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Effect of Kastamonu Red Clay Addition on the Properties of Matt Glazes in Art Ceramics Application

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ABSTRACT: *Pigments are widely used for colouring of ceramic products such as tiles, ceramic and artworks. These materials are normally classified as expensive colorants due to their expensive production costs. Due to this fact, recent researches are focusing on the development of cost effective colouring agents based on natural materials. In this study, the aim was to produce a type of matt glaze using locally available clay deposits of Kastamonu region. Four different matt glaze formulations were prepared and the effects of clay amount on the properties of glazed stoneware ceramic samples were investigated. Also some ceramic artwork pieces were designed and covered by the formulated glaze. The glazed samples and ceramic art works were sintered at 1150 °C for 1 hour in an electric furnace. Different characterization techniques were performed on the glazed bodies including after firing colour evaluation, phase analysis, microstructural studies and thermal behaviour. It is determined that with increasing the clay amount in the matt glaze formulations, the colour gradually changes from light to dark yellowish tones. The whole findings revealed that the local Kastamonu red clay raw material is potentially suitable for ceramic and glaze application and can be successfully used as colouring agent in the matt glaze formulations of ceramic art works.*

KEYWORDS *clay, matt glaze, characterization, microstructure, ceramic art work*

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I. INTRODUCTION

Turkish ceramic industry including tiles, porcelains, sanitary wares and building materials shows a rapid development during recent years which consumes various types of domestic and imported raw materials. Artistic ceramic sector is another important consumer of high quality raw materials especially for design, decoration and colouring of products. The fact that the sources of highly pure raw materials are decreasing gradually brings serious demand of researches on developing alternative raw materials (Karasu, Çakı, & Yeşilbaş, 2000). The substitution of toxic synthetic material by natural resources is another motivation of using sustainable materials in ceramic industry and art. Beside several technical properties requirements such as mechanical strength, physical durability, thermal behaviour and etc., traditional ceramic industry and art are strongly depended on high quality methods of decorations and design of final products (Yalçin & Sevinç, 2000). Ceramic bodies, glazes and engobes are generally coloured with different types of natural and synthetic pigments. The use of metal oxides is now well-established in further enhancement of decorative appearance of stone wares and other ceramic products. In this regards, the usage of colouring agents such as inorganic pigments is thought to be increased according to the wide consumption in ceramic industry. However, the preparation of dye mixtures from pigments or heavy metal oxides would increase the initial cost of the production process as well as the risk of environmental hazards. Natural pigments are kinds of inorganic colouring agents which generally can be found in nature such as clays (Çakı, Karasu, Karaveli &Mühürcü, 2007**;** Öztürk, Atay, Çaki, & Ay, 2015), limonite (Sarnıç, Güllü, & Yılmaz, 2011; Karasu & Bahşi, 2001) and basalt (Gültekin, 2017; Ergun & Çakı, 2010; Çetin, 2005). These natural inorganic materials can be used for glaze colouring instead of expensive synthetic pigments. It was also tried to evaluate the usage of herbal ashes in the composition of artistic ceramic glazes (Sarnıç, Güllü, & Yılmaz, 2011; Karasu & Bahşi, 2001). However the use of these natural resources seems to be difficult in some cases due to the impurities entrance or mixing inhomogeneity in glaze formulations. To overcome these problems, it needs to well developing of technical properties of natural sources in ceramic and glaze industries. Red clays are kinds of common and inexpensive ceramic raw materials which are normally available in the earth surface in the forms of alluvial or precipitated deposits. From the ancient ages, most of the human made ceramic products were fabricated from this natural material. Today, the use of red clays is still continuing in a wide range of ceramic art works, building materials and functional products. One of the main consumption areas of red clays is in building materials as roofing tiles and red construction bricks. In the ceramic glaze production, these types of clays are generally used for sub-lining and under-glaze decoration for artistic and industrial products (Çakı, Karasu, Karaveli &Mühürcü, 2007). Among the natural inorganic pigments, iron oxides would give different after firing colours in ceramic bodies. Raw materials containing Fe_2O_3 such as red clays, iron production by-products and hematite ores are widely used for colouring of ceramics, glazes and engobes (Gültekin, 2017). These materials are well-known colouring agents in ceramic industry and normally produce reddish to brownish colour after firing. In ceramic tile production, colouring agents are used in either body or glaze formulations alone or mixture with other oxide raw materials (Öztürk, Atay, Çaki, & Ay, 2015). Red clays are chemically composed of various types of iron bearing phases such as iron oxides and hydroxides. There are some reports were discussed the use of red clays in engobe and/or glaze formulation of traditional pottery production (Yastı, 2004; Çakı, Karasu, Karaveli & Çapar, 2007; Biçici, Çakı & Ercan, 2010; Öztürk & Gültekin, 2014). Özcan (2002), investigated the usability of Eskisehir red clay in the glaze production for some ceramic stone wares. It was demonstrated that this clay is suitable for the formulation design of stoneware glazes (Karasu & Bahşi, 2001). Çakı, Kaya, Karasu, & Başer (2012) evaluated the application of perlite mineral as raw material in ceramics industry. This mineral with high alkaline content was obtained from Kütahya region and tried as a substitution for albite, orthoclase and ulexite minerals in the stoneware glaze compositions. It was declared that perlite could be used as both melting and colouring agent in stoneware glazes. In addition, due to the high alkaline content, it can be used in the glaze recipes for artistic glaze applications (Çakı, Kaya, Karasu & Başer, 2012).

In this study, Kastamonu red clay was used in the formulation design of matt glazes at different amounts. The main aim was to prepare a colourful matt glaze formulation using this clay in the raw state for ceramic glazing instead of synthetic pigments and dyes. First, ceramic matt glazes were prepared and after characterizing, applied to some artistic ceramic forms. Technical and aesthetical properties of stoneware matt glaze compositions were investigated via different characterization techniques such as X-ray diffraction, scanning electron microscopy and colouring parameters.

II. MATERIALS AND METHODS

2.1. Raw Materials, Formulations and Glaze Preparation

The main used raw materials for glaze sample preparation were potassium feldspar (K-feldspar), marble ($CaCO_3$), kaolinite, quartz (SiO_2) and zinc oxide (ZnO, 99% purity) powders. All raw materials were commercially available and industrially-graded for use in ceramic and glaze industries in the form of sub-micron super-fine powders. These materials were used without any furthered purification or washing. The Kastamonu red clay material was obtained from Pınarbaşı mine near Kastamonu city (~120 km NW). The clay was previously washed several times using water and passed through -120 mesh sieve to remove impurities. After 24 h drying in an electric oven at 110 ^oC, the clay was ground using agate mortar to obtain -230 mesh fine powders. Glaze preparation was based on the recipes indicated in Table 1. After accurate weighing, raw materials were mixed with 0.25 wt.% STTP as deflocculating agent and wet-grounded in a porcelain jet-mill containing 1 cm dia. alumina balls. Each recipe was homogeneously mixed with 50 wt.% water and ground for 1 h. The obtained glaze slips were passed through -90 μm sieves to remove the coarse grains and then applied on the cover of 5 cm circular ceramic bodies by pouring. It was noticed that the entire surface was covered homogeneously with approximately same thickness and the extra slip was poured away. The glazed bodies were then dried at 105 °C for 24 h in an electric oven. Sintering of the glazed samples was done in a laboratory type electric resistance furnace (Protherm PLF 150/10, Turkey) at 1150 °C for 1 h. Some artistic ceramic pieces were also covered with the optimum formulation of glaze and fired with the same condition.

2.2. Characterization

Chemical composition of raw materials was found out by X-ray fluorescence spectroscopy (XRF, Xepos 3, Spectro, Germany). For this test, the powders were poured in polymer holders and directly exposed to X-ray. Glossiness properties measurement of the fired gazed products was carried out using a gloss meter (Multi-Gloss 268, Konica Minolta, Japan) system. The colour parameters measurement of glazes was conducted by measuring the chromatic coordinates (L, a*, b*) via a chroma meter (CM-2300, Konica Minolta, Japan) machine. L* parameter is called as the aperture axis and L*=0 characterizes black and L*= 100 defines whiteness. Other colouring parameters are a* and b* value which shows green-red and blue-yellow colours, respectively (Kaplan & Binal, 2017). The melting behaviour of the studied glazes was investigated with hot stage microscope (Misura 3.32 ODHT-HSM 1600/80, Italy) in the temperature range of 25-1400 °C. The surface morphology of glazes was characterized by FE scanning electron microscope (QUANTA 250, Czech) equipped with EDAX spectroscope (AMETEC, USA). The phase composition of glazes was obtained via X-ray diffraction (XRD) using D8 Advance diffractometer (Bruker, USA). The Cu Kα radiation source was used for diffraction measurements in the scan range of 10 to 80 ° and rate of 5 °/min.

Table 1. Matt glaze recipes (wt.%)

Raw Materials	S0	S10	S15	S20
K-Feldspar	55	55	55	55
Marble	15	15	15	15
Kaolinite	15	15	15	15
Quartz	10	10	10	10
ZnO	5	5	5	5
Kastamonu Red Clay	0	10	15	20

III. RESULT AND DISCUSSION

XRF chemical analysis of the used raw materials is shown in Table 2. As it can be seen, the Kastamonu red clay has the high contents of CaO (6.13 wt.%) and Fe_2O_3 (8.35 wt.%). It is thought that the high contents of iron oxide would alter the final tonality of after firing colour of ceramic products. Figure 1 shows the colour appearance of the ceramic samples covered with different glazes and sintered at 1150 °C for 1 h. It is obvious that depending on the amount of red clay in the glaze formulations, the obtained colours after firing changed from light to dark yellowish appearance. The content of these oxides is sensitive to firing temperature and often produces changes in fired colour of clay raw materials. Iron oxides are also responsible for the reddish colour of fired glazed tiles and artistic pieces.

Table 2. XRF chemical analysis of used raw materials (wt.%)

Raw Materials	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	CaO	MgO	Na_2O	K_2O	LOI
Kaolinite	57.68	26.98	0.94	1.42	0.12	0.34	0.29	2.06	10.03
Quartz	98.15	1.09	0.03	0.02	0	0.05	0.34	0.12	0.21
K-Feldspar	67.06	17.15	0.16	-	0.14	-	2.64	12.65	0.20
Marble	-	-	-	-	54.90	0.31	-	-	44.43
Kastamonu Red Clay	46.81	16.98	6.13	0.88	8.35	2.68	1.72	3.09	12.73

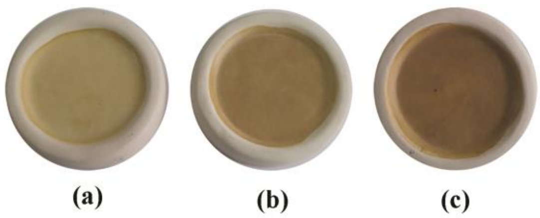

Fig. 1. Colour appearances of the fired matt glazes at 1150 °C: (a) S10, (b) S15 and (c) S20 samples

Table 3 list the measured optical parameters of the stoneware matt glazes fired at 1150 °C for 1 h. The L * value, which expresses the lightness/darkness of the colour, decreases due to the increase in the amount of red clay which is in accordance with the colour of the fired samples shown in Figure 1. The lowest L* value was obtained for matt glaze with 20 wt.% of Kastamonu red clay. A slight decrease in the whiteness of red clay containing glazes could be caused due to the Fe_2O_3 presence in clay. According to the listed data in Table 3, red clay addition has not a significant effect on a* value. Slight observed increase in a* values indicates the redness quality of samples. It is clear that a* value changes from 2.07 and 8.65 for sintered glazes. The positive b* value expresses the yellowness of the glazes. The values of b* parameter increase from 11.72 to 28.38 with an increase of red clay amount up to 20 wt.% in the glaze formulations.

Table 3. Optical parameters of the stoneware matt glazes fired at 1150 °C

Glaze	L^*	a^*	b^*
S 0	88.94	2.07	11.72
S 10	79.15	4.06	25.67
S 15	68.25	8.56	25.91
S 20	65.68	8.65	28.38

The brightness parameters values of the fired glaze samples are mentioned in Tables 4. According to these results, an increasing in the amount of red clay in glaze recipes had a negative effect on mattness property. The standard glaze sample has the highest mattness value amongst the others. By increasing the amount of red clay, the mattness values gradually decreases.

Table 4. Brightness test results of the stoneware matt glazes with different red clay content

Glazes	Brightness	
	20°	60°
S 0	1.3	5.2
S 10	1.3	6.0
S 15	1.3	7.4
S 20	1.3	8.7

The hot stage microscopy (HSM) analysis was conducted on S10 and S20 glaze samples from room temperature till 1400 °C. Figure 2 shows the hot stage curves and Figure 3 demonstrates the microscopic image of the studied samples during heating. According to Figure 2, the HSM graphs of the studied S10 and S20 glazes clearly show the melting behaviour of samples. Figure 3 shows the microscopic images during heating which reveals the shape deformation characteristic temperatures, percentage of the initial sample height and contact angles. As it can be seen in this picture, the sintering start and end stages of the S10 and S20 are in the temperature range of 1120-1226 °C. During the crystallization, the sample shrinkage stops as a result of the sintering process, and softening occurs when the crystallization ends. Higher temperatures were required to reach the softening point. By increasing the content of red clay in the glaze formulation, no significant changes were observed in the sintering behaviour of samples, however, the softening temperature was slightly decreased.

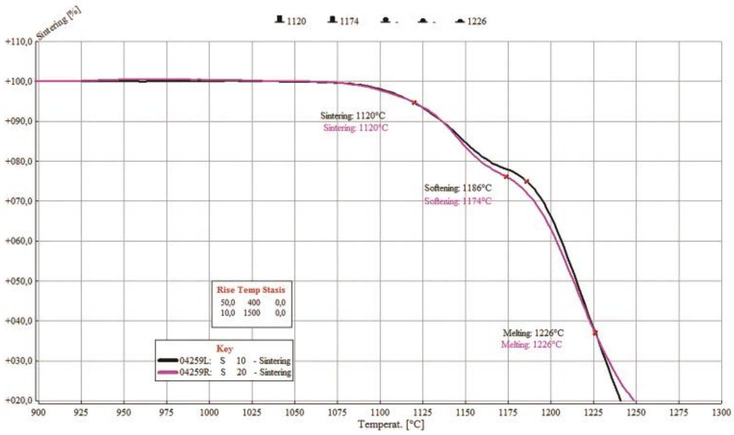

Fig. 2. Hot stage microscopy curves: (black) S10 and (pink) S20 samples

The melt spreading behaviour on the ceramic surfaces, movement of the gas bubbles and the crystallization process during cooling period are strongly depending on firing temperature, surface tension and viscosity of melted glaze. Glaze with a high surface tension normally leads to flocculation phenomenon and prevent air bubbles remove. High viscosity values and surface tension behaviour can cause high pinhole defects in the final fired glaze. The low viscosity growth of the crystalline nucleus, which is the starting of the crystallization process, is more preferable than the high viscosity glazes. In the hot stage microscopy analysis of S10, the sintering temperature was 1120 °C, the softening temperature was 1186 °C and the melting temperature was 1226 °C for S10 sample. At the end of the measurement, it was observed that the surface tension was low (Figure 3). In addition, the high yield point (1226 °C) has been seen to be suitable for use in glaze formulations of porcelain structures. In this test, it was visible that the thermal behaviour of the glaze sample was sufficient to allow for bubbles removing.

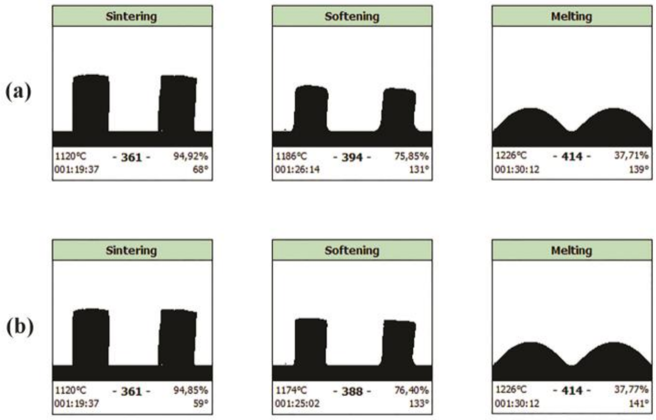

Fig. 3. Hot stage microscopic images of matt glazes: (a) S10 and (b) S20 samples

The crystalline phases formed after firing in the standard (S0) and high content red clay (S20) glaze samples were detected by means of XRD analyses and represented in Figure 4. It is clear that the standard S0 glaze sample has only quartz as the main characteristic phase, while the S20 glaze with high red clay content shows both anorthite and quartz in the phase composition. On the other hand, anorthite was the main constitution phase in S20 sample. From these XRD graphs, it is visible that the glassy amorphous phase content was increased by using red clay in the matt glaze formulation. In addition, by comparing the quartz peaks position in S0 and S20 samples, it is clear that the characteristic peaks are shifted toward low degrees for S20 sample. According to these results it can be concluded showed that the presented Fe_2O_3 from red clay could be dissolved in glassy phase and affected the quartz peaks position.

The surface microstructural features of S10 and S20 glaze samples were investigated by scanning electron microscopy (SEM) and shown in Figs. 5 (a) and (b), respectively. The overall microstructure of glazes is composed of an amorphous glassy phase of vitreous melt which surrounds other crystalline phases. The observed big dark grains in the microstructure are generally composed of remained non-reacted quartz particles from raw materials. This is due to the high melting point of quartz which is over 1700 ^oC. However most of the primary quartz was used in the formation of glassy phase as well as other crystalline phases such as anorthite. As the both SEM images of the glaze samples show, there are some needle shaped bright crystals in the structure. The EDS point chemical analysis of these crystals (Fig. 6) reveals that the anorthite is the possible component of them, which is also in agreement with the results obtained from XRD analysis. Table 5 also shows the semi quantitative chemical analysis of the highlighted point on the Fig. 6 and proves it is closed to the composition of anorthite phase ($CaAl_2Si_2O_8$). It is also observed that the glazes produced using high contents of Kastamonu red clay had no remaining open porosities after firing. Also there were not any visible formed defects such as cracks, lamination or exfoliation during cooling. These are kinds of important parameters in the quality control of ceramic glazes which are used industrially or for artistic pieces.

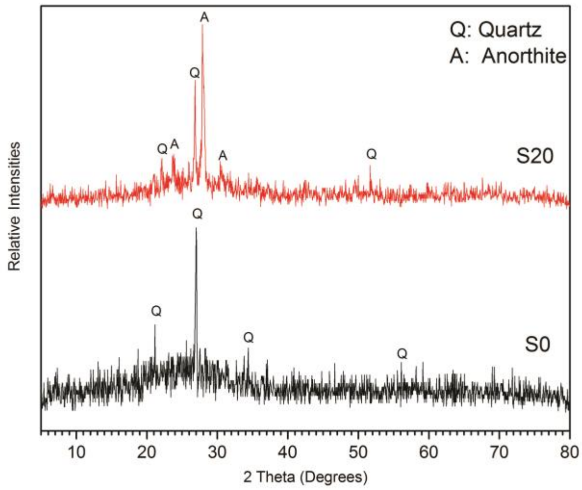

Fig. 4. XRD patterns of S0 and S20 glaze samples

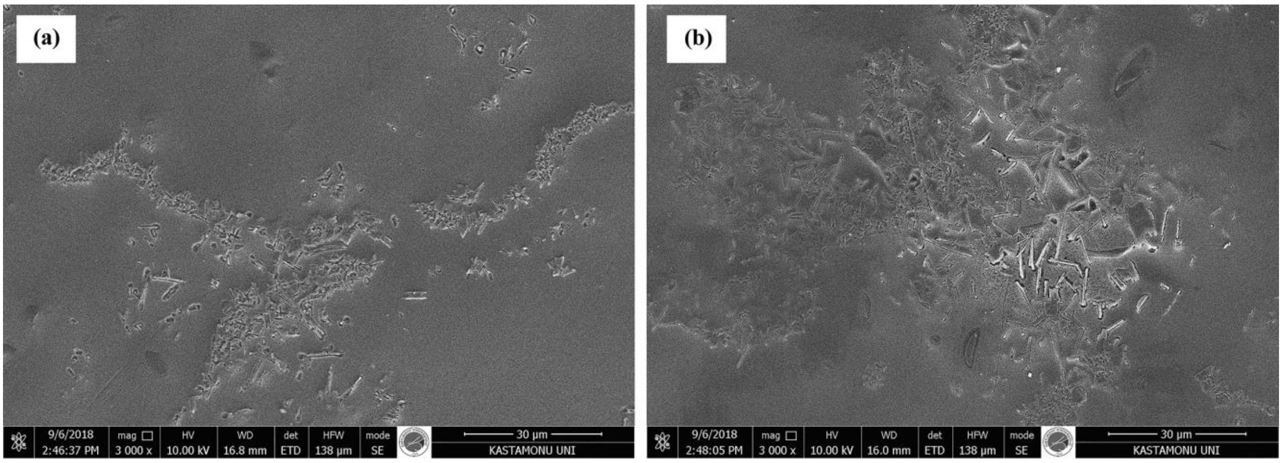

Fig. 5. SEM images of matt glaze surfaces: (a) S10 and (b) S20 samples

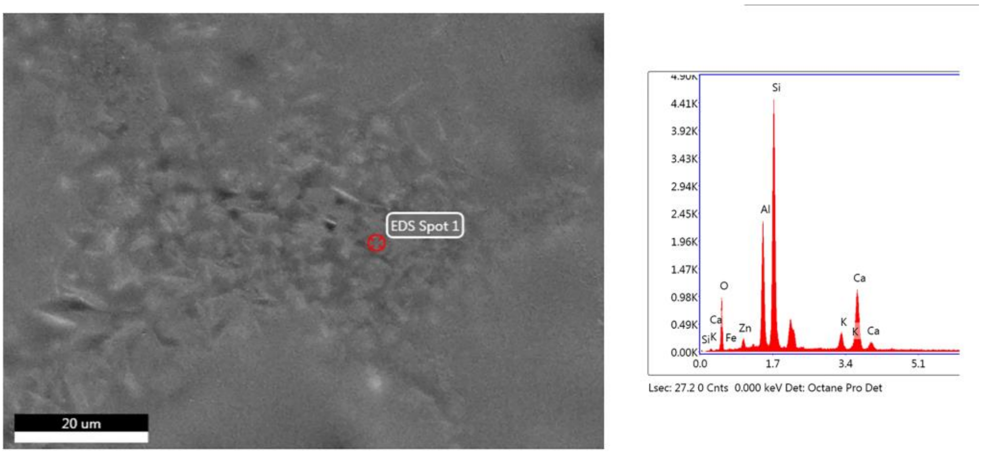

Fig. 6. SEM image and EDAX analyses of S20 matt glaze sample

Table 5. EDAX analysis of the highlighted point of Fig. 6

Element	Wt.%
Al_2O_3	23.64
SiO_2	55.96
K_2O	2.48
CaO	13.22
Fe_2O_3	2.12
ZnO	2.58

At the final part of the study, the S20 glaze which has the highest content of Kastamonu red clay (20 wt.%), was applied to cover and decorate some ceramic artwork pieces. Figure 7 shows both sides of the ceramic artwork glazed by S20. The glaze preparation, application and firing condition for these art works was exactly the same as the previously discussed test samples. The investigation of this art work shows the formation of high quality matt glaze on the stoneware ceramic body. The mattness quality seems to be interesting for artistic ceramic researchers. Also the thickness of the applied glaze looks to be homogeny in all part of the art work. The visible big defect such as pin hole, gas bubbles, laminations or crack were also not seen in this product.

Fig. 7. Artistic ceramic pieces covered by designed S20 matt glaze.

IV. CONCLUSION

In this research, the production of matt glaze using locally Kastamonu red clay was investigated. Four different formulations were designed and the effects of clay addition on the properties of glazed ceramic test samples and artworks were studied after firing at 1150 °C for 1 hour. The samples were characterized in terms of after firing colour, phase analysis, microstructural studies and hot stage thermal behaviour. The results showed that with increasing the clay amount in the matt glaze formulations, the firing colour gradually changes from light to dark yellowish. The high iron oxide contents of red clay, was determined as the main responsible for colour changes of the matt glaze samples. The hot stage microscopy study revealed the normal sintering behaviour of the developed glaze contained red clay at high content level of 20 wt.%. The phase and microstructural investigations showed the presence of quartz and amorphous glass as the main constitutional phases for the fired glazes. However by addition of red clay, the formation of anorthite phase was also proved in the samples. The high red clay content glaze formulation (S20) was also applied to a ceramic art work piece and the visual investigation revealed the formation of a homogenous cover on the product with not clear defects. The whole results showed that the Kastamonu red clay is potentially suitable for ceramic and glaze applications and can be used as a natural, sustainable and cost-effective colouring agent in the production of matt glazes for industrial and artistic ceramic products instead of commonly used inorganic synthetic pigments.

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