

Black ceramic pigments for porcelain tile bodies produced with chromite ores and iron oxide waste

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In this study, two different natural chromite ores and iron oxide waste from the steel rolling industry were used as less expensive alternative raw materials for the synthesis of black ceramic pigments to be used in porcelain tile bodies. The effects of chromite ore-iron oxide waste ratios and calcination temperature on the pigment properties were investigated. It was found that chromite ore with a higher $\text{Cr}_2\text{O}_3/\text{FeO}$ ratio can be used to synthesise black ceramic pigments when combined with the iron oxide waste. However, their color intensity was not as strong as commercial black pigments due to the presence of other phases and impurities coming from the chromite ores. When these pigments were used in combination with commercial black pigments, the consumption of the commercial pigments can be reduced, providing cost savings for coloration of porcelain tile bodies.

Key words: Black ceramic pigment, Chromite, Iron oxide waste, Spinel, Color.

Introduction

Inorganic natural and synthetic pigments find applications as coloring agents in glazes, ceramic bodies and porcelain enamels [1]. Most of the synthetic pigments are prepared with metallic oxides or salts of the desired metals and they must be of industrial chemical purity. However, this makes them rather expensive. Therefore, current trends are towards the use of less expensive natural raw materials [2-5] and/or industrial wastes [6-9].

Chromium containing structures have been widely studied as ceramic pigments [10, 11] for coloring glazes and ceramic bodies due to their interesting properties including high temperature resistance and chemical stability combined with suitable optical properties. Chromium-containing black ceramic pigments are either in the spinel or hematite structures. Black pigments based on the spinel system are widely used to decorate glazed wall and floor tiles, since they remain stable when mixed with glazes during high temperature firing. Spinel-based black pigments are based on cobalt ferrochromite, $(\text{Fe},\text{Co})(\text{Fe},\text{Cr})_2\text{O}_4$ or nickel ferrochromite, $(\text{Ni},\text{Fe})(\text{Fe},\text{Cr})_2\text{O}_4$ compounds. Black pigments based on the hematite system are synthesised by a traditional solid state reaction method to obtain a $(\text{Fe},\text{Cr})_2\text{O}_3$ solid solution and are mainly used in coloring porcelain-stoneware tile bodies. They are not suitable for glazes due to their instability [12-14].

Although many minerals contain chromium, chromite is the only commercial ore mineral of chromium. Pure chromite

ore has a spinel crystalline structure and the theoretical chemical composition is FeCr_2O_4 (or $\text{FeO}\cdot\text{Cr}_2\text{O}_3$ as oxides). However, the chemical composition of chromite ores could also be more generally written as $(\text{Mg},\text{Fe}^{2+})\text{O}\cdot(\text{Cr},\text{Al},\text{Fe}^{3+})_2\text{O}_3$, owing to the partial natural substitution of Fe^{2+} by Mg^{2+} , and Cr^{3+} by Fe^{3+} and Al^{3+} in a lower proportion [15, 16].

As far as ceramic pigments are concerned, chromite is a potential inexpensive natural pigment or a raw material because of its high thermal and chemical stability among natural oxides and is available on the market in a large amount [2]. Natural chromite has been used as a pigment for coloring porcelain tiles, producing dark gray shades on the fired tile. A mixture of 95 wt.% chromite and 5 wt.% CoO additions to a body at a certain amount was used to get black shades on the fired tile [17]. It is also reported that natural chromite combined with commercial black pigment reduced the cost of black coloring porcelain-stoneware tiles [4]. However, chromite used in these studies was neither calcined nor combined with hematite. Recent investigations on producing less expensive Fe-Cr pigments with natural raw materials have shown that limonite and chromite ores could be used to obtain brown pigments for transparent and opaque glazes for wall tiles [2, 14]. Colors from dark brown to light brown, depending on the calcination temperature and chromite-limonite content, were obtained and present a good alternative to commercial pigments produced from pure oxides.

Iron oxides are the most widely used raw materials for pigment production. The continually increasing importance of iron oxide-based pigments is due to their non-toxicity, chemical stability, wide variety of colors ranging from yellow, orange, red, brown to black and low price [18]. It is reported that hundreds and thousands of tons of

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practically unusable solid waste containing from less than 15 to more than 90% iron are formed annually by metallurgical, chemical, mechanical engineering and other industrial plants [19]. There are several studies on the synthesis of iron-chromium brown and/or black ceramic pigments for glazes and porcelain tile bodies from Fe-rich industrial wastes. For example, cast iron foundry grinding waste together with chromite [20], copper slag flotation waste with chromite, Cr_2O_3 , ZnO and CoO [21], Fe-rich galvanizing sludge generated during steel wire drawing with Cr/Ni-rich sludge [22, 23] generated from Cr/Ni plating have been used.

The aim of this study is to produce $(\text{Fe,Cr})_2\text{O}_3$ black ceramic pigments by using natural chromite ores and iron oxide waste from the steel rolling industry and to investigate their suitability for coloring porcelain tile bodies as a way to reduce their coloring cost. It is to be noted that $(\text{Fe,Cr})_2\text{O}_3$ black ceramic pigment is the most extensively used pigment in porcelain tile production.

Experimental

Raw materials

Chromite ores with different chemical compositions; namely chromite I (Kumas A.S., Turkey) and chromite II (Laviosa Chimica Mineraria S.P.A, Italy) and iron oxide waste from the steel rolling industry (Eregli Demir-Celik Fabrikaları T.A.S., Turkey) were used as raw materials.

Preparation and characterisation of pigments

As-received chromite ores and iron oxide waste was ground separately to the required particle-size by planetary wet ball-milling using distilled water and dried. Then, chromite ores and iron oxide waste containing 30-100 wt.% chromite I ore and chromite II ore were mixed by wet ball-milling for 20 minutes and the slurries were dried at 110 °C. This was followed by calcination firstly at 1200 °C for 5 hours dwell time. This temperature was selected from the previous studies on a similar system [24]. In order to see the effect of the calcination temperature on reaction products, a selected composition was also calcined at 1100 °C and 1300 °C using the same dwell time. The calcined pigments were ground by planetary wet ball-milling for 2 hours, filtered and dried at 110 °C in an oven. In order to evaluate the color development, 3 wt.% ground pigment was added to a porcelain tile body composition, supplied from a ceramic factory (Toprak A.S, Eskisehir, Turkey) by wet ball-milling. The dried porcelain powder

mix was pressed into 4 cm diameter pellets at 40 MPa and fired in an electric furnace at 1190 °C in 45 minutes from cold to cold.

The compositions of the raw materials were determined using an X-ray fluorescence spectrometer (XRF, RIGAKU ZSX Primus). A laser diffraction particle size analyser (MALVERN MASTERSIZER 2000G) was used to find out the particle size distribution of the raw materials and pigments. The crystalline phases in the samples were identified using an X-ray diffractometer (XRD, RIGAKU Rint 2200-Series). In the XRD analysis, metallic silicon (Si) powder was used as a reference to determine the exact d-spacings of the phases present and also to compare their relative amounts.

$L^*a^*b^*$ color parameters of fired porcelain tile samples colored with the pigments produced in this study were measured with an UV-Vis spectrophotometer (MINOLTA 3600 d). Measurements were recorded with a small aperture and a standard D 65 light source. The color coordinates, L^* , a^* and b^* , were measured according to the CIE- $L^*a^*b^*$ trichromatic system recommended by the CIE (Commission Internationale de l'Eclairage) [25]. In this system, L^* is the degree of lightness and darkness of the color in relation to the scale extending from white ($L^* = 100$) to black ($L^* = 0$). a^* is the scale extending from green ($-a^*$) to red ($+a^*$) axis and b^* is the scale extending from blue ($-b^*$) to yellow ($+b^*$) axis. The color difference (ΔE^*) was calculated according to $\Delta E^* = [(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2]^{1/2}$. The values ΔL^* , Δa^* and Δb^* correspond to the difference of each parameter recorded for the two samples that are being compared.

Results and Discussion

Characterisation of raw materials

Chemical compositions of the raw materials determined using the XRF technique are given in Table 1. When chromite I and chromite II ores were compared, they both contained similar amounts of Cr_2O_3 , chromite I was found to contain less FeO and consequently the $\text{Cr}_2\text{O}_3/\text{FeO}$ ratio was higher for chromite I. There were also differences in MgO, Al_2O_3 and SiO_2 contents in that chromite I was rich in MgO and SiO_2 whereas chromite II was rich in Al_2O_3 . The iron oxide waste was determined to contain over 97 wt.% Fe_2O_3 (Table 1). XRD analysis showed that the iron oxide waste contained only the hematite phase (Fig. 1(a)) and thus the iron oxide waste will be named as the "hematite waste" hereafter. XRD analysis also showed

Table 1. Chemical composition of raw materials obtained by using XRF analysis (wt.%)

Raw materials	Fe_2O_3	Cr_2O_3	Al_2O_3	SiO_2	FeO	MgO	CaO	Others	LOI
Iron oxide waste	97.5		0.8	0.9				0.4	0.5
Chromite I ore		42.5	8.4	7.4	17.7	17.8	1.8	1.0	3.4
Chromite II ore		40.9	13.4	3.4	31.1	8.9	1.3	0.9	

(LOI is loss of ignition at 1000 °C)

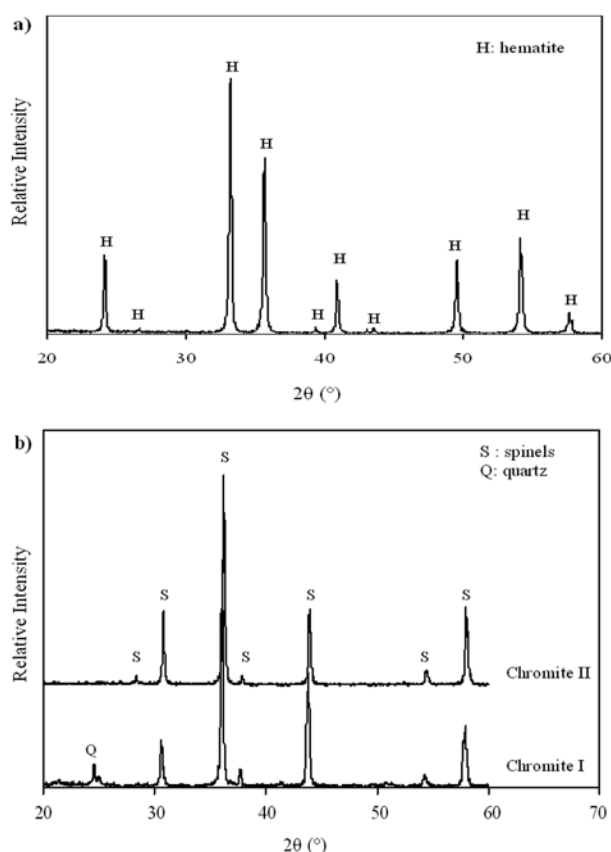


Fig. 1. XRD patterns of iron oxide waste (a) and chromite ores (b).

that both chromites contained only spinel type phases except that chromite I also contained a minor amount of quartz (Fig. 1(b)). It is rather difficult to differentiate different composition spinel phases in chromites. However, Sanchez-Ramos *et al.* [26] demonstrated that the iron present in the spinel phase of chromite had a +2 valency and thus identified the spinel phase as the generic magnesiochromite ferroan $[(\text{Mg}, \text{Fe}^{2+})(\text{Cr}, \text{Al})_2\text{O}_4]$. For this reason, the content of iron oxide is given as FeO in Table 1.

Table 2 gives the particle-size distribution of each raw material after planetary ball milling. The average particle-size was around 7 μm and 90% of the particles are below about 25 μm . It is known that solid state reactions between two components primarily depend on the particle size: the finer the particle size, the easier is the reaction between the components. However, milling into lower particle sizes by ball milling requires prolonged milling time that increases the cost of processing.

Characterisation of pigments

The XRD patterns of pigments produced with the use of different amounts of chromite I and hematite waste mixtures calcined at 1200 °C are shown in Fig. 2. When chromite I was calcined alone, the occurrence of a free Cr_2O_3 phase was evident together with predominant spinel phases. The free Cr_2O_3 phase was not seen in the XRD pattern of the as-received raw material (Fig. 1(b)). This

Table 2. Particle size distribution of ball milled raw materials (μm)

Raw materials	d_{10}	d_{50}	d_{90}
Iron oxide waste	1.1	7.8	24.9
Chromite I ore	0.9	7.1	23.0
Chromite II ore	1.0	6.7	20.2

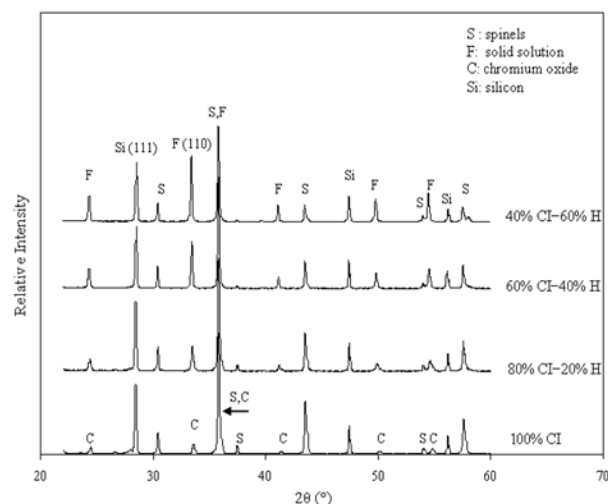


Fig. 2. XRD patterns of pigments produced by calcining different amounts of chromite I-hematite waste mixtures at a constant temperature of 1200 °C (CI : chromite I, H : hematite waste).

reveals that the chromium-containing spinel $[(\text{Mg}, \text{Fe}^{2+})(\text{Cr}, \text{Al})_2\text{O}_4]$ was separating to Cr_2O_3 and another type of spinel at high temperatures. This phenomenon was also observed by Sanchez-Ramos *et al.* [26] who demonstrated that the Cr_2O_3 segregates as a differentiable compound, being removed from the chromite spinel and remaining only in spinels as magnesium, aluminium and iron oxides above 800 °C. In the compositions containing hematite waste, in addition to the presence of the spinel phases, the generated free Cr_2O_3 reacts with the hematite (Fe_2O_3) to produce a solid solution phase $(\text{Fe}_{1-x}\text{Cr}_x)_2\text{O}_3$ (Fig. 2). In the phase diagram of Fe_2O_3 and Cr_2O_3 , these oxides can be observed to generate a complete $(\text{Fe}, \text{Cr})_2\text{O}_3$ solid solution for all the range of compositions up to 1400 °C [27]. As the same amount of silicon (Si) was used in the samples as an internal standard, the intensity ratio of the solid solution phase $(\text{Fe}_{1-x}\text{Cr}_x)_2\text{O}_3$ (F) and Si (F/Si) can be used to follow the development of the solid solution phase. In Fig. 2, F_{110}/Si_{111} ratio is 0.0, 0.48, 0.75 and 1.16 for the mixtures of 100% chromite I, 80% chromite I-20% hematite waste, 60% chromite I-40% hematite waste and 40% chromite I-60% hematite waste, respectively. The highest ratio is observed in the 40% chromite I-60% hematite waste sample, indicating that this sample contains the largest amount of the solid solution phase.

The XRD patterns of pigments produced with the use of different amounts of chromite II and hematite waste mixtures calcined at 1200 °C are presented in Fig. 3. The main phases were spinels and the solid solution phase $(\text{Fe}_{1-x}\text{Cr}_x)_2\text{O}_3$ in all compositions. No free Cr_2O_3 phase

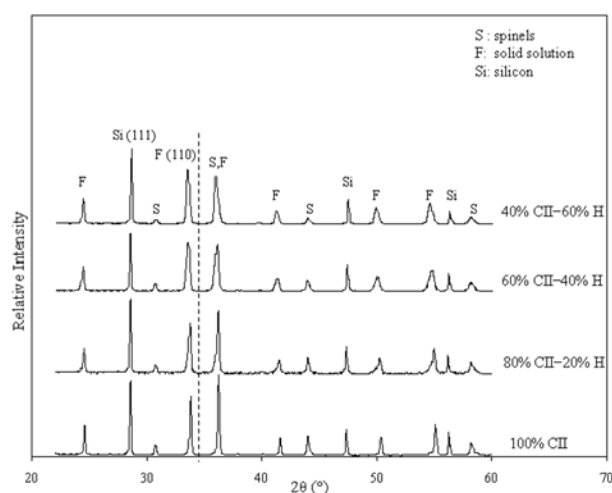


Fig. 3. XRD patterns of pigments produced by calcining different amounts of chromite II-hematite waste mixtures at a constant temperature of 1200 °C (CII : chromite II, H : hematite waste).

formation was observed in the pure chromite II after calcination in contrast to pure chromite I. This may be due to the higher amount of FeO content of chromite II which forms the solid solution phase directly upon calcination. Although the F_{110}/Si_{111} ratio (~ 0.8) was not changed substantially with the addition of hematite waste, the solid solution phase became rich in iron (see the shift of the solid solution peaks to lower 2θ values, indicated by a dotted line in Fig. 3). Similar shift of 2θ values of the solid solution phase with Fe_2O_3 was also observed by Munoz *et al.* [24].

In both chromite I and chromite II containing compositions, the highest amount of solid solution phase was obtained when 40% chromite I and 60% hematite waste were used. Therefore, to see the effect of temperature on the solid solution phase formation, this composition was kept constant and also calcined at 1100 °C and 1300 °C. The XRD patterns of pigments produced from 40% chromite I and 60% hematite waste mixtures calcined at between 1100 °C and 1300 °C are compared in Fig. 4. In the same figure, a diffraction pattern of the commercial black pigment (Coded as CP-2) is also shown for comparison. The XRD results showed that the samples calcined at all temperatures contained $(Fe_{1-x}Cr_x)_2O_3$ solid solution and spinel phases. The F_{110}/Si_{111} intensity ratios in Fig. 4 is 0.58, 1.16 and 0.86 at 1100 °C, 1200 °C and 1300 °C, respectively. This indicates that the highest amount of the solid solution phase was obtained at 1200 °C which was selected at the beginning of the study to find out the optimum composition for the formation of the highest amount of the solid solution phase. While the lower amount of the solid solution phase at 1100 °C may be due to incomplete reactions, its decreased amount at 1300 °C may be due to the decomposition of the solid solution phase possibly by an increased vapour pressure of Cr_2O_3 .

Color measurement

The measured $L^*a^*b^*$ values of colored porcelain tiles

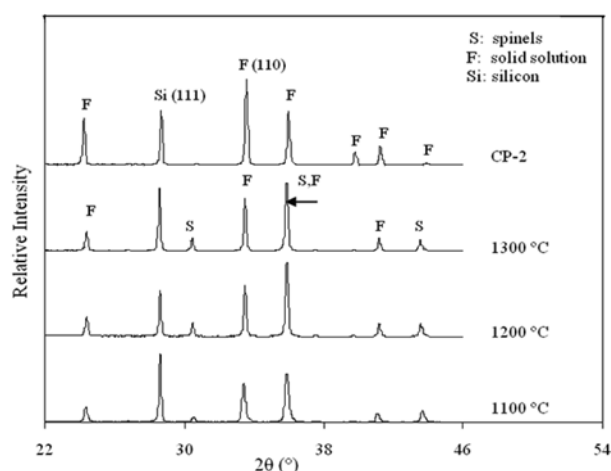


Fig. 4. XRD patterns of pigments containing 40% chromite I-60% hematite waste mixture calcined at different temperatures between 1100 °C and 1300 °C. An XRD pattern of black commercial pigment (CP-2) is also included for comparison purposes.

containing 3 wt.% pigments (produced at 1200 °C according to the procedure given above) are shown in Fig. 5. The pigment prepared with pure chromite I gives a yellow-brown color which has $L^*a^*b^*$ values of 41.6, 3.0 and 5.2. With an increasing hematite waste percentage in chromite I-hematite waste mixtures, $L^*a^*b^*$ values were all decreased and the lowest $L^*a^*b^*$ values of 35.9, 1.4 and 1.1, which indicate better black coloring, were obtained with the use of the 40% chromite I and 60% hematite waste composition. These results are in line with the XRD spectra that the use of 40% chromite I and 60% hematite waste gave the largest amount of the $(Fe_{1-x}Cr_x)_2O_3$ solid solution phase with a concurrent decrease of the spinel phase intensity. However, commercial black pigments, coded as CP-1 and CP-2 (Itaca, Spain) both gave L^* , a^* and b^* values of < 33 , < 1 and < 0.5 , respectively (Table 3). This indicates that even the lowest $L^*a^*b^*$ giving composition (40% chromite I-60% hematite waste) is not good enough to be used as a replacement for a commercial black pigment. This may be attributed to the dilution effect of impurity oxides. The other reason might be the difference in the particle size distribution of the pigment. However, please also note that the particle size distribution of the synthesised pigment used in this study was very similar to the commercial black pigments (Table 4). In order to increase the black coloring, that is, to decrease $L^*a^*b^*$ values, 0.5 and 1 wt.% of a commercial black pigment (CP-2) was used together with 3 wt.% the pigment (40% chromite I-60% hematite waste composition) in a porcelain tile body. CP-2 was selected as the commercial black pigment to be used together with the synthesised pigment in this study due to its better $L^*a^*b^*$ values (Table 3). The addition of the commercial pigment reduced the $L^*a^*b^*$ values as given in Table 3, approaching those of the pure commercial pigment. This indicates that chromite I and hematite waste mixtures can be a cost-effective complementary to the commercial black pigments and help to reduce their usage.

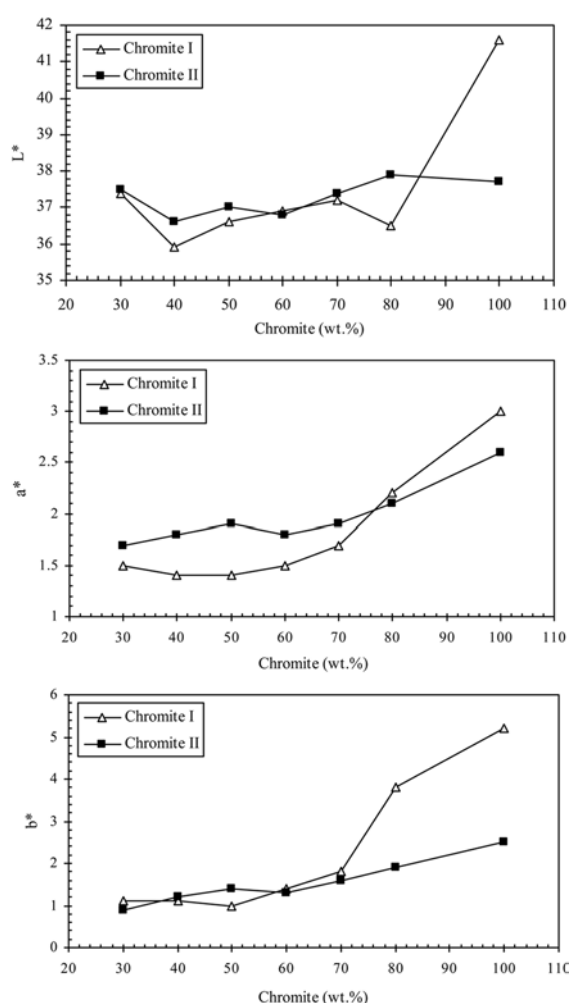


Fig. 5. The $L^*a^*b^*$ values of colored and fired porcelain tile samples containing 3 wt.% pigment, prepared by calcining different amounts of chromite I-hematite waste and chromite II-hematite waste mixtures at a constant temperature of 1200 °C.

Table 3. $CIE-L^*a^*b^*$ and calculated DE^* values of colored porcelain tile samples

Reference pigment	Pigment (wt.%)	CP-2 (wt.%)	L^*	a^*	b^*	$DE^*(1)$	$DE^*(2)$
CP-1	3	-	33.0	1.0	0.4	-	1.9
CP-2	3	-	31.4	0.3	-0.3	1.9	-
40CI-60H	3	-	35.9	1.4	1.1	3.0	4.8
40CI-60H	3	0.5	34.5	1.4	0.9	1.6	3.5
40CI-60H	3	1.0	33.8	1.0	0.2	0.8	2.5

(CP-1 and CP-2 : commercial black pigments, 40CI-60H designates 40% chromite I and 60% of hematite waste derived pigment)

Table 4. Particle size distribution of pigments (μm)

Pigment	d_{10}	d_{50}	d_{90}
CP-1	2.4	6.0	14.6
CP-2	1.5	4.7	10.4
40CI-60H	1.9	5.6	12.8

(CP-1 and CP-2 : commercial black pigments, 40CI-60H designates 40% chromite I and 60% of hematite waste derived pigment)

The measured $L^*a^*b^*$ values of pigments containing 40% chromite I and 60% hematite waste calcined at temperatures between 1100 °C and 1300 °C are given in Fig. 6. The $L^*a^*b^*$ values of pigments were influenced by the calcination temperature. L^* values decrease with a decreasing calcination temperature, whereas the values of a^* and b^* were considerably lower at a calcination temperature of 1200 °C in comparison to 1100 °C and 1300 °C. These coloring observations are in line with XRD data given in Fig. 4.

Pigments prepared with chromite II resulted in darker colors than those with chromite I where the chromite content was higher (> 80%) (Fig. 5). This is due to the formation of the solid solution phase even in the pure chromite II containing sample. However, at lower chromite contents, $L^*a^*b^*$ values of chromite II derived pigments were not as low as chromite I derived pigments. The better black coloring of chromite I and hematite waste

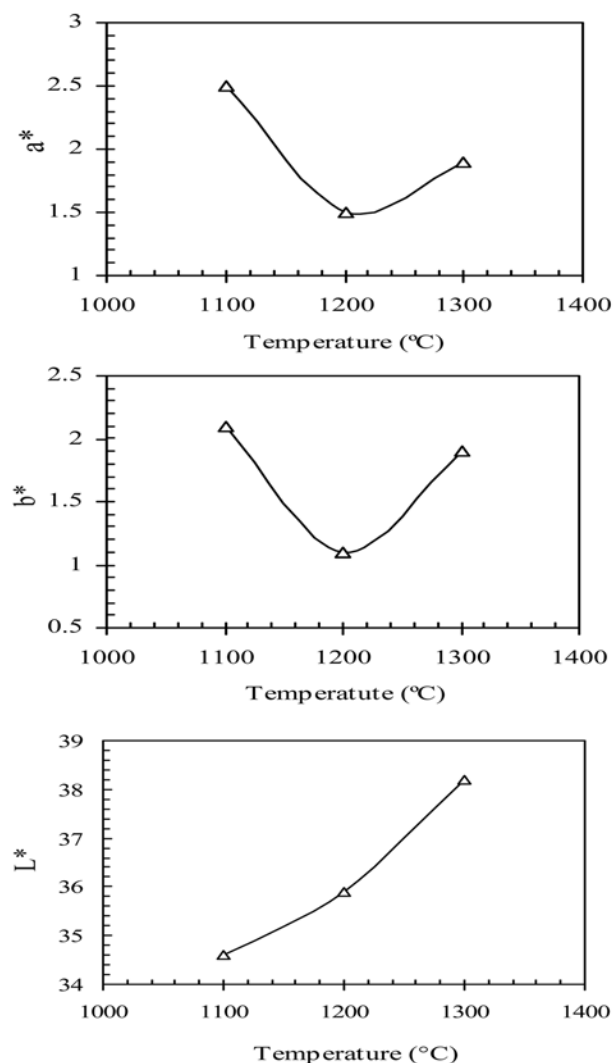


Fig. 6. The $L^*a^*b^*$ values of colored porcelain tile samples containing 3 wt.% pigment, synthesised by calcining a 40% chromite I-60% hematite waste mixture at temperatures between 1100 °C and 1300 °C.

mixtures, evidenced by lower L^* and a^* values, may be due to somewhat higher solid solution phase formation in chromite I and hematite waste mixtures. This may be due to the exsolution of Cr_2O_3 from chromite I, readily reacting with the hematite waste to form the solid solution phase.

Conclusions

By using less expensive chromite ores and hematite waste, black ceramic pigments suitable for porcelain tile body coloring can be produced. A black color close to commercial black pigments was obtained after calcination of 40% chromite I and 60% hematite waste mixture at 1200 °C. The black coloring phase is the $(\text{Fe}_{1-x}\text{Cr}_x)_2\text{O}_3$ solid solution phase. However, due to the presence of impurity oxides of Al_2O_3 , SiO_2 and MgO the color intensity is not as strong as commercial black pigments which are generally prepared with higher purity oxides. These pigments, when combined with a small amount of commercial black pigments, can reduce the consumption of the more expensive commercial pigments, providing cost savings for black coloration of porcelain tile bodies.

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