

# THE EFFECT OF CALCITE ADDITIVES ON CLAY FOR CERAMIC TILE MANUFACTORY

**Dr. Mayyasa Melhem**

Faculty of Civil Engineering - Damascus University - Syria

## **ABSTRACT**

The continuous use of suitable raw materials in ceramic manufacturing has caused a big shortage in the main resources for these materials. Consequently, manufacturers try day by day to find alternative materials satisfy their demand. We aim in our research to support the industry by improving available raw material with artificial or natural additives, which affect positively final product specification.

Many researchers have studied the important effect of calcium carbonate on fine soils. They have proved there is a reverse relation between calcite content in clay and its plasticity index. From this result, we focus on the change in plasticity, which is considered a very important property in ceramic tile manufactory.

The samples of clay have been chosen from some Syrian clay sites. These were before unacceptable soils in industry, because they did not achieve the minimum requirements for ceramic tile industry standards.

We have classified the soils according USCS after applying the essential tests on clay which include: mineralogy analysis, sieve analysis, chemical analysis and Atterberg limits. We have prepared the reference ceramic tile samples (without additive) and compared these with other samples (with calcium additives from 5% up to 30%) by applying technical tests such as: water absorption, flexural strength, linear shrinkage.

We have achieved a remarkable improvement in the original properties: flexural strength has increased; in contrast, water absorption has decreased. The best percentage for calcium carbonate additive is about 5%, which ensures technical properties in accordance with international standards. All changes in the strength and shrinkage and water absorption value became stable after an additive percentage 25%. The efficiency of the additive correlates with soil composition, chemically and mineralogy.

It is recommended to use calcite with percentage less than 5%, in the coming researches. Probably this percentage will present important results, in addition to using calcite additives with a mixture of two types of clay soil, in order to study its effect on this mixture.

## 1. INTRODUCTION

Interest in clays has increased in recent years due to their physico-chemical and plastic properties, which make them some of 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 a new technique and new raw material resources to improve the quality of their products and minimize their costs.

The raw materials, clay in particular, significantly affect the technical properties of the ceramics. It is well known that the mechanical properties of ceramics are an important parameter for defining their use and applications<sup>(1)</sup>. Consequently, a lot of studies and researches have focused on Clay soils and studied their properties during industrial processing.

The continuous and concentrated use of a suitable clay soil resource causes a remarkable shortage of these materials day after day. Therefore, the manufacturers always look for new resources, and they face many problems to find the ideal materials which achieve an economical product with the required specifications.

Calcium carbonates  $\text{CaCO}_3$  (CALCITE) have a remarkable effect after addition to fine soils<sup>(2)</sup>. It was proved<sup>(3)</sup> that the plasticity index is inversely proportional to calcium carbonate content<sup>(4)</sup>. Therefore, the addition of calcium carbonates to clay will change the plasticity property and subsequently, it will affect the technical specifications of the ceramic product during the manufacturing process.

In view of the above, this research with calcium carbonate additives is being carried out in order to improve different types of clay soil<sup>(5)(6)(7)</sup>. The nature and extent of the change in the final product were studied.

## 2. EXPERIMENTAL SECTION

### 2.1. MATERIALS AND METHODS

The samples of clay soil have been chosen from two Syrian Clay sites. These two sites are: **Sergaya** (referenced F), **Gdedt Yabous** (referenced GD) as shown in fig. 1. Many ceramic manufacturers have tried to use the soil from these two sites in the industry, but it does not achieve the minimum limits according to ceramic tile standards. Consequently, they have been considered unacceptable soils for the ceramic tile industry.

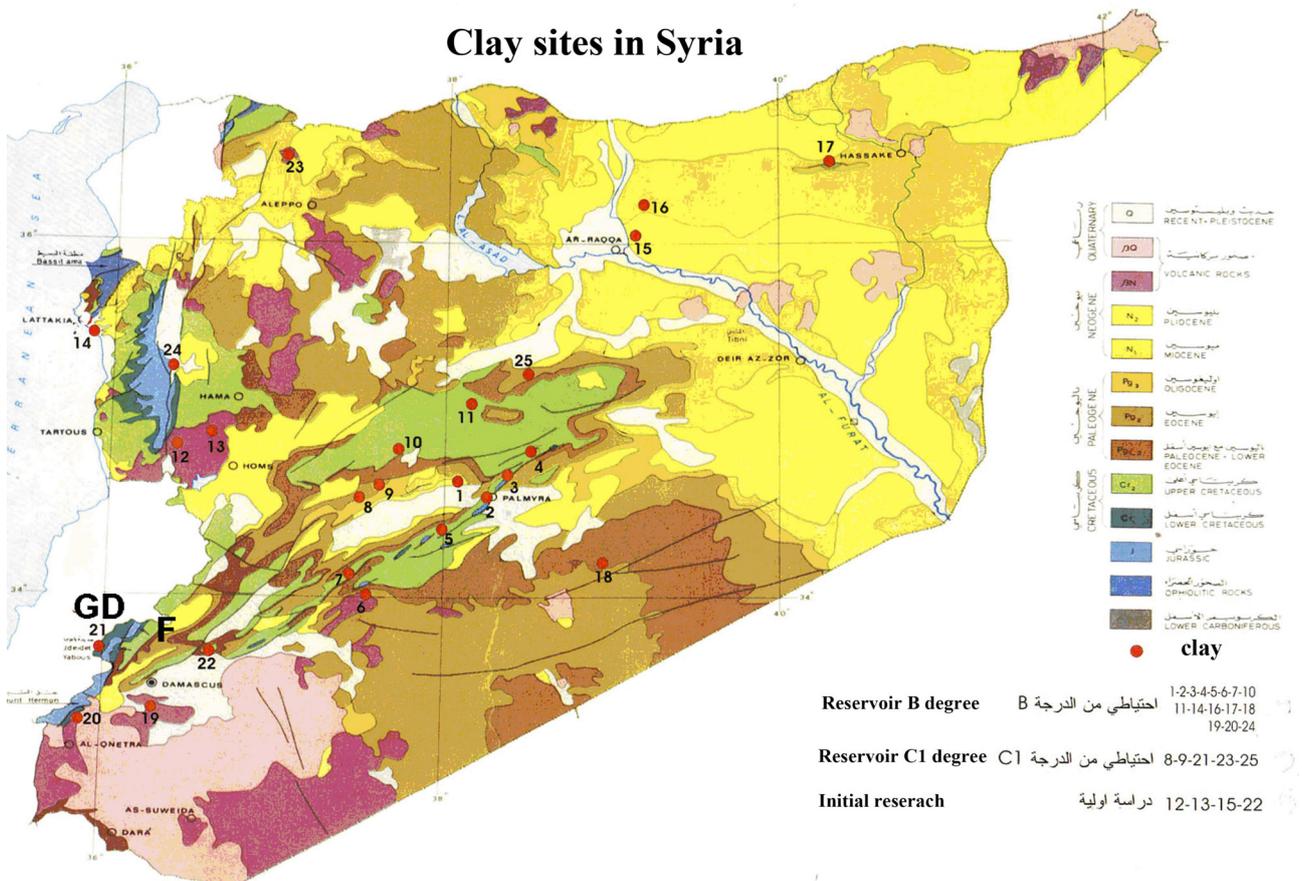


Figure 1: Clay sites (F, GD) in Syria<sup>(8)</sup>.

Calcium carbonate is the main component of limestone. Limestone (calcium material) is widespread in Syria, in the east, middle, and north area as illustrated in fig. 2. The geological reserves of unexploited limestone is quantified as approximately  $12 \times 10^9 \text{ m}^3$ . It is available and cheap. For this research, calcium carbonate was brought from the nearest site to the chosen soil sites (F & GD sites) in order to be as economical as possible.

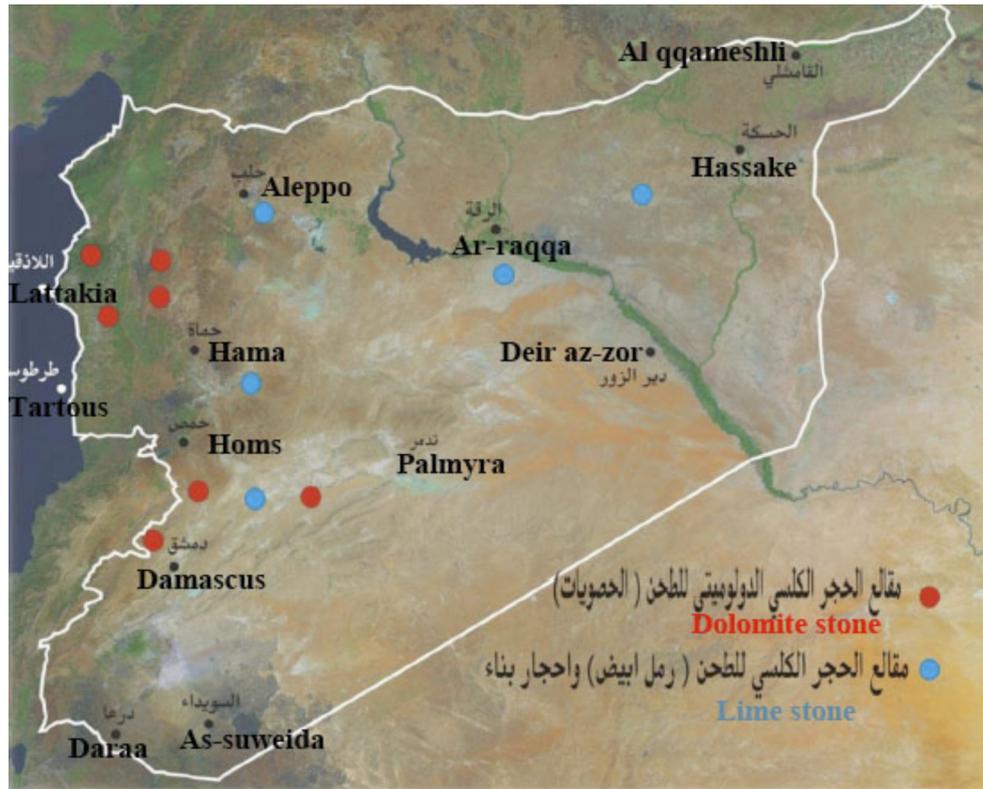


Figure 2: Limestone sites in Syria<sup>(8)</sup>.

### 2.1.1. CHARACTERIZATION OF RAW MATERIALS

The knowledge of the physico-chemical properties of clay soil is essential and very important<sup>(9)(10)</sup>. The oxides in clay soil undergo chemical and constitutional transformations (during the fire period), which in turn change the properties of those soils and define the specification of the final products. There are several factors that affect those transformations: **chemical composition, mineralogical composition, grain size distribution**<sup>(11)(12)</sup>.

The mineralogical analysis of clay samples (15 samples from each of two sites: F and GD) was carried out by XRD on oriented aggregates (normal, heated to 550°C for 2h and treated with ethylene glycol)<sup>(13)</sup>.

The mineralogical composition of GD clay was Kaolinite  $\text{Al}_4\text{Si}_4\text{O}_{10}(\text{OH})_8$ , Quartz  $\text{SiO}_2$ , small quantities of Illite  $\text{KAl}_2(\text{Al},\text{Si}_3)\text{O}_{10}(\text{OH})_2$  and Chlorite  $(\text{OH})_4(\text{SiAl})_8(\text{MgFe})_6\text{O}_{20}$ . Also, some samples contain small quantities of muscovite  $\text{KAl}_2[(\text{OH})_2/\text{AlSi}_3\text{O}_{10}]$ , montmorillonite  $(\text{Al},\text{Mg})_2[(\text{OH})_2/\text{Si}_4\text{O}_{10}](\text{Ca})x(\text{H}_2\text{O})n$ , calcite  $\text{CaCO}_3$  and organic materials (in traces) as shown in Table 1.

The mineralogical composition of **F** clay was Kaolinite  $\text{Al}_4\text{Si}_4\text{O}_{10}(\text{OH})_8$ , Quartz  $\text{SiO}_2$ , small quantities of Illite  $\text{KAl}_2(\text{Al},\text{Si}_3)\text{O}_{10}(\text{OH})_2$  and Calcite  $\text{CaCO}_3$  (trazas), as shown in Table 2.

The chemical analysis of the major and minor elements was performed by X-ray fluorescence (XRF)<sup>(13)</sup> using conventional techniques for the F soil and GD soil as shown in fig. 3. The highest percentage is for  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  in all samples. Table 3 presents the chemical analysis for calcium carbonate, after it was tested by X-ray fluorescence (XRF) using conventional techniques<sup>(14)</sup>.

Calcite CaCO <sub>3</sub>	Clorite (OH) <sub>4</sub> (SiAl) <sub>8</sub> (MgFe) <sub>6</sub> O <sub>20</sub>	Montmorillonite (Al,Mg) <sub>2</sub> [(OH) <sub>2</sub> / Si <sub>4</sub> O <sub>10</sub> ] (Na)x(H <sub>2</sub> O)n	Montmorillonite (Al,Mg) <sub>2</sub> [(OH) <sub>2</sub> / Si <sub>4</sub> O <sub>10</sub> ] (Ca)x(H <sub>2</sub> O)n	Muscovite KAl <sub>2</sub> [(OH) <sub>2</sub> /AlSi <sub>3</sub> O <sub>10</sub>	Illite KAl <sub>2</sub> (Al,Si <sub>3</sub> ) O <sub>10</sub> (OH) <sub>2</sub>	Quartz SiO <sub>2</sub>	Kaolinite Al <sub>4</sub> Si <sub>4</sub> O <sub>10</sub> (OH) <sub>8</sub>
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Table 1: Mineralogical analysis for soil GD<sup>(13)</sup>.

Calcite CaCO <sub>3</sub>	Illite KAl <sub>2</sub> (Al,Si <sub>3</sub> ) O <sub>10</sub> (OH) <sub>2</sub>	Quartz SiO <sub>2</sub>	Kaolinite Al <sub>4</sub> Si <sub>4</sub> O <sub>10</sub> (OH) <sub>8</sub>
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Table 2: Mineralogical analysis for soil F<sup>(13)</sup>.

(5% > \*\_) (5% < \*) (10% < \*\*) (15% < \*\*\*) (20% < \*\*\*\*)

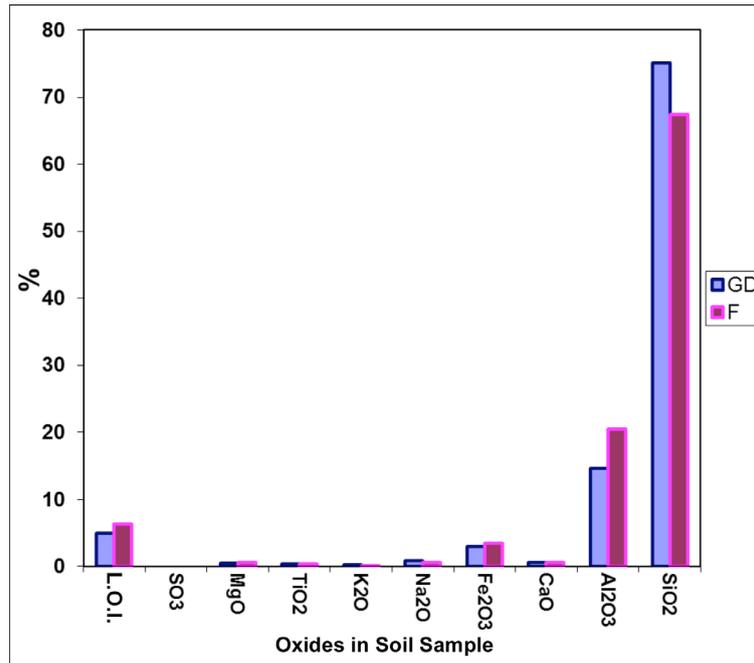


Figure 3: Chemical Analysis for soil samples (GD, F)<sup>(13)</sup>.

SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	Fe <sub>2</sub> O <sub>3</sub>	Na <sub>2</sub> O	K <sub>2</sub> O	TiO <sub>2</sub>	MgO	SO <sub>3</sub>	L.O.I.
0.93	0.46	82.70	0.2	0.01	0.02	-	0.19	0.07	15.42

Table 3: Chemical Analysis for calcium carbonate<sup>(14)</sup>.

The size distribution determinations were performed according to (ASTM D422-02)<sup>(15)</sup>. Obviously from (fig. 4 & fig. 5), the percentage of clay particles in the F soil (46.8%) is greater than in the GD soil (32.6%).

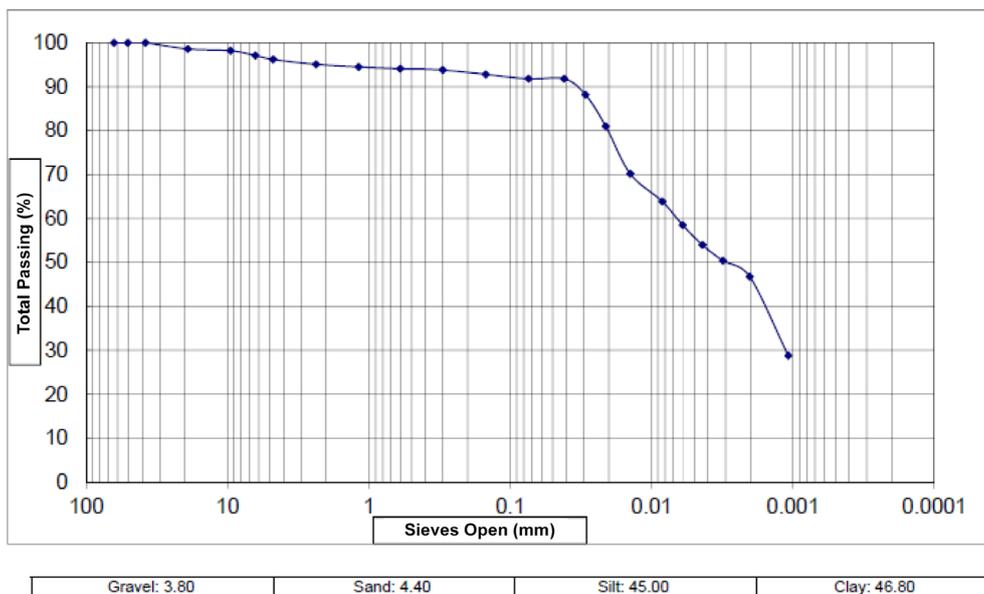


Figure 4: Size Distribution Curve for the F soil<sup>(16)</sup>.

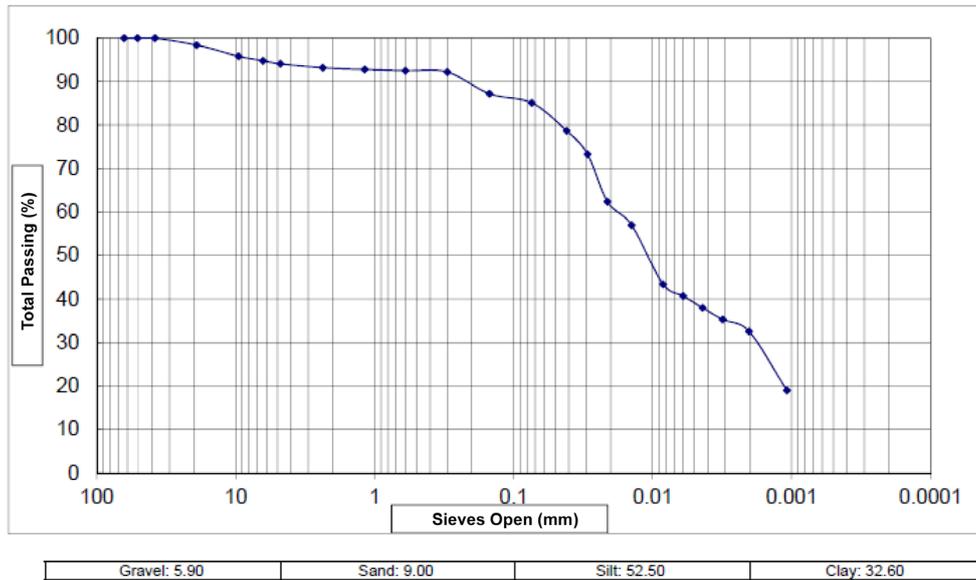


Figure 5: Size Distribution Curve for the GD soil<sup>(16)</sup>.

The size distribution for calcium carbonate ranges from 30  $\mu\text{m}$  to 300  $\mu\text{m}$ <sup>(17)</sup> as shown in fig. 6.

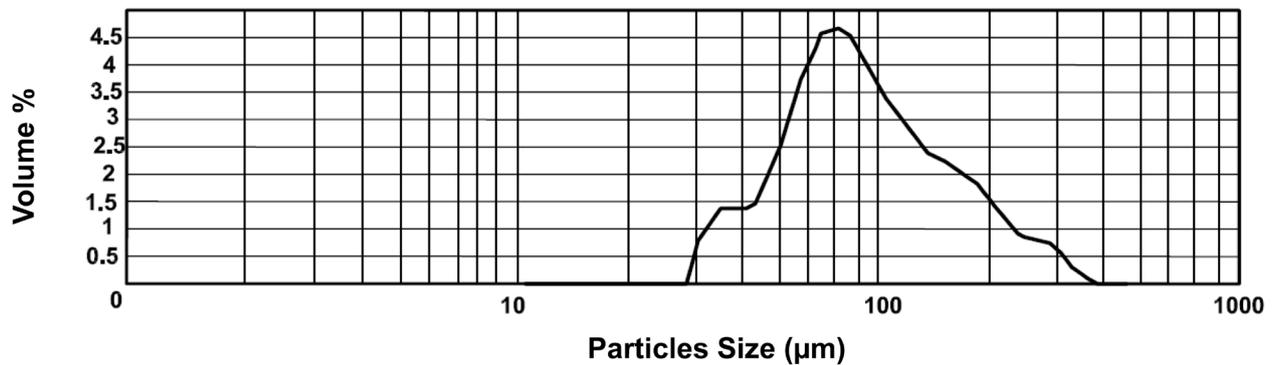


Figure 6: Size Distribution Curve for Calcium Carbonate<sup>(17)</sup>.

The Atterberg limits test was applied on three samples of each soil<sup>(18)</sup> (F and GD) according ASTM 4318-00<sup>(19)</sup>. Table 4 presents the average value for each of the following: Liquid Limit, Plastic Limit and Plasticity Index, and the classification of the F soil and the GD soil according to USCS.

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

Table 4: Average results of the Atterberg Limits for the soil samples.

The reason for the low plasticity index value for the two types of soils, F and GD, is the high content of kaolinite in the mineral composition. The hydrogen bonds between kaolinite layers prevent the water from entering between these layers. Also, the high content of quartz (in the mineral composition) affects the value of the plasticity index. Quartz is a deflocculating material so it lowers the plasticity.

### 2.1.2. CERAMIC SAMPLE PREPARATION

90 ceramic samples were prepared: 45 samples contain F soil (as a main component) and 45 samples contain GD soil (as a main component) according to the following methodology [EN 14411:2004]<sup>(20)</sup>:

The granulation process of the ceramic formulations was performed by three distinct operations: grinding, mixing, and agglomeration.

Each series of 45 ceramic samples was divided into 7 groups as follows: **first group** for reference samples only contains clay soil without calcite additives (termed RGD group or RF group), **second up to seventh** group (termed GD<sub>calcite</sub> group or F<sub>calcite</sub>) contains clay soil plus calcite additives in percentages from 5% to 30% (5% steps), respectively.

Each group was thoroughly mixed by wet ball milling for 12 h in a porcelain jar using agate balls. The slurry obtained was then screened with a screening residue of 4%, on screens with 63mm net openings (mesh no. 250). This was dried at 110 °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 desiccator for 24 h to homogenize their moisture content. The granulated powder is sieved to eliminate agglomerates larger than 2 mm.

Samples were prepared by uniaxial pressing 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 fired in the temperature range of 800–1150 °C in an electric muffle furnace. The heating and cooling rate was 5°C /min, and soaking time at the maximum temperature was 1 h. The physico-mechanical properties were determined using the following arrangement:

- 1) **18 samples:** 9 fired samples from each of RF and RGD: 3 samples for the flexural strength test according to [ASTM, C 674]<sup>(21)</sup>, 3 samples for the linear shrinkage test according to [ASTM, C 326]<sup>(22)</sup> and 3 samples for the water absorption test according to [ASTM, C 373]<sup>(23)</sup>.
- 2) **24 samples:** 12 fired samples from each of F<sub>calcite</sub> and GD<sub>calcite</sub> (2 at each percentage of calcite additives) for the flexural strength test according to [ASTM, C 674].
- 3) **24 samples:** 12 fired samples from each of F<sub>calcite</sub> and GD<sub>calcite</sub> (2 for each percentage of calcite additives) for the linear shrinkage test according to [ASTM, C 326].
- 4) **24 samples:** 12 fired samples from each of F<sub>calcite</sub> and GD<sub>calcite</sub> (2 for each percentage of calcite additives) for the water absorption test according to [ASTM, C 373].

## 2.2 RESULTS AND DISCUSSION

### 2.2.1. RESULTS FOR THE REFERENCE CERAMIC SAMPLES

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

**Flexural strength:** The value of the RF samples is 105kg/cm<sup>2</sup>, which is greater than its value for RGD samples which is 85kg/cm<sup>2</sup>. However, for the two groups it is still less than the minimum limit (200kg/cm<sup>2</sup>) according to ISO10545-4. The difference in the values between RF samples and RGD samples may be due to the size distribution where the clay percentage in the F soil is higher than in the GD soil as shown in fig. 4 and fig. 5. Consequently, the samples from the F soil exhibit the highest flexural strength.

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

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

The two types of soils could not be used separately in Ceramic manufacturing, because they do not provide the required strength according to the above technical specification results.

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

Table 5: Average value of the technical specification for the reference samples<sup>(24)</sup>.

### 2.2.2. RESULTS FOR CERAMIC SAMPLES WITH CALCITE

#### Flexural strength:

Fig. 7 displays the flexural strength values for the GD<sub>calcite</sub> samples according to [ASTM, C 674] and fig. 8 displays the flexural strength values for the F<sub>calcite</sub> samples. It is noted that, at 5% calcite additives, the flexural strength is approximately 256kg/cm<sup>2</sup> for the GD<sub>calcite</sub> samples and 214kg/cm<sup>2</sup> for the F<sub>calcite</sub> samples, and then it decreases to 244kg/cm<sup>2</sup>, 180kg/cm<sup>2</sup> respectively, at a calcite additive of 25%.

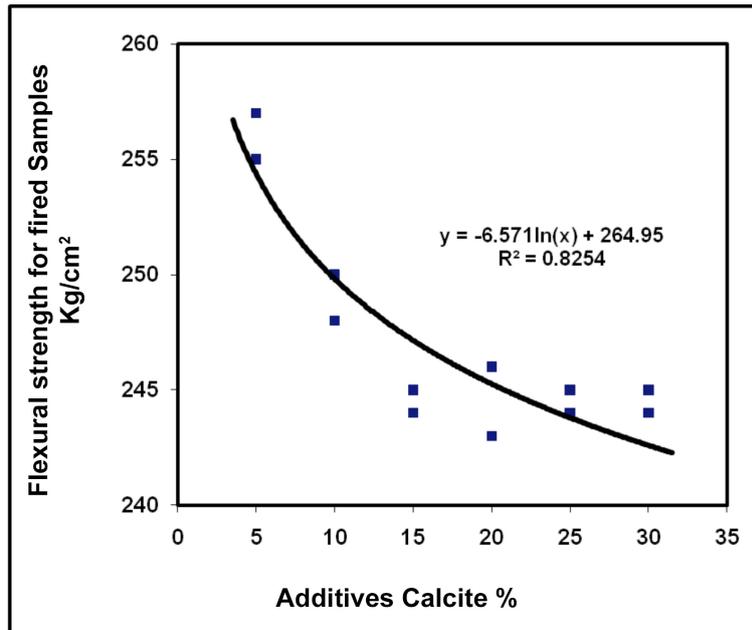


Figure 7: Flexural Strength for fired  $GD_{calcite}$  Ceramic Samples against Calcite addition percentages.

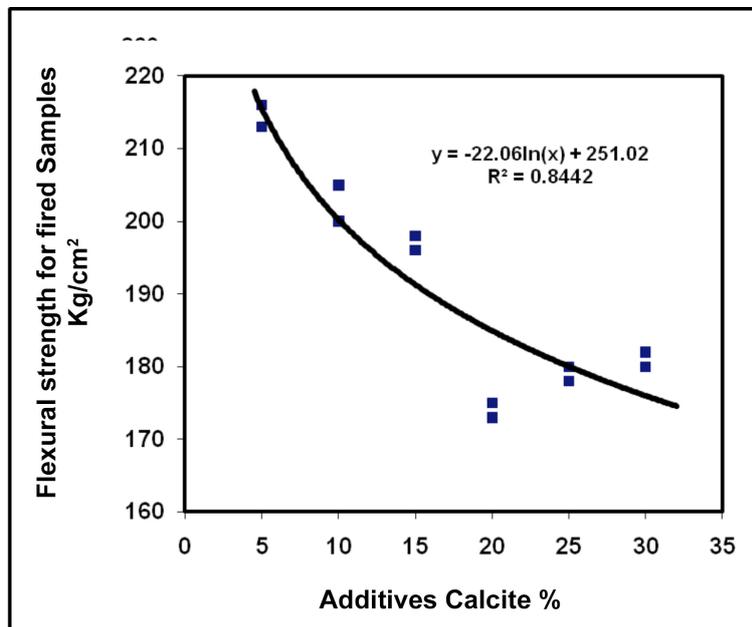


Figure 8: Flexural Strength for fired  $F_{calcite}$  Ceramic Samples against Calcite addition percentages.

However, by comparing the behaviour of the samples before and after using the additives from fig. 9, it is clear that there is a remarkable increase in flexural strength for the F group samples from 105kg/cm<sup>2</sup> to 214kg/cm<sup>2</sup> at a calcite percentage of 5%, and for the GD group samples from 85kg/cm<sup>2</sup> to 255kg/cm<sup>2</sup> at a calcite percentage of 5%. This could be explained as follows:

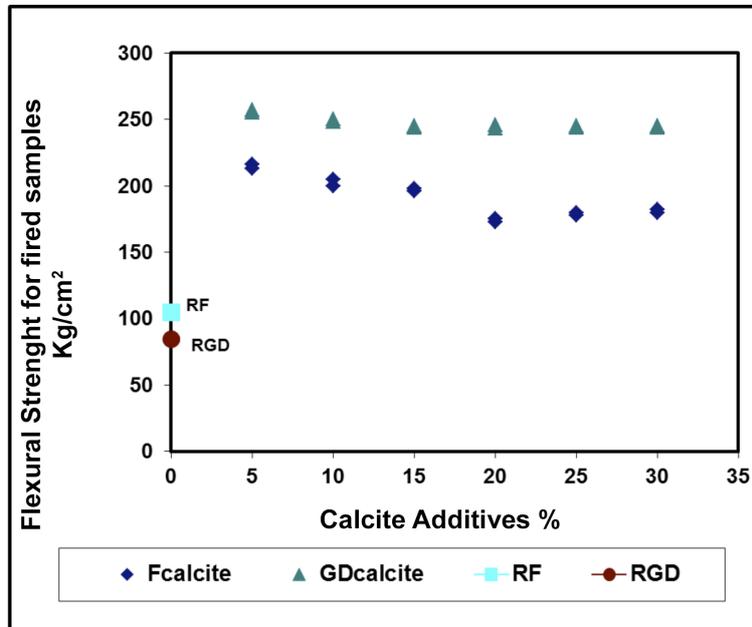
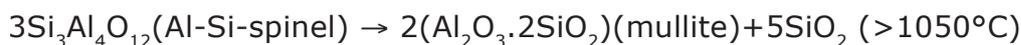
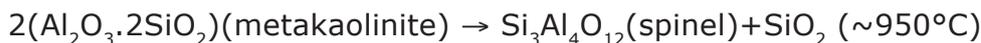


Figure 9: Flexural Strength for fired Ceramic Samples against Calcite addition percentages.

The thermal transformations before the calcite additives occur as follows<sup>(25)(26)(27)</sup>:



The mullite results from the above thermal transformations of kaolinite<sup>(28)</sup>. It is known that mechanical strength decreases as a result of the presence of mullite<sup>(29)</sup>.

After adding a low percentage of calcite, the transformation will change as follows:

(SiO<sub>2</sub>-CaO·SiO<sub>2</sub>-CaO·Al<sub>2</sub>-O<sub>3</sub>·2SiO<sub>2</sub> (quartz-wollastonite-anorthite). Where wollastonite forms according to the following reactions<sup>(30)</sup>:



Then anorthite forms from wollastonite and alumina at a temperature of 1025°C as follows:



Anorthite is considered the most effective mineral in increasing the mechanical strength of ceramic materials<sup>(31)</sup>. Consequently, the formation of anorthite is responsible for increasing the strength after adding calcite 5%.

Nevertheless, the addition of a high percentage of calcite with an elevated CaO content moves the final composition of the body to the  $\text{CaO}\cdot\text{SiO}_2\text{-CaO}\cdot\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2\text{-2CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{SiO}_2$  (wollastonite–anorthite–gehlenite); for this reason we note a decrease in strength after a 5% percentage of calcite, where a portion of the CaO did not react because its quantity was in excess of the free silica able to react with it<sup>(32)</sup>.

Returning to fig. 9, after the percentage 25% of calcite, there is no changing in value of flexural strength for the two types,  $F_{\text{calcite}}$  and  $\text{GD}_{\text{calcite}}$ . In other words, no new phases have been formed. Although there is a similar behaviour for two types of samples ( $F_{\text{calcite}}$  and  $\text{GD}_{\text{calcite}}$ ), it is obvious that the increase in strength of the  $\text{GD}_{\text{calcite}}$  samples is more the others, which brings us back to the mineral composition. The higher the content of quartz, the greater is the ability to form anorthite phases, which mean it has higher flexural strength.

### Linear Shrinkage

Fig. 10, displays the linear shrinkage percentage (LS%) for  $\text{GD}_{\text{calcite}}$  according to [ASTM C 326]. **LS%** is equal to 1.2% at 5% calcite, and then it decreases to 0.6% at 25% calcite. Similarly, from fig. 11, **LS%** for the  $F_{\text{calcite}}$  samples decreases from 1% at 5% calcite to 0.3% at 25% calcite. However, all these values for **LS%** are still less than the maximum value (2%) according to ISO10545-4.

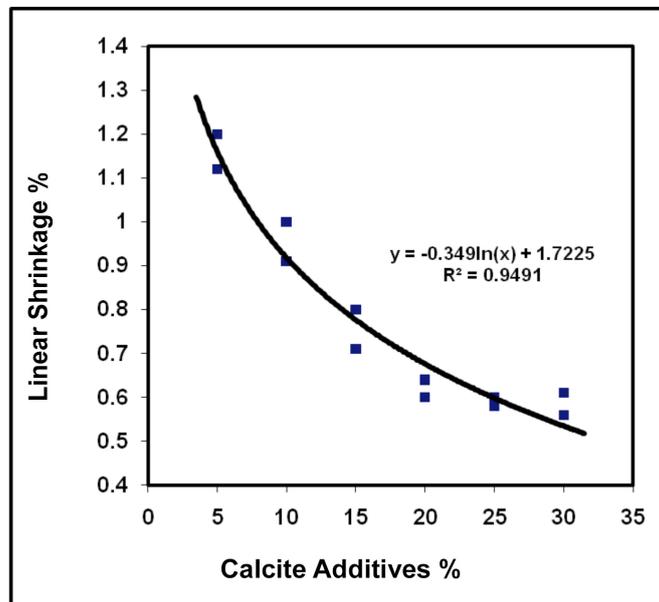


Figure 10: Linear Shrinkage for fired  $\text{GD}_{\text{calcite}}$  Ceramic Samples against Calcite addition percentages.

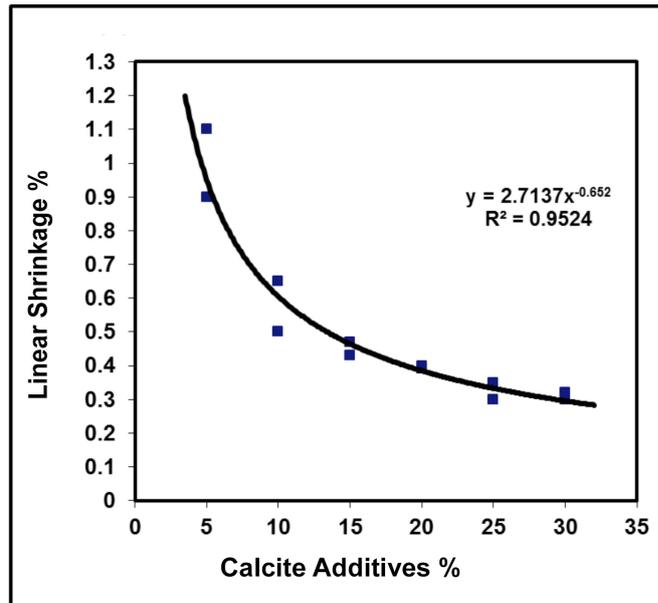


Figure 11: Linear Shrinkage for fired  $F_{calcite}$  Ceramic Samples against Calcite addition percentages.

Fig. 12 allows the behaviour of the GD group & the F group before and after calcite additives to be compared. For the F group samples: **LS%** decreases from 1.4% (RF) to reach 0.3% ( $F_{calcite}$ ) at 25% additives, then continues steadily. And, for the GD group samples: **LS%** decreases slightly from 1.23% (RGD) to 1.2% ( $GD_{calcite}$ ) at 5% calcite; afterwards it decreases to 0.6% at 25% calcite. As illustrated in the thermal reactions above when the reaction of calcium oxide and metakaolinite occurs, the 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<sup>(33)</sup>.

One of the methods for controlling firing shrinkage is the use of various calcium containing materials<sup>(34)</sup>, and this is consistent with the results of this research.

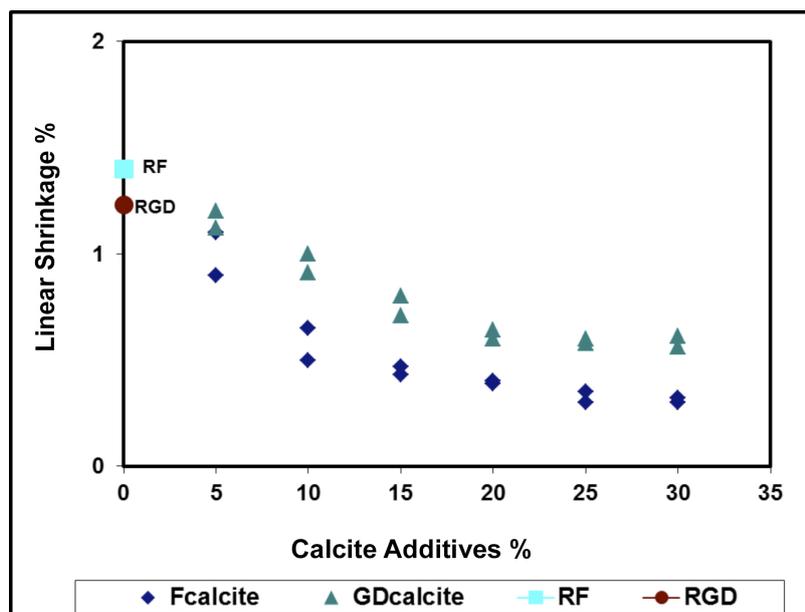


Figure 12: Linear Shrinkage for fired Ceramic Samples against Calcite addition percentages.

### Water Absorption

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

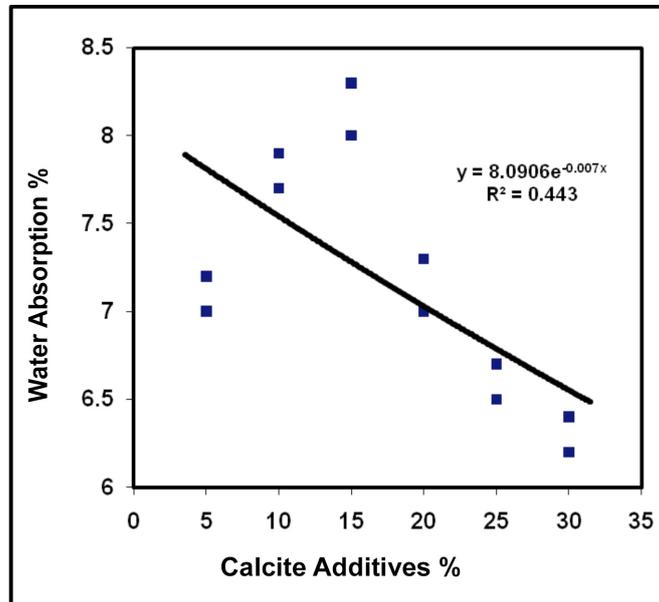


Figure 13: Water Absorption for fired  $GD_{calcite}$  Ceramic Samples against Calcite addition percentages.

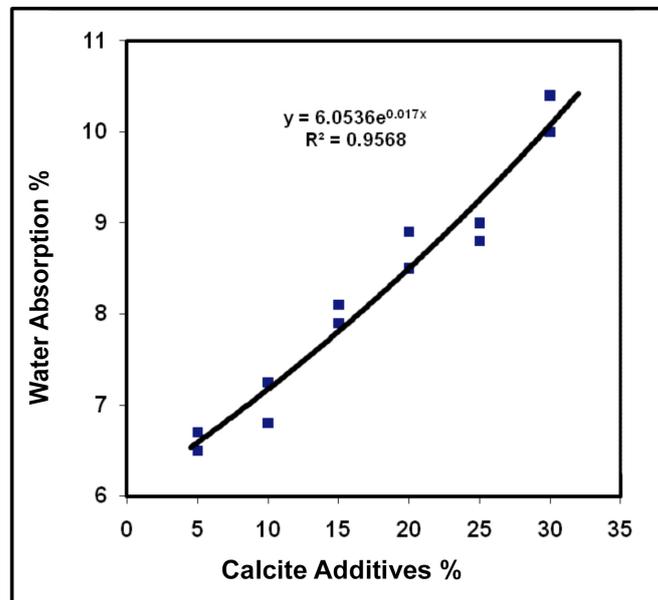


Figure 14: Water Absorption for fired  $F_{calcite}$  Ceramic Samples against Calcite addition percentages.

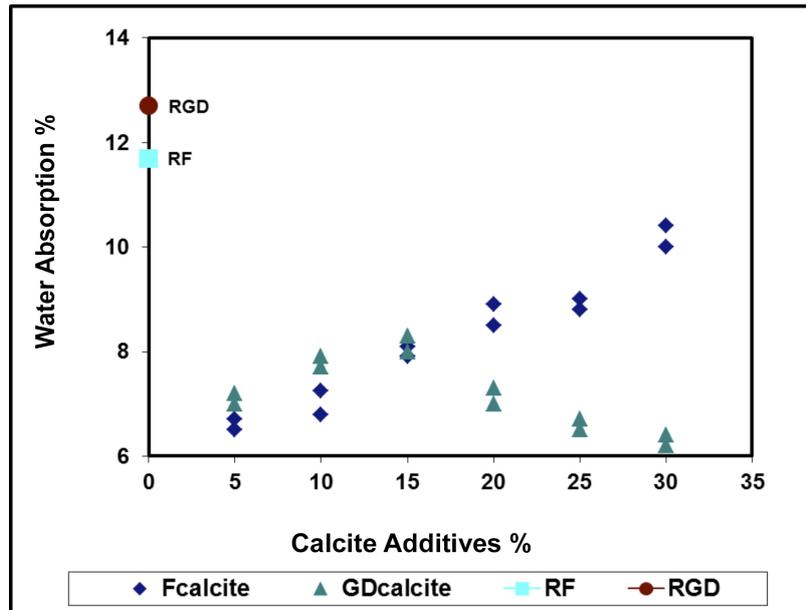


Figure 15: Water Absorption for fired Ceramic Samples against Calcite addition percentages.

However, for the  $F_{\text{calcite}}$  samples, there is a direct relation between **WA%** and calcite percentage, where fig. 14 shows the increase in **WA%** from 6.5% up to 10% at additive percentages 5% and 30% respectively.

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

After a studying the two figures 9 & 15, the difference was observed between the two graphs. The difference is quite logical; when the density of the ceramic samples increases during sintering, an increase in strength and a decrease in the porosity occur. The decrease in porosity is followed by decreased water absorption in the ceramic sample<sup>(35)(36)</sup>.

### 3. RESULTS

This research of additions of calcium carbonate into ceramic bodies has shown that it is adequate for improving the flexural strength of the final ceramic tiles. On the other hand, some technological properties can be improved with these additions. The results are summarized in the following points.

- 1) The use of calcite additives with the F soil and the GD soil has changed the properties of those soils, which subsequently improve the specifications of ceramic the samples prepared from these. The flexural strength has increased, water absorption and linear shrinkage has decreased.
- 2) It has been demonstrated that the calcite has a great reactivity and, therefore it reacts easily with the phyllosilicates and quartz, providing better sintering of the starting powders at lower temperature degrees. Subsequently, it reduces the cost of production, which is an economic advantage.
- 3) The natural stone production could supply an important amount of calcite. In other words, calcite is a low cost and available additive.
- 4) The mineral and chemical analysis, grain size distribution, and classification of soil affect directly the efficiency of the additive and its role in changing the properties of the soil.
- 5) In this research, the best additive percentage of calcite were defined at around 5% (for the F & GD soils), which achieved the best specification according to the international standards.

### 4. RECOMMENDATIONS

- 1) An exhaustive evaluation of the technological properties of industrial-size products is required in future research.
- 2) It is recommended to use calcite additive with a percentage of less than 5% in coming researches. This could present notable results.
- 3) In future research, it is recommended to study the effect of calcite additive on a mixture of two or more types of clay soils.

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