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Vermikülit (Yıldızeli/ Sivas) İlavesinin Seramik Porselenin Özellikleri Üzerinde Etkisinin Araştırılması

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Öz

Porselen, beyaz, ince taneli bir gövdeye sahip, genellikle yarı saydam olan gözeneksiz vitrifiye bir seramik üründür. Diğer seramik türlerine göre porselenin tokluğu, kuvveti ve yarı saydamlığı, esas olarak vitrifikasyondan ve bünyede mullit fazı oluşumundan kaynaklanmaktadır. Hidromikas grubunun doğal olarak meydana geldiği bir mineral olan vermikülit, 300 °C 'nin üzerine ısıtıldığında, yüksek verimli bir ısı yalıtım malzemesi haline gelir. Genleşmiş vermikülit, kendine has özellikleri düşük kütle yoğunluğu, düşük ısı iletkenliği, nispeten yüksek erime noktası, kimyasal atalet, dayanıklılık ve çevre güvenliği sayesinde, ısı yalıtıcı malzemeler için bir dolgu maddesi olarak kullanılabilir. Bu çalışmada Yıldızeli/Sivas (Organik madencilik) yöresinden temin edilen vermikülitin porselen bünye özellikleri üzerinde etkileri incelenmiştir. Bu amaç doğrultusunda; hazır porselen bünyelere (Refsan, Kütahya) ağırlıkça %0, 10 ve 20 kalsine vermikülit (1050 °C'de 1 saat) ilave edilerek bünye reçeteleri oluşturulmuştur. Alümina bilyeli değirmenlerde homojen hale getirilen (60 devir/dakika, 24 saat) karışımlar tek eksenli kuru presleme (100 MPa) yöntemi ile şekillendirilmiştir. Daha sonra hazırlanan preslenmiş numuneler 1050-1150 °C sıcaklıkta 1 saat süreyle pişirilmiştir. Üretilen porselen bünyeler üzerinde mikro yapı (SEM), faz analizi (XRD), mekanik (sertlik, 3-nokta eğilme) ve fiziksel özellik (% büzülme, su emme, gözeneklilik ve yoğunluk) testleri yapılmıştır. Sonuçlara göre, kalsine vermikülit katkısının artışı ile birlikte porselen özelliklerinin geliştiğini göstermiştir.

Anahtar kelimeler
Porselen;
Vermikülit;
Seramik;
Karakterizasyon.

Investigation of The Effect of Vermiculite (Yıldızeli/Sivas) Addition on The Properties of Ceramic Porcelain

Abstract

Porcelain is a non-porous vitrified ceramic product, usually semi-transparent, with a white, fine-grained body. The toughness, strength and translucency of porcelain compared to other ceramic types are mainly due to vitrification and mullite phase formation in the body. Vermiculite, a mineral in which the hydromycas group occurs naturally, becomes a high-efficiency thermal insulation material when heated above 300 °C. The expanded vermiculite can be used as a filler for heat insulating materials due to its unique properties, low bulk density, low thermal conductivity, relatively high melting point, chemical inertia, durability and environmental safety. In this study, the effects of vermiculite obtained from Yıldızeli / Sivas (Organic Mining) region on porcelain body properties were investigated. In accordance with this purpose; ready-made porcelain bodies (Refsan, Kütahya) %0.10 and 20 by weight calcined vermiculite (1050 °C 1 hour) was added to formed the body compositions. Mixtures homogenized in Alumina ball mills (60 rpm, 24 hours) were shaped by uniaxial dry pressing (100 MPa). Then, the prepared pressed samples were fired at 1050-1150 ° C for 1 hour. Microstructure (SEM), phase analysis (XRD), mechanical (hardness, 3-point bending) and physical properties (% shrinkage, water absorption, porosity and density) tests were performed on the porcelain bodies produced. According to the results, it has been shown that porcelain properties are improved with the increase of calcined vermiculite.

Keywords
Porcelain;
Vermiculite;
Ceramic;
Characterization.

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1. Introduction

Porcelain is a traditional ceramic that is widely used in many applications in households, science and engineering. The main technological features of porcelain are high mechanical strength, low water absorption, translucence and durability (Carty and Senapati 1998, Iqbal and Lee 1999, Norton 1978, Kingery et al. 1976). Typically, a porcelain body is produced of clay, feldspar and quartz together with other components to achieve required characteristics (Carty and Senapati 1998, Iqbal and Lee 1999). Clay offers plasticity to the material in the process of forming while feldspar is a fluxing agent that promotes the formation of glass by combining with amorphous clay silica and decreases the sintering temperature. Most of a sintered porcelain composed of mullite, glass and quartz (Carty and Senapati 1998, Norton 1978, Tarvornpanich et al. 2005). Mullite is formed in porcelain fired above 1100 °C and is found to be constant above 1200–1400 °C (Martin-Marquez et al. 2009, Seymour 2000, Lerdprom 2014). Thick glass stage starts to create at distinctive temperatures depending on the chemical composition of porcelain (for potash feldspar, shapes of eutectic dissolving at a temperature of 990 °C though the eutectic dissolving of soda feldspar shapes at a temperature of 1050 °C) and glass stage chemistry in terminated porcelain is found at the glass arrangement boundary between 1200 and 1400 °C (Lerdprom 2014, Lee and Carty 2004). Quartz dissolution is significant above 1200 °C (Seymour 2000, Carty 2002, Pinto et al. 2000, Rambaldi et al. 2007, Shah 2007) and has been shown to rise as a function of temperature and dwell time irrespective of heating rate (Lerdprom 2014). Many researchers have investigated the effects of pure oxides such as MgO, TiO_2 and industrial wastes such as fly ash, ceramic wastes on porcelain bodies (Iya et al. 2019, Gouvea et al. 2015, Xian et al. 2015, Tarhan et al. 2016, Shui et al. 2011).

Because of the curved, elongated and twisted columns generated when the crystals are suddenly subjected to elevated heat, the name “vermiculite” derives from the Latin – vermicularis (wormlike). Vermiculite could be a mica-like mineral with a sparkly flake, which is one part of the phyllosilicate group. Vermiculite is created under present conditions such as biotite or weathering or phlogopite hydrothermal alternation. Vermiculite material primarily comprises of SiO_2 (37–42 wt%), MgO (14–12 wt%), Al_2O_3 (10–13 wt%), Fe_2O_3 (5–17 wt%), H_2O (8–18 wt%) and FeO (1–3 wt%) (Suvorov and Skurikhin 2003). Considering the review findings, it is hopeful that vermiculite is used as a construction material. And also, can be used as aggregate in lightweight concrete and plaster for its good thermal insulation, fire resistance and sound insulation (Rashad 2016). Ngayakamo and Park (2019) reported that Kalalani vermiculite has a potential raw material for the production of high strength porcelain insulators. In this study, the effects of vermiculite on porcelain bodies were investigated.

2. Materials and Methods

The materials used in this study are calcined vermiculite and porcelain powder. Based on the results of the chemical analysis, a suitable recipe was prepared for the porcelains used in the ceramic industry. Raw vermiculite obtained from Organic Mining of Yıldızeli/Sivas region was calcined in 1 hour at 1050 °C in electric chamber type furnace. Ready-made porcelain bodies are supplied from Refsan/Kütahya. The chemical composition of calcined, raw vermiculite and porcelain powder are given in Table 1. All mixtures were stirred for 24 hours at a rotational speed of 60 rpm in dry media. Porcelain bodies %0, %10 and %20 by weight calcined vermiculite was added to formed the body compositions. The sample was coded as P20V1150 (P: porcelain; 20V: 20% vermiculite addition and 1150: 1150 °C firing temperature). Mixtures homogenized in alumina ball mills (60 rpm, 24 hours) were shaped 10x30x70 mm size under 100 MPa pressure by uniaxial dry pressing. Then, the prepared pressed samples were fired at 1050 °C, 1100 °C, and 1150 °C for 1 hour. Then, microstructure (SEM), phase analysis (XRD), mechanical (hardness, 3-point bending) and physical properties (% shrinkage, water absorption, porosity and density) tests were performed on the porcelain bodies produced.

The % shrinkage of the sintered samples was measured and calculated using a digital calliper. Density, porosity and water absorption tests were also calculated according to Archimedes's principle (ASTMC373-88). The 3-point bending strength tests of the samples were performed on a mechanical tester with a load sensitivity of 1 N and a power of 5 kN. Five measurements were made for each sample and average results were accepted as the strength values of the samples. The samples were polished on a velvet base using a 1 µm diamond solution after the 400, 800, 1200, 2000 grid sanding process, respectively. The diagonal field traces on the polished specimens were created using a square pyramid diamond tip with a 136° apex angle under 1 kg and 2 kg load on the Alfred Amsler & Co brand vickers hardness tester. When calculating the hardness values, five measurements were taken and the results were given as average. The samples were analyzed by X-ray analyzed in the range of 4^o to 70^o 2-theta using Panalytical X'Pert Powder X-ray diffraction (XRD) Analyzer. The phase analysis of the XRD patterns was determined using the Pananalitical X'Pert High Score program. Scanning electron microscopy (SEM) and energy dispersive spectrum (EDS) analysis of the samples were also performed with Mira3XMU FE-SEM (Tescan®, Czech Republic) brand within the Cumhuriyet University Technocity. The data obtained were presented in graphs and tables and their comments were made.

Table 1. The chemical composition of the raw, calcined vermiculite and porcelain powder.

%	Raw vermiculite	Calcined vermiculite	Porcelain powder
SiO_2	36.90	40.61	66.50
Al_2O_3	17.70	19.48	22.70
TiO_2	2.18	2.40	0.10
Fe_2O_3	11.20	12.31	0.30
CaO	3.54	3.90	0.20
MgO	16.4	18.05	0.10
Na_2O	0.15	0.17	3.00
K_2O	2.64	2.91	0.40
MnO	0.15	0.17	0.00
L.O.I.	9.14	0.00	6.70

3. Results and discussion

Specified to sintered samples; Physical Tests (total shrinkage, porosity, density and water absorption tests), mechanical tests (hardness and 3- point bending), scanning electron microscopy (SEM) for EDX analysis and XRD for phase analysis. Measurements and calculations were made with 3-5 replicates, and their arithmetic averages were obtained.

The results of physical measurements (water absorption, bulk density, porosity and shrinkage) are given in Table 2, and also shown between Figure 1 and Figure 4. The results indicate an increase in bulk density and % shrinkage values with increasing vermiculite addition, as well as a decrease in porosity and water absorption values with increasing additive.

Table 2. Physical test results of porcelain samples.

Samples	Water Absorption	Bulk density	Porosity	Total Shrinkage
	%		%	%
P0V1050	15.25	1.88	28.62	1.23
P0V1100	11.41	2.01	22.91	2.76
P0V1150	4.53	2.25	10.18	6.44
P10V1050	13.18	1.99	25.84	1.64
P10V1100	7.26	2.16	16.22	4.60
P10V1150	0.66	2.43	1.60	7.90
P20V1050	11.83	2.01	23.77	2.31
P20V1100	4.12	2.17	15.46	4.88
P20V1150	0.45	2.45	0.90	8.56

Referring to the graph of Figure 1, the increase in vermiculite addition and sintering temperature on porcelain samples increased by % shrinkage on the samples. The average shrinkage in P0V1050 samples was 1.23%, while the average shrinkage in P0V1150 samples was measured as 6.44%. Similarly, the mean shrinkage of P20V1050 samples was 2.31%, and the mean shrinkage of P20V1150 samples was 8.56%.

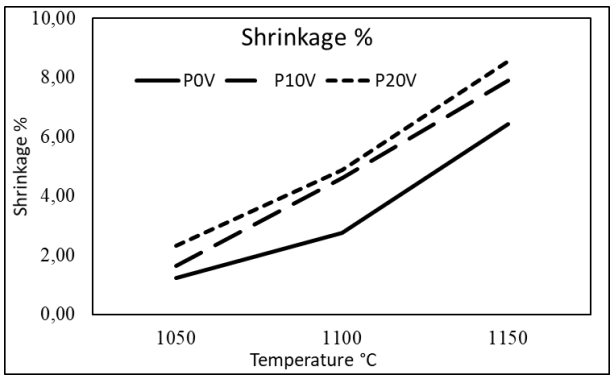

Figure 1. % Total shrinkage graph of porcelain samples.

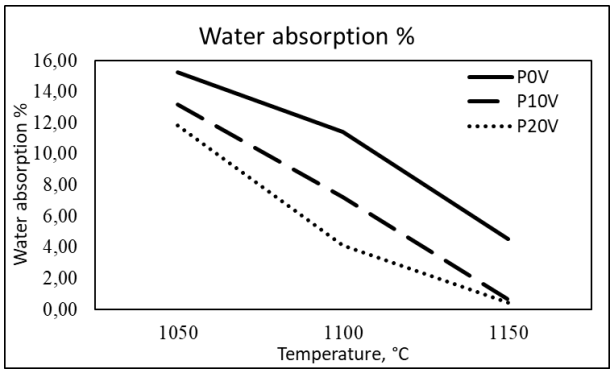

Figure 2. % Water absorption graph of porcelain samples.

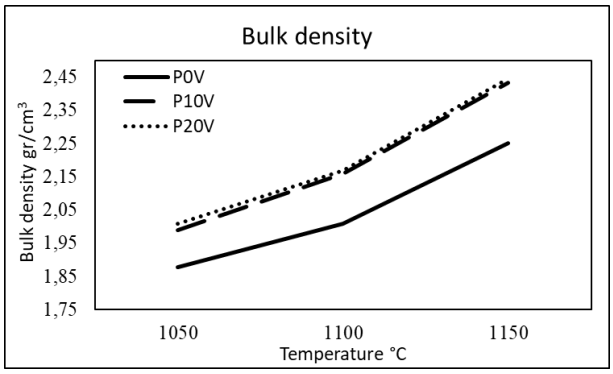

Figure 3. Bulk density graph of porcelain samples.

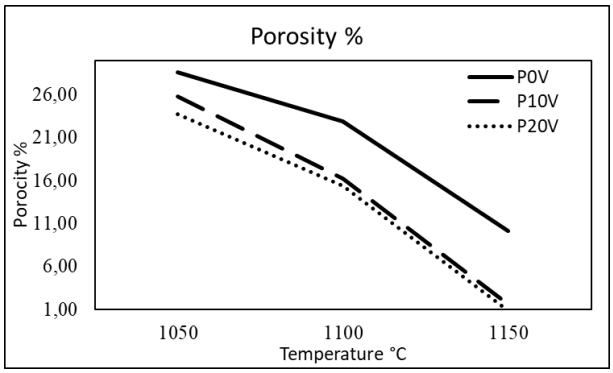

Figure 4. % Porosity graph of porcelain samples.

Figures 2, 3, and 4 show water absorption, bulk density and porosity graphs of the porcelain sample, respectively. In porcelain samples, with increasing sintering temperature, the amount of vermiculite increased, and the water absorption and porosity rates of the samples decreased while bulk density increased. The average water absorption in P0V1050 samples was 15.25%, the porosity was 28.62%, and the density was 1.88 g / cm^3, while the average water absorption in P0V1150 samples was 4.53%, the porosity was 10.18% and the density was 2.25 g/cm^3. In vermiculite doped compositions, the average water absorption in the P20V1050 sample was 11.83%, the porosity was 23.77%, and the density was 2.01 g/cm^3, while the average water absorption in the P20V1150 sample was 0.45%, the porosity was 0.90%, and the density was 2.45 g /cm^3.

Figure 5. Macro images of non-additive and vermiculite additive porcelain samples.

When the colour analysis results of the samples were examined in Figure 5, the brownish shade darkened in visible colours with increasing vermiculite contribution. Mechanical measurements (micro hardness and 3-point bending strength) are given in Table 3. Also, Figure 6 and Figure 7 are shown graphs of measurements. The results show an increase in the micro hardness and 3-point bending strength values with increasing vermiculite addition.

Table 3. Micro hardness and 3-point bending strength values of porcelain samples.

Samples	3-Point Bending Strength	Micro hardness
	MPa	Hv
P0V1050	17.52	65.00
P0V1100	23.45	143.00
P0V1150	24.70	490.00
P10V1050	25.45	84.00

P10V1100	29.15	175.00
P10V1150	36.92	569.00
P20V1050	30.26	111.00
P20V1100	34.52	211.00
P20V1150	40.54	629.00

Figure 6 shows that when the amount of vermiculite and the sintering temperature in the porcelain samples increase, the fracture strength of the samples increases. The average fracture strength in the P0V1050 sample was 17.52 MPa, while the average fracture strength in the P0V1150 sample was 24.70 MPa. Similarly, in vermiculite doped compositions, the average fracture strength in the P20V1050 sample was 30.26 MPa, while the average fracture strength in the P20V1150 sample was 40.54 MPa.

Figure 7 shows that when the amount of vermiculite and the sintering temperature in the porcelain samples increase, the hardness of the samples increases. The mean hardness in P0V1050 samples was 65 Hv, whereas the mean hardness in P0V1150 samples was 490 Hv. Similarly, the average hardness in P20V1050 samples was 111 Hv, while the average hardness in P20V1150 samples was 629 Hv.

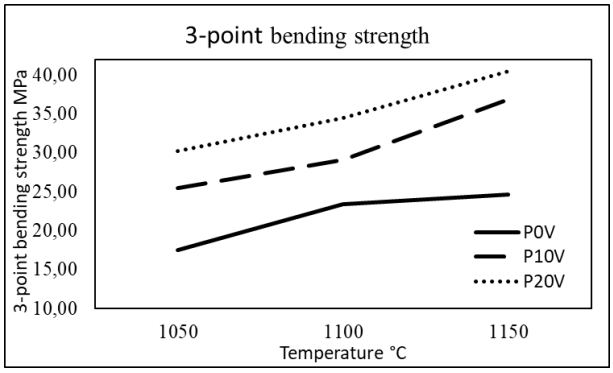

Figure 6. 3-point bending strength graph of porcelain samples.

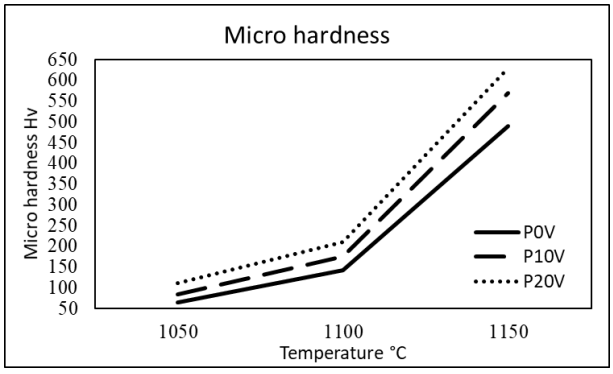

Figure 7. Microhardness graph of porcelain samples.

XRD pattern of porcelain starting powders used in the study is shown in Figure 8. When XRD result is examined, quartz, albite, muscovite and kaolinite phases are observed.

Figure 8 shows the XRD pattern of starting powders encoded as POV and given the chemical composition in Table 1. (96-900-9667) quartz, (96-900-1632) Albite, (96-101-1046) Kaolinite and (96-900-5014) Muscovite phases were determined in the pattern.

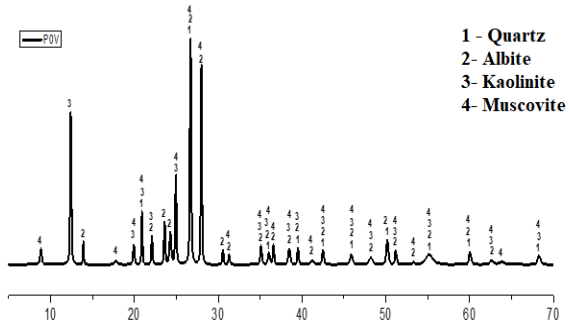

Figure 8. XRD pattern of porcelain raw materials.

Figure 9 shows the XRD graph of sintered undoped porcelain samples in 1050 ℃ and 1150 ℃. When the XRD patterns of P0V1050 and P0V1150 samples are examined, the peaks of Mullite, (96-900-1632) Albite and (96-900-9667) Quartz phases can be seen. The decrease in the intensity of albite peaks is thought to be related to the increase of the glassy phase in the samples where albite begins to transition to the liquid phase at 1150 ℃.

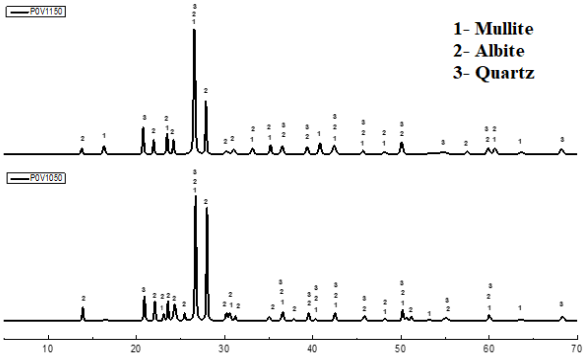

Figure 9. XRD patern of non-additive porcelain samples sintered 1050℃ and 1150℃.

Figure 10 shows the XRD patterns of P20V1050 and P20V1150 samples. Mullite, (96-900-1632) Albite, (96-900-9667) Quartz, (96-901-0898) Enstatite and

(96-900-0075) Phlogopite phases were detected in the sample coded P20V1050. In the sample coded P20V1150, four other phases except Phlogopite phase were detected. Enstatite and phlogopite phases formed the phase due to the addition of vermiculite mineral.

The apparent peak numbers and peak intensities of mullite and enstatite peaks increased in P20V1150 coded sample with increasing temperature. In the same sample, due to the increase in temperature, albite peak intensities decrease due to the formation of albite glassy phase in the structure.

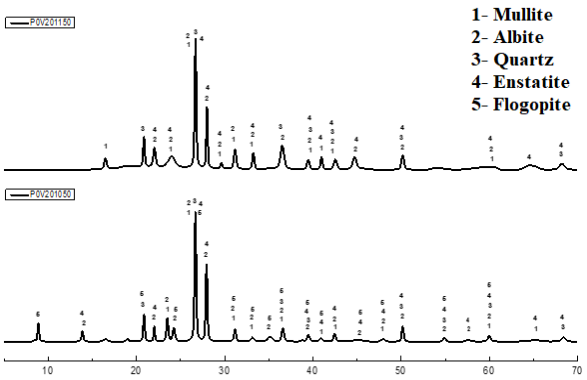

Figure 10. XRD pattern of %20 wt. vermiculite additive porcelain samples sintered 1050℃ and 1150℃.

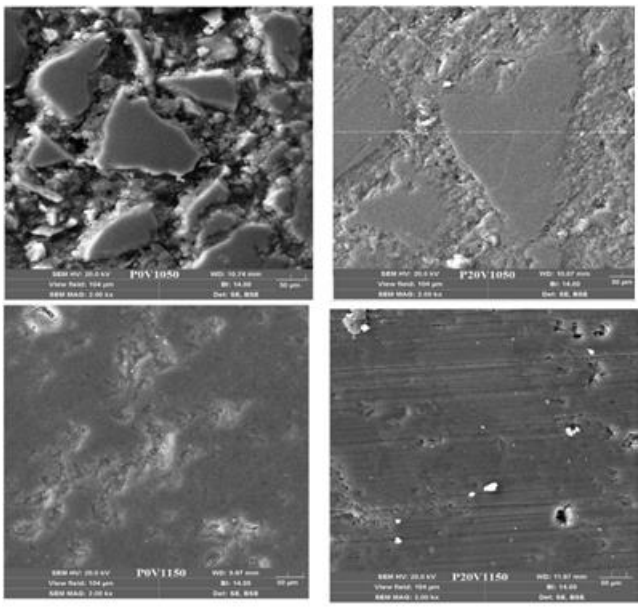

Figure 11. SEM images of non-additive porcelain samples sintered 1050°C and 1150°C and %20 wt. vermiculite additive porcelain samples sintered 1050°C and 1150°C.

Figure 11 shows SEM microstructure photographs of undoped and %20 wt. Vermiculite additive porcelain samples sintered at 1050 °C and 1150 °C. Figure 12 shows EDX analyses of %20 wt. Vermiculite additive porcelain sample sintered at 1150℃. It is evident from the SEM photographs, as seen in Figure 11, that the micro pores in the structure are reduced with increasing temperature and increasing vermiculite contribution. The evaluation of EDS analysis results on the P20V1150 sample in Figure 12 was performed according to the general A and B, C, D and E regional results. When the results of the field measurement are examined, the elemental values that meet the mineralogical recipe of the porcelain sample are seen. The EDS results from points B, C, D and E are consistent with the XRD patterns of the sample.

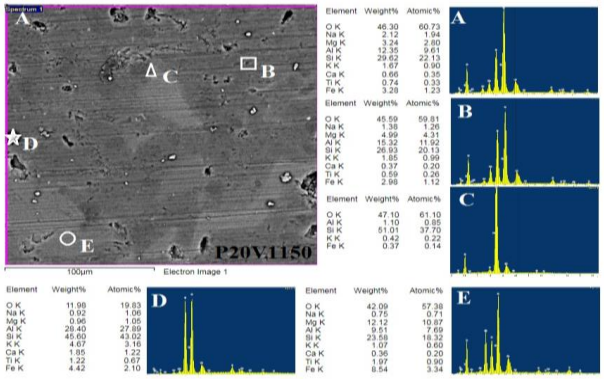

Figure 12. EDX analyses of %20 wt. Vermiculite additive porcelain samples sintered at 1150℃.

4. Conclusion

In this study, utilisation of vermiculite in the manufacturing of porcelain was investigated, and beneficial outcomes were achieved. The bulk densities of the products generated with the vermiculite additive also improved. The addition of vermiculite increased the bulk density of porcelain specimens and reduced their water absorption and porosity. With the increasing amount of additives, the shrinkage of the porcelain specimens increased. Based on the outcomes of colour assessment, darkening of brown tone was noted in visible colours with the rise of vermiculite additive. As a result of 3-point bending strength tests, increasing vermiculite additive increased the strength value of all materials. In all tests, the best values were obtained from doped samples. Also,

micro hardness values increased with increasing vermiculite additive. When the XRD results are examined, the Mullite phase is formed above 1000 °C with the conversion of the kaolin in the recipe into metakaolin and mullite, respectively. With increasing temperature, albite and quartz peak intensity decreases in the samples. This is thought to be due to increased mullite transformation with increasing temperature and feldspar formation of glassy structure. Together with vermiculite, enstatite phase was formed. It has also been reported in the literature that vermiculite forms an enstatite phase at temperatures above 1000 °C. The phlogopite phase of porcelain samples at 1050 °C sintering temperatures was also observed, which can be explained by the fact that vermiculite cannot completely convert to enstatite. When the microstructure photographs taken from the samples taken from the SEM analysis were examined, it was a known result that the increased firing temperature reduced the micro pores, and it was observed in all samples. It also reduces the amount of vermiculite in increasing pore structure is quite obvious from the SEM photographs and additives to enhance the formation of the glassy structure. In this case, the water absorption results of samples exactly compatible. It was discovered that the samples were consistent with the crystal structures identified in XRD patterns when interpreting the outcomes of the point element assessment.

5. References

Carty, W. M. (2002, January). Observations on the glass phase composition in porcelains. In Ceramic engineering and science proceedings (Vol. 23, No. 2, pp. 79-94). [Columbus, Ohio, American Ceramic Society].

Carty, W. M., & Senapati, U. (1998). Porcelain—raw materials, processing, phase evolution, and mechanical behavior. *Journal of the American Ceramic Society*, **81**(1), 3-20.

Gouvêa, D., Kaneko, T. T., Kahn, H., de Souza Conceição, E., & Antoniassi, J. L. (2015). Using bone ash as an additive in porcelain sintering. *Ceramics International*, **41**(1), 487-496.

Iqbal, Y., & Lee, W. E. (1999). Fired porcelain microstructures revisited. *Journal of the American Ceramic Society*, **82**(12), 3584-3590.

Iya, S. G. D., Noh, M. Z., Ab Razak, S. N., Sharip, N., & Kutty, N. A. A. (2019). Effect of Iron (111) Oxide (Fe2O3) as an Additive and Substitution of Quartz with POFA on Physico-Mechanical Properties of Porcelain. *International Journal of Nanoelectronics & Materials*, **12**(2).

Kingery, W.D., Bowen, H.K., Uhlmann, D.R., 1976, Introduction to Ceramics, Wiley, NY.

Lee, H., & Carty, W. M. (2004, April). Glass phase composition in porcelains and correlation with firing temperature. In Proceedings of the 106th Annual Meeting and Exposition of the American Ceramic Society (pp. 18-21).

Lerdprom, W., 2014, Firing of Porcelain: M.S Thesis, New York State College of Ceramics at Alfred University, Alfred, NY.

Martín-Márquez, J., De la Torre, A. G., Aranda, M. A., Rincón, J. M., & Romero, M. (2009). Evolution with temperature of crystalline and amorphous phases in porcelain stoneware. *Journal of the American Ceramic Society*, **92**(1), 229-234.

Ngayakamo, B., & Park, S. E. (2019). Evaluation of Kalalani Vermiculite for Production of High Strength Porcelain Insulators. *Science of Sintering*, ***51***(2).

Norton, F.H., 1978, Fine Ceramics: Technology and Applications, 2nd ed., Robert E. Krieger Publishing Company, Inc., FL.

Pinto, B., Carty, W., & Misture, S. (2000). Measurement of residual strain in quartz particles in porcelain. In Science of Whiteware (Vol. 3). Alfred University.

Rambaldi, E., Carty, W. M., Tucci, A., & Esposito, L. (2007). Using waste glass as a partial flux substitution and pyroplastic deformation of a porcelain stoneware tile body. *Ceramics International*, **33**(5), 727-733.

Rashad, A. M. (2016). Vermiculite as a construction material–A short guide for Civil Engineer. *Construction and Building Materials*, **125**, 53-62.

Seymour, D.I., 2000, Phase Evolution of Electrical Porcelains During Firing: M.S Thesis, New York State College of Ceramics at Alfred University, Alfred, NY.

Shah, A., 2007, The Glass Formation Boundary in Porcelains M.S. Thesis, New York State College of Ceramics at Alfred University, Alfred, NY.

Shui, A., Xi, X., Wang, Y., & Cheng, X. (2011). Effect of silicon carbide additive on microstructure and properties of porcelain ceramics. *Ceramics International*, **37**(5), 1557-1562.

Suvorov, S. A., & Skurikhin, V. V. (2003). Vermiculite—a promising material for high-temperature heat insulators. *Refractories and industrial ceramics*, **44**(3), 186-193.

Tarhan, M., Tarhan, B., & Aydin, T. (2016). The effects of fine fire clay sanitaryware wastes on ceramic wall tiles. *Ceramics International*, **42**(15), 17110-17115.

Tarvornpanich, T., Souza, G. P., & Lee, W. E. (2005). Microstructural evolution on firing soda–lime–silica glass fluxed whitewares. *Journal of the American Ceramic Society*, **88**(5), 1302-1308.

Xian, Z., Zeng, L., Cheng, X., & Wang, H. (2015). Effect of polishing waste additive on microstructure and foaming property of porcelain tile and kinetics of sinter-crystallization. *Journal of Thermal Analysis and Calorimetry*, **122**(2), 997-1004.