The Effect Of Raw Material's Fineness And Lime Saturation Factor On Clinker's Grindability And Energy Effeciency In The Gabes Cement Industry

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***Abstract*—The aim of the present research is to improve the manufacturing conditions of cement and therefore its quality. For this purpose, various reference samples of clinker were produced in the normal manufacture's conditions considered by the Company of Cement of Gabes, then compared to other samples which are variable in the Lime Saturation Factor and the raw material's fineness. All the samples are analyzed by X-Ray Fluorescence, X-ray diffraction and optical microscopy including a study of measurement of clinker's crystal sizes. Besides, tests of compressive strength were made after 2, 7 and 28 days. Finally, a study of clinker's grindability enabled us to evaluate the probability of grinding of these samples. In all cases, the best clinker is the one that has a vintage's fineness close to 13-15% for the refusal of 100 µm. This latter gives a well-formed clinker nodules, well homogenized phases and indicating cement's good quality. This clinker presents also the best grindability.**

Keywords— Cement; clinker; LSF; raw material's fineness; compressive strength; grindability

I. INTRODUCTION

Portland cement is a highly sought material. It is a fine powder produced by grinding Portland cement clinker (more than 90%), a limited amount of calcium sulfate (which controls the set time) and up to 5% minor constituents allowed by various standards. Portland cement clinker is typically composed of 42.9-75.4% alite (C_3S), 0.1-27.6% belite (C_2S), 0.4-10.9% aluminate (C_3A), and 0.6-14.4% ferrite(C_4AF)(1). The world production of cement was about 2.55 billion tons in 2006 (2), it increased to 3.2 billion tons in 2011 (3).

The global market economy has always forced industrials to be more competitive in monitoring their activities. This involves developing more efficient and economically viable means of production. The production of cement involves several steps which are particularly electrical energy consuming: raw materials grinding and heating and clinkers grinding.

The total electrical energy consumed by the cement manufacturing process is approximately 110 kWh/t. About 40% of this energy is consumed in grinding clinker (4). Therefore, the objective of cement producers is to make this phase of production more economical and this is the major goal of the present work. Several investigations studied the subject of clinker grinding. They were primarily articulated around the effects of the chemical (5, 6), structural (7) and morphological (8, 9) characteristics of the clinker. However, there are few studies which treat the effect of the vintage's chemistry on the grindability of clinker and the quality of cement.

The objectives of the present study were to determine the effects of the fineness and the lime saturation factor (LSF) of the raw materials on the cement's quality (chemical composition, fineness, resistance) and the clinker's characteristics and to study the influence of these two factors on the clinker's grindability.

II. EXPERIMENTAL MATERIALS AND PROCEDURE

Typical Portland cement raw mix and plant clinkers were obtained from the cement plant of Gabes (South of Tunisia).

A. X- Ray Fluorescence analysis

The chemical and potential compound compositions of the clinkers used in this study are listed in table I.

TABLE I. CHEMICAL AND MINERALOGICAL COMPOSITIONS OF THE CLINKERS (%).

Clinker samples		*CaO*	*SiO_2*	*Al_2O_3*	*Fe_2O_3*	*SO_3*	*K_2O*	*Free*	*C_3S*	*C_2S*
F	*F1*	66.34	21.65	4.91	3.12	1.31	0.60	0.84	60.93	16.13
	F2	65.78	21.75	5.03	3.24	1.29	0.59	1.06	56.07	20.08
L	*N1L1*	66.46	22.37	4.97	3.29	0.52	0.29	1.05	56.70	21.39
	N2L1	66.05	21.47	4.99	3.45	0.67	0.66	2.45	55.38	19.8
	N3L1	65.78	22.2	5.17	3.51	1.04	0.52	0.94	52.53	24.04
	N4L1	65.49	22.05	5.27	3.48	1.22	0.57	1.01	51.06	24.72
	N1L2	66.41	22.21	4.93	3.24	0.51	0.58	2.9	56.70	25.56
	N2L2	66.61	22.05	4.88	3.21	0.41	0.58	2.86	55.38	22.95
	N3L2	66.56	22.16	4.9	3.29	0.3	0.52	2.59	52.53	23.17
	N4L2	66.5	22.2	4.99	3.33	0.22	0.37	0.86	51.06	18.72
G	*G1*	65.97	21.66	4.97	2.79	1.42	0.59	1.52	57	19.2
	G2	65.43	20.6	5.26	3.07	2.64	0.62	1.36	58.4	15.1
	G3	66.1	21.18	4.88	2.91	1.16	0.48	1.3	63.4	12.8
	G4	66.52	21.37	4.93	3.02	0.41	0.42	0.89	67.1	10.8
	G5	65.85	21.82	5.14	3	1.03	0.46	1.06	57.2	19.5
	G6	65.39	21.65	5.17	2.88	1.04	0.6	0.95	57.4	18.9
	G7	65.07	21.42	5.06	2.88	1.77	0.75	1.27	55.5	19.6
	G8	65.17	21.54	5.01	2.89	1.45	0.63	1.19	56.2	19.5

The cement clinker produced under the normal conditions of manufacturing considered by the cement's company is designed clinker G. It is considered as the reference cement clinker. Clinker F is the cement clinker which is made by changing the raw mix fineness (8.5 – 14.93 % for the refusal of 100 µm (R100)). The product made by changing the Lime Saturation Factor (LSF) (94.9% - 98.7 %) is designed as clinker L. The global characteristics of the raw materials are shown in table II.

TABLE I. CHARACTERISTICS OF THE RAW MATERIALS COLLECTIONS USED IN THIS STUDY.

Raw	*G*	*F*		*L*	
	—	*F1*	*F2*	*L1*	*L2*
LSF (%)	98.6	98.	97.5	94.	98.7
R100 (%)	19.7	8.5	14.9	13.	15.1

B. *Optical microscopy analyses*

Microscopy gives visual form to the data from other methods of analysis. The microscopic observation of cement clinker is done in reflected light [9]. So we need the preparation of polished sections. At first, four to five nodules of clinker were selected and placed in a cylindrical mould made of polyethylene, 40 mm in diameter and 30 mm in height. Theses clinkers were completely immersed in a cold mounting resin. After 20 minutes of impregnation, we obtain a pellet clinker. The sample is cut with a saw to bring up the nodules and get a flat section of clinker.

This section was ready for polishing on disc by using abrasive paper with adhesive reverse of number 320, 400, 600, 800, 1000 and 1200 µm respectively until obtaining an increasingly polished section. The final phase of polishing is done on cloth by using an alumina suspension, diluted with alcohol and acting as a lubricant. Then the section is washed with alcohol in an ultrasonic cleaner (10).

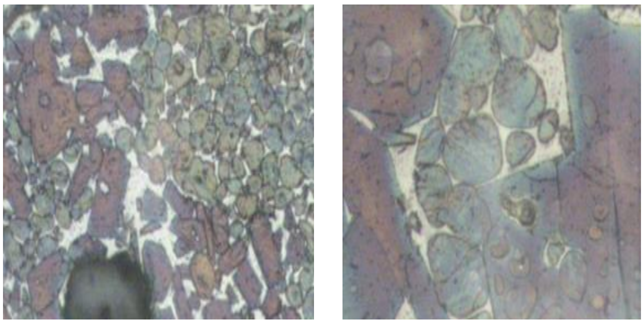
By taking account of the resemblance of the various phases of the clinker, a surface chemical attack must be made on all samples in order to make the various phases of the clinker apparent. The crystals of alite (C3S) are prismatic, those of belite (C2S) are rounded and the interstitial mass (C3A + C4AF) is clear (11). The samples used in this study were etched with hydrofluoric acid vapor or a solution of nitric acid HNO3 with 0.25 % in alcohol.

C. *Grinding tests*

Grinding tests were carried out using a standard laboratory apparatus consisting in a cylindrical ball mill uncoated type TTS50. The dimensions of the mill are typically 400 mm in length and 400mm in diameter. Its weight, including steel balls, is 380 kg. The feed charge was held constant at 1460g of clinker combined with 40g of fluogypsum, and then rotated for 10 minutes of grinding and 3 minutes of discharge. During experiments, the mill was rotated at 50 rpm. In order to compare the grindability of the three types of clinker described in Table 2, four samples of each collection are grinded for 13 minutes then two samples of them are grinded for 8 and after 18 minutes. The quality of cement is measured by the surface area or the Blaine index. This index is determined by the Blaine air permeability test. All stages of grinding are determining for the production of 3500 cm2/g Blaine surface area (12). This surface area of the cement powder depends on size distribution of cement particles; smaller particles have larger surface area. The breakage process is characterized by a selection function that represents the fractional rate of breakage of particles in each size class and so the probability of breakage. To obtain the specific selection function and the Blaine specific surface of this material, each sample was individually ground in dry conditions at different times of grinding, using a constant ball diameter (32 mm). The other operating conditions were also kept constant as those mentioned above. To compare the energies of grinding, we used the law developed by Bond (13).

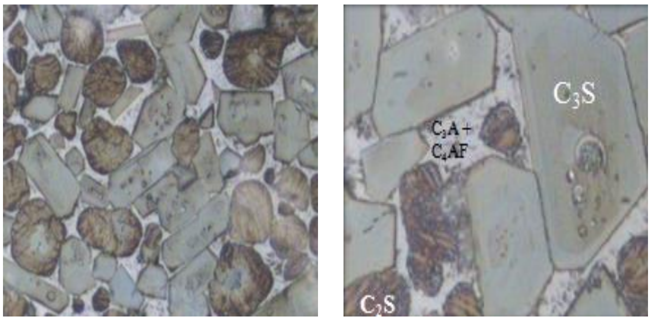
III. RESULTS AND DISCUSSION

The fundamental use of the microscope in Portland cement clinker analysis is to bring to the observer a visual appreciation of phase identities, sizes, conditions, and mutual relationships. If we compare the micrographs of the reference collection G (Fig.1) with the other collections which are represented in Fig.2 and Fig.3, we can note that the distribution of phases becomes more heterogeneous. This can indicate unstable conditions of manufactures, heterogeneous raw materials, insufficient smoothness and short burning time. Whereas, for the clinker collections F and L, we notice an improvement in global crystals characteristics such as the sizes of belite clusters which become smaller and the distribution of the phases appears generally less heterogeneous and sometimes very homogeneous. So the conditions of manufacturing become more stable and acceptable.



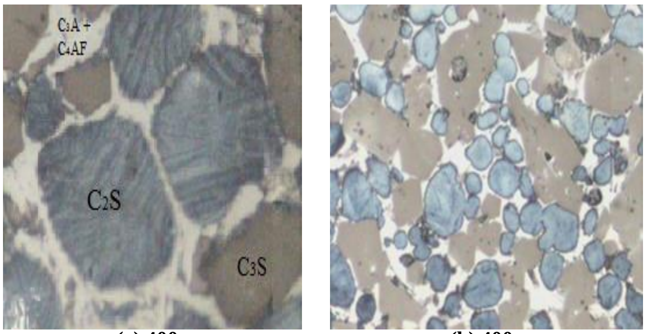
(a) 100x ***(b) 200x***

Fig. 1. Micrography of the clinker G attacked by the vaporized hydrofluoric acid (40%): Heterogeneous distribution of the phases and Clusters of belite are so frequent.



(a) 200x ***(b) 400x***

Fig. 2. Micrography of the clinker F attacked with a nitric acid solution in alcohol. The prismatic alite is light blue, the round belite is brown and the interstitial mass is white. Homogeneous distribution of the phases.



(a) 400x **(b) 400x**

Fig. 3. Micrography of the clinker L attacked by the vaporized hydrofluoric acid (40%).The crystals of belite are rounded and blue. The crystals of alite are prismatic and brown. The interstitial mass is well crystallized and white. ±Homogeneous distribution of the phases.

To confirm these qualitative interpretations, we made a quantification of the clinkers phases by measuring the sizes of alite and belite crystals.

Fig.4 shows the relationship between the length of alite, the diameter of belite and the raw material's fineness. On one hand, the crystal size of alite becomes smaller by decreasing the raw material's fineness. Thus, it seems clear that the raw smoothness has a great role on the phase of clinkerization. On the other hand, the crystal size of belite becomes larger by decreasing the fineness of the raw. These results are in good correlation with Ono's method (9).

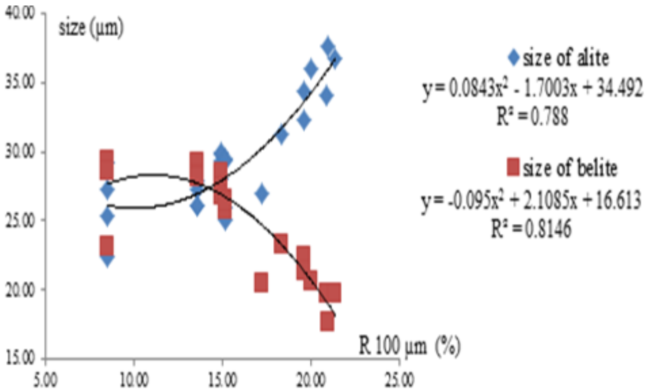


Fig. 4. Variation of crystals sizes with the raw material fineness.

The effect of the raw mix fineness on the compressive strength is appreciated in Fig.5. This diagram shows that the influence of the fineness is better sensed for early-age resistances (2 and 7 days). This result illustrates also that the fineness develop the alite's phase which is responsible of the 2 and 7 days resistances.

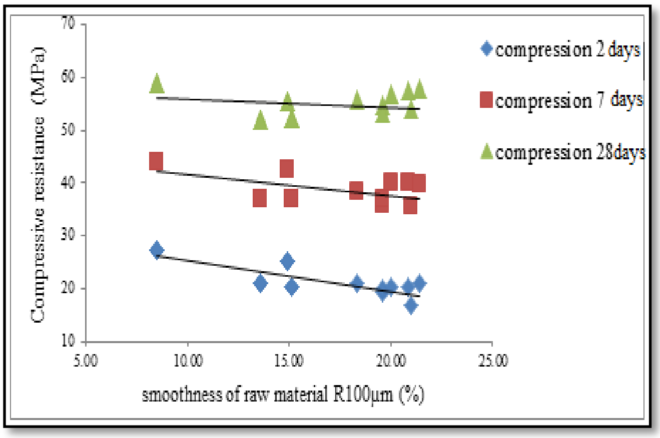


Fig. 5. Variation of compressive strength with the raw material fineness.

We can note that the crystal size of alite was controlled by two factors: (a) heating rate above 1000°C and, (b) the sizes of the raw meal components, mainly that of quartz which largely determines the size of the belite from which most of the alite is derived. So it is important to have a rapid heating rate and a finely ground raw meal. Belite size also can partially relate to the number of belite nests with large tightly packed crystals in the clinker, these crystals can be quite large and are usually determined by the number of large quartz grains in the raw meal. These grains are difficult to disaggregate during burning, thus the belite continues to grow. Belite crystals, in general, grow at high temperature and also during cooling; consequently, the cooling rate must be rapid.

The relationship between the clinker crystals size and the hydraulic activity of cement was shown in table III.

TABLE II. RELATIONSHIP BETWEEN THE SIZE OF ALITE (L) AND BELITE (D) CRYSTALS AND THE HYDRAULIC ACTIVITY (HA) OF CEMENT.

Samples	***Size of crystals***			
	Alite		***Belite***	
	L (µm)	***HA***	***D (µm)***	***HA***
F	27.66	Excellent	27.51	Excellent
L	27.17	Excellent	27.35	Excellent
G	33.62	Good	20.67	Average

With reference to Ono's method, the F and L collections of clinkers have an excellent hydraulic activity. However, this later varies between average and good for the reference collection G. The clusters size and surface are shown in Table IV.

TABLE III. SIZE AND SURFACE OF CLUSTERS.

Raw materials	***F1***	***F2***	***L1***	***L2***
Size of belite cluster(µm)	106	144	126	12
Area of cluster (10^{-2} mm^2)	4.2	6.8	2.2	2

The aptitude of grinding the clinker depends on its microstructural properties, like the crystals composition and size. However, the clinker's microstructure is influenced by the production's parameters especially the raw materials smoothness and the homogeneity, the burning time and the cooling rate. By knowing all these relations it will be possible to predict the grindability of the clinker and consequently its grinding energy.

Grindability is a measure of how much energy is required to change a particle from one size to another (13). There are many methods for assessing and studying grindability. At first we made a grading analysis. This latter consists to separate and classify the grains of the clinker according to their diameter and using a series of sieve. The sieved grains can be weighed to determine the proportion of each one in the aggregate.

Fig.6 indicates the variation of the cumulative percentage of passing with the opening sieve for the collections F1, F2, L1 and G. The time of grinding was constant and equal to 13 minutes.

The clusters present in clinker F1 are the smallest in size and area. Moreover, the microscopic observation shows that these clusters are dispersed. The most remarkable difference between L1 and L2 is the abundance of the clusters of belite in the latter. Fundal (1980) shows that the large clusters of belite associated with high contents of free lime are due to a high lime saturation factor (14).This remark is well applied to the example of clinker L2. It has the greatest ratio of free lime (1.9%) and the highest lime saturation factor (98.7%) which exceeds also the margin.

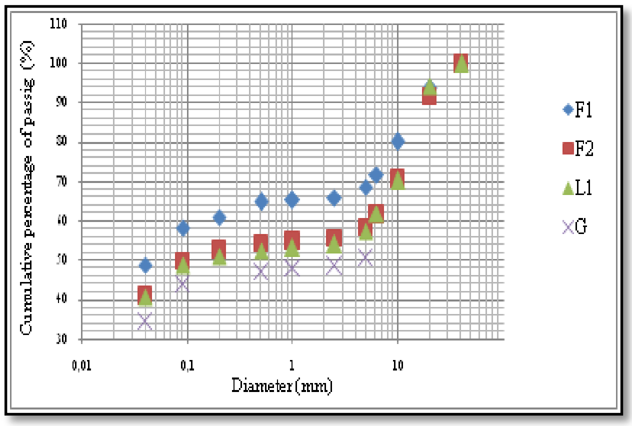


Fig. 6. Grading curve of the passing. The collections used in this part of study are F1, F2, L1 and G. We took 5 samples for each collection, then we calculated their cumulative percentage of passing and finally we made the average of these percentages.

Curve F1 shows the highest fractions of passing. While, curve G indicates the lowest fractions of passing. The margins of variation between the two curves before and after grinding, for clinker G and clinker F1, were shown in Fig.7.

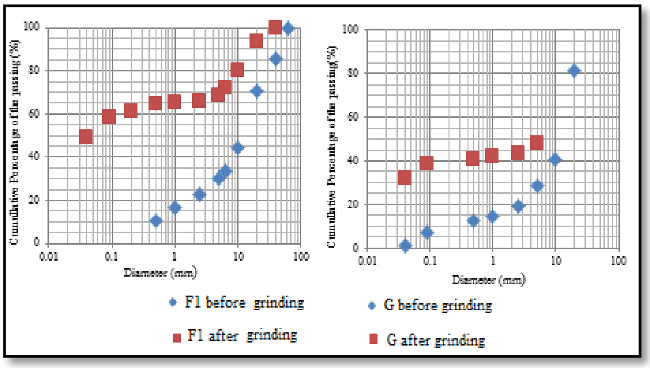


Fig. 7. Cumulative percentage of passing before and after grinding.

Clinker F1 which have the best fineness of raw (8.5 % for the refusal of 100µm) represents a margin of variation considerably elevated. Whereas, the reference clinker G which has the bad fineness of raw shows the weakest margin of variation. This results indicates that we produced further fine particles for sample F1.

Clinker grinding process is often monitored and controlled by measuring the product surface area using a simple air-permeability procedure such as the Blaine test and also measuring its energy of grinding and index of breakage (15). Table V shows the values of the index of breakage (I) of the collections used in this work.

TABLE IV. TABLE V. INDEX OF BREAKAGE.

Samples	***F1***	***F2***	***L1***	***L2***	***G***
SSB (cm^2/g)	3718	4044	3953	3564	3087
I	0.91	0.99	0.97	0.87	0.76

The reference collection G had the lowest index of breakage. It indicated also the highest value of the grinding energy. It was estimated to 1.014 kWh/t for clinker G. However it was valued to 0.814 kWh/t for the collection F1. For better studying the probability of breakage of each type of clinker, we calculated the specific selection functions corresponding to the fractions of sizes considered in this work.

Fig.8 and Fig.9 indicate the variation of the specific selection functions for the collections F1, F2, L1 and L2. The diameter of balls was considered constant in this study.

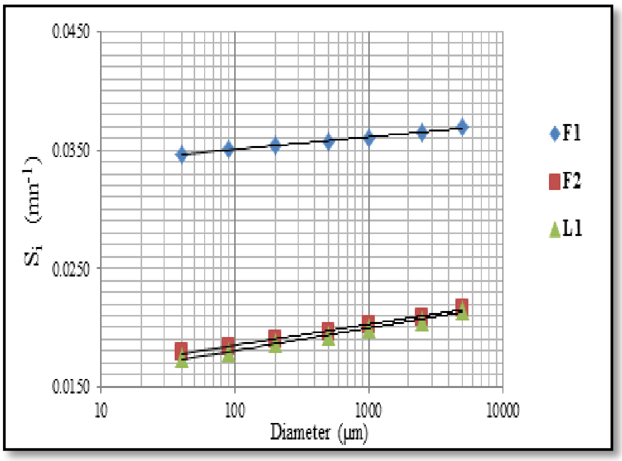


Fig. 8. Specific selection functions versus particle size for the collections F1, F2 and L1.

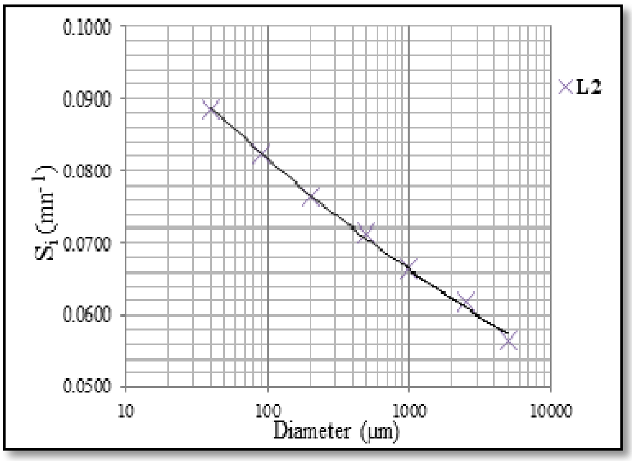


Fig. 9. Specific selection functions versus particle size for the collection L2.

Increasing trends for the collections F1, F2 and L1 were observed in figure 8. Contrary to the other curves, L2 follows decreasing trends. This can be explained by the fact that L2 was entered creased in the mill. So a problem of adaptation of the size of particles with the size of balls will be encountered. Thus, the experimental results showed that the grinding process is more efficient with a maximum specific selection function. Therefore, F1 had a better grinding probability while F2 and L1 had an acceptable grindability.

IV. 4. CONCLUSIONS

In this paper, we investigated the effects of the variation of the fineness and the lime saturation factor of the raw materials on the grindability of the clinker and the quality of the cement. The results are summarized as follows:

- With comparison to the reference situation G, the main structural modifications were: reduction of the alite size and growth of the belite size. A significant change in the distribution of phases was also observed. So a phase of homogenization appears when we improve the fineness of the raw material. The belite clusters become smaller.

- The lime saturation factor has a great role on the compressive strength of the cement. If this factor exceeds the margin (90-98%) we will have a heterogeneous distribution and so large clusters that adverse the grinding of the clinker.
- Reduction of the clinker's energy consumption with the improvement of the raw materials fineness.

So, we suggest having a raw material's fineness of about 13 to 15 % of the refusal of 100 µm because this margin indicates a good optimum for both sizes of alite and belite and also an energy improvement.

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