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Production and characterisation of iron-chromium pigments and their interactions with transparent glazes

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Abstract

In this study, production and characterisation of pigments by using less expensive raw materials such as limonite and chromite was undertaken. The resulting pigments were characterised by using X-ray diffraction (XRD) and UV-Vis spectrophotometer. The colour of glazed tiles containing 3 wt.% pigment change from dark brown to light brown depending on the calcination temperature and limonite content. With pigments prepared with 50% limonite content calcined at 1250 °C, the chocolate brown colour was obtained corresponding to the commercial brown pigments. An iron-chromium black pigment was synthesised from a mixture of pure chromium (III) oxide (Cr_2O_3) and iron (III) oxide (Fe_2O_3) powders and was used to determine possible interactions between a pigment and a transparent glaze. The interactions were studied using a scanning electron microscope (SEM) attached with an energy dispersive X-ray spectrometer (EDX). The results showed that black pigment particles give brown colour to the glaze. EDX analysis on pigment crystals embedded in the glaze clearly showed that Zn and Mg diffused into pigment crystals and caused a change of colour from black to brown.

Keywords: Colour; Microstructure-final; Pigments; Powders-solid state reaction; Spinels

1. Introduction

Ceramic pigments are used in the ceramic industry to colour ceramic glazes. The way to obtain colour in a vitreous matrix is to disperse in the matrix an insoluble crystal or crystals that are coloured and known as pigments. The colour of the crystal is then imparted to the transparent matrix.[1,2]

Most of the crystals used as ceramic pigments are oxides. The reason is the high stability of oxides in molten silicate glasses. Ceramic pigments must have the following properties such as thermal stability, insolubility in the glazes, resistance to attack by chemical agents (acids and basics) and should not produce gases to form faults in the glazes. Most of the oxides contained in such pigments are crystals of mixed oxides, such as silicates, spinels and zircon oxides.[3]

Although there are a number of different pigment systems, most of them are prepared through a similar procedure. The first step in pigment production is the close control over the selection of raw materials, which are mostly metallic oxides, or salts of the desired metals and they must be of industrial chemical purity. On the other hand, often less pure raw materials prove superior for producing a given pigment.[1]

The most important brown and black pigments used in ceramic coatings are the iron-chromite spinels and synthesised from mixture of iron oxide and chromium oxide by calcination above 1000 °C.[4,5] Some of the black pigments contain the oxides of cobalt, manganese, nickel or copper with iron and chromium. The cobalt free iron-chromium pigments have been the focus of renewed interest in recent years because of the increase in the price of cobalt-bearing black pigments and its pollution problems.[6]

Chromium (Cr) is a widely used element in ceramic pigment production, but depending on synthesis conditions, it can be found in different states of oxidation and these generate different properties, stability and colouration. Cr can appear in oxidation states of II to IV. Trivalent Cr is a mineral found in nature and it is not hazardous for living beings.[7]

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Chromite ($FeO.Cr_2O_3$) is an important mineral used in refractories and as a colouring agent in glass and enamels.[8,9] Because of its high thermal and chemical stability among natural oxides available on the market in a large amount, chromite is a potential inexpensive natural pigment or a raw material to produce pigments. It is also reported that chromite addition to commercial black pigment reduced the cost of colouring glaze.[9] However, when raw chromite used as a colouring agent in glaze, brown spots may form and the colour change from yellow to brown depending on the glaze composition. Recent investigations on the determination of thermal expansion of chromites and zinc spinels have shown that Cr cations are always in the trivalent state and exclusively located in the octahedral sites in chromite whereas Fe cations can be in divalent and trivalent state and located in both tetrahedral and octahedral sites.[10]

Iron oxide is a widely used natural pigment, but it has been a problem for the ceramic industry because it is the only one considered to give red colour but does not work at temperatures higher than 1100 °C. Hematite is a natural iron ore, with a stable red colour up to 1000 °C. However, the Fe^{+3} ions is very reactive with ceramic glaze compositions, frits and ceramic bodies.[11] Limonite ($2Fe_2O_3.3H_2O$) can widely be found in the Earth cluster and is a mixture of hydrated lepidocrocite, goethite and occasionally hematite.[12] The colour of limonite is in the shades of yellow and brown. Calcined limonite was recently used for colouring wall tile glazes.[13]

The aim of the present work is to synthesis ceramic pigments from relatively less expensive materials at spinel formation temperatures by using a various amount of limonite and chromite mixtures, to determine colour properties of pigments and to find out possible interactions between the pigment and transparent glazes.

2. Experimental procedure

2.1. Pigment preparation

Natural chromite and limonite, mined around Eskisehir in Turkey were used as raw materials. Chromite–limonite mixtures containing 10, 20, 30, 40 and 50 wt.% limonite and 4 wt.% sodium phosphate (Na_3PO_4) added as a mineraliser were prepared. The mixtures were ground in water in a ball mill for three hours to obtain very homogeneous slurries. The slurries were then dried at 100 °C. Calcination were carried out in an electric furnace between 900 and 1250 °C temperature range for three hours by applying a heating rate of 2 °C/min.

The calcined products were ground in water in a ball mill for an hour and washed with water to remove undesirable soluble salts that have negative effects during glazing.

3 wt.% pigments were added to a frited transparent glaze and applied to an engobed single firing ceramic biscuits. Finally, the colour-glazed biscuits were fired at 1125 °C for 45 min.

2.2. Characterisation of pigments and coloured glazes

In order to identify the crystalline phases present in the raw materials and pigments, XRD patterns were obtained using conventional powder diffraction technique in a RIGAKU diffractometer with Ni-filtered, Cu K_α radiation with a goniometer speed of 0.5°/s. In XRD analysis, metallic silicon (Si) powder was used as a reference material to find the exact d-spacing of spinels produced in this study.

The microstructure characterisation and quantitative analysis of raw materials and pigments were carried out by using SEM (CAM SCAN S4) attached with an EDX (LINK ISIS 300).

The thermal analysis of raw materials were determined by using simultaneous differential thermal and thermogravimetric analysis (DTA-TG/Linseis Thermowaage L81) with alumina crucible and a heating rate of 10 °C/min. Powdered alumina was used as the reference substance.

$L^*a^*b^*$ colour parameters and UV-Vis spectral curve of coloured glazes were measured with an UV-Vis spectrophotometer (Minolta 3600 d). These parameters were measured for an illuminant D65, following the CIE-$L^*a^*b^*$ colourimetric method recommended by the CIE (Commission Internationale del'Eclairage). In this system, L^* is the degree of lightness and darkness of the colour 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.

3. Results and discussion

3.1. Characterisation of raw materials

The XRD patterns (not shown here) and chemical analysis by EDX demonstrated that, limonite was rich in Fe_2O_3, quartz, alumina and nickel oxides whereas chromite was in the form of spinel and it also contains free Cr_2O_3. Approximate chemical analysis of natural limonite and chromite determined by EDX is given in Table 1.

The D–TG curve of limonite is shown in Fig. 1. The first peak at 100 °C corresponds to the physical water loss whereas the peak between 250 and 300 °C can be ascribed to the decomposition of limonite (loss of chemical water) to form hematite. The weight loss occurs above 600 °C is due to $MgCO_3$ decomposition to magnesium oxide and carbon dioxide.

Table 1
Composition of raw materials used throughout this study obtained by converting elemental EDX analysis to oxides (wt.%)

Raw materials	Cr_2O_3	Fe_2O_3	Al_2O_3	SiO_2	MgO	NiO
Chromite	61	27	4.0	1.4	6.6	–
Limonite	2	48	9	31	3.5	6.5

3.2. XRD analysis of pigments

The XRD patterns of pigments produced from chromite-limonite mixtures containing 50 wt.% limonite calcined at temperatures between 900 and 1250 °C are shown in Fig. 2. XRD combined with TG analysis showed that, limonite losses its chemical water content at 300 °C and transforms to hematite which is stable

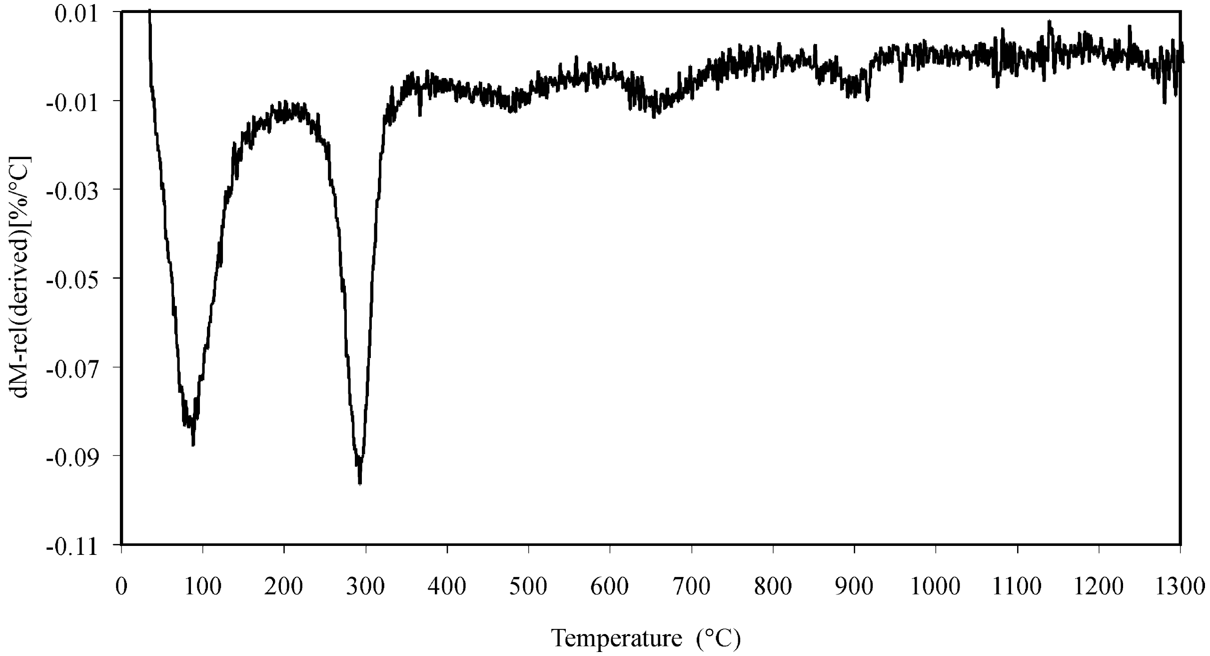

Fig. 1. D–TG curve of limonite.

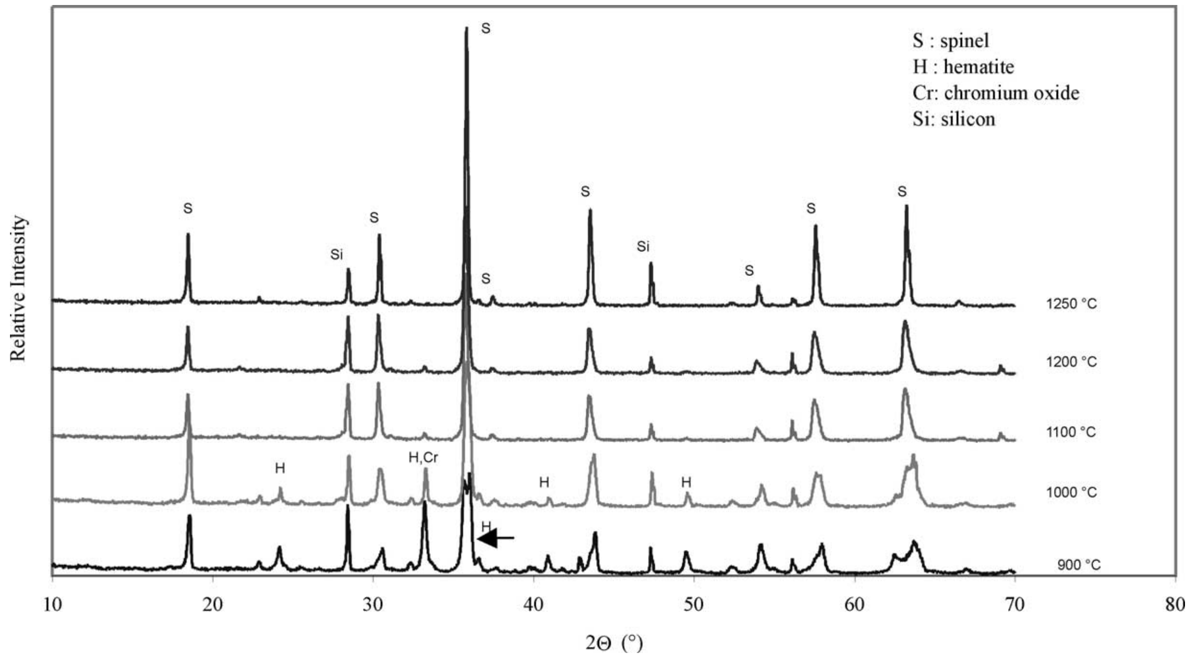

Fig. 2. XRD patterns of pigments synthesised from a chromite–limonite mixture containing 50 wt.% limonite calcined at temperatures between 900 and 1250 °C.

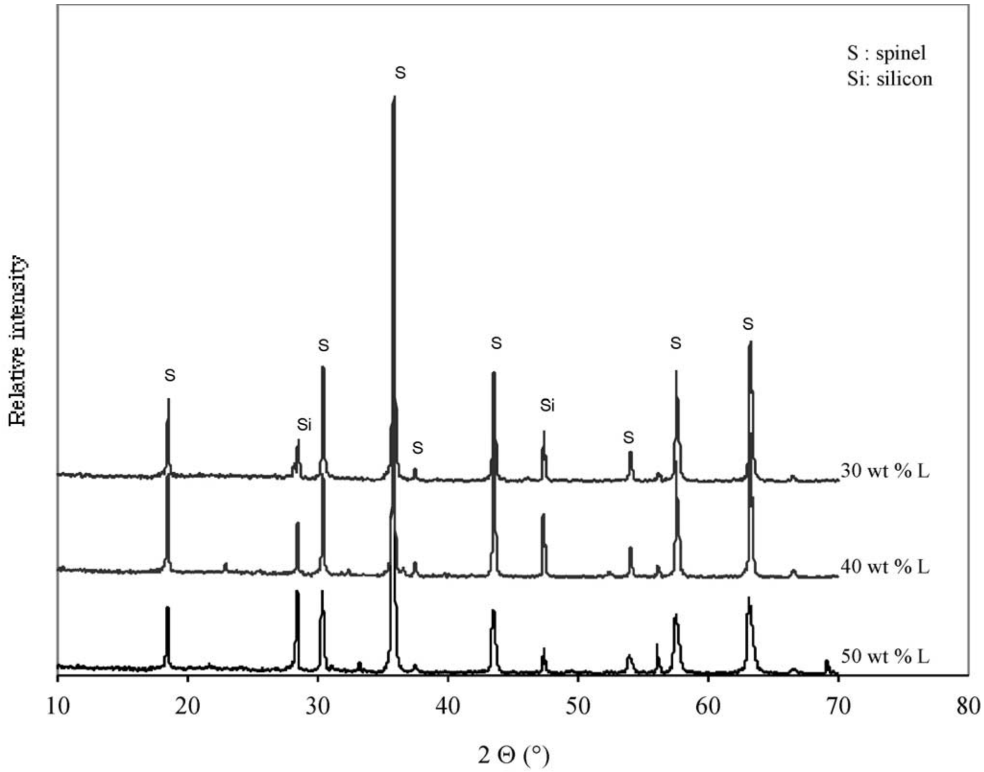

Fig. 3. XRD patterns of pigments produced from chromite–limonite mixtures containing 30, 40 and 50 wt.% limonite calcined at 1250 °C (L: limonite).

until 1200 °C. Above 1200 °C, it forms the spinel structure with free Cr_2O_3 from the chromite. Apart from this peak, all the others identified as spinel peaks. Therefore, all the other compounds (MgO, Al_2O_3, NiO) exist in the raw materials go into the spinel solid solution above the 1200 °C. As is known, the general formula of spinel group is AB_2O_4. The A represents divalent metal ions such as Mg, Fe and Ni. The B represents trivalent metal ions such as Al, Fe and Cr. Solid solutioning is common in this group of minerals and chromite spinels can contain certain percentages of different ions such as Ni-Mg, Al and Fe.[1]

The XRD patterns of pigments produced from chromite–limonite mixtures containing 30, 40 and 50 wt% limonite calcined at 1250 °C is given in Fig. 3. As it is shown in this figure, the XRD patterns of pigments were not change with increasing limonite content.

3.3. Colour measurements

When limonite content or calcination temperature decreases, the colour of glazes visually changes from dark brown to light brown. Pigments prepared with chromite-limonite mixture (especially 40 and 50 wt.% limonite) and calcined at 1250 °C gives the chocolate dark brown colour which has $L^*a^*b^*$ values of 26, 6.3, 6.5.

The measured $L^*a^*b^*$ values of pigments containing different amount of raw materials calcined at different temperatures are given in Fig. 4. $L^*a^*b^*$ values of commercial Fe–Cr brown pigments (CP) and Fe–Cr pigments prepared with pure Cr_2O_3 and Fe_2O_3 powders (PO) are also given in Fig. 4.

The $L^*a^*b^*$ values are influenced by the amount of limonite or chromite and the calcination temperature. a^* values slightly decrease with increasing calcination temperature and chromite concentration. The b^* values decrease with the increasing calcination temperature whereas slightly decrease with increasing ratio of chromite in the mixture. L^* values is less influenced by the increasing of chromite content in the mixture as long as the chromite concentration is above 50 wt.%, but the values of lightness decreased considerably with calcination temperature until around 1200 °C for the same composition. Above 1200 °C, the L^* parameter reaches values of about 25–28 which is lower than commercial pigment and corresponds to a very intense degree of darkness.

Spectral reflectance curves of glazed tiles with pigments containing different amount of limonite in the mixture calcined at different temperatures are given in Fig. 5. Here, the absorption is extended almost to 550 nm and the wavelength of absorption is centred in the blue-green.

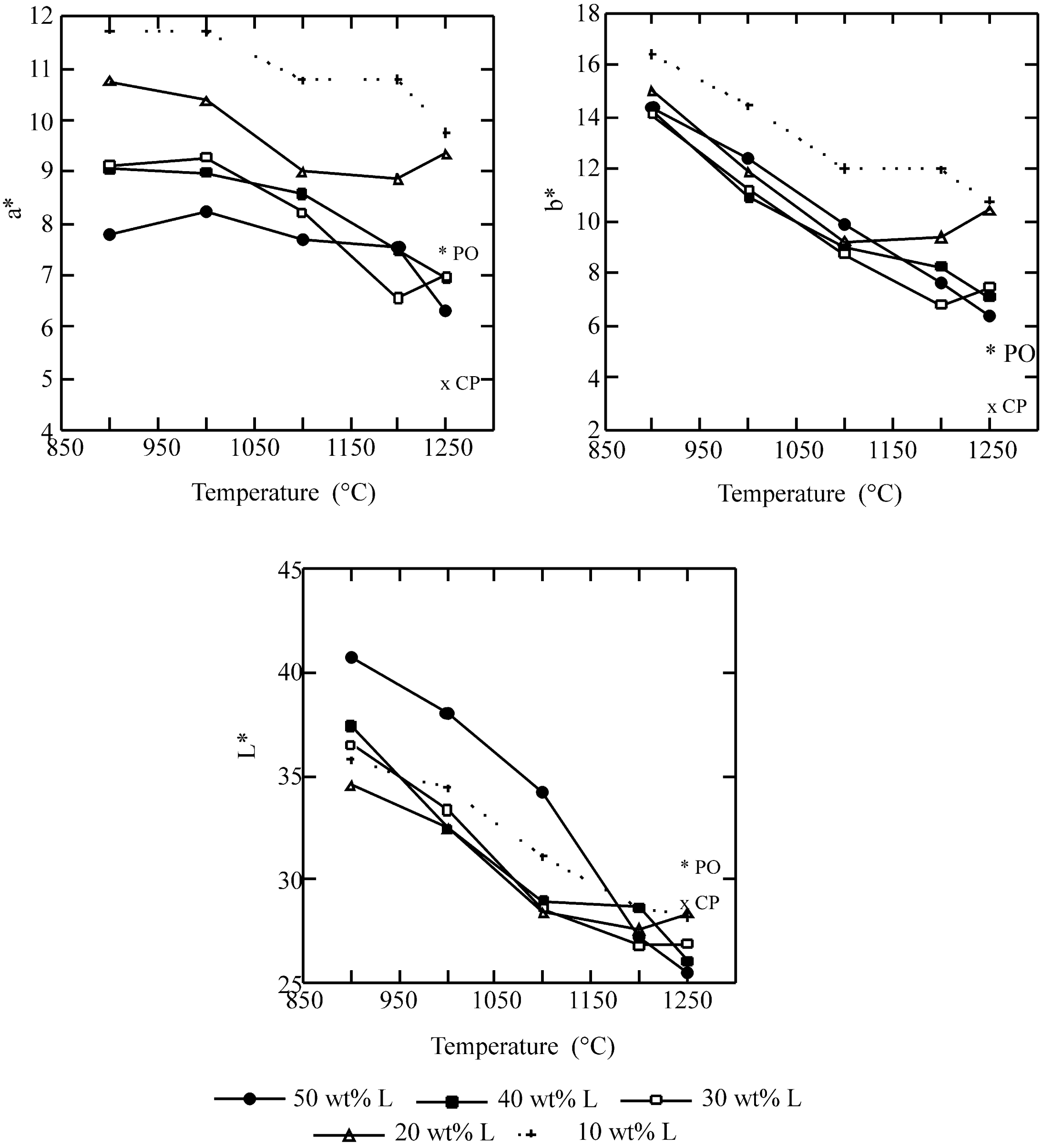

Fig. 4. The $L^*a^*b^*$ values of fired glazes containing 3 wt.% pigment synthesised from chromite-limonite mixtures containing 10, 20, 30, 40 and 50 wt.% limonite and calcined at different temperatures for 3 h (PO: pigment prepared with pure Fe_2O_3 and Cr_2O_3, CP: commercial pigment).

One of the concerns about using raw materials instead of pure oxides is that the variation of composition in the raw materials may alter the colour of the pigment. In order to clarify this point, colour properties of two most promising pigments (40 and 50 wt.% limonite) were compared. $L^*a^*b^*$ parameters of pigments prepared with 40 and 50 wt% limonite containing mixtures calcined at 1250 °C are very close and the spectral curves of these pigments are almost the same. The total colour difference ΔE (is the total difference or distance on the CIELAB diagram at ΔL^*, Δa^* and Δb^* values) between pigments prepared with 40 and 50 wt.% limonite content mixtures was found as 0.30. When the total colour difference $\Delta E < 1$, the colour differences can not be distinguished by human eyes. On the other hand, reflectance curves of 40 and 50 wt.% limonite containing pigments and pigment made from pure oxides are very similar. Therefore, small variations in raw material composition may not be effective on colour and raw materials can safely be used to produce pigments.

3.4. Interactions between iron-chromium pigments and transparent glaze

In previous studies, interactions between pigment and glazes were studied to show the colour differences of the iron-chromium pigments in zinc-based and zinc-free glazes.[14] It was reported that when the iron–chromium–

hematite black pigment is placed in a zinc oxide–containing glaze, it will react with the zinc oxide and form a zinc–iron–chromite brown spinel pigment.[15,16] Although it was indicated in these works[14–16] and also found in this work that cobalt free iron–chromium black pigments give brown colour in glazes containing ZnO, there is no experimental microscopy work to show direct evidence on how the colour change from black to brown in glazes.

In order to find out the interactions between glaze and iron-chromium pigments, the XRD patterns and SEM-EDX analysis of pigment crystals were obtained from glazed surfaces containing 3 wt.% pigments prepared from limonite and chromite mixtures calcined at 1250 °C, but investigations of interactions by XRD and SEM-EDX analysis could not be carried out since lots of elements existing in the pigment when raw materials are used to produce pigment. Therefore, to study the interactions between pigment and the glaze, the iron-chromium pigment was synthesised from a mixture of pure Cr_2O_3 and Fe_2O_3 powders and calcined at 1250 °C. The resulting black pigments were used in ZnO containing transparent glazes and fired at 1125 °C.

Although it is known that pigments must have small particle size distribution (≈5 μm), in this study, pigment crystals having larger particle size distribution (≈10 μm) were used in transparent glaze in order to make interactions between a pigment particle and the glaze visible for SEM analysis.

The SEM images and EDX analysis were obtained from glazed surface containing 3 wt.% pigments prepared using pure oxide mixtures. Fig. 6 shows a backscattered SEM image and results of line scan analysis of Al, Si, Ca, Fe, Cr and Zn elements in the pigment crystals embedded in the glaze. In Fig. 6(a), two regions were observed, the outer part of the pigment crystal is seen brighter than inner part of the pigment crystal indicating that outer part of the pigment crystal contains heavier elements than the inner part of the pigment crystal. Zn is the only element in the glaze that is heavier than Fe and Cr elements contained in the pigment.

In Fig. 6(b), through the line scan area the concentration of Fe and Cr increases while that of Al, Si and Ca decreases when the edge of the particle is reached. Zn concentration starts to increase at the edge of the crystal while the core of the pigment crystal is depleted of Zn and rich in Fe and Cr elements.

Fig. 6(c) shows EDX mapping of Al, Si, Ca, Cr, Fe and Zn elements in the pigment crystal embedded in the glaze. EDX analysis also indicates a higher Fe content in the core of pigment crystal and higher Zn content in the outer part of the pigment crystal confirming the corresponding line scan analysis [Fig. 6(b)]. Small amount of Al, Si and Ca ions from transparent glaze diffused into the pigment crystal [Fig. 6(b) and (c)].

Fe concentration gradually increases from the edge of the pigment to the core show that Fe in pigment crystals are very reactive with glaze as shown in a previous study,[11] Fe diffuses out to glaze while Zn from glaze diffuses into the pigment crystal. Further confirmation for Fe diffusion from the pigment to the glaze come from a recent study,[11] in which hematite particles were capsulated by occlusion in an amorphous silica matrix to protect red colour of hematite in glaze by preventing outward diffusion of Fe from the pigment crystal.

In accordance with the stabilisation energies of the crystalline field [157.6 kJ/mol for Cr^{+3} (d^3) and 0 for Fe^{+3} (d^5)], Cr will situate itself in the octahedral position and outward diffusion of Fe will occur into the glaze.[17] It is also known that compounds which melt at lower temperatures have higher ion diffusion coefficients than those melting at higher temperatures.[18,19] As a result, it can be explained why Zn diffusion from glaze into the pigment is much faster than Mg and Al in oxides form.

EDX line scan analysis and EDX mapping on pigment crystals embedded in the glaze clearly showed that change of colour from black to brown caused by Zn diffusion into the pigment crystal and outward diffusion

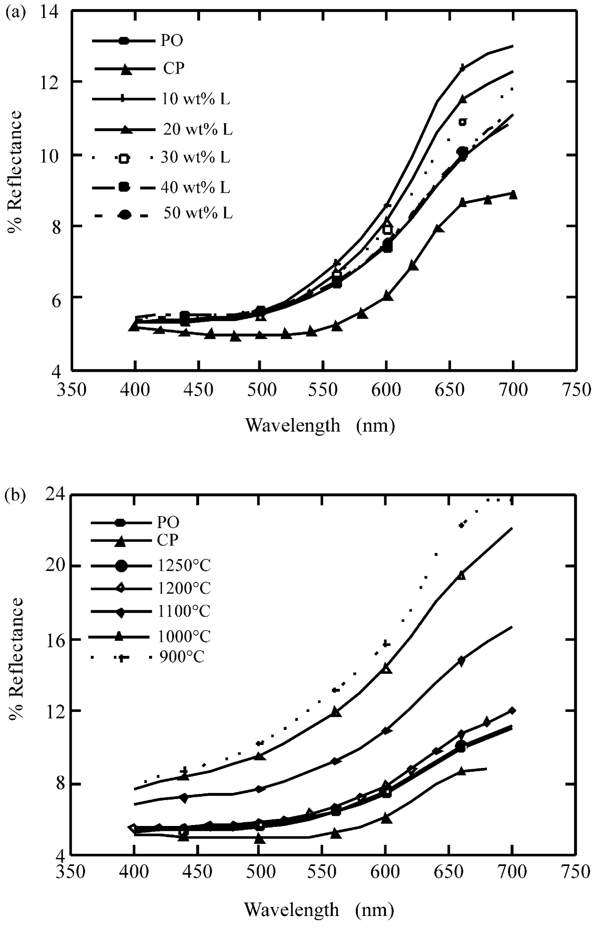

Fig. 5. The spectral reflectance curves of glazes containing 3 wt.% pigment synthesised from chromite–limonite mixtures containing 10, 20, 30, 40 and 50 wt.% limonite and calcined at different temperatures for (PO: pigment prepared with pure Fe_2O_3 and Cr_2O_3, CP: commercial pigment).

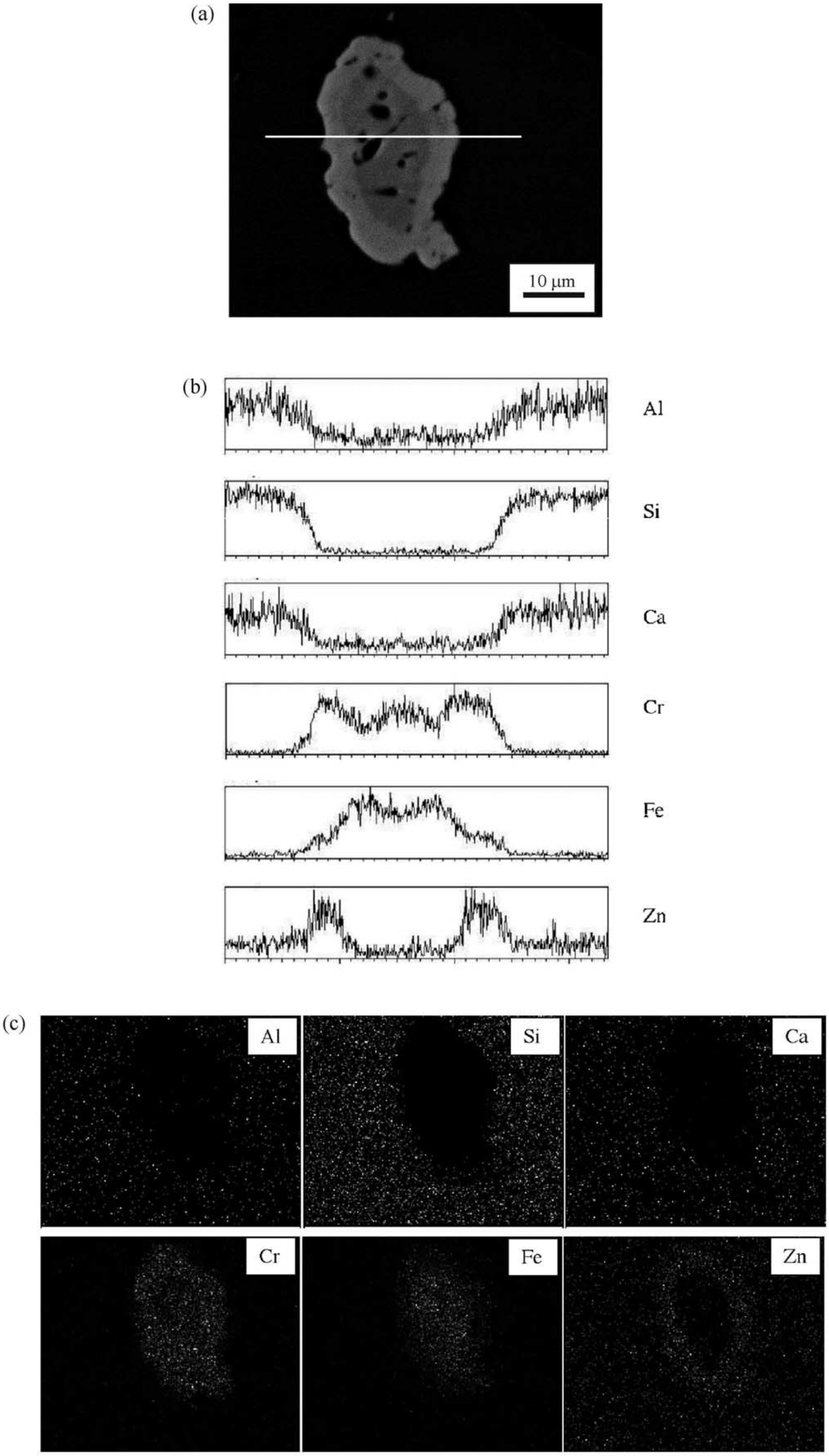

Fig. 6. (a) Backscattered SEM image, (b) line scan analysis and along the white line shown in (a), (c) EDX mapping of Al, Si, Ca, Cr, Fe and Zn elements of a pigment crystal embedded in the transparent glaze.

of Fe into glaze. In different studies based on black spinel pigment production with replacing the chromophore cations of metals of relative toxic risk (Ni, Co) by low toxicity metals (Mg, Al and Zn) shown that, it is possible to produce black pigments by decreasing percentage of the nickel, substituting this by inert magnesium and zinc ($(Fe_{0.7}Mg_{0.15}Zn_{0.15})(Fe_{0.3}Ni_{0.7}\ Cr_2O_4)$). However, with addition of high levels of Zn and Mg, the undesirable browned hues were obtained compared with the commercial pigment.[20]

The tendency of Zn ions to covalency involves lattice contraction, increasing the field in the sphere of Cr^{+3} octahedral antagonist coordination by shortening the Zn–O distance, so that a shift can be expected of the chromophore absorption bands towards higher wavelengths, producing colours towards yellow.[17,20]

4. Conclusion

Chromite and limonite can be used as raw materials to obtain colours from dark brown to light brown depending on the calcination temperature and chromite-limonite content and presents a good alternative to commercial pigments produced from pure oxides. The raw materials form spinel structure above 1200 °C independent of composition. $L^*a^*b^*$ values and reflectance curves of pigments produced from 40 and 50 wt.% limonite content were very similar to commercial pigments and pigments made from pure oxides.

Pigment crystals prepared with pure Cr_2O_3 and Fe_2O_3 and calcined at 1250 °C had interactions with transparent glazes and black colour turn into brown. SEM-EDX analysis on pigment crystals embedded in the glaze clearly showed that Zn ions diffused into the pigment crystal while Fe ions transport from the pigment to the glaze and caused a change of colour from black to brown.

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