In Turkey the annual natural stone production is about 1500 natural stone quarries, 2000 factory like workshops and about 9000 small scale workshops. The potential is estimated to be 5.1 billion m$^3$ – 13.9 billion m$^3$. In this branch of the industry there has been an increase in the need for natural stone usage rapidly due to the existing ones so many new stone quarries have been put into operation. Turkey is situated in the Alpine-Himalayan mountain range where world’s richest marble quarries are found. Turkey’s marble reserve potential is estimated to be 5.1 billion m$^3$ – 13.9 billion tons. This is about 33% of the estimated world reserve of 15 billion m$^3$. In this branch of the industry there are 1500 natural stone quarries, 2000 factory like workshops and about 9000 small scale workshops. In Turkey the annual natural stone production is about 11.5 million tons and plate production capacity of these processing plants is about 6.5 million m$^2$. (Republic of Turkey Ministry of Economy, 2016). During the process of these large numbers of natural stones, inevitably large quantities of stone wastes develop and accumulate. These stone wastes need to be economically recycled. In the ‘marble quarries and factories, during the process of bridge cutting, monolizing, ‘ST cutting and sizing, about 30% wastes (as much as dust wastes) develop from the bottom and side units of one block cut. The amount of wastes develop in the quarries is equal to 40% of the rock mass (Akbulut and Güzer, 2007). Only 40 marble processing plants located in the organized industrial zone in Afyonkarahisar produce annually 60,000 tons solid, and 120,000 tons aqueous marble wastes (Çelik and Tur, 2012). In the marble processing plants, during the block and plate cuts of the marbles, size...
of the produced dust waste material in the colloidal form is mostly below 250 μm before grinding (Demir et al., 2008). These wastes are used in the construction industry, lime production, concrete and autoclaved aerated concrete production, ceramic-glass-paper industries, agriculture, etc. Wastes not used in such fields are deposited in the waste storing areas causing various environmental problems. There are numerous studies on the evaluation of natural stone wastes in the literature. Gürü et al. (2005) used marble dust as filling material in the polyester composites and noticed that with the increased rate of filling material mechanical qualities have improved. Filiz et al. (2010) carried out a work to produce cobblestone by using waste marble dust and concluded that the material can successfully be used to produce cobblestones. Sütçü et al. (2015) studied on producing clay brick construction material by adding waste marble dust into the substance. They reported that by adding certain amount of waste marble dust into the brick material had a positive effect on to the porosity and crystal phase developments. Bilgi et al., (2012) investigated the use of waste marble dust in brick production and stated that the use of waste marble dust in industrial brick production provides great benefits to the production, the environment and the economy of the country. Along with all these works Aliabdo et al. (2014) also investigated the use of marble wastes in cement and concrete productions and they reported that by adding certain amount of marble waste into the cement have improved the physical and mechanical quality of concrete mixture. Arel (2016) also studied on the possibility of marble waste use in cement and concrete productions and concluded that by adding less than 20% waste marble dust added to the cement mixture greatly improved the physical and mechanical qualities of the concrete produced.

2. Materials and Method

2.1. Material

In traditionally produced wall tiles, mixtures containing SiO₂-Al₂O₃-CaO are heated (fired) at 1135-1155°C temperature interval (Cengiz and Kara, 2012). To be able to use the marble wastes to produce floor and wall tiles, a mixture suitable to SiO₂-Al₂O₃-CaO system was prepared. In preparation of the mixture, raw materials of 60% granite, 35% recrystallized limestone (metamorphic) and 5% Aluminium oxide (Al₂O₃) have been used. Granitoids are the magmatic rocks rich in silica (SiO₂ ≥ %66), alkalines (feldspars) and poor in CaO, Fe, MgO (biotite, amphibole) (Uz, 1990). Depending upon the mineral content, granitoids display colour variations from grey-white to grey, grey green and even to brown-red. Because of their magmatic origin and chemical compositions granitoids are rocks with strong resistance to acids (Gündüz, 1995). The granite (granitoid) used in the study is from the Aksaray region, it is massive with holocrystalline grain size. Mineralogical composition is; alkaline feldspars (orthoclase, microcline), quartz, plagioclase, mica (muscovite, biotite) and small amount amphibole. Recrystallized limestones are the sedimentary rocks subjected to metamorphism under high temperature and pressure, changed to become a metamorphic rock. Lime stones are basically made of calcite mineral (CaCO₃) with at least 90% calcite. Depending on the mineral content, recrystallized limestone may be in various colours and they are not resistant to acids (HCl, C₆H₈O₇, HNO₃, H₂SO₄ etc.). The recrystallized limestone used in the study is from Amasya region. It is massive with microcrystalline grain size. Mineral content consists of carbonate minerals (calcite) and has some fossils. Aluminium oxide (Al₂O₃) used in the study has been obtained by calcination of aluminium hydroxide (AlOH₃) used in the Bayer process. Its Al₂O₃ ratio is about 99%. It is used in the ceramic, glass, refractory industries, grinding material production, primary aluminium production, transparent armour production, ceramic cutter production.

2.2. Method

2.2.1. Material Definition Processes

Granites and recrystallized limestone have been ground, through 0.149 mm measuring range and then sieved in dry system. Following the sieving, 3 g of sample and 0.9 g of cellulose mixture were homogenously milled for 15 minutes, then compressed into a 33 mm diameter tablet under 40 kN pressure and made ready for analysis. Prepared materials were analysed by using Panalytical XRF with TSEN 15309 wave length dispersion standards. Mineralog of the specimens was pointed out by using XRD (Rigaku, Miniflex) with Cu Kα radiation between 20–60° angles at 2% min speed. To determine the grain size distribution of the samples used in the study, Malvern Mastersizer 2000 model instrument was used which measures with Mie dispersion principle at 0.02-2000 micron measuring range. For the grain size dispersion analyses, a suspension of 200 gr specimen were prepared and were analysed with wet system.
2.2.2. Shaping and Firing

The prepared watery mixture was mixed for 30 minutes at 180 rounds/minute speed in a Fritsch brand pulveriser and a homogeneous mixture was obtained, then dried at 100°C. 7% shaping water was added to the obtained mixture then the material was placed into a steel mold 75x20x50 mm in size and it was shaped at 70 MPa single axes pressure by using a German made Toni Technik Baustoffprüfsysteme GmbH hydraulic press. The shaped material was kept 24 hours at room temperature then dried for 24 hours at 100°C in a drying oven. Dried material has been fired (heated) in a Protherm brand PLF 160/15 electrical drying oven at 1140, 1150 and 1160°C temperatures with 5°C/min. rate, then were kept in the oven for 1 hour (Figure 1).

2.2.3. Tests Carried Out on The Fired Samples

To point out mineralogical composition of the fired material, ground specimens were studied by using Rigaku Miniflex brand diffractometer with Cu anode. X-Ray dispersion analyses of the samples were carried out. 3 points bending strength test was conducted by using a German made Toni Technik Baustoffprüfsysteme GmbH universal test instrument. By using Grindo-Sonic, J. W. Lemmens Inc., St. Louis, Mo. ‘Young’s Modulus’ measurements were made in accordance with ASTM C1259-15 standards. According to impulse excitation method in the undamaged tests samples are subjected to fixed impacts with a small hammer with fixed intervals. By using this method Young’s Modulus values of the prepared samples have been determined. By using Minolta CR300 chronometer L (white), a (green) and b (blue) colour values of the fired samples have been determined. To determine water absorption coefficient of the fired samples, the samples were dried at 70°C in the oven and then weighed at 24 hours’ interval and continued drying until samples came to a stable mass. Dried samples at room temperature were kept in water for 48 hours and weighed with 24 hours’ interval and kept them in water until they reached to fixed saturation. Apparent density analyses of the fired samples were determined in accordance to ASTM D 5550-14 standard by using ‘Micromeritics AccuPyc II 1340 helium pycrometer’. To measure apparent density, in the instruments using gas replacement method inert gasses helium or nitrogen are used as replacement gases. By using Micromeritics GeoPyc 1360 instrument, mass density tests of fired samples were carried out in accordance with ASTM D 6683-14 standard. The instrument operates in Archimedes principle and uses semi liquid replacement media of non-hazardous microspheres with high degree of flow rate. In accordance to apparent and mass density tests results open pore space values have been determined.

3. Research and Findings

3.1. Characteristics of Raw Materials

Grain size distribution of the prepared mixture is given in table 1. According to these results 10% of the mixture has grain size below 2.114 μm, 50% below 26.326 μm and 90% below 87.950 μm. Chemical analyses of granite and limestone are given in table 2. In the XRD chart pattern of the limestone used in the mixture shows that main mineral content of the mixture is calcite (Ka) (Figure 2). In the granite pattern of the XRD main mineral content is quartz (K) and orthoclase (O) (Figure 3).

<table>
<thead>
<tr>
<th>Mixture</th>
<th>d (10) (μm)</th>
<th>d (50) (μm)</th>
<th>d (90) (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grain size</td>
<td>2.114</td>
<td>26.326</td>
<td>87.950</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Samples</th>
<th>MgO (%)</th>
<th>Al2O3 (%)</th>
<th>SiO2 (%)</th>
<th>CaO (%)</th>
<th>Fe2O3 (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Granite</td>
<td>0.32</td>
<td>14.18</td>
<td>73.10</td>
<td>1.35</td>
<td>1.55</td>
</tr>
<tr>
<td>Limestone</td>
<td>0.31</td>
<td>0.03</td>
<td>0.10</td>
<td>55.9</td>
<td>0.01</td>
</tr>
</tbody>
</table>

3.2. Bending Strength and Young’s Modulus Tests

Three points bending and Young’s Modulus test results of the samples are given in figure 4. In the...
tests it was noticed that with the increasing firing temperature bending strength and Young’s Modulus values increase accordingly.

3.3 Colour Measurement

Results of the L, a, b colour measurements of the samples heated (fired) at different temperatures are given in table 3. With increased heating, whiteness of the samples represented by ‘L’ value decreases. ‘a’ representing greenness value of the heated samples. During the heating procedure of the samples, when temperature increases from 1140°C’ to 1150°C’ green colour value increases, on the other hand when temperature goes up from 1150°C’ to 1160°C then green colour value decreases. ‘b’ represent blueness value. During the heating process when temperature goes up from 1140°C’ to 1150°C’ yellow colour value decreases, when temperature goes up from 1150°C’ to 1160°C’ blue colour value increases.

3.4. Water Absorption and Density Tests

According to water absorption and porosity test results, when samples are heated (fired) to 1140°C-1150°C and 1160°C water absorption coefficient and porosity values decrease (Figure 5). It is considered that decrease in water absorption is related to decrease in open porosity values. According to apparent density and mass density results, when samples are fired (heated) to 1140°C-1150°C and 1160°C apparent density value decreases but mass density values increases (Figure 6).

3.5. Characteristics of The Heated (fired) Samples

Calcium Carbonate (CaCO₃) triggers phase development reactions. At 800°C’-900°C’ with the destruction of Calcium Carbonate (Ca CO₃ Calcium Oxide (CaO) develops. Calcium Carbonate reacts representing greenness value of the heated samples. During the heating procedure of the samples, when temperature increases from 1140°C’ to 1150°C’ green colour value increases, on the other hand when temperature goes up from 1150°C’ to 1160°C then green colour value decreases. ‘b’ represent blueness value. During the heating process when temperature goes up from 1140°C’ to 1150°C’ yellow colour value decreases, when temperature goes up from 1150°C’ to 1160°C’ blue colour value increases.

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Calcium Carbonate (CaCO₃) triggers phase development reactions. At 800°C’-900°C’ with the destruction of Calcium Carbonate (Ca CO₃ Calcium Oxide (CaO) develops. Calcium Carbonate reacts
with the amorphous phase (Metakaolinite). As a result, gehlenite and anorthite like crystal phases develop (Kara vd., 2006). Figure 7 and figure 8 show XRD patterns of the samples heated (fired) to 1140°C (Figure 7) and 1150°C (Figure 8) indicating gehlenite and wollastonite developments. In figure 9, the XRD pattern shows that when a sample is heated to 1160°C phases making up the structure are gehlenite, wollastonite and anorthite. It is considered that with the increase of temperature, anorthite will be more prominent.

4. Results

It was noticed that Despite the decline in water absorption values with the increase in cooking temperature, there was a slight change in the apparent and bulk densities; it is believed that the temperature and the total porosity are unchanged while the open pores are partially closed, but the glassy phase, which increases with temperature, does not completely fill the closed pores. In this study it was understood that changes in the bending strength and Young’s Modulus are related to the main skeleton forming the structure of the mineral rather than pores forming. Measuring the frequency difference developed as a result of sound waves advancing within the material has shown that change in the Young’s Modulus values with increased temperature is smaller than the changes in the bending strength values. As porosity in the materials acts as a barrier to the advancing sound waves this is in accordance with the small changes in the porosity and density and determined small increase in the Young’s Modulus values with increased temperature. Bending strength is related to porosity of the material but more so to the skeleton structure. When firing temperature goes up from 1150 °C to 1160 °C Young’s Modulus and bending strength values show respectively increase to 2.4% and 28%. When materials is fired (heated) at 1150 °C in respect to 1140 °C there was increase in the wollastonite and gehlenite developments. At 1160 °C along with increased wollastonite and gehlenite, anorthite also starts developing. In this study it was noticed that anorthite phase development has considerably effected the strength of the material.

The main purpose of this study is to study of the possibilities of using natural stone wastes as construction material in producing ceramic tiles. The material was evaluated in accordance with TS EN
14411 ceramic tiles standard given in Attachment L. As water absorption capacity of the tiles were above 10% at three different firing temperature, so they are in BIII group but as bending strength values are smaller than 12 N/mm² so they are below than the values stated in standard.

In this study, it was shown that two different types natural stone wastes used in this study are not suitable to produce ceramic tiles. It has been determined that the anorthite phase, which is an important phase in the production of fast-fired ceramic tile, begins to form at 1160 °C. However, it is considered that the other stone wastes can be used as filling substance in producing ceramic tiles.

References


