

The production of Ni and co-gahnite pigments using ZnO powder produced from metal slags

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In this study, Ni and Co-gahnite pigments were produced from Al_2O_3 powder and ZnO powder obtained from industrial metal slags. Different pigment compositions were prepared by adding metal oxides (NiO or Co_3O_4) and mineralisers (NaF, CaF_2 or Li_2CO_3). Pigments were calcined in an electric furnace at 1300, 1400 and 1450 °C for 4 h at a heating rate of 2 K·minute⁻¹. The pigment powders obtained were added to a transparent ceramic glaze and to porcelainised tile bodies. The pigment colours were determined using L*a*b* measurements from a spectrometer. On one hand, the results show that Ni-gahnite pigment is not useful for industrial applications because it has poor colour intensities and stabilities. On the other hand, our results also show that Co-gahnite pigments can be produced using ZnO from industrial metal slags, and that they have an intense blue colour.

Key words: Colour, Gahnite, Spinel, ZnO, Powders-solid state reaction, Pigment.

Introduction

In the ceramics industry, oxide pigments are preferred due to their thermal and chemical stability in molten glazes. Only a limited number of crystalline materials, such as zircon, corundum, rutile or spinel, can withstand the chemical corrosion of the liquid phase formed during the firing of bodies or glazes [1].

Cobalt-containing pigments are commonly used in the ceramics industry to obtain an intense blue colour. Spinel (CoAl_2O_4) and olivine (Co_2SiO_4) pigments are thermally stable at high temperatures and chemically stable in molten glazes. However, spinel blue is widely preferred to olivine blue, since a navy blue colour can be obtained from a lower cobalt content (33 wt.% in spinel vs. 50 wt.% in olivine), resulting in lower cost and toxicity [2, 3].

In recent years, extensive research has been conducted to characterise ceramic pigments with the goal of increasing the number of coloured materials and refining their colouring properties. One research focus has been developing new pigments by doping white or colourless structures with efficient chromophores. Apart from the blue spinel and olivine pigments, new blue pigments such as willemite (Zn_2SiO_4) and gahnite (ZnAl_2O_4) are interesting to the ceramics industry because they contain less Co, which translates to lower production costs compared to CoAl_2O_4 and Co_2SiO_4 [3-5].

Gahnite has a spinel structure, similar to CoAl_2O_4 ,

and high thermal and chemical stability. It is initially white in colour, but after doping with small amounts of transition metal ions, such as Co^{2+} and Ni^{2+} , it gains colour. The Co^{2+} and Ni^{2+} ions become lodged within the tetrahedral sites of the ZnAl_2O_4 spinel structure, as in Zn_2SiO_4 and CoAl_2O_4 [3, 4]. The resulting product has a low toxicity, it can be made from recycled material (industrial metal slags), and is environmentally friendly. Therefore, our goal with the present study is to synthesise Ni and Co-gahnite pigments using less expensive ZnO powder that is produced from industrial metal slags, and to determine the colour properties of these pigments.

Experimental Procedure

In this study, we used as raw materials Al_2O_3 (Riedel-de Haen), ZnO produced from industrial metal slags (Çorum, Turkey), Co_3O_4 (Ferro), and NiO (Merck) to produce a range of Ni- and Co- gahnite pigments. The chemical compositions of the Co_3O_4 and ZnO powders produced from industrial metal slag were determined by X-ray fluorescence spectrometry (XRF, Rigaku RZS Primus) as listed in Table 1. The ZnO powder contained certain impurities such as PbO, CuO, etc. as shown in Table 1. Despite this fact, the ZnO powder was successfully used as a raw material for several different pigment types [6].

We designed pigment compositions with $\text{Ni}_x\text{Zn}_{1-x}\text{Al}_2\text{O}_4$ and $\text{Co}_x\text{Zn}_{1-x}\text{Al}_2\text{O}_4$ stoichiometries; a 3 wt.% mineraliser (NaF, CaF_2 or Li_2CO_3) was added in order to test the mineraliser effect on colouration properties (Table 2).

The mixtures were ground for 3 h in a ball mill containing water to obtain homogeneous slurries. After drying

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Table 1. Chemical analyses of the Co₃O₄ and ZnO powder produced from industrial metal slags (wt.%)

	ZnO	Co ₃ O ₄	PbO	NiO	CuO	Fe ₂ O ₃	Al ₂ O ₃	CaO	K ₂ O	Na ₂ O	MgO	SiO ₂	SO ₃
ZnO	95.50	-	1.62	0.02	0.53	0.14	-	0.07	0.25	-	-	0.12	1.74
Co ₃ O ₄	-	96.70	-	-	-	0.053	0.105	0.024	-	1.49	0.034	0.043	1.56

Table 2. Prepared pigment compositions

Ni _x Zn _{1-x} Al ₂ O ₄			Co _x Zn _{1-x} Al ₂ O ₄		
Code	Ni	M ^a	Code	Co	M ^a
GNi1	x = 0.05	-	GC01	x = 0.05	-
GNi2	x = 0.10	-	GC02	x = 0.10	-
GNi3	x = 0.15	-	GC03	x = 0.15	-
GNi4		NaF	GC04		NaF
GNi5	x = 0.05	CaF ₂	GC05	x = 0.05	CaF ₂
GNi6		Li ₂ CO ₃	GC06		Li ₂ CO ₃
GNi7		NaF	GC07		NaF
GNi8	x = 0.15	CaF ₂	GC08	x = 0.15	CaF ₂
GNi9		Li ₂ CO ₃	GC09		Li ₂ CO ₃

M^a : Mineraliser

the slurries, calcinations were performed at 1300, 1400 and 1450 °C for 4 h with a 2 K·minute⁻¹ heating rate. The calcined products were ground in a ball mill containing water and were then washed with water. The 5 wt.% pigment powder were added to a commercial double firing glaze and a porcelainised tile body in order to test technical performance. The ceramic tile, glazes and porcelainised tile granules were obtained from a ceramic factory (Toprak San. and Tur. A.S.) in Eskisehir, Turkey. The coloured glazes were fired at 1050 °C and the porcelainised tile bodies were fired at 1200 °C.

The L*a*b* colour parameters of both fired powders and coloured glazes were measured using a spectrophotometer (Minolta 3600 d), with an illuminant D₆₅ and observer 10°, following the CIE-L*a*b* colourimetric method recommended by the CIE (Commission Internationale de l'Eclairage) [7]. In this method, L* is the lightness axis, a* is the green (-) → red (+) axis, b* is the blue (-) → yellow (+) axis, C* is chroma and h is hue.

In order to identify the crystalline phases of the calcined pigments, XRD patterns were obtained using a conventional

powder diffraction technique in an X-ray diffractometer (XRD, Rigaku d_{max}) with a Ni-filter, and Cu K_α radiation with a goniometer at a speed of 0.5°/s.

The microstructure and chemical homogeneity of the pigment powders were measured using scanning electron microscopy (SEM, Zeiss Supra 50 VP) with an attached energy dispersion X-ray spectrometer (EDX, Oxford Instruments).

Results and Discussion

Pigment characterization

The colour parameters of the pigment powders calcined at 1400 °C are listed in Table 3. The pigment colour properties were influenced by the Ni and Co contents and by the mineraliser. The blue colour is mainly governed by the parameter b*. The more negative the b* value, the more intense the blue colour. Neither increasing the Ni content nor adding different mineralisers were able to improve the Ni-gahnite pigment colour properties. Ni-gahnite pigments exhibited a less intense blue-green colour,

Table 3. Colour parameters of pigment powders calcined at 1400 °C

Ni-gahnite pigments						Co-gahnite pigments					
Code	L*	a*	b*	C*	h	Code	L*	a*	b*	C*	h
GNi1	87	-2.3	-0.6	2.6	164.7	GC01	65	-4.7	-39.1	39.8	263.1
GNi2	85	-3.2	-0.7	2.1	161.6	GC02	63	-2.1	-41.5	46.3	264.2
GNi3	84	-4.7	-0.9	2.3	170.2	GC03	57	-0.7	-49.8	47.9	266.4
GNi4	88	-2.5	-0.4	2.5	190.1	GC04	69	-6.4	-36.2	36.8	260.0
GNi5	87	-3.8	-0.8	2.5	164.7	GC05	66	-5.8	-39.8	40.3	261.7
GNi6	81	-6.7	-2.1	7.0	197.2	GC06	70	-6.4	-38.1	36.8	260.2
GNi7	84	-5.4	-1.7	5.7	197.6	GC07	59	-2.9	-47.8	47.9	266.5
GNi8	76	-9.3	-4.2	10.2	204.2	GC08	54	-0.9	-51.1	51.0	268.9
GNi9	78	-6.2	-3.2	7.9	196.2	GC09	48	-4.5	-50.2	48.9	263.1

and this observation was confirmed by the higher L^* and $-a^*$ values, and by the lower $-b^*$ and C^* values as listed in Table 3. As stated by Lorenzi *et al.* [4], the blue colour of the Ni-gahnite pigment is related to the presence of Ni^{2+} ions in the tetrahedral structure. This demonstrates that Ni^{2+} ions can be present simultaneously in both tetrahedral and octahedral sites within the gahnite structure, but they are preferentially present in octahedral sites. Octahedral Ni in the gahnite structure does not modify the colour, because the electronic transition of Ni in the octahedral site is of low intensity. We found that the fraction of tetrahedral Ni^{2+} was small, but strongly related to the blue pigment colour. The green colour was mainly attributed to NiO contamination in the Ni-gahnite solid solution. The NiO charge transfers are associated with high molar absorptivity values. As a consequence, NiO has a strong colouring effect and is responsible for the green colour even at very low concentrations [4].

Co-gahnite pigments display a blue colour, the intensity of which depends on both the Co content and the added mineralisers. As the cobalt oxide content in the pigment increases, L^* values decrease and $-b^*$ values increase. Furthermore, the addition of CaF_2 and Li_2CO_3 leads to an increase in $-b^*$ and C^* values, representing the intensity of the blue colour. Co^{2+} ions occupy the tetrahedral positions, substituting for the Zn ions in the gahnite structure, as in a spinel Co-aluminate. This substitution is responsible for the more intense blue colour [3].

The colour parameters of Co-gahnite pigments calcined at different temperatures are shown in Table 4. The $L^*a^*b^*$ values are slightly influenced by the calcination temperature. L^* values decrease as the calcination temperature increases. The $-b^*$ values increase as the calcination temperature increases from 1300 to 1400 °C, until the colour parameters change only slightly at 1450 °C. The calcination temperature was not further increased because of the formation of a glassy phase.

Reflectance curves of Ni-gahnite pigments calcined at 1400 °C are shown in Fig. 1. The reflectance values of Ni-gahnite pigment powder decreased with increasing Ni content in the pigment composition, and the addition of mineralisers slightly increased the pigment colour intensity (Fig. 1b). Fig. 2 shows the reflectance curves of Co-gahnite pigments calcined at 1400 °C. The reflectance values of Co-gahnite pigment powder were influenced by increasing the Co content and by adding different mineralisers into the pigment composition. The most intense blue colour was

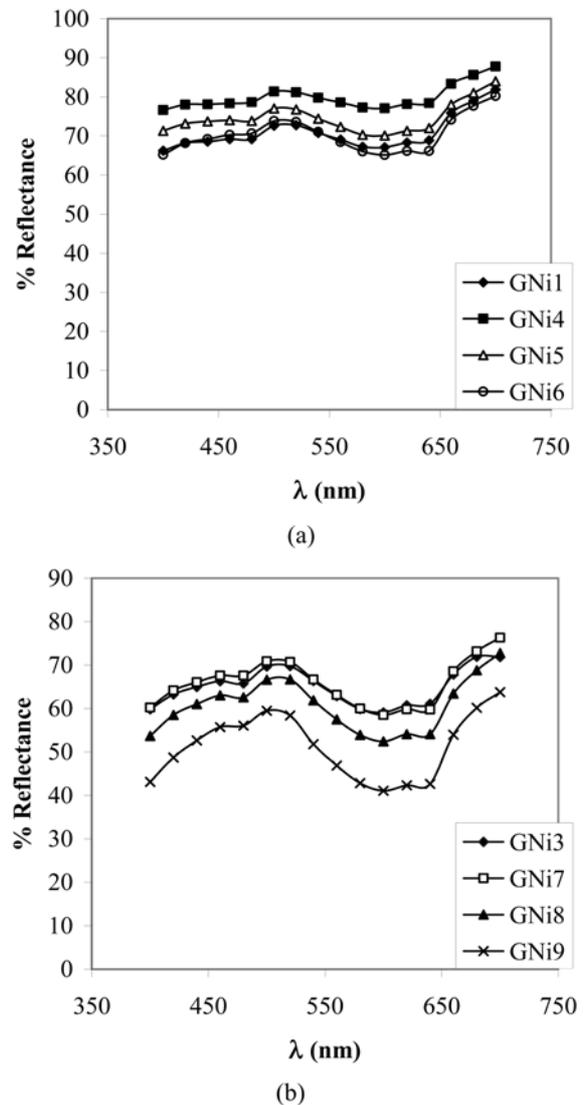


Fig. 1. Reflectance curves of Ni-Gahnite pigment powders prepared with a) 0.05 mol% Ni and different mineralisers and b) 0.15 mol% Ni and different mineralisers.

obtained with the GCo8 sample, which exhibited very low reflectance values.

XRD patterns of the Ni-gahnite pigments calcined at different temperatures are shown in Fig. 3. Consistent with these XRD patterns, the pigments primarily contained gahnite ($ZnAl_2O_4$; JCPDS file no.05-0669) phase. Additionally, the XRD patterns exhibited two peaks located at a diffraction angle (2θ) between 65 and 66°, indicating the presence of

Table 4. Colour parameters of Co-gahnite pigment powders calcined at different temperatures

Code	Calcination Temperature (°C)														
	1300					1400					1450				
	L^*	a^*	b^*	C^*	h	L^*	a^*	b^*	C^*	h	L^*	a^*	b^*	C^*	h
GCo3	61	-4.5	-41.8	42.1	263.8	57	-0.7	-49.8	47.9	266.4	57	-0.8	-47.9	45.6	268.9
GCo7	60	-3.1	-42.7	42.8	265.9	59	-2.9	-47.8	47.9	266.5	59	-4.4	-48.2	42.4	264.0
GCo8	57	-2.1	-44.0	44.9	267.4	54	-0.9	-51.1	51.0	268.9	53	-0.8	-51.3	46.7	268.9
GCo9	54	-6.2	-37.7	38.2	260.6	48	-4.5	-50.2	48.9	263.1	48	-1.74	-51.7	45.8	267.8

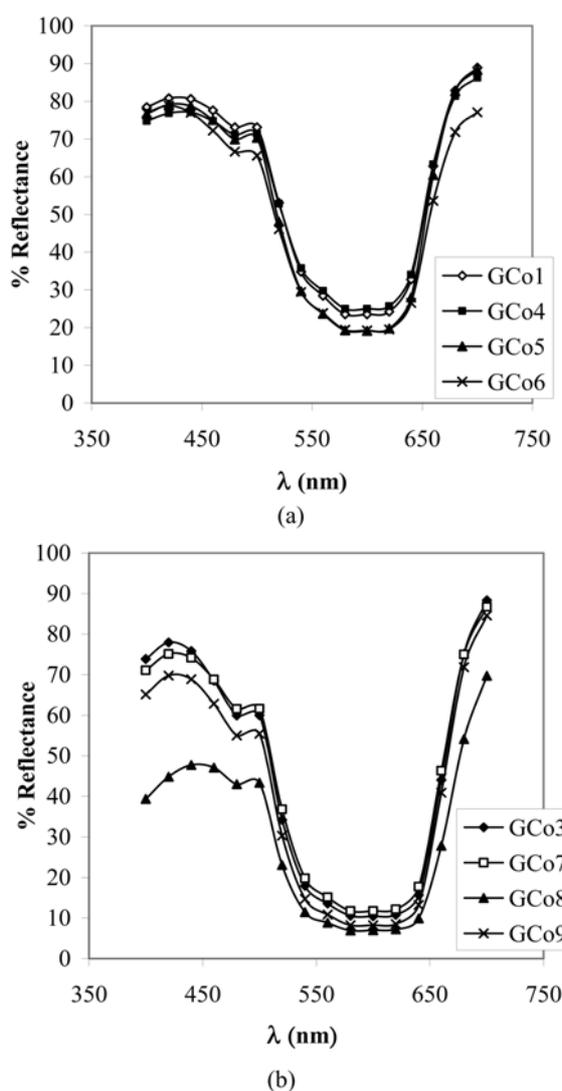


Fig. 2. Reflectance curves of Co-Gahnite pigment powders prepared with a) 0.05 mol% Co and different mineralisers and b) 0.15 mol% Co and different mineralisers.

NiAl_2O_4 (JCPDS file no.10-0339). The peak at $48^\circ 2\theta$ is associated with the only gahnite phase. The overlapped peaks appear in the all XRD patterns of the pigment powder calcined at all temperatures. The general spinel group formula is AB_2O_4 . The A represents divalent metal ions such as Mg, Fe, Ni, Co and Zn. The B represents trivalent metal ions such as Al, Fe, Cr. A solid solution is common in this group of minerals and could contain percentages of several different ions such as Ni, Mg, Al and Fe [1]. Additionally, we did not observe any residual phases containing Ni, such as NiO. But Ni-containing phases, which are sources of green contamination, might go undetected by XRD due to low concentrations or poor crystallinity, as hypothesised by Lorenzi *et al.* [4].

XRD patterns of Co-gahnite pigment powder (GCo3) calcined at different temperatures also show a non-uniform solid solution similar to the Ni-gahnite pigments (Fig. 4). At higher $2\theta^\circ$ values (65-66 $2\theta^\circ$), the peak is split into two overlapped peaks that belong to the CoAl_2O_4 (JCPDS

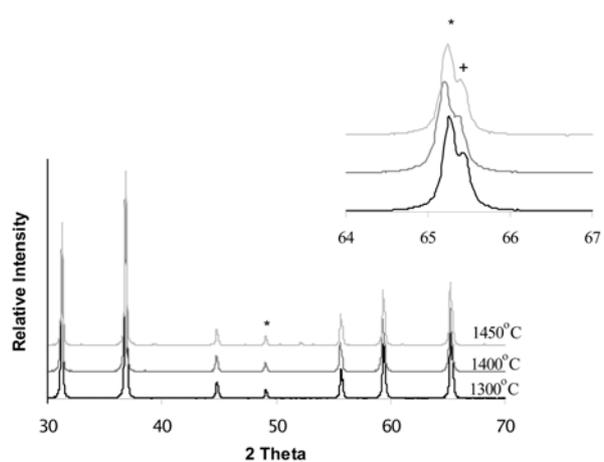


Fig. 3. XRD patterns of GNi3 pigment powders calcined at different temperatures. (+ : NiAl_2O_4 (10-0339) and * : ZnAl_2O_4 (05-0669))

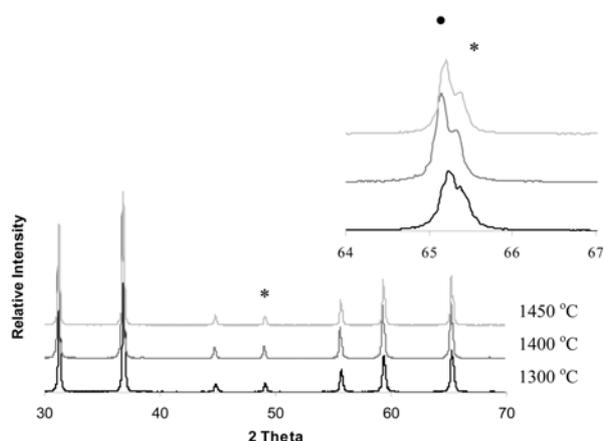


Fig. 4. XRD patterns of GCo3 pigment powders calcined at different temperatures. (• : CoAl_2O_4 (44-0160) and * : ZnAl_2O_4 (05-0669))

file no. 44-0160) and ZnAl_2O_4 (JCPDS file no.05-0669) phases in the pigment powder calcined at 1300 $^\circ\text{C}$. These phases were still present even when the calcination temperature was increased to 1450 $^\circ\text{C}$. These two peaks can also be seen in both the pigment powders prepared with no mineraliser (GCo3) and in the pigment prepared with CaF_2 (GCo8) and calcined at 1400 $^\circ\text{C}$ (Fig. 5). The XRD characterisation did not indicate the presence of any purely cobalt-containing oxide phases. We conclude that a solid solution of Co^{2+} in ZnAl_2O_4 and CoAl_2O_4 was present in the pigment powders.

Fig. 6 shows several backscattered SEM images of different sized Ni-gahnite agglomerates fired at 1400 $^\circ\text{C}$. A small number of brighter agglomerates were also observed. The agglomerate variation may be explained by the heterogeneity of the pigment composition. The elemental distribution was determined with EDX analysis. In Fig. 7, the EDX spectrum shows that the bright region (2) contains a large amount of nickel oxides when compared with the dark region (1). EDX mapping of Ni, Zn and Al elements in both bright and dark pigment agglomerates (GNi3) also indicates heterogeneity in nickel distribution, as illustrated in Fig. 8.

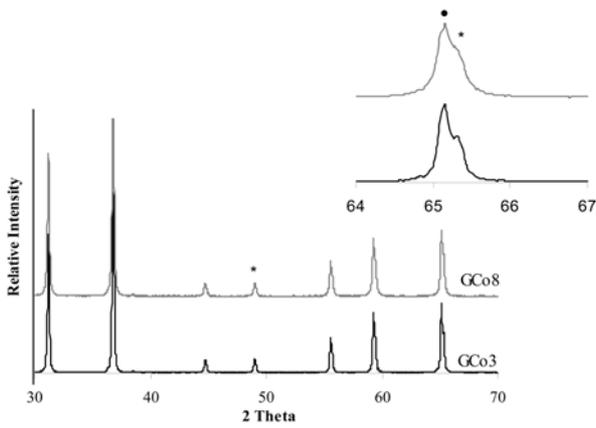


Fig. 5. XRD patterns of pigment powders prepared without mineraliser (GCo3) and with CaF_2 (GCo8) and calcined at 1400 °C.

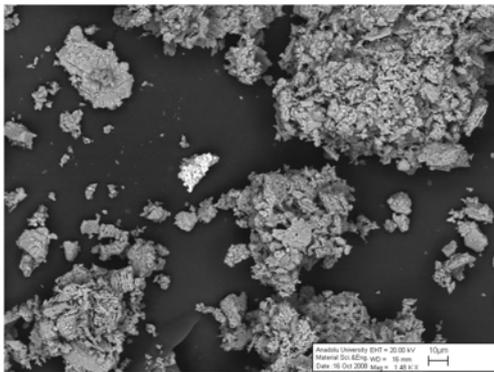


Fig. 6. SEM image of Ni-gahnite powder (GNi3) calcined at 1400 °C.

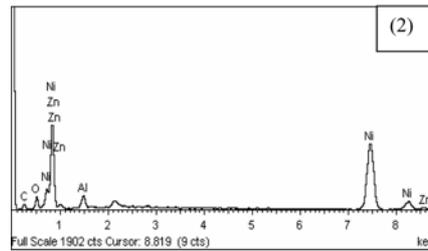
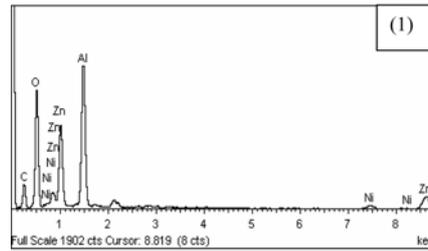
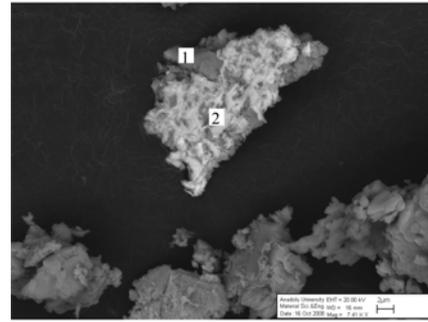


Fig. 7. EDX spectra of bright pigment agglomerates.

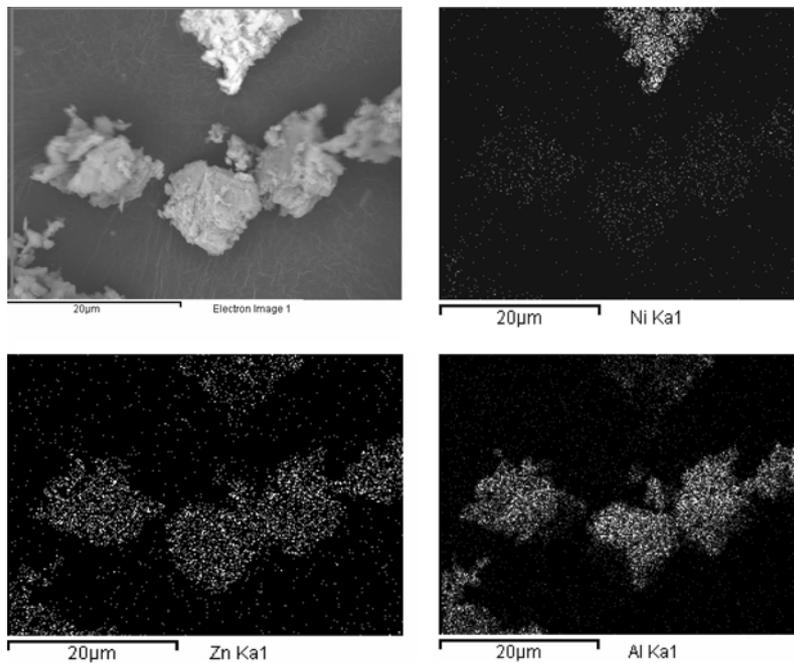


Fig. 8. EDX mapping of Zn, Al and Ni elements in pigment agglomerates (GNi3) calcined at 1400 °C.

A backscattered SEM image of GCo8 shows that large agglomerates can range in size between 10 μm and 30 μm (Fig. 9). The elemental distributions within

different pigment agglomerates were again determined using EDX analysis to assess particle homogeneity (Fig. 10). The EDX results show that the general chemical composition

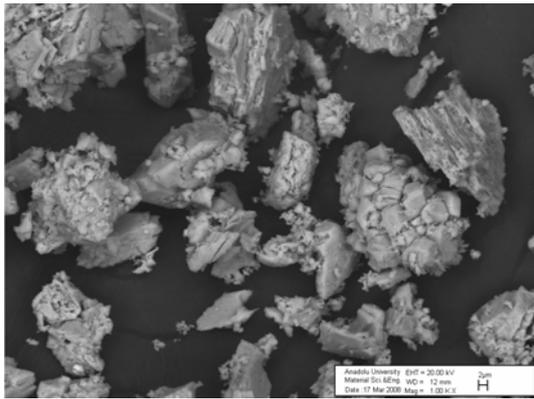


Fig. 9. SEM image of Co-gahnite powder (GCo8) calcined at 1400 °C.

of Co-gahnite pigments varies between 59-66 wt.% for Al₂O₃, 4-6 wt.% for CoO and 30-34 wt.% for ZnO. The EDX mapping of Co, Zn and Al in two GCo8 pigment agglomerates is shown in Fig. 11, indicating a homogeneous distribution of Al, Zn and Co elements across all regions of both agglomerates.

Pigment technical performance

In order to determine their technical performance, we added the pigments to a glaze and a porcelained tile body and we fired them at 1050 °C and 1200 °C, respectively. As expected from the appearance of the original Ni-gahnite pigment powder, the colour results in a yellow shade in the glaze and is not technically interesting. As indicated by Lorenzi *et al.* [4] the low crystallinity of the Ni-gahnite pigment and the formation of a small amount of NiO affect the pigment stability and cause an unstable colouration in the glaze.

In the case of the Co-gahnite pigments, various shades

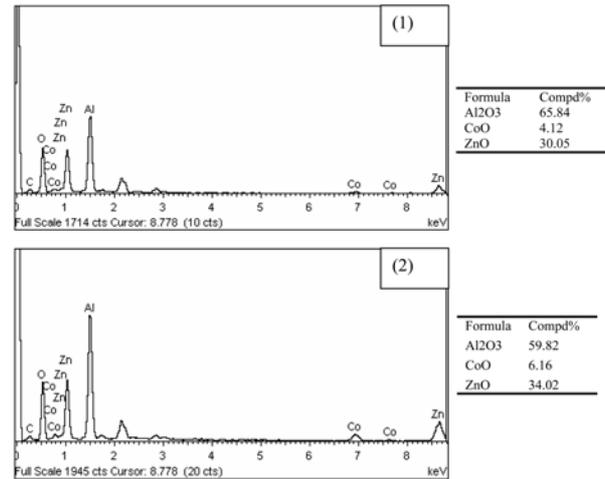
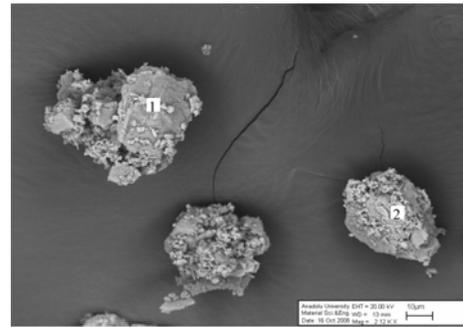


Fig. 10. EDX spectra of pigment agglomerates (GCo8) calcined at 1400 °C.

of blue were obtained in the transparent double firing glaze. By contrast, in the porcelained tile body the pigments gave a less intense blue colour because the porcelained tile body is opaque and caused a colour dilution. The colour parameters for the transparent glaze and the porcelained

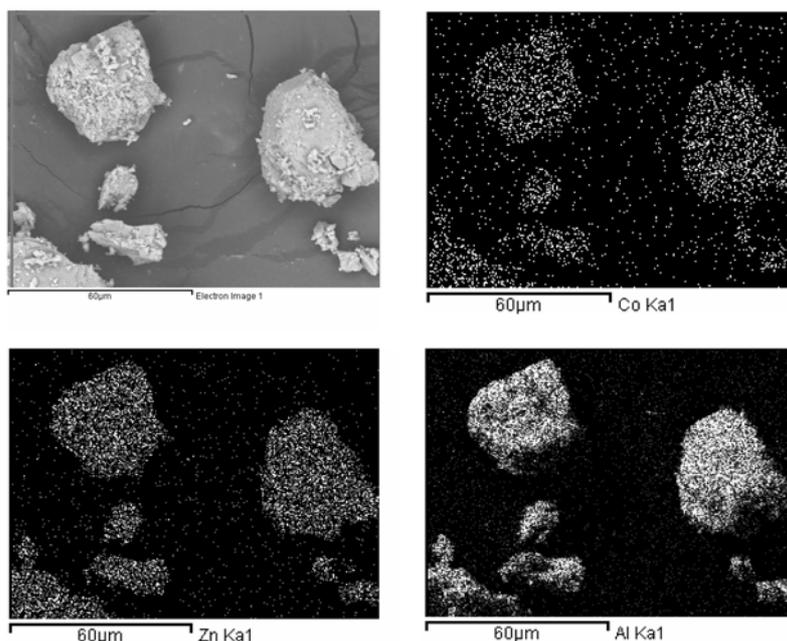


Fig. 11. EDX mapping of Zn, Al and Co elements in two different pigment agglomerates GCo8 calcined at 1400 °C.

Table 5. Colour parameters of coloured glazes and porcelained tiles containing 5 wt% Co-gahnite pigments

Code	In transparent glaze					In porcelained tile				
	L*	a*	b*	C*	h	L*	a*	b*	C*	h
GCo1	67	3.6	-24.1	24.3	278.5	63	-5.5	-10.2	11.6	241.6
GCo2	61	2.1	-32.8	26.8	274.4	63	-5.4	-12.1	11.8	242.7
GCo3	59	1.6	-37.7	27.1	276.4	57	-5.9	-15.0	16.1	248.5
GCo4	62	2.7	-26.2	29.2	275.3	62	-5.7	-9.5	11.1	238.9
GCo5	75	-3.7	-22.5	22.8	260.5	63	-5.3	-9.1	10.9	240.5
GCo6	70	-3.2	-29.8	27.0	263.2	67	-3.4	-4.6	5.8	233.5
GCo7	65	-1.3	-33.5	33.6	267.8	52	-6.5	-21.1	22.1	252.8
GCo8	56	-3.6	-39.5	39.7	275.3	54	-6.4	-19.4	20.4	251.7
GCo9	53	-4.2	-35.6	33.8	276.7	54	-5.3	-17.1	17.9	252.6

tiles containing Co-gahnite pigments are listed in Table 5. The intensity of the blue colour increased as the Co content increased. The colour properties improved with the addition of mineraliser to pigments GCo7, GCo8 and GCo9. The GCo8 pigment, prepared with CaF_2 , gives an intense and bright blue colour that has $L^*a^*b^*$ values of 56, -3.6, and -39.5, respectively, and a C^* value of 39.7 in the transparent glaze. The GCo7 pigment, prepared with NaF, has an intense blue colour that has $L^*a^*b^*$ values of 52, -6.5, -21.1, respectively, and a C^* values of 22 in the porcelained tile.

XRD patterns of the double firing glazes were evaluated in order to determine the pigment thermal stability (Fig. 12). The main crystalline phases in the coloured glaze include gehlenite ($\text{Ca}_2\text{Al}_2\text{SiO}_7$; JCPDS file no. 035-0755), sodium silicate ($\text{Na}_6\text{Si}_8\text{O}_{19}$; JCPDS file no.037-0186) and gahnite (ZnAl_2O_4). In addition to the crystalline phases, a glassy phase was observed consistent with the high background and characteristic hump in the 20-40° range of the diffraction patterns. The XRD results and glaze colour properties demonstrated that the Co-gahnite pigments can withstand molten glazing at high temperatures without any colour deterioration.

Conclusions

We have discussed the production and characterisation of Ni and Co-gahnite pigments fabricated using ZnO powder. We used the ZnO powder obtained from metal slags to produce gahnite pigments - in this manner, we converted a secondary product into a value-added product (pigments) for use in the ceramics industry.

Ni-gahnite pigments have a less intense blue-green colour and heterogeneity in their chemical composition, rendering them unsuitable for the ceramics industry. On the other hand, we were able to successfully prepare blue Co-gahnite pigments by using ZnO powder. Additionally, the Co-gahnite pigments exhibited stable colour properties in the double fired transparent glaze and porcelained tile body applications. The transparent glazes exhibited different shades of blue depending on the Co content and added mineralisers. Co-gahnite pigments with 0.15 mol% Co content and CaF_2 exhibit an intense blue colour. Since the blue

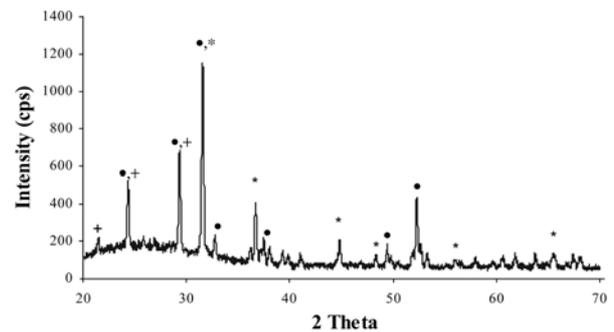


Fig. 12. XRD patterns of glazes containing 5 wt.% pigment (GCo3) and fired at 1050°C. (●: $\text{Ca}_2\text{Al}_2\text{SiO}_7$ (035-755), +: $\text{Na}_6\text{Si}_8\text{O}_{19}$ (037-0186) and *: ZnAl_2O_4 (05-0669))

Co-gahnite pigments use recycled material and less Co, they are an environmentally friendly alternative to commercial Co-aluminate spinel pigments.

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