INFLUENCE OF THE PHASES PRESENT IN CLAY-BASED WALL AND FLOOR TILES ON CERAMIC TECHNICAL PROPERTIES

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ABSTRACT

In this study, the end ceramic characteristics and the amorphous and crystalline phases present were determined in clays from various geological sites in the department of Cundinamarca-Colombia, each with a different chemical and mineralogical composition, after being fired at three temperatures (1050°C, 1100°C and 1150°C), in order to identify the influence of these phases on their technical ceramic properties. The clays were characterised chemically by X-ray fluorescence, followed by mineralogical characterisation, and the determination of phases after firing using X-ray diffraction. From this study, it can be concluded that the phases present in the end product affect its ceramic technical properties, which are conditioned by its mineralogy, the chemical composition of the raw materials, and by temperature. Thus, it was observed that the amorphous phase and mullite help to increase mechanical strength; however, the

percentage of amorphous phase should not be too high, as it causes deformations. High amounts of quartz can lead to a decrease in mechanical strength. Magnesium-based minerals such as chlorite act as fluxes and are responsible for liquid phase formation, which accelerates the sintering process, while anorthite is beneficial, because it helps to stabilise the ceramic tiles.

1. INTRODUCTION

Within the ceramic industry, there exists a wide variety of products that are mainly conditioned by the characteristics and behaviour of their clays at each stage of the production process, especially in the firing stage, where clays undergo a series of chemical reactions and physical transformations that significantly influence the ceramic technical properties of the end product [1-7]. However, these properties often vary depending on the chemical and mineralogical composition of the original clay [8-12], sometimes displaying exceptional and at other times, not so exceptional, properties. Therefore, it is necessary to understand the main causes that lead a clay to behave better or worse for the ceramic industry, taking into account that these materials are of very variable nature and origin, made up of a number of different clay minerals that rarely appear in a pure state, which is why it is important to ascertain what the most adequate mineralogical compositions are for manufacturing clay-based wall and floor tiles, and how those minerals react under production conditions, specifically in the firing stage [13-18].

In this sense, the purpose of this work was firstly to study the mineralogical changes that take place during the sintering process in different clay samples and to determine how those changes influence the properties of the end product. Thus, the relationship can be found between chemical composition, clay mineralogy and the phases formed in the firing process, since the technological properties of fired clays are strongly dependent on the mineralogy and chemical composition of the original clay, so that such knowledge would enable the firing process and the properties of the end product to be optimised. The second purpose was to attempt to establish what processing conditions need to be set to obtain a product with uniform characteristics and with suitable properties for use in the formulation of ceramic wall and floor tile bodies.

2. MATERIALS AND METHODS

The experimental stage of this study included the chemical and mineralogical characterisation of 18 clay samples and determining the phases in ceramic test-pieces obtained from those samples, which were subjected to firing at three different temperatures: 1050°C, 1100°C and 1150°C. These temperatures were chosen because they correspond to the temperatures used in the industrial firing of group BIIb ceramic tiles. For the chemical characterisation, a Philips MagixPro PW-2440 X-ray fluorescence spectrometer equipped with a Rhodium tube and maximum power of 4 KW was used. Both the initial and post-firing mineralogical composition were determined by X-ray diffraction (XRD) using a BRUKER ADVANCE D-8 diffractometer fitted with a copper anode. To obtain the necessary readings, the equipment was configured to operate at an intensity of 30 mA, voltage of 40 kV, typical 2θ range from 20 to 60°, speed of 2°/min, and steps of 0.02. The quantity of each mineral present in the clays was determined using the results obtained from the chemical analysis by taking each of the eight main oxides, calculating for each clay the percentages of the minerals assignable to each element starting with the most limiting ones, and then applying the traditional method of calculation using the gram molecular weight of each mineral and its components, which allowed for an approximately semi-quantitative definition to be made of the mineralogical composition of the clays [19]. The phases present in each of the fired clay test pieces were determined by identifying the various peaks in the diffractograms obtained using the interlaminar distances, as these provide the information required to identify the different phases present. The quantitative analysis was made using EVA software and the PDF2 database of the XPowder program, which is based on non-linear least squares fit for the full diffractogram versus a weighted combination of diffraction diagrams taken directly from the database.

3. RESULTS AND DISCUSSION

A total of 18 clays were included in the study, organised into groups based on their mineralogy. To do so, clays that had the same mineralogical composition or one predominant or common mineral were sorted into the same group, giving a total of six groups. To display the results, a sample was chosen for each group, given that clays in the same group returned very similar results and behaviour patterns. Table 1 outlines the groups, their mineralogical composition and respective samples. The minerals in bold type are the predominant or common mineral used to classify them, while the samples underlined and in bold type were the ones chosen from each group to present the results.

GR	MINERALOGY	SAMPLES
1	Caolinita, Illita, Montmorillonita, Illita-Montmorillonita, Cuarzo	0-0089; 0-0135; 0-0121; 0-0013 ;0-0124; 0-0128; 0-0105; 0-0134; **0-0118**
2	**Pirofilita**, Illita, Cuarzo, Illita-Montmorillonita.	**0-0104**; 0-0091
3	**Clorita**, Illita, Cuarzo, Montmorillonita, Illita-Montmorillonita	0-0109; **0-0096**; 0-0119; 0-0129
4	**Calcita**, Caolinita, Illita, Cuarzo, yeso.	**0-0093**
5	**Cuarzo**, Caolinita, Montmorillonita.	**0-0108**
6	**Pirofilita, Clorita, Dolomita,** Cuarzo, Caolinita, Illita.	**0-0103**

***Table 1**. Classification of clays according to their mineralogy*

3.1. CHEMICAL AND MINERALOGICAL COMPOSITION

Tables 2 and 3 show the results of the chemical and mineralogical characterisation of the clays chosen for the presentation of results.

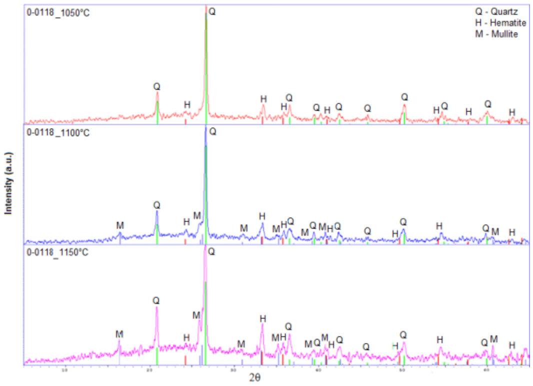
ELEMENT	SAMPLE CODE					
	0-0118	0-0104	0-0096	0-0093	0-0108	0-0103
	%	%	%	%	%	%
SiO_2	58.22	55.48	56.82	44.74	72.56	46.08
Al_2O_3	17.85	25.54	17.65	19.1	11.36	24.64
Fe_2O_3	8.02	2.06	7.6	3.77	5.22	8.77
K_2O	2.47	3.43	1.91	1.31	0.78	2.75
TiO_2	0.97	1.19	0.95	0.67	0.69	0.94
MgO	1.54	0.37	1.75	0.54	0.39	1.59
CaO	0.32	0.1	1.08	8.00	0.82	2.72
Na_2O	0.17	0.48	0.81	0.15	0.08	0.33
P_2O_5	0.17	0.07	0.1	0.32	0.28	0.25
MnO	0.05	0.01	0.07	0.01	0.05	0.05
LOI	10.22	11.27	11.26	21.39	7.77	11.88

Tabla 2: *Composición química de todas las arcillas*

MINERALOGY	SAMPLE CODE					
	0-0118	0-0104	0-0096	0-0093	0-0108	0-0103
	%	%	%	%	%	%
Kaolinite	31.23			46.72	25.92	17.63
Illite	10.98	16.10	21.47	10.96		16.71
Interbedded	10.27					7.08
Quartz	34.51	45.00	32.25	23.34	59.81	12.78
Hematite	8.02		4.37		5.22	7.91
Calcite				12.36		
Gypsum				6.62		
Montmorillonite	4.99		18.01		9.05	
Chlorite			23.90			7.68
Pyrophyllite		38.90				25.04
Dolomite						5.17

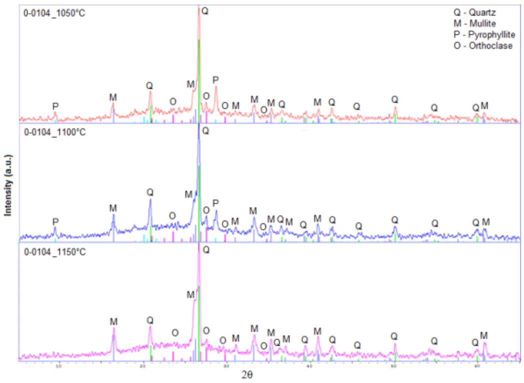
Table 3*: Mineralogical composition of all clays*

3.2. PHASE COMPOSITION AFTER FIRING



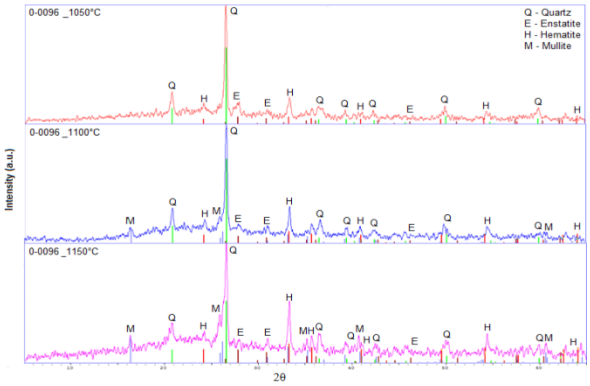
Graph 1: *Diffractograms of sample 0-0118 at the 3 temperatures*

As can be seen in Graph 1, the fired clay test pieces in Group 1, represented by sample 0-0118, generally comprised 4 main phases: quartz, mullite, hematite and amorphous phase. In all fired clay samples, quartz is a component of the original clay and diminishes as temperature increases, when part of the quartz dissolves in the matrix, forming more fluid and viscous liquid and therefore more amorphous phase, which grows as firing temperature increases. In all the fired clay samples in this group, mullite appeared at 1100°C and its proportion increased significantly at 1150°C. Hematite is also a component of the original clay and increases as temperature goes up [20].



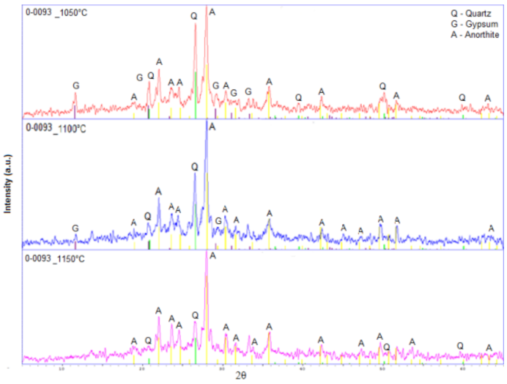
Graph 2: *Diffractograms of sample 0-0104 at the 3 temperatures*

Graph 2 shows the results obtained for clay 0-0104 that represents Group 2 clays, in which pyrophyllite is a common mineral among them. From these samples, the formation of mullite from 1050°C onwards is worth noting and can be explained by the pyrophyllite content in the samples, the presence of which increases mullite formation [21]. The diffractograms (Graph 2) show crystalline dehydroxylated pyrophyllite detected at temperatures of 1050°C and 1100°C, which, when thermally decomposed, forms mullite. The pyrophyllite gradually disappears as the temperature rises, while mullite increases. Apart from quartz, the presence of orthoclase is also observed, which is triggered by the high content in illite, which provides the potassium required for this phase to form. In addition to the presence of quartz.



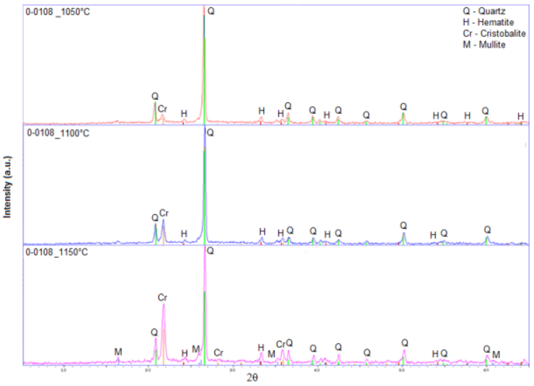
Graph 3: *Diffractograms of sample 0-0096 at the 3 temperatures*

In regard to the clays in Group 3, represented by sample 0-0096, in addition to quartz, mullite and hematite, the presence of enstatite is significant as a new phase, which can be seen from 1050°C onwards in all the samples in the group and which remains relatively constant at all three temperatures. The formation of an enstatite phase is mainly due to the presence of chlorite, because, as the results of the mineralogical composition (Table 3) reveal, this clay has more than a 20% proportion of chlorite. The diffractograms (Graph 3) also show quite a significant increase in amorphous phase as temperature increases. This is mainly due to magnesium compounds that act as fluxes, as well as the presence of illite.



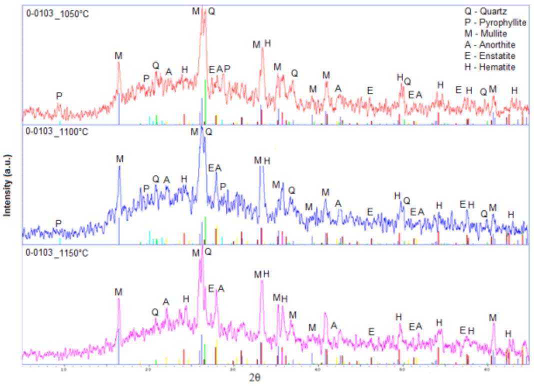
Graph 4: *Diffractograms of sample 0-0093 at the 3 temperatures*

Sample 0-0093 corresponding to Group 4 exhibits calcite and gypsum in its original composition, as can be seen in the mineralogy (Table 3). During firing, these minerals undergo transformations: for example, gypsum decreases as the temperature rises, as shown in the diffractograms (Graph 5), where its presence is no longer visible at a temperature of 1150°C. In this sample, it is important to highlight the formation of anorthite as a new phase, which is driven by the presence of calcite in the sample, since according to the results of the chemical and mineralogical analyses, the calcium oxide content is 8% and calcite mineral content is 12.36%. This new phase was observed from 1050°C and increased as temperature went up. Apart from the presence of quartz, which, as in all the groups, is a component of the original clay and decreases with increasing temperature.



***Graph 5**: Diffractograms of sample 0-0108 at the 3 temperatures*

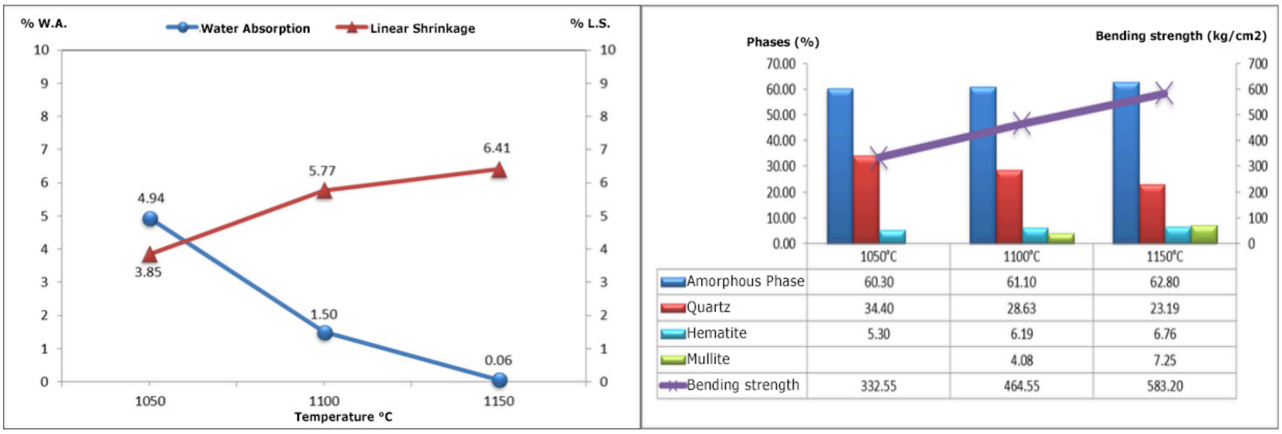
In the diffractograms of sample 0-0108 (Graph 5), the presence of cristobalite can be seen from 1050°C on, which could be explained by the high SiO_2 content this clay has, since according to the chemical analysis (Table 2), it appears in the highest proportion of all the clays under scrutiny. The amorphous phase decreases at 1150°C, because part of the amorphous silica recrystallizes to form cristobalite, which increases very sharply at 1150°C and also starts forming part of the mullite that develops at this temperature.



***Graph 6**: Diffractograms of sample 0-0103 at the 3 temperatures*

Interestingly, sample 0-0103 exhibits mullite after 1050°C, which may be explained by the presence of pyrophyllite in the sample, as was seen in the results of Group 2, where the common mineral was pyrophyllite, leading to the formation of mullite at such low temperatures. In this sample, the amorphous phase increased as the firing temperature went up and returned values of over 70%. Hematite increased with temperature, while quartz simultaneously went down. The presence of chlorite led to enstatite forming, as was observed in Group 3, where the fired clay exhibited enstatite as a phase thanks to the presence of chlorite in the sample. The presence of anorthite was also observed, thanks to the calcium provided by the dolomite.

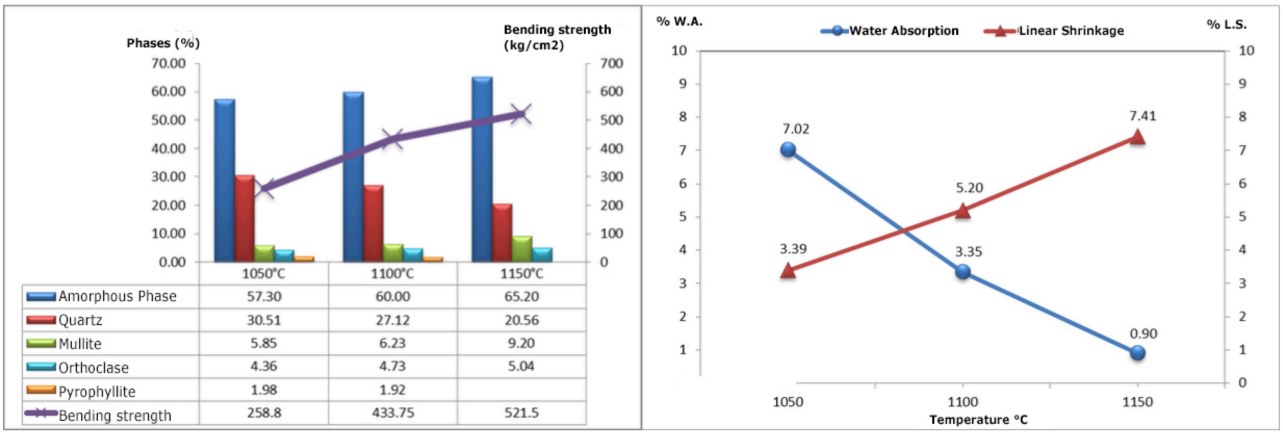
3.3. INFLUENCE OF PHASES ON CERAMIC BEHAVIOUR



	1050°C	1100°C	1150°C
Amorphous Phase	60.30	61.10	62.80
Quartz	34.40	28.63	23.19
Hematite	5.30	6.19	6.76
Mullite		4.08	7.25
Bending strength	332.55	464.55	583.20

FIgure 7*: Relationship between the phases and ceramic properties (water absorption, linear shrinkage and mechanical strength) in Sample 0-0118*

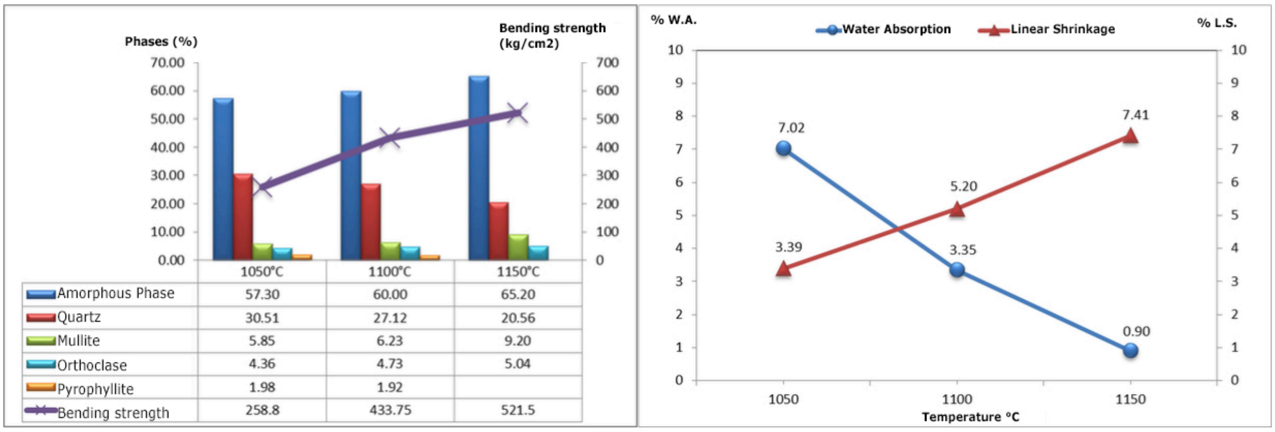
The vitrification curve (Figure 7) for fired clay sample 0-0118 exhibits typical behaviour, in which the sample's fired shrinkage increases as water absorption decreases. At 1150°C, water absorption is seen to be very low (0.06%), which indicates low porosity and therefore a significant increase in mechanical strength in excess of 500 kg/cm^2 at this firing temperature. These clay samples contain illite, which favours sintering, enabling liquid phase formation, in which the mullite phase crystallizes. The mullite phase also significantly helps increase mechanical strength.



	1050°C	1100°C	1150°C
Amorphous Phase	57.30	60.00	65.20
Quartz	30.51	27.12	20.56
Mullite	5.85	6.23	9.20
Orthoclase	4.36	4.73	5.04
Pyrophyllite	1.98	1.92	
Bending strength	258.8	433.75	521.5

Graph 8*: Relationship between phases and ceramic properties (water absorption, linear shrinkage and mechanical strength) in Sample 0-0104*

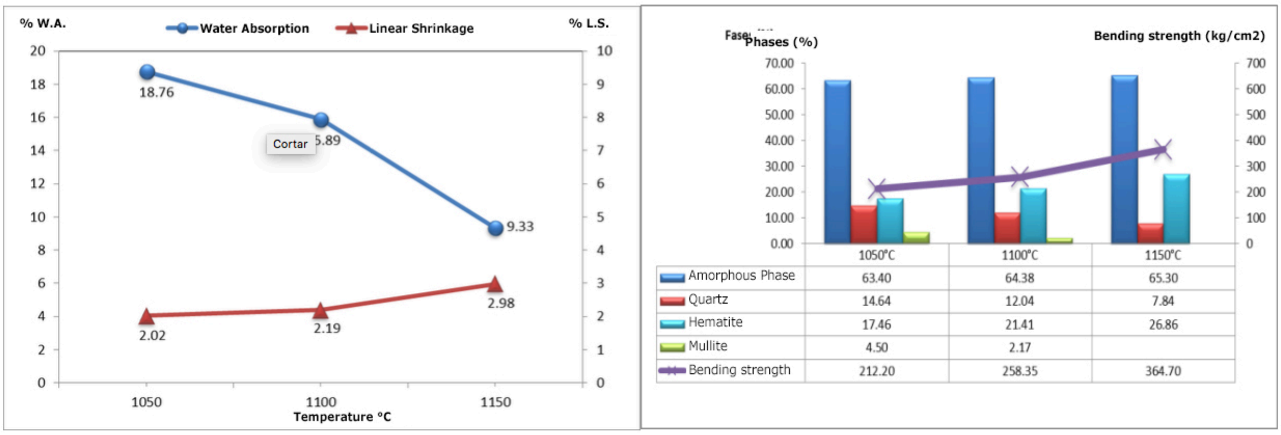
Graph 8 shows the data for the ceramic properties of Clay 0-0104, where the most prominent feature is the high mechanical strength displayed as firing temperature increases. Such high mechanical strength in these samples can be explained mainly by two factors: the first one is that a higher content of mullite results in higher strength, since it must be remembered that this sample exhibited the highest mullite content of all the samples analysed in the study and, furthermore, that it is present from 1050°C. The second factor is that these samples have a rather high amorphous phase, which reduces porosity, thus leading to diminished water absorption. As the graph shows, at a temperature of 1150ºC, water absorption is less than 1%, which leads to an increase in mechanical strength.



	1050°C	1100°C	1150°C
Amorphous Phase	57.30	60.00	65.20
Quartz	30.51	27.12	20.56
Mullite	5.85	6.23	9.20
Orthoclase	4.36	4.73	5.04
Pyrophyllite	1.98	1.92	
Bending strength	258.8	433.75	521.5

***Graph 9**: Relationship between phases and ceramic properties (water absorption, linear shrinkage and mechanical strength) in Sample 0-0096*

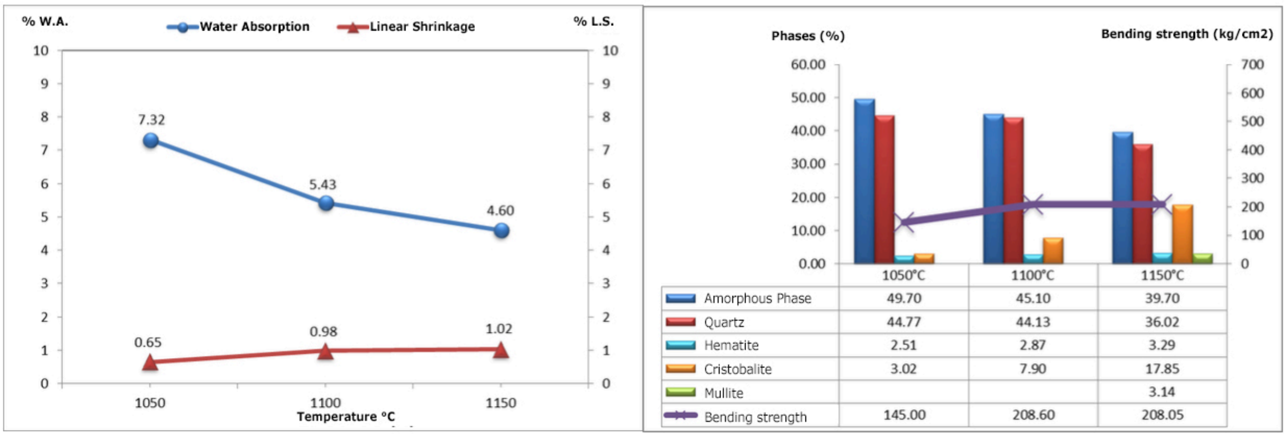
As can be seen in Graph 9, Sample 0-0096 has a significant amount of amorphous phase, leading to deformations in the sample, since high amorphous phase contents can generate defects [22]. That is why at a temperature of 1150°C, it was not possible to obtain data on ceramic properties and mechanical strength, since the specimen reached its sintering temperature at 1100°C. With a mineralogy rich in fluxing minerals such as illite, feldspars and chlorite, vitrification is achieved at lower temperatures. Thanks to the significant vitrification that takes place at this temperature range, resulting in higher amorphous phase content and therefore lower porosity, very low percentages of water absorption were obtained, which at 1100ºC, were already less than 1%. This is a very significant factor that may explain the high mechanical strength of these samples, apart from the presence of mullite.



	1050°C	1100°C	1150°C
Amorphous Phase	63.40	64.38	65.30
Quartz	14.64	12.04	7.84
Hematite	17.46	21.41	26.86
Mullite	4.50	2.17	
Bending strength	212.20	258.35	364.70

***Graph 10**: Relationship between phases and ceramic properties (water absorption, linear shrinkage and mechanical strength) in Sample 0-0093*

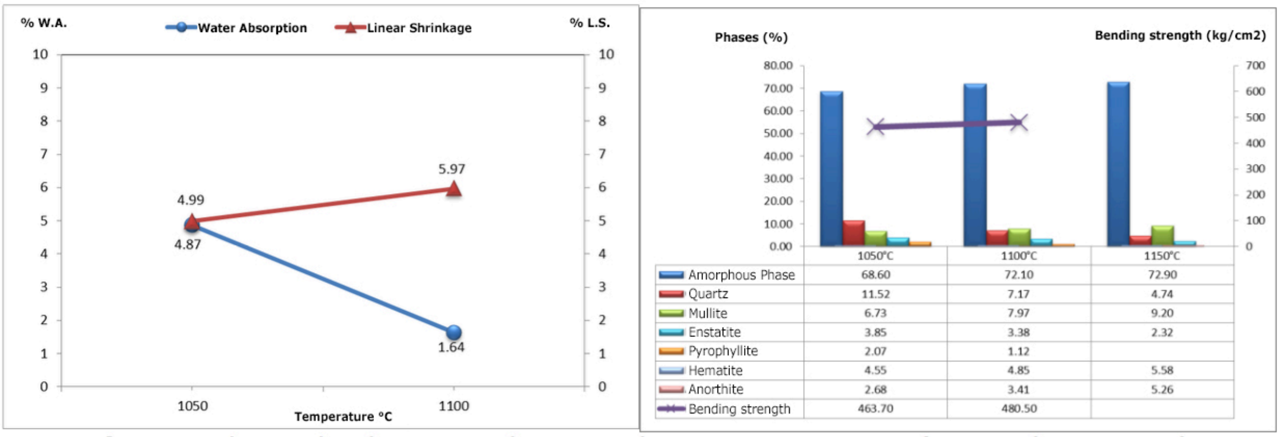
The vitrification curve for sample 0-0093 (Graph 10) shows that parameter readings do not vary significantly, with high percentages of water absorption and less shrinkage at each of the firing temperatures, indicating that it is not very sensitive to temperature change. Such behaviour is due to the presence of calcite (CaCO3), which, together with quartz (SiO2), enables anorthite crystallization, thus helping to stabilise dimensional changes, as well as the evolution of CO2 outside the structure of the fired samples, which tends to create a porous structure [23]. Total porosity gradually increases due to the evolution of a greater amount of CO2 outside the structure, so that, even with such high water absorption at 1150°C, it appears that a certain amount of porosity exists that influences the properties of this clay sample. The increase in mechanical strength observed at a temperature of 1150°C may be contradictory to the above, since mechanical strength is influenced by the sample's porosity, but it can be explained by the formation of anorthite (CaAl2Si2O8), which has high mechanical strength [24], and so the anorthite content offsets the high porosity. In clays with a high calcite content, flexural strength depends on the crystalline phase content and is directly related to the calcium carbonate content [25]. Generally, the presence of crystalline phases in the ceramic matrix affords the tile high mechanical strength.



	1050°C	1100°C	1150°C
Amorphous Phase	49.70	45.10	39.70
Quartz	44.77	44.13	36.02
Hematite	2.51	2.87	3.29
Cristobalite	3.02	7.90	17.85
Mullite			3.14
Bending strength	145.00	208.60	208.05

***Graph 11**: Relationship between phases and ceramic properties (water absorption, linear shrinkage and mechanical strength) in Sample 0-0108*

The high silica content in Sample 0-0108 could explain its very low mechanical strength, as demonstrated in Figure 11, since according to [26] "An increase in the percentage of silicon leads to the material having lower mechanical strength". Accompanied by the scant formation of the amorphous phase "The differences between the thermal expansion of the quartz grains and the liquid phase cause mechanical stress, which can produce microcracks". The vitrification curve (Graph 11) shows that this clay's reactivity with temperature is very low and indeed it has a refractory behaviour, in which, as temperature rises, shrinkage remains almost constant, while water absorption decreases slightly. Therefore, it is important to emphasise that the presence of high amounts of quartz in the samples can lead to lower mechanical strength in the material, as the results for this sample show.



	1050°C	1100°C	1150°C
Amorphous Phase	68.60	72.10	72.90
Quartz	11.52	7.17	4.74
Mullite	6.73	7.97	9.20
Enstatite	3.85	3.38	2.32
Pyrophyllite	2.07	1.12	
Hematite	4.55	4.85	5.58
Anorthite	2.68	3.41	5.26
Bending strength	463.70	480.50	

***Graph 12**: Relationship between phases and ceramic properties (water absorption, linear shrinkage and mechanical strength) in Sample 0-0096*

This fired clay sample has a high amount of amorphous phase, resulting in deformations of the sample, since high amorphous phase contents can cause defects, which is why, at a temperature of 1150°C, it was not possible to obtain water absorption, linear shrinkage and mechanical strength readings, since this sample reaches its sintering temperature at 1100°C. This behaviour may be because the mineralogy of this clay is rich in fluxing minerals, such as illite, feldspar or chlorite, which reach vitrification at lower temperatures. The high mechanical strength (Graph 12) displayed by this sample may be explained by several theories, the first being that a higher mullite content results in higher strength, as noted above. However, there is another factor that has an influence on the mechanical strength of the ceramic, namely that, as seen in earlier samples, the amorphous phase is quite high in this sample. A moderate increase in temperature means greater shrinkage and also a higher tendency to deform. An excessive increase in firing temperature causes tile bloating, while the significant decrease in viscosity in the liquid phase leads to a considerable increase in pyroplastic deformation in the tiles.

4. CONCLUSIONS

The phases present in the end product are the main factor affecting its technical ceramic properties, while it is also conditioned by the mineralogy, chemical composition of the raw materials, and temperature.

The most frequent phases that can be found in clay specimens following the firing stage are: glassy phase, quartz, hematite, mullite, cristobalite, enstatite when chlorite or dolomite are present in the clay, while the main feldspars are anorthite, when calcite or dolomite are present in the clay, and orthoclase, when it has a high K_2O content.

The glassy phase in a range of 57% to 66% helps to produce high mechanical strength, reduces porosity, but does not affect the final form of the calcined clay sample. However, above 66%, it is detrimental to the sample's ceramic properties, as it causes deformation.

Quartz decreases as the firing temperature increases, which indicates partly dissolution as the liquid phase forms. The presence of high amounts of quartz in the samples may lead to a decrease in the material's mechanical strength.

Firing temperature can be an important factor to reduce the problem of cracking caused by allotropic changes in the quartz, as it causes the quartz to dissolve.

The presence of anorthite and enstatite as phases help in the end properties of the fired clay samples, because they provide greater dimensional stability and low expansion coefficients.

Mullite ($3Al_2O_3 \cdot 2SiO_2$) is a characteristic constituent of ceramic products. Mullite has high refractoriness, low thermal expansion, low thermal conductivity, and it increases tile mechanical strength thanks to its crystallization and good thermal stability. Mullite usually forms from metakaolinite - the variables that can affect the formation of mullite include kaolinite content, firing behaviour, the presence of pyrophyllite, and the possible presence of alkaline and alkaline-earth oxides.

During the ceramic process, specifically in the cooling stage, attention should be paid to whether the tile has cristobalite as a phase, because the inversion of alpha to beta cristobalite occurs at a temperature of 220ºC to 275°C, with a cubic expansion or shrinkage of 5.6%, which would be detrimental to the end properties of the tile if not taken into account when the kiln cooling curve is being adjusted.

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