

Effects and Control of Chemical Composition of Clinker for Cement Production

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Abstract This research focused the role to study the effects and ways to control the chemical composition of clinker for better cement production. Cement is a substance produced by grinding a mixture of a clay and limestone and heating to a temperature of 1450°C, in which the chemical transformation occurs inside the kiln to form new compound called clinker. The methodology of this research work are; the 10 samples of clinker were collected on the apron conveyor, 10g of each sample were weighted, milled and pelletized with the aid of pyridine and binding agent. Then the sample were subjected to XRD analyzer machine for determination of mineralogical composition of clinker, the minerals and oxides detected are; C₃S, C₂S, C₃A and C₄AF and CaO, SiO₂, Al₂O₃ and Fe₂O₃. The other cement modulus such as LSF, AM, and SM were calculated using Bogues equation. From results fig.8 shows increases of early strength of cement as a result of increases of AM, fig.10 shows the decrease of early strength of cement as a result of the increase of SM, fig 9 also is the chart of LSF and free lime (FCaO) and the result shows how the free lime increase as the LSF increases, which leads to requires more energy consumption for clinker formation, poor quality clinker, volume expansion and poor strength of cement. Therefore the chemical composition of cement raw materials and clinker are critical to cement plant efficiency and energy consumption. To ensure constant and consistent chemical compositions and quality of cement clinker with lowest possible energy consumption, attention must be paid to kiln feed and clinker chemical compositions.

Keywords Chemical, Cement, Clinker, Composition, Kiln, Consumption

1. Introduction

Effects and control of chemical composition of clinker is an important of the cement manufacturing process. In cement production the effects of chemical composition of clinker in the process materials and finished products has to be analyzed, monitored and effectively control to optimize the process and a consistent desired product quality of cement.

Cement substance is produced by grinding a mixture of a clay and limestone together and heating to a temperature of 1450°C. In which the chemical transformation occurs inside the kiln to form new compound called clinker. Clinker formed from burning of kiln stage, it can be described as lumps or nodules usually 3 mm to 25 mm in diameter. CaO, SiO₂, Al₂O₃ and Fe₂O₃ are the major component of cement clinker, they accounting for more than 95% and MgO, TiO₂, P₂O₅ and alkalis are the minor components in initial less than 3% they are not present in individual oxide, but exist as

compound formed by two or more oxides (Mohammad A. Aldies, et al 2010). C₃S, C₂S, C₃A and C₄AF are the composition minerals of the clinker and these minerals is as a result of the pyro processing or reaction of oxides in the kiln which leads to the formation of lime saturation factor (LSF). LSF is the ratio of CaO to SiO₂, Al₂O₃, and Fe₂O₃. Clinker with LSF close to or beyond 1.0 indicate a likelihood of the presence of free lime, this will results to the high burn of clinker and hence difficult in grinding (Nuhu.S, et al 2019). However LSF also control the proportion of C₃S to C₂S in clinker, high value of LSF causes free lime (CaO) not combine with these oxides, stay as free lime and excess free lime leads to undesirable effects such as increases setting time, difficult in grinding of clinker, volume expansion and reduces strength of cement (CCNN-Sokoto, 2013). Therefore from the chart figure 9 below confirms that chemical composition of cement clinker are critical to energy consumption, because the grinding of cement clinker depends on LSF and free lime compositions which any slide deviation from these composition can significantly affect the performance of the installation, that's including the energy consumption and quality of the cement. This research paper focused to study the role of the effects and ways to control the chemical composition of clinker for better production of

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quality cement with lowest possible energy consumption. The study was done based on the analysis of the clinker chemical compositions obtained from Sokoto cement plant.

1.1. Raw Feed Chemistry

In order to achieved the required clinker chemical composition during sintering the raw feed chemistry must be set. Different chemical parameters can be used for controlled depends on the number of raw materials used to prepare the feed. Usually the number of target parameters which can be controlled is one less than the number of raw materials. However also raw mix control using calcium carbonate requires two raw materials – high grade and low grade stone, if the iron content must also be controlled then a third raw material containing iron oxide must be added in order proper adjustment (CCNN - Sokoto, 2009). Normally the raw feed target applied at a plant is the available raw materials and the important clinker parameters. Usual combinations for raw feed target parameters may be based on:

- Chemical composition – CaCO_3 , SiO_2 and Fe_2O_3
- Calculated mineralogy of C_3S , C_3A and C_4AF
- Calculated ratios such as LSF, SM and AM
- Or a combination of parameters from all three groups.

1.2. Burning Process

The modern technology system of cement manufacture, the retention time of the material inside the kiln is 30 to 40 minutes, of which the large part is in burning zone. The temperature of the material increases rapidly from 850°C to 1250°C to 1300°C , at which temperature of clinker melt is, formed (Mohamed A. Aldieb, 2010). The chemical and physical changes of the material take place in the burning zone simultaneously; it is importance with respect to the kinetics of clinkerization reactions and agglomeration process. The actual temperature of melt formation depends on the chemical composition of the feed.

However, the kiln operator needs to keep the temperatures stable in each part of the kiln system, in order to convert the raw materials (kiln feed) in the kiln into clinker minerals, because with the deviation of temperature, kiln operation become unstable and clinker minerals are not properly formed making cement performance variable (CCNN - Sokoto, 2009). Moreover too long heating the feed in the kiln would make the minerals in the clinker grow larger and hence the clinker become less reactive and produces a poor quality of cement.

Fig.1 Below described the process of clinker formation. The primary clinker phases conclude transformation and properties (Mohamed A. Aldieb, 2010):

- The most important constituent is alite (C_3S), 50-70% in normal Portland cement clinkers. It is tricalcium silicate (Ca_3SiO_5) modified in composition and crystal structure by ionic substitutions. It produces most strength up to and including 28 days. Each 10%

increase in C_3S content increases the 28 day EN 196 mortar strength by about 5 MPa (Mohamed A. Aldieb, 2010).

- Belite (C_2S) constitutes 15-30% of normal Portland cement clinkers. It is dicalcium silicate (Ca_2SiO_4), it reacts slowly and improves later strength (≥ 28 days).
- Aluminate (C_3A) constitutes 5-10% of normal Portland cement clinker; it is tricalciumaluminate ($\text{Ca}_3\text{Al}_2\text{O}_6$). It releases a lot of heat, shortens setting time and improves very early strength, but it lead the cement to make prone to sulphate attack.
- Ferrite (C_4AF) it constitutes up to 5-15% of normal Portland cement clinkers. It is a tetracalcium aluminoferrite ($\text{Ca}_4\text{AlFeO}_5$). It make little effect on strength but it gives cement the dark coloring.

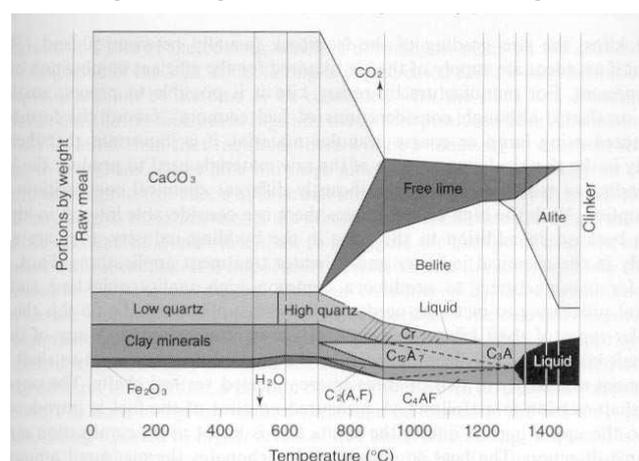


Figure 1. A schematic views of the clinker formation reactions (markus, 2003)

The transformation reaction taking place in rotary kiln is illustrated in fig.1. From the fig left hand side is the feedstock comprising in this case are calcite (CaCO_3), low quartz (SiO_2), clay minerals ($\text{SiO}_2\text{-Al}_2\text{O}_3\text{-H}_2\text{O}$) and iron oxide (Fe_2O_3). From 200 up to a temperature of about 700°C , activation through the removal of water and crystal structure changes take place, 700 to 900°C ranges de-carbonation of the calcium carbonate occurs, together with the initial combine of the alumina, ferric oxide and activated silica with lime. From 900 to 1200°C Belite forms. Above 1250°C and up to 1300°C , the liquid phase appears and this promotes the reaction between Belite and free lime to form Alite (Mohamed A. Aldieb, 2010).

Burning process of the kiln feed depends on:

2. Materials and Methods

The materials and methods used in carrying out chemical analysis using x-ray diffraction machine in cement industry to determine the presence and amount of minerals species in samples, as well identify phases. And method for compressive strength test.

2.1. Materials

- Distilled water
- 10 Samples of weighted of clinker
- Compressive strength testing machine
- Jolting machine
- The prism mould
- Mixer

2.2. Experimental Procedure

- The 10g of each clinker samples were weighed, milled and pelletized with the aid of pyridine and binding agent.
- Pelletized samples were subjected to XRD/XRF analysis machine, this were done to determine the mineralogical chemical compositions of the clinker samples and their respective elemental oxides. The clinker minerals whose compositions were determined using XRDF/XRD were; C_3S , C_2S and C_4AF , while the elemental oxides compositions determined also are: CaO , SiO_2 , Al_2O_3 , and MgO . The silica modulus, alumina modulus, lime saturation factor were found from the elemental oxides compositions using Bogues equation stored as a program in the XRD/XRF analyzer.
- For the compressive strength. 1350g, 450g and 225g of standard sand, cement sample and distilled water were weighed respectively and then mixed in the automatic mixing machine. The mixtures then transferred into the prism mould mounted to the jolting machine and jolted for 2 minutes. The prism mould then remove away for curing 24 hours inside curing chamber and then de mould it to remove cube at different periods 2days, 7days and 28days. Then the cube were remove from curing chamber to the compressive strength testing machine, then cube were placed on the resting point on the machine and were operated at low speed and reading were taken.
- The free lime was determined using wet chemistry method.
- **Lime saturation factor (LSF)**

The lime saturation factor is a measure of the degree of conversion of silica, alumina, and iron oxide into the corresponding lime and it can be calculated using the formula:

$$LSF = \frac{CaO \times 100}{2.8(SiO_2) + 1.18(Al_2O_3) + 0.65(Fe_2O_3)}$$

LSF is usually between 93 and 97% for Portland cement clinker to get a good balance cement properties and reasonable burnability.

- **Silica modulus**

Silica modulus essentially governs the proportion of silica phases in clinker or is the indicator of burnability of the feed or clinker and it can be calculated using the formula:

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

Silica modulus is one of the main components of C_2S & C_3S which make up the liquid phase and help in alite formation (Taylor and Francis Group, 2018).

- **Alumina modulus**

The alumina modulus is also used as an indicator of burning temperature and flux characteristic in the kiln. It is the measure of the proportion of alumina to iron oxide in the mix, and it can be calculated using the formula:

$$AM = \frac{Al_2O_3}{Fe_2O_3}$$

Alumina modulus of about 1.4 would leads to the formation of liquid phase or flux at lowest temperature in the kiln. Earlier formation of liquid phase or flux in the kiln allows alite formation to start sooner and go for a longer time, which improve the conversion of belite into alite. However AM with above or below these target 1.4, the amount of liquid phase would reduce at lower temperature, the length of burning zone coating would reduce, the flux becomes less fluid which slowing down alite formation, and subsequently more fuel is needed in order to obtain a given free lime clinker level (Taylor and Francis Group, 2018).



Figure 2. Concrete compressing machine

The machine used for testing the strength of the cubes mortar of cement usually it is done by applying force on a specimen. Strength is defined as the maximum load carried divided by the average cross-sectional area. The load is applying on the specimen until it fails.



Figure 3. Jolting machine

The machine used to compact cement mortar prisms in three gang mould the apparatus consist of flat table for

holding the mould and can be raised or lowered by means of compressed air.



Figure 4. Weigh balance

It is a instrument measuring equipment used to measure the weight of the samples usually set in grams.



Figure 5. Chemical analyzer

XRD/XRF is a machine used in the cement or any chemical industry to determine the presence and amount of minerals species in samples, as well identify phases.



Figure 6. Prism mould



Figure 7. Curing chamber

It is used after modeled the cubes of cement to prepare well cement specimens for compressive strength tests.

3. Results and Discussion

3.1. Table 1: XRD Analysis of Clinker Samples

Table 1

Clinker Samples	CaO %	SM	AM	C3S %	C2S %	C3A %	C4AF %	LSF %	FCaO %	2days Mpa	7days Mpa
1	66.79	2.06	1.47	59.73	15.03	7.5	11.52	97.21	4.75	17.1	31.23
2	66.8	2.1	1.47	63.07	11.14	7.9	11.86	98.56	4.37	17.7	30.02
3	66.6	2.15	1.48	54.21	17.82	7.54	12.77	99.33	3.99	17.6	32.56
4	66.1	2.16	1.32	60.22	12.92	8.64	12.79	99.51	2.81	17.7	30.45
5	66.79	2.18	1.34	63.06	11.29	8.77	12.09	99.65	2.66	16.7	39.45
6	66.4	2.2	1.37	60.68	13.1	8.89	11.47	99.72	2.47	18.1	38.5
7	66.3	2.2	1.5	59.64	13.81	9.2	11.37	99.88	2.47	18.3	38.1
8	66.96	2.2	1.48	60.9	11.94	9.01	10.21	100.33	2.41	18.3	39.1
9	66.72	2.27	1.63	59.01	15.55	8.23	9.78	100.52	2.35	20.1	39.04
10	65.89	2.3	1.81	63.17	25.85	8.34	9.76	102.65	2.29	17.7	38.9

Table 1 are the results of analysis of clinker samples that were subjected to XRD analyze for the minerals compositions, results shows that samples were collected at random because of the variation of calcium oxide (CaO). The modulus composition of AM, SM, and LSF are the factors concerning the proportions of SiO₂, CaO, Al₂O₃ and Fe₂O₃ in the clinker samples.

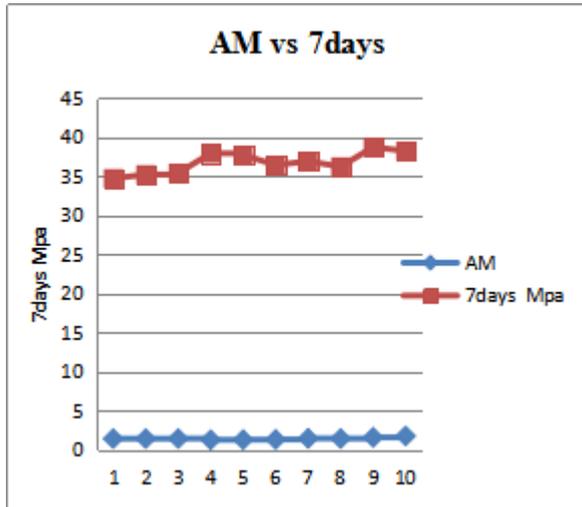


Figure 8. Alumina Modulus and 7days Compresses Strength

Fig 10 of alumina modulus (AM) and 7days compressed strength shows increases of 7days strength as the AM increases this is to confirm from the introduction that, less AM lead to less early strength and heat of hydration. AM contributes to the formation of C₃S which will leads to increase of early strength of cement product. If AM is above the target causes clinker sticky in the kiln, which leads to thick coating inside the kiln.

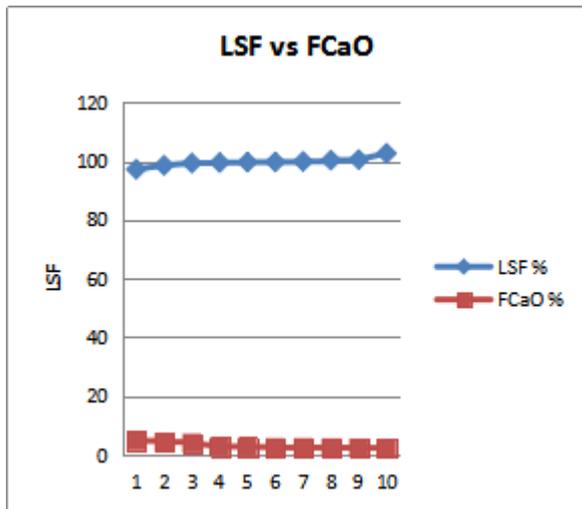


Figure 9. Of Lime Saturation Factor and Free Lime

The chart 3.0 shows how the lime saturation factor enhances the formation of free lime. Over 100% of LSF leads to incomplete conversion of lime there by leaving as free lime no matter how long or how hot the clinker is burned, which will eventually affect the fuel consumption, life span

of the bricks and strength of the cement, and it make cement unsound. Hence high LSF lead to more formation of alite (C₃S), hard to burn to clinker and also dusty clinker.

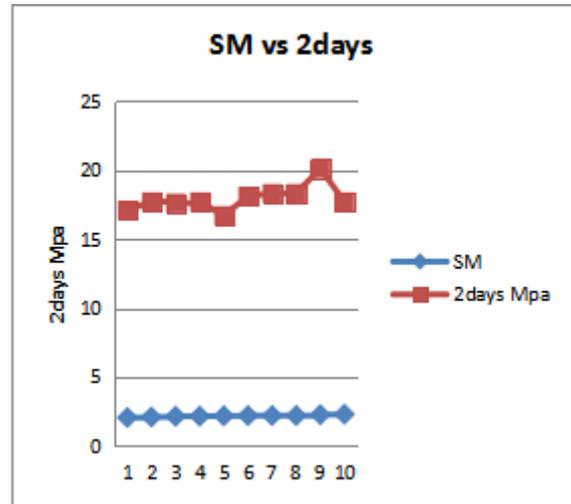


Figure 10. Silica Modulus and 2days Compressed Strength

SM and 2days compressed strength shows how the silica modulus affect the early strength of cement. From the chart point 3, 9 and 10 of SM draw down to point 20.1 and 20Mpa strength of 2days compressed strength, this is the fact that silica modulus is an indicator of the burnability of the feed or clinker. High level of silica in the raw feed makes the feed difficult to burn and result to poor clinker formation (Nwokedi, 2014).

4. Conclusions and Recommendations

4.1. Conclusions

The quality of cement is typically assessed base on the compressive strength development mortar and concrete. The ingredient ratio of cement raw materials affects the quality and property of cement clinker and Portland cement, and also the optimal ingredient ratio promotes and stabilizes cement clinker. From the fig 8 shows increases of compressive strength as the AM increases, this is to confirm that, more formation of AM leads to the formation of liquid phase or flux in the kiln with lowest temperature, and early formation of liquid phase or flux in the kiln allows formation of alite which is the major component for early strength of cement. And fig 10 shows how the SM affects the early strength of cement. Point 3, 9 and 10 of SM draw down to point 20.1 and 20Mpa strength of 2days compressed strength, this is the fact that silica modulus is an indicator of the burnability of the feed to clinker. Increases of SM affect the formation of liquid phase, difficult in burning of clinker and poor quality of the cement, so attention must be paid to achieve the desired target of the SM. In fig.9 the results shows increase of the free lime because of the increase of LSF. However this to confirm that more LSF above the target leads to incomplete conversion of free lime, staying as free lime in clinker and

hence these result to more energy require to burning the clinker, volume expansion, and poor quality of cement. Therefore the chemical composition of cement raw materials and clinker are critical to cement plant efficiency and energy consumption. However in order to ensure constant and consistent chemical compositions and quality of cement clinker with lowest possible energy consumption, attention must be paid to kiln feed and clinker chemical compositions.

4.2. Recommendations

The attention should be paid during the pre –calcination of the kiln feed in the free calciner and correlation between the kiln feed and clinker LSF should also be done for elimination of the high free lime.

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