusses the process engineering of cement manufacturing. Despite the increasing tendency to use substitute materials (fly ash, and blast furnace slags, pozzolans or volcanic ash, etc.), clinker is still today the most used material for producing cement. In this work, we discussed the mechanisms and parameters controlling the reactivity of the clinker phases, whether it was major or minor phases. Alite ($(CaO)_3.SiO_2$) or C3S) remains the most important phase in the mineralogical structure of clinker. We have also addressed the question of the partial melting of the charge, which the literature attributes to the presence of two oxides considered as the most melting (Al_2O_3 and Fe_2O_3), which are found in the form of aluminate phases ($(CaO)_3.Al_2O_3$ or C_3A) and Ferrite ($(CaO)_4.Al_2O_3.Fe_2O_3$ or C_4AF). The kinetic parameters of different clinkerization reactions are also discussed. The limitation of the CaO_{free} and MgO_{free} contents in the clinker is appropriate for a good reactivity of the clinker. The process evolution is also commented and discussed.

KEYWORDS: Clinkerization Reactions, Clinker, Cement, Kinetic Constants, Alite, Belite, Aluminate, Ferrite, Free Lime, Periclase.

RÉSUMÉ: Le présent article a pour objectif de passer en revue les aspects liés à la chimie du ciment, plus particulièrement au processus de clinkérisation au sein du four tournant. L'article présente également l'ingénierie de procédé de fabrication de ciment. Malgré la tendance accrue d'utilisation de matériaux de substitution (cendres volantes, et laitiers de hauts fourneaux, pouzzolanes ou cendres volcaniques,…), le clinker est encore aujourd'hui le matériau le plus utilisé pour produire du ciment. Dans ce travail, nous avons discuté des mécanismes et les paramètres contrôlant la réactivité des phases du clinker, que ça soit les phases majeures que mineures. L'alite ($(CaO)_3.SiO_2$) ou C_3S) reste la phase la plus important dans structure minéralogique du clinker. Nous avons également abordé aussi la question sur la fusion partielle de la charge, que la littérature l'attribue à la présence de deux oxydes considérés comme les plus fondants (Al_2O_3 et Fe_2O_3), qui se retrouvent sous formes de phases aluminate ($(CaO)_3.Al_2O_3$ ou C_3A) et Ferrite ($(CaO)_4.Al_2O_3.Fe_2O_3$ ou C_4AF). Les paramètres cinétiques de différentes réactions de clinkérisation sont également discutés. La limitation des teneurs en CaO_{free} et en MgO_{free} dans le clinker est de mise pour une bonne réactivité du clinker. L'évolution de procédé est également commentée et discutée.

MOTS-CLEFS: Réactions de clinkérisation, Clinker, Ciment, Constantes cinétiques, Alite, Bélite, Aluminate, Ferrite, Chaux libre, Periclase.

1 INTRODUCTION

Cement production is at the heart of the construction industry. It is an economic indicator, linked on the one hand to the number of inhabitants, and on the other hand to the growth of each country on a specific period [1]. Demand for cement has increased significantly as a result of rapid development in the construction sector worldwide, especially as a result of the construction boom in emerging countries. Global cement production has increased in recent decades. It went from 2.6 billion tons in 2006 [2] to 4.2 billion tons in 2016 [3]. The large share of production is in Asia, with China remaining by far the largest cement producing country, with production estimated at about 57.5% of world production. In Europe, Turkey is in first place, with a production of 70 million tons in 2013, or 1.75% of world production, and in Africa it is Egypt which is in the lead, with production of 46 million tons, or 1.15% of world production (source USGS[1]). The main goal of the cement industry is to produce cement on a large scale while consuming the least amount of energy. Measurements of energy consumption in a cement plant, and in the cement industry as a whole, are generally expressed in energy/weight of clinker, which is the cornerstone of the process [4]. The production of the clinker requires very high temperatures, of the order of 1450 °C, to initiate the clinkerization and phase-change reactions required to form clinker mineral compounds, which give the cement its unique properties [5,6]. Energy requirements in the dry process are on the order of 3200 kJ / kg clinker (of which 86 % for clinker production) [1]. This last value corresponds to a plant with a daily capacity of 3270 tons of clinker [7], having an average fuel flow of 540 t/day of coal. The overall emissions of the process (in terms of CO_2) amount to 0.8 t_{CO2}/t of clinker [8], resulting for one part in the combustion of fossil fuels and another for the decarbonation of limestone ($CaCO_3$, $CaCO_3.MgCO_3$ or $CaMg(CO_3)_2$), the main raw material [9–11]. The cement industry is responsible for 5 % of global CO_2 emissions, and faces some challenges including the introduction of the European Emissions Trading Scheme (called the quota system) [12]. The cement manufacturing process is based on the production of clinker, which is an artificial rock, produced after cooking in the rotary kiln, serving as raw material for the manufacture of Portland cement (and/or specific cement). It is therefore a mixture of hard or soft calcareous rocks and finely ground clays, dried and then cooked in the rotary kiln. The clinker thus comprises two phases: the major phases ($(CaO)_3.SiO_2$, $(CaO)_2.SiO_2$, $(CaO)_3.Al_2O_3$, and $(CaO)_4.Al_2O_3.Fe_2O_3$) and the minor phases (CaO_{free}, MgO_{free}, Na_2SO_4, K_2SO_4 and $CaSO_4$). These phases are formed following the process of clinkering, which involves different chemical reactions, taking place in very precise times along the rotary kiln. Studies are currently being conducted on the kinetics of these reactions, in order to be able to control the clinkering process that several authors describe as complex [12–17]. In this work, we will begin by describing the cement manufacturing process, where the different steps are briefly described. Then we talk about the raw materials used in the manufacture of cement, where we discuss the composition and dosage of raw materials. Then, we address the issues related to cement chemistry (clinkerization reactions). During clinker formation in the rotary kiln, reactions such as decarbonation of $CaCO_3$ and $MgCO_3$, clinkerization reactions and formation of a liquid phase take place in the kiln. These reactions may be endothermic or exothermic. The combustion of fossil fuel and/or alternative fuels (in the case of waste substitution) which provides the energy required for the various reactions taking place in the kiln is also presented. Finally, we deal with aspects related to the process (process engineering). A description of the existing processes is given. We also present in detail the dry process, giving the key characteristics of different types of kilns encountered in this process. The inputs and outputs of the kiln system are also presented.

2 CEMENT MANUFACTURING PROCESS

There are five main steps constituting the cement manufacturing process:

- Extraction and pre-homogenization of raw materials;
- Preparation of raw materials to form raw meal (or paste for wet process);
- Cooking of the flour leading to the creation of the clinker;
- Grinding clinker and additions to make cement, and;
- Storage and shipment of cement.

The schematic diagram of cement manufacturing is given in Figure 1.

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[1] United States Geological Survey (USGS) is an American government agency dedicated to earth sciences.

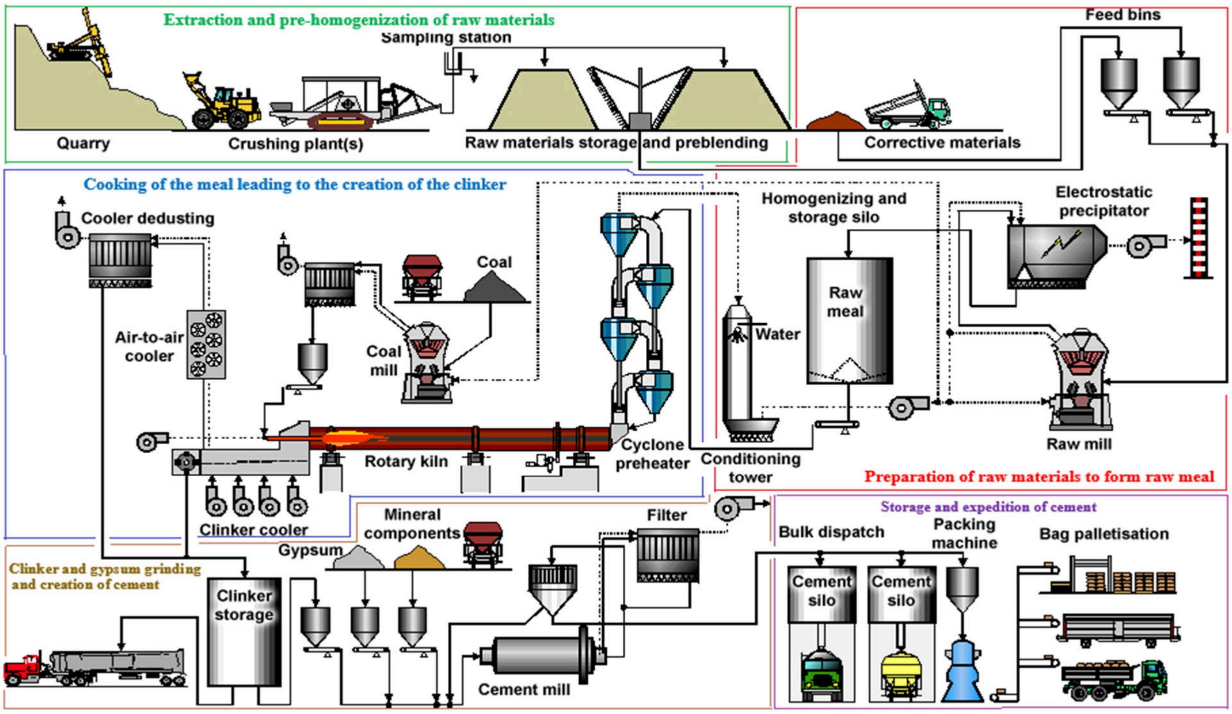

Fig. 1. Cement manufacturing - schematic diagram [18]

2.1 EXTRACTION AND PRE-HOMOGENIZATION OF RAW MATERIALS

Cement factories usually have one or more quarries, from which raw materials are extracted. Limestone and clay are the main materials used in the manufacture of cement. The limestone ore may be Calcium Carbonate ($CaCO_3$), Dolomite ($CaCO_3.MgCO_3$ or $CaMg(CO_3)_2$), or Calcium and Magnesium Dioxide ($CaO.MgO$). As for clay, it can be in the following forms:

- Kaolinite: $Al_2O_3.2SiO_2.(OH)_4$;
- Halloyisite: $Al_2(Si_2O_5).(OH)_4$;
- Montmorillonite : $(Na, Ca)_{0,3}(Al, Mg)_2Si_4O_{10}(OH)_2.nH_2O$;
- Illite or Phyllosilicates : $K_{0,65}Al_2(Al_{0,65}Si_{3,35}O_{10})OH$;
- Chlorite : $Mg_5(Al,Fe)(OH)_8(Al,Si)_4O_{10}$;
- Sepiolite : $Mg_4Si_6O_{15}(OH)_{22}.2H_2O$;
- …

The extraction of these two materials can be done in the same career or in different careers. Limestones are extracted from rock walls by blasting and /or mechanical shovels. Transport to the crushing halls is provided by conveyor belts, or by skips of different tonnages. After crushing, the limestones are stored in the storage hall of raw materials (limestone), whose capacity can go up to several thousand tons. For clay, extraction is most often done by direct excavation (on the surface). The pre-homogenization of the clay is done on the same site of excavation. This operation determines the nature of the clinker that is desired.

2.2 PREPARATION OF RAW MATERIALS

The material is extracted from the stock by means of a lateral recovery scraper, which moves on rails on one of the longitudinal sides of the stock. The capacity of the recovery scraper is about 150 tons per hour (Source CINAT). The extracted products are conveyed by conveyor belts to the limestone and clay dosers to adjust the proportions of limestone and clay. The average composition used is 80 % limestone and 20 % clay.

The mixture obtained is then sent to the mill, in order to obtain a homogeneous mixture called raw or "flour" in the form of very fine powder (diameter less than 200 microns [9,19]) having a fixed composition. The composition of the raw usually stays in the following proportions [20] :

- Calcium carbonate ($CaCO_3$): from 77 to 83 %
- Silica (SiO_2): from 13 to 14%
- Alumina (Al_2O_3): from 2 to 4%
- Iron oxide (Fe_2O_3): 1.5 to 3%. (These are the oxides that give Portland cement its gray color).

In modern installations, the grinder allows both the drying and grinding of raw materials. This is made possible by the hot gas circuit from the rotary kiln. The grinding of raw materials has been in the focus of better energy utilization [21]. Several types of grinders are used (grinders with pebbles, grinders with balls ...), in which are arranged loads to grind (pebbles, balls ...).

These grinders (or mills) are often equipped at their output with a system (screen) to separate the sufficiently crushed fractions, those insufficiently crushed. The flour obtained at this stage is called "raw meal" and is conveyed by pneumatic transport to the storage and homogenization silos. Homogenized flour is often referred to in the cement language as "kiln flour".

2.3 COOKING THE FLOUR AND CREATING THE CLINKER

From homogenizing silos, the flour is extracted by means of air boosters, and is conveyed by screw conveyors, then by bucket elevators to the dosers (which regulate the flow of flour to be sent to the kiln). From the dosers, the flour is sent by pneumatic transport to the preheater tower, where the first transformations of the flour begin.

The flour inlet temperature in the preheat tower can vary from 60 to 80 ° C. It is brought to 900 ° C in the cyclone exchangers before being brought to the entrance of the rotary kiln. Inside the kiln, several physicochemical transformations are observed, especially the collapse of the crystalline structure of the clay, the decarbonation, and the clinkering.

As an order of magnitude of energy consumption, Charron [1] gives an average value of 3200 kJ/kg of clinker. At the outlet of the kiln, the clinker is still at very high temperatures (1200 °C), hence the need to cool. The clinker is transported to the cooler, where it leaves a maximum temperature of 200 ° C. Figure 8 shows the hot clinkers coming out of the kiln.

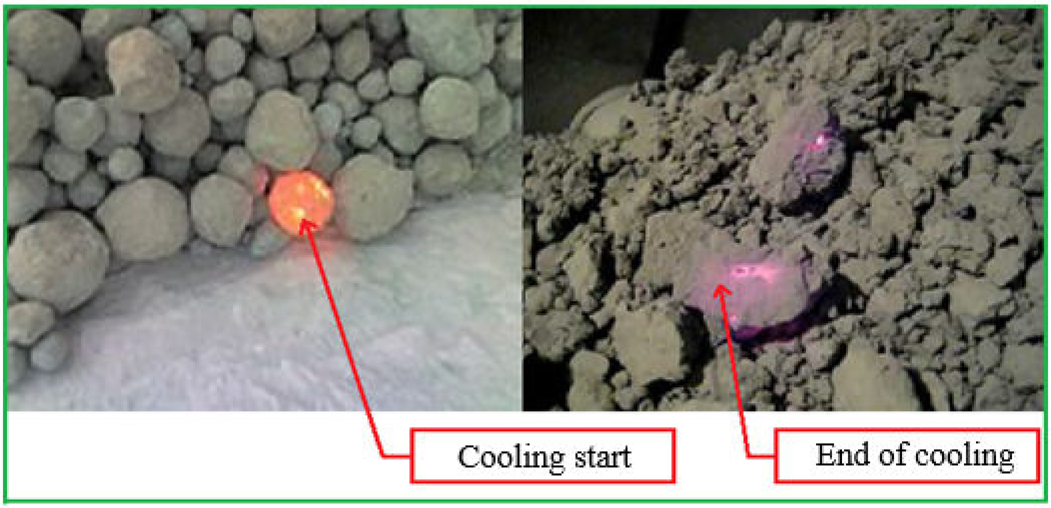

Fig. 2. Hot clinkers coming out of the rotary kiln [22,23]

2.4 GRINDING OF CLINKER AND MANUFACTURE OF CEMENT

At the outlet of the cooler, the clinker is transported to the clinker storage hall, whose capacity can be up to several thousand tons. From the storage hall, the clinker is extracted with a trench and transported to the cement mill using belt conveyors and then bucket elevators. Cement standards require that the grinding be made of 97% clinker and 3% gypsum ($CaSO_4.2H_2O$). Clinker and gypsum are fed in the mill using two feeders, which ensure the dosage between the clinker and the gypsum (from the gypsum storage hall).

2.5 STORAGE AND SHIPMENT OF CEMENT

From the cement mill, the cement thus produced is conveyed by pneumatic lines to the cement storage silos. The storage capacity in a cement plant can range from a few tons to several thousand tons. The cement is extracted from the silos by pneumatic extractors, which convey it to the bagging workshop, using screw conveyors, then by bucket elevators. The bagging of the cement is done by means of a bagger with flow whose capacity can go from a few tons to several hundreds of tons per hour. The cement is thus placed in valve bags, generally made of paper weighing 50 kilograms. The shipping of the cement is made possible by toboggans, and by conveyor belts to the place of loading of trucks and wagons of railway.

3 RAW MATERIALS

3.1 COMPOSITION OF RAW MATERIALS

The preparation of raw materials is an important step in the cement manufacturing process. Obtaining a good quality clinker depends heavily on it. In general, the flour introduced into the rotary kiln consists of 80 % of limestone ($CaCO_3$, $MgCO_3$, ..) and 20 % of clay (SiO_2, Al_2O_3, Fe_2O_3, H_2O, ...). It should be noted that these compositions differ from one career to another. Nielsen [24] and Varas et al.[25] present raw meal as consisting of limestone, a source of calcium ($CaCO_3$, $CaMg(CO_3)_2$), clay and/or sand, sources of silicon, aluminum and iron (Al_2O_3, SiO_2, Fe_2O_3). As for the proportions, they give 75 - 80 % in mass of limestone, 20 – 25 % in mass of clay. The cement industry may have to correct the contents above. The overall composition is sometimes adjusted to meet the requirements of the type of cement to be produced. The transformation of flour into clinker takes place through many chemical reactions that the various authors frequently group into 5 major reactions (see paragraph 4.2.5. below), involving the following compounds: $CaCO_3$, CaO, SiO_2, Al_2O_3, Fe_2O_3, $(CaO)_2.SiO_2$, $(CaO)_3.SiO_2$, $(CaO)_3.Al_2O_3$, $(CaO)_4.Al_2O_3.Fe_2O_3$. Some compounds are often neglected because they are considered as minor elements with low levels [26,27]. Witsel et al. [28] study the overall dynamic behavior of the rotary kiln system, the impact of different control variables, and the analysis of disturbances on the temperature profile. They model the furnace by considering that the solid phase consists of the following chemical species at the input (flour) $CaCO_3$, SiO_2, Al_2O_3, Fe_2O_3, CaO. Mastorakos et al. [15] consider that the feed consists of $CaCO_3$, CaO, SiO_2, Al_2O_3, Fe_2O_3, C_2S, C_3S, C_3A and C_4AF, species linked by the five major chemical reactions described below. In the interest of developing a rotating furnace model capable of simulating the formation and production of clinker along the kiln, Darabi [29] consider the following species as part of the flour at the entrance of the kiln: $CaCO_3$, SiO_2, Al_2O_3, Fe_2O_3. Nørskov [30] in its model of solid fuel combustion in cement kilns considers that the raw materials consist of CaO, Al_2O_3, Fe_2O_3, SiO_2, MgO, Na_2O and K_2O. He also considers that the major part of $CaCO_3$ is converted into the pre-calciner, with a pre-calcination rate of between 90 – 95 % before being admitted to the rotary kiln. Bhad et al. [13] in their work on the development of a mathematical model of a cement kiln with a multi-channel burner, present the cement manufacturing process as composed at the entrance of the following species: CaO, Al_2O_3, Fe_2O_3, SiO_2 , and other oxidized metals. Hiromi Ariyaratne et al. [31] give the following composition (by weight) of the raw flour: 66 % CaO, 21 % SiO_2, 5 % Al_2O_3, 3 % Fe_2O_3 and 5 % other compounds. Hassaan [32] is studying the possibility of using basalt as a raw material to compensate for the lack of iron in the clay and silicate in the clinker mixture.

3.2 DOSAGE OF RAW MATERIALS

3.2.1 LIMITATION AND PROPORTION OF RAW MATERIALS

The production of quality cement is possible only if the composition of the mixture of raw materials is made optimally. Kohlhaas and Labahn [33] gave the limit values at which the limestone-clay mixture finely ground must satisfy.

Table 1. Limit values of chemical composition of cement raw materials [33,34]

Oxide	**Limit Value [%]**	**Content [%]**
CaO	60 - 69	65
SiO_2	18 – 24	21
Al_2O_3	4 - 8	6
Fe_2O_3	1 - 8	3
MgO	< 5	2
K_2O, Na_2O	< 2	1
SO_3	< 3	1

Wilson et al. [35,36] in their studies on the proportions of the various oxides within the limits given in the Table 1 above. The dosage (proportion) of the main constituents of the clinker is done by well-defined criteria, in the form of ratios, modules or chemical indices.

3.2.2 MODULES AND LIME SATURATION FACTOR

In the cement plant, it is customary to determine the quantity of different constituents of the flour and/or clinker in the form of ratios, modules or factors. These latter result from the many works on the mechanisms of formation, reaction, and production of Portland cement.

3.2.2.1 HYDRAULIC MODULE

Hydraulic Module (HM) allows to calculate the optimum amount of lime (CaO) contained in the mixture:

$$HM = \frac{CaO}{SiO_2 + Al_2O_3 + Fe_2O_3} \tag{1}$$

Limit values of HM are between 1,7 and 2,3 [37,38].

Table 2. Chemical criteria for the composition of clinker and/or flour [37]

Modules and Factors	Range	Consequences
Hydraulic Module	≥ 1.5	Initial weak resistances
	≤ 2.5	Volume stability, swelling
Silica Module	≥ 1.5	Decreased clinker temperature; Fast setting and hardening; Promotes crusting
	≤ 3.5	Difficult cooking due to lack of Substances; Curing plug Slow ; Reduction of crusting in the oven
Alumino-Ferric Module	≥ 1.5	Low heat of hydration; Cement without C_3A
	≤ 2.5	Quick Start Aluminous cement
Lime Saturation Factor	≥ 0.85	Low heat release
	≤ 0.95	High initial resistances High final resistances

3.2.2.2 SILICA MODULE

Silica Module (SM) is often between 1,5 and 5, and is calculated as follows [38]:

$$SM = \frac{SiO_2}{Al_2O_3 + Fe_2O_3} \tag{2}$$

According to SCAEK [37], a high value of SM corresponds to a high value of silica (S) to the detriment of the fondants agents (A and F), whereas a small value causes excessive crusting in the clinkerization zone, thus being able to cause nuisances to the good oven running. For Sorrentino [39], the silica module controls the grindability.

3.2.2.3 ALUMINO-FERRIC MODULE OR IRON MODULUS

As its name suggests, this module (AF or IM) allows to estimate the ratio Al_2O_3 and Fe_2O_3 in the mixture. It is calculated by the following relation:

$$AF = \frac{Al_2O_3}{Fe_2O_3} \tag{3}$$

Alumino-Ferric Module is between 1,5 and 2,5 [37,38]. Currently, the Lime Saturation Factors are more used to judge the quality of the clinker[33,37,40].

3.2.2.4 LIME SATURATION FACTORS

Lime Saturation Factors (LSF) express the ratio between the lime present in the mixture and the amount of lime capable of combining with the silica to form C_3S and C_2S.

- **Saturation Factor of Kuhl**

$$LSF\ I = \frac{CaO}{2.8SiO_2 + 1.1Al_2O_3 + 0.7Fe_2O_3} \tag{4}$$

- **Saturation Factor of Lea Parker** [38,41]

$$LSF\ III = \frac{CaO + 0.75MgO}{2.8SiO_2 + 1.18Al_2O_3 + 0.65Fe_2O_3}\ ;\ with\ MgO < 2\% \tag{5}$$

The saturation factor of Lea and Parker is between 0.85 and 1.0. It is also in the following form [37]:

$$LSF\ III = \frac{CaO + 1.5MgO}{2.8SiO_2 + 1.18Al_2O_3 + 0.65Fe_2O_3}\ ;\ with\ MgO > 2\% \tag{6}$$

LSF « Lime Saturation Factor » represents the ratio of CaO present in the Clinker and the possibility of it to bind with the most basic compounds [42]. When the lime saturation factor is greater than 100 %, there is imbalance between the constituents. The HM provides the means to calculate the maximum proportion of CaO that can be combined with the oxides. It should be noted that all the lime cannot be saturated, hence the existence of a non-combined portion (CaO_{free}). Both LSF formulas provide a criterion for determining the optimal CaO content. They express the CaO content present in the flour (or in the clinker) as a percentage of maximum CaO content that can be combined with the acid oxides (SiO_2, Al_2O_3, Fe_2O_3) in the clinker richer in lime, under the technical conditions of cooking or cooling [33]. According to Chatterjee [9] and Sorrentino [39], the Lime Saturation Factor (LSF), the Silica Module (SM) and the Alumina Module (AM) make it possible to follow the grinding process of the raw materials. C3S is the main phase controlling the reactivity of cement and clinker [39].

4 CLINKERIZATION REACTIONS

4.1 COMPOSITION OF CLINKER

Clinker is the main component of the cement, which results from the baking at about 1450 °C of a mixture of clay and limestone, finely ground. It is composed of the following minerals: $(CaO)_3.SiO_2$, $(CaO)_2.SiO_2$, $(CaO)_3.Al_2O_3$, $(CaO)_4.Al_2O_3.Fe_2O_3$, and minor elements such as CaO_{free}, MgO, Na_2SO_4, K_2SO_4 , $CaSO_4$. The above clinker minerals are generally represented by the following respective specific notation C3S, C2S, C3A and C4AF, which are of use in a cement plant, where C = CaO, S = SiO_2, A = Al_2O_3, and F = Fe_2O_3. The final composition of the clinker depends on a cement plant to another (function of raw materials), the type of cement that is desired. Some clinkers have minimal levels of minor compounds. Witsel et al. [28] in their studies give the following composition of clinker: C_3S, C_2S, C_3A, C_4AF. Bhad et al.[13], Mastorakos et al. [15], Mujumdar and Ranade [26], Hiromi Ariyaratne et al. [31], Sorrentino [39], Ghabezloo [43], Opoczky and Gavel [44], and Cyr et al. [45] consider also the same composition as [28]. Darabi [29] give the following composition and clinker mineral contents: 45 - 65% C_3S, 10-25% C_2S, 7-12% C_3A, and 5-11% C_4AF. As for Nørskov [30], it gives the following composition and contents: 65 % C_3S, 15 % C_2S, 10 % C_3A, 10 % C_4AF, 1 % CaO_{free}, 2 % MgO, 1 % K_2SO_4, 0.5 % Na_2SO_4 . Hassaan [32] presents the clinker composition in two forms, oxide and mineral. The standard composition deduced from the formulas of Borgue [33] is as follows:

Table 3. Standard mineralogical composition of clinker [19]

Components	[% in wt.]
C_3S	≥ 55
C_2S	≤ 22
C_3A	≥ 8
C_4AF	≥ 8
$CaSO_4$	≤ 2,5

4.2 CLINKERIZATION REACTIONS

The physico-chemical reactions leading to the formation of clinker can be represented as follows (Source CINAT):

- 100 °C: Evaporation of free water
- 100 – 400 °C: Dehydration of crystalline water

$$Al_2O_3.SiO_2.mH_2O \rightarrow Al_2O_3.SiO_2 + mH_2O^{\nearrow}$$

- 400°C: Dissociation of $MgCO_3$

$$MgCO_3 \rightarrow MgO + CO_2{}^{\nearrow}$$

- 800°C: Dissociation of $CaCO_3$

$$CaCO_3 \rightarrow CaO + CO_2{}^{\nearrow}$$

- 800 – 900°C: Formation of $CaO.SiO_2$ or CS
- 900 – 950°C: Formation of $(CaO)_5(Al_2O_3)_3$ or C_5A_3
- 950 – 1200°C: Formation of $(CaO)_2\,SiO_2$:

$$2CaO + SiO_2 \rightarrow (CaO)_2.SiO_2$$

Or

$$2C + S \rightarrow C_2S$$

- 1200-1300°C: Formation of $(CaO)_3\,Al_2O_3$ or C_3A and of $(CaO)_4\,Al_2O_3\,Fe_2O_3$ or C_4AF
- 1260-1450°C: Formation of C_3S with progressive and total disappearance (possibly) of the free lime.

4.2.1 DECARBONATION REACTION ($CACO_3$ & $MGCO_3$)

4.2.1.1 DECOMPOSITION OF $CACO_3$

Decarbonation (equation (7)) is a very important reaction (because it is very endothermic) in the cement manufacturing process. It allows the formation of the key species, lime (CaO). Calcium carbonate ($CaCO_3$) is in most cases about 79 % by weight of the raw meal. It decomposes around 800 °C. In practice, its decomposition begins between 550 °C and 600 °C [33].

$$CaCO_3(s) \rightarrow CaO(s) + CO_2(g) \tag{7}$$

At atmospheric pressure, the Gibbs free energy (in J/mol) at the equilibrium of the decarbonation reaction can be expressed as a function of temperature, following the relationship (8) below [46] :

$$\Delta G_r^0 = 182837 + 13{,}402\; lnT - 251{,}059T \tag{8}$$

Decarbonation (decomposition of $CaCO_3$) is therefore an endothermic reaction. Several values of the $CaCO_3$ reaction enthalpy are available in the literature. Kohlhaas and Labahn [33] give 1660 kJ/kg, while Boateng [46] gives 1768 kJ/kg.

4.2.1.2 DECOMPOSITION OF $MGCO_3$

Magnesium carbonate ($MgCO_3$) dissociates according to the following chemical reaction:

$$MgCO_3(s) \rightarrow MgO(s) + CO_2(g) \tag{9}$$

The reaction (9) starts at 250 °C, and can end around 410 °C, at atmospheric pressure [46]. As for $CaCO_3$, the decomposition of $MgCO_3$ is also an endothermic reaction, its enthalpy of reaction is evaluated at 1298 kJ/kg [46].

4.2.2 MAJOR PHASES OF THE CLINKER

4.2.2.1 ALITE (C_3S : CA_3SIO_5)

Alite or tricalcium silicate, of formula $3CaO.SiO_2$ or C_3S in cement notation, is the principal anhydrous constituent of clinker [34]. This species gives it his hydraulic properties. Its proportions in the clinker are evaluated at more than 60 % of the total mass, containing 71 – 75 % by weight of CaO, 24 – 28 % by weight of SiO_2, and 3 – 4 % by weight of substituted ions or impurities (MgO, Al_2O_3, Fe_2O_3, TiO_5, and others) [9,47]. The quantities of the oxides depend very particularly on the composition of the clinker, the temperature with which they were cooked, and finally the way in which they were cooled [33]. Alite mainly controls the initial and final strengths of the cement. The best cement would be that which consists only of C_3S. C_3S is formed at temperatures ranging from 1350 to 1450 °C, according to the reaction (10):

$$C_2S(s) + CaO(s) \rightarrow C_3S(s) \tag{10}$$

If the cooling is too slow, the formed C_3S can decompose into C_2S and CaO, depending on the reaction (11):

$$C_3S(s) \rightarrow C_2S(s) + CaO(s) \tag{11}$$

The retrogradation reaction ((11)) occurs only at temperatures below 1250 °C, and often in the presence of Fe_2O_3 or of the ion Fe^{2+} (in C_3S), which results from combustion under reducing conditions [33]. Because of the chemical reaction leading to the creation of C_3S takes place in the cooking zone (characterized in its entirety by the partial melting of solids), it should be affirmed that the C_3S is formed only in the presence of the liquid phase (see paragraph 4.2.4. below).

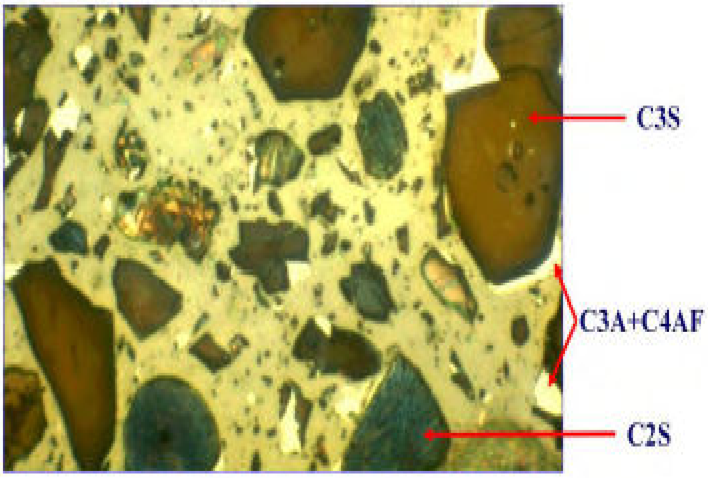

Fig. 3. Microscopic visualization of mineral compounds of clinker [1]

According to some studies Svinning et al. [48] and Aldridge [49], the influence of C_3S decreases with increasing age of curing while the influence of C_2S increases. Liu and Li [50], have studied the Effect of MgO on the composition and properties of alite-sulphoaluminate cement. They found that the addition of MgO at about 2–5 % can improve the burnability of raw meal, promote the absorption of free lime and the formation of C_3S.

4.2.2.2 BELITE (C_2S : CA_2SIO_4)

Belite or dicalcium silicate ($2CaO.SiO_2$) is considered to be the second most important species of clinker. It is formed mainly in solid form, at the clinkerization temperature, and is present in the clinker in proportions of 15 to 30 % by weight. Regarding the presence of oxides, C_2S consists of 60 – 65 % by weight of CaO, 29 – 35 % by weight of SiO_2 and 4 – 6 % by weight of substituted oxides or impurities (Al_2O_3 and Fe_2O_3, but also K_2O, Na_2O, MgO, SO_3 and P_2O_5). Its resistance after hydration in cement is almost similar to that of Alite, but its hydration speed is much slower than that of C_3S [33,47,51]. The belite is formed according to the chemical reaction (12):

$$2CaO(s) + SiO_2(s) \rightarrow C_2S(s) \tag{12}$$

4.2.2.3 TRICALCIUM ALUMINATE (C_3A : $CA_3AL_2O_6$)

Tricalcium aluminate ($3CaO.Al_2O_3$) is the phase of clinker with a high degree of reactivity, whose content in clinker is between 5 and 10 % by weight. Pure C_3A consists of 62 % by weight of CaO, and 38 % by weight of Al_2O_3 and does not have polymorphs dependent of the temperature [33,47]. The tricalcium aluminate may also contain foreign ions or alkalis (Na_2O, K_2O) [9], each in amounts greater than 5% by weight [33]. Tricalcium aluminate is formed according to the reaction (13) below:

$$3CaO(s) + Al_2O_3(s) \rightarrow C_3A(l) \qquad (13)$$

4.2.2.4 TETRACALCIUM ALUMINO-FERRITE (C_4AF : $2(CA_2ALFEO_5)$)

Tetracalcium alumino-ferrite ($4CaO.Al_2O_3.Fe_2O_3$) represents 5-15 % by weight of clinker. Pure C_4AF contains 46 % by weight of CaO, 21 % by weight of Al_2O_3, 33 % by weight of Fe_2O_3. However, it is possible to find a content of 10 % by weight of MgO, its often the case of industrial clinkers [47]. Kohlhaas and Labahn [33] consider that the ferrite phase does not have a constant chemical composition, but rather being part of a series of solid solutions theoretically extending from C_2A to C_2F (whether C_2A…C_6A_2F…C_4AF…C_6AF_2…C_2F), whereas Rompaey [40] considers that the ferrite phase, in the majority of the cases, belongs to a series of solid solutions whose compositions are between C_6A_2F and C_6AF_2. He states that the C_6A_2F is the brightest pole of the solid solution, since the C_2A pole is stable only at high pressures. Telschow [47] as for him, considers the ferrite phase as consisting of solid solutions of the form $Ca_2(Al_xFe_{1-x})_2O_5$, with $0 < x < 0,7$. According to Tao et al [34], C_3A accounts for the early development of compressive strength of cement due to the highest rate of reactivity among four main clinker phases. Tetracalcium Alumino Ferrite is formed according to the reaction (14) below:

$$4CaO(s) + Al_2O_3(s) + Fe_2O_4(s) \rightarrow C_4AF(l) \qquad (14)$$

4.2.3 MINOR PHASES OF THE CLINKER

4.2.3.1 FREE LIME (CAO_{FREE})

Free lime (CaO_{free}) is considered as one of the minor phases of clinker. It is therefore the fraction of CaO not combined with the oxides (SiO_2, Al_2O_3, Fe_2O_3). Its content can reach values greater than 2 % by weight of the clinker [52]. The presence of CaO_{free} in the clinker is due to several factors (from the preparation of raw materials, to clinker cooling): the inadequate preparation of raw meal (inhomogeneity or grinding too coarse), insufficient combustion (so that was not combined with other oxides), the clinker cooling rate too low, leading to the partial decomposition of C_3S (C_3S retrogradation reaction), the lime content too high in the raw materials (if LSF III > 100, there is an imbalance between the constituents) [33]. These factors can be both exclusive and inclusive. In cement, it is likely to cause expansion phenomena in mortar and concrete (**expansion of lime**), by reacting with water to give slaked lime or Portlandite ($Ca(OH)_2$) [53], depending on the chemical reaction (15) below:

$$CaO(s) + H_2O(l) \rightarrow Ca(OH)_2(s) \qquad (15)$$

According to Kohlhaas and Labahn [33], free lime is undesirable in appreciable concentrations, often above about 2.5 % by weight of the clinker. In view of the above, free lime can therefore be considered as an essential parameter for judging the quality and the degree of cooking of the clinker produced. Clinkers well-cooked resulting from a well-balanced vintage and a good grain size have CaO_{free} contents less than 2 % [54].

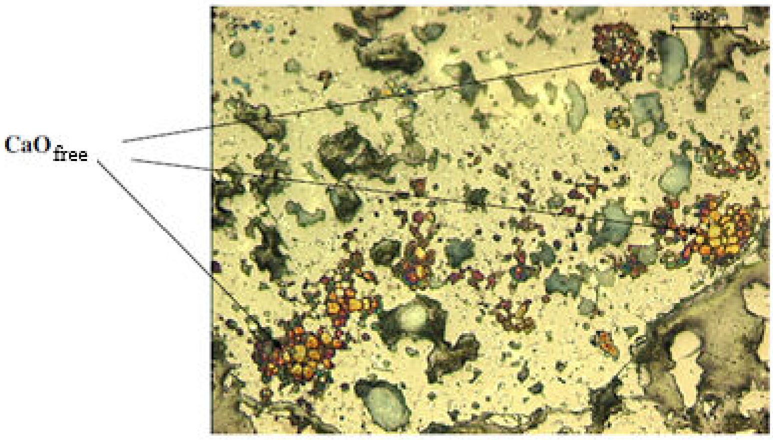

Fig. 4. Microscopic visualization of free lime [55]

4.2.3.2 PERICLASE (MGO$_{LIBRE}$)

Periclase or magnesia (MgO$_{free}$) can come from various sources: raw materials, more precisely limestone, and in rare cases clays, or decomposition of $CaCO_3.MgCO_3$ or CaO.MgO, or even of $MgCO_3$ alone. Rompaey [40] affirms that periclase occurs in clinker when MgO concentrations exceed 2 % of clinker weight, and when maximum concentrations of MgO have been reached in the clinker phase. For Kohlhaas and Labahn [33], clinkers rich in MgO may contain MgO$_{free}$. They affirm that 2 to 2.5 % by weight of MgO combine in the form of solid solutions in the other clinker phases, and we can only talk about the MgO$_{free}$ when the contents exceed 2.5 to 3% (values according to standard specifications for a compliant cement). As for free lime, periclase produces Brucite ($Mg(OH)_2$) when its hydrated. Brucite can also cause in long-term the problem of expansion in cement (**expansion of magnesia**), in some cases the damage it causes may remain unnoticed for years. The proportion of MgO that is combined in other phases will depend on the chemical composition of the clinker and his state of production [33].

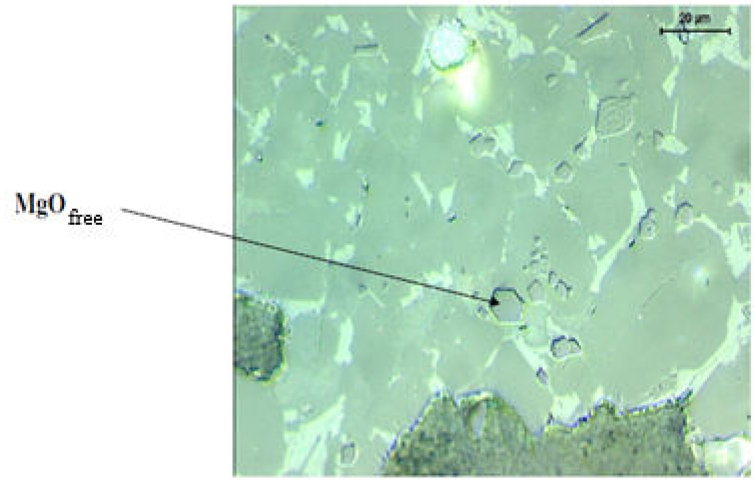

Fig. 5. Microscopic visualization of Periclase [55]

4.2.3.3 ALKALINE SULPHATES

The alkaline sulfates (Na_2SO_4, K_2SO_4 and $CaSO_4$) also originate from the raw materials. They are the fruits of the reactions of K_2O, Na_2O, SO_3 present in the flour in the form of impurities. The chemical reactions leading to the formation of alkaline sulfates are as follows ((16) below):

$$\begin{gathered} Na_2O(s) + SO_3(g) \leftrightarrow Na_2SO_4(s) \\ K_2O(s) + SO_3(g) \leftrightarrow K_2SO_4(s) \\ CaO(s) + SO_3(g) \leftrightarrow CaSO_4(s) \\ MgO(s) + SO_3(g) \leftrightarrow MgSO_4(s) \\ CaSO_4(s) + CO(g) \leftrightarrow CaO(s) + CO_2(g) + SO_2(g) \end{gathered} \tag{16}$$

Rompaey [40] speaks of alkaline sulfates in the form of $3K_2SO_4.Na_2SO_4$, and $2CaSO_4.K_2SO_4$. The high concentration of alkaline sulfates in the rotary kiln can cause some anomalies: crystallization of anhydrite ($CaSO_4$) which is very unstable compared to other alkalis [56]. This crystallization causes clogging and / or plugging inside the kiln, reducing the diameter of the kiln [27,57].

4.2.4 FORMATION OF THE LIQUID PHASE (SOLID FUSION)

The formation of clinker in cement rotary kilns takes place at very high temperatures and at residence times of about 30 minutes [58], which promote solid-solid and solid-liquid reactions, essential reactions for the formation of four mineralogical clinker compounds: C_2S, C_3A, C_4AF and C_3S. According to Mujumdar and Ranade [14], the liquid phase is mainly due to the formation of C_3S. Some authors attribute the formation of the liquid phase to the presence of aluminum and iron in the flour.

They also attribute the formation of the additional coating of the kiln (collage) to the liquid phase, which they consider to be an advantage for the protection against wear of the refractories. Mujumdar and Ranade [26] state that the formation of the liquid phase is highly dependent on the local temperature. They estimate the fraction of the liquid formed due to the melting of solids by the relation (17) below:

$$y_{fa}^{Liq} = max\left[0, \frac{T - T_S}{T_L - T_S}\right] \tag{17}$$

Where T_L and T_S are respectively the temperature at which the whole mass is liquid ("LIQUIDUS") and the temperature at which the first drop of liquid is formed ("SOLIDUS"), and T the temperature of the mixture. These depend strongly on the composition of solids in the kiln, and are likely to vary inside the kiln. The values of liquidus and solidus retained are respectively 1927 °C and 1287 °C. Nielsen [24] and Hewlett [59] consider that alumina (Al_2O_3) and iron oxide III (Fe_2O_3) at temperatures above 1300 ºC are at the base of the liquid phase. They affirm that, Alumina and Iron Oxide III although not being essential to the constitution of the final product (Portland cement), allow the formation of the liquid phase, and that they act like lowering flow of energy requirements at the clinkerization stage. They retain the chemical reactions (18) below as characteristic reactions of the liquid phase:

$$\begin{gathered} 3CaO(s) + Al_2O_3(l) \rightarrow 3CaO.Al_2O_3(s) \\ 4CaO(s) + Al_2O_3(l) + Fe_2O_3(l) \rightarrow 4CaO.Al_2O_3.Fe_2O_3(s) \end{gathered} \tag{18}$$

Aluminate and Ferrite crystallize from the liquid phase when the temperature drops to around 1230 ºC (**Erreur ! Source du renvoi introuvable.**). According to Nielsen [24], the liquid phase acts as a carrier for increasing diffusion transport, and thus accelerates the formation of belite (C_2S), Alite (C_3S) and free lime (CaO_{free}) crystals.

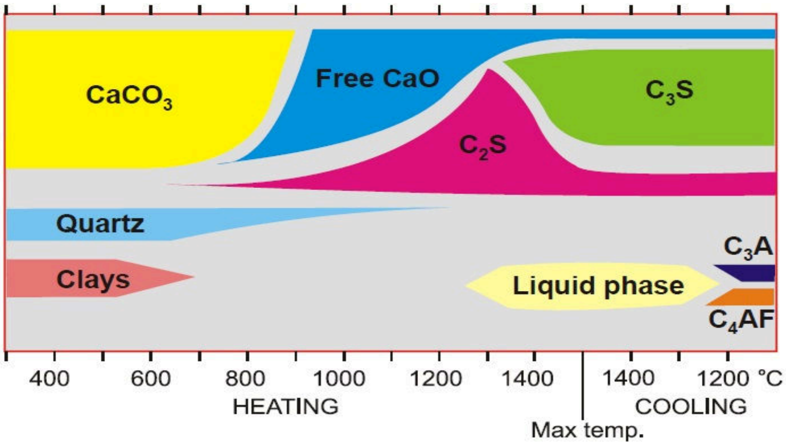

Fig. 6. Phase diagram of clinker production [24]

Mastorakos et al. [15] take into account the formation of the liquid phase in cement rotary kilns, establishing a model that assumes that the formation of the liquid phase varies linearly. They limit the fraction of the liquid in the bed to 30 %. This latter value is supposed to remain constant thereafter, in the combustion zone until the solids exit. The model considers the bed temperature to be greater than or equal to the melting temperature (1560 K). Nørskov [30] considers C_3A and C_4AF as the main catalysts of the liquid phase in the solids bed, at temperatures of 1330 °C. He states that the liquid phase accelerates the clinkerization reactions by forming alite, belite, and free lime, according to the figure 7 below.

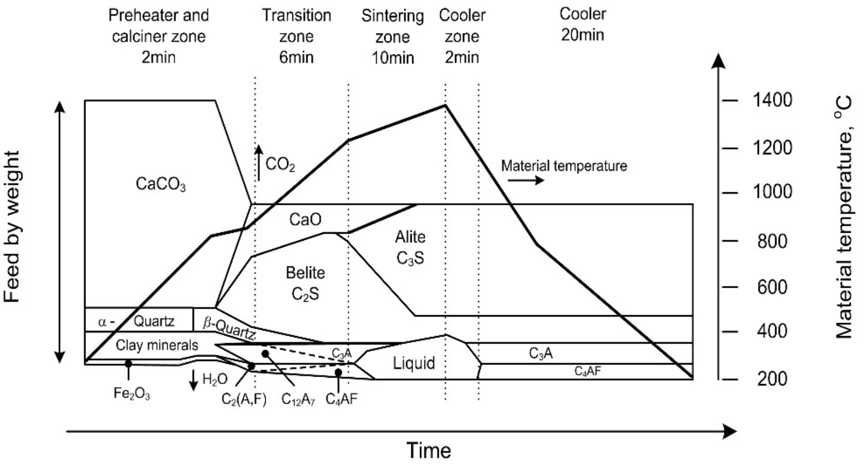

Fig. 7. Pyroprocessing with indications of reaction time [30]

Romero Valleötzl [60] restart the model of the fraction of the liquid formed by the fusion of solids developed by Mujumdar and Ranade [26], retaining the temperatures of 2570 °C and 1390 °C respectively LIQUIDUS and SOLIDUS.

4.2.5 THE FIVE MODEL REACTIONS

The mechanism of transformation of flour into clinker is most often described in the literature by the following five reactions (equations (19) below):

$$\begin{gathered} CaCO_3(s) \rightarrow CaO(s) + CO_2(g) \\ 2CaO(s) + SiO_2(s) \rightarrow C_2S(s) \\ C_2S(s) + CaO(s) \rightarrow C_3S(s) \\ 3CaO(s) + Al_2O_3(s) \rightarrow C_3A(l) \\ 4CaO(s) + Al_2O_3(s) + Fe_2O_4(s) \rightarrow C_4AF(l) \end{gathered} \tag{19}$$

Mujumdar and Ranade [26] develop a bed model that considers only five reactions for clinker formation. Hiromi Ariyaratne et al. [31] present a mathematical model that also takes into account five major chemical reactions of the solid inside the rotary furnace: calcination, endothermic melting and exothermic clinkerization. Bhad et al. [13], Mastorakos et al. [15], Darabi [29], and Spang [61] also model clinker formation reactions using the five reactions above.

4.2.6 KINETIC CONSTANTS AND ENTHALPIES OF CLINKERIZATION REACTIONS

4.2.6.1 INTRODUCTION

There is very little information in the literature concerning the kinetics of clinkerization reactions. Some researchers attribute this to complex physicochemical reactions, to multiple phases and especially to several simultaneous processes at very different time scales, which take place during clinker formation [13,14]. In view of the above, Mujumdar and Ranade [14] discuss the importance of identifying key issues and using appropriate methodology to develop mathematical models for rotary kilns dedicated to clinker production.

4.2.6.2 KINETIC CONSTANTS AND ENTHALPIES OF REACTIONS

In the literature, we find different values of enthalpies of clinkerization reactions (Table 4**Erreur ! Source du renvoi introuvable.**). To evaluate the net enthalpy of solid reactions, Hiromi Ariyaratne et al. [31] use the specific equations (20) below established by the German Cement Association (VDZ), given below:

$$
\begin{aligned}
\Delta h_{CaCO_3} &= r\,\dot{m}_{rm} w_{CaCO_3,rm}(1-\eta_{cal}) \\
\Delta h_{C_4AF} &= 3{,}043\; s\,\dot{m}_{cl}\, w_{Fe_2O_3,cl} \\
\Delta h_{C_3A} &= t\,\dot{m}_{cl}\big(2{,}65\; w_{Al_2O_3,cl} - 1{,}692\; w_{Fe_2O_3,cl}\big) \\
\Delta h_{\beta-C_2S} &= u\,\dot{m}_{cl}\big(2{,}868\; w_{SiO_2,cl} - 0{,}754\; w_{C_3S,cl}\big) \\
\Delta h_{C_3S} &= z\,\dot{m}_{cl} w_{C_3S,cl} \\
h_R &= \Delta h_{CaCO_3} - \Delta h_{C_4AF} + \Delta h_{C_3A} - \Delta h_{\beta-C_2S} - \Delta h_{C_3S}
\end{aligned} \tag{20}
$$

Where Δh_{CaCO_3} and Δh_{C_3A} represent respectively the energy quantities absorbed for the dissociation of $CaCO_3$ and the formation of C_3A, whereas Δh_{C_4AF}, $\Delta h_{\beta-C_2S}$ and Δh_{C_3S} represent respectively the quantities of energy released by the formation of C_4AF, C_2S, and C_3S. In previous expressions $\dot{m}_i$ is the mass flow of the components (kg/s), η_{cal} the real degree of calcination, and $w_{i,j}$ the fraction by weight of the component i in j (i= species and j=clinker). This study led them to determine enthalpies of formation (Table 4), represented in the equations (20) above by letters r, s, t, u and z. Subscripts rm and cl refer to raw materials and clinker, respectively. The enthalpies of clinkerization reactions are given in Table 4 concern to the five model equations below:

$$CaCO_3(s) \rightarrow CaO(s) + CO_2(g) \tag{21}$$

$$2CaO(s) + SiO_2(s) \rightarrow C_2S(s) \tag{22}$$

$$C_2S(s) + CaO(s) \rightarrow C_3S(s) \tag{23}$$

$$3CaO(s) + Al_2O_3(s) \rightarrow C_3A(l) \tag{24}$$

$$4CaO(s) + Al_2O_3(s) + Fe_2O_4(s) \rightarrow C_4AF(l) \tag{25}$$

Several chemical reactions take place during the cooking of the flour, involving different species, both solid and liquid. Several authors consider that clinkerization reactions follow the Arrhenius law, and are of the first order [15,26,29,46]. The kinetic constants given by [15], were chosen by trial and error, in order to obtain the desired composition (clinker) at the exit of the kiln. As for reaction rates, Mastorakos et al. [15], Mujumdar and Ranade [26], and Darabi [29] give the reaction rates in mass form. The kinetic values found in the literature are given in Table 4 below:

Table 4. Kinetics and enthalpies of clinkerization reaction

Equations	References	A	E [kJ/mol]	ΔH [kJ/mol]
(21)	[26]	$1,18.10^{3}$ (kmol/m^{2}/s)	185	179,4
	[15]	10^{8} (s^{-1})	175,728	-
	[46]	$9,67.10^{24}$ (h^{-1})	1092, 947#	-
	[29]	$4,55.10^{31}$ (s^{-1})	781	+$1,782.10^{6}$@
	[13]	-	-	+1660 ¤
	[31]	-	-	1778 ¤
(22)	[26]	$1,0.10^{7}$ (m^{3}/kg/s)	240	-127,6
	[15]	10^{7} (s^{-1})	240,	-
	[46]	$1,41.10^{15}$ (h^{-1})	346,014#	-
	[29]	$4,11.10^{5}$ (s^{-1})	193	-$1,124.10^{6}$@
	[13]	-	-	-603 ¤
	[31]	-	-	700 ¤
(23)	[26]	$1,0.10^{9}$ (m^{3}/kg/s)	420	16,0
	[15]	10^{9} (s^{-1})	420	-
	[46]	$4,18.10^{8}$ (h^{-1})	461,352#	-
	[29]	$1,33.10^{5}$ (s^{-1})	256	+$8,01.10^{4}$ @
	[13]	-	-	-448 ¤
	[31]	-	-	495 ¤
(24)	[26]	$1,0.10^{8}$ (m^{3}/kg/s)	310	21,8
	[15]	10^{8} (s^{-1})	310	-
	[46]	$1,81.10^{9}$ (h^{-1})	251,208#	-
	[29]	$8,33.10^{6}$ (s^{-1})	194	-$4.34.10^{4}$ @
	[13]	-	-	-37 ¤
	[31]	-	-	74 ¤
(25)	[26]	$1,0.10^{8}$ (m^{3}/kg/s)	330	-41,3
	[15]	10^{8} (s^{-1})	330	-
	[46]	$5,59.10^{11}$ (h^{-1})	188,406#	-
	[29]	$8,33.10^{8}$ (s^{-1})	185	-$2,278.10^{5}$ @
	[13]	-	-	-109 ¤
	[31]	-	-	67 ¤

 # : in [kJ/kg/mol] ; @ : in [J/kg de CaO] ; ¤ : in [kJ/kg]

5 ENGINEERING OF THE PROCESS

5.1 EXISTING PROCESSES

There are four cement manufacturing processes: wet, semi-wet, semi-dry, and dry. Each process corresponds to one or more types of kilns.

5.1.1 WET PROCESS

The wet process has been used for a long time. Currently, it is considered obsolete, and energy consumer (see Figure 8). The wet kilns are known to be very long, sometimes reaching 220 meters [1]. These kilns have three zones: drying, decarbonation, and clinkering. The raw material is fed in paste form, made of limestone and clay finely ground with water (28 to 42 % of water). For thermal reasons, the walls at the entrance of the kiln (about 20 % of the total length of the kiln) are coated with marine chains. The wet process kilns are characterized by daily production capacities of 250 to 3600 tons [62].

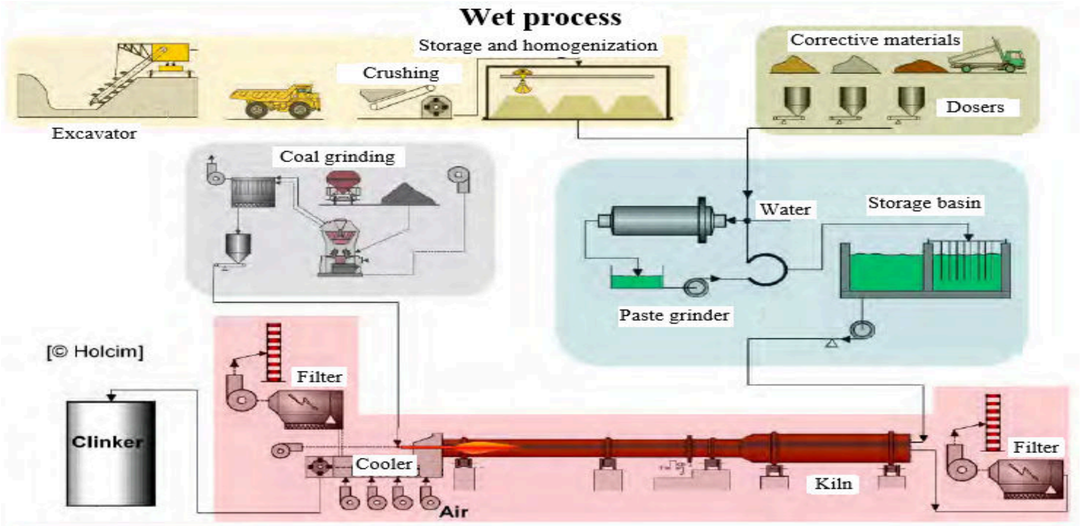

Fig. 8. Wet process [1]

5.1.2 SEMI-WET PROCESS

The semi-wet process is a derivative of the wet process, but with the particularity of the presence of a filter press, a preheater tower or a Lepol grate and a short rotary cylinder. And also the low water content in the paste, evaluated between 17 to 21 %. The filter press is used to filter the paste before its introduction into the preheating tower [1]. The material enters the preheating tower in form of the paste, and comes out as flour. The latter is then admitted to the rotary cylinder to give clinker. In the case of kilns with Lepol grate, the paste from the filter press is fed into a Lepol grate preheater. The paste falls on perforated grids through which pass the combustion gases from the kiln [1]. At the exit of the Lepol grate, the flour is admitted to the rotary kiln or rotary cylinder (see Figure 9).

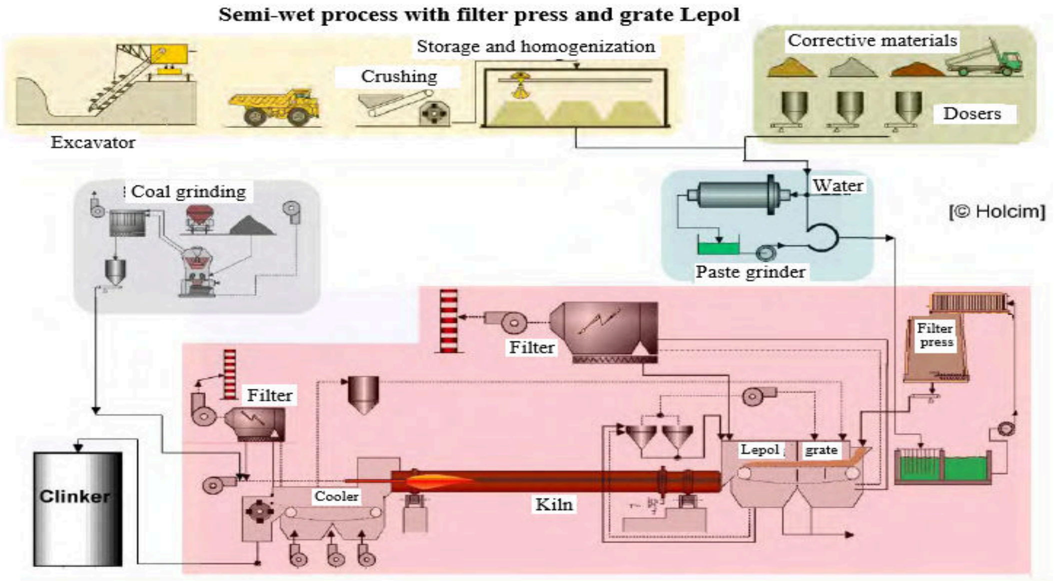

Fig. 9. Semi-Wet process with filter press and grate Lepol [1]

5.1.3 SEMI-DRY PROCESS

The semi-dry process is very similar to the semi-wet process. The difference between the two categories resides on the fact that in the case of the "semi-dry", we do not manipulate the material in the form of paste, but rather in the form of granules or flour. This process developed from the 1930s as an alternative to the wet process. There was then a big reduction in the specific thermal consumption, of the order of 20 to 30 % [62]. After grinding and homogenization, the raw materials are introduced into a granulation sole (granulator), where they are mixed with water (10 to 12%) to give granules [1]. These latter are then sent to the Lepol grate, before their admission to the rotary kiln (see Figure 10).

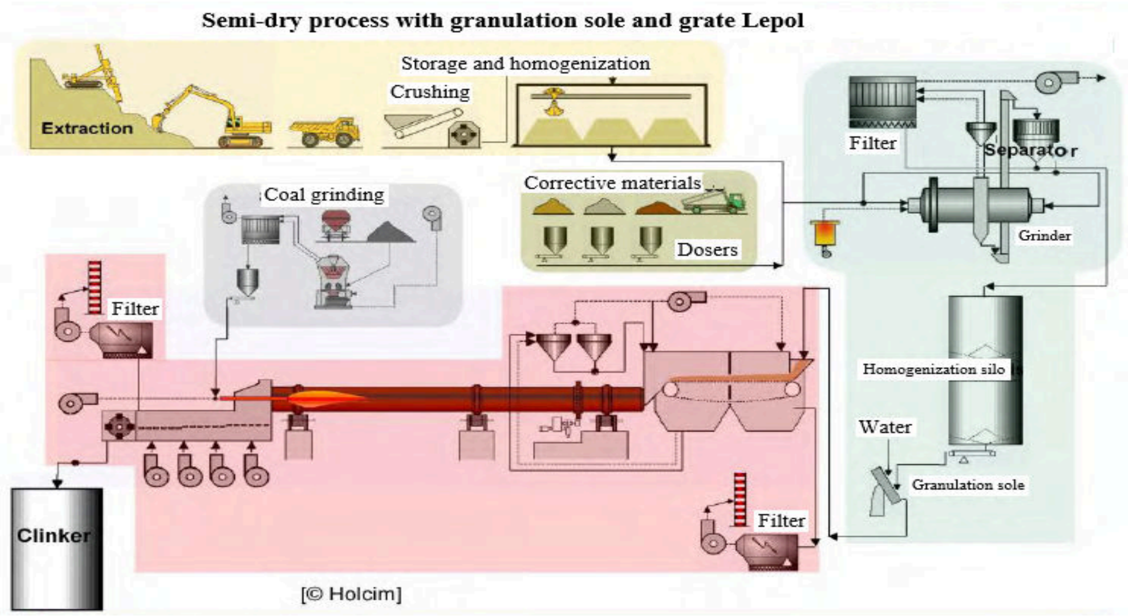

Fig. 10. Semi-dry process with granulation sole and grate Lepol [1]

5.1.4 DRY PROCESS

The dry process is the most widely used (see Figure 1). It has been developed in order to eliminate the step of drying the paste and/or granules. The material (raw meal) sent into the kiln contains no water. This is due to the presence of a grinder, able to grind and dry the raw materials at the same time. There has been a great evolution of these types of kilns, in so far as several technologies have emerged, with the aim of improving energy and production yields. We can cite for example preheater kilns without precalcination, preheater kilns with precalcination, without tertiary air, and preheater kilns, with precalcination and with tertiary air.

5.2 THE HEART OF THE DRY PROCESS: THE ROTARY KILN

The dry cement manufacturing process has developed significantly over the past three decades, particularly with regard to the baking kiln. Several types of rotary kilns have emerged: preheater kilns (the first since the advent of the process), preheater kilns with precalciner, without tertiary air, and preheater kilns with precalciner and tertiary air. These rotary kilns are equipped with different types of coolers: grates, balloons (or planetary), and rotary. In this paper, we present the schematic diagram of different types of rotary kilns in the dry process. We also give some information about the inputs, outputs, geometric characteristics and temperature levels of these kilns.

5.2.1 SCHEMATIC DIAGRAM OF ROTARY KILN BY DRY PROCESS

We present the schematic diagrams of three large families of rotary kilns encountered in the dry process, as well as the types of coolers used.

5.2.1.1 ROTARY KILNS WITH PREHEATERS WITHOUT PRECALCINER

Preheater rotary kilns without precalcination are the first kilns that have emerged since the advent of the dry process. So they are old, although they still work today. These kilns, equipped with preheating towers, whose stages can range from 4 to 6, were developed in order to overcome the energy problem. More the number of stages is high, more the rotary cylinder (rotary kiln) is of short length. The number of stages depends highly on the humidity of the raw materials. Preheater kilns thus allow a balance between the heat available in the gases exiting the exchanger, at temperatures of 350 to 380 ° C, and the need for heat to evaporate moisture from raw materials, often 8 at 9 % [62]. Figure 11 illustrated 4-stage preheater kilns. For the industrial realization of preheating towers, we can find preheaters with 4 stages of cyclones, KHD-FLS exchanger, Polysius exchanger, and Prerov exchanger. Preheater rotary kilns without precalciner can be equipped with balloon (planetary) coolers, either grate coolers or rotary coolers.

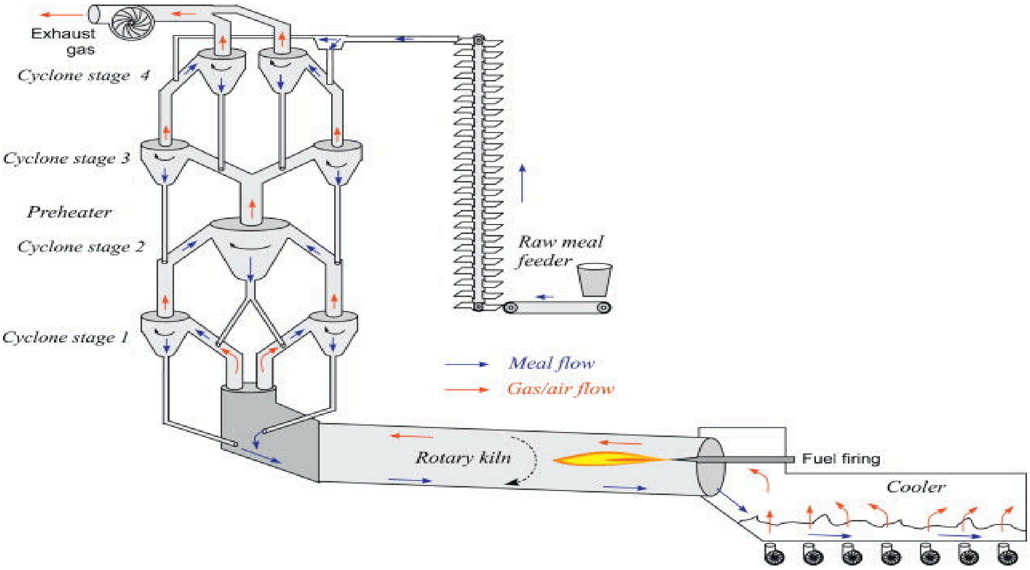

Fig. 11. Four-stage cyclone preheater kiln [63,64]

5.2.1.2 PREHEATER ROTARY KILNS WITH PRECALCINER, WITHOUT TERTIARY AIR

The concept was developed in 1970 by the Japanese cement industry, with the aim of improving the thermal performance and production of existing plants. Kilnss equipped with precalciner have low specific consumptions, because of the quality of heat exchange, and have large production capacities. Bastier et al. [65] talk of increasing production by a factor of 2 to 2.3 compared to other types of kilns. The air used for the combustion of the coal (or heavy fuel oil) injected into the pre-calcination furnace comes from the excess air of the main burner of the rotary kiln. In this configuration, it is necessary to have a large excess of air at the main burner of the furnace, if we wants to have better combustion yields in the precalciner. The precalcination rate is limited to 20 % [33,65], value not to be exceeded for fear of cooling the flame produced by the main burner of the kiln. Figure 12 illustrates rotary kilns with precalciner, without tertiary air.

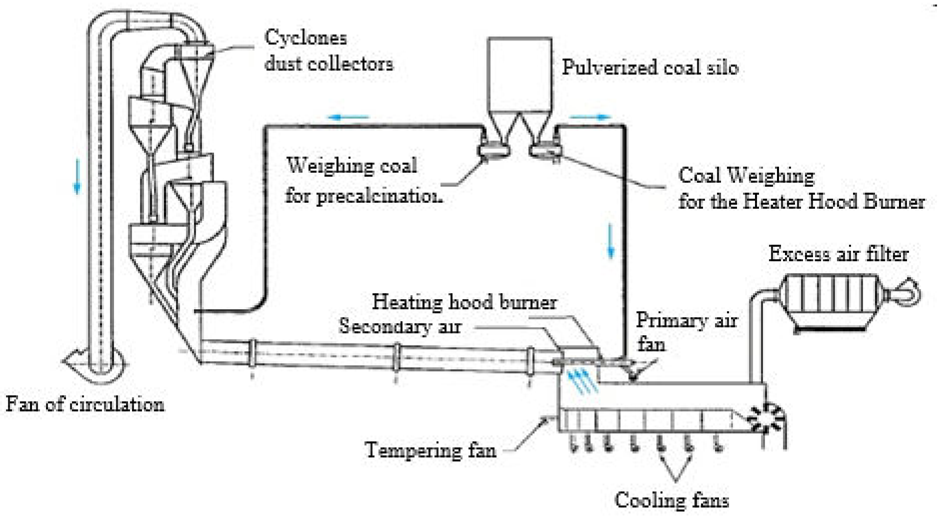

Fig. 12. Rotary kiln equipped with a precalciner, without tertiary air [62]

5.2.1.3 PREHEATER ROTARY KILNS WITH PRECALCINER, WITH TERTIARY AIR

All that is said about precalciner kilns without tertiary air duct remains valid, the difference lies in the rate of precalcination, which can reach 95 %. The air used for the combustion of the coal (or heavy fuel oil) injected into the precalciner is extracted from the cooling air of clinker, directly from the grate coolers, as illustrated on the **Erreur ! Source du renvoi introuvable.**Figure 13 below. It's not necessary to have the high excess of air in the main burner of the kiln. In most cases, rotary kilns with precalciner and tertiary air are equipped with grate coolers.

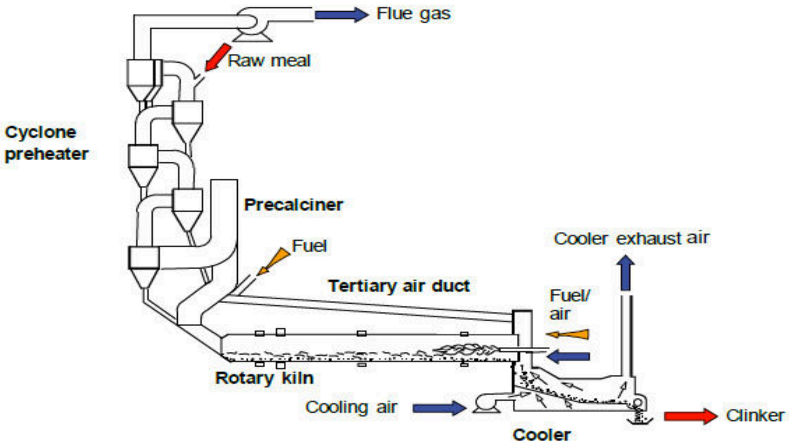

Fig. 13. Rotary kiln equipped with precalciner and tertiary air [66]

5.2.1.4 TYPES OF COOLERS

There are three types of coolers in the cement plant: balloon (planetary), grates (grid), and rotary.

5.2.1.4.1 BALLOON COOLERS (PLANETARY)

In these types of coolers, the clinkers leaving the kiln are divided almost equitably into different planetary tubes, generally 10 in number (Figure 14). These tubes are equipped with levers, to improve the thermal exchange hot clinker-air. This air (secondary air) is then sent to the rotary kiln as combustion air. The demand for air in kilns equipped with planetary coolers is estimated at 0.899 Nm^3/kg of clinker (ie 1.16 kg/kg of clinker), for kilns with a specific consumption of 3450 kJ/kg [67]. Clinkers generally come out at temperatures above 150 °C [33].

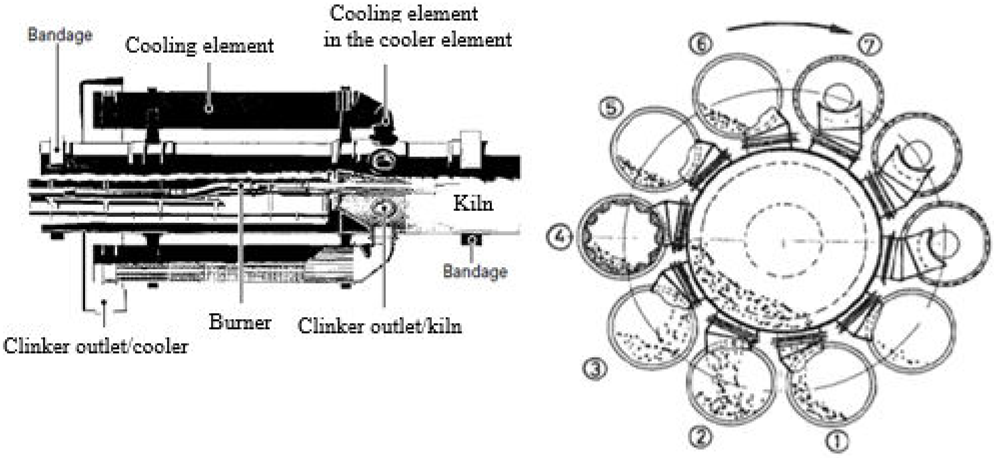

Fig. 14. Balloon or planetary cooler [33]

5.2.1.4.2 GRATE COOLER

Here, the final temperature of 80 °C for cooled clinkers can easily be reached. This is made possible by fan batteries placed below the grate, sending air cross currents when passing hot clinkers on the grate, as show in Figure 15. In these types of coolers, the cooling air consumption is 1.4 to 1.8 Nm^3/kg of clinker [67]. These values explain the better thermal efficiency of kilns equipped with a grate cooler. The secondary air temperature at the furnace inlet can easily reach 1000 °C.

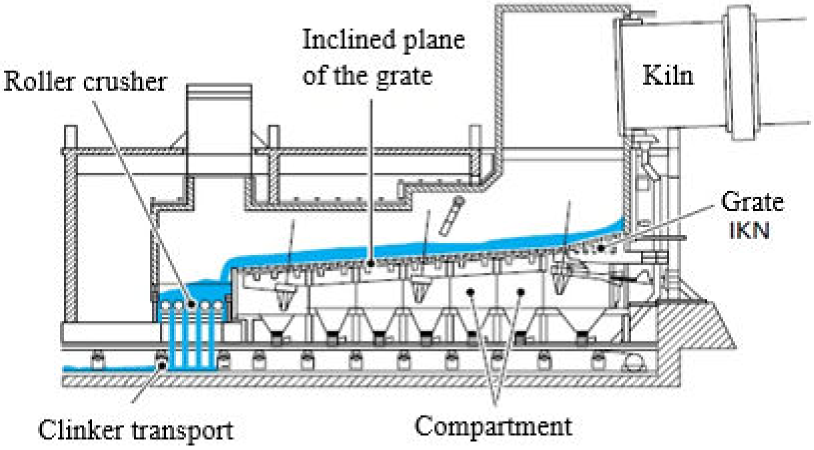

Fig. 15. Inclined grate cooler with pendulum suspension, with IKN grate and roller crusher [67].

5.2.1.4.3 ROTARY COOLERS

Rotary coolers are very old systems. They were often used on high capacity kilns. Their dimensions (length and diameter) are almost equal to those of the rotary kiln, illustrated Figure 16. For example, for a kiln with a daily capacity of 3200 tons, the length and diameter of the rotary cooler are 54 and 5.6 meters respectively. As with planetary coolers, cooling is not fast in rotary coolers. The temperature of the clinkers leaving the cooler is of the order of 180 to 300 °C [67].

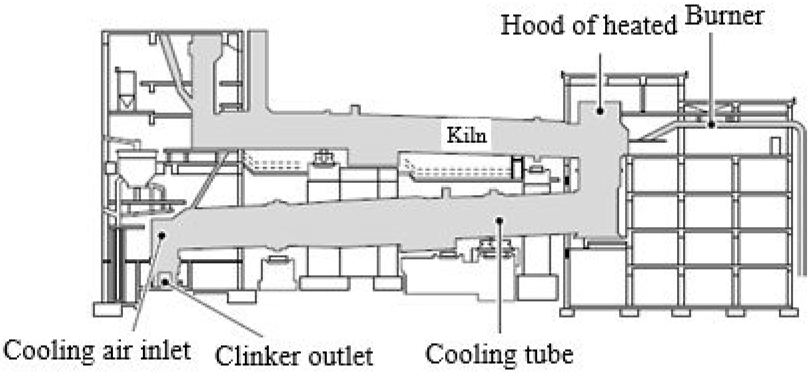

Fig. 16. Rotary or tubular cooler KHD [67]

5.2.2 INPUTS

The main inputs in this type of kiln are flour, fossil and/or alternative fuels, and air (primary and secondary). The main input of flour in the rotary kiln circuit is located at the last stage of the preheater tower. In the rotary section, it enters through a derivative channel (independent of the exit gases in the kiln) located just below the last cyclone (first stage). The fossil fuel (coal, heavy fuel oil, or natural gas) is introduced by means of a feed circuit to the main burner. As for alternative fuels, they are introduced either in the same input as the flour (below the last cyclone) or in the main burner (specific burner), at the same time as fossil fuel. And finally, the primary air is introduced via primary air fans, which send air into the burner. Primary air is also used to transport the fuel to the kiln. While the secondary air is introduced through the secondary air fans, which send air to the clinker cooler, before entering the rotary section.

5.2.3 EXITS

The main outputs are clinker and exhaust gas. The clinker leaves the rotary cylinder a few meters after the head of the main burner (end of clinkerization zone), at the cooler inlet. It is at the cooler outlet that the clinker definitely leaves the rotary kiln circuit. The gases exit the rotary section of the kiln through the riser pipe, connecting the rotary cylinder (rotary kiln) to the last cyclone of the preheater tower. They exit the rotary kiln circuit on the last stage of the preheater tower.

6 CONCLUSIONS

We have just presented a state of the art modeling of cement chemistry and engineering of the cement manufacturing process. The article focused on presenting and discussing the work and information available in the literature on cement chemistry, the cement manufacturing process, and the technologies used to produce cement, point of view of energy saving. The different phases of the clinker have been presented in detail. Their kinetics being strongly coupled, it is not possible to decouple. The kinetic models of clinkerization proposed in the literature follow the Arrhenius law, the most elaborate of which are those based on the dynamic model of Spang [61], which gives the different reaction rates as a function of the mass concentration of CaO, and takes into account the enthalpies of clinkerization reactions in the enthalpy balance. The aluminate phases ($(CaO)_3.Al_2O_3$ or C_3A) et Ferrite ($(CaO)_4.Al_2O_3.Fe_2O_3$ or C_4AF) are precursors of the liquid phase in the bed material, mainly due to the presence of Alumina (Al_2O_3) and Iron Oxide III (Fe_2O_3). The aspects related to the crystallography of clinker phases have not been addressed in this work, we reserve them for a future publication. Mineralogical analyzes of the clinker reveal that the CaO_{free} and MgO_{free} contents in the clinker must imperatively be limited, in order to avoid the phenomenon of expansion which causes damage in the mortar and/or in the concrete. This work is an open path for the aspects related to cement chemistry to be fully elucidated.

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