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Investigation of thermal transformation of composite material obtained from granite and recrystallized limestone natural stone wastes

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Research Article

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Waste, Limestone, Thermal-Mechanical Behavior, Granite, Natural Stone.

ABSTRACT

In this study, the usability of granite (magmatic) and recrystallized limestone (metamorphic) natural stone wastes as alternative raw materials in ceramic tile production was investigated. Based on the CaO, SiO_2, and Al_2O_3 compounds found in waste powders, mixtures containing 65% granite and 35% recrystallized limestone (by mass) were prepared to obtain the ceramic phases of gehlenite, wollastonite and anorthite as a result of thermal transformation. The grain size of both raw materials is -149 µm (d_{90} = 110.957 µm). The powder mixtures were moistened with 7% (by mass) water and shaped in a steel mold with dimensions of 75x20x50 mm with a uniaxial press with a setting of 127 MPa. The first series samples were called as natural building stone (DYT), and the second series samples, in which wood chips of 2% (by mass) -1 mm grain size are added to obtain porous material, were called as natural building stone - porous (DYT-G). The samples belonging to both series was applied heat treatment at 1.160°C. Phase analysis of samples obtained after heat treatment was measured by X-Ray Diffraction (XRD) and Scanning Electron Microscope (SEM-EDS) methods, and sintering properties were measured using water absorption coefficient, flexural strength, modulus of elasticity, density-porosity and color measurement tests. Gehlenite and wollastonite phases were detected in the heat treated samples, but no anorthite phase was observed. According to the test results, it was determined that the flexural strength (22.64 MPa) of the DYT marked sample was in accordance with the ceramic tile standards. In the DYT-G example, despite the decreasing unit volume mass value, it was determined that the bending strength (16.50 MPa) was in the range of ceramic tile strength values.

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1. Introduction

Increasing pace of urban development and housing parallel to industrialization in our country has led to an increased usage of natural stones. To meet the increasing demand, production capacities of factories were improved and new natural stone deposits were found. Türkiye holds approximately 40% of the planet's natural stone reserves with 5.1 billion m^3 of minable marble, 2.8 billion m^3 of minable travertine and 1 billion m^3 of granite reserves. Annual natural stone production of Türkiye is around 11.5 billion tons with a total production capacity of plate manufacturing factories being approximately 6.5 billion m^2. Almost all of the production is handled by the private sector (Ministry of Trade, the Republic of Türkiye, 2014).

Block and plate productions reaching massive volumes has led to large amounts of natural stone waste which in return became an environmental issue.

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Due to the inability to reuse the waste in its entirety, it has also caused economic losses. Erol and Pekdemir (2018) has prepared mixtures consisting raw materials of 5% pure aluminum oxide (Al_2O_3) powder, 35% recrystallized limestone (metamorphic) and 60% granite (magmatic). In the mentioned study, an increase in the intensity of wollastonite and gehlenite phases were observed for the samples with firing temperature of 1.150 °C in contrast to samples that were treated with 1.140 °C. An even further amount of increase in these two phases were observed for 1.160 as well as an observation of an additional anorthite phase. They stated that the occurrence of anorthite phase greatly contributes to the resistance of the sample. It was detected in the study that when the firing temperature was increased from 1.150 °C to 1.160 °C, the elasticity modulus and flexural strength values of the samples increased by 2.4% and 28%, respectively. In red ceramic ware production process, natural stone wastes can be used as potential additive material. (Gustavo, 2019). Genç et al. (2019) researched the possibilities of usage of zeolitic tuffitites in wall tiles and consequentially discovered them to be a usable raw material in wall tiles ingredients. Pastor et al. (2019) states that the natural stone industry produces large amounts of industrial waste annually and that these wastes could be used as binding ingredient to decrease the negative environmental effects arising from waste storage processes. In their study, they respectively added 5, 10, 15, 20 and 25 percent limestone by dry mass to the clay raw material and as a result determined an increase in the endurance and a decrease in deformation properties of the samples.

Stoichiometrically, wollastonite phase is calcium meta-silicate ($CaSiO_3$), a mineral visually white in color and needle shaped. Properties related to its alkali form and crystal structure ensures it to become a commercially valuable product (Ciullo, 1996). Wollastonite dissolves in strong inorganic acids (such as HCl) and has a low level of dissolution in organic acids (such as CH_3COOH) (Kogel et al., 2006). It could be used as a substitute material for raw materials such as feldspar, calcite, quartz and dolomite in ceramic industry in which it is used widely. It is also used as a preventative material for deformation due to its property of preventing thermal expansion. Moreover, it increases the strength of the raw and fired ceramic products as well as reducing drying times and energy costs while reducing ceramic firing times (DPT, 2001).

On the other hand, stoichiometric gehlenite phase is calcium aluminosilicate ($Ca_2Al_2SiO_7$). It is considered to be a product of CaO and alumina silicate reaction. (Sousa and Holanda, 2005). In the production of wall tiles, marble powders, talc and dolomite are used as calcium sources. Gehlenite and anorthite phases are formed as a result of the reaction of metakaolin, which is the transition phase of kaolinite in the tile, and CaO, which is formed as a result of thermal decomposition of calcium carbonate (Kara et al., 2006). The Gehlenite phase ($Ca_2Al_2SiO_7$) is formed by hydrated lime and cement components that have been heat-treated at low temperatures (<1.200 °C). Since the stable temperature range of the Gehlenite phase is 900-1.150 °C, it can form at low temperatures. The reason for the absence of gehlenite in the cement is that the clinker is heat treated above this temperature range. Calcium alumina silicate compounds, which are more stable at high temperatures, are formed in cement (Callebaut et al., 2001).

In this study, it is aimed to bring an alternative solution to the environmental pollution that occurs with the economic revaluation of the large amount of waste generated as a result of natural stone mining activities.

2. Materials and Methods

2.1. Materials

The samples determined as granite and limestone according to the XRD results in accordance with the TS EN 12407 standards. Chemical composition of the aforementioned samples determined as crystallized limestone and granite by XRF (X-ray Fluorescence) results in accordance with the TS EN 15309 are given in Table 1. Granitoids are rocks of magmatic origin rich in silica ($SiO_2 \geq 66\%$) and alkalies (feldspars) and poor in calcium, magnesium and iron (amphibole, biotite etc.) contents. Granitoids are rich in range of color starting with gray-white, gray, gray-green and even brown-reddish tones. As a rock type they are also quite durable against acids due to their formation and chemical content. (Gündüz, 1995). The origin of the granitoid rock used in the study is the Eskişehir district and is granular in texture. Mineralogical composition

Table 1- Chemical properties of the raw materials used in the study.

Raw Material	SiO_2 (%)	Al_2O_3 (%)	MgO (%)	CaO (%)	Na_2O (%)	Fe_2O_3 (%)	LoI (%)	Other (%)
Granite (Magmatic)	65.9	17.0	0.9	3.8	4.6	3.0	0.5	4.3
Recrystallized Limestone (Metamorphic)	0.3	0.1	0.3	55.2	<0.1	0.1	43.70	0.2

LoI: Loss on Ignition.

of the rock is of plagioclase, quartz, biotite, alkali feldspar and amphibole. Recrystallized limestones are formed due to neomorphism under the effect of heat and pressure. Essentially, they are made up of calcite minerals and contain a minimum of 90% carbonate ($CaCO_3$). Color range can differ due to the minerals in their composition and are not durable against acids (HCl, $C_6H_8O_7$, HNO_3, H_2SO_4 etc.). The origin of the limestones used in the study is the Bilecik district and are massive fine grained in texture. Mineralogical composition of this rock belonging to carbonate group minerals (calcite) are intraclast, pellet and ooid and houses fossilized shells.

2.2. Method

Appropriate mixtures were prepared in consideration of the wastes being used as replacement material in production of floor and wall tiles in accordance with the SiO_2-Al_2O_3-CaO system (Figure 1). In preparing the mixtures, 35% recrystallized limestone (metamorphic)and 65% percent granite (magmatic)raw materials were used, respectively.

In the beginning of the study, mixtures prepared with natural building stone samples ground to -149 µm (-100 mesh) are ball milled into homogeneity for 30 minutes with a speed of 180 rpm and subsequently dried at a temperature of 100 °C. 7% (6% carboxymethyl cellulose) forming water was added to the mixture and small pellets were pressed under 127 MPa pressure, in continuation of the study. (Figure 2). Pellets were then fired at 1.140, 1.150 and 1.160 °C with an electric oven (Protherm Model PLF 160/15) at a temperature of 5°C/minute and kept in

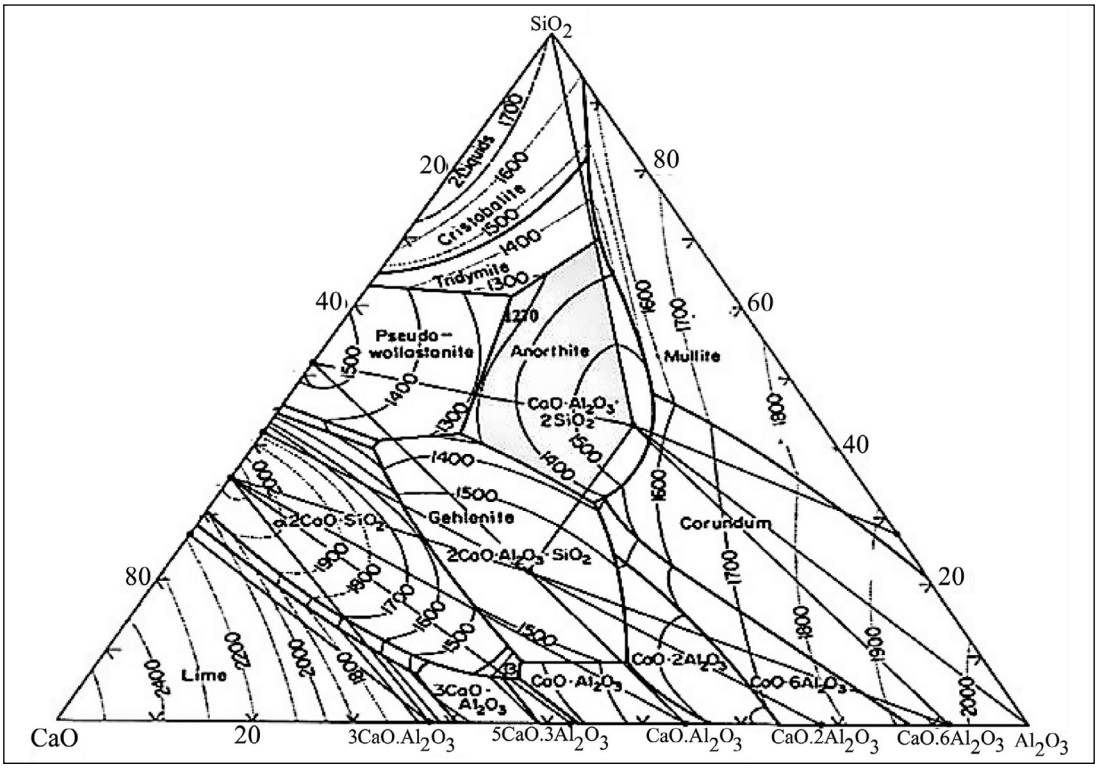

Figure 1- CaO-SiO_2-Al_2O_3 phases and isotherms (Sletson and Reed, 1988).

the last temperature for 1 minute. In the second study conducted, (Figure 3), the first procedure was repeated for samples ground to -74 µm (-200 mesh).

In the continuation of the study, samples that were fired in the oven were sent to XRD analysis. According to the analysis results (Table 2), target phases of wollastonite and gehlenite were determined for all three separate temperature points. Considering the endurance point to be higher due to results, firing temperature and the mixture size of the samples were determined to be 1.160 ºC and 149 µm, respectively.

Table 2- XRD analysis results of fired samples.

Heat, °C	More	Medium	Less
1.140	Wollastonite	Gehlenite	Quartz, Akermanite
1.150	Wollastonite	Gehlenite	Quartz, Akermanite
1.160	Wollastonite	Gehlenite	Quartz, Akermanite

Upon determining the process temperature and grain size, raw material samples were ground to a size below -149 µm and then dry sieved. Using laser grain size analyzer (Malvern Mastersizer 2000), operating according to the TS ISO 13320 (Laser Radiation Diffraction Method) standards, a suspension was prepared for the mixture grain size distribution analyses, and were analyzed using the device (Table 3). According to these results, 10% of the grain size of the mixture is below 6.961 µm, 50% is below 41.546 µm, and 90% is below 110.957 µm.

Table 3- Particle size distribution of the mixing materials (% distribution).

Mixture	d_{10} (µm)	d_{50} (µm)	d_{90} (µm)
Particle size	6.961	41.546	110.957

To obtain the DYT (Natural Building Block, working code) product, samples of -149 µm were mixed, the mixture was molded in a 75x20x50 mm steel mold using 7% molding water (6% carboxymethyl cellulose) and under 127 MPa pressure (Figure 4), subsequently fired at 1.160 °C. Following the process, 1 mm wood chip additive material with a content of 2.1% was added to mixture for the DYT-G (Natural Stone - Porous, working code) process to obtain a more porous product and the process was repeated.

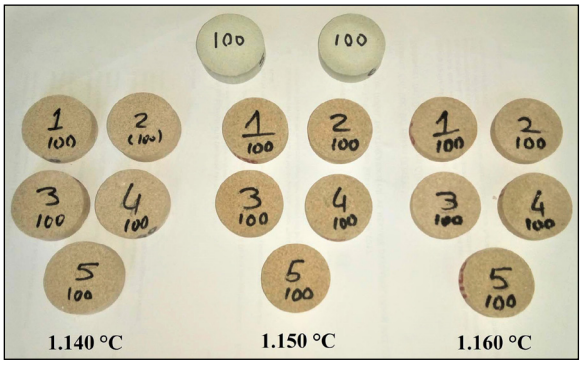

Figure 2- -100 Mesh product samples.

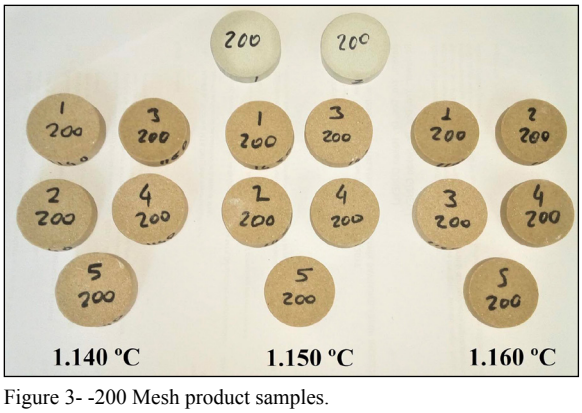

Figure 3- -200 Mesh product samples.

3. Research and Findings

3.1. Physical Tests

In the tests performed on the samples, results of the Modulus of Elasticity experiment, performed in accordance with the ASTM C1259-15 (2015) standards and a three-point flexural strength test device (Toni Technik Baustoffprüfsysteme GmbH, Germany), as well as the apparent density analyses

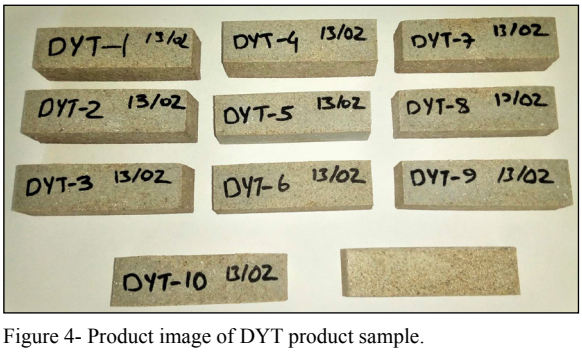

Figure 4- Product image of DYT product sample.

performed in accordance with the ASTM D5550-14 (2014) standards were given in Table 4. To determine the water absorption rates of the fired samples, first the samples were dried at 70 °C in the drying oven and weighted 24 hours apart until there was no more mass change. Dried samples were kept under water for 48 hours in room temperature and then weighted 24 hours apart until they reached stable saturation while still being kept underwater besides the weighing process. Physical test results of the samples from the 1.Ç (first study) (Erol and Pekdemir, 2018) were given in Table 4. While the flexural strength of the DYT sample, its modulus of elasticity and apparent density values in comparison to the values of DYT-G sample were respectively, 37.2%, 15% and 4.8% higher, total-open porosity and water absorption coefficient were respectively, approximately 43.7% - 11.3% and 65.9% lower. Flexural strength, the modulus of elasticity and apparent density values of the DYT-G sample in comparison to 1.Ç sample are respectively and approximately 123%, 98.5% ve 21.2% higher, total-open porosity and water absorption coefficient on the other hand are respectively and approximately 56.7% - 25.2% ve 67.6% lower.

3.2. Color Measurement Tests

L (white), a (green) and b (blue) color values (Figure 4) of fired samples were made using a color measurement device (Minolta CR300 Chromameter), results of which from the DYT and DYT-G samples are given in Table 5. For the L value representing the whiteness degree, it was determined that the DYT sample (58.37) had a lower value then the DYT-G sample (61.40). For the remaining colors, it was determined that DYT sample had lower amounts of green a (1.50) and blue b (8.847) values in comparison to DYT-G which respectively had values of a (0.98) and b (7.830).

Table 5- Color measurement results of fired samples.

Firing Temperature 1160 °C	**Parameters**		
	L	a	b
DYT	58.37	1.50	8.847
DYT-G	61.40	0.98	7.830

3.3. SEM-EDS Analyses

SEM and EDS analyses (Figure 5 and Table 6) are performed for the samples of DYT product. According to the results, point of the image marked as 1, unreacted calcium oxide (CaO) can be seen. On point marked as 2, wollastonite ($CaSiO_3$) and gehlenite [$Ca_2Al(AlSiO_7)$] phases, on points marked as 3, 4 and 5 silicon dioxide (SiO_2) and on points 6 and 7, alkali-rich wollastonite ($CaSiO_3$) and gehlenite [$Ca_2Al(AlSiO_7)$] phases were detected. On point 8, porosity of approximately 150 ηm can be seen, and many micro, meso and macro porosities are found in the structure. According to SEM imaging (Figure 6) and the EDS analysis results (Table 7) of the DYT sample, it is determined that wollastonite ($CaSiO_3$) and gehlenite [$Ca_2Al(AlSiO_7)$] phases started to crystallize at points marked as 1-7.

According to the SEM imaging sample (Figure 7) and EDS analyses of the DYT (Table 8), formation of inert calcium oxide (CaO) phases can be seen on point 1. At points 2, alkaline-rich wollastonite ($CaSiO_3$) and gehlenite [$Ca_2Al(AlSiO_7)$] phases were formed and the contact point was determined. Strength decreases due to these contact points. SEM imaging belonging to the DYT sample (Figure 8) porosity distribution is determined to be quite homogeneous.

According to the SEM image (Figure 9) and EDS analyses (Table 9) of the DYT-G sample, inert calcium oxide (CaO) is seen in points marked as 9.2 and 7; wollastonite ($CaSiO_3$) and gehlenite [$Ca_2Al(AlSiO_7)$]

Table 4- Physical test results of fired samples.

Sample	**Flexural Strength (MPa)**	**Modulus of Elasticity**	**Visible Density (g/cm³)**	**Real Density (g/cm³)**	**Open Porosity (%)**	**Total Porosity (%)**	**Water Absorption Coefficient (%)**
DYT	22.64	37.25	1.98	2.78	8.0	28.9	4.1
DYT-G	16.5	32.39	1.89	2.78	14.2	32.17	6.8
1.Ç*	7.40	16.32	1.56	2.75	32.8	43.0	21.0

1.Ç* (Erol and Pekdemir, 2018).

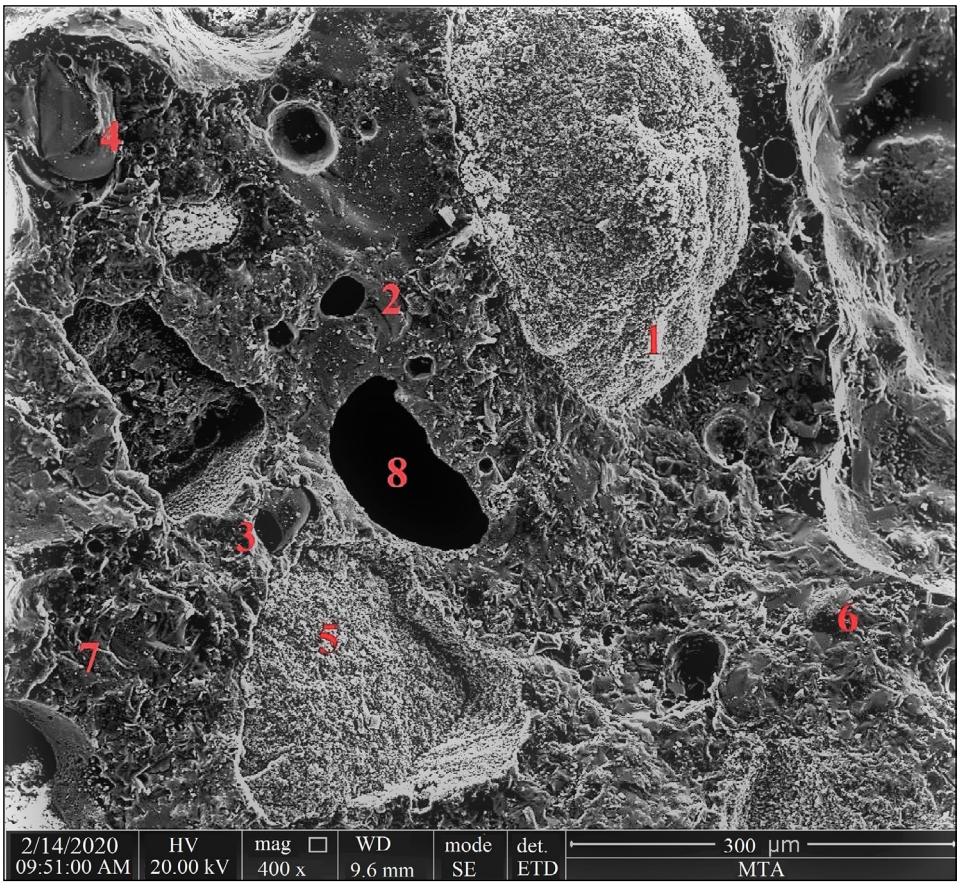

Figure 5- SEM image of the DYT product sample.

Table 6- EDS analysis of DYT product sample.

Point	O (%)	Mg (%)	Al (%)	Si (%)	Ca (%)	Na (%)	K (%)	Fe (%)	C (%)	Ti (%)
1	23.65	0.15	0.33	1.35	74.53	-	-	-	-	-
2	40.70	1.01	10.69	31.44	3.25	8.00	4.20	0.71	-	-
3	45.80	-	-	54.20	-	-	-	-	-	-
4	45.65	-	1.40	48.41	4.54	-	-	-	-	-
5	52.49	0.82	0.12	0.25	34.40	-	-	0.28	11.65	-
6	36.68	1.00	13.46	24.26	11.00	6.54	2.49	6.30	-	-
7	23.65	0.15	0.33	1.35	74.53	-	-	-	-	-

phases rich in alkali can be seen in points marked as 1, 3, 4, 5, 6 ve 8. On point marked as 10, porosity of apporoximately 164 ηm can be seen, in many micro, meso and macro forms. According to the SEM image of the DYT-G product sample (Figure 10) and EDS analyses (Table 10), formation of inert calcium oxide (CaO) at point marked as 3, wollastonite ($CaSiO_3$) and gehlenite [$Ca_2Al(AlSiO_7)$] phases rich in alkali at points 1 and 2 can be observed as the contact points. Strength decreases due to these contact points. The porosity distribution of the DYT-G product sample is determined to be quite homogeneous in the SEM imaging (Figure 11). Additionally, it is determined that the porosity ratio of the DYT-G product sample is much higher than the DYT product sample, as expected.

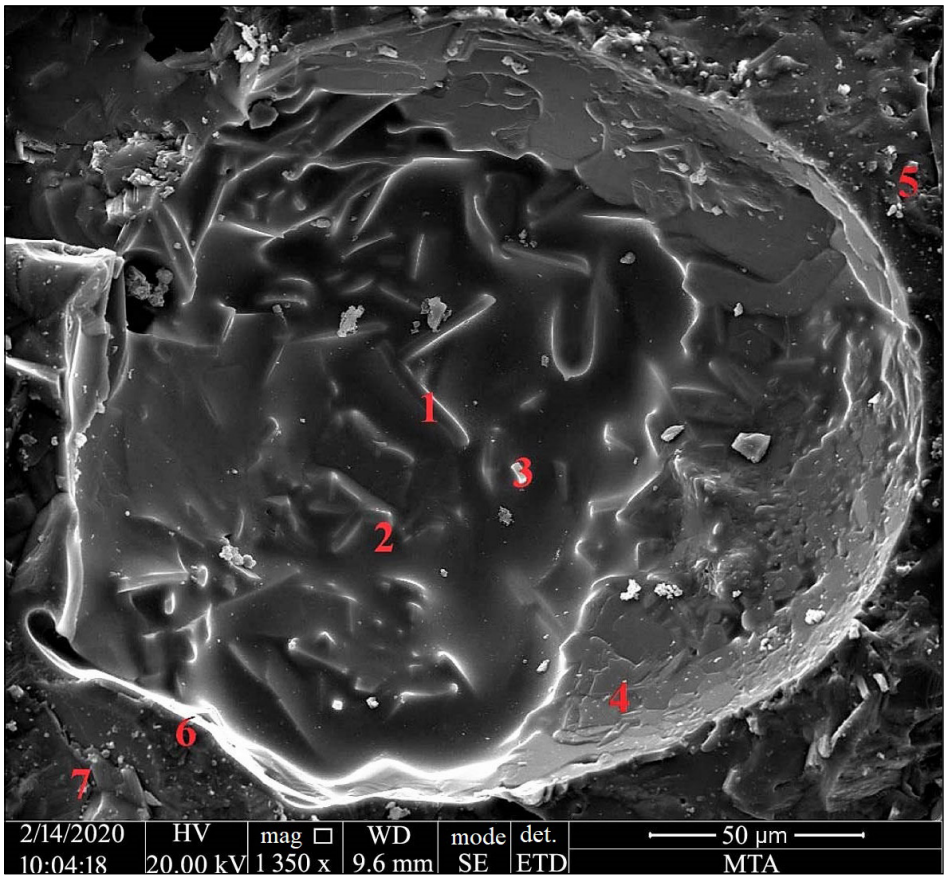

Figure 6- SEM image of the DYT product sample.

Table 7- EDS analysis of DYT product sample.

Point	O (%)	Mg (%)	Al (%)	Si (%)	Ca (%)	Na (%)	K (%)	Fe (%)	Ti (%)
1	35.57	0.94	5.72	22.26	26.08	3.58	1.86	3.42	0.58
2	37.44	0.81	11.51	27.47	8.04	7.05	3.73	3.65	0.31
3	41.55	1.09	6.88	23.03	19.04	4.67	1.60	2.09	0.05
4	41.84	-	1.02	22.38	31.60	2.07	0.25	0.85	-
5	34.22	1.49	14.12	27.99	8.03	7.62	3.85	2.69	-
6	22.12	0.96	11.50	28.69	20.41	3.81	3.69	8.02	0.82
7	29.65	2.18	11.48	27.08	14.54	6.86	3.00	4.89	0.32

4. Discussion

In this study, only natural stone wastes were used and mixtures were prepared using 35% recrystallized limestone (metamorphic), 65% granite (magmatic) raw materials. According to the XRD results obtained by firing samples prepared at 1.140 - 1.150 - 1.160 °C, target phases of wollastonite and gehlenite were reached.

According to the results of the physical tests performed, comparing the samples of DYT and DYT-G with wood chip added, the flexural strength, modulus of elasticity and the apparent density of DYT-G sample was determined to be lower. True density of the samples was determined to be the same, yet their total-open porosity and water absorption values were higher. According to TS EN 14411 (Table 11) Ceramic Tile Standards, as the water absorption

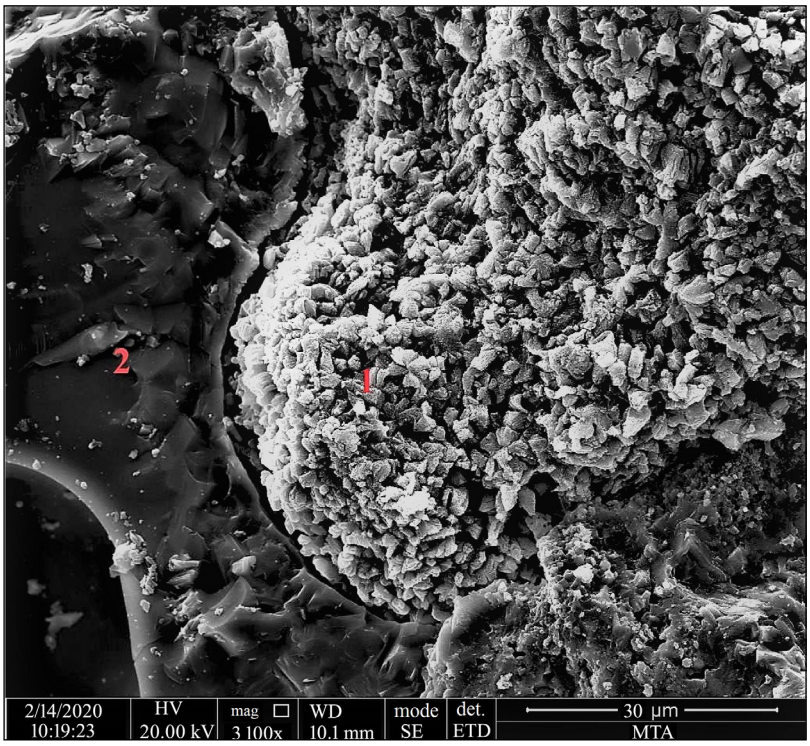

Figure 7- SEM image of the DYT product sample.

Table 8- EDS analysis of DYT product sample.

Point	O (%)	Mg (%)	Al (%)	Si (%)	Ca (%)	Na (%)	K (%)	Fe (%)	Ti (%)
1	39.56	0.28	0.08	0.61	59.47	-	-	-	-
2	32.93	0.49	13.08	33.18	6.61	6.34	6.23	1.14	-

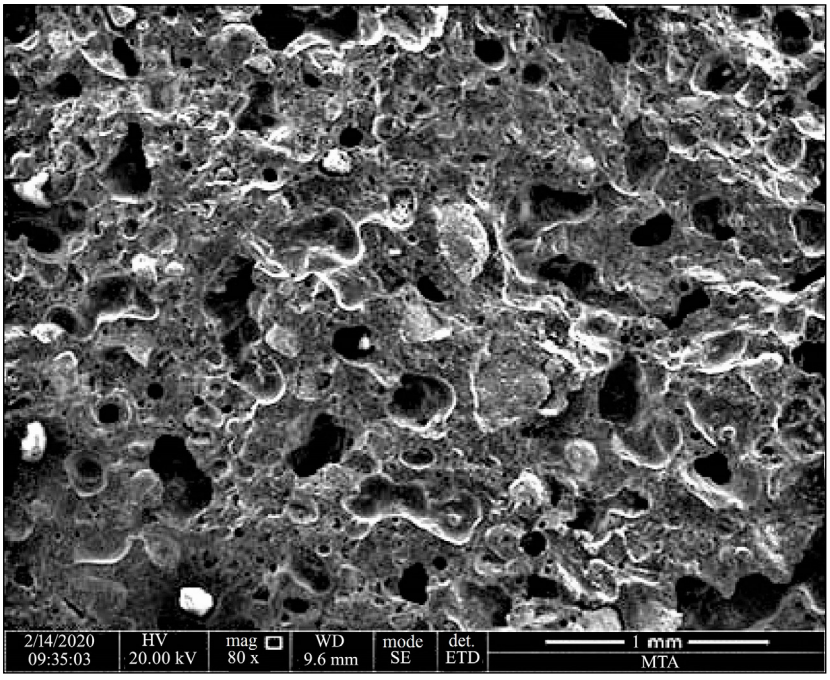

Figure 8- SEM image of the DYT product sample.

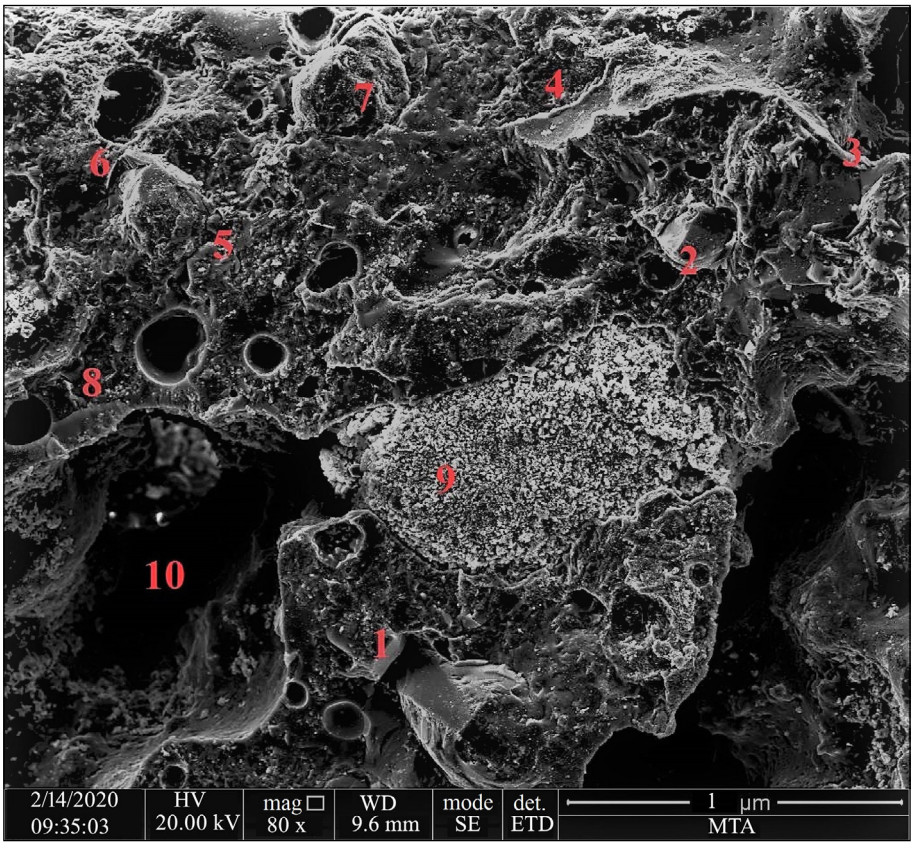

Figure 9– SEM image of the DYT-G product sample.

Table 9- EDS analysis of DYT-G product sample.

Point	O (%)	Mg (%)	Al (%)	Si (%)	Ca (%)	Na (%)	K (%)	Fe (%)	Ti (%)
1	43.05	0.68	0.27	0.77	55.23	-	-	-	-
2	33.29	1.15	11.81	22.27	21.09	6.16	1.57	2.67	-
3	46.48	-	1.57	49.26	2.68	-	-	-	-
4	36.34	1.33	12.10	25.07	7.70	7.65	3.62	5.65	0.53
5	39.49	2.29	10.72	19.71	17.68	7.15	1.02	1.94	-
6	42.10	0.71	1.17	24.36	29.06	1.55	0.42	0.63	-
7	36.38	0.72	12.64	24.75	13.91	7.12	3.06	1.42	-
8	55.44	-	1.03	42.66	0.87	-	-	-	-
9	31.05	-	14.61	26.21	12.40	6.33	4.52	4.88	-

rate DYT sample was determined to be 4.1%, in accordance with the standards, it is classified to be in the BIIa group. As the flexural strength value (22.64 MPa) is higher than the limit value of the standard (22 MPa) and single sample (20 MPa) value, it is above the values requested by the standards. According to TS EN 14411 (Table 11) Ceramic Tile Standards, as the water absorption rate of the DYT-G sample is determined to be 6.8%, it is classified to be in the BIIb group. Although the flexural strength value (16.5 MPa) is slightly lower than the limit values of the standard (18 MPa), as it is higher than the single sample (16 MPa) value, it is above the values determined by the standards.

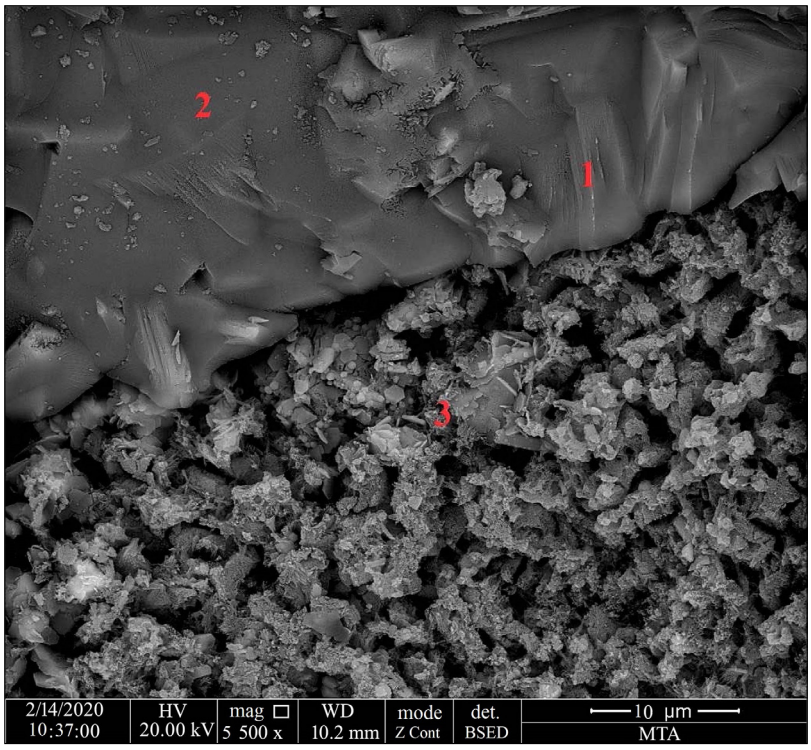

Figure 10- SEM image of DYT-G product sample.

Table 10- EDS-2 analyzes of DYT-G product sample.

Point	O (%)	Mg (%)	Al (%)	Si (%)	Ca (%)	Na (%)	K (%)	Fe (%)	Ti (%)
1	44.18	0.55	0.15	0.56	54.56	-	-	-	-
2	25.32	0.52	11.20	21.28	26.49	6.28	2.02	6.89	-
3	21.38	0.15	13.69	28.14	21.17	4.64	5.11	4.82	0.91

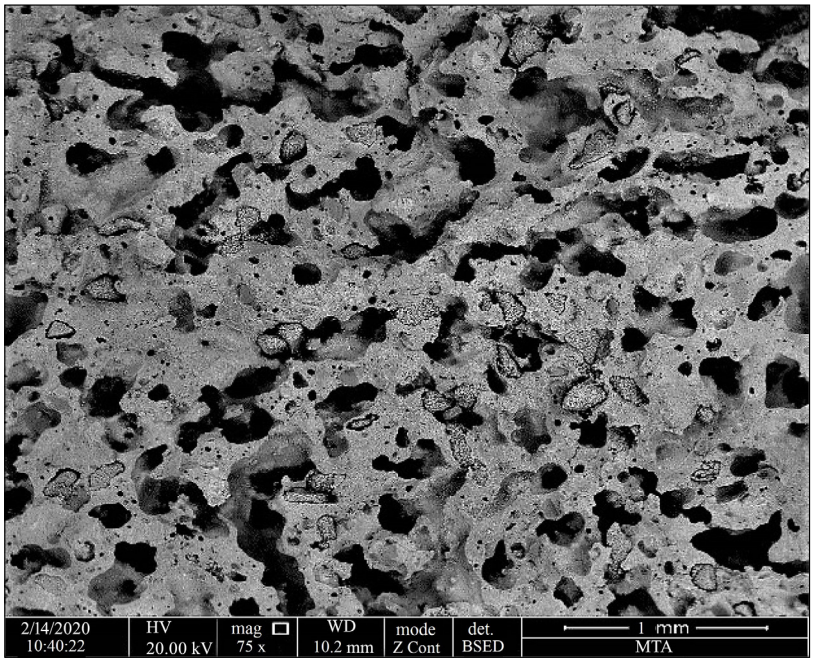

Figure 11- SEM image of the DYT-G product sample.

Table 11- Limit values of TS EN 14411 standard.

Standard Group	Water Absorption (%)	Flexural Strength (MPa)	
BIIa	$3 < w_a \leq 6$	Average at least	22
		One sample at least	20
BIIb	$6 < W_a \leq 10$	Average at least	18
		One sample at least	16

5. Results

The aim of this research is to obtain similar products to floor and wall tiles, completely from natural stone wastes. As a result, it is observed that anorthite, as the dominant phase in tiles, did not form through pyrolysis of natural stone wastes. A large volume of deformation is observed in the samples in anorthite formation temperature due to the melting effects of Na-feldspar and K-feldspar, contained in granite. Thus, for the temperatures above 1.160°C, no heat treatment was able to be performed. The glassy phase with high viscosity formed due to the melting effect prevented the diffusion of Al_2O_3. Therefore, Al_2O_3 needed for the formation of anorthite did not react. Flexural strength values of the seramics without the formation of anorthite were 22.64 MPa for DYT and 16.5 MPa for DYT-G. While it is undesirable for floor tiles, porosity is desired for wall tiles to adhere with mortar. Hence, porosity substance was made using wood chip additives which resulted in partial deformation in glassy phase samples of high volume formed post-firing of ceramic samples. In the light of all the aforementioned results, in contrast to producing building material solely using natural stone wastes, it is recommended only for the usage as an additive material in production of ceramic tiles. In case it is preferred to be used as a building material without the aim of tile production, it was observed that the polishing capacity of the fired samples is also good and that they can be ready for use by applying the polishing processes used in natural stones after firing. In conclusion, it is observed to be useful in disposal and re-introduction of large quantities of wastes resulting from natural stone production to the economy.

References

ASTM C1259-15. 2015. Standard test method for dynamic Young's modulus, shear modulus, and Poisson's ratio for advanced ceramics by impulse excitation of vibration, ASTM International, West Conshohocken, PA.

ASTM D5550-14. 2014. Standard test method for specific gravity of soil solids by gas pycnometer, ASTM International, West Conshohocken, PA.

Callebaut, K., Elsen, J., Van Balen, K., Viaene, W. 2001. Nineteenth century hydraulic restoration mortars in the Saint Michael's Church (Leuven, Belgium): natural hydraulic lime or cement?. Cement and Concrete Research 31(3), 397-403.

Ciullo, P. A. 1996. Industrial Minerals and Their Uses, Noyes Publications, New Jersey, 607.

DPT. 2001. Madencilik Özel İhtisas Komisyonu raporu Endüstriyel Hammaddeler Alt Komisyonu Toprak Sanayi Hammaddeleri çalışma grubu raporu. Devlet Planlama Teşkilatı, Ankara (unpublished).

Erol, G., Pekdemir, D. 2018. Investigation of thermal and mechanical behavıors of construction materials obtained from some natural stone waste. Bulletin of the Mineral Research and Exploration 157(157), 185-190.

Genç, Ş. C., Kayacı, K., Yıldırım, Y., Keskin, A., Çırpın, A. 2019. Biga yöresi zeolitik tüfitlerin karakterizasyonu ve duvar karosu bünyelerinde kullanım olanaklarının araştırılması. Afyon Kocatepe Üniversitesi Fen ve Mühendislik Bilimleri Dergisi 19, 310-320.

Gustavo, A. 2019. Evaluation of the effect of natural stone processing waste incorporation on red ceramics physical properties. London Journal of Research of Engineering Research 19(1).

Gündüz, L. 1995. Dekoratif taş endüstrisinde granit. Endüstriyel Hammaddeler Sempozyumu, İzmir.

Kara, A., Özer, F., Kayacı, K., Özer, P. 2006. Development of a multipurpose tile body: phase and microstructural development. Journal of the European Ceramic Society 26(16), 3769-3782.

Kogel, J. E., Trivedi, N. C., Barker, J. M., Krukowski, S. T. 2006. Industrial Minerals and Rocks (7th Edition). Society for Mining, Metallurgy, and Exploration Inc., Colorado, 1507.

Pastor, J. L., Tomás, R., Cano, M., Riquelme, A., Gutiérrez, E. 2019. Evaluation of the improvement effect of limestone powder waste in the stabilization of swelling clayey soil. Sustainability 11(3), 679.

Sletson, L. C., Reed, J. S. 1988. Microstructure development in a vitrified anorthite porcelain. The American Ceramic Society Bulletin 67(8), 1403-1408.

Sousa, S. J. G., Holanda, J. N. F. 2005. Development of red wall tiles by the dry process using Brazilian raw materials. Ceramics International 31(2), 215-222.

T. C. Ekonomi Bakanlığı. 2014. Doğal Taş Sektör Raporu. Ankara (published).

TS EN 12407. 2019. Natural stone test methods-petrographic examination. Turkish Standards Institute.

TS EN 14411. 2006. Ceramic tiles-definitions, classification, characteristics and marking. Turkish Standards Institute.

TS EN 15309. 2008. Characterization of waste and soil - determination of elemental composition by x-ray fluorescence. Turkish Standards Institute.

TS ISO 13320. 2009. Particle size analysis - laser diffraction methods. Turkish Standards Institute.