ESKİŞEHİR TEKNİK ÜNİVERSİTESİ BİLİM VE TEKNOLOJİ DERGİSİ B- TEORİK BİLİMLER

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RESEARCH ARTICLE

APPLIED RESEARCH INTO MUTTALIP CLAY IN ESKISEHIR

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ABSTRACT

Although the brick-tile industry is one of the industrial establishments in Turkey, the search for raw materials that can meet the needs is one of the important problems. According to the 9th State Development Plan, clay reserves are insufficient and in the group that should be sought. There are not enough studies on the analysis of clays in our country. For this reason, the suitability of clay in the tile sector in the Muttalip region of Eskisehir province was investigated. As a result of X-Ray Diffraction (XRD), X-Ray Fluorescence Spectrometer (XRF), Scanning Electron Microscopy (FESEM), particle analysis, the clay, which was found to be suitable for tiles, was slurred and inserted into Vacuum Press devices as a result of moisture analysis, and tablet tiles were obtained. The tiles obtained were baked at 80°C during the drying phase and cracks were formed on the surface. These cracks in the drying stage can be resolved by natural drying method or drying at lower temperatures, and tile, which is an industrial product with high strength, can be obtained from Muttalip clay.

Keywords: Clay, FESEM, Industrial product, Roof tile, XRD

Anahtar Kelimeler: Kil, FESEM, Endüstriyel ürün, Kiremit, XRD

1. INTRODUCTION

Brick-tile industries in Turkey are one of the important branches of industry. Due to the increasing needs and quality problems in Turkey, many industrial raw materials have been purchased from abroad. The clay group used in the production of tiles is also included in the group of minerals that need to be sought, whose reserves are insufficient. Generally, granular material smaller than 0.002 mm is called clay. According to the 9th State Development Plan, when the demand projection for brick-tile soil is examined, it is planned to increase by 5%, and when the production projection is considered, a growth of 7.3% has been observed [1].

Natural clay minerals have been well known to mankind since the early days of civilization [2]. Clay content consists of silica, alumina, and water, and significant amounts are often found in iron, alkalies, and alkaline earth. Clays are used as raw materials in the production of ceramic tile from industrial areas [4]. The suitability of clays in production depends on their composition, tight structure, and physical properties [5]. These features are important in determining ignition cycles in production [6]. Common ingredients that play a key role in the performance of the products are kaolins for plasticity, silica as a filler, and feldspar as a melting agent to lower the temperature required to form a glassy phase that promotes densification [7]. Studies [2, 6-11] on the characterization of clays are important for obtaining a good product in tile production.

In this study, chemical, physical, mineralogical, and microstructure analyzes of Muttalip clay were made and its role in tile production as an application area was examined. The positive and negative aspects of Muttalip clay in the production stages in the tile industry are discussed. R&D laboratory of the Hatipoglu Gunes Tile and Brick Industry Joint Stock Company factory was used for the production stages in the tile industry.

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2. MATERIAL AND METHOD

2.1. Properties and Characterizations of Muttalip Clay

The clays used in the study were obtained from the Muttalip region of Eskisehir province in Turkey. The chemical, physical and mineralogical properties and microstructures of these clays were investigated. Mineralogical analysis was measured with the Panalytical Empyrean model X-Ray diffraction (XRD) device, the minerals in the composition of the mud were determined and the oxides of these elements were determined as % by measuring with the Panalytical brand Axios MAX model Wavelength Discrimination X-Ray Fluorescence (WD-XRF) Spectrometer device. The microstructure of the structure was analyzed using the Hitachi Regulus 8230 Field Emission Scanning Electron Microscopy (FE-SEM) instrument.

2.2. Preparation of Roof Tablet Tile

The clay to be used to produce the earthen tile was purchased from the Muttalip region. Grain size distribution of Muttalip clay was made by passing the clay through laboratory sieves of different scales (the largest 2 mm, the smallest 63 µm) (Figure 1.a.) in the R&D laboratory of the Hatipoglu Gunes Tile and Brick Industry Joınt Stock Company factory.

Muttalip clay (Figure 1.b.) passed through a sieve was mixed with water and the humidity rate was measured as 23.02% with the Moisture Determination device the next day. Tablet tiles of approximately 5 cm x 10 cm x 20 cm dimensions were obtained from the mixture poured into the Vacuum Press device by adjusting the humidity rate above a certain level (Figure 1.c.). The width, height and weight values of each tablet tiles were noted (Figure 2.a.). The general properties of the tablet tiles, which were dried in an oven at 80 °C for 1 day, were examined (Figure 2.b.).

(a) (b) (c)

Figure 1. (a) Passing Muttalip clay through sieves of different sizes, **(b**) Screened Muttalip clay, **(c)** Tablet tiles pressed from vacuum press

(a) (b)

Figure 2. (a) Physical measurements of tablet tiles, **(b)** Tablet tiles dried in an oven at 80 ºC

3. RESULTS

Muttalip clay, which was purchased for tile production in the tile factory, was taken from the field by trucks and buckets. Some of the incoming clay was brought to the Hatipoglu Gunes Tile and Brick Industry Joınt Stock Company factory and left to dry naturally. Then, the clay was passed through different scale laboratory sieves, the largest of which was 2 mm and the smallest 63 µm, and was pulverized. When the XRD results of the powdered Muttalip clay were examined (Figure 3), it was found that it consisted of calcite, Albite, clinochlore, biotite, muscovite and quartz.

Calcite is a carbonate mineral. Other polymorphs of calcium carbonate are aragonite and vaterite. Aragonite can transform into calcite under favorable conditions. Vaterite is less stable [12]. Clinochlore is one of the best-known members of the Chlorite group [13]. Chlorites are also a group of phyllosilicate minerals. Chlorites are defined by the elements Mg, Fe, Ni and Mn in the silicate lattice [14]. Biotite is rich in iron, consisting of aluminum silicate and potassium [15]. Muscovite, commonly known as mica, is a hydrated phyllosilicate mineral of aluminum and potassium [16].

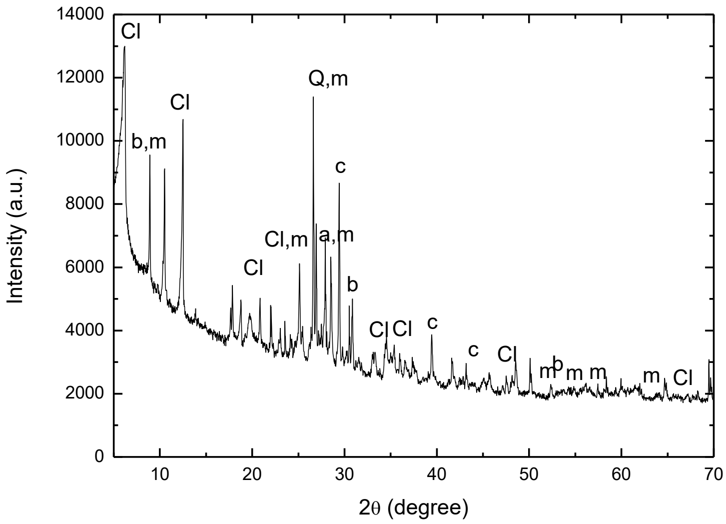


Figure 3. Minerals detected in Muttalip clay by XRD (Cl:clinochlore, a:albite, b:biotite, c:calcite, Q:quartz, m:muscovite)

Elemental analysis of Muttalip clay was measured by XRF (Table 1). When the clay is examined in terms of chemical components in XRF analysis, it is seen that it is basically SiO_2, Al_2O_3, Fe_2O_3, TiO_2, CaO, MgO, K_2O, SO_3. When the Muttalip clay XRF analysis is examined, it consists of approximately

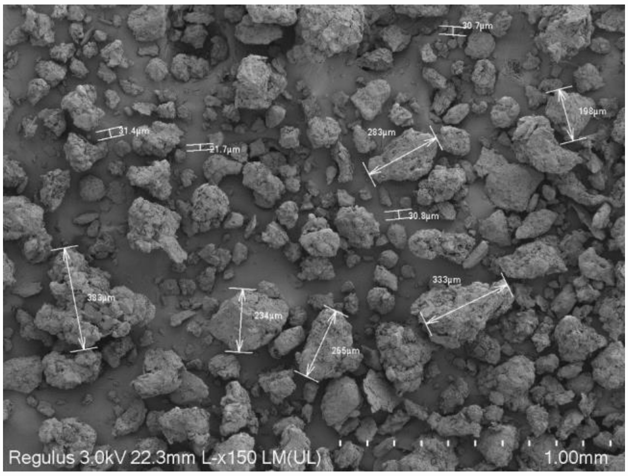
67.29% corresponding SiO_2 and Al_2O_3. It is seen that alumina and silica oxide are found in high amounts in clay, while other minerals are found in trace amounts. In another study[6] with industrial applications of clays, this rate is 91% and 82%. In another study [2] on clays, this value was 82.66%, and it has a higher value than the clay value in our study. The amount of alkali oxides (K_2O and Na_2O) in Muttalip clay, which functions as flux materials, is 1.91%, lower than the clays made by Celik [6] (4.11% and 2.11%). The low alkali oxide content in Muttalip clay is a result of kaolinitic clays that naturally have low flux content [17]. The amount of CaO and MgO in Muttalip clay is 2.4% higher than in a study [6] on other industrial applications, which shows that carbonates are higher in the clays in our study. The high ignition loss (10%) is related to low SiO_2 and high Al_2O_3 content and is due to the content of clay minerals in Muttalip clay[10]. Muttalip clay has a higher Fe_2O_3 content compared to other studies [6]. Fe_2O_3 gives a red color to the baked products and also plays a melting role. CaO, MgO, MnO, and TiO_2 components also play important roles in the coloring of baked clays [9]. The amount of Al_2O_3 is another factor that plays an important role in cooking temperature [10].

Table 1. Chemical components of Muttalip clay

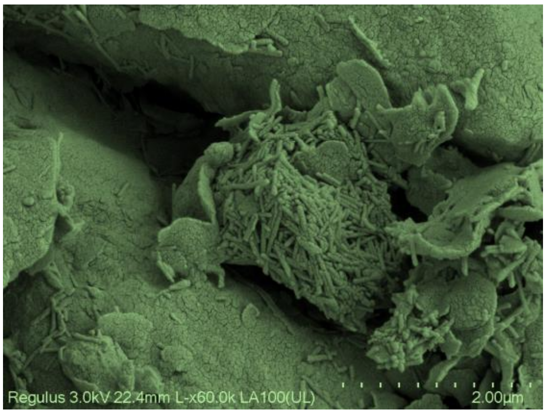
Muttalip clay	
Materials	**(%wt.)**
SiO_2	53.77
Al_2O_3	13.50
Fe_2O_3	8.34
TiO_2	1.28
CaO	1.53
MgO	0.87
Na_2O	0.00
K_2O	1.91
SO_3	0.03
L.O.I.	18.77
Total	100.0

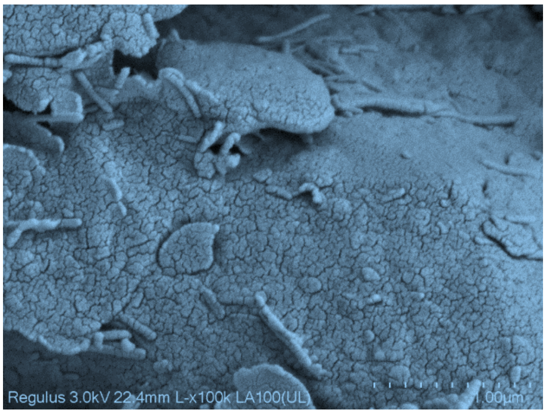
The FESEM microscope works with electrons released by field emission. The examined clay is scanned by electrons in random directions. FESEM images can distinguish very small topographical details on the surface of the studied clay. The electron beam is bombarded on the clay surface and secondary electrons are released from the impinging electrons on the clay. Secondary electrons are captured by a detector and produce an electronic signal that provides a digital image on the monitor. The detector used in this study was an In-Lens detector[11].

When the Muttalip clay was examined in the FESEM device at 150x magnification (Figure 4.a.), dimensional analysis was carried out with dimensions ranging from 21-383 µm. When the magnification of the clay was increased to 60kx in the FESEM (Figure 4.b.), it was revealed that rod-shaped extensions were clustered in the clay content and formed in the form of rods on other structures. When the clay structure is examined in the FESEM device at 100kx magnification (Figure 4.c.), small crack formations in the structures draw attention. There are similar studies [8, 18-21] on FESEM images of clays. In a study [18], in the FESEM image of kaolinites, a structure consisting of longitudinal packages belonging to the same or different crystals and consisting of differently oriented flakes is seen. Particles ranging from 21-383 µm in the FESEM image of Muttalip clay in our study are in the appropriate range for tile production [22].



(a) 150x





(b) 60kx (c) 100kx

Figure 4. FESEM image of clay at different magnifications **(a)** 150x; **(b)** 60kx; **(c)**100kx

Sieve analysis was carried out to determine the size distribution of Muttalip clay to be examined. The samples were broken in the jaw and roller crushers and their sizes were reduced. Afterward, the dry clay was sieved in different sizes of 4 mm, 2 mm, 1 mm, 500 µm, 250 µm, 125 µm, 63 µm sieves, and the size distribution of the clay was determined. The size distribution of Muttalip clay is shown in Table 2.

Table 2. Size distribution of Muttalip clay

Size Range (mm)	**Muttalip clay Residue (%)**
-4+2	0.00
-2+1	0.00
-1+0.05	55.97
-0.05+0.025	24.19
-0.025+0.0125	10.58
-0.0125+0.0062	6.98
-0.0062	2.28

The width, length, and weight values of the tablet tiles (called 5, 6, 7) obtained by the vacuum press device are shown in Table 3. In order to comply with TSE EN 1304 standards, tablet tiles should be dried by taking into account the tensile and strength values. Drying tablet tiles is known as the process of removing water from the raw material [22]. In the study, the drying temperature was determined as 80°C. Drying is known as mass transfer between the object and the atmosphere surrounding the object [23]. Tablet tiles in Muttalip clay showed cracks on their surfaces after being heated in drying ovens. (Fig. 5). Micro cracks around sand grains can be avoided when the drying shrinkage value is between 0 - 0.5% [22, 24, 25]. Drying sensitivity is one of the criteria for evaluating ease during drying. There are many studies that have been studied [23, 26] with drying sensitivity. Drying Sensitivity Index (DSI) of clays can be calculated using Bigot's curve method [23]. Due to the fact that Muttalip clay is an oily clay, it shrinks, cracks, and deforms more than other clays during firing. For this reason, if it is used in tile production, it will be blended with other clays, and clays with high strength will be obtained.

Table 3. Physical values of tablet tiles produced from vacuum press device

		no. 5 tablet tile	**no. 6 tablet tile**	**no. 7 tablet tile**
After	Length (mm)	144.7	149.7	149.4
Vacuum	Width (mm)	49.6	124.8	144.5
Press device	Weight (gr)	244.7	214.5	245.0

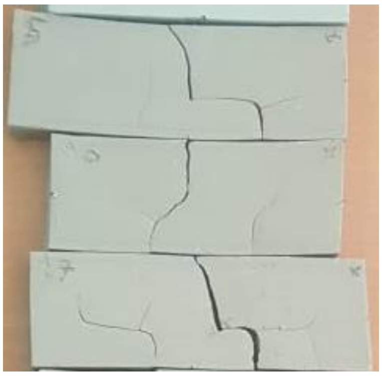


Figure 5. Post-drying images of tablet tiles obtained from Muttalip clay

4. CONCLUSIONS

The Muttalip clays from the Eskisehir region, Turkey, were characterized by chemical, mineralogical, physical, and microstructure analysis. The characterization of Muttalip clay has not been widely studied before. Thus, the information obtained will contribute to the improvement of the studies to be carried out. Tablet tiles were obtained in the vacuum press device. The tablet tiles given to drying at 80°C cracked during drying and the causes of cracking were analyzed by making XRD, XRF, and FESEM analyses and comparing other structures in the literature and the source of the problem was examined. To prevent cracking, efficient results will be obtained by natural drying in the factory environment or drying at low temperatures in the laboratory environment. Muttalip clay has sufficient chemical, physical, mineral, and microstructural properties for soil tile production.

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CONFLICT OF INTEREST

The author stated that there are no conflicts of interest regarding the publication of this article.

REFERENCES

[1] Presidency of the Republic of Turkey, Strategy and Budget Department, Ninth Development Plan report 2007-2013. Turkey, 2006.

[2] Nayak PS, Singh BK. Instrumental characterization of clay by XRF, XRD and FTIR. Bulletin of Materials Science 2007; 30(3): 235-238.

[3] Grim RE. Clay mineralogy. New York: McGraw-Hill,1968.

[4] Chang LLY. Industrial mineralogy: Materials, processes, and uses. Upper Saddle River, New Jersey: Prentice Hall, 2002.

[5] Grim R. Some applications of clay mineralogy. Am Mineral 1960; 45: 259-269.

[6] Celik H. Technological characterization and industrial application of two Turkish clays for the ceramic industry. Applied Clay Science 2010; 50(2): 245-254.

[7] Kamseu E, Leonelli C, Boccaccini DN, Veronesi P, Miselli P, Pellacani G, Melo UC. Characterisation of porcelain compositions using two China clays from Cameroon. Ceramics International 2007; 33(5): 851-857.

[8] Zhang MY, Sun H, Song C, Li Y, Hou M. Pores Evolution of Soft Clay under Loading/Unloading Process. Applied Sciences-Basel 2020; 10(23) 8468.

[9] Kreimeyer R. Some notes on the firing color of clay bricks. Appl. Clay Sci. 1987; 2: 175-183.

[10] Fisher P. Some comments on the color of fired clays. Ziegelindustrie Int. 1984; 37: 475-483.

[11] Wijeyesekera DC, Ho MH, Bai X, Bakar IBH. Strength and Stiffness Development in Soft Soils: A FESEM aided Soil Microstructure Viewpoint IOP Conf. Series: Materials Science and Engineering 2016; 136: 012041.

[12] Staudigel PT, Swart PK. Isotopic behavior during the aragonite-calcite transition: Implications for sample preparation and proxy interpretation. Chemical Geology 2016; 442: 130-138.

[13] Ulian G, Moro D, Valdre G. Infrared and Raman spectroscopic features of clinochlore Mg6Si4O10(OH)(8): A density functional theory contribution. Applied Clay Science 2020; 197.

[14] Cloutier J, Piercey SJ, Huntington J. Mineralogy, Mineral Chemistry and SWIR Spectral Reflectance of Chlorite and White Mica. Minerals 2021; 11(5).

[15] Kwon S, Kim Y, Roh, Y. Cesium removal using acid- and base-activated biotite and illite. Journal of Hazardous Materials 2021; 401.

[16] Wang YB, Wang Y, Wen K, Dang W, Xun J. Strengthening the inhibition effect of sodium silicate on muscovite by electrochemical modification. Minerals Engineering 2021; 161.

[17] Monteiro SN, Vieira CMF. Influence of firing temperature on the ceramic properties of clays from Campos dos Goytacazes, Brazil. Applied Clay Science 2004; 27(3-4): 229-234.

[18] Clausell JV, Bastida J, Serrano FJ, Pardo P, Huertas FJ. A new FESEM procedure for assessment of XRD microstructural data of kaolinites. Applied Clay Science 2007; 37(1-2): 127-132.

[19] Sun H, Hou MX, Chen C, Ge X. Microstructure investigation of soft clay subjected to triaxial loading. Engineering Geology 2020; 274.

[20] Guo M, Liang Y, Cai M, Nie J, Ju M, Liu M, Jiang G. Improved slag resistance of taphole clay due to in situ formation of TiCN from ferrotitanium slag. Ceramics International 2021; 47(16): 23630-23636.

[21] Muleja AA, Mubiayi MP, Hassard F, Mamba BB. Titania containing natural clay doped with carbon nanotubes for enhanced natural photocatalytic discoloration of wastewater. Journal of Nanoparticle Research 2021; 23(4).

[22] Celik H. Technological Characterization and Comparison of two Ceramic Clays Used for Manufacturing of Traditional Ceramic Products in Turkey. Scientific Mining Journal 2017; 56: 137-147.

[23] Aungatichart P, Wada S. Correlation between Bigot and Ratzenberger drying sensitivity indices of red clay from Ratchaburi province (Thailand). Applied Clay Science 2009; 43(2): 182-185.

[24] Baccour H, Medhioub M, Jamoussi F, Mhiri T. Densification Behaviour of a Red Firing Tunisian Triassic Clay. American Journal of Applied Sciences 2008; 5: 263-269.

[25] Mahmoudi S, Zargouni F. Simultaneous Optimisation of Drying Parameters of Ceramic Bodies. Current Research in Geoscience 2014; 4(1): 1-7.

[26] Schneider HE, Hanke W. Determination of the Drying Crack Sensitivity of Structural Ceramics and Heavy Clay Raw Materials. Ziegelindustrie International 1996; 7(8):168-480.