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Production of brown pigments for porcelain insulator applications

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Abstract

In this study, production of brown pigment for the ceramic insulator applications by using inexpensive natural raw materials or waste materials was undertaken. Different pigment compositions were designed, synthesised and examined. As a source of chromium, chromite, Cr_2O_3 and ferrochrome were used. Limonite, grinding waste, flotation waste and iron oxide scale were used as an iron source whereas manganese oxide and ferromanganese were used as a manganese source. The colour of glazed insulator bodies change from dark brown to light brown depending on the pigment composition. The pigments prepared with ferrochrome, manganese oxide, flotation waste (C6) or iron oxide scale (D4) and calcined at 1300 °C have a darker brown colour and possess suitable $L^*a^*b^*$ values as 30.1, 2.7, 1.6 for C6 and 30.9, 2.1, 0.3 for D4, which are closer to the $L^*a^*b^*$ values (30.1, 2.9, 0.1) of commercial Mn—Fe—Cr pigments. The results indicate that waste materials containing iron can be used to produce brown pigments to be used in the insulator application in ceramic industry and as a result of this waste material can be converted into a value-added product. Also, ferrochrome can be used successfully as chromium source and help to reduce the cost of the pigment.

Keywords: Insulators; Colour; Spinels; Thermal properties; Pigment

1. Introduction

Insulator materials are used to prevent or regulate current flow in electrical circuits by being inserted as a barrier between conductors. Ceramics are widely used as insulating materials. Because of the fact that they are used in environmentally sensitive applications the ceramic insulator porcelain must be dense, moisture impervious, and must have minimal mechanical flaws. Ceramic insulators are used to provide good mechanical support, high dielectric strength, a low loss factor, heat dissipation and protection of conductor from severe environment, like humidity and corrosion. The main advantage of ceramics as insulator is their capability for high-temperature operation without hazardous degradation in chemical, mechanical or dielectric properties.[1] To reduce the surface contamination, ceramic insulators are coated with transparent glaze. Although, the glaze itself is an insulator, an electrical-conducting surface layer is produced through the action of water extracting alkali ions from the glaze surface.[2] These problems have been overcome by the use of conducting glazes including Fe_2O_3 with additions of other oxides, for example Cr_2O_3, CoO, MnO, CuO, NiO and ZnO. The conducting spinel phases were formed and distributed uniformly throughout the fired glaze. Another way to obtain conducting glaze is to disperse spinel pigments based on these oxides. Addition of 10–20% by volume of pigments in the glaze composition is necessary to develop a continuous conducting network.[2]

Ceramic pigments are inorganic products of metal oxides or compounds capable of forming metal oxides; they must show thermal and chemical stability at high temperatures and must be inert to the chemical action of the molten glaze.[3] The development of brown pigments that are stable at high temperatures because of the spinel structure is of great interest to the ceramic insulator applications. Brown coloured spinel pigments improve physical properties and give aesthetic appearance to the porcelain insulator. Although, the presence of manganese in the pigment composition will often lead to a poor surface and unstable colour and the use of this pigment is limited, the most important brown pigment in this

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field is the manganese–iron brown spinel, which is the deep brown colour associated with electrical porcelain insulators.[4]

Higher percentage levels of pigment produced from expensive pure metal oxides and used to be in ceramic ware can affect the final cost of product. Use of new raw material sources or wastes containing valuable metals in the pigment production is important in order to reduce the pigment prices. In recent years, natural limonite, chromite[5,6] and iron containing grinding waste[7] were successfully used in the pigment production. Also, Samsun copper flotation waste was used as iron source to produce brown and black pigments to be used in the tile glaze and body and convert the waste into value-added products.[8]

Based on this consideration, the aim of this study is to produce and characterise brown inorganic pigments by using different inexpensive raw materials and wastes containing iron for porcelain insulator applications.

2. Experimental procedure

2.1. Preliminary study

A preliminary study was first performed on suitable raw material selection from different raw materials and wastes. Limonite, hematite, Samsun copper flotation waste, grinding waste and iron oxide scale waste were used as iron source, Cr_2O_3 (Merck), ferrochrome (Gensa A.Ş.) and chromite were used as chromium source, and manganese requirement was supplied from MnO_2 (Ege Ferro A.Ş.) and ferromanganese (Gensa A.Ş.). The chemical compositions of the raw materials and wastes (wt.%) determined by energy dispersive X-ray spectrometer (EDX) are given in Tables 1 and 2. The compositions of pigment mixtures were chosen to match commercially available brown pigment. Therefore, the amounts of the oxides were taken up fixed, only the sources of the iron, chromium and manganese were changed (Table 3).

The mixtures were ground for 3 h in a ball mill containing water and were dried. This was followed by calcination for 3 h at 1300 °C. The calcined product was again ground for an hour in a ball mill containing water, washed, filtered and then dried. Pigments of 12 wt.% were added to glaze and applied onto the unfired porcelain body. Glazed ceramic body were fired at 1300 °C for 2 h. The unfired porcelain body and glazes were supplied from a ceramic factory (Ankara Seramik A.Ş) in Ankara, Turkey and also firing was carried out in the same factory.

The crystalline phases present in the pigments after calcination were determined by using X-ray diffractometer (XRD-RIGAKU Dmax IIIC) with Cu Kα radiation. Colour measurements were made by using a spectrophotometer (MINOLTA-3600 d) and the results were expressed in $L^*a^*b^*$ values. These parameters were measured for an illuminant D65, following the CIE-$L^*a^*b^*$ colorimetric 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.

2.2. Composition study

After studying the effect of the starting raw material on the colour properties, the amount of oxides in the pigment composition was changed to improve colour properties by using chosen suitable materials (Flotation waste, iron oxide scale, ferrochrome, chromite, Cr_2O_3 and MnO_2) and pigment compositions prepared (group C and D pigments) were calcined

Table 2
Elemental analysis of metallic materials determined by EDX (wt.%)

	Grinding waste (G)	Ferrochrome (FC)	Ferromanganese (FM)
Metallic materials			
Mg	0.30	–	–
Al	0.70	–	–
Si	8.30	3	3
Ca	0.40	–	–
Cr	0.30	65	–
Fe	71.5	25	25
Zn	–	–	–
Mn	–	–	65
C	–	7	7
O_2	18.5	–	–

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

	Chromite (C)	Limonite (L)	Hematite (H)	Samsun flotation waste (S)	Iron oxide scale (I)	MnO_2 (M)
Oxide materials						
MgO	22.4	3.5	–	0.4	–	–
Al_2O_3	12.2	9	–	1.9	1.0	4.0
SiO_2	4.8	31	5	33.8	2.5	5.0
CaO	0.2	–	–	0.6	–	–
Cr_2O_3	46.7	2	–	–	1.5	4.0
Fe_2O_3	13.5	48	95	58.6	95.0	10.0
ZnO	0.2	–	–	3.4	–	–
CuO	–	–	–	1.3	–	–
NiO	–	6.5	–	–	–	–
MnO_2	–	–	–	–	–	77.0

Table 3
Pigment compositions prepared in this study (wt.%)

Code	L	H	S	G	I	C	FC	Cr_2O_3	MnO_2	FM	Al_2O_3	SiO_2
CP[a]	–	28	–	–	–	–	–	24	32	–	4	12
A1	50	–	–	–	–	–	–	18	32	–	–	–
A2	–	27	–	–	–	–	–	24	33	–	4	12
A3	–	–	35	–	–	–	–	22	30	–	3	10
A4	–	–	–	31	–	–	–	23	32	–	3	11
A5					32			29	39			
A6	36		–	–	–	–	32	–	32	–	–	–
A7	–		23	–	–	–	32	–	30	–	4	11
A8	–	–	21	–	–	36	–	–	30	–	2	11
A9	33	–	–	–	–	37	–	–	30	–	–	–
A10	–	–	–	21	–	–	34	–	32	–	4	9
A11				20	–	39			31	–	2	8
B1	–	–	25	–	–	–	–	22	–	38	4	11
B2	–	–	–	23	–	–	–	24	–	41	4	8
B3	21	–	–	–	–	–	33	–	–	40	2	4
B4	–	–	–	14	–	–	34	–	–	39	4	9
B5	38	–	–	–	–	–	–	23	–	38	1	–
B6	–	–	14	–	–	–	33	–	–	39	4	10
C1	–	–	33	–	–	40	–	–	27	–	–	–
C2	–	–	29	–	–	44	–	–	27	–	–	–
C3	–	–	25	–	–	48	–	–	27	–	–	–
C4	–	–	35	–	–	–	32	–	33	–	–	–
C5	–	–	31	–	–	–	36	–	33	–	–	–
C6	–	–	26	–	–	–	40	–	33	–	–	–
C7	–	–	49	–	–	–	–	19	32	–	–	–
C8	–	–	45	–	–	–	–	23	32	–	–	–
C9	–	–	41	–		–	–	27	32	–	–	–
D1	–	–	–	–	19	50	–	–	31	–	–	–
D2	–	–	–	–	25	54	–	–	31	–	–	–
D3	–	–	–	–	21	–	41	–	38	–	–	–
D4	–	–	–	–	17	–	45	–	38	–	–	–
D5	–	–	–	–	33	–	–	28	39	–	–	–
D6	–	–	–	–	36	–	–	25	39	–	–	–
D7	–	–	–	–	28	–	–	33	39	–	–	–

Composition of this pigment was determined by using XRF analysis. L: limonite; H: hematite; S: Samsun flotation waste; G: grinding waste; I: iron oxide scale; C: chromite; FC: ferrochrome; Cr: Cr_2O_3; M: MnO_2; FM: ferromanganese.

[a] CP: Commercial pigment.

at 1300 °C. Pigments of 12 wt.% (the percentage of pigments were chosen constant as used in ceramic insulator factory) were added to the glaze and applied onto the unfired porcelain body. The glazed ceramic bodies were fired at 1300 °C for 2 h.

3. Experimental results and discussion

3.1. Preliminary study

The $L^*a^*b^*$ values and reflectance curves of coloured glazes containing pigments prepared with different raw materials and waste are given in Fig. 1. The colour properties of glazed porcelains containing pigments were influenced by pigment composition prepared with different starting mixtures and different shades of brown colour were obtained. Darker chocolate brown were observed with iron chromite pigments containing MnO which is similar to NiO containing iron chromite pigments.[9] In contrast, iron chromite pigments produce a wide palette of tan and reddish brown shades with the addition of ZnO.[3] It is clear that replacement of Mn^{2+} (0.97 Å) ions (larger than Fe^{2+} (0.72 Å) Fe^{3+} (0.78 Å) and Cr^{3+} (0.77 Å) ions) could change the lattice parameter. Accommodation of a larger ion induces a lattice distortion involving even a variation of the distance between the colouring ion and its ligands, that shifts the energy required to produce an electronic transition, thus leading to different colours.[10]

In group A pigments, MnO_2 was used as manganese source. The pigment prepared with hematite and Cr_2O_3 (A2) has a higher a^* and b^* value compared to the limonite or flotation waste containing Cr_2O_3 (A1 and A3). From this point of view, it can be concluded that, the sources of the iron oxide affect the $L^*a^*b^*$ values (Fig. 1a). Flotation waste and iron oxide scale were selected as an iron oxide source, because of the lower total colour difference ΔE^* (is the total difference or distance on the CIELAB diagram at ΔL^*, Δa^* and Δb^*) value. The more intense chocolate brown colour was obtained with pigment containing ferrochrome (A6) compared to pig-

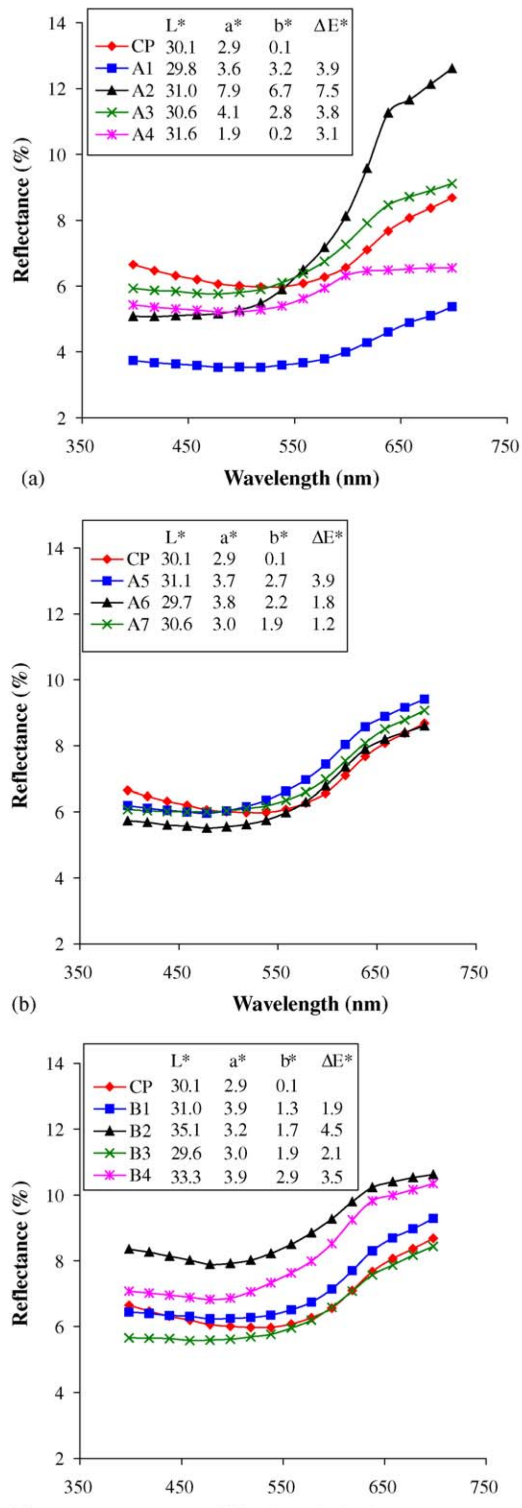

Fig. 1. Reflectance curves of coloured porcelain samples containing 12 wt.% pigment prepared with different raw materials and different types of wastes.

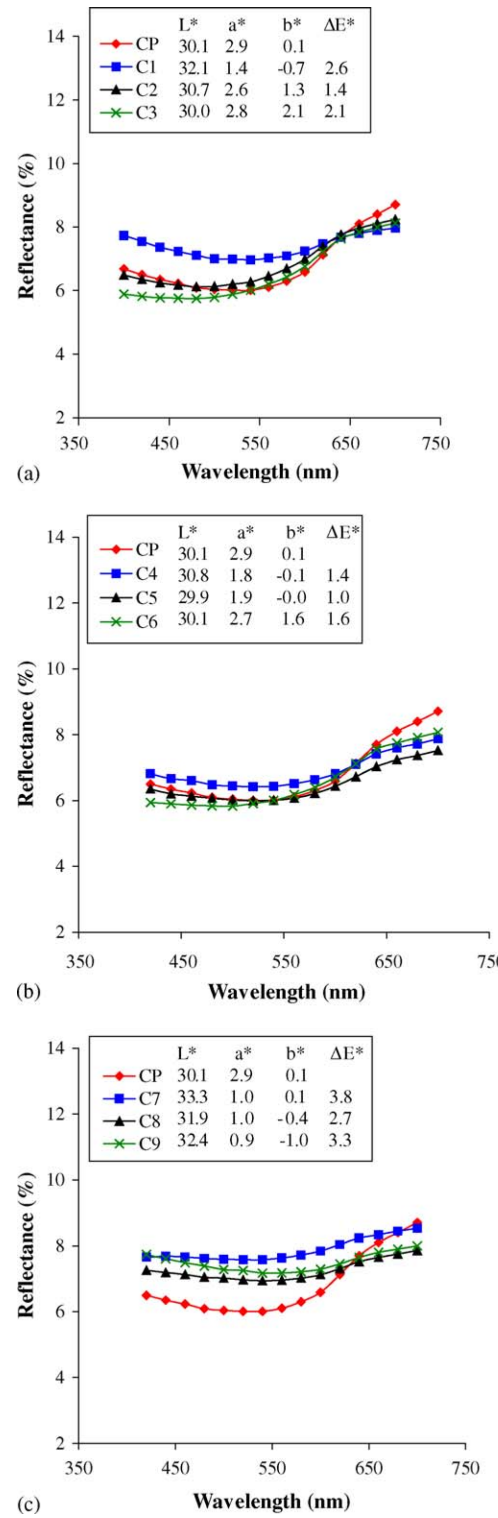

Fig. 2. Reflectance curve of coloured porcelain samples containing 12 wt.% pigment prepared with a mixture of flotation waste and either chromite (a), ferrochrome (b) or Cr_2O_3 (c).

ment containing Cr_2O_3 (A1) (Fig. 1b). Ferrochrome is an alloy that can be regarded as a solid solution of chromium and iron. It is thought to be a homogeneous spinel formation which occurs easily between ferrochrome and other compounds due to its homogeneity of iron and chromium in atomic scale and affect colour quality.

In group B pigments, ferromanganese was used as manganese source. When the grinding waste replaced by

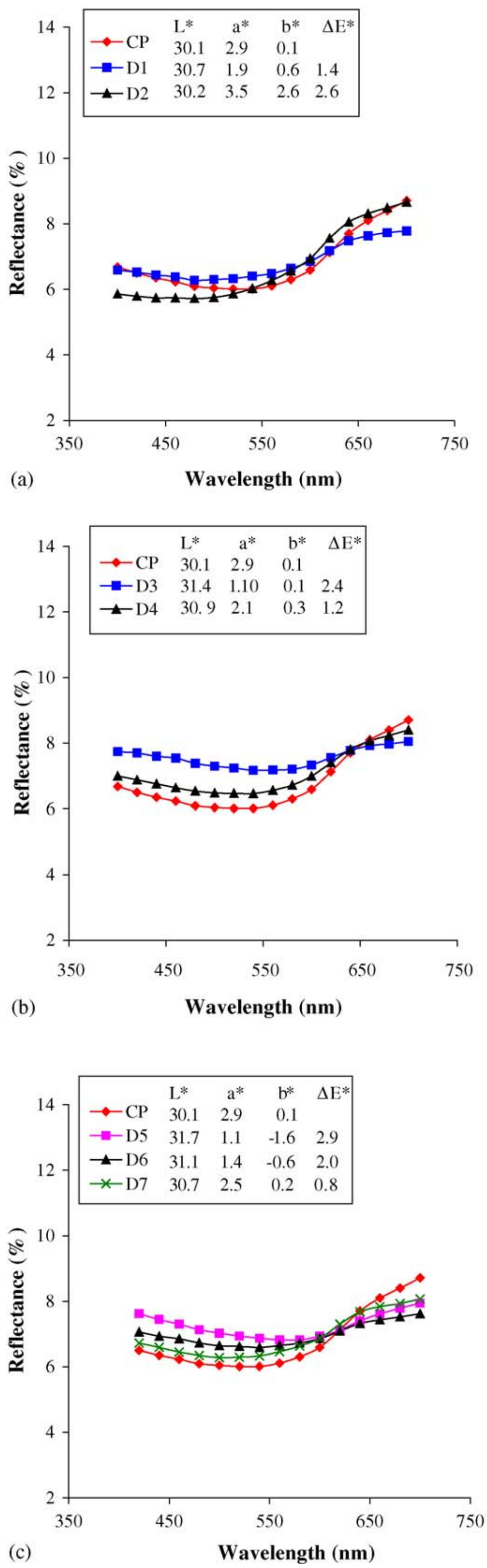

Fig. 3. Reflectance curve of coloured porcelain samples containing 12 wt.% pigment prepared with a mixture of iron oxide scale and either chromite (a), ferrochrome (b) or Cr_2O_3 (c).

the limonite in the same composition, the $L^*a^*b^*$ values increased. Although, grinding waste was successfully used as iron source in pigments for wall tile glaze and porcelainised tile,[7] desired colour properties by using grinding waste were not obtained for porcelain insulator applications and crystallisation on the glaze surface was occurred (B2 and B4). However, B1 composition containing flotation waste showed more desirable colour compared to the B3 pigment composition containing limonite (Fig. 1c).

3.2. Composition study

After establishing which starting material yielded the best colour, the effect of oxide composition on the colour properties were studied with these materials (Table 3).

In group C, flotation waste was used as iron source with different chromium sources (chromite, ferrochrome and Cr_2O_3) while iron oxide scale were used in group D. When the chromium content in the pigment composition prepared with chromite and ferrochrome increases, *a** and *b** values increase and desirable brown colour were obtained (Fig. 2a and b). In contrast, the colour of glazes visually changes from dark brown to black colours with increasing Cr_2O_3 content as shown in Fig. 2c. Similarly, brown colour was affected by chromium content in the group D pigment compositions prepared with iron oxide scale (Fig. 3).

Reproducibility of pigments is necessary to achieve colour stability. Although, chemical composition of copper flotation waste does not change much from region to region,[8] iron oxide scale can be used more safely and reliably due to having

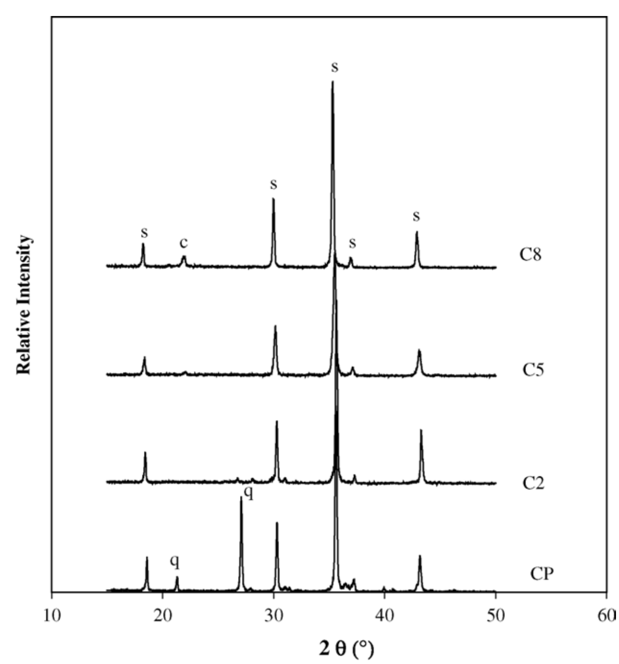

Fig. 4. XRD patterns of pigments prepared with flotation waste and different chromium sources (chromite, ferrochrome, Cr_2O_3) and calcined at 1300 °C, showing the existence of mainly spinel(s) phase and the other phases (c: cristobalite and q: quartz).

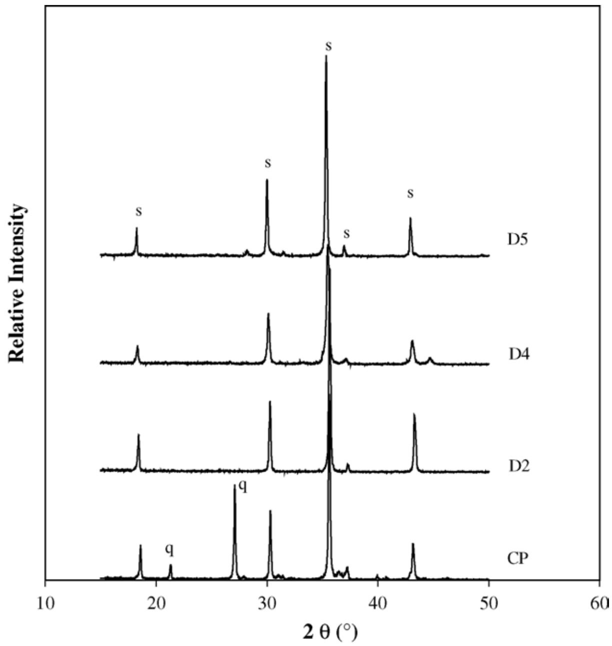

Fig. 5. XRD patterns of pigments prepared with iron oxide scale and different chromium sources (chromite, ferrochrome, Cr_2O_3) and calcined at 1300 °C, showing the existence of mainly spinel (s) phase and quartz phase (q).

high iron oxide content and stability of chemical composition in comparison to flotation waste.

The XRD patterns of pigments prepared with chromite, ferrochrome, Cr_2O_3 and flotation waste calcined at 1300 °C are shown in Fig. 4. Spinel phase was observed for all the pigment compositions and commercially available brown pigment. As a difference, commercially available brown pigment contain quartz (SiO_2) phase. It is well known that, all elements of first transition series (Cr, Ti, Fe, Zn, Mn, Cu, Ni and Co) can form different compounds with the spinel structure.[11]

The pigments prepared with chromite, ferrochrome, Cr_2O_3 and iron oxide scale calcined at 1300 °C (Fig. 5) have spinel phase when compared to pigments prepared with flotation waste. It is clear that although all pigments have similar spinel phase, colour of pigments were influenced by the type of raw material compositions and the impurities.

4. Conclusions

In this study, production and characterisation of brown pigments for porcelain insulator application by using less expensive raw materials and waste was undertaken. The glazed insulator bodies containing pigments have a different shade of brown colour depending on the raw material used. Black–brown were obtained with Cr_2O_3 containing pigments whereas pigments prepared with ferrochrome, flotation waste (C6) or iron oxide scale (D4) give more intense and bright brown colour with a low ΔE^* and were found to be within the acceptable values according to the insulator porcelain manufactures. Furthermore, if ferrochrome is used instead of Cr_2O_3 in pigment composition, use of ferrochrome is more advantageous because of its lower cost.

Flotation waste and iron oxide scale were chosen as an iron source because of the lower $I\Delta E^*$ values. In this way, flotation waste and iron oxide scale can be used as iron source to produce brown pigments to be used in the ceramic insulators and convert the waste into a value-added product and in addition, environmental damage can be reduced with the waste disposal in this way.

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