DYNAMIC STUDY OF THE CEMENT FLOUR CRUDE FIRING IN CLAYS AND LIMESTONES CONDITIONS OF DR CONGO

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ABSTRACT

The cement industry is one of the most standardized industries from the raw materials preparation to the cement manufacture, through the raw materials grinding and the crude flour firing. The raw materials used are mainly limestone (if Dolomite $CaCO_3.MgCO_3$) and Clay (If Kaolinite: $Al_2O_3.2SiO_2.(OH)_4$; if Montmorillonite : $(Na,Ca)_{0,3}(Al,Mg)_2Si_4O_{10}(OH)_2.nH_2O$). At each stage or level of the process, there are existing standards and principles to be respected. These Cement standards require especially that the free lime active (CaO_{free}) value be significantly less than 2 % by weight. The CaO free causes damage to the mortar, combining with water (H_2O) to produce slaked lime ($Ca(OH)_2$), when it is in high content in clinker.

Thus, the present article is concerned with the study of specific parameters which help to judge the quality of the clinker produced; those are clinker liter weight and free lime content (CaO_{free}) in the clinker which are strongly linked to the dosing and grinding of raw materials. It present also in a precise way the various aspects related to the raw materials preparation, the various causes leading to the presence of CaO_{free} in the clinker, and finally establish a correlation between the density of the clinker (weight of the liter) and free lime, which is important for the adjustment of raw materials (upstream) and cement produced (downstream).

The results show that clinker density decreases exponentially with the increasing of free lime content. The weight of the liter for an economic step of the furnace is thus between 1100 and 1250 g/l, where the content of free lime is clearly less than 2 % of the weight.

Key words: Cement rotary kiln, Clinker, Raw material dosage, Weight of the liter, Free lime, Alite (C_3S: Ca_3SiO_5), Belite (C_2S: Ca_2SiO_4), C_3S retrogradation reaction, Cooling rate

1. INTRODUCTION.

Rotary kilns are mainly used in cement plants, and have the role of producing the clinker used for the manufacture of portland cement. Clinker is obtained after cooking raw meal (fine material), consisting of a mixture of clay and limestone finely ground. The production of clinker requires very high temperatures to initiate the clinkerization reactions and the phase changes necessary to form the complex mineral compounds of the clinker, which give the cement its unique properties [1]. Clinker is an artificial rock, produced after firing in the rotary kiln, used as raw material for the manufacture of portland cements and specific cements. It is therefore a mixture of hard or soft calcareous rocks and finely crushed clays, dried and then cooked in the rotary kiln. The purpose of the cooking process is to transmit to the raw meal, in function of quality of the raw material, the quantity of heat which ensures the desired quality of the baked product in order to manufacture hydraulic cements according to the specifications of the standards and of the customer, the minimizing production cost, optimizing the flow rate of the cooking product, minimizing energy expenditure, and finally minimizing variations of product quality.

This article studies the quality of the clinker produced (degree of cooking), starting from the raw material preparation stage. Thus, two variables are involved, the weight of the liter of clinker and free lime content in the clinker. The weight of the liter is calling also the bulk density of the clinker. The method consists in measuring the weight of one liter of a granulometric fraction of the clinker. While free lime (CaO_{free}), a compound derived from the decarbonation of $CaCO_3$, is a parameter mainly used by cement manufacturers to judge the quality and degree of cooking of flour. The value of free CaO is often desired to be low, because in case of excess, it causes damage in the mortar or in concrete (it reacts with water to give slake lime $Ca(OH)_2$ [2].

Increases in free lime content may result from a malfunction of the cooking process or a failure in the preparation of the raw material (excessive lime saturation factor (LSF), coarse grinding or flour heterogeneity, Decomposition of alite (C_3S) caused by a drop in temperature, overcooking or slow cooling of the clinker, reducing conditions in the cooking zone).

The main objective of this study is to provide an account of the degree and quality of cooking of the flour in the cement rotary kiln by establishing a mathematical equation (Correlation) linking the variables cited above, namely the weight of Liter of the clinker and the free lime content in the clinker.

For so doing, we use data from the Unax rotary kiln of the National Cement Plant (CINAT) in the Democratic Republic of Congo. One thousand and twenty-eight (1028) random samples were examined, including three hundred and seventy (370) September 1974 samples, one hundred and forty-eight (148) October 1974 samples, one hundred and two (102) January-February 1983, two hundred fifty-one (251) samples from May 1985 and one hundred and fifty-seven (157) samples from January-February 2009.

2. PRODUCTION OF CEMENT.

The cement industry has an important role in the production-based economy. During the production of cement, natural resources are consumed in large part. The main raw materials used in the manufacture of cement are limestone (if Dolomite $CaCO_3.MgCO_3$) and Clay (If Kaolinite: $Al_2O_3.2SiO_2.(OH)_4$; if Montmorillonite : $(Na,Ca)_{0,3}(Al,Mg)_2Si_4O_{10}(OH)_2.nH_2O$) and/or marl, a material in which both components are already naturally mixed. After quarrying, these components are crushed and then ground and dried by combustion gases from the rotary kiln. Depending on the type of cement to be produced, the following products can be added: pyrite ash, fly ash from coal-fired power stations, clay sand and ash from electrostatic filters [3]. The mixture obtained is ground and then fired in a cement rotary kiln.

For heating, different fuels and other combustible materials are used, coal, petroleum coke, etc. At CINAT, the kiln is heated by the combustion of heavy fuel oil. The latter is heated by means of the superheated steam produced by the WEISCHAUPT boiler at a temperature of 120 °C and a pressure of 19.62 bar (20 kgf /cm^2), in order to allow a good spraying in the kiln burner.

At the inlet cyclones, the raw meal (materials) is at an average temperature of 80 °C, it undergoes vortex movements, caused by the hot gases coming out of the kiln. The flour is heated during its passage from the inlet to the outlet cyclones. At the inlet of the kiln, the materials have a temperature so-called outlet temperature of the last cyclone or precalciner, depending on whether it is a kiln with precalciner or not. In the Unax rotary kiln, for example, this temperature is close to 800 °C. In the kiln, under the effect of gravity and rotation, the flour is gradually heated as it advances by the hot air flowing countercurrent. Under the action of heat, the flour undergoes a series of physicochemical transformations until a partial melting process which converts it into clinker at around 1450 °C. The clinkers produced are ground with gypsum, to finally give cement.

Combustion, oxygen is drawn from the atmosphere by means of primary air and secondary air fans. The primary air fan adjusts the amount of air to be sent to the burner, which has an impact on cooking (long flame or short flame, fault or excess air).

3. BRIEF DESCRIPTION OF THE UNAX ROTARY KILN OF CINAT.

The firing kiln of the CINAT factory is a rotary kiln of the Unax type with a diameter of 4.15 m, a length of 58 m and a tilt of 3 %. At its outlet end, it is equipped with a 1.65 x 13.2 m Unax type balloon cooler, consisting of ten planetary cylindrical tubes, in which the clinker is cooled by the air circulation, thus enabling to lower the temperature of the clinker to about 150 °C [4]. Heating of the Unax rotary kiln is ensured by the combustion of fuel oil. Specific consumption amounts to approximately 3.5 MJ/tonne of clinker.

4. ASPECTS RELATED TO THE PREPARATION OF RAW MATERIALS.

In the cement production, it is necessary to mix raw materials whose chemical composition is within certain limits. In general, the intimate mixture of raw materials consists of 80 % of calcareous grains ($CaCO_3$, $MgCO_3$, if dolomite $CaCO_3.MgCO_3$ or $CaMg(CO_3)_2$) and 20 % clay grains (If kaolinite: $Al_2O_3.2SiO_2.(OH)_4$; if montmorillonite : $(Na,Ca)_{0,3}(Al,Mg)_2Si_4O_{10}(OH)_2.nH_2O$ and/or marl), subsequently who passed in a crusher for obtaining very fine raw meal (raw powder). The grinding of the grains is controlled by means of screens of different sizes. It should be noted that the grinding conditions greatly influence the cooking of the flour in a rotary kiln. [5] stated that when limestone is crushed to a fineness that does not allow a 200 µ sieve rejection, the combination of CaO with SiO_2 (C_3S and/or C_2S) is complete at the operating temperatures of kiln.

The final stage of the preparation of raw materials takes place in so-called homogenization silos, where the mixture reaches a perfect dosage of respective constituents of raw materials. At the exit of the homogenization silos, the mixture is flour oven, homogenized flour and ready to be sent to the oven for cooking.

4.1. Composition of raw materials in terms of oxides.

The production of quality cement is only possible if the composition of the raw material mixture is made optimally. [2] gave the limit values to be met by the finely ground limestone-clay mixture.

Table 1: Chemical composition limit values for cement raw materials

[2]

Oxide	Limit values [%]	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

4.2. Modules and saturation factor of lime.

In the cement plant, it is customary to determine the quantity of different constituents of flour and/or clinker in the form of ratios, moduli or factors. The latter are the result of numerous studies on the mechanisms of formation, reaction and production of Portland cement.

4.2.1. Hydraulic Module.

The hydraulic module (HM) makes it possible to calculate the optimum quantity of the quicklime (CaO) contained in the mixture:

$$HM = \frac{C}{S + A + F} \quad (1)$$

The limit values for HM are between 1.7 and 2.3.

4.2.2. Silica Module.

The silica modulus (SM) is often between 1.5 and 5, and is calculated as follows:

$$SM = \frac{S}{A + F} \quad (2)$$

The high value of SM corresponds to a high value of silica (S) to the detriment of the fluxing agents (A and F), whereas a low value causes excessive crusting in the clinkerization zone, Nuisances to the proper operation of the furnace.

4.2.3. Alumino-Ferric Module.

As its name indicates, this module (AF) makes it possible to estimate the ratio Al_2O_3 and Fe_2O_3 in the mixture. It is calculated by the following relation:

$$AF = \frac{A}{F} \quad (3)$$

The Alumino-Ferric module is between 1.5 and 2.5.

At present, more use is made of lime saturation factors to judge the quality of clinker [2], [6].

4.2.4. Lime saturation factors.

Saturation factors (LSF) express the ratio of the lime present in the mixture to the amount of lime that can combine with the silica to form C_3S and C_2S.

- Kuhl saturation factor

$$LSF\ I = \frac{C}{2.8S + 1.1A + 0.7F} \quad (4)$$

- Lea Parker saturation factor

$$LSF\ III = \frac{C + 0.75M}{2.8S + 1.18A + 0.65F}\ ;\ avec\ MgO < 2\% \quad (5)$$

The saturation factor of Lea and Parker is between 0.85 and 1.0. It is also in the following form, where the values must be between 85 and 100:

$$LSF\ III = \frac{C + 1.5M}{2.8S + 1.18A + 0.65F}\ ;\ avec\ MgO > 2\% \quad (6)$$

The LSF "Lime Saturation Factor" represents the ratio of the CaO present in Clinker to its ability to bind with the most basic compounds [6,7]. When the saturation factor in lime is greater than 100 %, there is imbalance between the constituents. HM provides the means to calculate the maximum proportion of CaO that can be combined with the oxides. It should be noted that not all lime can be saturated, hence the existence of an uncombined portion.

The two 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 rich in lime under technical conditions Cooking or cooling [2].

Table 2: Chemical criteria for the composition of clinker and / or flour (Unpublished)

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

5. PHYSICO-CHEMICAL ASPECTS RELATED TO COOKING.

The rest of the reactions in the cooking process can be represented as follows:

- 100 °C: Evaporation of free water
  $$Al_2O_3.SiO_2.mH_2O \rightarrow Al_2O_3.SiO_2 + mH_2O^{\nearrow}$$
- 400 °C. Dehydration of the crystalline water
- 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 C3A and $(CaO)_4.Al_2O_3.Fe_2O_3$ or C_4AF probably.
- 1260-1450 °C: formation of C_3S with gradual disappearance and practically total free lime.

These reactions may in fact be simultaneous or overlapping and are in any case only intermediate steps, since at the maximum cooking temperature the only solids present are C_2S and C_3S and, incidentally, a little free Lime (CaO). All of the alumina, iron oxide III and minor components are then found in the liquid phase and will crystallize more or less [8,9], depending on the cooling rate, into C_3A-C_4AF and other complex constituents. The only stable compounds at the lowest temperature are C_2S and C_3A. CaO is not desirable in cement, follows the excessive expansion of the mortar it causes[10]. By lowering the liquid forming temperature, C_3A accelerates the combination of CaO with SiO_2. C_3S pure would be the ideal cement, but the difficulties of its production make it uneconomical. This is confirmed by [11], who say that from the point of view of resistance, the best cement would therefore be that corresponding to the proportion of lime such that C_2S = 0, that is to say that in which all the silica would be combined with the lime in the form of C_3S.

Table 3: Mineralogical composition deduced from the Borgue formulas [12].

Elements	**[%]**
C_3S	≥ 55
C_2S	≤ 22
C_3A	≥ 8
C_4AF	≥ 8
$CaSO_4$	$\leq 2{,}5$

Table 4: Chemical composition of the clinker of the national cement plant in the form of oxides [12,13].

Elements	[%]
PF	0,2 - 2
CaO	64 - 67
SiO_2	20 -22
Al_2O_3	5 - 6
Fe_2O_3	2,5 - 3
MgO	0,5 - 2
SO_3	0,5 - 2
K +Na	-

6. FREE LIME IN THE CLINKER.

The free lime in the clinker must be rigorously monitored to ensure the quality of the cement. Its excess is likely to cause adverse effects such as volume expansion, increased setting time, or decreased strength of cement [14].

In view of the above, free lime can be considered as one of the most essential parameters, making it possible to judge the quality and degree of cooking of clinker. Well-cooked clinkers, resulting from a well-dosed raw and well-graded, have contents of less than 2 % CaO_{free} [15].

Free lime in clinker may come from the following sources: overdosage, insufficient cooking, retrogradation of C_3S (caused by overcooking or slow cooling of the clinker), and the effects of particle fineness (Coarse grinding or heterogeneity of the flour) [11,15].

6.1. Overdose of raw meal.

In this case, the free lime is due to the excess of unreacted CaO. The work of any chemist in a cement plant is to make a good mix of raw mix. He must ensure that the lime saturation factor (LSF) is less than or equal to 100 %. This is equivalent to saying that overdosage of the vintage is a rare case.

6.2. Insufficient cooking.

The absence of a sufficient quantity of oxygen (too little draft) leads to insufficient combustion, which causes a drop in temperature in the cooking zone (insufficient cooking temperature). In this case, there is a high carbon monoxide content (reducing conditions in the cooking zone) and uncombined lime (free lime). The cooker work is to regulate the draft so that there is a sufficient supply of oxygen. This is why, it is always required an excess of air to avoid bad combustion. Excessive air (high draft) causes a drop in temperature in the cooking zone as well as an increased speed of the air passing through the kiln.

6.3. Downgrading of C_3S.

During a too slow cooling of the clinker or of overcooking, the C_3S decomposes in C_2S according to the equation:

$$C_3S \rightarrow C_2S + C \qquad (7)$$

If the free lime content is low, CaO will normally be extinguished during grinding. On the other hand, if its content is important, the clinker is unusable without prior extinction. Once extinguished, free lime is no longer dangerous, it brings finesse and plasticity. For artificial portland cement, a free lime content of less than or equal to 2.5 % [5,11].

The chemical reaction of downgrading C_3S to C_2S is a first order reaction. The reaction rate is as follows:

$$V = -\frac{d[C_3S]}{dt} = +\frac{d[C_2S]}{dt} = +\frac{d[C]}{dt} \qquad (8)$$

$$V = -\frac{d[C_3S]}{dt} = k[C_3S] \qquad (9)$$

Where

k =rate constant.

$[i]$= concentration of the species i.

6.4. Effects of particle fineness. The amount of free lime remaining after cooking depends on the fineness of the particles (coarse grinding or heterogeneity of the flour). As stated in paragraph 4, the fine grinding of the limestone must not allow a rejection on a sieve of 200 µ, in order to have very low levels of CaO_{free}. At CINAT, the fineness of raw meal (raw powder) is as follows [16]:

- Refusal on sieve of 200 µ : 2 % max ;
- Refusal on sieve of 90 µ : 15 % max.

In practice, the rejection on sieves of 90 µ rarely exceeds 13.5 %. From what is mentioned above, we will always expect to have a certain amount of free lime after cooking.

7. THE WEIGHT OF THE LITER.

According to Ghomari [17], the weight of the liter or bulk density of the clinker ranges from 800 to 1300 kg/m^3 (0.8 to 1.3 kg/l) on average. In a cement plant (Rotary kiln), the weight of the liter is always checked every hour during the clinker production campaign. At the CINAT, the sample of the clinker is taken manually from the planetary coolers, on the horizontal chain.

8. COOLING RATE OF CLINKER.

The cooling rate of the clinker is also one of the important parameters to be controlled during the production of the clinker, because, as said above, cooling too slow can lead to a retrogradation reaction of C_3S, resulting in a considerable amount of the free lime in the clinker at the exit of the kiln. The relationship below makes it possible to estimate the cooling rate of the clinker:

$$V_{ref} = \frac{dT}{dt} \quad (10)$$

Where

- V_{ref} : the speed in K/min,
- dT : the temperature variation in K, and ;
- dt : the time variation in min.

8.1. Rapid cooling rate.

A rapid cooling rate of clinker, in the high temperature range, has a great influence on the formation of clinker minerals, and therefore on the strength of the cement [18]. The condition for asserting that that we are in the case of rapid cooling of the clinker is given by the relation below:

$$V_{ref} = \frac{dT}{dt} > 40\ K/min. \quad (11)$$

The properties of the clinker (depending on the cooling rate) can thus be represented as follows:

- No retrogradation (decomposition) of C_3S to C_2S, consequence high content of C_3S;
- Slower setting of the cement because the cryptocrystalline C_3A reacts with water more slowly than the well crystallized C_3A.

8.2. Slow cooling rate.

The case of slow cooling is often at the base of high CaO content in the clinker. It is therefore dealt with briefly in this section. The slow cooling take place when:

$$V_{ref} = \frac{dT}{dt} < 20\ K/min. \quad (12)$$

The properties of the clinker (depending on the cooling rate) can thus be represented as follows:

- Perturbation of crystalline networks by a beginning of C_3S decomposition (stop at 1200 °C as the extreme case of slow cooling);
- Rapid setting of the cement because the well-crystallized C_3A (ie, which has not been mixed with C_4AF) reacts intensely with water.

The clinker is cooled in two steps: **The first step** (or the first phase) takes place in the cooling zone of the rotary kiln, before entering the cooler, this is the decisive phase. The clinker is cooled from 1450 °C to 1300-1200 °C. **The second step**, however, takes place in the cooler. The clinker is cooled from 1300-1200 °C to 500 °C. The cooling rate for these two steps, based on the practical ENKEGAARD cooling curves and the optimum regime of cooler for rich clinkers in C_3S of ONO, KAWAMURA and SODA, is:

-1st step : 1450 °C→1200 °C ; $V_{ref} = \frac{dT}{dt} < 20\ K/min.$

In this part of the furnace, the cooling gradient is between 15 and 20 K/min. The modification of the length and / or the position of the flame has an effect (modified) on the duration of cooling of the clinker in the furnace.

-2nd step : $V_{ref} = \frac{dT}{dt} < 70\ K/min.$

In the case of the CINAT/Kimpese plant, in the province of Kongo Central, DR Congo, the following values were found:

- Rapid cooling of the clinker: $V_{ref} = 56\ K/min.$
- Slow cooling of the clinker : - 1st step : $V_{ref} = 19\ K/min.$;

- 2nd step : $V_{ref} = 31\ K/min.$.

For the decisive step, the velocity is three times less than that which had to be obtained, in order to avoid the decomposition of C_3S (rapid cooling). Which implies that when the cooling time is much longer than 8 minutes (residence time of the clinker in the cooling zone when the furnace is running at a speed of 1.5 to 1.6 rpm), the reaction of decomposition of C_3S into C_2S will then take place.

9. CORRELATION BETWEEN THE WEIGHT OF THE CLINKER AND THE FREE LIME PRESENT IN THE CLINKER.

It is important to emphasize that the correlation that we establish in this paragraph is specific to the Unax rotary kiln of CINAT, but can be adapted to other kilns, in function of specific parameters of theses kilns.

9.1. Influence of clinker mineralogical compounds.

In terms of percent by weight, the four mineralogical constituents of the clinker have generally the following mean weight [2,5,9,10,19]:

- C_3S : 62 %
- C_2S : 22 %
- C_3A : 8 %
- C_4AF: 8 %

For [15], C_3S can reach a maximum weight of 80 %. Considering ideal conditions, ie no overdosage of the raw, good fineness of grinding, good homogenization of the flour, good combustion (complete) and proper coating of the kiln (good insulation). If the above conditions are verified, we could be concluded that the presence of free lime in the clinker is due solely to the retrogradation of C_3S, according to the chemical reaction (7). We can be understood that the weight of the liter of clinker is due essentially to the weight of the C_3S.

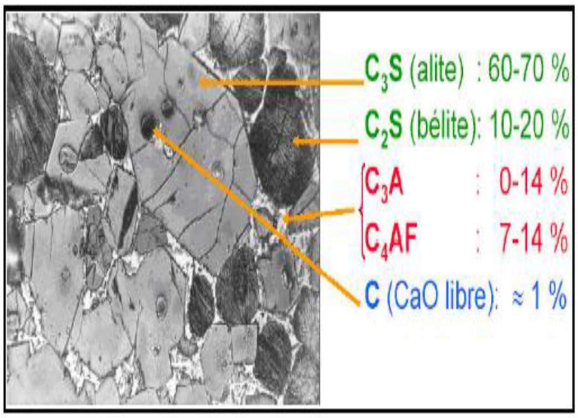

Figure 1 – Polished section of a clinker sample (1 cm≈10µm) [20]

9.2. Establishment of the mathematical relationship.

Equation (9) above allows to write:

$$-d[C_3S] = k\ dt\ [C_3s] \quad (13)$$

To simplify the writing, we write equation (13) as follows:

$$-dC_3S = k\ dt\ C_3S \qquad (14)$$

The cooling time being too slow, because dt very large. This is reflected in the relationship below:

$$k\ dt\ = \lambda\ dC \qquad (15)$$

Where

- λ : downgrade constant of C_3S en C_2S, in m^3/kg.
- C : concentration of free lime, in kg/m^3.

By substituting the relation (15) in (14), he comes:

$$-dC_3S = \lambda\ C_3S\ dC \qquad (16)$$

In practice, to control the degree of cooking, it is important to determine the weight of the liter of clinker and free lime, carbon monoxide and oxygen contents. Since the weight of the liter of clinker is mainly due to the weight of the C_3S, we can replace the C_3S by the weight of the liter, denoted "ρ". In view of the above, equation (16) takes the following form:

$$-d\rho = \lambda\ \rho\ dC \qquad (17)$$

(17) Can still be written as in this form:

$$\frac{d\rho}{dC} + \lambda\ \rho = 0 \qquad (18)$$

Où ρ is the solution of the differential equation (18). Written in the form above, equation (18) can be easily integrated.

$$\int \frac{d\rho}{\rho} = -\int \lambda\ dC \qquad (19)$$

The trivial solution is of the form:

$$\rho = a.exp(-\lambda\ C) \qquad (20)$$

Where:

- a : the integration constant;
- ρ : the weight of the liter;
- λ : the demotion constant, and;
- C: The free lime content.

Because of free lime is not desired, pure C_3S would be the ideal cement [21]. Hence, when cooking of flour, we will seek to have a low content of free lime.

If $C = 0, \rho = a.exp(0) = a$

Let's call ρ_0, the weight of the liter when $C = 0$, the equation (20) is written

$$\rho = \rho_0.exp(-\lambda\ C) \qquad (21)$$

This last expression expresses the way in which the weight of the liter of clinker can vary (decay) exponentially following the increase of free lime. It is therefore the correlation between the weight of the liter of clinker and the content of free lime present in the clinker.

10. RESULTS AND DISCUSSIONS.

Figure 2 shows that the weight of the liter decreases when the free lime increases, but this happens exponentially. Because of free lime is undesirable, a low content of free lime (< 2.5 %) is sought for artificial cements. The European Union standards that we use do not limit free lime content, but limit expansion to 10 mm on the test of Le Chatelier à chaud [2,11].

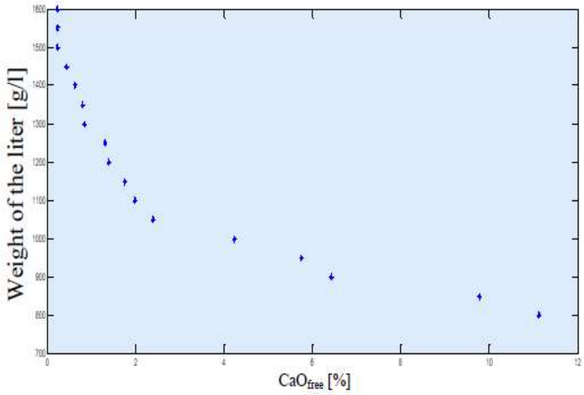

Figure 2 - Weight of liter according to free lime

According to the results presented in Table 5, we have economical cooking when the weight of the liter varies from 1100 to 1250 g/l and the free lime content varies from 1.97 to 1.30 %. However, in 16 % of the cases, we have seen a decrease in the weight of the liter due to overdosage of the raw

(raw meal). The weight of the liter then varies from 800 to 1050 g/l while the free lime content oscillates from 11.12 to 2.38 %. And an increase in the weight of the liter in almost 9 % of cases due to overheating of the kiln, the weight of the liter varies from 1350 to 1600 g/l, while the free lime content is ≤ 0.79 % (Table 5 and Figure 4 below).

Based on the results presented in Table 5, the retrogadation of C_3S to C_2S can be considered as a statistical phenomenon, because we cannot predict exactly what proportion of C_3S could be transformed into C_2S. For this, we have defined the probability λ (retrogradation constant) for the C_3S to be transformed into C_2S and to release lime.

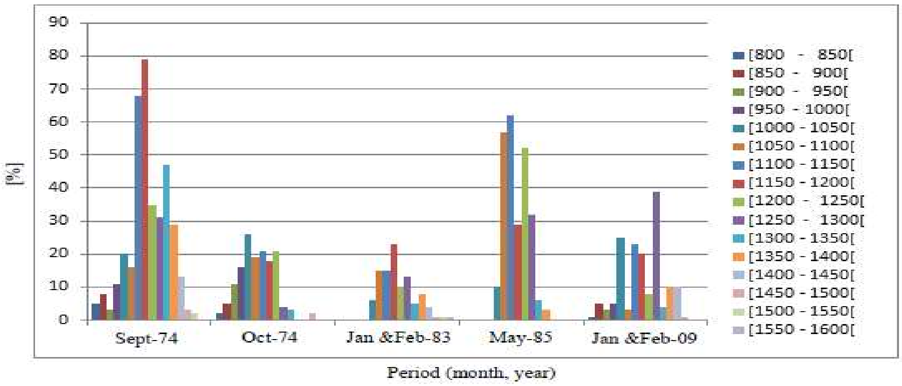

Figure 3: Effect of the weight of the clinker of different CINAT productions.

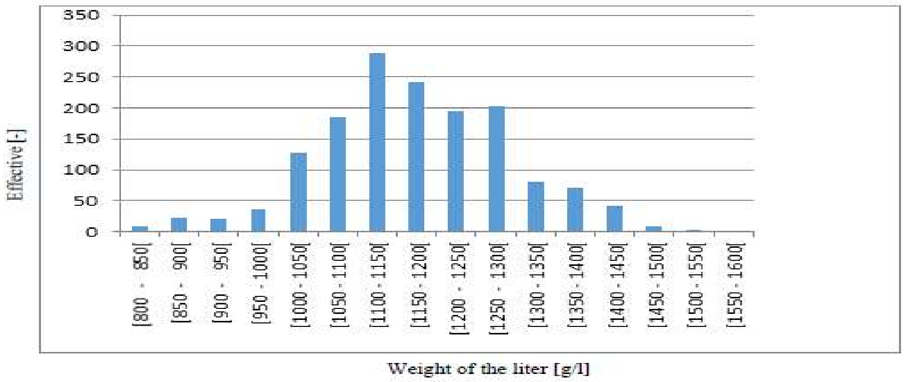

Figure 4: Average strength (total) of the weight of the clinker of different CINAT productions.

We have determined ρ_0 graphically by extending the curve at the abscissa point C=0, $\rho_0 = 1650$ g/l (figure 3).
The equation (21) is written:

$$\rho = 1650\, exp(-\lambda\, C) \qquad (22)$$

This expression is the retrogradation equation of C_3S in C_2S for the case of the Unax rotary kiln of the Kimpese national cement plant (CINAT) in DR Congo. λ can be determined (read) graphically or calculated.
Considering the data given in Table 1 and 3, it is found that 73 % of samples have a weight of liter varying between 1050 and 1300 g/l (figures 1 and 2), and the free lime content decreases from 2.38 to 0.83 %. This variation in the weight of the liter, is well observed in figures 3 and 4, is in agreement with that given by [17].

Taking all these considerations into account, after calculation, λ would be equal to 0.21.
The equation (22) becomes:

$$\rho = 1650\, exp(-0.21\, C) \qquad (23)$$

If ρ is expressed in kg/l, the equation (23) becomes:

$$\rho = 1.65\ exp(-0.21\ C) \qquad (24)$$

But for energy reasons, CINAT does not prefer to overheat nor to cool the kiln. For this reason, the weight of the liter must vary from 1100 to 1250 g/l, and the free lime will oscillate from 1.97 to 1.30 %. The weight of the liter ranging between 1050 and 1300 g/l are tolerable.

Table 5: Weight of the liter and free lime.

	sept 1974		oct 1974		jan-feb 1983		may 1985		jan-feb 2009		CaO l(%)	effective
Weight of the liter (g/l)	CaO l(%)	effective	CaO l(%)	effective	CaO l(%)	effective	CaO l(%)	effective	CaO l(%)	effective	Weight average	total
800	-	0	-	0	-	0	-	0	-	0	-	0
825	10.63	5	13.70	2	-	0	-	0	8.42	1	11.12	8
850	9.96	5	11.69	2	-	0	-	0	8.21	3	9.78	10
875	8.67	3	9.24	3	-	0	-	0	6.37	2	8.31	8
900	6.90	2	6.41	4	-	0	-	0	6.11	3	6.42	9
925	6.21	1	5.87	7	-	0	-	0	-	0	5.91	8
950	5.83	6	5.42	4	-	0	-	0	5.91	5	5.75	15
975	5.69	5	4.89	12	-	0	-	0	-	0	5.13	17
1000	5.23	11	3.27	9	5.23	1	5.00	2	3.84	13	4.23	36
1025	5.14	9	2.97	17	3.53	5	1.93	8	3.54	12	3.38	51
1050	3.01	13	2.41	15	3.11	6	1.85	28	3.34	2	2.38	64
1075	2.41	3	1.79	4	2.97	9	1.72	29	3.28	1	2.05	46
1100	1.94	32	1.37	12	2.72	14	1.63	60	2.80	22	1.97	140
1125	1.78	36	1.27	9	2.69	1	1.50	2	2.19	1	1.70	49
1150	1.70	40	1.24	7	2.42	10	1.45	22	2.04	19	1.75	98
1175	1.70	39	1.16	11	2.28	13	1.34	7	1.92	1	1.69	71
1200	1.57	17	1.00	14	2.14	2	1.31	36	1.85	6	1.38	75
1225	1.20	18	0.76	7	1.93	8	1.18	16	1.65	2	1.27	51
1250	1.17	22	0.72	3	1.53	7	1.15	24	1.60	21	1.30	77
1275	0.87	9	0.67	1	1.24	6	1.00	8	1.54	18	1.23	42
1300	0.82	27	0.63	3	0.96	2	0.78	1	1.37	1	0.83	34
1325	0.71	20	-	0	0.89	3	0.75	5	1.25	3	0.79	31
1350	0.63	17	-	0	0.80	7	0.67	3	1.18	8	0.79	35
1375	0.54	12	-	0	0.78	1	-	0	1.15	2	0.64	15
1400	0.54	11	-	0	0.72	1	-	0	0.98	2	0.62	14
1425	0.51	2	-	0	0.46	3	-	0	0.90	8	0.74	13
1450	0.28	3	-	0	-	0	-	0	0.82	1	0.42	4
1475	-	0	0.43	2	0.41	1	-	0	-	0	0.42	3
1500	0.15	2	-	0	0.36	1	-	0	-	0	0.22	3
1525	-	0	-	0	-	0	-	0	-	0	-	0
1550	-	0	-	0	-	0	-	0	-	0	-	0
1575	-	0	-	0	0.22	1	-	0	-	0	0.22	1
Total		370		148		102		251		157		1028

11. CONCLUSION.

Working under ideal conditions, the presence of free lime in the Portland clinker is due solely to the retrogradation of C_3S to C_2S. The retrogradation reaction of C_3S to C_2S is a first order reaction. For this reason, the weight of the liter and the free lime in the case of the rotary furnace of the national cement plant in the DR Congo are linked by the mathematical expression (23) or (24). For an economical operation of the oven, the weight of the liter must fluctuate between 1100 and 1250 g/l and the free lime will always be below 2.0 %. The mean clinker weight varies from 1050 to 1300 g/l while the free lime remains below 2.5 % [17]. Starting from practical cases, we have been able to give the mathematical equation (21) between the weight of the liter of the clinker and the free lime. This work is only an open path for the correlation between the weight of the liter and the free lime to be completely elucidated.

ABBREVIATION (Cement notations).

A = Al_2O_3 (Alumina)
C = CaO (Lime)
F = Fe_2O_3 (Iron III oxide)
M = MgO (Periclase)
S = SiO_2 (Silica)

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