Investigation of the Effects of Red Clay on the Structural Properties of Chamotted Clay Bodies

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Abstract: Chamotte, also known as fired clay or Grog, comes in a range of particle sizes, from fine to coarse. When mixed with various clay compositions, it forms chamotte mud (CM), a vital component in crafting artistic ceramics. The primary muds used for this purpose are chamotte mud and red pottery mud (R-PM). These muds' properties, including sintering, linear shrinkage, water absorption, and color, vary based on their components and firing temperatures. Chamotte mud excels at high temperatures (1150-1200°C) but tends to deform during high-temperature firing, and also exhibits a greater tendency to absorb more water. In contrast, red Kınık pottery mud suits lower temperatures, typically 900-1000°C. Combining both mud types allows ceramic artists to enhance color effects and shaping properties. This study aims to decrease water absorption while increasing firing shrinkage, improving sintering by adding red pottery mud to chamotte mud. The goal is also to optimize R-PM's behavior at different temperatures, ensuring products, especially those meant for outdoor artistic use, have a longer lifetime. Experimental studies involve creating six recipes with specific chamotte and red mud ratios, followed by examining changes in properties such as water absorption, linear shrinkage, color, gloss, microstructure, and sintering behavior during firing at 1160°C.

Keywords: Clay, Ceramics, Ceramic art, Characterization, Design, Glaze.

1. Introduction

The word ceramic is derived from the Greek terms keramos, which means “potter’s clay” and keramikos which means “clay products” [1]. Ceramics have been around since 70,000-35,000 BC because a container of burned clay was discovered at that time [2]. Ceramic art has survived to the present day by being influenced by various civilizations, different life perspectives, different techniques, and aesthetic values in the historical development process. Today, it is reshaping and constructing its own identity due to the conditions and mentality of the age [3].

The term 'clay' refers to a naturally occurring material composed primarily of fine-grained minerals, which is generally plastic at appropriate water contents and will harden when dried or fired. Although clay usually contains phyllosilicates, it may contain other materials that impart plasticity and harden when dried or fired [4]. Red clays are one of the commonly used clays soils in the production of artistic objects, building materials and structural products [5]. Such clays are also used directly in artistic and industrial ceramics for under-glaze and intra-glaze decoration purposes [6]. Owing to the higher percentages of fluxing oxides (especially $K_2O$, $Na_2O$ and $Fe_2O_3$ with clay minerals illite and montmorillonite), red clay is capable of vitrifying at low temperature compared to China clay and ball clay [7].

In ceramic art, the mud from which the designed form will be shaped is chosen by considering features such as formability, glazed and unglazed firing colour, shrinkage, water absorption, expansion and
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...melting behaviour. The colour and texture of the mud after firing are critical. Chamotte mud and potter's mud with red firing colours are the preferred mud types for easy shaping in artistic ceramic production.

The texture of fired ceramic products can form as rough, coloured, stained, or speckled. The roughness on the surface is formed by adding chamotte in varying proportions to the ceramic mud. Grog is bisque, fired clay, used to reducing plasticity and shrinkage, and promoting drying. Grog is available in a variety of sizes from very fine to coarse and is usually tan to brown. Big particle sizes can be used to create texture in clay bodies [8-10]. Although chamotte-added bodies are unsuitable for tableware or other similar ceramic products, they have a pleasing visual and tactual appearance. As a result, these types of mud are best suited for indoor and outdoor ceramics such as sculptures, handmade pottery, and decorative ceramic objects [5].

Chamotte clay is added into the body to add texture, prevent bending and deformation, and increase strength and refractory quality. It acts as a filler and in colours such as brick red, brown, buff and white [11].

Clay is fired to produce chamotte, a material specially prepared to be added to clay or mud bodies; it is crushed to 0.5 cm or less depending on the desired fineness and classified according to mesh size by passing through a dry sieve [12].

Clay is a part of the soil in our 4.543-billion-years-old Earth that contains clay minerals that activate plasticity when it is wet. Water between the particles of clay minerals allows each particle to move easily in relation to each other, and this produces its plasticity [13]. Each type of clay has its own characteristics and allows us to obtain different shaping, firing, colour and texture properties.

The most common secondary clay group is red clay (Red earthenware clay). It can be found in almost every part of the world. They have many of the same properties as ball clay, but they have a high iron content, which gives them a "red terracotta" colour when fired [14]. In the production of red mud, one or more of these red earthenware clays, which have a high iron oxide content and differ in their sintering, melting, and vitrification properties, are generally used.

In the present study, the changes in properties such as microstructure, sintering behaviour, linear shrinkage, water absorption, colour and texture of the bodies obtained by mixing chamotte and red mud with different mineralogical, physical, and chemical properties in specific ratios as a result of firing at 1160 °C were investigated.

2. Materials and Methods

The chamotte mud (CM) used in this study was obtained from Aslan Tuğla A.Ş. and the traditional red pottery mud (R-PM) was obtained from the Kınık (Bilecik) region.

The ratios of the mixture recipes were determined using the Line Blend method. The Line Blend method is a method for producing variations of two materials. In this system, the amount of one material is increased while the amount of the other is decreased. It is usually done at 10% intervals by incrementing and decrementing. The combined value of the two materials should always be 100 [15]. This method is used to obtain a recipe in the production of glaze, mud, primer, or pigment.

Mixtures with 10 to 60% R-PM added to undoped CM based on the ratios determined in Table 1 are coded as R1, R2, R3, R4, R5, and R6. First, CM and R-PM were dried. The dry mud, which was weighed according to the determined ratios, was mixed with water to make it homogeneous, and then the slurry mixture was poured into the plaster mold and turned into plastic mud. The mixtures were
shaped in plaster molds measuring 50x20x15 mm to determine their water absorption and size reduction properties. The samples, which were dried in a furnace at 100 oC, were fired at 1160 oC in a Nabertherm brand electric chamber-type furnace. Furthermore, the samples formed in a different plaster mold to determine color change were fired under the same conditions as glazed and unglazed. Within the scope of the study, an unfritted stoneware glaze recipe to be applied to ceramic bodies was developed. Alkaline-boron-containing transparent stoneware glaze (ST), for which the Seger formula is given in Table 2, was applied to the plates that were bisque fired at 1000 oC. Seger formula was studied by Hermann Seger in the late 1800s. Since ceramic materials were so varied and complex, he decided to work on basic building block of matter, the atom, to try to establish a coherent system which might enable him to predict glaze behavior.

Table 1. Recipe compositions created in the binary system (wt. %)

<table>
<thead>
<tr>
<th>Raw Material</th>
<th>Composition (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>R1</td>
</tr>
<tr>
<td>CM</td>
<td>90</td>
</tr>
<tr>
<td>R-PM</td>
<td>10</td>
</tr>
</tbody>
</table>

When the Seger Molecular Type of a ceramic glaze is known, that is when we know the quantity of each oxide in moles, and then it is sure that we can create it from different raw material and in different quantities, taking under consideration the cost, the ecological impacts, and the availability of each raw material [16, 17].

Table 2. Seger Formula of ST coded Unfritted Transparent Glaze

<table>
<thead>
<tr>
<th>Glaze Code</th>
<th>Seger Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>ST</td>
<td>0.762 Na₂O</td>
</tr>
<tr>
<td></td>
<td>0.108 K₂O</td>
</tr>
<tr>
<td></td>
<td>0.310 Al₂O₃</td>
</tr>
<tr>
<td></td>
<td>2.295 SiO₂</td>
</tr>
<tr>
<td></td>
<td>0.129 CaO</td>
</tr>
<tr>
<td></td>
<td>0.468 B₂O₃</td>
</tr>
</tbody>
</table>

Chemical analyses of the raw materials used in the study were determined by using X-ray fluorescence spectrometry. In order to examine the sintering behavior of the prepared binary mixtures, optical dilatometer analyses of each mixture were made with a Misura, 3.32 ODHT-HSM optical dilatometer. For this purpose, 15x5x5 mm rectangular prism sticks were cast from each mixture and placed in the device for measurement. The water absorption values of the samples were made according to the TS EN 997 standard (Equation 1).

\[
\text{Water Absorption} \% = \left( \frac{A-B}{B} \right) \times 100
\]

\(A\): wet weight of the sample
\(B\): dry weight of the sample

Color measurements of ceramic plates were made with a Konica Minolta CM-2300D model spectrophotometer. L*- was evaluated as the lightness coordinate (L*=0 indicates black and L*=100 indicates white), a*- as the red/green coordinate (+a* indicates red, -a* indicates green), and b*- as the yellow/blue coordinate (+b* indicates yellow, -b* indicates blue) [18].
The shrinkage ratios were calculated by measuring the size of the samples before and after the sintering process. The linear shrinkage for length of a ceramics structure was determined by using the formula as shown in Equation 2 [19].

\[
\text{Percentage shrinkage for length} = \frac{L_0 - L_1}{L_0} \times 100\%
\]  

(2)

The formation and evolution of crystalline phases in ceramic bodies monitored by XRD. The microstructural analysis of fired samples was examined via SEM equipped with an energy dispersive X-ray spectrometer (EDX).

In addition to these characterization tests, Eskisehir Technical University's Ceramic Research Center, Standard Testing Laboratory performed frost resistance tests following the TS EN ISO 10545-12 standard to determine the suitability of the produced ceramic bodies for outdoor use in the presence of water under freezing conditions.

3. Results and Discussion

Chemical analyses of the CM and R-PM used in this study are given in Table 3. R-PM, as one can see, has a high percentage of Fe₂O₃.

Table 3. Chemical analysis of CM and R-PM (wt. %)

<table>
<thead>
<tr>
<th>Raw Material</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>CaO</th>
<th>MgO</th>
<th>Na₂O</th>
<th>K₂O</th>
<th>TiO₂</th>
<th>* L.O.I.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CM</td>
<td>59.30</td>
<td>25.93</td>
<td>3.28</td>
<td>0.20</td>
<td>0.64</td>
<td>0.98</td>
<td>2.40</td>
<td>1.05</td>
<td>6.22</td>
</tr>
<tr>
<td>R-PM</td>
<td>58.27</td>
<td>18.09</td>
<td>7.98</td>
<td>1.88</td>
<td>2.10</td>
<td>1.17</td>
<td>2.50</td>
<td>1.29</td>
<td>6.72</td>
</tr>
</tbody>
</table>

*L.O.I.: Losses on ignition

The linear shrinkage and water absorption values of ceramic bodies are shown in Table 4.

It was determined that the total shrinkage values of the mixtures obtained by gradually adding R-PM to CM increased while the water absorption values (Table 4) decreased. The body produced by firing CM at 1160 °C has a very high-water absorption value (8.19%). This value has an impact on the strength of the produced ceramic under usage conditions. This may cause issues, particularly with outdoor products, depending on atmospheric conditions. For this reason, ceramics that are much more resistant to freezing and have low water absorption are preferred outdoors [20].

The red mud added to the chamotte mud is not suitable for firing at high temperatures (≥1160 °C) since it deforms. As a result, the problem of high-water absorption in chamotte mud and deformation in red clays during the high-temperature firing were eliminated in the mixtures produced within the study. The linear shrinkage and water absorption results in Table 4 can be explained by considering the sintering behavior of red clay bodies. The densification of a red clay body takes place by two mechanisms; solid state sintering is prominent below 950 °C and liquid phase sintering is prominent above 950 °C. During firing, various thermal reactions and sintering processes take place in clay which strongly influences thermal reactions in bodies made thereof. In addition, the liquid phase sintering has a more significant effect on the densification than the solid-state sintering. The presence of the liquid phase aids in the increase of densification and reduces the sintering temperature. Therefore, the ratios of Fe₂O₃, Na₂O, and K₂O in the mixtures affect the firing color and vitrification of the body, as well as the reduction in size and water absorption rates [7]. Increasing the sodium and iron compounds in the specimens, leading to more glass phase. The glass phase filled the interstices
of specimens, thereby increasing bulk density and sintering shrinkage, and decreasing water absorption [21].

Table 4. Linear Shrinkage and water absorption values of CM and R-PM mixtures at 1160 °C.

<table>
<thead>
<tr>
<th>Recipe</th>
<th>Linear Shrinkage</th>
<th>Water Absorption</th>
</tr>
</thead>
<tbody>
<tr>
<td>CM</td>
<td>9.85</td>
<td>8.19</td>
</tr>
<tr>
<td>R1</td>
<td>9.26</td>
<td>6.27</td>
</tr>
<tr>
<td>R2</td>
<td>9.32</td>
<td>4.94</td>
</tr>
<tr>
<td>R3</td>
<td>9.4</td>
<td>3.92</td>
</tr>
<tr>
<td>R4</td>
<td>10.15</td>
<td>3.27</td>
</tr>
<tr>
<td>R5</td>
<td>10.5</td>
<td>2.86</td>
</tr>
<tr>
<td>R6</td>
<td>10.75</td>
<td>2.17</td>
</tr>
<tr>
<td>R-PM</td>
<td>13.2</td>
<td>0.27</td>
</tr>
</tbody>
</table>

Besides, industrial, and artistic ceramics with visually and aesthetically advanced color and texture effects can be produced. When fired at the same temperature, chamotte mud produces a light-colored tone. Red clays usually contain minerals such as kaolinite, illite along with high content of iron minerals, coloring the raw as well as fired bodies [22]. The high iron oxide content of red mud causes a significant change in color tone. Dark-colored clays have a high impurity content and a high Fe$_2$O$_3$ content. Their color is a deep earthen red. They have high fluxing properties and used at high temperatures to change or regulate the color and melting of the body [23].

Figure 1. Optical dilatometer curves of chamotte, red clay and produced bodies

After 100 cycles of frost resistance testing, no damage was observed in the samples.
Fig. 1 depicts the sintering behavior of the body against time as well as the sintering rate as temperature increases. The curves were created by comparing the results of CM and R-PM with the recipes produced in the study.

The use of red clay appears to increase the sintering speed of the bodies. When the comparative graphs were examined, it was discovered that the red clay had the fastest sintering speed compared to the other compositions and showed a significant amount of shrinkage. It is observed that gradually adding red clay to the chamotte mud increases the sintering speed and total shrinkage value of the sample. The decrease in water absorption values also coincides with this situation. Furthermore, the sintering behavior of the samples supports the firing shrinkage data presented in Table 4.

After firing, the colors of the mixtures darkened and changed from light terracotta to red-brown when 10-60 % red mud was added to chamotte mud. Fig. 2 depicts the color tones obtained after firing at 1160 °C based on the total amount of Fe₂O₃ in the mud mixtures between R1 and R6.

![Color images and tables](image_url)

**Figure 2.** Colors and textures obtained as after unglazed firing of CM- and R-PM mixtures at 1160 °C

**Table 5.** Color measurement values of unglazed samples fired at 1160 °C

<table>
<thead>
<tr>
<th>Recipe No</th>
<th>L*</th>
<th>a*</th>
<th>b*</th>
</tr>
</thead>
<tbody>
<tr>
<td>CM</td>
<td>69.96</td>
<td>13.75</td>
<td>29.28</td>
</tr>
<tr>
<td>R1</td>
<td>56.60</td>
<td>19.85</td>
<td>27.20</td>
</tr>
<tr>
<td>R2</td>
<td>49.12</td>
<td>19.83</td>
<td>22.33</td>
</tr>
<tr>
<td>R3</td>
<td>47.09</td>
<td>19.52</td>
<td>20.44</td>
</tr>
<tr>
<td>R4</td>
<td>44.37</td>
<td>18.16</td>
<td>17.72</td>
</tr>
<tr>
<td>R5</td>
<td>42.61</td>
<td>16.80</td>
<td>15.70</td>
</tr>
<tr>
<td>R6</td>
<td>42.07</td>
<td>15.14</td>
<td>13.52</td>
</tr>
</tbody>
</table>

The color measurement values in Table 5 also confirm that as the red mud ratio in the mixture increases, the whiteness (L*) decreases and the redness (a*) increases. The presence of Fe₂O₃ at a
concentration of 7.98 % in red mud naturally influences the color change. The term "earthenware clay" refers to the majority of usable clays found in nature. Depending on the mineralogical and chemical properties of the clay and the firing temperature, red clays in this group can be multicolored after firing, ranging from pink to buff tan, red, brown, or black [5].

Fig. 3 shows the glazed firing results of the samples from the mixtures (CM-R-PM) at 1160 °C. The terracotta color is dominant in bodies containing 10, 20, 30, and 40% red mud in these results, and after applying this ratio, a darker surface appearance was observed.

Figure 3. Glazed firing results of samples of chamotte mud-red mud mixtures at 1160 °C

![Glazed firing results](image1)

Figure 4. XRD patterns of the produced ceramic bodies

![XRD patterns](image2)
The mineralogical characterization by XRD of the raw materials identified the mineral quartz, mullite, cristobalite and hematite (Fig. 4). While only quartz, cristobalite, anorthite and mullite phases are observed in chamotte clay without R-PM addition, the hematite phase was also observed in R3-R6 coded samples with R-PM additions of 30% and above.

Fig. 5 shows microstructure images of the R2, R4 and R6 coded bodies, which produce the most effective color and texture effects.

![Figure 5](image)

**Figure 5.** SEM micrographs of fired samples (a) R2 (b) R4 (c) R6 coded samples fired at 1160 °C

When evaluated together with the XRD analysis results, residual quartz, round-shaped cristobalite, primary and secondary needle-like mullite and small amount of anorthite crystals are detected according to SEM images and EDX analyses (Fig. 6).

In Fig. 7, the microstructure image taken at 500X magnification from the R6 coded body containing 60% R-PM and the EDX scan of the white crystals in this area are presented.

When the back-scattered electron SEM images and EDX analysis for the hematite phase observed in the XRD graph with the addition of 30% or more R-PM to the CM are evaluated together, it is thought that the high-contrast white areas are the hematite structure since they are the regions with the highest iron content.
Figure 6. EDX results of (a) R2 (b) R4 (c) R6 coded samples

Figure 7. SEM image and EDX analyses of R6 coded body
4. Conclusions

This study focused on chamotte, also known as fired clay or Grog, and its role in ceramic production. Chamotte offers a range of particle sizes and is used in clay compositions collectively called chamotte mud (CM). Artists often prefer using chamotte mud in conjunction with red pottery mud (R-PM) due to their unique properties.

The primary goal was to reduce water absorption and enhance firing shrinkage in ceramic bodies by mixing red pottery mud with chamotte mud. This improves the durability of ceramics, especially for outdoor use. Six recipes with different chamotte and red mud ratios were fired at 1160 °C, and various properties were assessed. The results showed that adding red mud increased shrinkage and reduced water absorption, addressing deformation issues during high-temperature firings. This led to denser and more vitrified bodies with improved resistance to freezing. Moreover, the addition of red mud resulted in darker color tones, offering opportunities for visually appealing ceramics. Frost resistance tests confirmed their suitability for outdoor use.

In summary, this research highlights the benefits of combining chamotte and red mud to create versatile ceramics with enhanced properties, making them suitable for various applications.

Acknowledgments

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Authors’ Contributions

SY and MC conceived the research idea and formulated the study's structure. SY was responsible for sourcing materials, developing recipes, writing the literature review, conducting characterization tests, and interpreting the results. MC contributed to composing the research materials, production, conducting literature research, evaluating the results, and participating in recipe and product development. The paper was jointly authored by SY and MC.

Competing Interests

The authors declare that they have no competing interests.

References


