A Study to Improve Clay Soil by Using Calcite Additive in Ceramic Tile Manufactory

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ABSTRACT

Many researchers have studied the important effect of calcium carbonate addition on fine soils. They have proved a reciprocal relation between calcium carbonate (calcite) content in clay and its plasticity index. We aim in our research to support the industry by improving available raw materials through adding artificial or natural additives, which positively affect the specifications of the final product. So, we focus on changing the plasticity of clay which is considered a very important property in the manufactory of ceramic tiles. The samples of clay have been chosen from some Syrian clay sites. This clay was previously unacceptable in ceramic industry, because it couldn't achieve the minimum requirements for ceramic tile industry standards. We have classified the soils according to the Unified Soil Classification System (USCS) after applying the essential tests on clay soil. Then, we have prepared the reference ceramic tile samples (without additives) and compared them with the other samples (with calcium additives from 5% up to 30%) by applying technical tests such as: water absorption, flexural strength and linear shrinkage tests. We have achieved remarkable improvements. Flexural strength has increased while water absorption has decreased. The best percentage for calcium carbonate additive is about 5%, which ensures technical properties' matching with international standards. All changes on strength, shrinkage and water absorption values became steady after a percentage of 25% of calcite additives. The efficiency of the additives correlates both chemically and mineralogically with soil composition.

KEYWORDS: Ceramic tile, Clay, Calcite, Flexural strength, Linear shrinkage, Water absorption.

INTRODUCTION

Interest in clays has increased in recent years due to their physical, chemical and plastic properties, which make them among the most important materials in many industries. One of the most widespread industries is ceramic tile manufacturing, which is very competitive. Tile manufacturers are constantly looking for new techniques and new raw material resources to improve the quality of their products and minimize their cost.

Raw materials, particularly clay, affect significantly the technical properties of ceramics. It is well known that mechanical properties of ceramics are important parameters for defining their use and applications (Zweben, 1991). So, numerous studies have focused on clay soils and were concerned with their properties during industrial processing.

Continuous and concentrated usage of suitable clay soil resources causes a remarkable shortage of these materials day after day. Therefore, manufacturers always look for new resources and face many obstacles to find the ideal materials which lead to achieve economical products with the required specifications.

Calcium carbonates $CaCO_3$ (CALCITE) has a remarkable effect when added to fine soils (Buchan and

Smith, 1999). It was proved (Beringen et al., 1982) that plasticity index of clay is inversely proportional with calcium carbonate content (Tonnisen et al., 1985). The addition of calcium carbonates into clay will change the plasticity property and subsequently, it will affect the technical specifications of the ceramic product during manufactory processing.

Following this trajectory, this research with additives of calcium carbonates was carried out in order to improve different types of clay soil (Hauser, 2000; Dondi et al., 1997; Dondi et al., 2002). The nature and extent of the change in the final product have been studied.

EXPERMENTAL SECTION
MATERIALS AND METHODS

The samples of clay soil have been chosen from two Syrian clay sites. These two sites are: **Sergaya** (term F) and **Gdedt Yabous** (term GD), as shown in Fig.1. Many manufacturers of ceramics have tried to use the soil from these two sites in the industry, but it didn't achieve the minimum requirements according to ceramic tile standards. So, that soil has been remarked as unacceptable for ceramic tile industry.

Figure (1): Clay sites (F, GD) in Syria (General Establishment of Geology and Mineral Resources)

Calcium carbonates is the main component of lime stone. Lime (calcium) stone is located on many sites in Syria; in the east, in the middle and in the north, as illustrated in Fig.2. The geological reserve of unraveled lime stone is approximately quantified at $12*10^9$ m^3. It is available and cheap. For this research, calcium carbonates was brought from the closest site to the site of our study (F & GD soil sites) in order to be more economical.
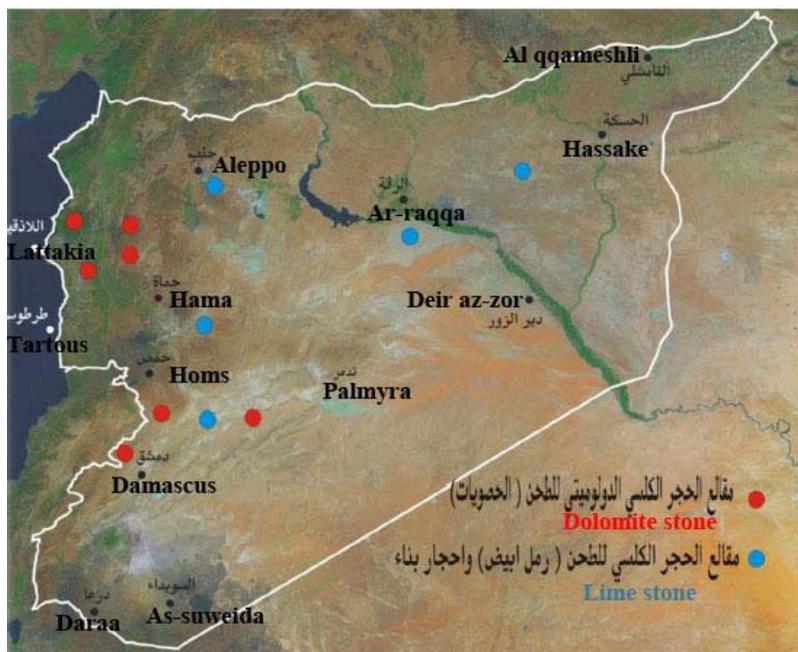
Figure (2): Lime stone sites in Syria (General Establishment of Geology and Mineral Resources)

CHARACTRIZATION OF RAW MATERIALS

The knowledge of physiochemical properties of clay soil is essential and very important (Mesenguer et al., 2009; Sanfeliu and Jordan, 2009). The oxides in clay soils submit chemical and constitutional transformations (during the fire period), which in turn change the properties of those soils and define the specifications of the final products. There are several factors which affect those transformations: chemical composition, mineralogical composition and grain size analysis (Maggeti, 1982; Moropoulou et al., 1995).

Mineralogical analysis on clay samples (15 samples from each of the two sites: **F** and **GD**) was carried out by XRD, where the samples were heated to 550°C for 2h and treated with ethylenglycol (General Establishment of Geology and Mineral Resouces, 2010).

The mineralogical composition of **GD** clay was: Kaolinite $Al_4Si_4O_{10}(OH)_8$, Quartz SiO_2, small quantities of Illite $KAl_2(Al,Si_3)O_{10}(OH)_2$ and chlorite $(OH)_4(SiAl)_8(MgFe)_6O_{20}$. Also, some samples contain small quantities of muscovite $KAl_2[(OH)_2/AlSi_3O_{10}$, montmorillonite $(Al,Mg)_2[(OH)_2/Si_4O_{10}](Ca)x(H_2O)_n$, calcite $CaCO_3$ and organic materials (in traces), as shown in Table 1.

The mineralogical composition of **F** clay was: Kaolinite $Al_4Si_4O_{10}(OH)_8$, Quartz SiO_2, small quantities of Illite $KAl_2(Al,Si_3)O_{10}(OH)_2$ and calcite $CaCO_3$ (in traces), as shown in Table 2.

The chemical analysis of major and minor elements was carried out by X-ray fluorescence (XRF) using conventional techniques for **F** soil and **GD** soil as shown in Fig. 3. The highest percentage is for SiO_2 and Al_2O_3 in all samples. Table 3 presents the chemical analysis for calcium carbonates (Syrian Carbonates Company, 2011).

Table 1. Mineralogical analysis for GD soil (General Establishment of Geology and Mineral Resources, 2010)

Sample No.	Calcite	Chlorite	Montmorillonite (Na)	Montmorillonite (Ca)	Muscovite	Illite	Quartz	Kaolinite
1		*-				*	* *	* * *
2		*-				*	*	* * *
3			*-			*	* *	* * * *
4	*	*-		*-		*	*	* * *
5		*-				*_	*	* * *
6			*-		*		* *	* * *
7		*		*		*	* *	* * *
8		*-	*-		*		* * *	* * *
9				*		*-	* *	* * *
10		*				*	* *	* *
11		*				*	*	* *
12	*		*-			*-	*-	*
13		*-	*		*	*-	* *	* * *
14		*				*	*	* *
15		*-				*-	*-	* *

Table 2. Mineralogical analysis for F soil (General Establishment of Geology and Mineral Resources, 2010)

Sample No.	Calcite $CaCO_3$	Illite $KAl_2(Al,Si_3)O_{10}(OH)_2$	Quartz SiO_2	Kaolinite $Al_4Si_4O_{10}(OH)_8$
1		*	* *	* * * *
2	*	*	*	* * *
3		*	* *	* * *
4	*	*	*	* * * *
5			*-	* * *
6		*	* *	* * *
7	*		*	* * *
8		*	* *	* *
9		*	*	* * *
10		*	* *	* *
11		*	*	* *
12	*		*-	* * * *
13			* *	* *
14		*	*	* *
15			*	* *

(5% > *-) - (5% < *) - (10% < **) - (15% <***) - (20% < ****)

Figure (3): Chemical analysis for (GD, F) soil samples (General Establishment of Geology and Mineral Resources, 2010)

Table 3. Chemical analysis for calcium carbonates (Syrian Carbonates Company, 2011)

SiO_2	Al_2O_3	CaO	Fe_2O_3	Na_2O	K_2O	$Ti)O_2$	MgO	SO_3	L.O.I.
0.93	0.46	82.70	0.2	0.01	0.02	-	0.19	0.07	15.42

Grain size analysis was performed according to (ASTM D422-02). Obviously, we notice from Fig. 4 and Fig. 5 that the percentage of clay particles in F soil (46.8%) is greater than that in GD soil (32.6%).

| Gravel: 3.80 | Sand: 4.40 | Silt: 45.00 | Clay: 46.80 |
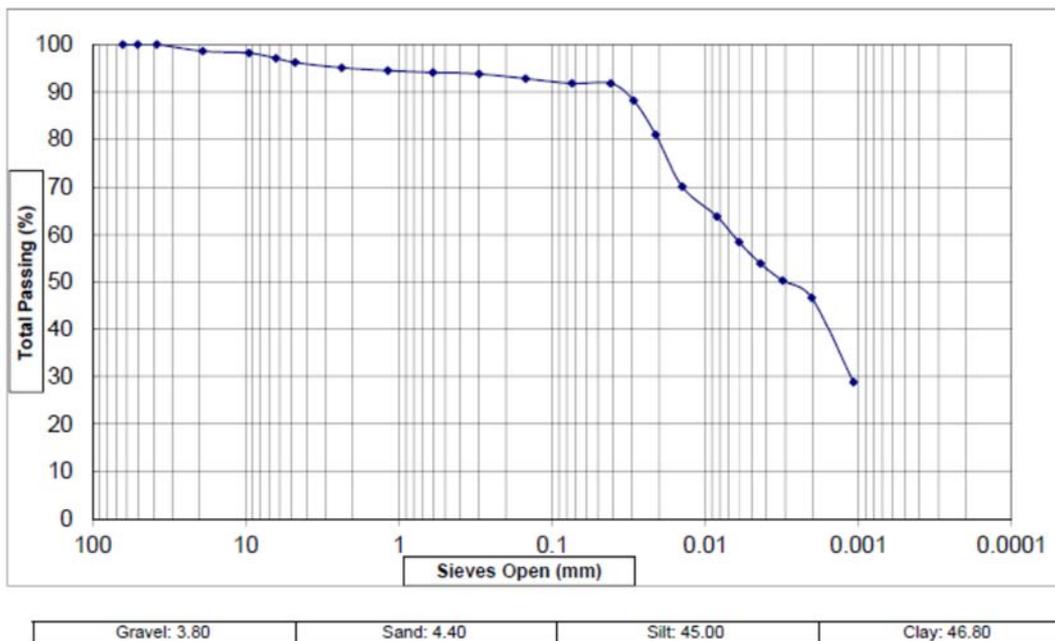
Figure (4): Size Distribution Curve for F soil (General Company for Studies and Consultations, 2010)

| Gravel: 5.90 | Sand: 9.00 | Silt: 52.50 | Clay: 32.60 |
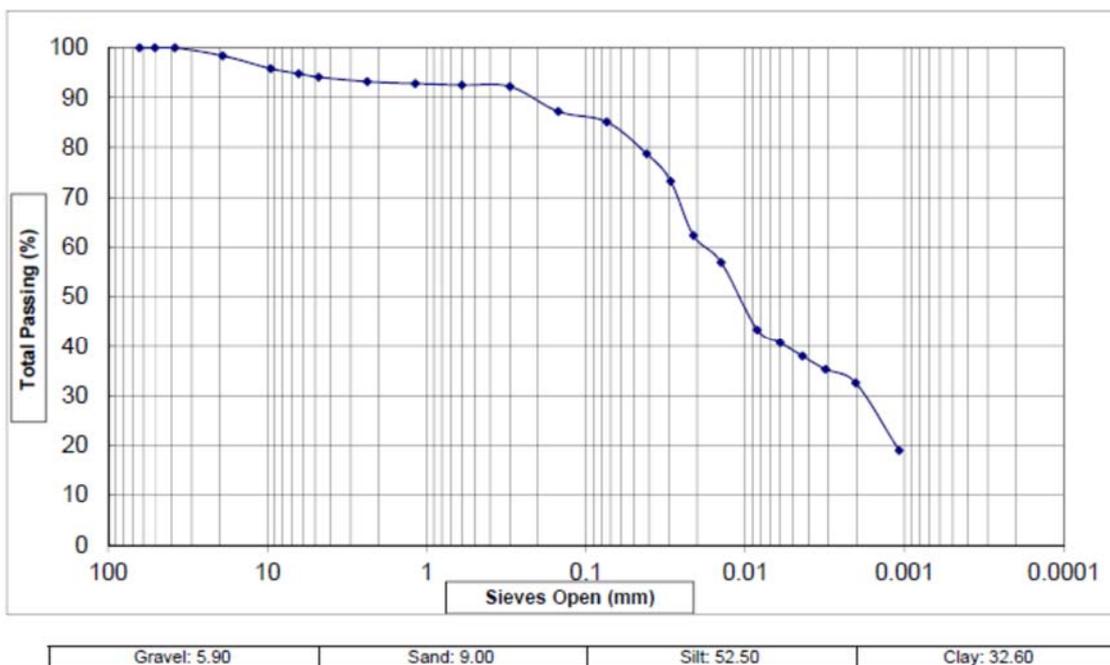
Figure (5): Size distribution curve for GD soil (General Company for Studies and Consultations, 2010)

The grain size for calcium carbonates ranges from 30 μm up to 300μm (Syrian Carbonates Company, 2011), as shown in Fig.6. Atterberg limits test was applied on three samples from each type of soil (Damascus University, 2010) (F and GD) according to ASTMD 4318-00. Table 4 presents the average value for each of:

Liquid Limit (LL), Plastic Limit (PL), Plasticity Index (PI) and classification of F soil and GD soil according to

the Unified Soil Classification System (USCS).
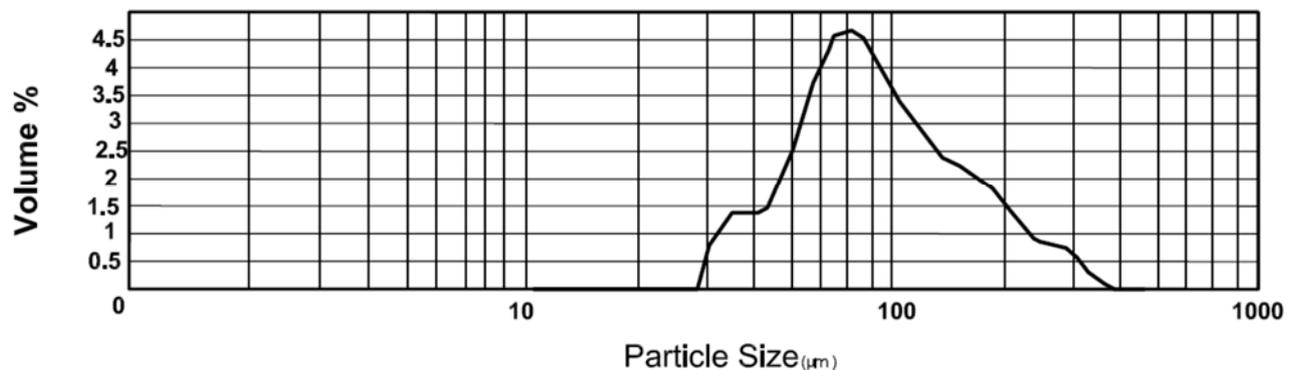
Figure (6): Size distribution curve for calcium carbonates (Syrian Carbonates Company, 2011)

Responsible for the low value of plasticity index for both types of soil (F and GD) is the high content of Kaolinite mineral in their composition. The hydrogen bonds between Kaolinite layers prevent water from penetrating between these layers. Also, the high content of quartz (in mineral composition) affects the value of plasticity index. Quartz is a deflocculating material. So, it reduces plasticity.

Table 4. Average results of Atterberg limits for soil samples

	GD	F
LL	0.206	0.27
PL	0.18	0.22
PI	0.027	0.05
classification	**CL-ML**	**CL**

CERAMIC SAMPLE PREPARATION

90 ceramic samples were prepared and divided as follows: **45** samples contain F soil (as a main component) and **45** samples contain GD soil (as a main component). The samples were prepared according to the following methodology: [EN 14411:2004].

The granulation process of the ceramic formulations

was performed by three distinct operations: grinding, mixing and agglomeration.

Each 45 ceramic samples were subdivided into 7 groups: **first group** (reference samples) containing clay soil only (GD or F) without calcite additives. It is termed **RGD** group or **RF** group, respectively. **Second group up to seventh group** (termed **GD**$_{calcite}$ group or **F**$_{calcite}$ group) contain clay soil (GD or F) plus calcite additives in percentages from 5% up to 30% (in 5% steps), respectively.

Each group was thoroughly mixed by wet ball milling for 12 h in a porcelain jar using agate balls. Then, the obtained slurry was screened with a screening residue of 4%, on screens with 63mm net openings (mesh no. 250). It was dried at 110 ^{o}C overnight, powdered, homogenized and granulated in a high intensity mixer with moisture content of 14% (moisture mass/dry mass). After reducing the moisture content to 7%, the granules were kept in a dissector for 24 h to homogenize their moisture content. The granulated powder was sieved to eliminate agglomerates larger than 2 mm.

Samples were prepared by uniaxial pressing technique in a rectangular die (10.3 cm x 21.6 cm x 1cm) under a pressure of 30 MPa and dried at 110°C overnight. Then, samples were fired in the temperature range of 800°C –1150 °C in an electric muffle furnace.

Heating and cooling rate was 5°C/min and soaking

time at maximum temperature was 1 h. The physico-mechanical properties were determined as follows:

1) **18 samples**: 9 fired samples from each of RF and RGD: 3 samples for flexural strength test according to [ASTM, C 674], 3 samples for linear shrinkage test according to [ASTM, C 326] and 3 samples for water absorption test according to [ASTM, C 373].
2) **24 samples**: 12 fired samples from each of $F_{calcite}$ and $GD_{calcite}$ (2 samples at each percentage of calcite additives) for flexural strength test according to [ASTM, C 674].
3) **24 samples**: 12 fired samples from each of $F_{calcite}$ and $GD_{calcite}$ (2 samples at each percentage of calcite additives) for linear shrinkage test according to [ASTM, C 326].
4) **24 samples**: 12 fired samples from each of $F_{calcite}$ and $GD_{calcite}$ (2 samples at each percentage of calcite additives) for water absorption test according to [ASTM, C 373].

RERSULTS AND DISCUSSION

RESULTS FOR REFERNECE CERAMIC SAMPLES

Table 5 displays the average values of flexural strength, linear shrinkage and water absorption for reference ceramic samples (RGD & RF).

Flexural Strength: The value for RF samples equals 105kg/cm^2, which is greater than that for RGD samples which equals 85kg/cm^2. But, for the two groups it is still less than the minimum requirement (200kg/cm^2) according to ISO10545-4. The difference in values between RF samples and RGD samples may be due to grain size, where the clay particle percentage in F soil is higher than that in GD soil, as shown in Fig.4 and Fig.5. So, the samples from F soil exhibit higher flexural strength.

Linear Shrinkage: It is observed that the linear shrinkage (**LS%**) of RGD samples (1.23%) is lower than that of RF samples (1.4%). This may be due to the presence of more quartz in GD soil than in F soil. But, for both soils, (**LS%**) is less than the maximum percentage (2%) according to ISO10545-4.

Water Absorption: For both samples (RF and RGD), the highest flexural strength value corresponds to the lowest water absorption percentage (**WA%**). This is logical as will be explained later.

The two types of soil couldn't be used separately in ceramics manufactory, because both do not meet the required strength according to the technical specification results mentioned above.

Table 5. Average value of technical specifications for reference samples (Syrian Ceramics Company, 2010)

Soil Type	Flexural Strength (kg/cm^2)	Water Absorption (%)	Linear Shrinkage (%)
RGD	85	12.7	1.23
RF	105	11.7	1.4

RESULTS FOR CERAMIC SAMPLES WITH CALCITE

Flexural Strength

Fig. 7 displays the values of flexural strength for $GD_{calcite}$ samples according to [ASTM, C 674] and Fig. 8 displays the values of flexural strength for $F_{calcite}$ samples. It is noted that at 5% calcite additives, the value of flexural strength approximately equals 256kg/cm^2 for $GD_{calcite}$ samples and 214kg/cm^2 for $F_{calcite}$ samples, then it decreases to 244kg/cm^2 and 180kg/cm^2 respectively, at calcite additives of 25%.
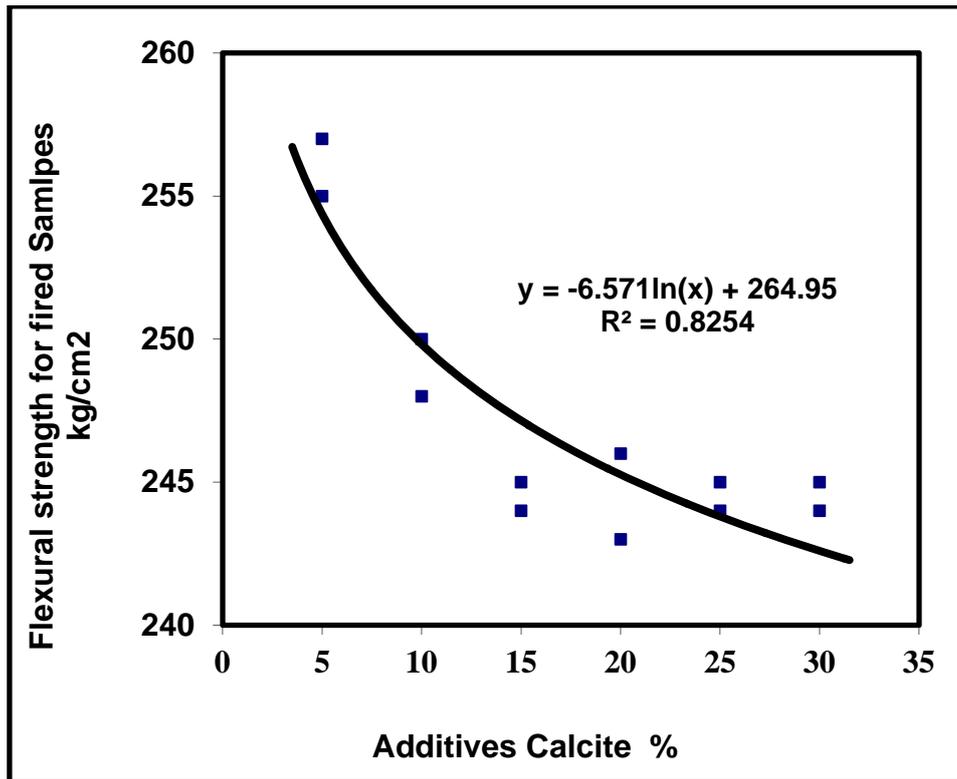
Figure (7): Flexural strength for fired GD$_{Calcite}$ ceramic sammples against calcite addition percentage
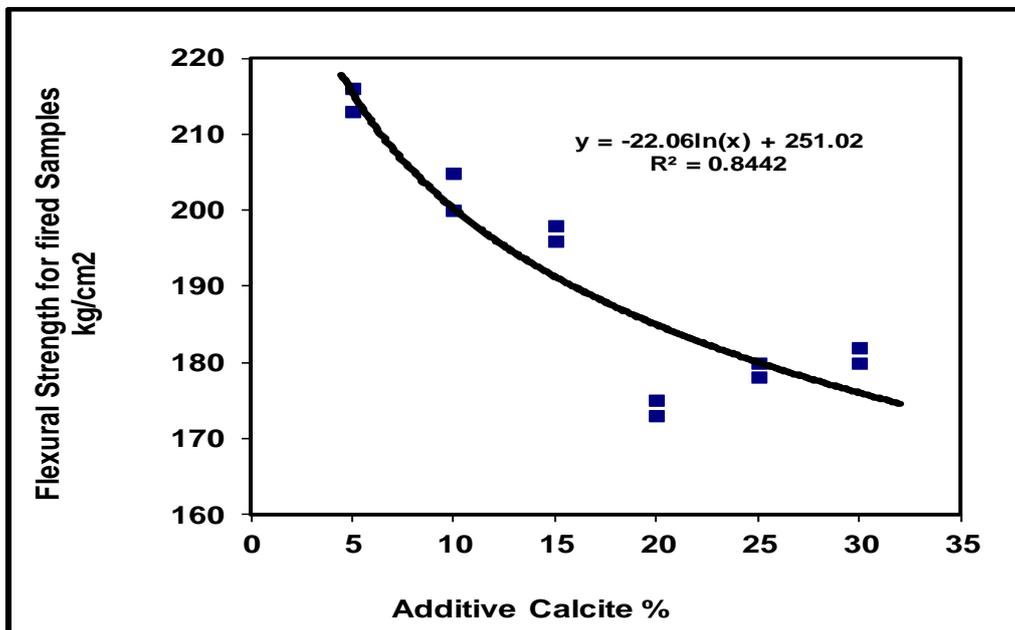

Figure (8): Flexural strength for fired F$_{Calcite}$ ceramic samples against calcite addition percentage

But, by comparing the behavior of samples before and after using the additives, from Fig.9, it is clear that there was a remarkable increase of flexural strength value for F group samples from 105kg/cm² to 214kg/cm²

at a calcite percentage of 5%, whereas the increase for GD group samples was from 85kg/cm² to 255kg/cm² at the same calcite percentage. This could be explained as follows.
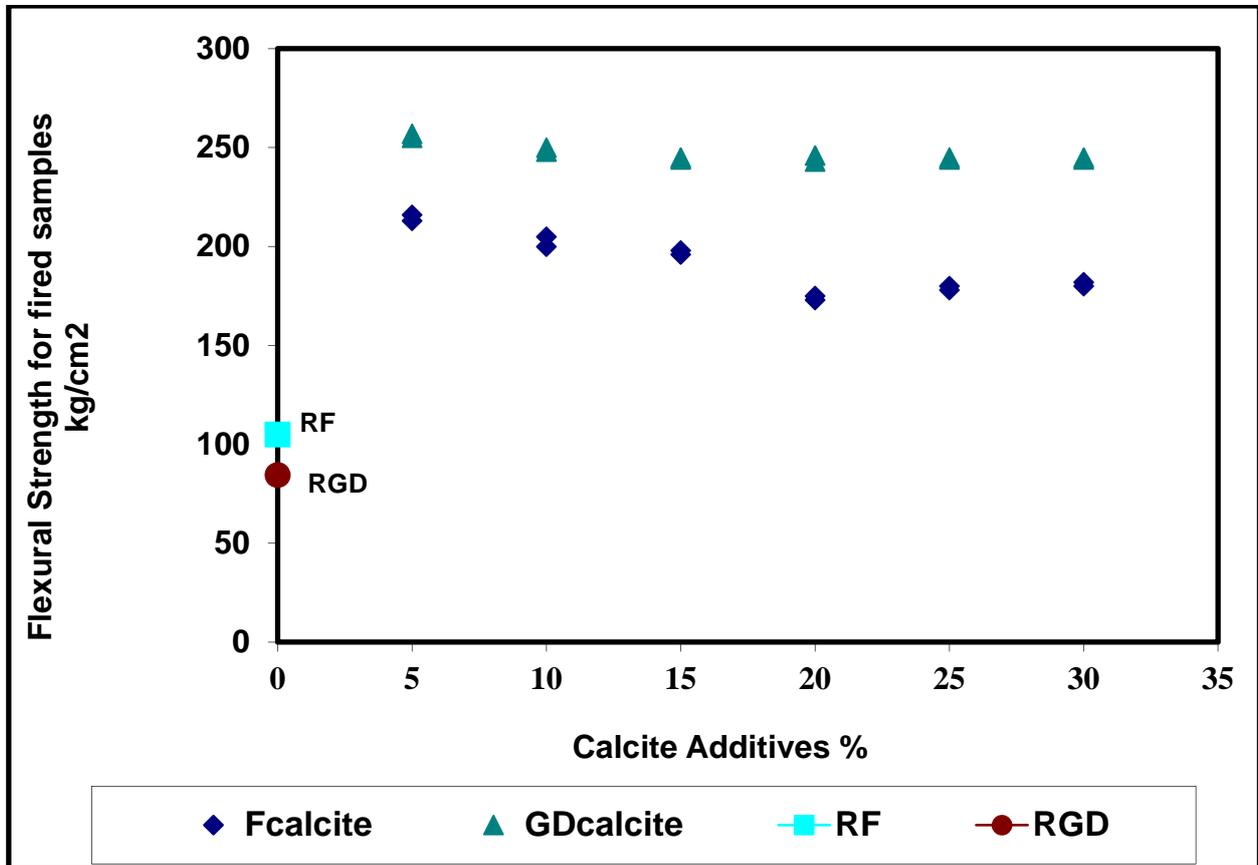
Figure (9): Flexural strength for fired ceramic samples against calcite addition percentage

Thermal transformations before calcite addition occur as follows (Brindley and Nakahira, 1959; Brindley and Nakahira, 1959; Brindley and Nakahira, 1959):

- $Al_2O_3.2SiO_2.2H_2O$ (Kaolinite) $\rightarrow$ $Al_2O_3.2SiO_2$ (metakaolinite) + $2H_2O$ (400-500°C).
- $2(Al_2O_3.2SiO_2)$ (metakaolinite) $\rightarrow$ $Si_3Al_4O_{12}$ (spinel) + SiO_2 (~950°C).
- $3Si_3Al_4O_{12}$(Al-Si-spinel) $\rightarrow$ $2(Al_2O_3.2SiO_2)$ (mullite) + $5SiO_2$ (>1050°C).
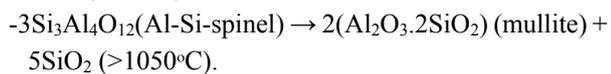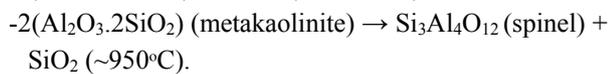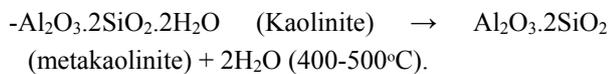
Mullite results from the above thermal transformations of Kaolinite (Seynou et al., 2011). It

was approved that mechanical strength decreases as a result of mullite occurrence (De Noni Junior et al., 2010).

After adding a low percentage of calcite, the transformations will change as follows: (SiO_2-$CaO \cdot SiO_2$–$CaO \cdot Al_2O_3$. $2SiO_2$ (quartz -wollastonite–anorthite)), where wollastonite forms according to the following reaction (Sandoval and Ibanez, 1999):

$CaCO_3 + SiO_2 \rightarrow$ $CaSiO_3 + CO_2$ (960-980°C).

Then, anorthite forms from wollastonite and alumina

at a temperature of 1025ºC as follows:

$$CaSiO_3 + Al_2O_3 + SiO_2 \quad \rightarrow \quad CaAl_2Si_2O_8.$$

Anorthite is considered the most effective mineral in increasing the mechanical strength of ceramic materials (Kurama and Ozel, 2009). So, the formation of anorthite is responsible of increasing the strength after adding calcite at a percentage of 5%.

Nevertheless, the addition of a high percentage of calcite with an elevated CaO content transforms the final composition of the body to $CaO \cdot SiO_2$–$CaO \cdot Al_2O_3 \cdot 2SiO_2$–$2CaO \cdot Al_2O_3 \cdot SiO_2$ (wollastonite–anorthite– gehlenite). For this reason, we note a decrease of the strength after the addition of 5% of calcite, where a portion of CaO did not react, because its quantity was in excess of the freeable silica to react with it (Montero et al., 2009).

Returning to Fig. 9, after the addition of 25% of calcite, there is no change in the value of flexural strength for both types, $F_{calcite}$ and $GD_{calcite}$. In other words, no new phases have formed. Although there is a similar behavior for both types of samples ($F_{calcite}$ and $GD_{calcite}$), it is obvious that the increase in the strength of $GD_{calcite}$ samples is more than that in the other samples, which is due to the mineral composition. The higher content of quartz is responsible of more ability to form anorthite phases, which means higher flexural strength.

Linear Shrinkage

Fig.10 displays the linear shrinkage percentage (LS%) for $GD_{calcite}$ according to [ASTM C 326]. **LS%** equals 1.2% at 5% calcite additives, then it decreases to 0.6% at calcite additives of 25%. Similarly, from Figure 11, **LS%** for $F_{calcite}$ samples decreases from 1% at 5% calcite additives to 0.3% at 25% calcite additives. But, all these values for **LS%** are still less than the maximum percentage (2%) according to ISO10545-4.
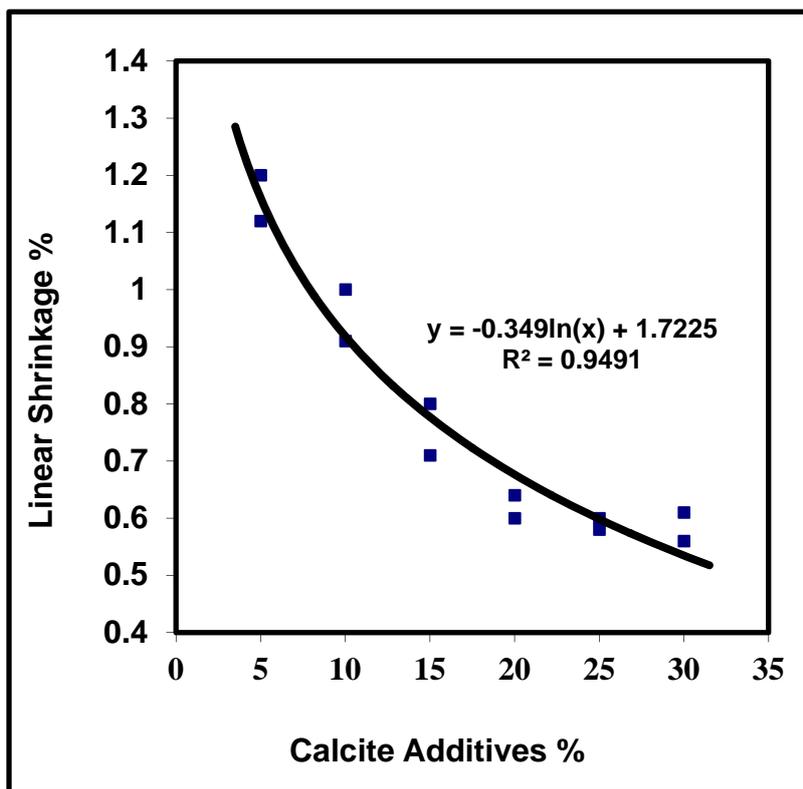

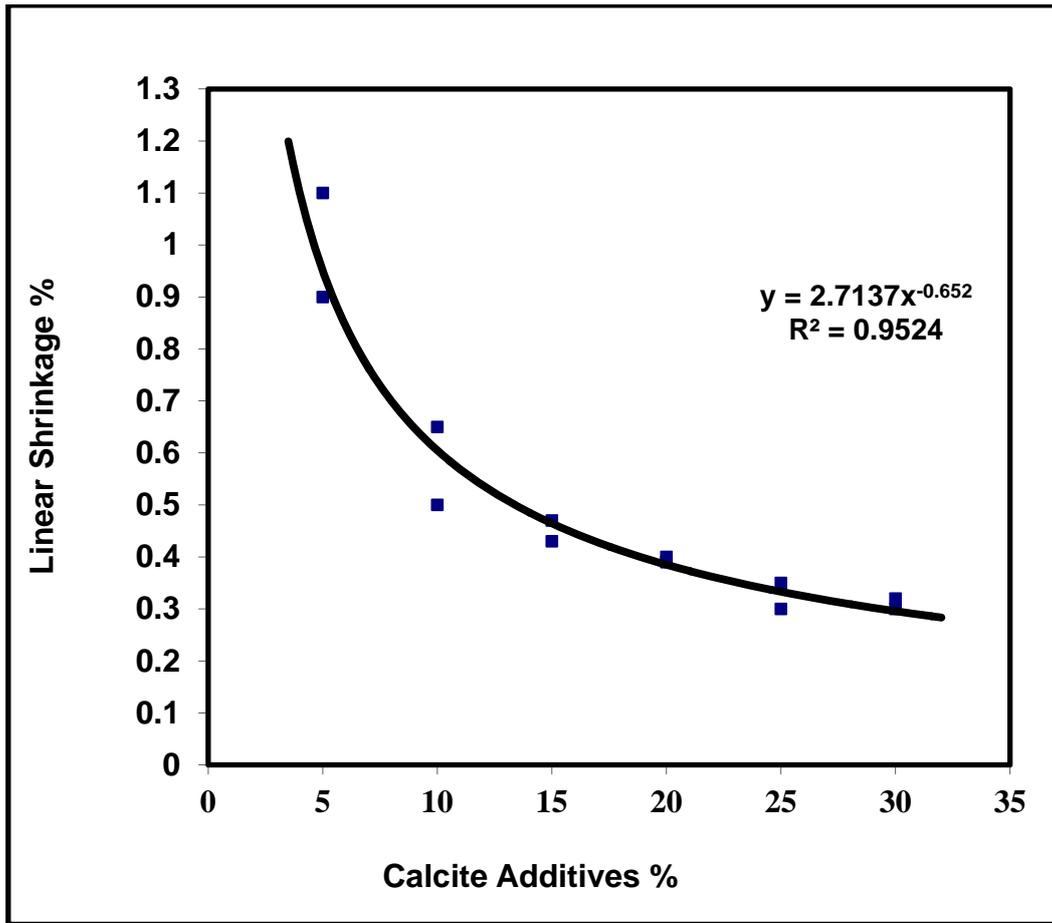**Figure (10): Linear shrinkage for fired GD_calcite ceramic samples against calcite addition percentage**

Figure (11): Linear shrinkage for fired F_{calcite} ceramic samples against calcite addition percentage

From Fig. 12, compared could be the behavior of GD group and F group before and after calcite addition. For F group samples, **LS%** decreases from 1.4% (RF) to reach 0.3% (F_{calcite}) at 25% of additives, then continues steadily. For GD group samples, **LS%** decreases slightly from 1.23% (RGD) to 1.2% (GD_{calcite}) at 5% of additives; afterwards it decreases to 0.6% at 25% of calcite additives. As previously explained in the thermal reactions, when the reaction of calcium oxide and metakaolinite occurs, silica is consumed for the formation of aluminosilicates and will not be available to form liquid phase. Thus, the formation of calcium aluminosilicates seems to involve a smaller amount of liquid phase during sintering, thereby resulting in a smaller firing shrinkage (Lira et al., 1998).

One of the methods for controlling firing shrinkage is the use of various calcium-containing materials (Das et al., 2005), which conforms to the results of this research.
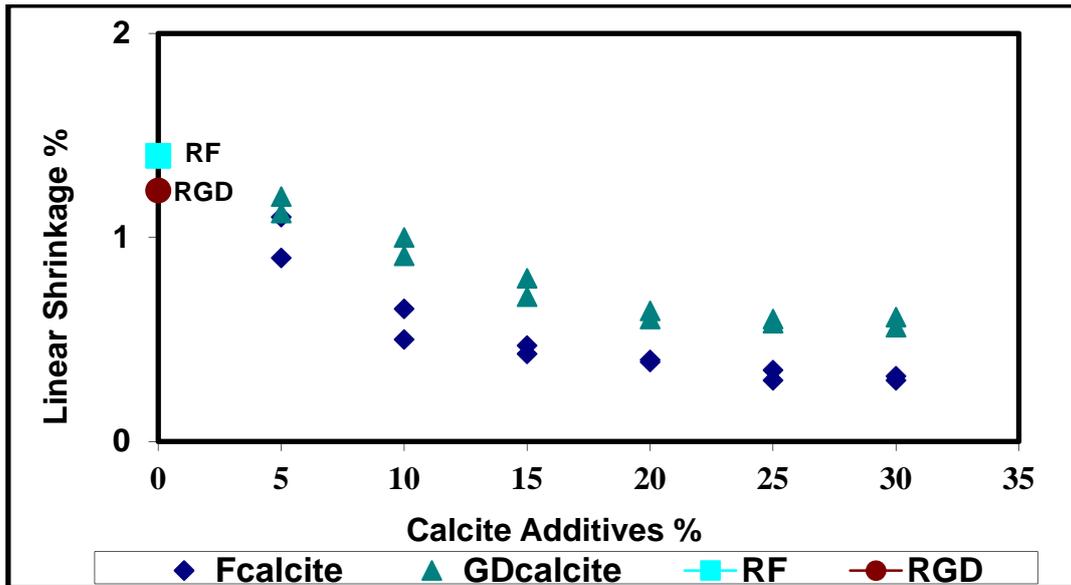
Figure (12): Linear shrinkage for fired ceramic samples against calcite addition percentage

Water Absorption

Figure 13 displays water absorption percentage **WA%** for $GD_{calcite}$ samples according to [ASTM, C 373]. **WA%** increases from 7% to 8% at 5% and 15% of calcite additives, respectively, then decreases to 6.3% at 30% of calcite additives.
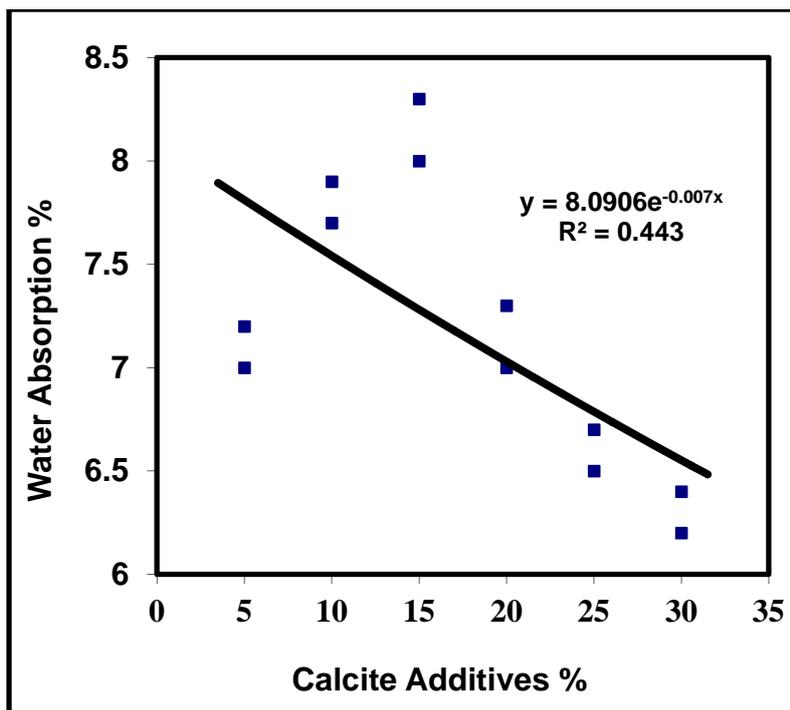

$$y = 8.0906e^{-0.007x}$$
$$R^2 = 0.443$$

Figure (13): Water absorption for fired $GD_{calcite}$ ceramic samples against calcite addition percentage

However, for $F_{calcite}$ samples, there is a direct relation between **WA%** and calcite percentage. Figure 14 shows an increase in **WA%** from 6.5% to 10% at calcite additives of 5% and 30%, respectively.
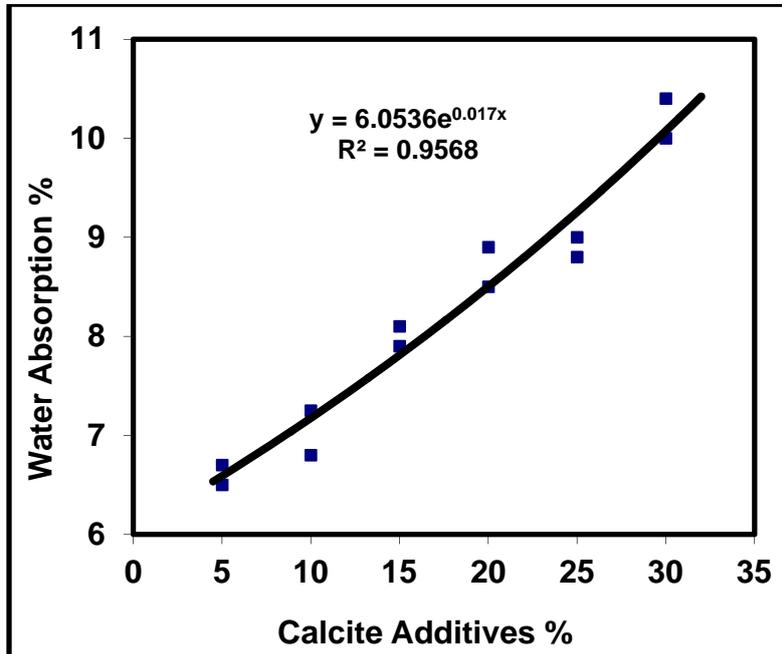

Figure (14): Water absorption for fired $F_{calcite}$ ceramic samples against calcite addition percentage

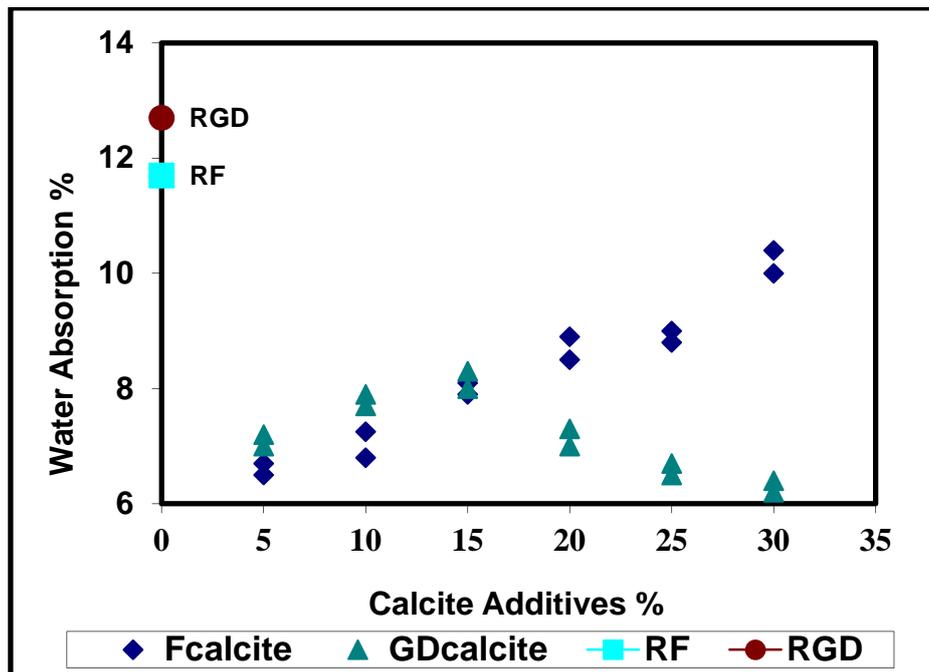$$y = 6.0536e^{0.017x}$$
$$R^2 = 0.9568$$

Figure (15): Water absorption for fired ceramic samples against calcite addition percentage

Figure 15 presents a comparison between GD group samples and F group samples. **WA%** decreases for GD group samples from 12.7% to 7% and for F group samples from 11.7% to 6.5%, at 0% and 5% of calcite additives, respectively.

After studying the two Figures 9 and 15, it was observed that there is a difference between the two graphs. The difference is logical, as the density of ceramic samples increases during sintering and subsequently, an increase in strength and a decrease in porosity occur. The decrease in porosity is followed by a decrease in water absorption in ceramic samples (Mesenguer et al., 2010; Jordan et al., 2006).

CONCLUSIONS

This research has shown that the addition of calcite into ceramic bodies is adequate for improving flexural strength of final ceramic tiles. On the other hand, some technological properties can be improved with these additives. Conclusions are summarized in the following points:

1) The use of calcite additives with each of F soil and GD soil has changed the properties of those soils, which subsequently improves the specifications of prepared ceramic samples. Flexural strength has increased, whereas water absorption and linear shrinkage have decreased.

2) It has been demonstrated that calcite has great reactivity and therefore, it reacts easily with phyllosilicates and quartz, providing better sintering of original powders at lower temperatures. Subsequently, it reduces the cost of production, which is an economical advantage.

3) Natural stone production could provide an important amount of calcite. In other words, calcite is a low-cost and available additive.

4) Mineral analysis, chemical analysis, grain size distribution and classification of soil affect directly the efficiency of the additive and its role in changing the properties of soil.

5) In this research, the best added percentage of calcite was around 5% (for both F and GD soils), leading to achieve the best specifications according to international standards.

RECOMENDATIONS

1) An exhaustive evaluation of technological properties of industrial-size products is required in future research.

2) It is recommended to add calcite with percentages less than 5% in coming research. This may present remarkable results.

3) In future research, it is recommended to study the effect of calcite addition on a mixture of two or more types of clay soil.

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