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Synthesis of black ceramic pigments from secondary raw materials

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Abstract

Black ceramic pigments were prepared from industrial wastes as raw materials, namely, Cr/Ni-rich sludge generated from Cr/Ni plating and Fe-rich galvanizing sludge generated during steel wiredrawing. The pigment was based on the chrome–iron–nickel black spinel (Ni,Fe)(Fe,Cr)$_2$O$_4$ catalogued as 13-50-9 in the DCMA classification and prepared by the common solid-state reaction method, under optimal formulation and processing conditions. The characterised synthesised pigments were tested in typical ceramic glazes and ceramic bodies. Optimal colour development was achieved when the spinel compound with the three elements Fe, Ni and Cr was the major phase formed. This situation was obtained for mixtures in which the amount of Cr/Ni-rich sludge varied between 50 and 75%. The colouring properties were similar to those imparted by a commercial black pigment.

Keywords: Black ceramic pigments; Iron–nickel–chromium spinel; Industrial sludges; Recycling

1. Introduction

Both synthetic and inorganic black pigments are widely used in the ceramics industry as colourants either for glazes and for ceramic bodies. Indeed, ~25% of pigments used in the ceramic industry are black and these are obtained from two main crystalline structures, namely, hematite and spinel [1]. Commercial black pigments normally have a spinel structure, owing to its higher stability and are derived from iron–cobalt–chromite (Fe,Co)(Fe,Cr)$_2$O$_4$ (DCMA 13-40-9) and chrome–iron–nickel (Ni,Fe)(Fe,Cr)$_2$O$_4$ (DCMA 13-50-9) black spinels [1,2]. However, it is easy to find several industrial pigments which contain several other cations, such as Mn. The DCMA catalogue also lists Co-free black spinels such as CuCr$_2$O$_4$ (13-38-9) and (Fe,Mn)(Fe,Mn)$_2$O$_4$ (13-41-9) as black pigments [2].

There has been a great interest within the ceramic industry in the development of high stability pigments that show intense tonality and which satisfy both technological and environmental requirements [3]. While the first step in pigment production involves the judicious choice of raw materials, current trends are towards alternative and less expensive raw materials [4–6]. Normally, such raw materials are of high chemical purity, but less pure raw materials are often tried since these can prove to display adequate stability and are less expensive [5–7]. Selected industrial wastes have been investigated for this purpose and, in particular, metal-rich sludges [8–12]. Indeed, industrial processes such as galvanizing or surface coating consume large amounts of water, yielding high volumes of sludge which requires both environmental and economic treatments [13]. This paper concerns spinel based pigments prepared by combining two different sludges, namely, Cr/Ni-rich sludge generated from Cr/Ni plating and Fe-rich galvanizing sludge generated during steel wiredrawing.

The above-mentioned spinel has a cubic structure involving two dissimilar cationic sites, one tetrahedral, the other

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octahedral. The unit cell contains 32 anions and thus form 64 tetrahedral interstices, of which eight are occupied by cations and 32 octahedral interstices, of which 16 are also occupied by cations. The distribution of metal ions in the structure is such that each oxygen atom is surrounded by four metal atoms in the form of a slightly distorted tetrahedron; the oxygen atoms do not form a perfect face-centred cubic sub-lattice [14,15]. The structure–field map for AB_2O_4 or $B(A,B)_2O_4$ shows that the spinel structure is stable for $0.06 < r_{Tet.} < 0.1$ nm and $0.055 < r_{Oct.} < 0.1$ nm, where r is the ionic radius. As these requirements are satisfied by the transition metals of the first period, the spinel structure is the most common structure found in the materials used as ceramic pigments and is very suitable for ionic substitution [14]. The formulations which simultaneously formed the correct spinel structure and which gave high intensity black pigments belong to the complex system $CoO-NiO-MnO-CuO-FeO-Fe_2O_3-Cr_2O_3-Mn_2O_3-V_2O_3-Al_2O_3$. However, oxides, other than those cited, may also be present, although in minor amounts (not exceeding $\approx 3\%$) [14].

2. Experimental

2.1. Raw materials and formulations

The galvanizing sludge from Cr/Ni plating (sludge C) and Fe_2O_3-based sludge (sludge F) generated from steel wiredrawing industrial wastes were collected and analysed.

Their characterisation included determinations of chemical composition (XRF, Philips X'UNIQUE II) while the main crystalline phases were identified by X-ray diffraction (XRD, Rigaku Geigerflex D/max – Series). Toxicity levels were accessed by leaching tests performed according to DIN-38414-S4 so as to determine the metal's mobility under neutral conditions (using distilled water).

2.2. Preparation and characterisation of pigments

The starting batch formulations of the pigments are shown in Table 1. In order to obtain fine, homogeneous slurries, the mixtures were prepared by wet ball-milling in ethanol for 1 h. The prepared suspensions were dried at 110 °C and then calcined in an electric kiln at temperatures varying between 1000 and 1100 °C (3 h dwell time and 5 °C/min heating rate); the calcined powders were manually disintegrated.

Table 1
Pigments' formulations (wt%) and corresponding codes

Reference	Formulation [wt%]	
	C sludge	F sludge
Bs-100C	100	0
Bs-75C25F	75	25
Bs-50C50F	50	50
Bs-25C75F	25	75
Bs-100F	0	100

Bs = black spinel, 75C25F gives the formulation and means 75% of C sludge and 25% of F sludge.

Preliminary characterisation involved the identification of the main crystalline phases formed upon firing using powder XRD, microstructure and chemical homogeneity using scanning electron microscopy (SEM – Hitachi, SU 70) with energy-dispersive X-ray spectroscopy (EDX – Detector: Bruker AXS, software: Quantax), particle size distribution (Beckman Coulter LS 230) and measurement of the CIE-$L^*a^*b^*$ coordinates under illuminant D_{65} and 10° standard observer [4] from the diffuse reflectance spectra of the pigments recorded on a Jasco V-560 UV–vis spectrophotometer, using MgO as reference.

Finally, to evaluate the colour development in common products, the pigment was added (5%) to commercial glazes and (10%) to ceramic bodies:

(i) a transparent and lustrous, lead-free glaze, referred to as TSG, with SiO_2, Al_2O_3, B_2O_3, CaO as main constituents >8%, 2–8% Na_2O and <2% K_2O fired at 1050 °C;
(ii) an opaque and gloss glaze, referred as OSG, with SiO_2, B_2O_3, ZrO_2 as main constituents >8%, 2–8% Al_2O_3, Na_2O, CaO, and <2% K_2O, MgO, ZnO, CoO also fired at 1050 °C;
(iii) a transparent gloss glaze, referred as TSHG, with SiO_2, Al_2O_3, CaO as main constituents >8%, 2–8% B_2O_3, MgO, K_2O, Na_2O, and <2% ZrO_2, BaO, fired at 1200 °C;
(iv) a "porcellanato" ceramic body, referred to as CB, also fired at 1200 °C.

For comparison purposes, a commercial, black iron–nickel–chromium spinel pigment (Bc-pigment) was also evaluated.

The mixtures were prepared by wet ball-milling for 30 min and were dried at 110 °C. As in the preparation of the pigments, the use of ethanol accelerated the drying process. The ensuing powders were then used to press pellets or buttons (Ø = 2.5 cm) that were fired (30 min dwell time and 5 °C/min heating rate) in an electric furnace in air.

3. Results and discussion

3.1. Waste characterisation

Table 2 gives the average chemical composition of the wastes and of the black commercial pigment, while the full characterisation of the sludges is detailed elsewhere [10,11]. The F sludge mainly composed Fe_2O_3 (up to 60%); zinc and calcium were the prevalent minor elements, the latter being incorporated during the wastewater treatment (lime additions). The C sludge was produced by the physical–chemical treatment of wastewaters generated in a Ni/Cr plating plant. Accordingly, NiO and Cr_2O_3 were the main constituents, but significant amounts of SiO_2, PbO and CuO were also detected. The metal species when combined, form nitrogen, oxygen, hydrogen, sulphur and carbon-containing compounds. Their chemical diversity requires careful sampling and homogenising to ensure consistency; indeed, previous work showed

Table 2
Average chemical composition of the wastes and that of the commercial pigment (as determined by XRF)

Component (wt%)	C sludge	F sludge	Bc-pigment
Fe_2O_3	1.13	62.1	32.1
NiO	24.1	0.01	31.6
Cr_2O_3	9.57	0.09	30.6
CuO	3.32	0.01	0.03
MnO	0.00	0.37	0.16
Al_2O_3	0.49	0.14	1.99
ZnO	1.87	2.96	0.08
SiO_2	6.81	0.41	0.24
CaO	0.30	5.31	0.06
PbO	8.88	0.00	0.00
P_2O_5	1.08	3.09	0.00
MgO	0.00	0.21	0.41
Na_2O	2.58	2.61	0.00
K_2O	0.16	0.00	0.00
TiO_2	0.00	0.01	0.00
V_2O_5	0.00	0.02	0.00
SnO_2	0.08	0.00	0.00
BaO	0.00	0.00	0.55
ZrO_2	0.00	0.00	0.03
SrO	0.00	0.00	1.34
Co_3O_4	0.00	0.00	0.65
SO_4	2.39	0.11	0.06
Cl	0.00	1.40	0.19
LOI	37.2	21.2	–

LOI = loss of ignition at 1000 °C.

significant variations accompanied by processing changes [16]. Such variations were found to be more prevalent in the case of sludge C.

Table 3 shows the average chemical composition of the eluates obtained from the water leaching of sludges according to DIN-38414-S4. The values in bold correspond to potential toxicity. The concentration limits used to define the hazardous nature of the leachates are defined by European Council Decision 2003/33/EC; these are also given in Table 3. Of the metallic species, nickel displayed the highest leachability and is responsible for the hazardous nature of sludge C, whereas sludge F was classified as non-hazardous and can therefore be disposed of in non-special landfills and, consequently, at lower cost.

Table 3
Leaching of the sludges according to DIN-38414-S4

Parameter	Material		
	C sludge	F sludge	Concentration limit
pH	6.80	6.67	<4 or >13
Conductivity (mS/cm)	5.44	15.8	50–100
Cr^{6+} (mg/l)	0.40	–	0.1–0.5
Total Cr (mg/l)	0.690	<0.05	0.5–5
Pb (mg/l)	<0.06	0.23	0.5–2
Cu (mg/l)	0.328	0.026	2–10
Zn (mg/l)	0.058	0.215	2–10
Ni (mg/l)	**60.3**	0.12	0.4–1.0

Concentration limits used to define the hazardous nature of the leachates, as defined by the European Council Decision 2003/33/EC, are also given.

3.2. Pigment preparation and characterisation

Table 1 shows the prepared formulations. Sludge C was used as a source of nickel and chromium species, while sludge F was the main source of iron. In order to explore the consequences of the compositional complexity of the sludges, a complete range of mixtures (from 0 to 100% of sludge C) was prepared.

Both extreme formulations, Bs-100C and Bs-100F, corresponding to the single use of each sludge, did not reveal the desirable trevorite phase after calcination at 1000 °C. The XRD spectra (Fig. 1) showed the prevalence of hematite (Fe_2O_3) in Bs-100F (the sample fully composed of sludge F), while the franklinite spinel ($ZnFe_2O_4$) was the secondary phase (Table 4). These two phases were responsible for the undesirable brown colour of the product. The Bs-100C pigment was more complex, with the major phases being nichromite ($NiCr_2O_4$) and nickel oxide (NiO), the former being responsible for the greenish grey hue of the product; Table 4 shows the minor phases.

Amongst a large variety of spinel structures involving the relevant elements in the system, trevorite ($Fe(NiFe)O_4$) seems to be the one that better fits the XRD patterns. This is explained by the fact that Ni^{2+} and Fe^{3+} are the dominant divalent and trivalent species in the mixtures. Accordingly, all formulations involving a combination of the two sludges revealed the presence of trevorite as the main phase. In particular, the Bs-50C50F pigment displayed maximum peak intensity in the XRD spectra (Fig. 1), while hematite was detected in minor (vestigial) amounts.

Fig. 2 shows the XRD spectra of Bs-50C50F pigments that were calcined at different temperatures (1000 and 1100 °C). In the same figure, the spectrum of the commercial black pigment is also shown for comparison. $(Fe,Ni)(Ni,Fe,Cr)_2O_4$ seems to be the dominant phase, in which the Ni:Fe:Cr molar ratio of ~1:1:1 was achieved, as confirmed by XRD and EDX (Table 5); previous studies [17] have shown that the best black pigments are obtained when this particular ratio was obtained. As expected, increasing the firing temperature improved the reactivity and, as a consequence, the amount of unreacted components reduced, while the crystallization degree of the formed spinel increased. The similarity of the XRD spectra of the Bs-50C50F formulation calcined at 1100 °C and that of the commercial pigment is remarkable. However, it must be emphasised that the commercial pigment required a higher sintering temperature (at least 1200 °C including the use of added mineralising/fluxing agents) [17], in order to develop desirable chromatic properties.

Table 4 also gives the estimated values of the unit cell parameter of the sintered powders. Those of the commercial pigment differ significantly from those of the sludges-based pigments, indicating that the spinel in the commercial pigment is probably not trevorite probably due to the higher amount of chromium oxide in the commercial formulation (Table 2). Theoretically, the lattice parameter of the iron–nickel–chromium spinel with Fe:Ni:Cr = 1:1:1 was 8.302 Å, a value that is close to that measured for the commercial pigment

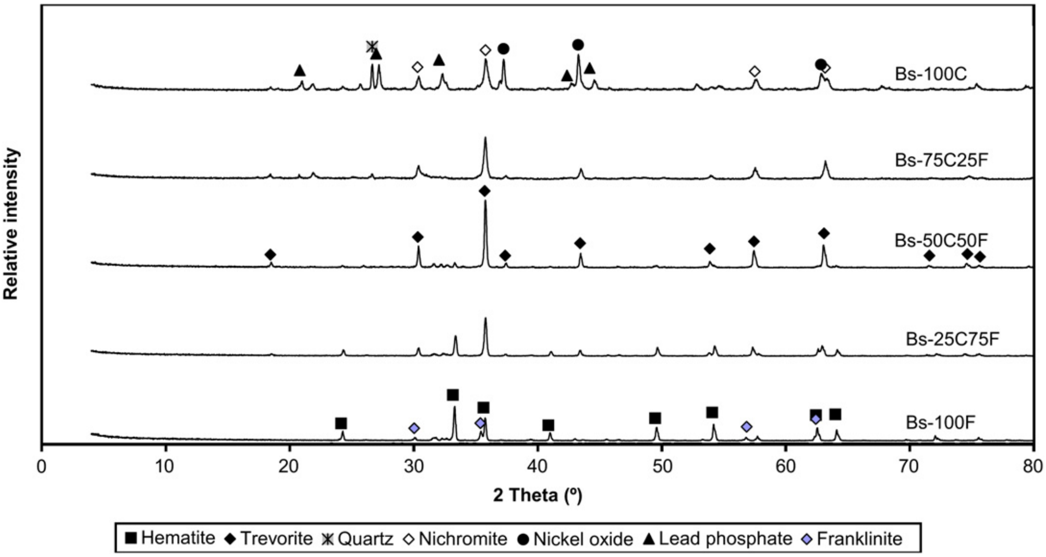

Fig. 1. XRD patterns of pigments calcined at 1000 °C.

Table 4
Phases identified by XRD and unit cell parameter of the formed cubic spinel ($a = 8.337$ Å; 8.3225 Å for trevorite, 8.302 Å for $(Fe_{0.5}Ni_{0.5})(Ni_{0.25}Fe_{0.25}Cr_{0.5})_2O_4$ spinel) on the pigments

Reference	a (Å) for $(Fe,Ni)(Ni,Fe,Cr)_2O_4$	Phases identified by XRD	
		Major phases	Minor phases
Bs-100C/1000 °C	–	Nickel oxide, nichromite	Quartz, lead-rich phases, olivine
Bs-75C25F/1000 °C	8.322	Trevorite[a]	Quartz, lead-rich phases, nickel oxide or rich-nickel phases
Bs-50C50F/1000 °C	8.339	Trevorite	Hematite, calcium sulphide phosphate
Bs-50C50F/1100 °C	8.349[a]	Trevorite	Hematite, calcium sulphide phosphate (traces)
Bs-25C75F/1000 °C	8.347	Trevorite	Hematite, halite, chlorapatite
Bs-100F/1000 °C	–	Hematite	Franklinite, halite, chlorapatite
Bc-pigment	8.308	$(Fe_{0.5}Ni_{0.5})(Ni_{0.25}Fe_{0.25}Cr_{0.5})_2O_4$ spinel	–

For comparison, the Bc-pigment was also characterised.

[a] Less accurate determination, due to the complex shape of the peak.

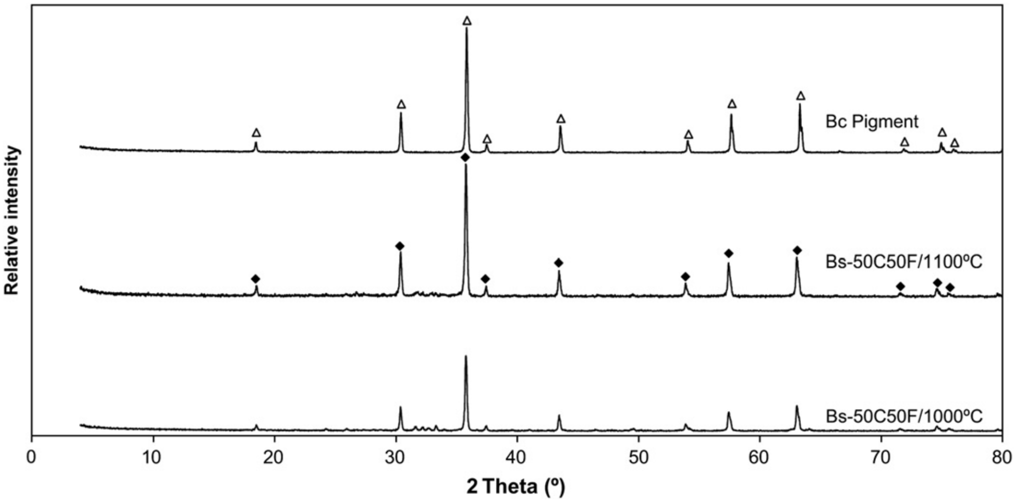

Fig. 2. XRD patterns of Bs-50C50F pigments calcined at 1000 and 1100 °C and of the black commercial Bc-pigment (◆ = phase identified as trevorite; △ = phase identified as nickel, iron, chromium spinel).

Table 5
EDX analysis of some grains showed in the SEM micrograph (see Fig. 3) of the Bs-50C50F/1000 °C (grains A–C) and of the Bc-pigment (grains D and E)

Elements (mol.%)	A grain	B grain	C grain	D grain	E grain
Fe	17.1	14.3	17.3	12.0	10.4
Ni	5.26	4.18	5.42	11.2	10.0
Cr	2.51	2.21	2.86	11.8	11.0
Zn	3.14	2.74	3.46	–	–
Cu	1.32	1.03	1.33	–	–
P	–	–	0.56	–	–
Ca	–	–	1.31	–	–
O	70.6	75.6	67.8	65.0	68.6
Molar ratios					
Fe:Ni:Cr	6.81:2.10:1	6.47:1.89:1	6.05:1.90:1	1.02:0.95:1	0.95:0.91:1
Zn:Cr	1.25:1	1.24:1	1.21:1	–	–
Cu:Cr	0.53:1	0.47:1	0.47:1	–	–
(Fe + Cr): (Ni + Zn + Cu)	2.02:1	2.08:1	1.98:1	2.12:1	2.14:1

Molar ratios of relevant elements were also determined.

(8.308 Å). The dimensions of the cubic cell parameter decreased with increasing proportion of sludge C, since the formed spinel tended to incorporate higher amount of chromium ions.

From the above stoichiometry, the best black spinel should be obtained when:

(i) the ratio of Fe:Ni:Cr = 1:1:1, achieved by mixing 87.5% sludge C and 12.5% sludge F to set the Fe:Cr ratio at 1:1; in this situation, the molar ratio of Ni was 2.8 which is compatible with the formation of reasonable amounts of secondary nickel-rich phase (probably NiO);
(ii) the molar ratio of trivalent:divalent elements should be 2:1, achieved by mixing 52.5% sludge C and 47.5% sludge F; in this situation, the amount of secondary phases is minimised, but the black hue obtained is not as strong as in the previous case.

Fig. 1 shows the maximum XRD peak intensity and minimum of sharpness for trevorite Fe(NiFe)O_4 in the Bs-50C50F sample because the trevorite stoichiometry was close to this composition. For Bs-25C75F, a large amount of unreacted hematite was detected, while for Bs-75C25F, the best pigment, the intensity and sharpness of the trevorite peaks decrease, probably due to a mixture of trevorite and nickel-rich phases. Indeed, the EDX data for Bs-50C50F (Table 5) suggest this possibility, since grain analysis indicates a high proportion of iron in this sample (Fe/Ni ~ 3). Trevorite peaks might also superimpose those of nichromite or NiO (if the amount of sludge C is >52.5%), but Eppler [18] suggests that the ternaries $NiCr_2O_4$–$NiAl_2O_4$–$NiFe_2O_4$ and $NiFe_2O_4$–$NiMn_2O_4$–$NiCr_2O_4$ were single-phase spinels. Table 5 also shows that the (Fe + Cr):(Ni + Zn + Cu) ratio was ~2 in all selected particles, which is predictable when one single spinel is the dominant phase formed.

SEM characterisation of the synthesised pigments (Fig. 3a) revealed an homogeneous microstructure, mainly composed of particles of 0.5–1.5 µm in size, with a regular octahedral shape typical of the spinel. Furthermore, the spinel seems to be a single crystalline phase, confirming the stability of the calcined pigments and indicating that most impurities present

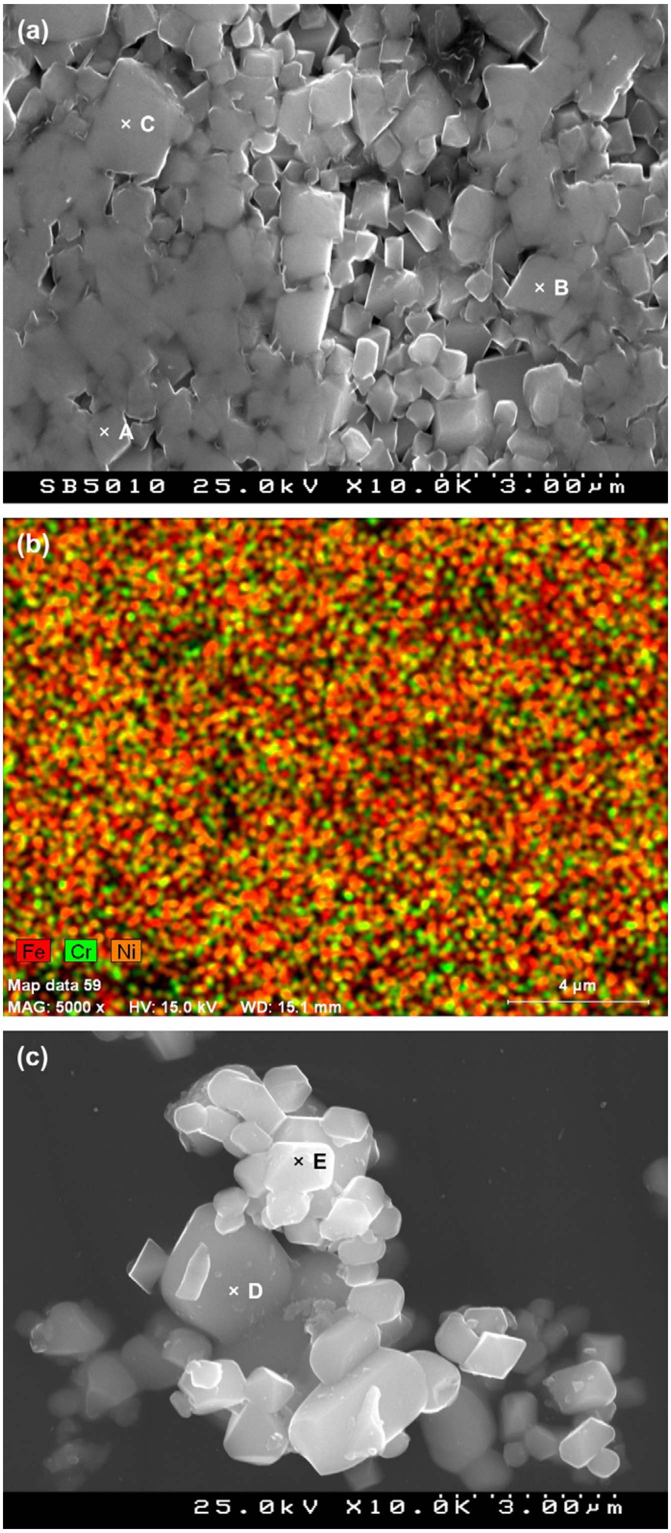

Fig. 3. (a) SEM micrograph of the Bs-50C50F button fired at 1000 °C. EDX analysis of the new pigment was performed on signed grains (see Table 5). (b) EDX maps of Cr, Fe and Ni in the Bs-50C50F pigment and (c) typical microstructure of the Bc-commercial pigment.

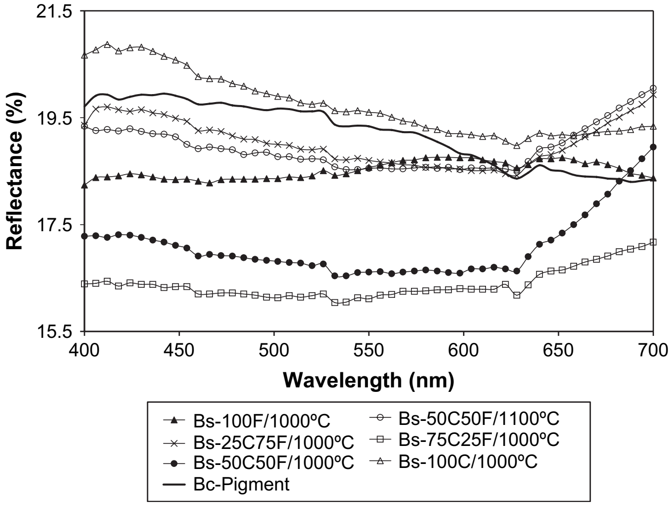

Fig. 4. Visible diffuse reflectance spectra of the new pigments. For comparison, the commercial pigment was also tested.

Table 6
$L^*a^*b^*$ values for the sintered pigments and the applications (glazes + 5 wt% of pigment and ceramic body + 10 wt% of pigment)

Reference	Product type	Colour parameters			Hue
		L^*	a^*	b^*	
Bs-100C/ 1000 °C	Pigment	26.0	0.5	5.3	Dark olive green
	TSG	27.2	−1.9	2.8	Dark green
	OSG	58.4	−2.5	5.2	Light greenish grey
	TSHG	35.6	−4.0	1.4	Green
	CB	38.1	1.6	5.9	Ochre brown
Bs-75C25F/ 1000 °C	Pigment	21.5	2.9	3.1	Dark brown
	TSG	24.7	−0.5	1.5	Black
	OSG	50.6	−0.5	2.2	Grey
	TSHG	29.7	−1.0	1.3	Black
	CB	33.7	1.7	4.5	Brownish grey
Bs-50C50F/ 1000 °C	Pigment	20.4	3.0	0.9	Dark brown
	TSG	25.4	−0.6	2.0	Black
	OSG	51.5	0.1	2.2	Grey
	TSHG	27.0	−1.0	0.7	Black
	CB	31.8	0.8	2.1	Grey
Bs-50C50F/ 1100 °C	Pigment	24.9	1.8	0.0	Dark brown
	TSG	24.4	−0.1	1.4	Black
	OSG	52.2	0.3	2.3	Grey
	TSHG	28.8	−1.9	0.7	Dark brown
	CB	33.2	1.8	3.6	Brown
Bs-25C75F/ 1000 °C	Pigment	24.8	1.2	−0.6	Dark brown
	TSG	26.6	−0.2	4.1	Dark yellow
	OSG	54.3	0.8	4.8	Yellowish grey
	TSHG	32.7	1.1	9.8	Ochre
	CB	31.1	0.3	0.6	Dark grey
Bs-100F/ 1000 °C	Pigment	27.3	0.4	−1.5	Dark grey
	TSG	38.5	7.5	20.3	Ochre
	OSG	71.7	1.8	20.4	Light orange
	TSHG	24.9	−0.5	−2.0	Brown
	CB	32.9	0.2	−1.1	Black
Bc-pigment	Pigment	28.8	−1.2	0.7	Black
	TSG	24.7	−1.3	1.0	Black
	OSG	34.2	−1.0	−0.8	Grey
	TSHG	26.8	−0.8	1.2	Black
	CB	31.5	0.9	2.5	Black

TSG and OSG glazes were fired at 1050 °C, while TRHS glazes and ceramic bodies were fired at 1200 °C.

in the wastes were completely incorporated into the spinel structure. As predicted, EDX analysis (Table 5) showed major quantities of Fe and Ni, but Cr, Cu and Zn were detected as secondary elements. This also confirms the homogeneity of the sample, as proven by the EDX maps of Cr, Fe and Ni (Fig. 3b).

The microstructure of the commercial pigment was very similar to that of the synthesised pigments, as revealed by Fig. 3c. It comprised mainly 0.2–2.7 μm sized particles of octahedral structure. EDX analysis (grains D and E in Table 5) revealed the presence of Fe:Cr:Ni in ∼1:1:1 molar ratio, confirming the expected high purity degree of the commercial pigment. Moreover, the relative amount of Fe was lower than in the synthesised pigments.

UV–vis spectroscopy (Fig. 4) showed an absorption band across the visible wavelength range that was characteristic of low reflectance systems. Maximum reflectance was ∼20%. The Bs-75C25F/1000 °C pigment displayed optimal reflectance and, whilst the behaviour of Bs-50C50F/1000 °C pigment was very similar, calcination at a higher temperature (Bs-50C50F/1100 °C pigment) lowered its absorption ability.

Table 6 shows the colorimetric coordinates of the sintered pigments and of glazes and ceramic bodies into which they were inserted. As previously mentioned, three different glazes (5% pigment) and a "porcellanato" ceramic body (10% pigment) were used. Fig. 5 shows that some of the $L^*a^*b^*$ coordinates were close to zero.

The common washing step in the preparation of the pigments was not undertaken since no significant amounts of soluble salts were expected due to the absence of added mineralisers. However, the leached concentrations (Table 7) of some toxic species (e.g. Ni) were above the limit for inertness, as defined in Table 3, and recommend its implementation in further preparations. The commercial pigment was inert, presumably due to the use of careful washing.

The colours developed by the extreme formulations, Bs-100C and Bs-100F, were substantially distinct. Bs-100C tended to give intense green-olive hue in glazes and an ochre hue in ceramic bodies, while Bs-100F developed a lighter brown hue in glazes and a reasonably good black hue in a ceramic body (Table 6). However, the use of the latter pigment improved the fusibility of the mixtures and developed bubbles, the size of which was greater in ceramic bodies, while the formation of pinholes was the dominant defect in the case of glazes. This kind of defect was not visible in the case of the Bs-100C pigment which may be attributed to the chemical nature and stability of the main phases present The dominant nickel–chromium spinel in Bs-100C showed high stability in the glaze matrix, while hematite (dominant in Bs-100F) is known to have a lower thermal/compositional stability in glazes. Moreover, gas formation was expected to occur due to the reduction of Fe_2O_3, which is a known expansive reaction that is often explored to obtain lightweight bodies [19].

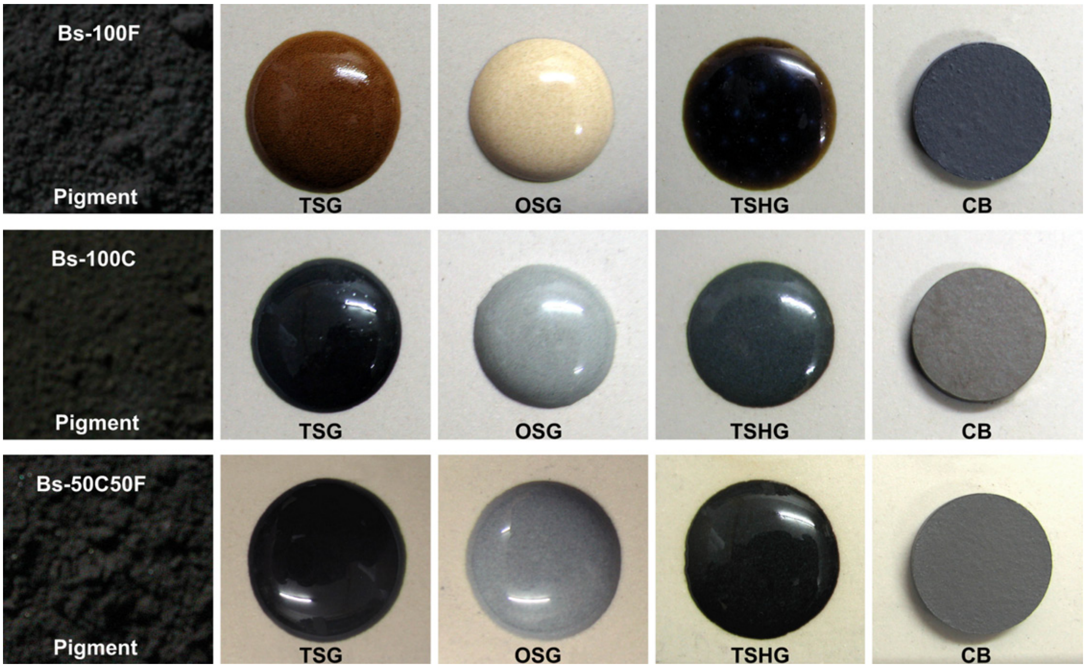

Fig. 5. Colours developed by the pure pigments calcined at 1000 °C (left), by the glazes (centre) containing 5 wt% pigments, and by ceramic bodies containing 10 wt% pigments.

All of the sludge combinations developed a reasonably strong black hue. Formulations containing 50–75% sludge fired at 1000 °C gave optimal colour; however, bluish spots were apparent in the case of the TSHG glaze, perhaps due to the higher fusibility of the mixture; this aspect deserves further refinement.

The commercial pigment performed better in all matrixes as indicated by the hue column in Table 6. Particularly interesting was the L^* value for the zirconia opaque glaze OSG. However, the Bs-50C50F formulation calcined at 1100 °C showed strong bubble formation (pinholes) denoting clear signs of overfiring without visible improvement of colour once added to glazes (Table 6 and Fig. 4).

Results can be improved via the amount of chromium in the pigment, by the formation of the iron–nickel–chromium partial inverse spinel, $(Fe_{0.5}Ni_{0.5})(Ni_{0.25}Fe_{0.25}Cr_{0.5})_2O_4$. This compound has been proposed by different authors [14,17] and is present in the commercial pigment.

Tighter control of the grain size distribution, by controlled milling of the most promising formulations, may prove

Table 7
Leaching of relevant species from the Bs-50C50F/1000 °C pigment, determined according to the DIN-38414-S4 protocol

Parameter/material	Bs-50C50F/1000 °C	Bc-pigment
pH	6.94	7.46
Conductivity (mS/cm)	4.25	0.220
Cr^{6+} (mg/l)	n.d.	n.d.
Total Cr (mg/l)	<0.05	0.260
Pb (mg/l)	1.48	<0.06
Cu (mg/l)	<0.025	<0.025
Zn (mg/l)	0.179	0.130
Ni (mg/l)	32.08	0.055

For comparison, Bc-pigment was also tested. Values signed in bold are over the legal limits of harmfulness. (n.d. = not detected).

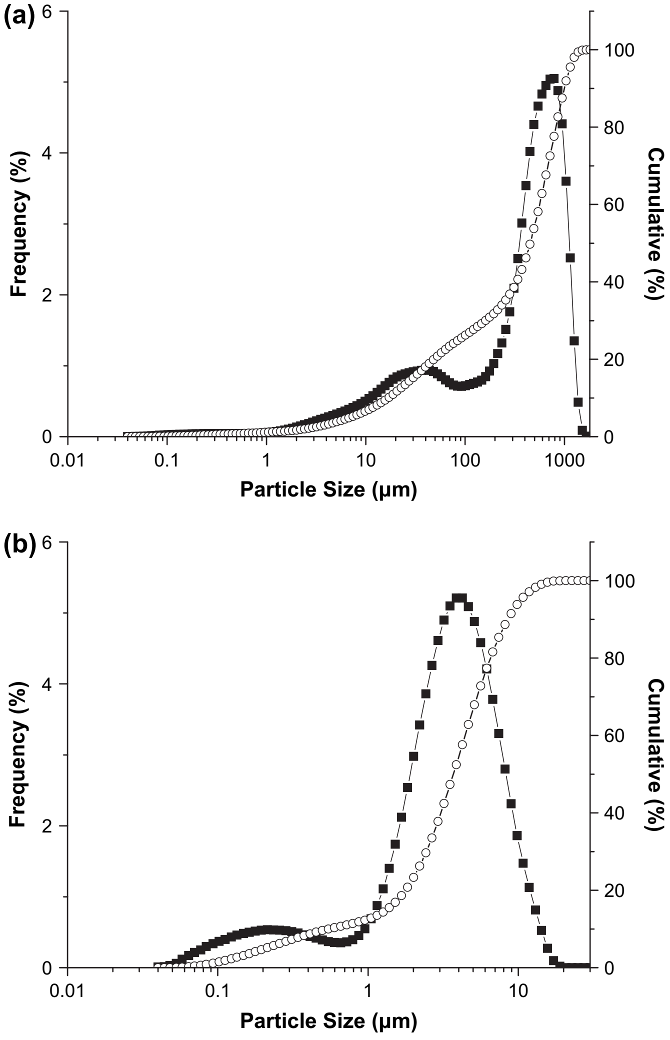

Fig. 6. Grain size distribution of pigments: (a) Bs-50C50F/1000 °C and (b) commercial Bc.

Table 8
Particle size distribution of the new pigments calcined at 1000 °C and of the commercial pigment

Pigments	Grain size (μm)				
	<100%	>75%	>50%	>25%	>10%
Bs-100C	1660	491.0	310.9	100.9	8.75
Bs-75C25F/1000 °C	256.80	39.09	17.51	6.14	0.90
Bs-50C50F/1000 °C	1822.0	750.5	452.7	85.93	16.81
Bs-50C50F/1100 °C	594.9	220.6	107.2	29.29	7.44
Bs-25C75F/1000 °C	1143	330.7	57.47	9.06	3.62
Bs-100F/1000 °C	2000	584.1	229.1	40.56	11.68
Bc-pigment	22.73	5.87	3.70	2.12	0.54

advantageous, since the synthesised pigments were simply manually disintegrated after calcination, and therefore showed much coarser particles than the commercial pigment (see Fig. 6 and Table 8).

4. Conclusions

Pigments based on the chrome−iron−nickel partial inverse spinel $(Fe,Ni)(Ni,Fe,Cr)_2O_4$ formulated from industrial waste sludges generated from Cr/Ni plating and from steel wiredrawing were successfully prepared using a solid-state reaction method. The colour of the pigments is comparable to that of a commercial pigment. Optimal formulations were obtained by using 50−75% sludge C.

The work shows that it is possible to transform two wastes, one of which is hazardous, into a technically promising product. In addition, the process negates the potentially toxic components, by firing at high temperature.

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