

Article

Firing Parameters Effect on the Physical and Mechanical Properties of Scheelite Tailings-Containing Ceramic Masses

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Abstract: The firing parameters in ceramic masses incorporated with 0, 5, and 10 wt% of scheelite tailings were investigated. The ceramic masses were characterized by X-ray fluorescence, granulometric, mineralogical analysis, and Atterberg limits determination. The samples were obtained by uniaxial pressing (20 MPa), sintered at different temperatures (800, 900, and 1000 °C), and heating rates (5, 10, 15, and 20 °C·min⁻¹). Physical and mechanical tests (water absorption, apparent porosity, and flexural strength) and mineralogical tests were accomplished from the sintered samples. Natural aging tests were also carried out to assess carbonation resistance. For this, some samples were kept in an internal environment (inside the laboratory) for 3 months. The results showed a high content of calcium oxide in the scheelite tailings and a reduction in the plasticity index of the ceramic masses with the tailings addition. The best results were observed for the ceramic mass with 5% tailings. The best results were observed regarding the firing parameters for the temperature equal to 1000 °C, increasing the heating rate to 10 °C·min⁻¹ without compromising the material properties. The samples kept in an internal environment for 3 months showed a loss of physical and mechanical properties. Such behavior probably occurred due to the onset of the carbonation phenomenon.

Keywords: scheelite tailings; sustainable ceramic mass; red ceramic; firing parameters



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1. Introduction

The increase in the global population results in an unrestrained rise in waste generation (industrial, mining, domestic, hospital, etc.), which often does not have the correct disposal, causing severe social and environmental problems. The massive tailings amount generated in mining activities has stimulated research interest to use these tailings to develop friendly construction materials [1–4]. Thus, the construction industry has been the target of research due to its potential tailings reuse [5–7]. The construction industry has been considered the largest consumer of waste, generating sustainability, conserving natural resources, and mitigating the adverse effects of tailings on the environment.

On the other hand, the tailings incorporation into the ceramics industry makes it possible to reduce the extraction of natural raw materials, avoid degrading native areas, apply correct disposal and recycling of waste, and generate a product higher-value-added [8]. Traditional ceramic products, such as roof tiles, blocks, and ceramic tiles, allow incorporating different tailings types due to their diversified composition. In recent years, some research has been carried out to incorporate the most varied types of tailings in

ceramic masses destined for traditional ceramic pieces production [9–14]. In this sense, several mining tailings, such as kaolin waste [9,10], waste from phosphate mines [11], iron ore tailings [12], red mud from the Bayer process [13,14], tailings from silver mines [15], quartzite [5,16,17], and scheelite [5,6] have been successfully reused in the production of sustainable ceramic materials.

Scheelite (CaWO_4) is a typical tungstate mineral, which is used to produce tungsten, which is usually associated with other minerals that contain calcium, such as calcite (CaCO_3), fluorite (CaF_2), and fluorapatite [$\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$] [1,18,19]. In beneficiation, the ore goes through the screening, crushing, and grinding processes, placed in jigs that feed the vibrating tables which separate the concentrate from the tailings. In this last stage, the scheelite tailings are generated, which has no use for the industry and is improperly deposited.

An important issue for the use of waste as an alternative raw material in the ceramic field is the knowledge of its chemical components, in addition to the mineralogical and physical characteristics [20]. Products obtained with clay-based compositions can be reinforced using mixtures of clay and calcite to form micro-composites, such as anorthite grains ($\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) in the silico-aluminous matrix, which favors a significant increase of resistance [21]. Therefore, the addition of tailings rich in calcium oxide, such as scheelite tailings, may favor the formation of anorthite.

It is well known that the increase in the firing temperature in clay-based ceramics produces a series of reactions and transformations that lead to the formation of new phases and the disappearance of others [22]. Therefore, it is necessary to analyze the quality of the ceramic masses, monitor, and understand the mineralogical transformations that occur during the firing process. The insertion of rapid firing in the ceramic material firing stage has been studied [23,24]; however, much still needs to be investigated, especially in masses containing tailings.

On the other hand, calcium silicate phases, such as gehlenite and anorthite, are potential sources of CaO and can favor carbonation. Carbonation is the process in which the CO_2 present in the atmosphere reacts with calcium hydroxide forming calcium carbonate that precipitates inside the microstructure, which can change its porosity [25,26]. Carbonation occurs mainly in materials rich in calcium oxide and can deteriorate the material with property loss [22]. Most research on carbonation is carried out with a focus on concrete and cementitious materials [27,28]. However, the carbonation process also occurs in ceramic construction materials, and studies aimed at these materials still need to be better explored since carbonation can affect its durability [29].

Although the use of scheelite tailings in the production of ceramic materials has already been reported in the literature, the influence of these tailings on the properties of traditional ceramic products, especially regarding carbonation resistance, still needs to be studied. Therefore, the objective of this work was to analyze the physical and mechanical properties and the carbonation resistance of samples obtained from the ceramic masses (used in the manufacture of ceramic blocks) containing 0, 5, and 10% scheelite tailings. The influence of different firing parameters (temperature (800, 900, and 1000 °C) and heating rate (5, 10, 15, and 20 °C·min^{−1}) on physical and mechanical properties (water absorption, apparent porosity, and strength flexural) was investigated. The carbonation resistance was evaluated in the specimens after 3 months of exposure to natural environmental conditions.

2. Materials and Methods

2.1. Raw Materials

Scheelite tailings were obtained from a tungsten mining company (Brejuí mine) located at Currais Novos city, Rio Grande do Norte state, Brazil. Three types of scheelite tailings from different mining stages were used to obtain the samples. Such tailings were denominated ST1, ST2, and ST3. The ceramic mass used as standard (MR) was donated by a red ceramic company located at Soledade city, Paraíba state, Brazil. The as-received scheelite tailings (ST1, ST2, and ST3) are shown in Figure 1a–c.



Figure 1. Scheelite tailings investigated (a) ST1, (b) ST2, and (c) ST3.

2.2. Incorporation of Scheelite Tailings in the Ceramic Mass and Preparation of Specimens

The scheelite tailings (ST1, ST2, and ST3) were added to MR at different contents (0 wt%, 5 wt%, and 10 wt%). The choice of incorporation contents of 5 wt% and 10 wt% of scheelite tailings were based on previous studies developed by Machado et al. [30]. The new ceramic masses were inserted into a porcelain jar containing alumina balls and dry homogenized (7 wt% humidity) for 24 h in a ball mill. The consistency of the masses was also evaluated by liquidity and plasticity limits using the Casagrande method [31]. Table 1 shows the nominal composition of the prepared ceramic masses.

Table 1. Nominal composition of the ceramic masses incorporated with scheelite tailings.

Ceramic Masses	Addition Content (%wt)	Scheelite Tailings Type
MR	0	-
M5S1	5	ST1
M5S2	5	ST2
M5S3	5	ST3
M10S1	10	ST1
M10S2	10	ST2
M10S3	10	ST3

The new ceramic masses were uniaxially pressed (20 MPa) in a hydraulic press (Servitech, model CT-335, Tubarão, Brazil) to obtain samples with dimensions of 50 mm × 15 mm × 5 mm. The samples were dried (110 °C for 24 h) and fired in an electric oven (Flyever Equipment, model FE50RP, São Carlos, Brazil) at different temperatures (800, 900, and 1000 °C) and heating rates (5, 10, 15 and 20 °C·min^{−1}). An isothermal treatment of 30 min was accomplished at each firing temperature and then the samples were cooled for room temperature at 10 °C·min^{−1}.

2.3. Characterizations

The chemical composition of scheelite tailings and of ceramic masses were determined by X-ray fluorescence (XRF) (Shimadzu, model EDX 720, Kyoto, Japan). The analysis was carried out in triplicate and performed under vacuum, with a collimator of 10 mm, a Rh X-ray tube, and an EDS detector. The mineralogical composition was determined by X-ray diffraction (XRD) (Shimadzu, model XRD 6000, Kyoto, Japan) with Cu-K α radiation (40 Kv/30 mA); goniometer speed 2°·min^{−1}; 0.02° step; and 2 θ scanning from 2° to 60°. The granulometric analysis (GA) of ceramic masses was determined by laser diffraction (Cilas, model 1064, Orléans, France). All raw materials were sieved (74 μ m) before XRF, XRD, and GA analyses.

Water absorption (WA), apparent porosity (AP), and 3-point flexural strength (FS) tests were performed on the specimens after firing. WA and AP were measured by Archimedes method. In summary, the samples were immersed in distilled water for 24 h to obtain the wet weight (W_w) and the immersed weight (W_i). Before immersion in distilled water, sintered samples were weighed to obtain their dry weight (W_d). Equations (1) and (2) were used to calculate WA and AP, respectively.

The flexural rupture module experiments were carried with the aid of a universal mechanical testing machine (Shimadzu, model Autograph AG-X 50 kN, Kyoto, Japan), with 5 kN load cells, the distance between the support points of 30 mm, and a test speed of $0.5 \text{ mm} \cdot \text{min}^{-1}$. The results of physical and mechanical tests were obtained from an average of 10 samples. The mineralogical phases formed after firing was analyzed by X-ray diffraction (XRD).

$$\text{WA}(\%) = \frac{W_w - W_d}{W_d} \times 100, \quad (1)$$

$$\text{AP}(\%) = \frac{W_w - W_d}{W_w - W_i} \times 100, \quad (2)$$

where W_w , W_d , and W_i are the weights of the specimens, wet, dry, and immersed, respectively.

2.4. Carbonation Resistance

The carbonation resistance evaluation was carried out on fired samples at 1000°C at a heating rate of $5^\circ\text{C} \cdot \text{min}^{-1}$, which were submitted to the natural aging test in an internal environment. The samples were kept protected from external climatic actions (inside the laboratory, at room temperature, and under air humidity $\sim 74\%$) for 3 months. After this period, the samples were evaluated to physical and mechanical (WA, AP, and FS), mineralogical (XRD), and fracture surface analysis using scanning electron microscopy (SEM).

3. Results and Discussion

3.1. Chemical and Mineralogical Composition of the Scheelite Tailings and Ceramic Masses

Table 2 presents the chemical composition of the scheelite tailings used in this research and the ceramic masses without and with scheelite tailings. The ceramic mass without scheelite tailings was denominated MR, while with tailings were denominated M5S1, M5S2, and M5S3 (with 5 wt%) and M10S1, M10S2, and M10S3 (with 10 wt%). The calcium oxide (CaO) was a major component detected in the scheelite tailings, which contents ranging from 37.6 to 40.2%, and is related to the presence of calcite or dolomite [5]. Additionally, SiO_2 (18.1 to 22.9%), Al_2O_3 (7.6 to 10.8%), and Fe_2O_3 (7.2 to 9.8%) contents were detected in the scheelite tailings. The ceramic masses presented a typical composition for the manufacture of red ceramic products. A high Fe_2O_3 content (8.2–9.0 wt%) is responsible for the reddish color of the pieces after firing. SiO_2 and Al_2O_3 were the major oxides detected. These oxides have origin from the clay minerals, feldspar, and free silica presented in the scheelite tailings. In the ceramic masses containing scheelite tailings (M5S1, M5S2, M5S3, M10S1, M10S2, and M10S3), an increase in the CaO content in relation to the MR mass (without tailings) is observed due to the higher concentration of this oxide in the tailings. In general, ceramic masses containing tailings have a high content of fluxing oxides (K_2O , CaO, and MgO), responsible for forming glass phases, reducing the firing temperature, and improving the physical and mechanical properties [7]. The loss on ignition (LOI) measured from the scheelite tailings is associated with free water loss and carbonate decompositions. In the ceramic masses, LOI is due to free water loss, clay mineral dehydroxylation, organic matter, and carbonate decompositions. All ceramic masses containing scheelite tailings (M5S1, M5S2, M5S3, M10S1, M10S2, and M10S3) presented a higher percentage of LOI compared to the ceramic mass without the tailings (MR). Such behavior is probably due to the increase in carbonate content.

Figure 2a shows XRD patterns measured from standard ceramic mass (MR), i.e., without the scheelite tailings. Quartz (JCPDS 46-1045), feldspar (JCPDS 84-0710), and kaolinite (JCPDS 79-1570) were the main crystalline phases identified in MR. On the other hand, mica (JCPDS 83-1808) and calcite (JCPDS 72-1937) phases were identified to a lesser extent. The XRD patterns measured from scheelite tailings (ST1, ST2, and ST3) are shown in Figure 2b. In general, all scheelite tailings presented the following mineralogical phases: calcite (JCPDS 72-1937), quartz (JCPDS 46-1045), and diopside (JCPDS 89-0837). Diopside usually occurs as an accessory mineral and is associated with calcite. Peaks referring to dolomite (JCPDS 89-5862) were identified at ST2 and ST3. These peaks may be associated

with a higher MgO (3.3%) and CaO (38.5 and 40.2%) content detected in these tailings, compared to ST1, which presented 2.7% MgO and 37.6% CaO. In general, the minerals detected in scheelite tailings are generally present in the masses used in traditional ceramics, which favor the incorporation of these tailings in this sector.

Table 2. Chemical composition of scheelite tailings (ST1, ST2, and ST3) used in this study and of ceramic masses without (MR) and with scheelite tailings (5 and 10%). The results were determined by X-ray fluorescence.

Raw Materials/Samples		Oxides (%wt)										
		SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	K ₂ O	TiO ₂	CaO	MgO	WO ₃	Others	LOI *	SiO ₂ /Al ₂ O ₃
	ST1	18.1	8.7	7.2	0.4	0.6	37.6	2.7	0.4	1.3	23.0	-
	ST2	21.8	7.6	9.8	0.6	0.7	38.5	3.3	0.2	1.8	15.7	-
	ST3	22.9	10.8	9.6	0.6	0.4	40.2	3.3	0.7	1.7	9.8	-
	MR	47.5	20.9	8.9	3.0	1.2	2.1	2.6	-	0.5	13.3	2.27
	M5S1	45.0	19.8	8.2	2.9	1.2	3.5	2.5	-	0.6	16.3	2.27
	M5S2	43.7	19.4	9.0	2.7	1.0	4.8	2.5	-	1.0	15.9	2.25
	M5S3	45.8	20.0	9.0	2.9	1.2	3.0	2.5	-	0.6	15.0	2.29
	M10S1	43.5	19.4	8.5	2.8	1.1	3.7	2.5	-	0.8	17.7	2.24
	M10S2	43.0	19.0	9.0	2.7	1.0	5.7	2.5	-	0.9	16.2	2.26
	M10S3	42.9	18.9	8.7	2.6	1.1	7.2	2.4	-	0.6	15.6	2.27

* LOI—Loss on ignition measured after drying at 110 °C and firing at 1000 °C.

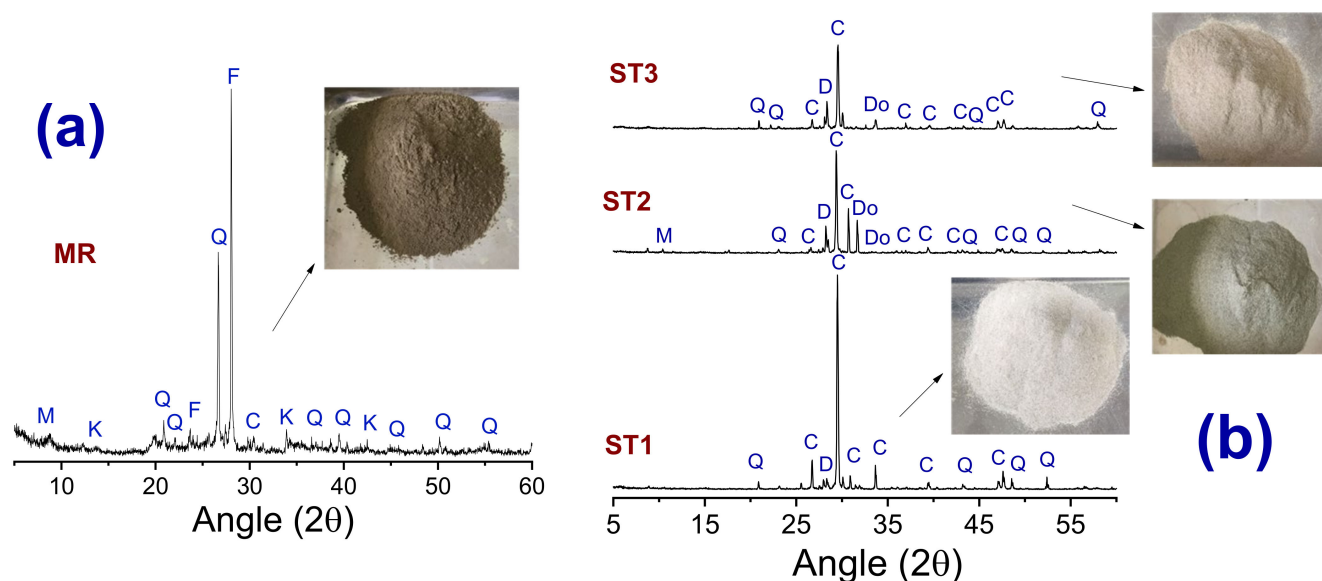


Figure 2. XRD patterns measured from ceramic mass (MR) (a) and of the scheelite tailings (ST1, ST2, and ST3) (b). M—Mica; K—Kaolinite; F—Feldspar; Q—Quartz; C—Calcite; D—Diopside; Do—Dolomite.

3.2. Granulometry and Consistency of Ceramic Masses

Knowledge of the particle size distribution and consistency of the ceramic masses is extremely important before the molding step of the ceramic product. Through the results of granulometry and consistency values, it is possible to assess whether the raw materials used are suitable for the molding and manufacturing process of ceramic pieces. In addition, the variation in particle size distribution and plasticity of the ceramic masses can cause changes in their behavior during processing and significantly affect the properties of the final products.

The accumulated mass percentage for different particle size ranges and the average diameter of particles obtained from the ceramic masses are presented in Table 3. All ceramic masses showed similar particle size distributions, being approximate: 21% clay

fraction ($<2\ \mu\text{m}$), 57% silt fraction (between 2 and $20\ \mu\text{m}$), and 21% sand fraction ($>20\ \mu\text{m}$). The average diameter of the ceramic masses was approximately $12\ \mu\text{m}$. In general, the ceramic masses have a wide granulometric distribution, which can favor the packing of the particles during compaction and the reactivity during firing temperature. It is worth mentioning that the reactivity between the particles favors the reactions for the formation of new crystalline phases based on calcium and/or magnesium, which significantly affects the physical and mechanical properties of the sintered parts [32,33].

Table 3. Accumulated mass for different particle size distribution ranges and average diameter of the ceramic masses.

Samples	Accumulated Mass (%)			Average Diameter (μm)
	Fine ($x < 2\ \mu\text{m}$)	Medium ($2\ \mu\text{m} < x < 20\ \mu\text{m}$)	Gross ($x > 20\ \mu\text{m}$)	
MR	22.1	55.5	22.4	12.5
M5S1	20.4	58.8	20.8	12.2
M5S2	21.5	57.3	21.2	12.9
M5S3	20.9	56.2	22.9	12.6
M10S1	20.6	57.6	21.8	12.1
M10S2	20.5	57.6	21.9	12.6
M10S3	20.6	57.8	21.6	12.4

* x: particle size.

Figure 3 shows the Atterberg limits measured from the ceramic masses with and without scheelite tailings. In general, there is a plasticity index reduction with the incorporation of scheelite tailings. Such behavior is probably related to the non-plastic characteristic of the scheelite tailings. However, the plasticity and liquidity indices and plasticity limits are within the range of the literature for use in red ceramics [34]. Ceramic masses with a plasticity index between 7 and 15% are classified as moderately plastic and values above 15% as highly plastic. In this way, the ceramic masses studied in this work are highly plastic, making them viable for the red ceramics pieces production.

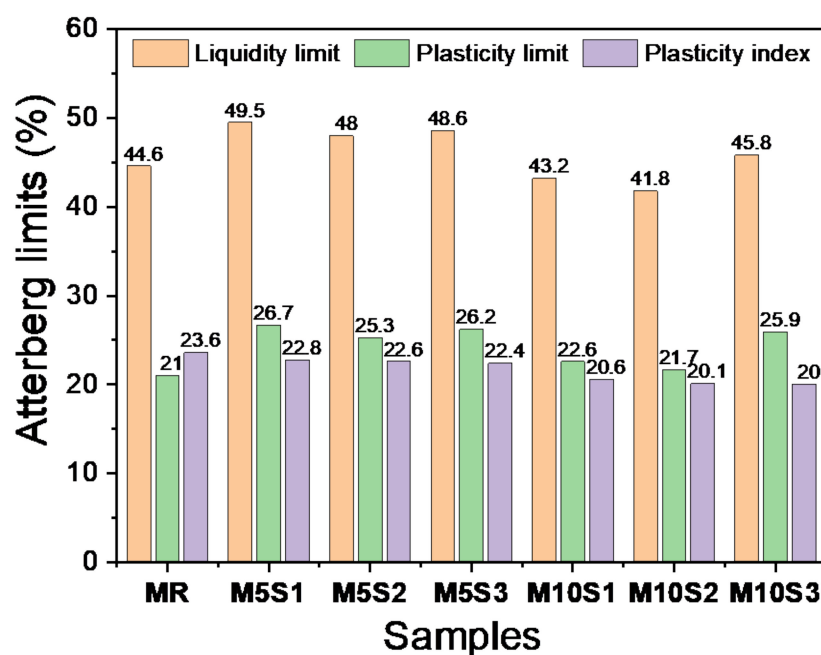


Figure 3. Atterberg limits (liquidity limit, plasticity limit, and plasticity index) of the ceramic masses investigated.

3.3. Mineralogical Phases of the Samples after Firing

Figure 4 shows the X-ray diffraction patterns of samples sintered at 800, 900, and 1000 °C, with a heating rate of 5 °C min^{−1}. The following crystalline phases were observed: mica ($\text{KMg}_3(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_2$, JCPDS 83-1808), quartz (SiO_2 , JCPDS 46-1045), feldspar (JCPDS 84-0710), anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$, JCPDS 89-1472), and gehlenite ($\text{Ca}_2\text{Al}(\text{AlSi})\text{O}_7$, JCPDS 35-0755). Peaks characteristic of the mica phase were detected only at 800 and 900 °C, where it was possible to observe a reduction in its intensity when the temperature increased from 800 °C to 900 °C. Feldspar is present in all compositions and temperatures; however, the peak intensity decreases as the temperature increases. The kaolinite phase was not identified in any investigated samples after sintering, showing that this phase detected in the ceramic mass before firing (see Figure 2a) disappeared due to dehydroxylation between 500 and 600 °C [35,36]. After dehydroxylation, the layered structure of kaolinite is destroyed, transforming into an amorphous phase called metakaolinite. At temperatures around 900 °C, metakaolinite reorganizes and forms other crystalline phases such as mullite, hematite, gehlenite, and anorthite. The formation of these phases depends on the amount of other minerals present in the material [26].

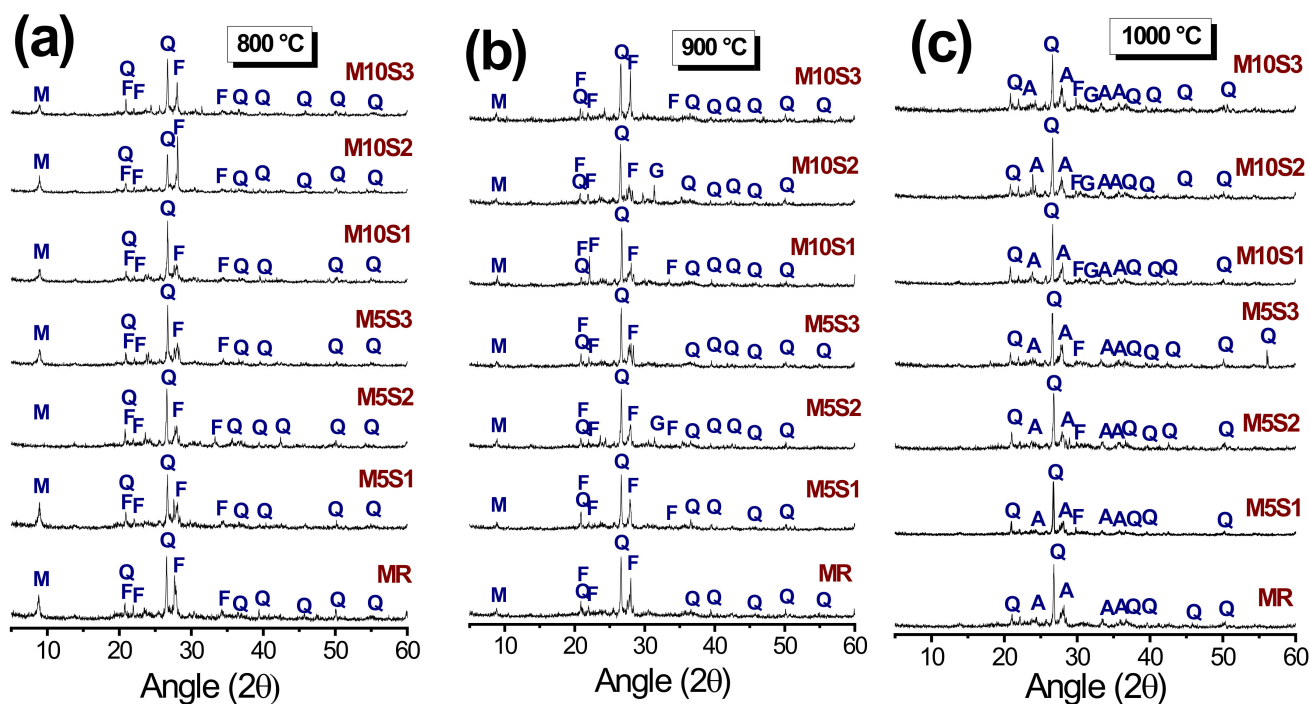


Figure 4. XRD patterns measured from samples sintered at 800 (a), 900 (b), and 1000 °C (c). All samples were fired at a heating rate of 5 °C·min^{−1}. M—Mica; F—Feldspar; Q—Quartz; A—Anorthite; G—Gehlenite.

In the scheelite tailings (ST1, ST2, and ST3), incorporated MR calcite (CaCO_3) was the main mineralogical phase identified (see Figure 2b). According to Baccour et al. [28], when the temperature increase from 850 to 950 °C, CaCO_3 decomposes ($\text{CaO} + \text{CO}_2$), and the formed CaO reacts with the amorphous phase (metakaolinite), forming crystalline phases, such as gehlenite and anorthite. It is worth mentioning that the first peaks related to the gehlenite phase occurred for the ceramic masses fired at 900 °C and 1000 °C to the anorthite. The appearance of the anorthite probably is related to the gehlenite into anorthite transformation. According to the literature, the presence of structural iron favors the metakaolinite to gehlenite transformation, which, later combines with aluminum, silicon (from metakaolinite), and quartz, form anorthite [21,37].

According to Jiang et al. [38], the gehlenite into anorthite transformation can be attributed to the high diffusion rate of Ca^{2+} . In anorthite, the $\text{Ca}^{2+}:\text{Si}^{4+}$ ratio is 1:2, while for gehlenite is 2:1. The Ca^{2+} and O^{2-} ionic bond can be more easily destroyed because it is less stable than the Si-O covalent bond. As a result, at low temperatures, the Ca^{2+} diffusion rate was much faster than that of Si^{4+} , causing the appearance of gehlenite peaks at $\sim 900^\circ\text{C}$.

Clays compositions containing high CaO contents, fired at 950 and 1100°C , were studied by González-García et al. [39]. In such a study, the researchers associated the transformation of the gehlenite into anorthite with the presence of the illite, SiO_2 , and CaCO_3 . It was observed that the increase in temperature favored the gehlenite into anorthite transformation. The authors also highlighted the mullite absence in clays with significant CaCO_3 proportions. According to Ouahabi et al. [40], the CaO presence in the limestone clays prevents mullite formation. Quartz was detected in the ceramic masses before firing. No phase transformation was observed during the different heat treatments for this mineral, only reducing peak intensity at a firing temperature of 1000°C .

3.4. Physical and Mechanical Properties of Sintered Samples

Table 4 presents water absorption (WA), apparent porosity (AP), and flexural strength (FS) values measured from samples fired at 800, 900, and 1000°C using different heating rates (5, 10, 15, and $20^\circ\text{C min}^{-1}$). For samples fired at 800°C , an increase in the scheelite tailings contents resulted in a slight increase in the WA and AP values. Such behavior can be credited to carbonate decomposition. During the firing step, the calcite (CaCO_3) present in the scheelite tailings decomposes ($\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$), and CO_2 formed increases the pressure inside the pores of the material, compromising the densification process [6]. Besides, for all heating rates used, it is observed that samples containing scheelite tailings (M5S1, M5S2, M5S3, M10S1, M10S2, and M10S3) tend to have higher FS values than the sample without tailings (MR), which is probably related to the interaction between the crystalline phases [21,41].

At heating rates above $10^\circ\text{C min}^{-1}$, a reduction in mechanical strength was observed. Such behavior may be associated with the microcracks formation due to the faster cycle, especially at cooling, which occurs during the quartz polymorphic transformation ($\beta \rightarrow \alpha$). In general, the samples fired at 800°C presented the potential to be used in the production of bricks because they showed water absorption values (range 15.5%–20.6%) within the maximum limit of 22% (ASTM C20-00 [42]) and flexural strength between 1–5 MPa. According to ASTM C67 [43], the minimum requirement for flexural strength of bricks is 0.65 MPa.

For samples sintered at 900°C , the best condition (lowest WA and AP values and highest FS value) was obtained for M5S1 and M5S3 samples (5% scheelite tailings). These results were higher than those measured to MR samples (without tailings). Taking account of the crystalline phases formed during the firing step (at 900°C) (Figure 4b), it is possible to observe a reduction in the intensity of the mica phase peaks and an increase in the intensity anorthite peaks. Such behavior can improve properties since the anorthite favors increased resistance and chemical stability of the material [21,41]. In general, the increase in firing temperature from 800°C to 900°C resulted in improved properties (WA and AP reduction and increase of FS), with the best results observed for samples heated to a rate of 5°C min^{-1} . The FS values obtained were higher than those found by other researchers who worked in the same temperature range [44].

At 1000°C and heating rates of 5 and $10^\circ\text{C min}^{-1}$, the M5S1 sample showed FS values higher than the MR sample. This indicates that for this composition, the firing time can be reduced by increasing the rate from 5 to $10^\circ\text{C min}^{-1}$ without loss of mechanical properties. In general, the best properties were observed for samples fired at 1000°C . This probably was due to the increase in the anorthite amount (Figure 4c), which contributes to the rise in the material's chemical resistance and stability and improves the physical properties [21,41,45].

Table 4. Physical and mechanical properties of the standard mass (MR) and ceramic masses with 5 and 10% scheelite tailings after sintering at 800, 900, and 1000 °C.

Rate (°C·min ^{−1})	Samples	Physical and Mechanical Properties of the Masses								
		Water Absorption (%)			Apparent Porosity (%)			Flexural Strength (MPa)		
		800 °C	900 °C	1000 °C	800 °C	900 °C	1000 °C	800 °C	900 °C	1000 °C
5	MR	17.7 ± 0.3	17.5 ± 0.2	13.2 ± 0.1	32.2 ± 0.4	31.7 ± 0.3	26.0 ± 0.2	2.0 ± 0.2	3.2 ± 0.3	6.4 ± 0.4
	M5S1	19.9 ± 0.3	16.0 ± 0.3	12.4 ± 0.3	35.1 ± 0.4	30.6 ± 0.6	24.5 ± 0.5	2.0 ± 0.4	5.6 ± 0.5	7.0 ± 0.8
	M5S2	17.6 ± 0.4	18.0 ± 0.2	13.9 ± 0.2	32.6 ± 0.6	32.9 ± 0.6	26.7 ± 0.3	3.6 ± 1.2	2.5 ± 0.2	5.5 ± 0.6
	M5S3	15.5 ± 0.1	14.7 ± 0.2	11.9 ± 0.2	29.8 ± 0.2	27.9 ± 0.3	23.8 ± 0.3	5.0 ± 0.3	4.7 ± 0.4	6.7 ± 0.5
	M10S1	18.9 ± 0.3	16.0 ± 0.2	13.0 ± 0.2	34.5 ± 0.4	29.9 ± 0.3	25.3 ± 0.3	2.3 ± 0.5	4.1 ± 0.2	5.1 ± 0.3
	M10S2	18.8 ± 0.5	16.9 ± 0.3	13.1 ± 0.3	33.7 ± 0.4	31.4 ± 0.4	27.3 ± 0.4	3.5 ± 0.5	2.3 ± 0.2	4.1 ± 0.5
	M10S3	18.6 ± 0.4	14.6 ± 0.3	13.7 ± 0.4	34.1 ± 0.5	27.9 ± 0.4	26.8 ± 0.4	4.5 ± 0.2	4.0 ± 0.2	5.2 ± 0.3
	MR	17.2 ± 0.5	17.4 ± 0.3	13.4 ± 0.2	31.1 ± 0.5	31.6 ± 0.4	26.2 ± 0.3	1.4 ± 0.4	3.1 ± 0.2	6.4 ± 0.4
	M5S1	19.5 ± 0.4	16.3 ± 0.3	12.8 ± 0.4	34.5 ± 0.6	30.8 ± 0.5	25.1 ± 0.5	1.8 ± 0.2	5.0 ± 0.4	6.6 ± 0.4
10	M5S2	17.5 ± 0.3	18.3 ± 0.2	14.4 ± 0.4	32.3 ± 0.5	33.2 ± 0.5	27.5 ± 0.6	3.6 ± 1.6	2.1 ± 0.1	4.5 ± 0.5
	M5S3	15.6 ± 0.2	14.8 ± 0.1	12.4 ± 0.3	29.8 ± 0.3	28.0 ± 0.2	24.6 ± 0.5	4.0 ± 0.3	4.5 ± 0.4	5.4 ± 0.3
	M10S1	19.8 ± 0.4	16.4 ± 0.4	15.1 ± 0.3	35.5 ± 0.5	30.3 ± 0.5	28.1 ± 0.5	1.5 ± 0.2	3.2 ± 0.3	3.6 ± 0.4
	M10S2	19.5 ± 0.3	17.3 ± 0.3	15.3 ± 0.4	34.4 ± 0.4	32.1 ± 0.4	28.4 ± 0.6	3.4 ± 0.2	2.0 ± 0.1	3.6 ± 0.2
	M10S3	19.0 ± 0.2	14.6 ± 0.3	14.8 ± 0.2	34.5 ± 0.2	28.0 ± 0.4	27.8 ± 0.3	3.8 ± 0.3	3.6 ± 0.4	4.7 ± 0.4
	MR	17.5 ± 0.2	17.6 ± 0.1	13.2 ± 0.9	31.5 ± 0.3	31.9 ± 0.2	25.9 ± 1.3	1.0 ± 0.4	2.8 ± 0.2	6.7 ± 1.0
	M5S1	19.8 ± 0.2	16.5 ± 0.3	13.3 ± 0.3	34.8 ± 0.3	31.0 ± 0.4	25.9 ± 0.5	1.6 ± 0.2	4.5 ± 0.2	5.6 ± 0.5
	M5S2	17.5 ± 0.4	18.4 ± 0.2	15.1 ± 0.3	32.3 ± 0.5	33.3 ± 0.5	28.4 ± 0.4	3.0 ± 1.2	2.0 ± 0.2	4.1 ± 0.5
	M5S3	15.8 ± 0.3	14.8 ± 0.2	13.1 ± 0.5	30.0 ± 0.4	28.0 ± 0.4	25.5 ± 0.7	3.7 ± 0.5	4.4 ± 0.3	4.7 ± 0.6
15	M10S1	19.9 ± 0.2	17.3 ± 0.5	16.0 ± 0.4	35.5 ± 0.2	31.6 ± 0.7	29.2 ± 0.4	1.5 ± 0.3	2.9 ± 0.4	2.9 ± 0.2
	M10S2	19.5 ± 0.2	18.0 ± 0.3	15.7 ± 0.3	34.4 ± 0.3	32.9 ± 0.4	28.9 ± 0.4	2.9 ± 0.2	1.9 ± 0.2	3.6 ± 0.3
	M10S3	19.4 ± 0.5	15.1 ± 0.3	15.1 ± 0.4	35.0 ± 0.7	28.4 ± 0.5	28.2 ± 0.6	3.4 ± 0.2	3.1 ± 0.2	4.4 ± 0.2
	MR	17.7 ± 0.2	17.6 ± 0.2	13.9 ± 0.2	31.7 ± 0.3	31.8 ± 0.3	26.8 ± 0.3	1.0 ± 0.1	2.6 ± 0.2	5.7 ± 0.4
	M5S1	19.8 ± 0.3	16.6 ± 0.3	14.3 ± 0.5	34.9 ± 0.4	31.0 ± 0.5	27.2 ± 0.7	1.4 ± 0.3	4.3 ± 0.4	4.3 ± 0.8
	M5S2	18.2 ± 0.5	18.6 ± 0.2	15.8 ± 0.4	33.1 ± 0.6	33.5 ± 0.6	29.2 ± 0.5	2.3 ± 1.2	1.6 ± 0.2	3.4 ± 0.4
	M5S3	16.4 ± 0.3	15.0 ± 0.2	13.9 ± 0.7	30.9 ± 0.4	28.2 ± 0.2	26.7 ± 1.0	2.6 ± 0.3	3.8 ± 0.3	3.5 ± 0.6
	M10S1	20.0 ± 0.1	18.8 ± 0.5	16.6 ± 0.5	36.5 ± 0.3	33.4 ± 0.6	30.0 ± 0.7	1.3 ± 0.3	2.1 ± 0.1	2.5 ± 0.3
	M10S2	19.8 ± 0.6	19.0 ± 0.3	15.7 ± 0.2	35.1 ± 0.3	33.9 ± 0.4	29.0 ± 0.2	2.1 ± 0.1	1.4 ± 0.2	3.4 ± 0.2
20	M10S3	20.6 ± 0.8	15.4 ± 0.2	15.0 ± 0.3	36.1 ± 0.9	29.0 ± 0.3	28.0 ± 0.5	2.3 ± 0.1	2.9 ± 0.1	4.6 ± 0.3

Sintering is one of the main steps during processing a ceramic product; because it is at this stage, the consolidation of the part occurs. Factors such as firing temperature and heating rate can affect the sintering degree and, consequently, the physical and mechanical properties of the material [23]. Therefore, it is worth noting that the samples' quick-firing (i.e., higher heating rates) did not significantly compromise the mechanical properties. At temperatures of 800 and 900 °C, there was no considerable variation in the properties with the increase in the heating rate. This fact is relevant for the industry since rapid burning in the manufacture of ceramic parts reduces energy expenditure and saves companies.

Regarding the incorporation of the scheelite tailings, in general, the difference in the tailings type (ST1, ST2, and ST3) did not cause significant changes in physical and mechanical properties. This is because the three tailings had similar chemical compositions (see Table 2). Such behavior indicates that the tailings from different stages of processing of scheelite can be incorporated into masses for the manufacture of red ceramic products without significantly compromising the physical and mechanical properties.

3.5. Carbonation Resistance

Figure 5a–d presents the physical and mechanical properties comparison before and after carbonation of samples sintered at 1000 °C and a heating rate of 5 °C min^{−1}. Such condition was chosen due to the better properties compared to the others. After 3 months of natural aging, the samples significantly reduced physical and mechanical properties (increasing WA and AP and decreasing FS). These changes may be related to the carbonation process. In general, all samples showed similar WA, AP, and FS values, except for M5S2 sample that presented the highest FS value and closed those measured before the carbonation study. Under the percentage viewpoint, the M5S2 sample showed less loss of mechanical strength (~3.6%), while the M5S1 sample showed more significant loss (~57%).

Carbonation is a physical-chemical process in which the CO₂ present in the atmosphere reacts with calcium hydroxide to form calcium carbonate, precipitating inside the microstructure [25]. This process can cause variation in porosity due to the destruction of the mineral through the action of carbonic acid-producing irregular surfaces and an increase in macro and mesoporosity. The precipitation of carbonates fills the micropores and increases the nanoporosity [29,46].

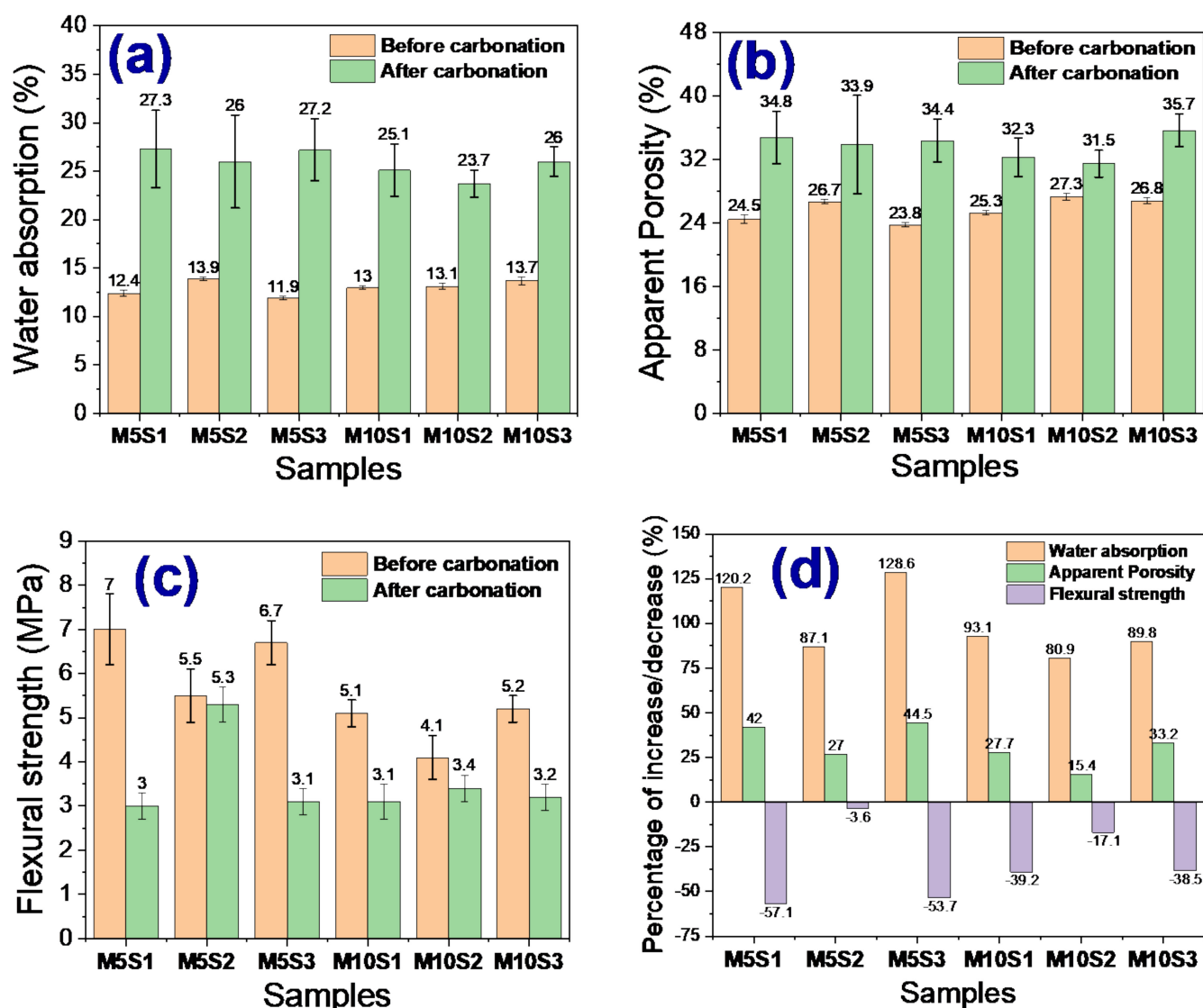


Figure 5. Physical and mechanical properties of the samples fired at 1000 °C (heating rate equal to 5 °C min^{−1}) before and after carbonation: water absorption (a), apparent porosity (b), flexural strength (c), and percentage of increase/decrease (d). The carbonation was evaluated after 3 months of natural aging.

In this study, the increase in porosity may be related to the dissolution of the material and the decrease in the flexural strength associated with new asymmetric crystal growth that can generate tensions within the material that contributes to the formation of the cracks. Therefore, pieces obtained with ceramic masses containing tailings rich in CaO (as in the case of scheelite tailings) must be evaluated after the fired step, as the carbonation phenomenon may compromise its function over time.

The X-ray diffraction patterns of samples submitted to the natural aging test for 3 months are shown in Figure 6. The following crystalline phases were observed: quartz (SiO₂, JCPDS 46-1045), anorthite (CaAl₂Si₂O₈, JCPDS 89-1472), calcite (CaCO₃, JCPDS 72-1937), and monohydrocalcite (CaCO₃·H₂O, JCPDS 83-1923). Compared with the diffractograms present in Figure 4c, it is possible to notice an increase in the intensity of the peaks in the region where the anorthite phase is located, probably due to a new phase of monohydrocalcite. The monohydrocalcite from the beginning of the carbonation process will be transformed into carbonate to form calcite later. The newly formed calcite arises from the reaction of the CO₂ present in the environment with the calcium hydroxide contained in

the samples. It is probably still present in the samples after the firing step; however, the peaks were not identified due to the low quantity or amorphous form.

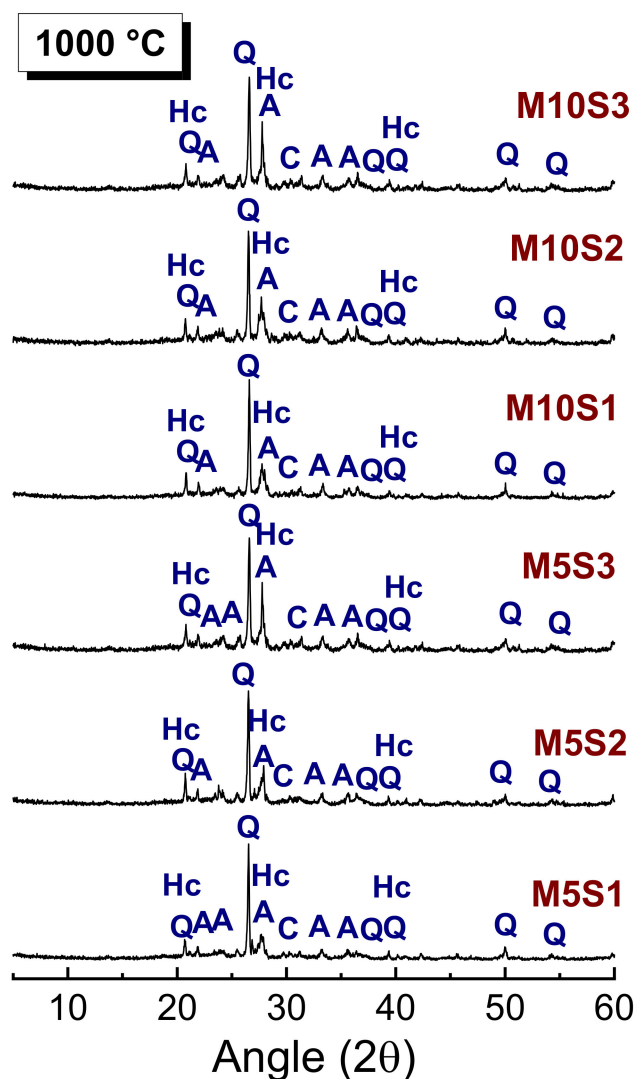


Figure 6. XRD patterns measured from samples sintered at 1000 °C and heating rate of 5 °C min^{−1} after 3 months of natural aging in an internal laboratory environment. Q—Quartz; A—Anorthite; C—calcite; Hc—Monohydrocalcite.

Figure 7 shows the SEM images acquired from the fractured surface of the M5S1, M5S2, and M5S3 samples, sintered at 1000 °C and heating rate of 5 °C min^{−1}, before and after carbonation. It is possible to visualize particle agglomeration of different sizes and shapes, as well as quartz grains. Spherical particles are present in all samples (red circles in the images). Those particles are probably relative to the anorthite phase, confirming the peaks in Figures 4 and 6. After carbonation, the samples presented more pores on their surface. Furthermore, needles were observed (squares highlighted in blue in the images). Those needles are probably relative to the monohydrocalcite phase, which corroborates with the XRD peaks identified in Figure 6. A similar structure was observed by Martín et al. [46].

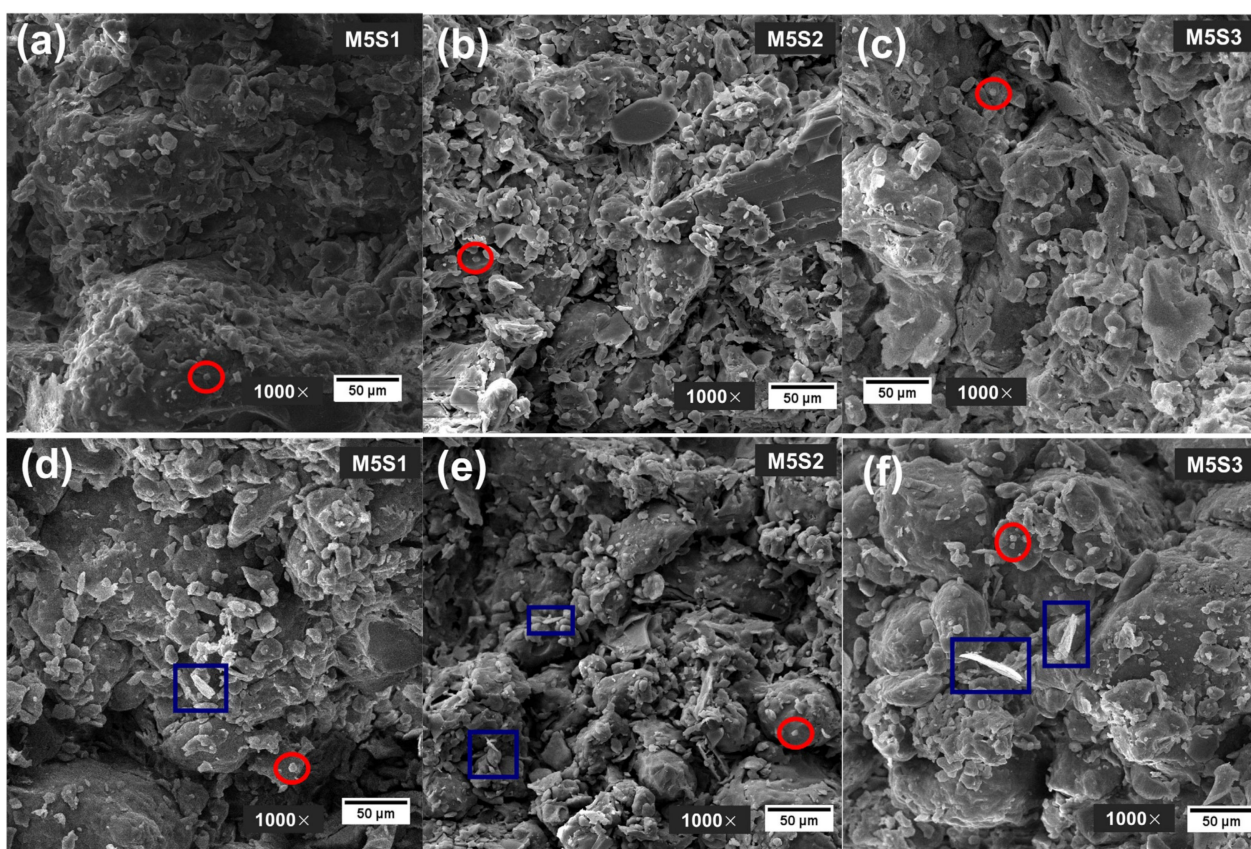


Figure 7. Scanning Electron Microscopy images of samples before (a,c,e) and after (b,d,f) carbonation.

4. Conclusions

Based on the results of this study, it is possible to conclude that incorporating scheelite tailings in ceramic masses for application in red ceramics is a viable alternative. After studying the firing parameters, the following conclusions can be drawn:

- The DRX standards of the 900 and 1000 °C sintered samples identified the gehlenite and anorthite phases, which contributed to the increase of the mechanical resistance of the materials.
- No significant differences were observed in the physical and mechanical properties as a function of the different types of scheelite tailings (ST1, ST2, and ST3) incorporated into the ceramic masses.
- The best physical and mechanical properties (lower water absorption and porosity values and higher flexural strength values) were obtained for samples with 5% scheelite tailings and heated at a rate of 5 °C min^{−1}. For samples with 5% tailings and sintered at 1000 °C, the increase in the heating rate from 5 to 10 °C min^{−1} did not significantly compromise the properties.
- Samples exposed to ambient conditions for 3 months showed a loss of physical and mechanical properties, probably due to the onset of the carbonation phenomenon. The M5S2 and M10S2 samples were the ones that presented the lowest percentages of resistance loss.
- The incorporation of scheelite tailings presented the potential for application in red ceramics and an alternative to reduce environmental pollution and conserve mineral resources.

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