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Chapter

Limestone Clays for Ceramic Industry

Herbet Alves de Oliveira and Cochiran Pereira dos Santos

Abstract

Limestone clays are used in the ceramic segment in the manufacture of bricks, ceramic tiles, and in the production of cement, among others. Limestone can be present in soils in pure form or as a contaminant, but always from marine environments. The limestone after burning can present a high loss of mass (35–45%), which can cause serious problems with the sintering of ceramic products such as bricks, tiles. The calcium or magnesium carbonate once dissociated forms calcium oxide (CaO) and releases carbon dioxide (CO_2). CaO in contact with water subsequently experiences very high expansions that can cause cracks in the materials. Researchers have studied procedures to inhibit limestone action on clays as well as to set the correct temperature for firing. In this chapter, examples of clays with different percentages of calcium carbonate ($CaCO_3$) that are used in the ceramic segment and their characteristics will be given.

Keywords: clays, ceramic, limestone clays, calcium carbonate

1. Introduction

Clays are inorganic, natural, earthy, and fine-grained materials that acquire plasticity when mixed with water [1]. For sedimentologists, a clay is a raw material whose grain size is less than 2 μm. Like clays, in turn, there are rocks made up of clay minerals and may contain other minerals such as quartz, feldspar, mica, calcite, hematite, and organic matter as accessories [2]. A clay, once ground and mixed with water, in addition to presenting excellent workability in the fresh state, after drying, becomes extremely rigid. After burning normally above 800°C, it acquires great resistance [3]. Clays are used worldwide in the ceramic industry, especially in bricks, coatings, and others. However, clays are formed from the weathering of explosion and can be contaminated with several minerals among them or carbonate, which can alter the shape that causes the following burns. Limestone may be present in colloidal form, or coarse particles. However, in all cases it is impossible to separate or calculate this. Some researchers have tried to reduce the size of the variations to improve the chemical changes. According to Barba et al. [4], calcium carbonate and magnesium carbonate are the main constituents of carbonate sedimentary rocks. Anionic carbonate groups are strongly activated units and share oxygen with each other. They are responsible for the properties of these minerals. The most important anhydrous carbonates belong to three isostructural groups: the calcite group, the aragonite group, and the dolomite group. Among these, the minerals most used in the ceramic industry are calcite and dolomite, as they are

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low-cost raw materials, in addition to having favorable physical and chemical properties and available deposits. Second, Padoa [5] adds that when $CaCO_3$ is small, a decomposition can be complete and the calcium oxide reaches later with other mass components forming calcium silicates and silicon aluminates (wollastonite, anortite, gehlenite etc.) during sintering. Barba et al. [4] mentioned that the raw materials of clay when burned at high temperatures produce crystal phases that influence the properties of ceramic products. Calcite exerts a bleaching action on burnt products when added to a formulated mass of clays (in proportions above 5% and less than 30%) and at the same time decreases its expansion by legislation, as it forms crystalline and liquid phases, including cycles temperature and firing adopted. Calcite and dolomite are the most important representatives of carbonates in the ceramic industry. They are used as main components in the manufacture of ceramic tiles with high water absorption. These coatings include "porous coatings" or "tiles." These products are designed or used on walls and are not suitable for application on floors, as they have undesirable technical characteristics, such as mechanical resistance, incompatibility with use. According to Amorós [6], properties of parts of a ceramic product are registered by crystalline phases formed based on calcium and magnesium as ghelenite ($SiO_2{\cdot}Al_2O_3{\cdot}2CaO$) and anortite ($2SiO_2{\cdot}Al_2O_3{\cdot}CaO$). To achieve these phases, use the dolomite calcium oxide and/or magnesium reaction with a remaining clay structure proven by its thermal decomposition.

The calculation in general can affect the ceramic product in two ways: low percentages (up to 3%) and high temperature (above 1180°C) result in flow agents, that is, materials that contribute to reduce water absorption and increase the resistance of ceramic products. Above 3%, they can act as a foundation at temperatures above 1170°C [7].

In this chapter, we will highlight properties of limestone clays and their application in the ceramic industry.

2. Clays

Clays are hydrated aluminum silicates with crystalline structure arranged in layers, consisting of continuous sheets of SiO_4 tetrahedrons, ordered in a hexagonal shape, condensed with octahedral sheets of di and trivalent metal hydroxides, usually below 2 μm. They are materials that in contact with water become plastic, a fundamental characteristic for conformation of ceramic products because it provides mechanical resistance in the pressing, extrusion, or gluing process. Clays are mixtures of various clay minerals such as kaolinite, illite, and montmorillonite, which may or may not contain impurities [3, 8].

2.1 Kaolinite

The kaolinite with structural formula $Al_2O_3{\cdot}2SiO_2{\cdot}2H_2O$ has a dioctahedral structure, which consists of a tetrahedral layer linked by an octahedral layer. Pure kaolinites usually have low plasticity, see **Figure 1**.

2.2 Montmorillonite

Montmorillonites are a set of family of clay minerals, composed of dioctahedral and trioctahedral silicate sheets, see **Figure 2(a)** and **(b)**. The most outstanding feature of these minerals is their ability to absorb water molecules [8, 9]. It has 80% of exchangeable cations in the galleries and 20% on the lateral surfaces. The modification of montmorillonite clays has aroused scientific and technological interest

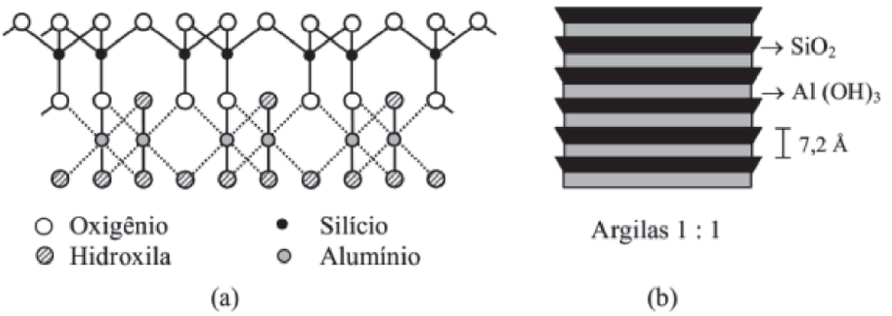


Figure 1.
Kaolinite structure. (a) Si—O tetrahedra on the bottom half of the layer and Al—O,OH octahedra on the top half. (b) Dioctahedral structure.

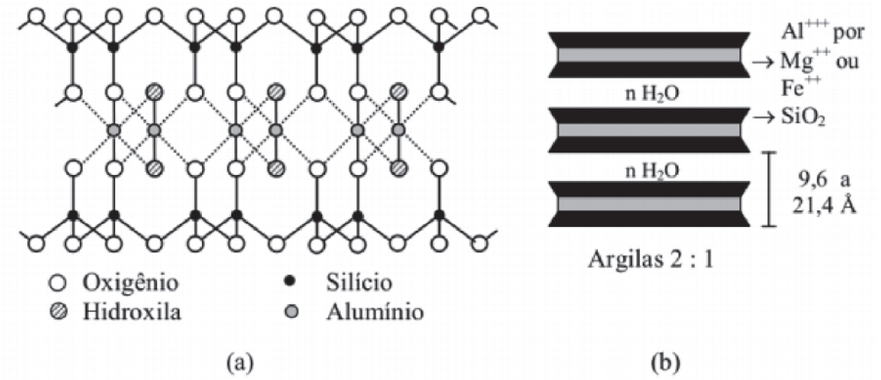


Figure 2.
Crystalline structure of a montmorillonite. (a) Montmorillonite structure, composed of Si, Al, and O. (b) Sheets of dioctahedral and trioctahedral silicates.

for providing significant improvements when incorporated into pure polymeric materials and conventional composites. The clay modification process occurs preferably through the ionic exchange of the exchangeable cations of its crystalline structure.

2.3 Illite

The basic structural unit of the illites is the same as that of the montmorillonites except that in illites, the silicon atoms in the silica layers are partially replaced by aluminum. Therefore, there are free valences in the boundary layers of the structural units, which are neutralized by K cations, arranged between the overlapping units. The structural scheme of the illites is shown in **Figure 3**. The K cation is the one that best adapts to the hexagonal meshes of the oxygen planes of the layers of silica tetrahedron and is not displaced by other cations. The water adsorption and cation exchange capacity is due only to the broken connections at the ends of the layers. The average diameter of the illites varies between 0.1 and 0.3 μm. When the replacement of silicon in the tetrahedron layers by aluminum in the illites is small, the connections between the structural units provided by the K cations may be deficient and will allow water to enter. When this occurs, the properties of the illites are close to the properties of montmorillonites [3].

2.4 Chlorite

Chlorites are minerals made up of four hydrated aluminum and magnesium silicate layers, containing Fe (II) and Fe (III) as shown in **Figure 4**.

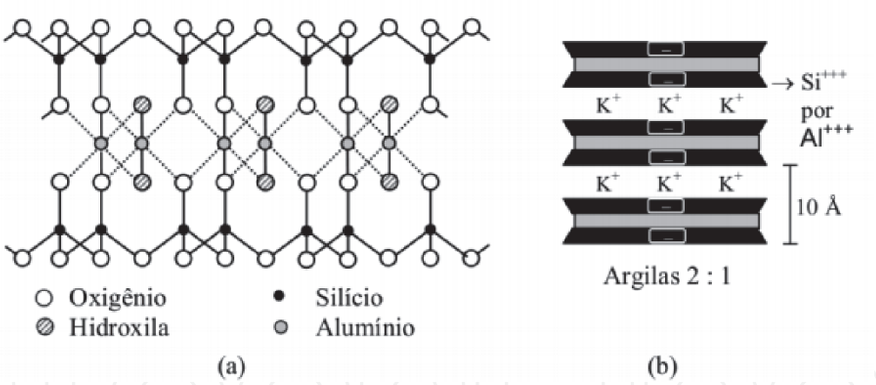


Figure 3.
Crystalline structure of an illite. (a) Silicon atoms in the silica layers partially replaced by aluminum in the illites. (b) Structural scheme of illites.

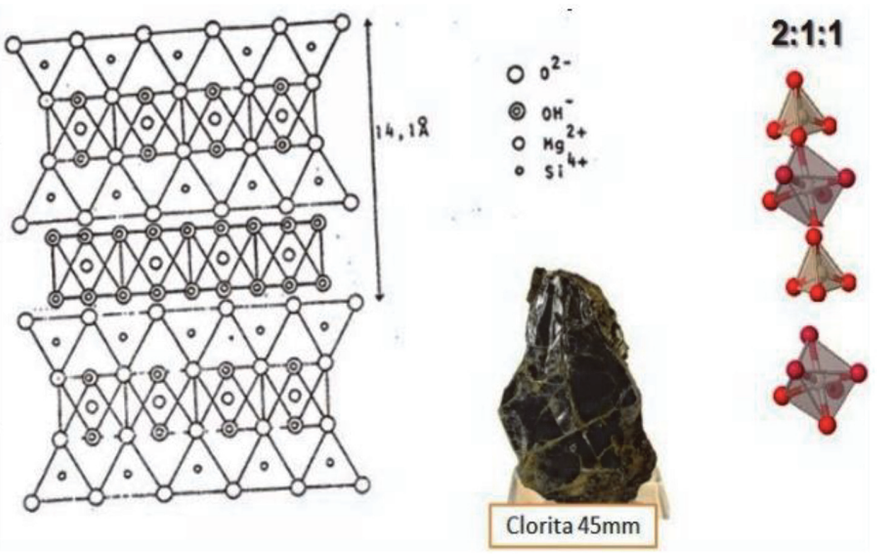


Figure 4.
Crystalline structure of chlorite [9].

The most common clay minerals are interstratified, characteristic of mixtures of clay minerals, classified by subgroup and mineralogical species, see most common classification in **Table 1**. Clay minerals are divided into several classes. A large majority of clays do not have in just one crystalline phase. Two or more chemical species may be present.

3. Clays used in the ceramic manufacturing process

The clays used in the ceramic manufacturing process can be classified into:

- Carbonitic clays: they are formed by associations of illitic-chloritic and eventually illitic-kaolinite clay minerals. The amount of calcium carbonate present can be variable. These clays give the dough plasticity. Generally, after burning they have colors ranging from beige to orange [4].

- Non-carbonitic clays: they are characterized by the almost total absence of carbonates. The clay minerals present are of the illitic-chloritic type. It has the function of giving plasticity to the dough, and generally after firing they give rise to well-sintered materials.

Subgroup	Chemical species	Minerals
Kaolin $X_n(Y_2O_5)(OH)_4$	Kaolinites	Nacrite $(Al_2(Si_2O_5)(OH)_4)$ Dikite $(Al_2(Si_2O_5)(OH)_4)$ Livesite $(Al_2(Si_2O_5)(OH)_4)$ Halloysite $(Al_2(Si_2O_5)(OH)_4)$
Talc $X_B(Y_2O_5)(OH)_2Z_mH_2O$	Montmorillonites	Montmorillonites $(Al_{1,51}Fe_{0,07}Mg_{0,60})(Al_{0,28}Si_{3,72})O_{10}(OH)_2Na_{0,33}$
		Beidellite $(Al_{1,46}Fe_{0,50}Mg_{0,08})(Al_{0,36}Si_{3,64})O_{10}(OH)_2Na_{0,4}$
		Nontronite $(Fe_{1,67}Mg_{0,33})(Si_4O_{10})(OH)_2Na_{0,33}$ and $Fe_{2,22}(AlSi_3O_{10})(OH)_2Na_{0,33}$
		Hectorite $(Mg_{2,67}Li_{0,33})(Si_4O_{10})(F,OH)_2Na_{0,33}$
		Saponite $Mg_3(Al_{0,33}Si_{3,67})O_{10}(OH)_2Na_{0,33}$
	Illites	Wide variety of minerals
Chlorite	Chlorites	Chlorite
$X_{2n}(Y_2O_5)_2(OH)_2$		$[Mg_2(Al,Fe(III))(OH)_6][Mg_3(AlSi_3O_{10})(OH)_2]$

Source: Barba et al. [4].

Table 1.
Subgroups of clay minerals.

- White plastic clays: the clay matrix is kaolinitic, with little illite. They give plasticity to the dough, and after burning they have a white color.

- Kaolinitic clays: clays of low plasticity and normally free of fluxing oxides such as K_2O and Na_2O, therefore, with refractory characteristics.

3.1 Heat action on clays

According to Mackenzie [10], when a ceramic raw material is subjected to the action of heat, it experiences volumetric variations, usually permanent and irreversible, which can be classified as:

- Oxidation of organic matter

- Decomposition of compounds containing oxygen, such as sulfates, carbonates, etc.

- Dehydroxylation of the clayey mineral

- Crystallization by increasing the temperature

- Vitreous phase formation

- Solid solutions: adjacent crystals of two different materials but of similar structure can react with each other, forming a solid solution.

Kaolinitic clay: the scheme according to **Figure 5** shows an endothermic peak between 560 and 590°C referring to the elimination of hydroxyls from the constitution water present in the clays, and an exothermic peak between 980 and

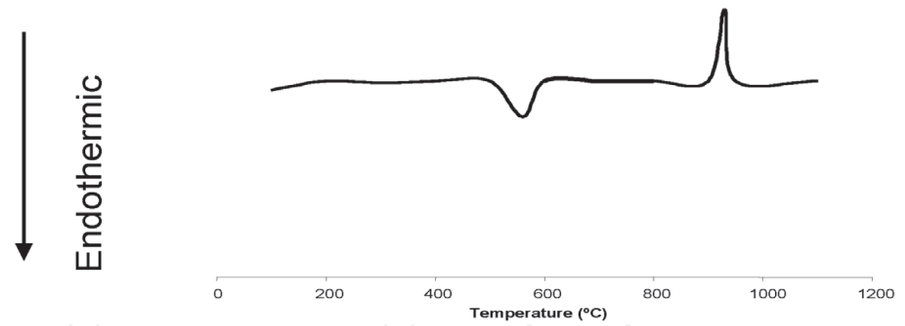


Figure 5.
Differential thermal analysis of a kaolinitic clay [10].



Figure 6.
Differential thermal analysis of a montmorillonite clay [10].

1000°C, due to the formation of mullite, which can be represented by the reactions 1 and 2 [8].

$$Al_2O_3.2SiO_2.2H_2O \xrightarrow{580\text{-}600} Al_2O_3.2SiO_2 + 2\,H_2O \quad (1)$$

$$3(Al_2O_3.2SiO_2) \xrightarrow{980\text{-}1000} 3Al_2O_3.2SiO_2 + 4SiO_2 \quad (2)$$

Montmorillonite: montmorillonites have water that lodges in the mineral structure, that is, hydration water of adsorbed ions. The elimination of hydroxyl groups occurs at 700°C. At 850°C, a small endothermic peak may occur due to the loss of montmorillonite crystallinity. Illites can present loss of adsorbed water between 100 and 200°C and water loss in the constitution between 550 and 600°C, see **Figure 6**.

3.2 Most common impurities present in clays

Quartz: it appears in clays in colored or colorless round grains, whose percentage ranges from 0 to 60%. For high levels of quartz, the clay is called sandy and has low plasticity [11].

Hematite: iron can be present in the forms of hematite (α-Fe_2O_3), goethite (α-FeO·OH), and lemonade (a mixture of iron oxides and hydroxides of a weakly crystalline nature), or simply as Fe^{3+} ions in the clay structure. In the illite group, Fe^{3+} ions can replace Al^{3+} ions in the octahedral structure [11]. Fe_2O_3 is formed during sintering under oxidation conditions and from minerals in the clays, giving a reddish color to ceramic materials.

Feldspar: feldspars refer to a group of aluminum silicate minerals. The feldspar contained in the clays is a source of sodium and potassium oxides and plays an important role in ceramic materials with quality of flow agents, temperatures such as sintering temperatures, porosity after firing and facilitating phase formation [6]. The most representative are the orthoclase ($KAlSi_3O_8$) and albite ($NaAlSi_3O_8$).

Carbonates: calcium or magnesium carbonates can appear as coarse or small grains. If they are presented as large grains (>125 μm), they may not react completely and the resulting oxides may rehydrate causing expansion according to reactions [12, 13].

$$CaCO_3 \xrightarrow{\Delta} CaO + CO_2 \quad (3)$$

$$CaO + H_2O \longrightarrow Ca(OH)_2$$

3.3 Use of calcite in the ceramic and chemical industry

Ceramic enamels and frits: can be used in matte enamels as a source of CaO to form crystals such as wollastonite, anorthite, gehlenite or in transparent enamels giving shine.

Masses for ceramic coating: as a source of CaO up to the limit of 3%, $CaCO_3$ assists in the formation of the vitreous phase. CaO levels that vary from 8 to 14% favor the formation of crystalline phases such as gehlenite, wollastonite, pseudo wollastonite, and anortite.

Putties for limestone porcelain: calcium carbonates provide the CaO that are used as a flux in limestone porcelain masses.

Ceramic pigments: the calcium carbonate provides calcium oxide, which together with SnO_2 produces pink pigments.

Glasses: glasses based on NaOH and CaO use $CaCO_3$ in their composition.

Obtaining settlement mortars: as a plasticizing agent for water retention and aggregate incorporation.

Steel: $CaCO_3$ acts as a flux and pH regulator in water treatment and as lubricant for drawing steel rebars.

3.4 Specifications of raw materials for ceramic tiles

Sánchez et al. [14] defined some specification parameters for choosing raw materials for formulations of coating masses, as shown in **Table 2** below.

Calcium or magnesium carbonates can appear as coarse or small grains. If they are presented as large grains (>125 μm), they may not react completely, and the resulting oxides may rehydrate causing expansion.

In compositions of ceramic floor covering with low water absorption, $CaCO_3$ acts as a flux until the limit of 3%; above this value, $CaCO_3$ increases porosity and can be accepted up to 40% in porous coatings.

Product	(%) of carbonates	Max. particle size of $CaCO_3$ (μm)	Organic matter (%)	Sulfate content max. (%)	IP (%)
Stoned	≤3	≤125	≤0.3	0.2	20–40
Porous	≤40	≤125	≤0.3	0.2	20–40

IP: index of plasticity.

Table 2.
Specifications for choosing raw materials.

Enrique [15] recommends that the $CaCO_3$ particle size should be less than 125 μm, because particles of larger sizes, the CaO resulting from the dissociation of carbonates when calcined at 900°C, do not react with the SiO_2 present in the clays and feldspars that should form the pseudo-wollastonite and wollastonite phases, which can give rise to $Ca(OH)_2$ formed by the hydration of CaO, when the part comes into contact with the humidity of the air, generating problems of expansion by humidity, with consequent cracking.

The ceramic tile and brick industry have grown enormously in recent years in Brazil. The clays must have sufficient plasticity to provide mechanical resistance when forming by pressing, in order to guarantee the integrity of the piece in the path between the press and the oven. The feldspar contained in the clays are sources of sodium and potassium oxides, acting as fluxes at temperatures above 800°C for bricks and above 1100°C for ceramic tiles, which facilitates the formation of a vitreous phase and reduces porosity [16, 17].

Quartz is mixed with clay during geological formation. If it is present in a smaller proportion, it helps in the formation of the vitreous phase, in the degassing of organic matter and water. However, large proportions of quartz lead to a drastic reduction in mechanical strength after firing [18]. Iron oxide is present in ceramic raw materials in the form of hematite or goethite, giving the finished product a red color.

Calcite, which appears in most clays used in the production process of ceramic tiles of type BIIb, is a mineral that needs special care in its use due to its high loss to fire. When present in a proportion equal to or less than 3%, this mineral acts as a flux. However, in higher proportions, calcite can cause an increase in the final porosity of the product. In addition, the size of the calcite particle for processing ceramics must be less than 125 μm. For larger sizes, it is observed that the CaO resulting from the dissociation of carbonates can hydrate after burning, promoting variations in the dimension of the piece. Therefore, the use of limestone clays is a challenge, requiring care in processing and control in the formulation and burning of coatings. To ensure the correct sintering of the product, proper grinding and pressing of the raw material are necessary, in addition to efficient, fast burning with the lowest possible energy consumption.

4. Characterization of raw materials

4.1 Chemical analysis

Table 3 shows the chemical compositions of a typical Brazilian limestone clay used in ceramics [19]. The chemical compositions of the raw materials were determined by X-ray fluorescence spectroscopy by wavelength dispersion (WDFRX), in a Bruker S8 Tiger equipment, in which the percentages of constituent oxides were estimated by the method semi-quantitatively. For these measurements, samples with a mass of 10.0 g were pressed as discs with 40.0 mm diameter and 4.0 mm thickness. During measurements, the samples were kept in a vacuum of 10^{-6} bar. A mixture of P-10 (90% argon and 10% methane) was used in the proportional counter.

The results show that all clays are composed mainly of SiO_2 and Al_2O_3. These elements are associated with clay minerals, quartz, and feldspar structures [17]. The highest amount of SiO_2 was determined for sample C1. This component is important for the manufacture of ceramic tiles, as it improves workability and favors compaction. However, SiO_2 can also cause low mechanical strength of sintered ceramic bodies, in addition to reducing shrinkage during firing.

Oxide (%)	C1	C2	C3	C4
SiO_2	63.0	52.1	50.2	45.3
Al_2O_3	16.7	18.6	15.5	14.1
Fe_2O_3	4.7	6.8	6.2	7.1
CaO	0.9	2.1	7.2	12.7
K_2O	3.8	4.7	3.2	3.2
Na_2O	0.6	0.4	0.5	0.7
MgO	1.5	2.3	2.2	2.3
TiO_2	0.6	0.8	0.7	0.8
L.O.I	8.2	12.1	14.3	13.8

Source: Santos [19].

Table 3.
Chemical compositions of raw materials by X-ray fluorescence (XRF).

The amount of Fe_2O_3 detected in the samples was between 4.7 and 7.1%. These values are acceptable for use in ceramic tiles, such as bricks and tiles, this element being responsible for the reddish color of the sintered pieces as well as being a powerful flux [20]. The high content of calcium oxide in C4 (12%) and C3 (7%) stands out, characterizing these clays as limestone [21]. C4 clay was previously studied in Alcântara [16], which reports the formation of stains on the ceramic bodies produced with this material, after sintering at 1120°C. This behavior was associated with a high content of CaO, estimated at 10%, which during the burning phase, the dissociation of $CaCO_3$, promotes a high mass loss. C4 (13%) generates many pores, reducing water absorption and resistance of the final product. Thus, the higher the CaO content, the higher the $CaCO_3$ content and in addition, the higher the mass loss.

Analyzing the levels of alkaline oxides, it is observed that the sample C2 has the highest concentration of K_2O, while the concentration of Na_2O is approximately the same in the four samples studied. Alkaline and alkaline earth compounds have a melting effect, which facilitates the formation of liquid phase and linear shrinkage during burning [13].

Table 4 was arranged according to the increasing amount of CaO present in the clays. Note that C1 and C2 have CaO content below 3%. According to Enrique [15], CaO acts as a flux until the limit of 3% in masses of ceramic coating. The percentage of alkali oxides (Na_2O and K_2O), also presented in **Table 3**, is another major factor for the densification process, due to the great tendency of liquid phase formation during burning. Considering the sum of the percentages of CaO and alkali oxides in samples C3 and C2, it can be concluded that C2 has a higher proportion of fluxing oxides, suggesting that this sample is the most promising. On the other hand, clays

Clay	CaO (%)	$Na_2O + K_2O$ (%)
C1	0.9	4.4
C2	2.1	5.1
C3	7.2	3.7
C4	12.7	3.9

Source: Santos [19].

Table 4.
Percentage of fluxing oxides in clays determined via XRF measurement.

with a high limestone content, such as C3 and C4, tend to have greater porosity and less mechanical resistance after firing. Additionally, these two raw materials have lower alkaline oxide ratios than those observed for C3 and C2.

4.2 X-ray diffractometry

The X-ray diffraction patterns of the clays are shown in **Figure 7** and correlate positively with the results observed by X-ray fluorescence. The X-ray diffractometry (XRD) technique was used to determine the crystalline phases. The samples were dried in an oven at 110 °C for 24 h, ground, and passed through a 150-μm mesh sieve. The diffraction patterns were obtained in a Rigaku D-MAX 100 equipment, using Cu Kα1 radiation (λ = 1.5418 Å). All measurements were carried out in the continuous scanning mode with speed of 1°/min, in the range of 5 to 65° and in the range of 2 to 15° in samples saturated with ethylene glycol for 1 h to identify montmorillonite by displacing the diffraction peaks at smaller angles compared to dry sample testing. The crystalline phases were identified through Match! (Phase Identification by Powder Diffraction) in the demo version, according to the ICSD (Inorganic Crystal Structure Database).

The main phases identified were quartz, kaolinite, muscovite, montmorillonite, calcite, feldspar, and hematite. Minerals from kaolinite and montmorillonite clay were identified in all analyzed clays. According to Celik [20], these clay minerals provide the necessary plasticity to guarantee conformation through the pressing process. The percentage of each crystalline phase present in the samples was estimated from the relative intensity of the main peaks in each phase. The values are shown in **Table 5**. The percentage of carbonates increases from 0.9% in C1 to 12.4% in C4.

4.3 Dilatometric tests

To verify the dimensional changes of expansion and thermal retraction of the samples, dilatometry tests were performed on a Netzsch dilatometer, model DIL

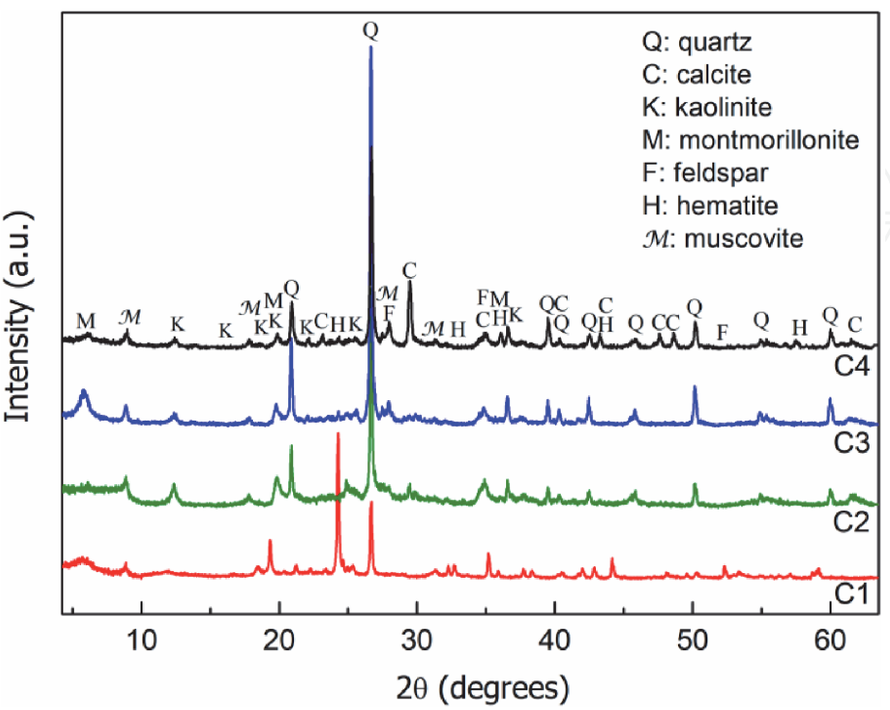


Figure 7.
X-ray diffraction patterns of the clays [19].

Minerals (%)	C1	C2	C3	C4
Quartz	55.7	51.8	65.1	57.1
Kaolinite	6.3	10.7	7.4	5.5
Muscovite	11.8	14.0	11.2	12.1
Montmorillonite	5.6	4.9	4.6	6.7
Calcite	8.6	2.8	1.1	13.7
Feldspar	6.3	9.9	6.2	3.2
Hematite	5.7	5.9	4.4	1.7

Table 5.
Mineralogical compositions of clays determined by XRD.

402PC, under synthetic air flow at 130 ml/min. For these analyses, the samples were compacted in a cylindrical shape, 12.0 mm in length and 6.0 mm in diameter. Under a constant heating rate of 10°C/min, the length of the compacted body is measured as a function of time and temperature, which varied from room temperature to 1150°C.

In **Figure 8** we can observe a slight expansion in all curves up to approximately 850°C, and at 573°C, the expansion was more pronounced due to the transformation of α quartz to β [22, 23], except for C2, which presents a lower percentage of free quartz. From 573°C, there was a gradual reduction in the expansion rate, occurring or starting with sintering, followed by an exponential retraction [22].

The results shown in **Table 5** with the percentages of CaO, Na_2O, and K_2O recommended by XRF measurements point out that sample C2 has a greater amount of funds (calcium carbonate up to a limit of 3% and alkaline oxides), or what is known as a greater linear shrinkage. Despite its advantages over the other samples, the C2 clay underwent deformation during firing up to 1150°C. This effect, known as pyroplastic deformation, may be due to the large proportion of funds in the sample, a high content of Fe_2O_3, and, even, the amount of organic matter [24]. One of the ways to control deformation during firing is to adjust the thermal cycle

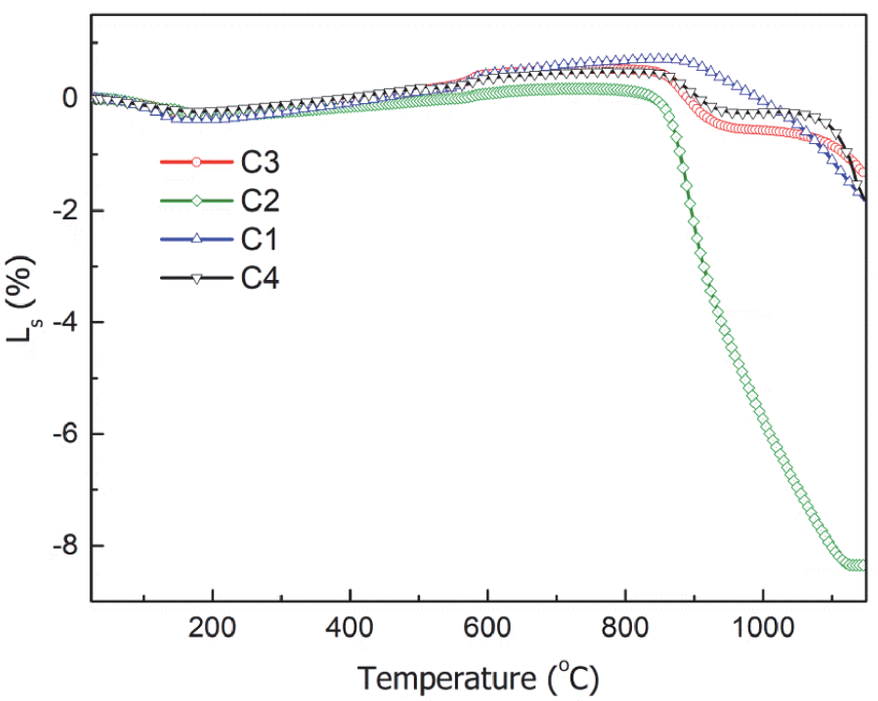


Figure 8.
Dilatometric curves of clays at a heating rate of 10°C/min [19].

through the dilatometric curves, so that the plate remains within the required standards [25].

4.4 Firing clays with limestone

Clays containing limestone when subjected to burning, $CaCO_3$ after heating, in the temperature range between 850 and 920°C, form CaO and release CO_2. An

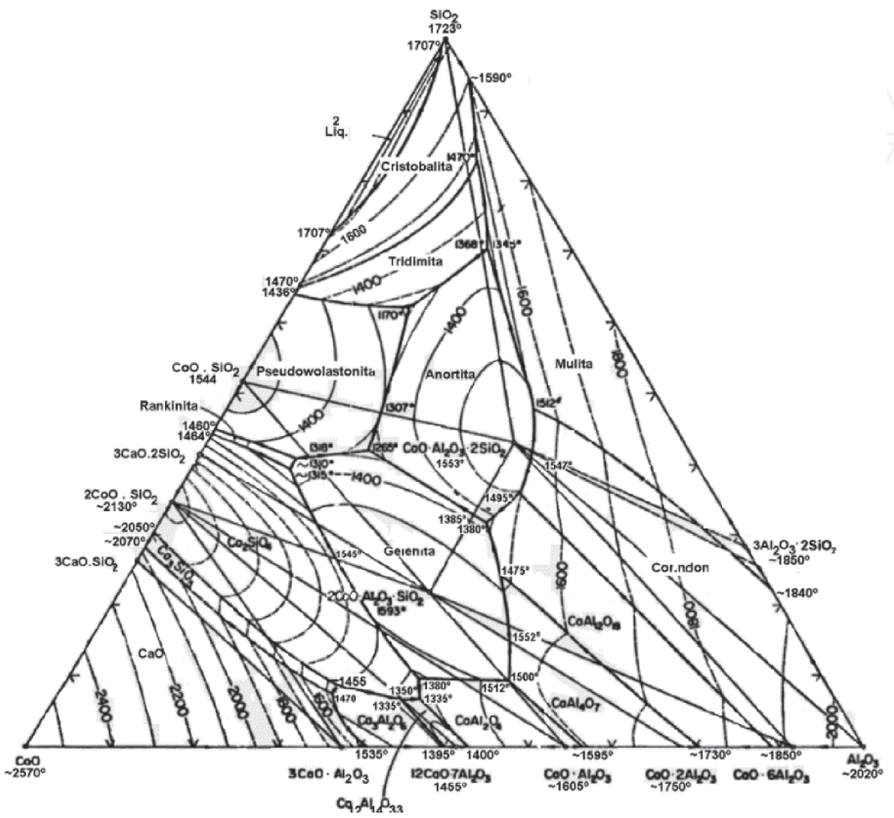


Figure 9.
Ternary diagram of CaO, SiO_2, and Al_2O_3.

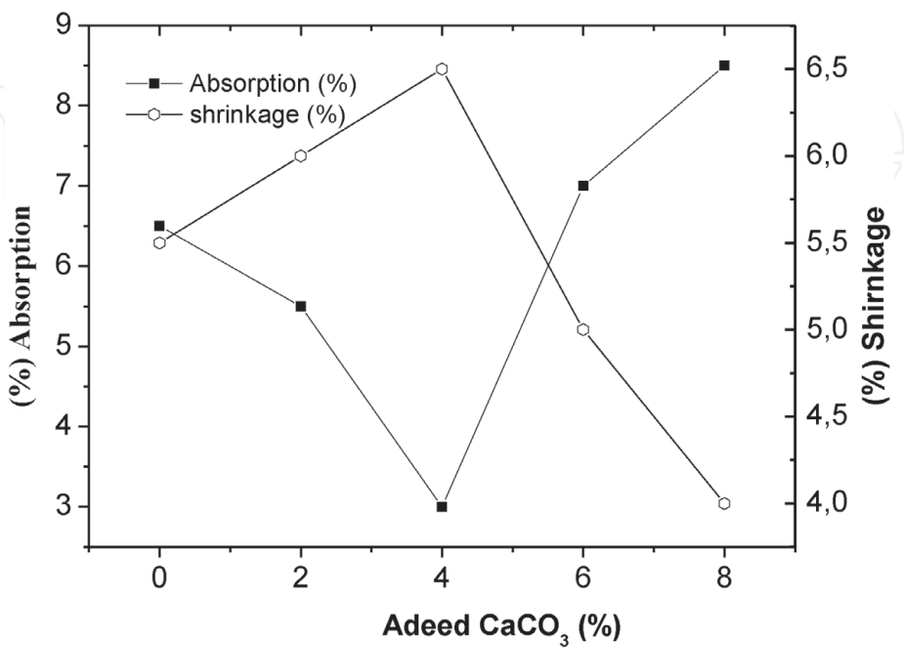


Figure 10.
Ceramic coating mass with incorporated calcite waste.

intense endothermic peak of approximately 35–44% of the mass loss can be observed in differential thermal analysis. In ternary diagrams, it is observed that there is a eutectic point (above 1170°C), which reduces the dimensional stability in ceramic products, which can melt quickly (**Figure 9**).

Clays when mixed with limestone can behave differently, as shown by Sánchez [25]. **Figure 10** shows a standard clay with 5 and 10% of incorporated limestone. It was observed that as the limestone and temperature increase, respectively, the dimensional instability increases. In other words, the retraction increases constantly, when it undergoes an exponential increase, reaching the melting point.

This phenomenon can be explained as follows: when exhibiting CaO up to the limit of 3%, this, associated with SiO_2 and Al_2O_3 present in clays and feldspars,

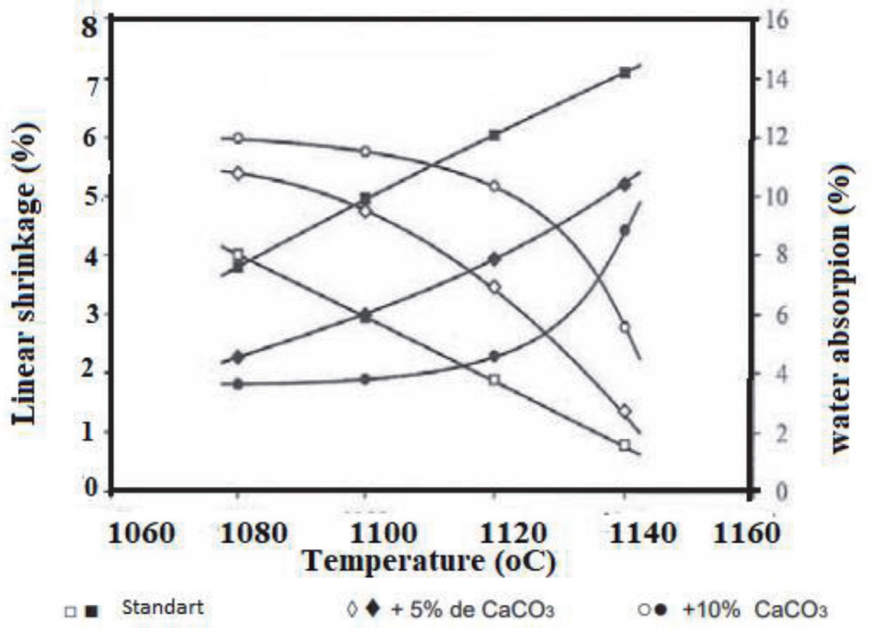


Figure 11.
Firing curve of a calcite clay.

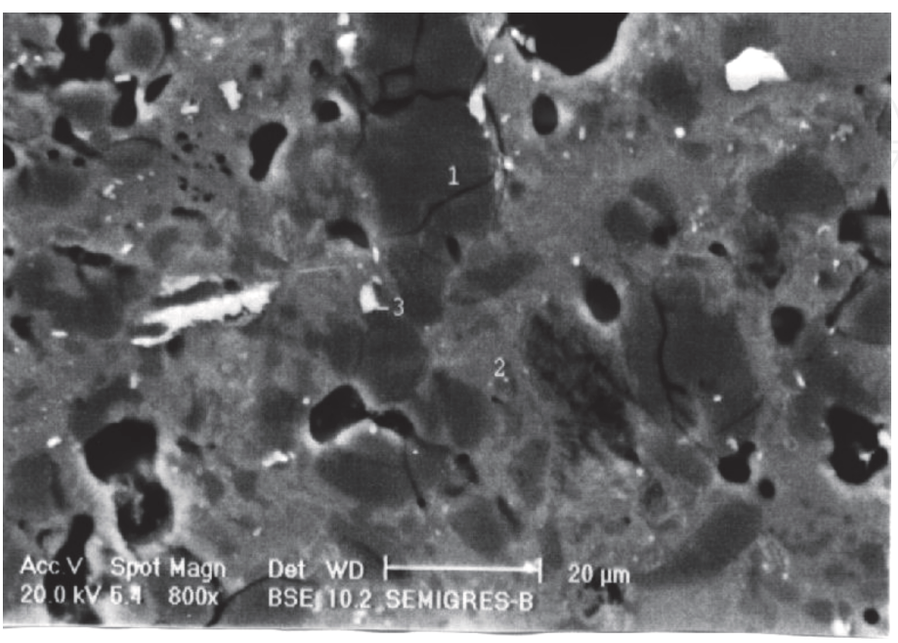


Figure 12.
Scanning electron microscopy of a ceramic with 10% of CaO.

helps in the formation of eutectic systems at 1170°C, with consequent formation of liquid phase and contributing to obtain the desired mechanical strength and porosity. When introduced in percentages above 4%, $CaCO_3$ levels are increased, and the composition moves from the eutectic line, forming crystalline phases such as $CaSiO_3$ (pseudo-wollastonite) and $2CaO{\cdot}Al_2O_3{\cdot}SiO_2$ (gehlenite). So, a larger number of pores is left by the eliminated CO_2. In this way, the porosity of the final product is increased, as shown in **Figure 11**. In **Figure 12** is shown a photo of a clay mass with 10% calibration in which the porosity exerted can be observed.

5. Conclusions and perspectives

Limestone is a contaminant for clay that above 125 μm can cause expansion and consequently cracks.

Rapid tests that mix clay with HCl can promote effervescence due to the release of CO_2 and contribute to decrease the amount of limestone.

In the ceramic industry, wet grinding of components is carried out in ball mills and grinding will be more efficient if the sieves are 150 to 325 μm. In ceramic mass formulations, the amount of CaO up to 3% contributes to the formation of the vitreous phase, however, between 8 and 14%, it favors the formation of crystalline phases, reducing the absorption of water and increasing the mechanical resistance.

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