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Investigation of the Use of Pink Pigment Obtained by Using Different Mineralisers in Wall Tile Glaze Recipes

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Abstract

Oxide and pigment components are used in the colouring of glazes applied to ceramic products. Pigment production process is a complex process involving different stages. Pigment production process, such as grinding, mineraliser addition and calcination are the most important parameters in the emergence of colour. The rapid firing process in the wall tile production process affects the colour intensity and colour quality of the pigment component used in the glaze recipe in the final product.

In this research, pigments were produced using Ca-borate and Mg-sulfate mineralizers, and their impact on pigment synthesis was examined. The glazes exhibited colors ranging from pink to light brown, dependent on the pigment composition. The choice of mineralizer had a notable effect on the crystal structure of the pigments. The Lab* values of the glazes were measured using a spectrophotometer. Characterization of the pigments was conducted through XRD and SEM-EDX analysis, respectively.

Keywords: Pigment, mineralizator, color.

1. Introduction

Ceramic glazes are glassy structures with glossy, matt or opaque effect that cover the surfaces of ceramic products and provide technical, aesthetic and hygienic properties. This glassy structure in the glaze product gives the ceramic body a shiny smooth surface and provides many advantages such as durability, easy cleanability, chemical resistance and colour effect. The colour effect in ceramic glazes is achieved by using natural and synthetic oxide and ceramic pigments, under-glaze and over-glaze colourants, fired over-glaze colourants and solution-based colourants added to the glaze [1].

Ceramic pigments are homogeneously distributed in the ceramic glaze system without dissolution and chemical reaction at high temperatures. Ceramic pigments can form physical and chemical bonds with the ceramic body and can vary depending on the sintering temperature (especially in terms of colour quality and amorphisation process in the glaze). Especially in industrial and artistic applications, colour effect, surface quality, physical and mechanical properties vary depending on glaze type and sintering temperature [2,3].

The production process of ceramic pigments used in ceramic body and glaze colouring includes grinding of colouring oxides in natural raw materials, homogenisation by salt addition, calcination, grinding, washing and recalcination when necessary. Colour is obtained by sintering the pigments produced by this step-by-step process after they are used in the composition and glaze recipes [4,5]. The appearance and perception of pigment colour by the

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human eye is related to its range in the wavelength scale of the electromagnetic spectrum, which is described as a physical effect. Pigment formation processes from natural raw materials have been investigated by various researchers. The initial chemical structure of the natural raw material, mineralogical structure, grain size effect due to grinding, mineraliser effect, effect of sintering stages have been investigated for various ceramic glaze materials in different articles [6,7].

In this study, olivine-based ceramic coloured pigments were synthesised by comparing the effects of two different mineralisers at two different temperatures (l250°C-1300°C). SEM observation of the powder heat-treated at 1250°C and 1300°C was performed to reveal the heterogeneous powder morphology. The synthesised colours exhibited a pink-brown colour when compared with two different mineralisers and two different calcination temperatures.

2. Experimental Procedure

2.1. Pigment Preparation

In this research, Mn_2O_3 (Kutahya, Turkey) and olivine (Kütahya, Turkey) were employed as raw materials for the production of Mn-olivine pigments. The chemical composition of Mn2O3 and olivine powders was determined using X-ray XRF, Panalytical Axios Max), as detailed in Table 1. Pigment compositions were adjusted by incorporating Mn_2O_3 in proportions ranging from 0% to 20%.

Table 1. The chemical analysis of Manganoxide and Olivine.

Oxide (wt%)	Olivine	Manganoxide
MgO	28,84	0,48
Al_2O_3	0,56	0,95
SiO_2	26,50	30,30
P_2O_5	0,00	0,08
SO_3	0,03	0,02
K_2O	0,02	0,10
CaO	0,78	1,10
TiO_2	0,03	0,11
Cr_2O_3	5,52	0,01
MnO	0,10	32,10
Fe_2O_3	7,79	0,72
NiO	0,49	0,02
ZnO	0,01	0,02
Cl	0,01	0,00
LOI	29,31	34,00
Total	100,00	100,00

The obtained manganese oxide and olivine raw materials were ground separately and then dried. Subsequently, mixtures of manganese oxide and olivine, with manganese oxide content ranging from 0% to 20%, were prepared through wet ball milling for 30 minutes, and the

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resulting slurries were dried at 110 °C. These mixtures underwent calcination at temperatures ranging between 1250 °C and 1300 °C, with a heating rate of 5 °C/min and a dwell time of 1 hour. The calcined pigments were then subjected to cyclic milling for 1 second, followed by filtration and drying at 110 °C in an oven. Prepared pigment mixture compositions and their codes are in Table 2.

Table 2. Prapared pigment mixture compositions and codes.

Mangan oxide additive for pigments	$MgSO_3$ Mineralizator		CaBorat Mineralizator	
	1250°C	1300°C	1250°C	1300°C
0%	M0S3	M0S4	C0S3	C0S4
5%	M1S3	M1S4	C1S3	C1S4
10%	M2S3	M2S4	C2S3	C2S4
15%	M3S3	M3S4	C3S3	C3S4
20%	M4S3	M4S4	C4S3	C4S4

To evaluate the colour improvement, we added 3 wt% pigments to the formulation of the porcelain tile body. These pigments were obtained from a ceramic factory (Kütahya Seramik A.Ş, Turkey).

2.2. Characterization

The analysis of both the raw materials and the produced pigments involved several key assessments. Chemical composition was determined through EDX, in a SEM, Supra 40VP-41-14. Particle size distribution was examined using a Malvern Mastersizer 2000G, while the identification of crystalline phases in the samples was accomplished through X-ray diffraction (XRD) using a RIGAKU Rint 2200-Series instrument.

The L*a*b* color parameters of the samples were measured using a UV-Vis Spectrophotometer. The color coordinates, L*, a* and b*, were determined based on the CIE-L*a*b* trichromatic system recommended by the CIE. In this system, L* represents the degree of lightness and darkness on a scale. The a* axis extends from green (-a*) to red (+a*), and the b* axis extends from blue (-b*) to yellow (+b*). The color difference (ΔE*) was determined using the formula: (ΔE*= [(ΔL*)2+(Δa*)2+((Δb*)2]1/2.

3. Results and Discussion

3.1. Characterization of Raw Materials

Table 1 provides the mean chemical composition of the raw materials. Olivine raw material contained Lizardite, Chromite, Olivine and Clinochlore minerals. Mn_2O_3 contained predominantly Mn_2O_3 phase together with minor amount of Kuvars. Table 3 presents the particle size distribution of raw materials following planetary ball milling. The average particle size measured approximately 20.4 µm, and 90% of the particles are below approximately 116 µm.

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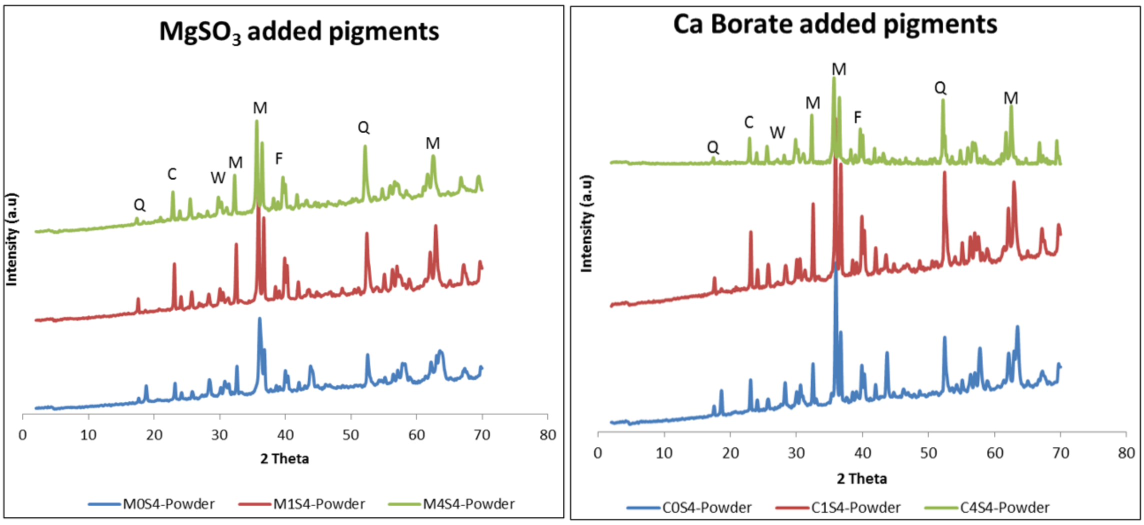
Table 3. Particle size distribution of milled raw materials before mixing.

Raw material	d10 (µm)	d50 (µm)	d90 (µm)
Olivine	2,36	20,4	116
Mangan oxide	2,93	14,4	60,3

3.2. XRD Analysis of Pigments

The XRD patterns of pigments produced from olivine-mangan oxide mixtures containing 0-5-20 wt.% mangan oxide with calcium borate and magnesium sulphate mineralizator calcined at temperatures between 1250°C and 1300°C are given in Figure 1a-1b. In the same figure, the spectrum of raw olivine calcined pigment (M0S4 and C0S4) is also shown for comparison.



a) $MgSO_3$ added pigments for 1300 °C . **b)** CaBorate added pigments for 1300 °.

Figure 1. $MgSO_3$ and Ca Borate added pigments for 1300 °C (Q: Kuvartz, C: Cristobalite, W: Wollastonite, M: Maghemite, F: Clinoferrosilite).

The pigment powders XRD results showed that samples calcined at 1300 °C contained ($FeSiO_3$) solid solution phase (denoted as F) together with maghemite, minor kuvarts.

Figure 2 showcases the XRD patterns of olivine-manganese oxide mixtures, incorporating 0-20 wt.% manganese oxide, along with pigments that include magnesium sulfate and calcium borate mineralizer. These pigments were calcined within the temperature range of 1250°C to 1300°C and combined with glazes.

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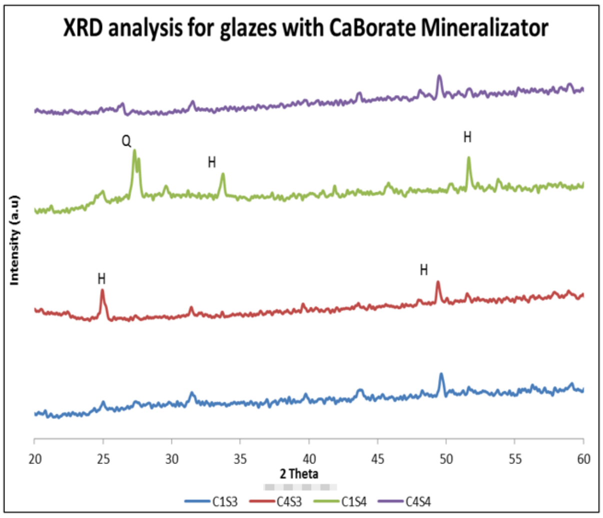
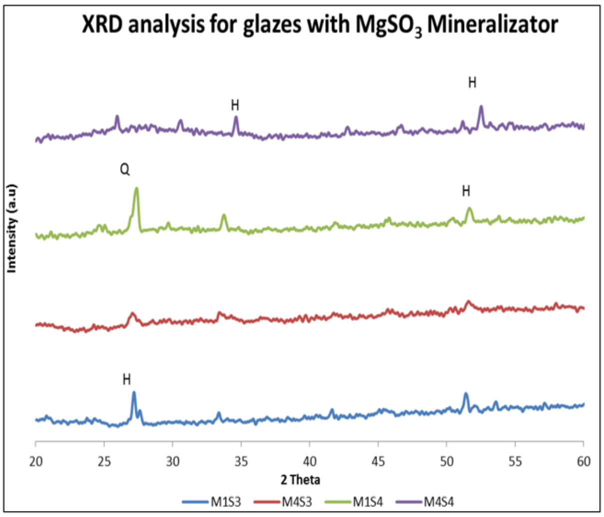


a) Glaze with Caborate-pigments.



b) Glaze with $MgSO_3$ pigments.

Figure 2. The XRD analysis of glazes with $MgSO_3$ pigments and Caborate pigments.

3.3. Colour Properties of Pigments

Change of L*a*b* values with composition is given in Figure 3 and Table 4. Pigment prepared with impure Mn_2O_3 with olivine gives the pink-brown colour. With increasing Mn_2O_3 percentage in olivine-manganoxide mixtures, L*a*b* values were all decreased for rising manganoxide recipes and rising sintering temperatures.

Table 4. CIE Lab colour coordinates (L*,a*,b*) for pigments in coloured wall tile samples.

$MgSO_3$ Mineralizator adding pigment powder						
Sample	L*		a*		b*	
	1250°C	**1300°C**	**1250°C**	**1300°C**	**1250°C**	**1300°C**
M0	50,97	52,42	9,43	9,16	15,35	14,81
M5	75,71	74,91	3,44	5,29	10,01	9,57
M10	78,63	74,42	2,13	4,53	9,23	9,16
M15	73,99	72,26	3,08	4,64	9,24	8,92
M20	71,38	69,69	4,22	5,64	9,00	8,74

CaBorat Mineralizator adding pigment powder						
Sample	L*		a*		b*	
	1250°C	**1300°C**	**1250°C**	**1300°C**	**1250°C**	**1300°C**
Ca0	50,44	51,21	8,72	9,09	10,25	11,45
Ca5	75,07	75,47	2,96	3,77	10,47	10,77
Ca10	73,64	73,43	3,57	4,23	9,72	9,31
Ca15	73,80	71,73	3,40	4,09	10,00	8,32
Ca20	72,22	69,45	3,58	4,61	9,52	8,02

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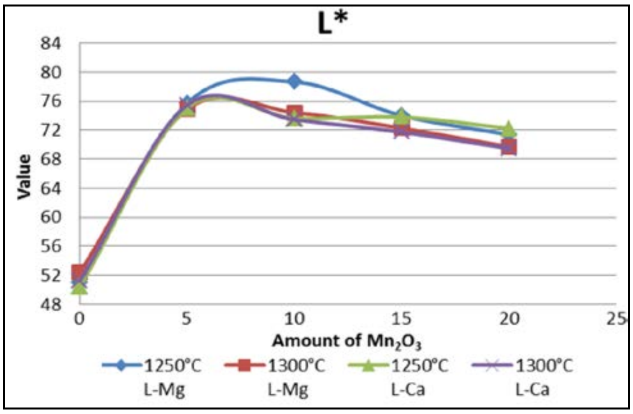
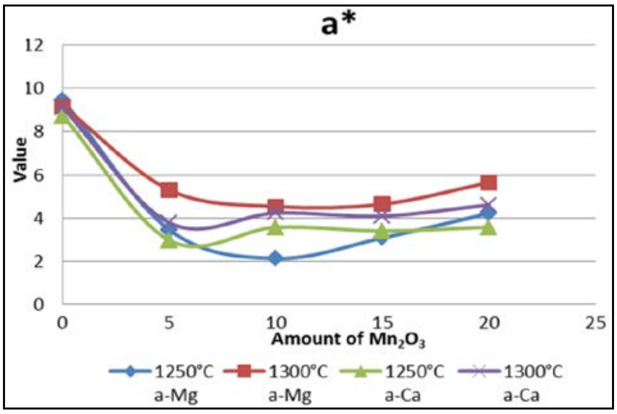
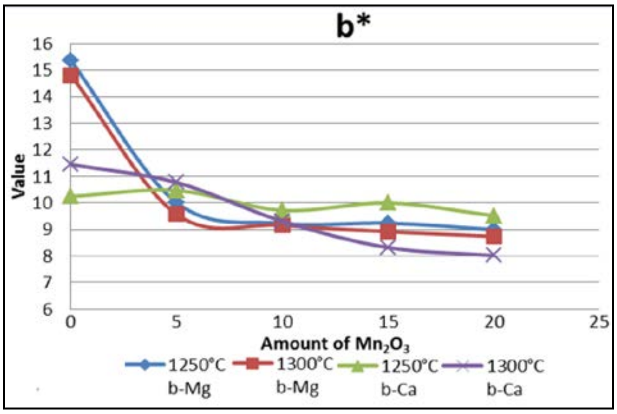


a) The L* values of 1250 °C and 1300 °C.



b) The a* values of 1250 °C and 1300 °C.



c) The b* values of 1250 °C and 1300 °C.

Figure 3. The L*a*b* values of coloured wall tile glazes samples containing 3 wt.% pigment prepared with mixture of olivine-manganoxide.

Figure 3 shows changes of color parameters versus Mn substituded content. Increase in Mn_2O_3 content up to 5%wt decreased L* and b* (M0 to M10 and Ca5 to Ca10). However, more addition of Mn_2O_3 showed no significant effect on these color parameters.

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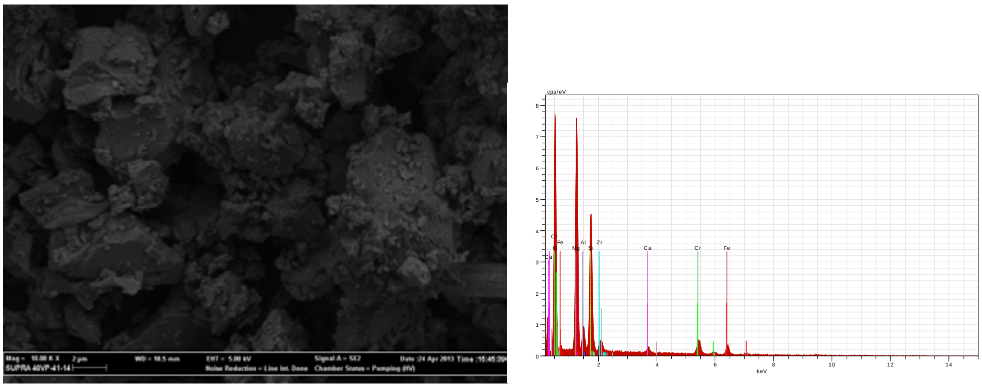
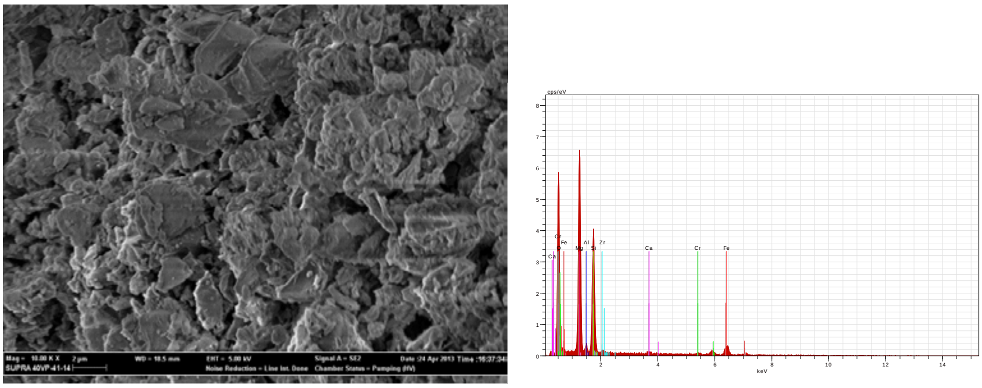
It is obvious that a small addition of Mn_2O_3 decreases a*, therefore, the red hue dereases. M20 and Ca20 have the highest a* among the obtained pigments. Color parameters of colored glazes including 20 wt% of the obtained pigments are presented in Table 4 and Figure 3. These results show the same trend as seen for the powder pigments, indicating thermal and chemical stability of pigments in the glaze.

3.4. SEM Analysis of Pigments

In Figure 4, secondary electron SEM images and EDX analysis of inhomogeneous pigment powder obtained from pink-brown glazes layer are shown for M0S4, M1S4, M4S4 and C0S4, C1S4, C4S4 powders. EDX analyses of the glazed surfaces were conducted to explain the tendency of crystal phase occurrences. White inhomogeneous areas are seen in pigment agglomerate in detail with higher magnification. In back scattered SEM images, brighter appearance shows the elements relative to other with higher atomic number. The white areas were identifed as hematite with EDX and also confirmed with XRD analysis. EDX analysis for these pigment powders as a general view.



a) C0S4 Powders



b) C1S4 Powders

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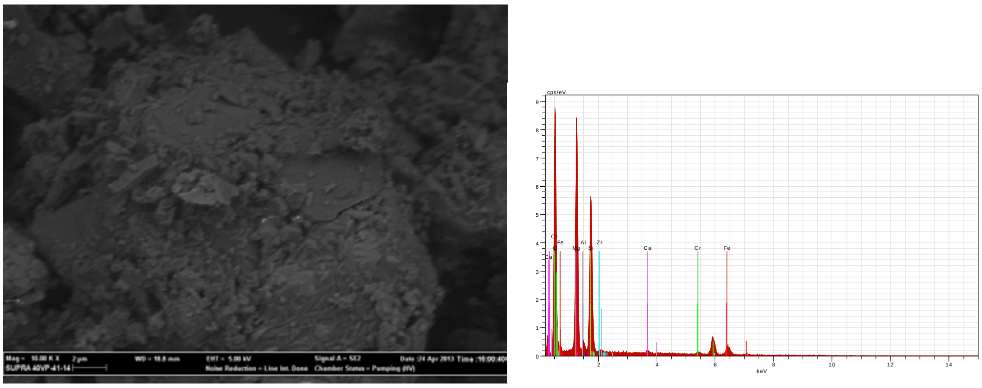
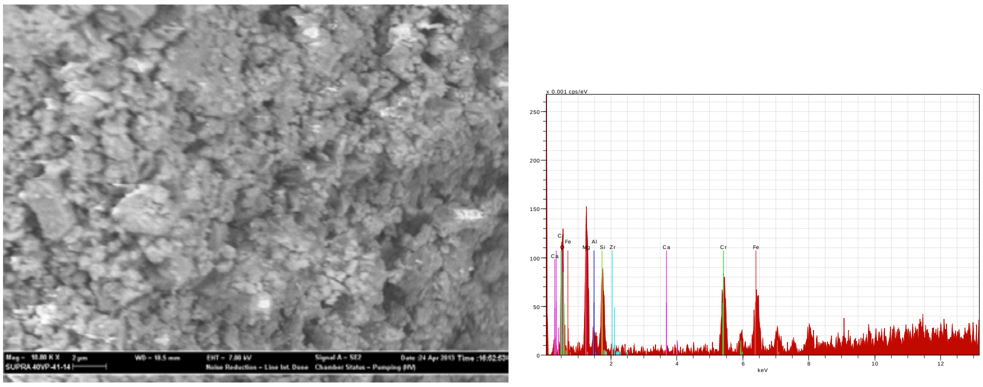
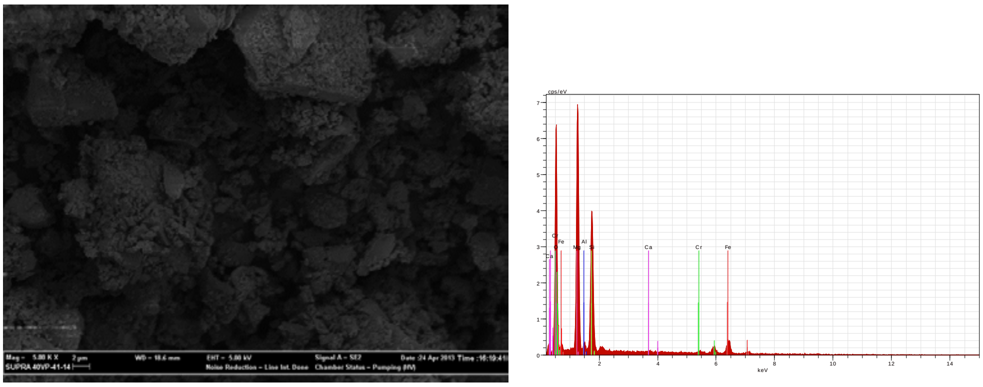


c) C4S4 Powders



d) M0S4 Powders



e) M1S4 Powders

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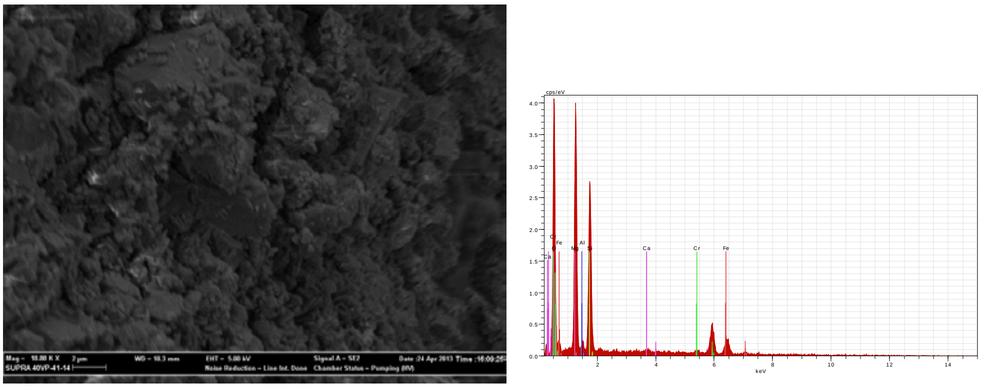
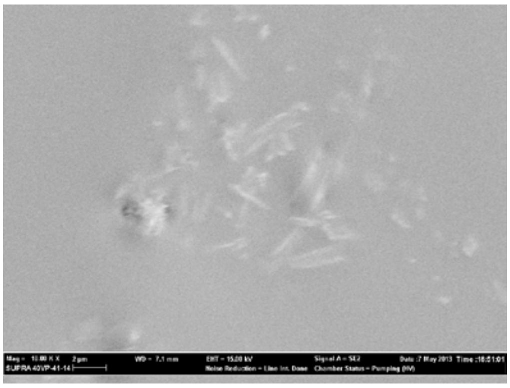


f) M4S4 Powders

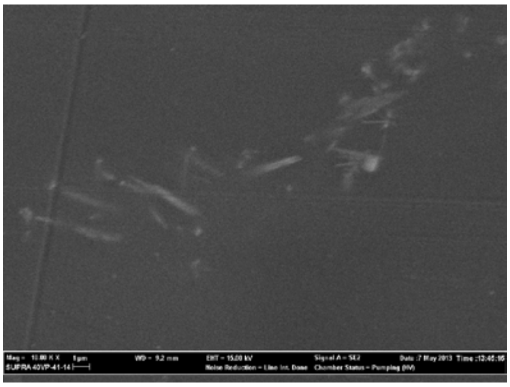
Figure 4. The SEM photos of different Mn_2O_3 and minerlizator adding pigment powders.

In Figure 5, secondary electron SEM images were obtained from the glazed wall tile surface containing 3% wt different olivine pigment. (M1S4, M4S4, M1S3, M4S3and C1S4, C4S4, C1S3,C4S3).

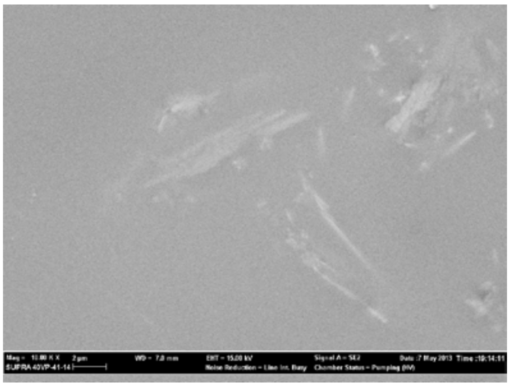


a) M1S3

b) M4S3



c) M1S4



d) M4S4

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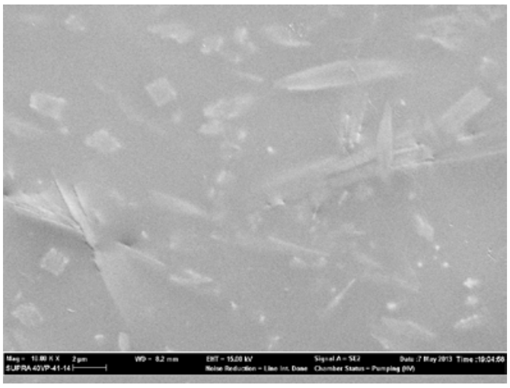
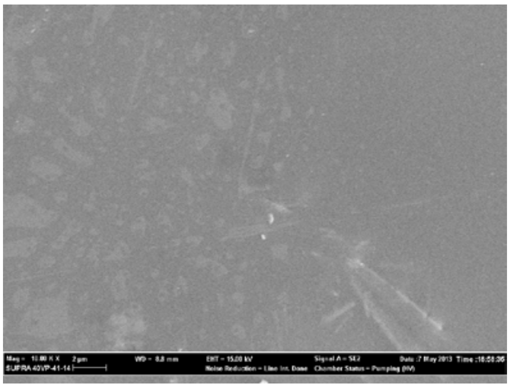
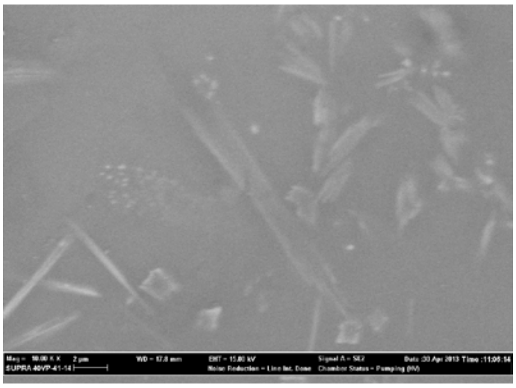
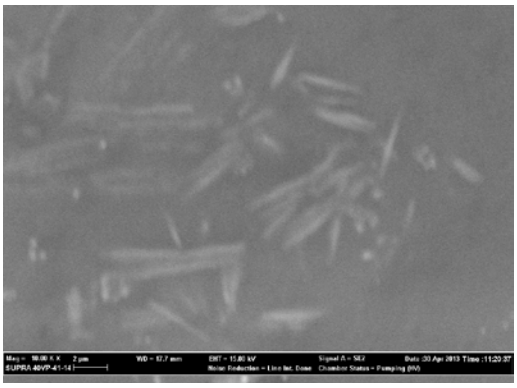




e) C1S3 f) C4S3





g) C1S4 h) C4S4

Figure 5. Secondary electron figures of glazes prepared with different pigments.

CONCLUSION

Olivine and manganoxide mixtures are calcined to produce pink-brown pigments from natural raw materials. The optimum composition was 15 wt.% manganoxide-85 wt. % olivine and 1 wt.% magnesium sulphate and calcium borate as mineralizator. The best calsination temperature was found to be 1250 °C. However, the intensity of the pink-brown was not as good as commercial pink-brown pigments due to the impurities in olivine.

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