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Influence of calcined halloysite on technological & mechanical properties of wall tile body

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ABSTRACT

The effect of adding 0.1, 0.3, 0.6, 1.0 wt.% halloysite clay, which calcined at 600, 800, 1000 and 1200°C, to the standard wall tile slurry was studied. Wet milled halloysite was sieved with different sizes to examine the halloysite grain size effect. The granulated samples were pressed by applying a pressure of 30 MPa using a hydraulic press and made ready for sintering at 1150°C for 30 minutes. Detailed technological, mechanical and microstructural characterization studies were done on sintered samples. Compared to standard wall tile, almost all the halloysite added samples displayed similar technological properties but higher green and fired strength values. The produced sample with adding 0.6% halloysite (at 600°C calcined) by weight showed a higher firing strength with 28.75 MPa value than the minimum requirement (17.75 MPa). Observation of needlelike microstructure in the porcelain body led to establishing a simple relationship between the interlocking effects of thin needlelike mullite grains and increasing strength values. This study has shown that the addition of calcined halloysite may be an alternative to produce a thinner section wall tile product.

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KEYWORDS
Calcined halloysite; wall tile; bodies; green & fired properties

1. Introduction

With the rapid increase in the consumption of ceramic materials worldwide, manufacturers and researchers have focused on developing innovative products. In recent years, very large size (1 m x 3 m etc.) tile production has been added to innovative works such as the application of functional coatings (photocatalytic coatings, hydrophobic coatings, antislip surfaces, etc.) to tile surfaces. The large size and thin section tile production has become widespread, especially for wall tiles to take their place in spaces with more esthetic designs. With the production of standard tiles from 11 mm section thickness to 6 mm section thickness, there is a weight reduction of approximately 45% in a product. Thin wall tiles with 6 mm section thickness are generally preferred in large and rectangular sizes. The large and rectangular shape of the dimensions causes critical measures to be taken in terms of deformation and strength in traditional ceramic material production. To produce products of this thickness and sizes, alternative shaping methods other than the existing dry press and additional binder materials or alternative raw materials that increase the tile green strength and baked strength are preferred. Manfredini et al. [1] conducted studies on inorganic binder compositions in floor tile compositions. They added bentonite clay as a binder to the mixture of 35% by weight illicit and kaolinitic clay mixtures and 65% by weight of non-plastic (feldspar and quartz) raw material mixture. They used natural bentonite and activated bentonite in the study. They investigated the effect of natural bentonite and sodium carbonate ($NaCO_3$) activated bentonite on the green strength of floor tiles. They stated that especially activated bentonite increases the green strength value of floor tiles. While the standard green strength value they used in the study was 1.71 MPa, this value increased to 2.69 MPa by adding the activated bentonite to the standard sludge by 7.5% by weight. Here, bentonite appears to increase some strength. However, the specified strength values are quite low and the effects of bentonite on floor tile mud rheology have not been systematically investigated. There are some studies in the literature involving boron derivatives as binders. These studies are especially aimed at the evaluation of tinkalkonite and colemanite concentrator wastes [2–8] used ulexite in the composition of three-component porcelain (tableware) and measured the changes in dry strength values. They stated that the addition of ulexite has a positive effect on dry strength value. As can be seen from the studies in the literature, alternative inorganic raw materials can be preferred frequently to use the wet and fired strength of ceramic tiles. In this study, halloysite clay, which was previously subjected to calcination pre-treatment, was used to help the thin section production of wall tiles and increase their wet

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and dry strength. Halloysite is also clay with the formula $Al_2Si_2O_5(OH)_4.2H_2O$, which naturally contains nano-sized tubes [9]. Halloysite nanotubes are often used in the literature to create a template [10]. Halloysites are generally used by forming polymer nanocomposites. Shi et al. [11] compared the thermal, electrical and dimensional stability performances of bulk polymers and halloysites reinforced with modification agents. In traditional ceramics, the mechanical properties of bodies have been studied for almost a century. Three theories offered to explain the green and firing strength of the porcelains during this period. These are:

(1) Mullite hypothesis
(2) Dispersion enhancement hypothesis and
(3) Matrix reinforcement hypothesis.

The mullite hypothesis is related to the interlocking of thin needlelike mullite grains in porcelain body microstructure. The higher the mullite content and the higher the clamping of the needlelike mullite crystals cause the higher the breaking strength [12].

In this study, it is aimed to reach high green and fired strength values that will allow the production of wall tiles in thinner form by using the needlelike structures that halloysite has due to its nature was used. Halloysite clay was calcined at four different temperatures (600, 800, 1000, 1200) to remove the impurities and obtain stable rod-like structure formation to obtain high green strength bodies at the beginning of the process. Calcined halloysite clay has been incorporated into the wall tiles in various proportions. The effect of calcined halloysite clay on wall tile green strength and fired strength was investigated.

2. Materials and methods

2.1. Preparation of the compositions

In this study, firstly halloysite raw material (Esan Industrial Raw Materials, Turkey) was prepared to add the standard wall tile composition Chemical characterization was carried out by means of wavelength dispersive X-ray fluorescence spectrometry (XRF), using Philips Model PW 2400 XRF Instrument fitted with an Rh white florescent tube. The sample was prepared as fused beads using a Philips PERL'X3 instrument. Chemical analysis of the halloysite clay (denoted as HAL) and standard wall tile body composition (denoted as STD) are given in Table 1.

Table 1. Chemical composition of halloysite clay (HAL) and standard wall tile body (STD).

Compounds	HAL-SD	STD-SD
SiO_2	45.20 ± 2.00	55.30 ± 2.00
Al_2O_3	38.80 ± 2.00	18.70 ± 2.00
Fe_2O_3	0.58 ± 0.10	1.20 ± 0.10
TiO_2	0.27 ± 0.10	0.36 ± 0.10
CaO	0.10 ± 0.01	8.50 ± 0.01
MgO	0.26 ± 0.10	0.30 ± 0.10
Na_2O	0.10 ± 0.01	0.82 ± 0.01
K_2O	0.26 ± 0.01	2.58 ± 0.01
L.O.I.	14.43 ± 2.0	12.24 ± 2.0

SD*: Standard deviation
L.O.I*: Lost of Ignition

The main steps of the preparation of samples are shown in Figure 1. The process configuration of calcined halloysite preparation is given in process (1) in Figure 1. The process of adding calcined halloysites to wall tiles is expressed in process (2) in Figure 1.

Halloysite firstly was wet-milled by a laboratory jar mill containing 60 wt.% solid and 1.0 wt.% deflocculant, for 20 minutes. The slurry was sieved with an aperture of 90 microns and 45 microns. The slurry sieved through 45-micron aperture was denoted as HAL-F, while sieved through the 90-micron gap was denoted as HAL-C. In this way, the halloysite grain size effect was also investigated – the particle size distribution of slurries determined by laser diffraction analysis (Malvern Master Sizer 2000). The particle size of two different slurries is given in Figure 2. The samples have nearly unimodal type particle size distribution having maxima points 11 and 18 μm for fine and coarse, respectively.

After the grinding process of the raw materials, the slurry dried at 100°C for 24 hours. For granulation of the dried powders, they were moistened by spraying water on them. Formed granules were passed through sieves with aperture sizes of 600 and 250 microns to collect between them. After granulation, the powders were calcined at 600, 800, 1000, and 1200°C with 10°C/min heating cycle. The second step was the addition of calcined granules with 0.1, 0.3, 0.6, 1.0 wt% to the standard wall tile (STD) slurry as given in the flow chart in Figure 1. The granules were mixed into the slurry, then dried at 100°C for 24 hours. After drying, they were moistened by spraying water on them and granulated. Then, the test specimens were prepared from the granules of each composition. The weighed granules powders were put into the cavity of a steel die and shaped by applying a pressure of 30 MPa by using a hydraulic press. The rectangular-shaped samples were prepared for the mechanical study. The discs' dimensions were 31.5 mm in diameter, and rectangular bars were 75 mm × 7 mm × 5 mm. Samples were fired

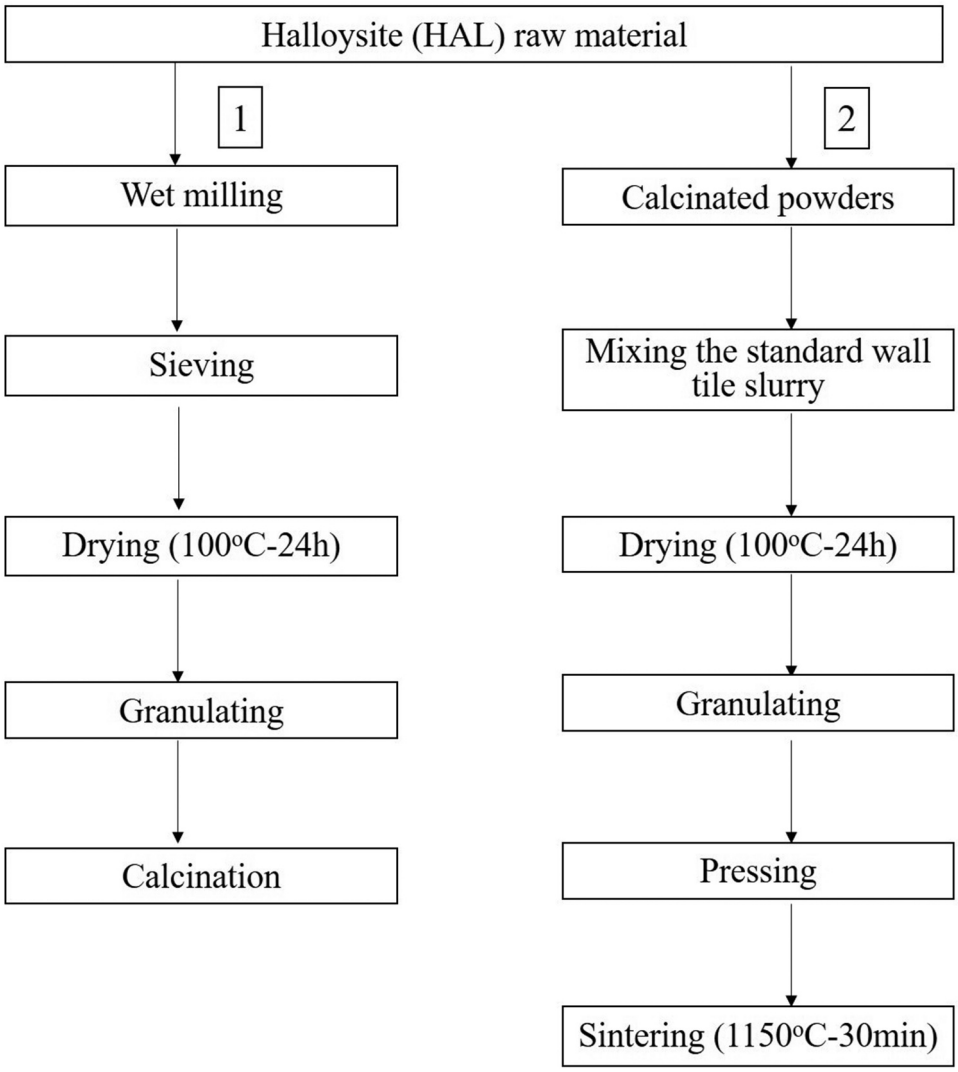

Figure 1. A schematic diagram showing the main processes (noted 1 and 2) used in this study, for the preparation of samples.

at 1150°C for 30 minutes in laboratory furnace (Nabertherm Furnace). Sample numbers and details are summarized in Table 2.

Water absorption value of the samples was determined by water saturation under vacuum and Archimedes' principle (ISO 10545–3) by using related equations (Eqs. (1)).

$$\%Water\ absorption\ (w_a) = [(w_w - w_d)/w_d]\ x100 \quad (1)$$

where, w_d, dry weight of the sample, w_w, wet weight of the sample, w_a, weight of solid suspended in water. The color values of the new compositions and standard composition were measured by a spectrometer (Minolta CR, 300 Colourmeter). The colorimeter operates on the CIELab method, which is utilized technique in the ceramic production to determine the whiteness and color of the tiles by measuring three main parameters (Hunter parameters) L* (brightness) from absolute white L = 100 to absolute black L = 0, an (red–green), bn (yellow–blue) elaborated from the visible spectra. According to the standard wall tile sample (STD), the color change value (ΔE) depend on the new compositions was measured with a spectrometer (Minolta CR, 300 Colourmeter). ΔE value is below 0.5, which means that the color variation can not be distinguished by the eye.

2.2. Characterization of the samples

2.2.1. Differential thermal analysis (DTA)

Using a differential thermal analysis (Q-600 model DTA-TA Instrument) a powder sample in a platinium crucible and tested at a heating rate of 10°C/min in a stationary air atmosphere. The sample was heat-treated from room temperature to 1000°C.

2.2.2. FT-IR spectroscopy

The FT-IR spectra of the calcined halloysite samples were recorded on a Perkin Elmer Spectrum-100 FT-IR spectrophotometer. Halloysite powders were placed in an infrared spectrometer for testing in the frequency range of 650–4000 cm^{-1} at room temperature. Approximately 2–5 mg of halloysite powder was removed from each specimen for ATR-FTIR analysis.

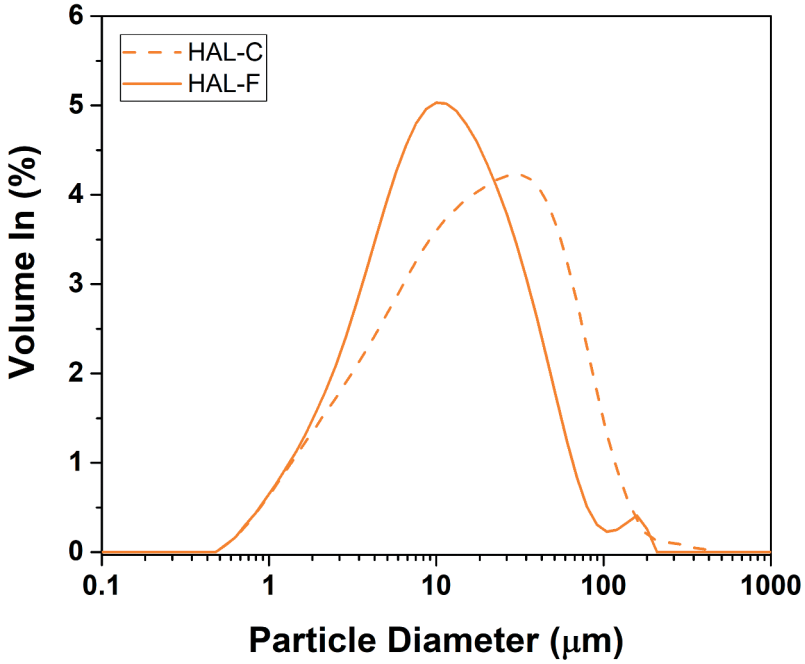

Figure 2. Particle size distribution of the halloysite slurries.

Table 2. Samples and details.

Calcination Temperature	600°C		800°C		1000°C		1200°C	
Grain Type	Fine	Coarse	Fine	Coarse	Fine	Coarse	Fine	Coarse
Sample No & Weight %	1. (%0.1)	17. (%0.1)	5. (%0.1)	21. (%0.1)	9. (%0.1)	25. (%0.1)	13. (%0.1)	29. (%0.1)
	2. (%0.3)	18. (%0.3)	6. (%0.3)	22. (%0.3)	10. (%0.3)	26. (%0.3)	14. (%0.3)	30. (%0.3)
3. (%0.6)	7. (%0.6)	23. (%0.6)	11. (%0.6)	27. (%0.6)	15. (%0.6)		19. (%0.6)	
4. (%1.0)	8. (%1.0)	24. (%1.0)	12. (%1.0)	28. (%1.0)	16. (%1.0)		20. (%1.0)	

2.2.3. Flexural strength and fracture toughness of the samples

The flexural strength of green and sintered samples was measured by three-point bending test using an electronic universal tester (Model 5569, Instron Ltd.). Tests were carried out according to ASTM C1161-90 standard with a lower span of 50 mm and crosshead speed of 1 mm/min. Microhardness measurements were carried out by hardness testing equipment (Instron Wolpert Tester 2100) with the help of the Vickers indentation method. Fracture toughness was determined by the fraction indentation method using Evan's equation [13].

2.2.4. X-ray diffraction analysis

X-ray diffraction (XRD) method was applied to detect the crystalline phases formed in the microstructure of sintered samples. In the analyses, the samples were used in powder form. They were scanned at 2°/min speed in the range of 5-70° with CuKα radiation, (λ = 0.154 nm), at 40 kV and 40 mA conditions using RIGAKU 2200 DMAX diffractometer.

2.2.5. Scanning electron microscopy

The microstructures of the samples were examined by scanning electron microscopy (SEM) analysis with the use of Philips XL30-SFEG-SEM equipped with energy dispersive X-Ray analysis (EDX). Firstly, the surface of the samples was made suitable for SEM analysis by grinding with a series of SiC abrasive papers and then polished using diamond paste. The polished surfaces were chemically etched in an aqueous solution containing 3% HF for about 2 min to reveal the crystalline structure, then the sample surfaces were coated with gold. Needlelike crystals width (a), length (L), and aspect ratio (L/a) measurements were carried out in microstructural analysis. Two hundred needlelike crystals were taken into account for each sample. SEM samples were prepared from different regions of the same sample, and all microstructural properties measurements were measured using the Fiji Image J software program.

3. Results and discussion

3.1. Differential thermal analysis of the halloysite powder

In this study, halloysite powders' TG-DTA analyses were also carried out. The analyses result of the initial halloysite powders is given in Figure 3. The DTA curve shows two endotherm and one exotherm peaks,

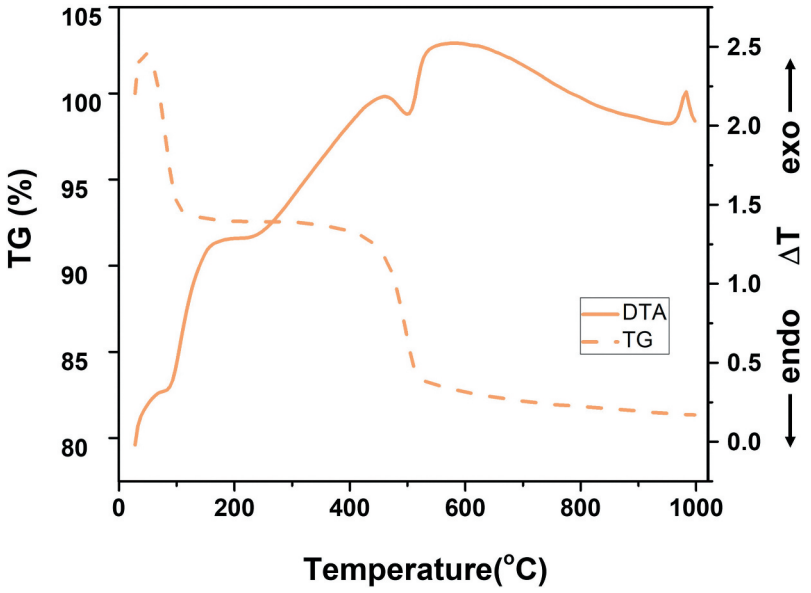

Figure 3. TG-DTA curve of raw halloysite powder.

centered at 92.5°C, 499°C and 982°C, respectively. The mass loss in halloysite is about 18.65% between 25°C and 1000°C because of endothermic dehydroxylation and dehydration. The surface water loss presents the first endothermic peak centered at 92.5°C with the % 2.1 weight loss. This water was already highlighted by FTIR (band at 1630 cm^{-1}) [14]. There is a second endothermic peak at 499 □ (with the weight loss % 11.2) due to metahalloysite transformation, which is structural dehydroxylation, into the mentioned mullite formation and up to the 982°C it remains stable [15]. The exothermic peak at about 982°C is about thermal decomposition of the halloysite mineral without any mass loss [16].

3.2. FT-IR spectra of the calcined halloysite powders

Figure 4 shows the infrared spectra of the samples calcined at different temperatures (600–800-1000-1200°C). A well-resolved peak found in the spectra of Hal, Hal600, and Hal800, Hal1000 and Hal1200 at

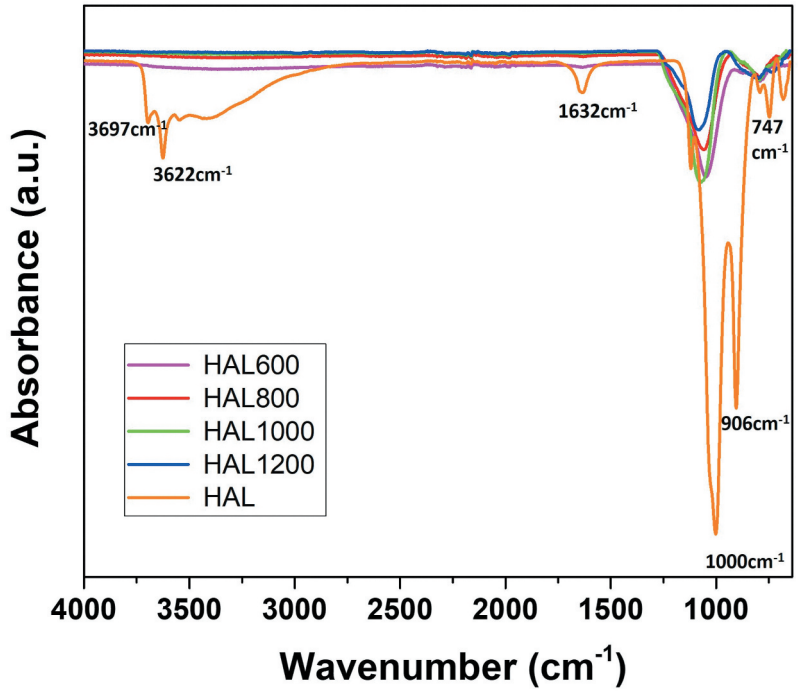

Figure 4. FTIR spectra of the calcined halloysite powders.

1000 cm^{-1} is typical of in-plane Si-O stretching vibration. Compared with initial halloysite (Hal) spectrum, the O-H stretching bands of the inner hydroxyl groups (3622 cm^{-1}) and inner-surface hydroxyl groups (3697 cm^{-1}) disappeared from the others' spectrum. It means dehydroxylation of halloysite after calcination at 500°C. A weak one at 1630 cm^{-1} appeared and was assigned to O-H deformation of physically adsorbed water. Furthermore, the presence of the adsorbed water bands (3413 and 1630 cm^{-1}) on the FTIR spectrum of initial halloysite (Hal) means that halloysite was more hydrophilic than the others. The band at 906 cm^{-1} and 747 were caused by Al-O vibration associated with four coordinated Al [17,18].

Table 3. Technological properties of the standard wall tile body (STD).

Sample No	Water Absorption (%)	Color Value
STD	15.2 ± 0.1	L*: 81.12 a*:5.67 b*: 16.17

Table 4. Technological properties of the compositions.

Sample No	Water Absorption (%)	Color & Color Variation Value (ΔE)	Sample No	Water Absorption	Color Variation Value (ΔE)
1	15.4 ± 0.1	<0.5	17	15.1 ± 0.1	<0.5
2	15.5 ± 0.1	<0.5	18	15.2 ± 0.1	<0.5
3	15.7 ± 0.1	<0.5	19	15.5 ± 0.1	<0.5
4	15.5 ± 0.1	<0.5	20	15.6 ± 0.1	<0.5
5	16.2 ± 0.1	<0.5	21	16.3 ± 0.1	<0.5
6	16.5 ± 0.1	<0.5	22	16.6 ± 0.1	<0.5
7	16.8 ± 0.1	<0.5	23	16.8 ± 0.1	<0.5
8	17.0 ± 0.1	<0.5	24	17.1 ± 0.1	<0.5
9	15.4 ± 0.1	<0.5	25	15.1 ± 0.1	<0.5
10	15.5 ± 0.1	<0.5	26	15.4 ± 0.1	<0.5
11	15.3 ± 0.1	<0.5	27	15.1 ± 0.1	<0.5
12	15.5 ± 0.1	<0.5	28	15.0 ± 0.1	<0.5
13	16.8 ± 0.1	<0.5	29	16.8 ± 0.1	<0.5
14	16.6 ± 0.1	<0.5	30	16.5 ± 0.1	<0.5
15	16.2 ± 0.1	<0.5	31	16.6 ± 0.1	<0.5
16	16.5 ± 0.1	<0.5	32	17.2 ± 0.1	<0.5

3.3. Technological and mechanical properties of the samples

This study, first, examined the technical properties of the standard wall tile represented in Table 3. Then, water absorption, and color values of all the studied compositions were evaluated.

The technological properties of the new compositions are presented in Table 4. As can be seen here, the water absorption values of wall tiles are almost similar to the standard. Although the addition of coarse halloysites to the bodies increases the water absorption value, it is among the accepted limits (10–20 wt.%). The color change value (ΔE) in new compositions measured using a reference sample (standard wall tile), and this value should be below 0.5. This value shows that study range of calcined halloysite does not cause large differences in the body color.

In the study, the effects of the initial halloysite grain size on the green and fired strength of the wall tiles were examined by using two different grain sizes. The change in the green strength values of the wall tile according to the sample compositions is given in Figure 5. Some compositions appear to increase the wall tile green strength considerably. In particular, compositions that increase the standard tile green strength approximately 3 times or more have been considered. Sample No. 3, which calcined at 600°C and incorporated 0.6 wt% into the body provided the highest increase in green strength. This is followed by Samples 2 and 4, which are calcined at the same temperature. Sample number 19 calcined at 1000°C, is followed by samples no 26 and 28 calcined at 1200°C. In addition to this, when the results of fine-grained halloysite and coarse-grained halloysite are compared, it is seen that the fine-grained ones increase the green strength more.

Figure 6 shows the fired strength of the wall tile bodies depends on the compositions. When evaluating this graph, the addition of halloysite caused an

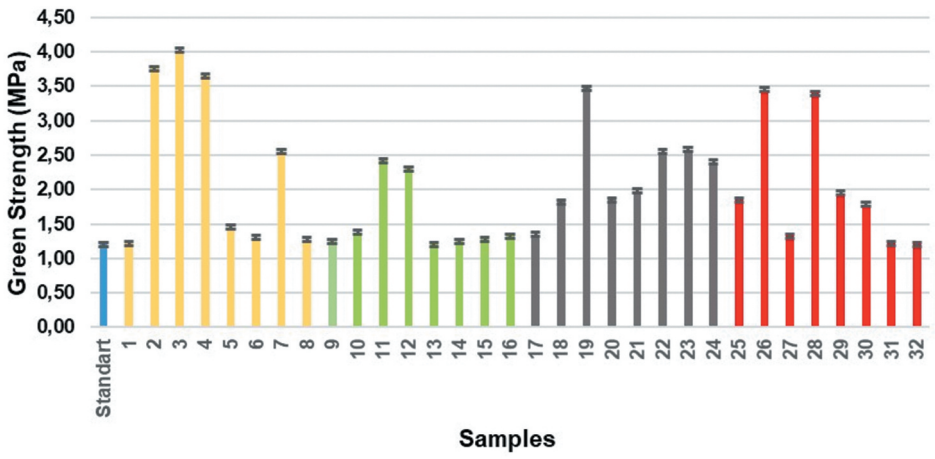

Figure 5. Green strength of the wall tile bodies depending on the compositions.

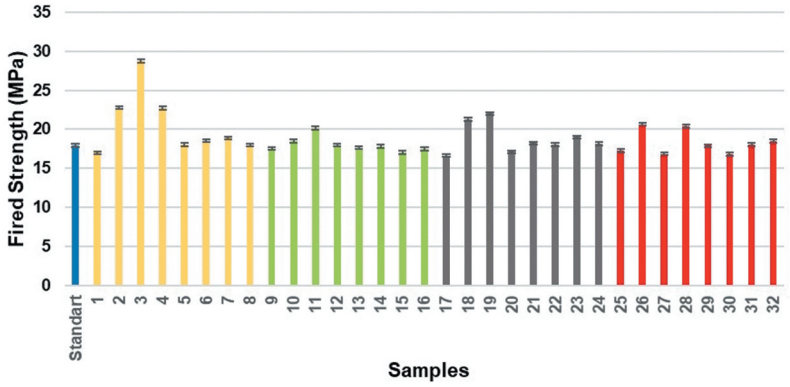

Figure 6. Fired strength of the wall tile bodies depending on the compositions.

increase in the fired strength value. The minimum requirement for a standard wall tile body is 17 MPa according to ISO-10545 standard. However, in this study generally halloysite addition caused higher fired strength than this value, since 20 MPa fired strength value was accepted as a threshold value. The composition calcined at 600°C and added 0.6% by weight showed the highest firing strength value (28.75 MPa). This sample was then calcined again at 600°C and the composition added at a rate of 0.3% by weight followed. In fired sample, unlike green sample, composition calcined at 1200°C and added at a ratio of 0.3 and 1.0% by weight have achieved a fired strength value higher than 20 MPa.

Fracture toughness of the standard and five compositions are given in Figure 7. It shows that fracture toughness is affected by the compositions. The addition of fine calcined halloysite to the compositions increased fracture toughness compared to the standard. As a result, the fracture toughness values of samples 2, 3, 4, 19, and 26, which have incredibly high strength values, are higher than the standard. From the graph, it can be seen that the composition calcined at 600°C and added 0.6% by weight (Sample no:3) showed the highest fracture toughness value (0.832 MPa.m$^{1/2}$). This value is only 0.484 MPa.m$^{1/2}$ for standard wall tile. The formation of mullite crystals in calcined halloysite added wall tile compositions caused an increase in fracture toughness values compared to standard wall tiles. Some results in the literature also support this situation. Mullite crystals have been used as reinforcing material in some studies, and it has been found to increase the fracture toughness value in these compositions [19–21].

When the relationship between fired strength (Figure 6) and fracture toughness (Figure 7) was examined, it was observed that samples with high fired strength values (Sample No: 2, Sample No: 3, Sample No: 4, Sample No: 19, Sample No: 26), fracture toughness values were also found to be high. The strength value of the standard sample (STD) is the lowest (17.74 MPa), and the fracture toughness value is also the lowest (0.484 MPa.m$^{1/2}$). In particular, it is seen that sample No. 3 (28.75 MPa), which has the highest fired strength value, shows highest fracture toughness value (0.76 MPa.m$^{1/2}$).

3.4. Phases and microstructural analyses of the samples

The crystalline phase composition of initial halloysite powder and calcined halloysite powders by XRD analyses are given in Fig. 8 and 9. The initial halloysite powder showed a (001) reflection at ~8.96° (2θ) belonged halloysite-(10A) form (JCPDS # 029–1489) as well as traces of quartz (JCPDS # 046–1045). The

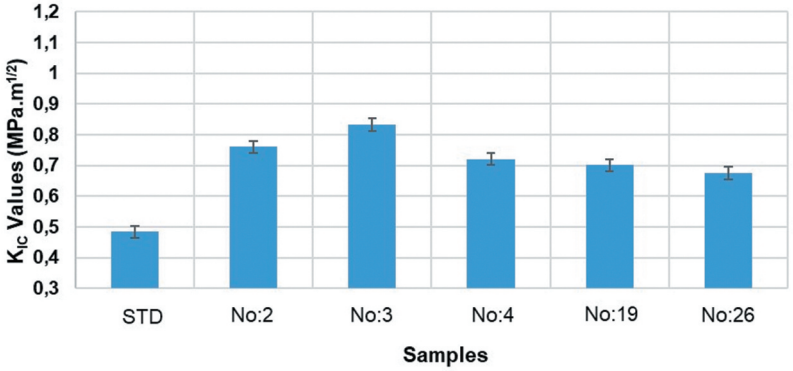

Figure 7. Fracture toughness of the 6 compositions tested.

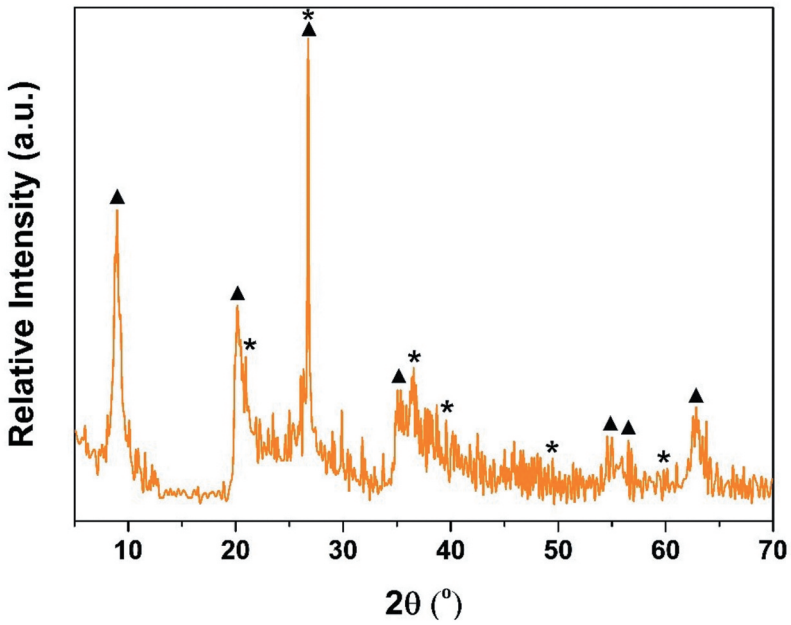

Figure 8. XRD pattern of initial halloysite composition (▲: halloysite,*: quartz).

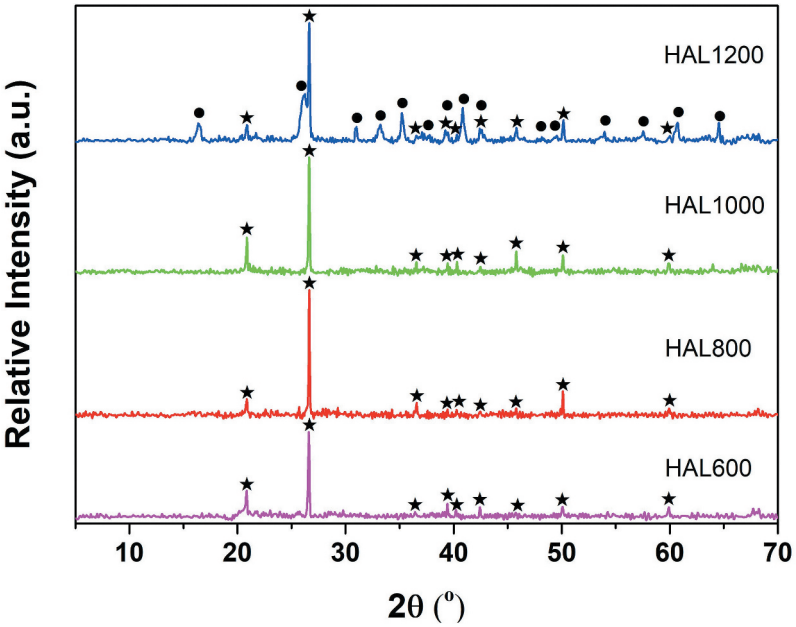

Figure 9. XRD patterns of calcined halloysite powders (□: quartz, ●: mullite).

characteristic peaks of hydrated halloysite were observed at 20.218, 26,742, 35.058 as seen from diffraction pattern (Figure 8).

After subjecting to temperatures from 600 to 1200°C, initial halloysite powders lost the peak at 8.96° (2θ). This is a significant sign for the absence of the 10 Å form and converting to the dehydrated state (Figure 9) [22]. After heat treatment at 600, 800 and 1000°C, all the halloysite powders showed quartz which exists already in the initial form, but halloysite crystalline phase was not observed. Because the heat treatment demolishes the halloysite crystalline phase by the well-known dehydroxylation process and transformed to an amorphous phase which was not detected by XRD [23,24]. Finally, when the temperature reached 1200°C, the mullite diffraction peaks (JCPDS # 015–0776) appeared beside the quartz as seen from Figure 9. At high temperature, it is obvious that recrystallization reactions take place to form mullite.

After the calcined halloysite powders added to the compositions incorporated into the wall tiles, they fired. In this study, characterization studies were continued with fine-grained halloysite-added compositions, since fine-grained halloysite powder gave better results. The focus has been on phase analysis and microstructure properties of the composition with fired strength higher than 20MPa. The XRD graphic of

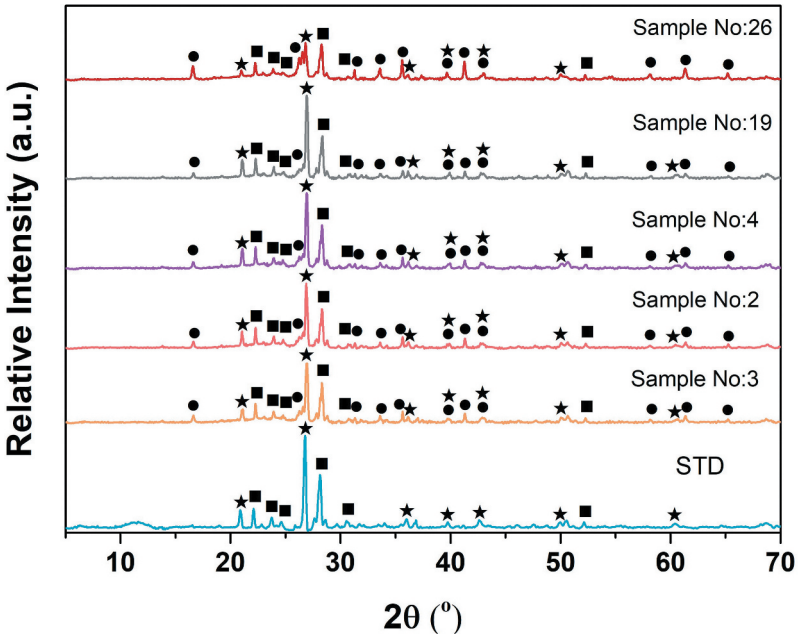

Figure 10. XRD patterns of samples containing calcined halloysite after firing (■: anorthite, □: quartz, ●: mullite).

the wall tiles fired with halloysite is given in Figure 10. The observed crystalline phases were anorthite (JCPDS # 041–1486) and quartz in standard wall tile. Compared to the STD, the mullite crystalline peaks were present in all the samples due to the addition of halloysite. This result is in good agreement with the reported studies in the literature. Harabi et al. [25] used halloysite and calcite ($CaCO_3$) to fabricate mullite and anorthite based porous membrane supports. The presence of both mullite and anorthite phases in the sintered sample was observed by XRD analysis. Haddar et al. [26] carried out a study to produce refractory ceramics with the use of non-hydrated halloysite, carbonate-containing raw materials (marl, diatomite) and silica sand mixture. The evidence of the formation of mullite, quartz, anorthite, and a small amount of cristobalite phases was obtained by XRD spectra.

The microstructures of the halloysite samples at different temperatures are given in Figure 11. Depending on the calcination temperature, morphological change

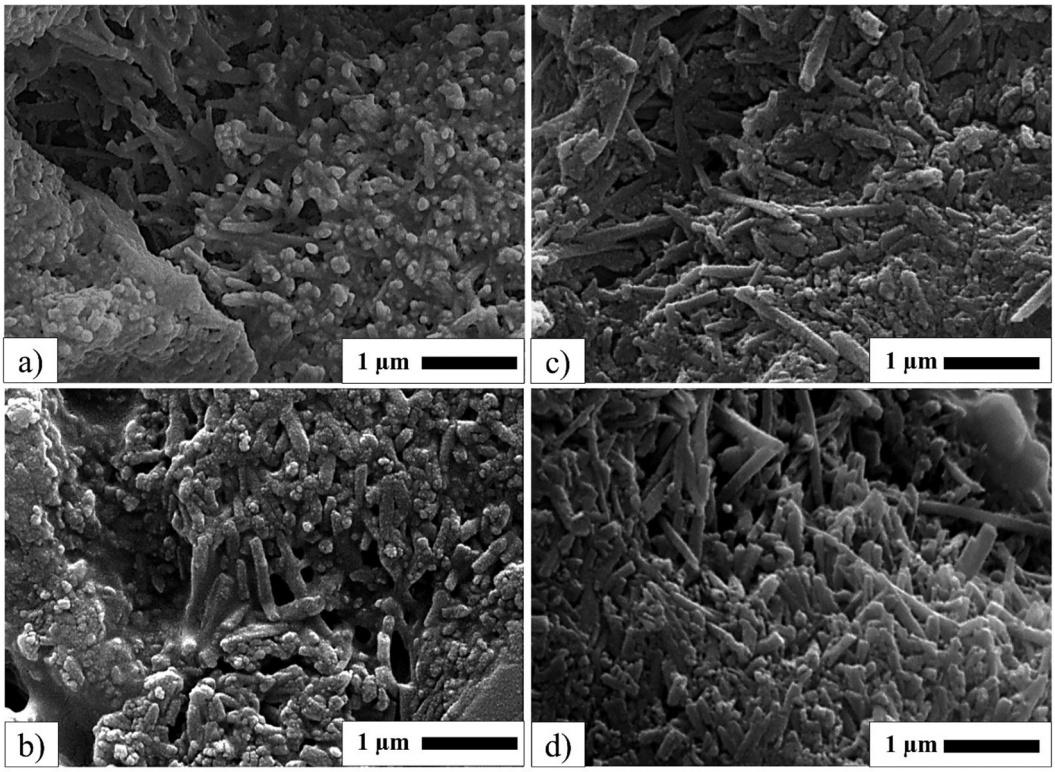

Figure 11. Microstructures of the halloysite samples calcined at different temperatures (a) 600°C, (b) 800°, (c) 1000°C, (c) 1200°C.

of the rod-like structure is observed. It can be seen that the length and aspect ratio of the rods increases with the increase in calcination temperature. The increase in the calcination temperature did not cause any degradation in the rod-like structure of the halloysite. In addition to this, fired samples' microstructures were also examined. First, SEM and EDX analyses of the standard wall tile body were carried out. The view of the microstructure is represented in Figure 12(a). Angular grains and round grains in microstructure attract attention. In the analysis taken from the region specified as 1, there is only a silicon peak in the EDX analysis Figure 12(b). It shows that these grains are quartz. In EDX analysis made from round grains (Figure 12(c)), calcium (Ca), aluminum (Al) and Silicon (Si) peaks are dominant. It shows that the grains belong to anorthite crystals. The results are also consistent with the XRD results (Figure 10).

EDX results and microstructure details of Sample 19 are given in Figure 13(a). The result of EDX analysis taken from angular grains given in Figure 13(b), there is only silicon (Si) peak, and it shows that these grains are quartz. The analysis result is taken from the section with round grains given in Figure 13(c). Calcium (Ca), aluminum (Al), and silicon (Si) peaks are dominant. These crystals are anorthite crystals. The EDX analysis result made from needlelike grains is also included in Figure 13 (d). Silicon and aluminum peaks are dominant. This shows that these needlelike grains are mullite grains. Microstructural analysis of various samples with high fired strength is given in Figure 14. Quartz, anorthite and mullite crystals also observed in these microstructures. In order to understand the increase of the high strength value in some samples, microstructure analyses were carried out from the fractured surfaces. Images of the Sample No:3, 2, 26, and finally 19 are represented in Figure 15(a–d), respectively, as can be seen from the red-framed areas in the images, especially needlelike mullite grains filled into the pores and cracks. These images can be considered evidence of the high strength and fracture toughness of these samples.

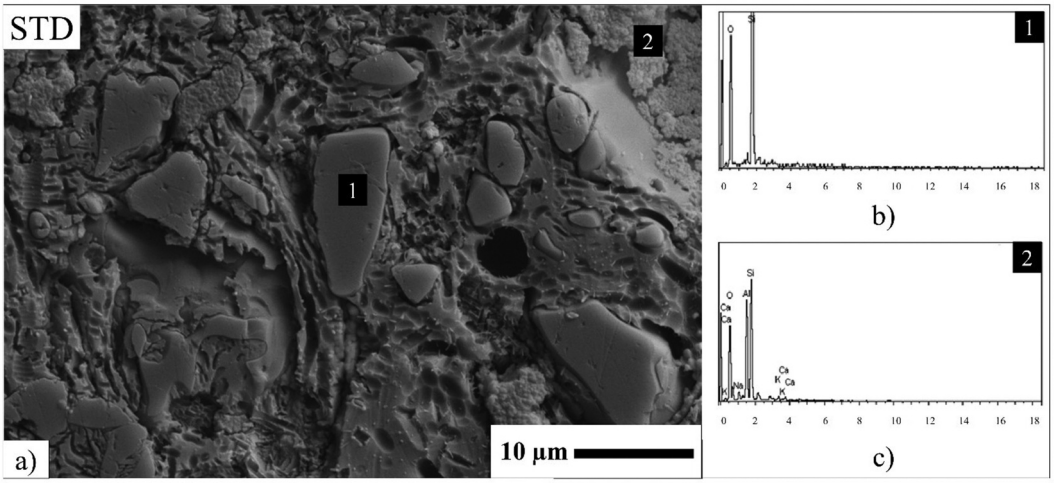

Figure 12. Microstructure and EDX analyses of the standard wall tile body.

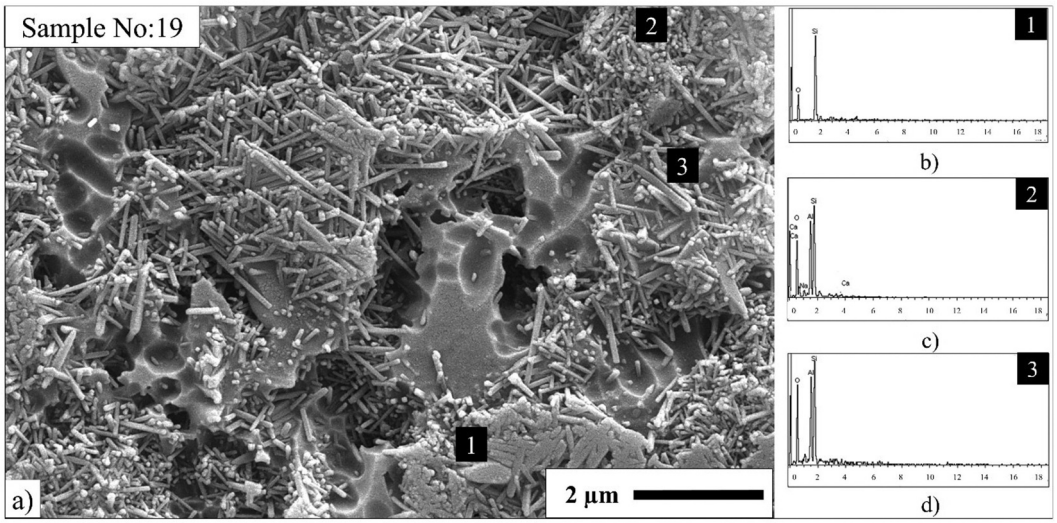

Figure 13. Microstructure of the fired wall tile sample (Sample No:19) (a) and EDX analyses results of different region (b)-(c)-(d).

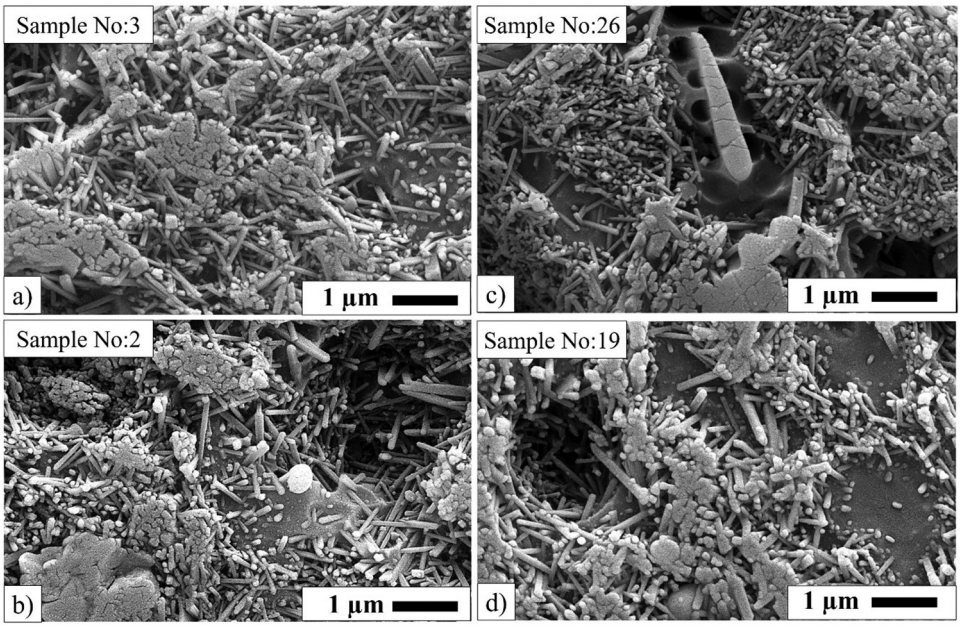

Figure 14. Microstructures of some fired samples.

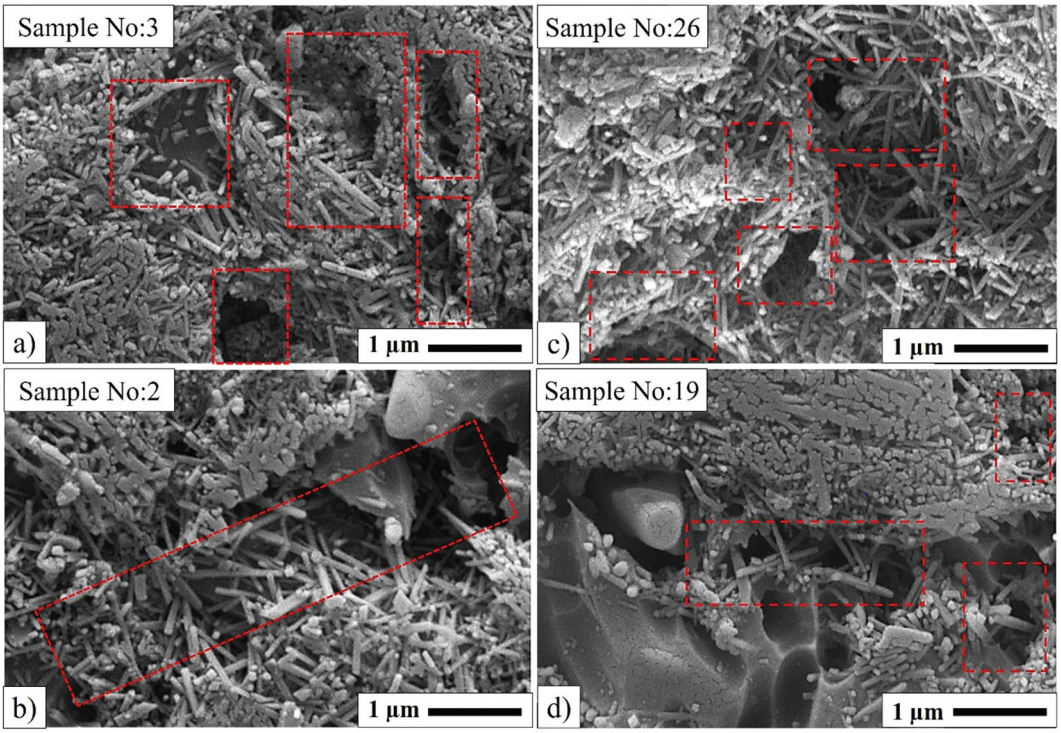

Figure 15. Microstructure images of the samples taken from fractured surfaces.

The microstructure analysis of the compositions added to the wall tile at the same rate, calcined to different degrees and provide high fired strength, was also analyzed-results presented in Figure 16. In the microstructure of the halloysite composition (Sample No: 2) calcined at 600°C, added to the structure of wall tiles at a ratio of 0.3% by weight, cause to formation of mullite grains with an average of 409 ± 6 nm length and 5.82 ± 0.1 aspect ratio. Halloysites (Sample No: 18) calcined at 1000 degrees and added to the composition at the same rate form mullite crystals with an average length of 433 ± 6 nm and an aspect ratio of 7.05 ± 0.1. In the microstructure (Sample No: 26) of the composition added at 1200 degrees and the same rate, there are mullite crystals with an average length of 464 nm ± 6 nm and aspect ratio of 7.25 ± 0.1. As the calcination temperature increases, there is an increase in the size and aspect

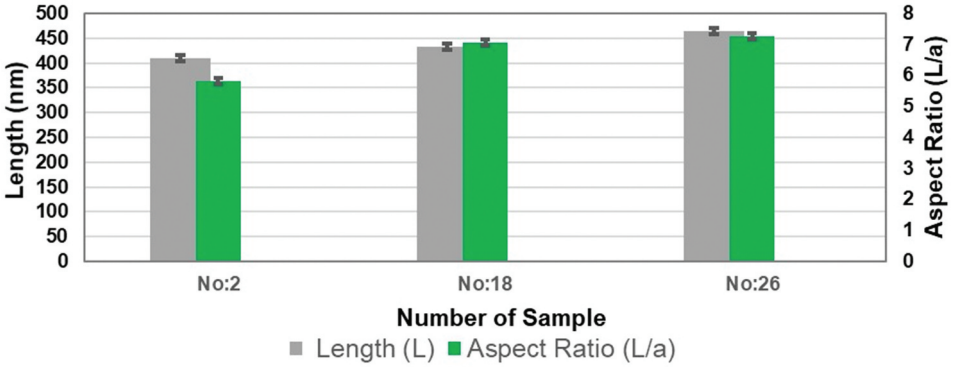

Figure 16. Microstructural analyses of the samples depending on the compositions.

ratio of mullite crystals. However, it was observed that this increase did not make a significant difference in the strength value of these samples. The mechanism of increase in strength and fracture toughness was carried out by filling mullite needlelike grains into discontinuities such as cracks or pores, as indicated in Figure 15. Therefore, it can interpret that the contribution of calcined halloysite provides the "mullite hypothesis" [12] results, thus increasing the strength& fracture toughness values.

Unlike these, the addition of halloysite compositions calcined at 800°C to the wall tile increased the fired strength (providing standard value), but not as high as the other compositions (18.5 MPa). For this, the composition's microstructure (Sample No: 10), which was calcined at 800 degrees and added at a ratio of 0.3% by weight, was examined (Figure 17). Here, it shows that mullite crystals are clumped, especially in the areas framed in black. It is noteworthy that the stacked crystals overlap and that the individual needlelike grains do not distribute literally. Therefore, it is understandable why the expected increase in these samples did not occur.

4. Conclusions

In this study, effect of calcined halloysite on the microstructure and properties of the wall tile bodies were studied. The following conclusions can be drawn:

TG-DTA analyses show that halloysite main transformation with temperature. The DTA curve shows two endotherm and one exotherm peaks, centered at 92.5°C, 499°C and 982°C, respectively. FT-IR spectroscopy studies show that the primary IR absorption peak shifts to the low wave-number, indicating the dehydroxylation of the halloysite with increasing calcination temperature. The addition of calcined halloysite powders to standard wall tiles did not cause a significant change in technological properties such as water absorption, and color values. However, it has been observed that it causes a considerable increase, especially in green strength and fired strength values. The addition of halloysite powders, which are calcined at 600–1000°C and 1200°C in particular, to the wall tile caused a significant increase in the green strength and fired strength values. It is thought that the biggest reason for the rise in fired strengths is

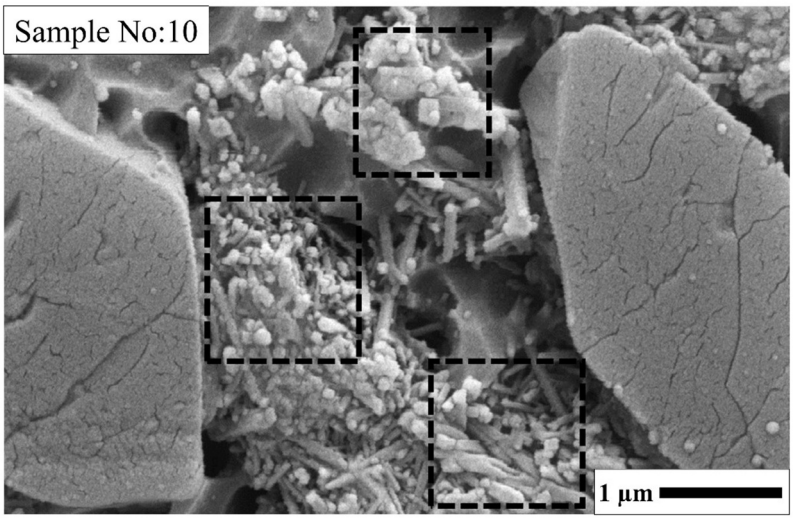

Figure 17. Microstructure image of the sample number 10.

related to mullite crystallization. Especially in the microstructures taken from the fractured surfaces, it was observed that the needlelike mullite grains filled into the cracks and pores. This situation explains the high strength and fracture toughness values in the samples with calcined halloysite addition. Besides, the study concluded that the mixing procedure is significant in the process. Especially during the addition of calcined halloysite to the standard body slurry, homogeneous integration of needlelike grains into the system becomes critical. The results considering both green and fired strength may allow for thinner section wall tile production without changing the existing forming process.

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Declaration of competing interest

The authors declare that they have no known competing financial interest or personal relationship that could have appeared to influence the work reported in this paper.

Disclosure statement

No potential conflict of interest was reported by the author(s).

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