



Evaluation of metal-ions containing sludges in the preparation of black inorganic pigments

W. Hajjaji, M.P. Seabra, J.A. Labrincha*

Ceramics and Glass Engineering Department, CICECO, University of Aveiro, 3810-193 Aveiro, Portugal

ARTICLE INFO

Article history:

Received 4 February 2010

Received in revised form 31 August 2010

Accepted 17 September 2010

Available online 25 September 2010

Keywords:

Waste valorization

Pigments

Spinel

Nichromite

Trevorite

ABSTRACT

Inorganic pigments were prepared from industrial wastes: galvanizing sludges resulting from Cr/Ni plating processes (S, G, and T) and a sludge generated from steel wiredraw process that is Fe-rich (F). These industrial wastes were characterized in order to determine the main compositional variations and discover their influence on the colour characteristics of pigments for glazes and ceramics. The toxic character was also investigated and established. Attempting to form the black spinel structure, several combinations of sludges were prepared and then calcined at 1000 °C. XRD and microscopy analysis confirmed the presence of nichromite for compositions with higher Ni amounts, while trevorite was detected in iron-rich formulations. The combination of S and F sludges (SF compositions) generates pigments with higher black colorimetric quality, which is similar to, and sometimes better than, a commercial black pigment. Pigments containing GF and TF sludges develop brown hues on glazes and on porcelain stoneware bodies, being this effect more evident upon industrial firing trials. The addition of minor amounts of cobalt or manganese enhances the black coloration, and might adjust some formulation deviations.

© 2010 Elsevier B.V. All rights reserved.

1. Introduction

The spinel structure has an $A^{II}B^{III}_2O_4$ form where divalent A^{2+} (Mg, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd and Sn) and trivalent B^{3+} (Al, Ga, In, Ti, B, Cr, Mn, Fe, Co, Rh and Ni) sites are occupied by metal ions in tetrahedral ($A^{2+}O_4$) and octahedral ($B^{3+}O_6$) interstitial positions [1–3]. The unit cell is composed of 32 cubic close-packed O^{2-} ions, which are located at the corners and in the center of the faces of 8 small cubes. Assembled, these cubes form a larger one with 56 atoms (general formula: $A_8B_{16}O_{32}$). In a normal spinel such as nichromite ($NiCr_2O_4$), A^{2+} ions occupy tetrahedral sites while B^{3+} ions assume octahedral coordination [4,5]. In inverse spinels like hematite ($FeFe_2O_4$) and trevorite ($Fe(Ni,Fe)O_4$), the tetrahedral sites are occupied by half of the B^{3+} ions. The other half of the trivalent species and all A^{2+} ions assume octahedral coordination [5–8].

In the ceramic industry, synthetic inorganic pigments are the current raw materials, being used to colour glazes, inks and even ceramic bodies. In particular, black pigments are extensively utilized, representing nearly 25 wt.% of the total consumption. Commercial formulations of black pigments are mostly based on the spinel structure: iron cobalt chromite ($Fe,Co)(Fe,Cr)_2O_4$ (DCMA 13-40-9), chrome iron nickel ($Ni,Fe)(Fe,Cr)_2O_4$ (DCMA 13-50-9), and manganese ferrite ($Fe,Mn)(Fe,Mn)_2O_4$ (DCMA 13-41-9). This

is explained by their high stability [9–12]. However, their synthesis is hard, and is difficult to obtain single phase systems and also to assure thermostability of formed phases [12–14].

Due to technological, commercial and environmental concerns there has been a great interest in developing pigments showing intense tonalities, at low cost, and that are environmentally-friendly. An innovative suggestion to decrease the price and, at the same time, to try to preserve natural resources was achieved by substituting wastes for pure reagents [15,16]. Obviously, the selection and preparation of wastes is fundamental to reach those objectives. In particular, the control of the amount of colouring is very important, to avoid unwanted changes on developed hues or creation of surface defects. This paper describes the use of distinct galvanizing sludges as sources of Ni and Cr. In the spinel formulation, the iron is introduced from another sludge, that is generated from the steel wiredraw process. Some of these wastes contain hazardous contaminants that constitute a threat to water, natural resources and human health. However, their use as raw materials of ceramic pigments neutralizes their harmful environmental effects, since the thermal treatment involved assures the desirable inertness [17]. Therefore, this process would be doubly environmentally beneficial as it both removes hazardous wastes from the environment and reduces the use of raw materials.

2. Experimental procedure

Galvanizing sludges from three Cr/Ni plating processes (named G, T and S) and a Fe_2O_3 -based sludge (sludge F) from

* Corresponding author. Tel.: +351 234370250; fax: +351 234370204.
E-mail address: jal@ua.pt (J.A. Labrincha).

Table 1
Tested formulations and main crystalline phases detected by XRD.

	GF1	GF2	GF3	TF1	TF2	TF3	SF1	SF2	SF3	GF5Co	GF5Mn	TF5Co	TF5Mn	SF2Co	SF2Mn
Raw materials (wt.%)															
Sludge G	85.0	72.3	60.0	–	–	–	–	–	–	69.5	69.5	–	–	–	–
Sludge T	–	–	–	50.0	35.9	25.0	–	–	–	–	–	33.5	33.5	–	–
Sludge S	–	–	–	–	–	–	83.0	60	48.5	–	–	–	–	49.0	49.0
Sludge F	15.0	27.7	40.0	50.0	64.1	75.0	17.0	40	51.5	25.5	25.5	61.5	61.5	49.0	49.0
Co ₃ O ₄	–	–	–	–	–	–	–	–	–	5.0	–	5.0	–	2.0	–
MnO ₂	–	–	–	–	–	–	–	–	–	–	5.0	–	5.0	–	2.0
Pigments' main crystalline phases (after calcination at 1000 °C)															
Trevorite	–	•	•	•	•	•	–	•	•	•	•	•	•	•	•
Nichromite	•	–	–	–	–	–	•	–	–	–	–	–	–	–	–
Hematite	–	–	–	–	–	–	•	–	•	–	–	–	–	–	–
Nickel oxide	•	–	–	–	–	–	•	–	–	–	–	–	–	–	–
Chloroapatite	•	•	•	•	•	•	•	•	•	•	•	•	•	•	•
Anhydrite	•	•	•	–	–	–	–	–	–	•	•	–	–	–	–

a steel wire drawing plant were collected and fully characterized. Main crystalline phases present were detected by X-ray powder diffraction (XRD) analysis, using a Rigaku Geigerflex D/MAX-B diffractometer (Bragg-Brentano geometry, CuK α radiation $\lambda = 1541 \times 10^{-10}$ m, 40 kV/30 mA, graphite monochromator, step 0.02°, velocity of 3° 2 θ /min.) between 4° and 80° 2 θ .

The X-Ray Fluorescence (XRF) was conducted using Philips X'UNIQUE apparatus. The WD-XRF spectrometry was performed on glass beads, obtained from a mixture of 66 wt.% lithium tetra-borate and 34 wt.% lithium meta-borate, where 10 wt.% of the sample was dissolved at high temperature. The bead was then analyzed for elemental composition, according to the calibrated procedure, employing the following reference materials as standards (organized by producers):

- South Africa Bureau of Standards (SABS): SARM1, SARM48, SARM50
- Centre de Recherches Pétrographiques et Géochimiques (CRPG): AC-E, MICA-Fe, GH, FK-N,
- Himalayan geoanalytical reference standards (WIHG): AM-H, DG-H
- The International Association of Geoanalysts (GeoPT): AMH-1, BNV-1, CH-1, GBPG-1, HTB1, LOESS, MBL-1, MGT-1, MSAN, OPY-1, OShBO, OU-2, OU-3, OU4, OU-5, OU-6, OU-7, OU-8, OU-9, OU-10
- Canadian Certified Reference Material Project (CCRMP): LKSD-1, LKSD-2, LKSD-3, STSD-2, STSD-3, STSD-4, TILL-4.

Analysis was done on dried samples. Mass loss on ignition was determined between room temperature and 1000 °C. The sludge's toxicity levels were determined by leaching tests performed according to DIN-38414-S4 in order to establish the metals' mobility under neutral conditions (using distilled water). The dried sample/distilled water proportion was 10 being this suspension kept under agitation (0.5 rpm) during 24 h. After filtration, a quantitative analysis (Cu, Cr total, Ni, Pb and Zn) of the eluate was done by atomic absorption spectroscopy (AAS, GBC 904 AA). The amount of Cr(VI) was obtained by molecular absorption spectrometry and was inferred from measurements of absorbance intensity at 540 nm. First a calibration curve was obtained by using known concentrated dichromate solutions obtained by dissolving K₂Cr₂O₇ (Sigma–Aldrich) in deionized water. The particle size distribution was determined using a Laser Coulter LS230.

The sludges resulting from the wastewater treatment of Ni/Cr plating plants were used as sources of nickel and chromium, while sludge F was the main source of iron. The tested formulations are presented in Table 1, attempting to replicate the (Ni,Fe)(Fe,Cr)₂O₄ black spinel composition. Before being used, each sludge was dried and crushed (<100 mm). Homogeneous slurries were obtained by wet ball-milling with water for 1 h. The mixtures were then dried

at 110 °C and calcined, in an electric kiln, at 1000 °C (2 h dwell time and 5 °C/min heating rate). The emerging crystalline phases were identified by X-ray diffraction (XRD). The microstructure and phase composition were also checked by scanning electronic microscopy, SEM/EDS (Hitachi SU 70 coupled with EDAX Bruker AXS detector). The thermal (DTA-TG) behaviour of some pigments was analyzed in a Setaram apparatus, between 30 and 1300 °C with a heating rate of 10 °C/min (in air atmosphere) in alumina crucibles.

The evaluation of pigments and application colours was done based on the three-dimensional CIEL*a*b* projection [9]. The respective coordinates: lightness L* (black–white), a* (green–red) and b* (blue–yellow), were measured by a Konica–Minolta Chroma Meter CR-400.

At laboratory scale, the colour development was evaluated by adding pigment (1/20 ratio) to a commercial transparent lead-free glaze (SiO₂, Al₂O₃, B₂O₃, CaO as main constituents >8%, 2–8% Na₂O, and <2% K₂O). The mixtures were wet ball-milled for 30 min and dried at 110 °C. Pellets (2.5 cm diameter) were pressed and fired at 1050 °C (30 min dwell time and 5 °C/min heating rate) in an electric furnace in air.

After laboratory trials some pigments were selected to be industrially tested (Revirés, PT) for the colouring of two very different kinds of ceramic support:

- (I) *Glazes* (1/25 weight ratio): transparent bright (TB), opaque bright (OB) and transparent mate (TM). The homogenization process was conducted by wet-mixing. The obtained mixture was applied, as a uniform layer, over a ceramic tile that was subject to a fast firing process (T_{max} , 1050 °C and 50 min cycle time).
- (II) *Porcelain stoneware body* (3/100 weight ratio): the coloured powders were obtained by wet-mixing and drying (110 °C). Then pellets were pressed, which were fired at a maximum temperature of 1200 °C (firing cycle of 60 min).

Note: The pigment/ceramic support ratio used in the industrial tests was the normally utilized in the factory.

3. Results and discussion

3.1. Characterization of sludges

Table 2 presents the average chemical composition of the sludges. G, T and S sludges have significant but also variable contents of NiO and Cr₂O₃ that seems dependent on the generating source (galvanizing condition) and/or the wastewater treatment. The NiO/Cr₂O₃ ratio is naturally variable, as seen in Table 2. Sludge T is richest in NiO (55.8 wt.%) which is almost 6 times greater than the amount of Cr₂O₃ amount. On other hand, sludges G and S are richer

Table 2
Average chemical composition of the selected sludges, as determined by XRF.

Component (wt.%)	Sludge G	Sludge T	Sludge S	Sludge F
Al ₂ O ₃	3.76	1.61	0.10	0.14
BaO	0.06	0.03	–	–
CaO	15.5	0.29	11.0	5.31
CeO ₂	–	0.05	–	–
Cl	0.18	0.32	–	1.40
Cr ₂ O ₃	10.2	7.32	15.1	0.09
CuO	2.87	8.07	13.37	0.01
Fe ₂ O ₃	1.25	0.36	0.26	62.1
K ₂ O	0.15	0.48	0.03	–
MgO	0.81	0.32	0.28	0.21
MnO	–	–	–	0.37
Na ₂ O	2.72	3.29	0.95	2.61
NiO	13.8	42.9	21.9	0.01
P ₂ O ₅	6.96	2.60	8.57	3.09
PbO	0.14	0.06	0.04	–
SO ₃	8.43	1.79	2.00	0.11
SiO ₂	10.3	4.98	0.16	0.41
SnO ₂	–	0.05	–	–
SrO	0.02	–	0.02	–
TiO ₂	–	–	–	0.01
ZnO	2.11	2.27	0.05	2.96
ZrO ₂	0.01	–	–	–
V ₂ O ₅	–	–	–	0.02
LOI (at 1000 °C)	20.7	23.2	26.1	21.2

(–) Not detected.

in chromium content and have a NiO/Cr₂O₃ ratio close to 1. The sum of NiO and Cr₂O₃ is also variable, sludge T being the richest in these two oxides (65.3 wt.%). Sludge G has less than half this quantity (30.2 wt.%). Nickel and chromium appears in the calcined sludge (Fig. 1) as nichromite (NiCr₂O₄) and liebenbergite ((Ni,Mg)₂SiO₄). Relatively important amounts of calcium oxide were observed in sludges G and S (insignificant in sludge T); resulting from lime additions to adjust the pH and reduce the level of free phosphorous and sulphates by precipitation in an alkaline media [17,18]. This reaction explains the identification of calcite and apatite in sludge G (Fig. 1). Significant amounts of SiO₂, associated with cristobalite and liebenbergite, were also detected in this sludge. The persistence of sulphur-based compounds in the calcined materials means that the sulphate decomposition was incomplete during firing, this being particularly apparent in sludge G. The phase composition of sludge S is similar to sludge G, apart from the absence of silicates. Differences are more notable for sludge T, since the NiO content is higher.

The iron-rich sludge F is mainly composed of Fe₂O₃ (62 wt.%). The zinc and calcium are present in minor quantities and can form complexes such as franklinite (ZnFe₂O₄) and apatite (Ca₅(PO₄)₃(OH,F,Cl)) after calcination at 1000 °C (Fig. 1). As in the case of the sludges generated by Ni/Cr process, calcium, chlorine and sodium oxides are incorporated during the wastewater treatment (lime addition).

Fig. 2 shows the particle size distribution of Ni/Cr galvanizing and Fe-rich sludges. Particles of the galvanizing waste are slightly coarser, as a probable effect of aggregation during the treatment process. However, both wastes show a fine distribution, the maximum size being inferior to 10 μm, and D₅₀ = 4 and 1 μm respectively for the Ni/Cr and Fe-rich sludges. This means that a milling operation is not necessary in order to assure suitable mixing of components and enough reactivity upon firing.

The concentrations of leachates released from the sludges evaluated in normalized conditions (DIN-38414-S4) are given in Table 3. According to European Council Decision 2003/33/EC, which defines the legal limits of hazardousness character of leachates, the Ni/Cr sludges are harmful wastes, since the amount of chromium and nickel is in excess (bold values, Table 3). The F sludge is classified as

Table 3
Leaching test of the sludges performed according to DIN 38414 S4.

	Legal limits	Sludges			
		G	T	S	F
pH	4–13	8.8	9.5	7.8	6.67
Cr(VI) (mg/L)	0.1	<0.05	<0.05	0.93	<0.05
Cr (total) (mg/L)	2	12.4	5.56	1.12	<0.05
Pb (mg/L)	1	<0.06	<0.06	<0.06	0.23
Cu (mg/L)	5	0.04	0.86	0.14	0.026
Zn (mg/L)	5	<0.008	<0.008	<0.008	0.215
Ni (mg/L)	1	0.1	1.9	0.26	0.12

In bold are values exceeding the allowed limit defined by the European Council Decision 2003/33/EC.

non-hazardous, since the concentration of toxic elements is below the limits.

3.2. Pigment characterization

The crystalline phases detected in the pigments are listed in Table 1. The diffraction patterns of spinels having magnetite (Fe₃O₄), trevorite (NiFe₂O₄), and nichromite (NiCr₂O₄) [19] as end members are very similar, so the discrimination of the formed/expected structure – (FeNi)(FeCr)₂O₄ – is difficult [20,21]. In the actual conditions, it can be assigned to trevorite, since it shows the nearest arrangement and composition.

The SF3 composition shows trevorite as the main crystalline phase (Fig. 3), this being the phase present in all the pigments, except in GF1 and SF1 (Table 1 and Fig. 3). These two formulations develop nichromite instead of trevorite, due to the excessive amount of nickel and chromium that results from the use of a higher percentage of galvanizing sludge (>83 wt.%). Its presence is accompanied by free NiO [21,22]. On the opposite side, non-stoichiometric mixtures richer in F-sludge (TF3 and SF3) show hematite (α-Fe₂O₃). The presence of anhydrite (CaSO₄) in the pigments prepared with sludge G, can be explained by its higher sulphate concentration (10.6 wt.% on Table 2).

The microstructure and elementary composition of the SF1 and SF3 samples were investigated by SEM/EDS (Fig. 4). These pigments are representative of the rest. In both samples, particles showing high amounts of calcium and phosphorous were detected (Fig. 4 – Ap1 and Ap2). These particles can be attributed to the chloroapatite phase, in accordance with XRD results (Fig. 3). The presence of iron, chromium, nickel and copper is related with interference of co-existing phases, making any accurate assignment impossible. In the SEM micrographs, these phases were identified as clear small sized crystals. In the SF1 sample (Fig. 4), grain B contains Cr and Ni as major elements, confirming the prevalence of (NiCr₂O₄) and NiO phases. The small particles in the SF3 pigment (particle C) have an iron/chromium ratio close to two, so they can be associated to the trevorite phase (Fig. 4).

The colorimetric parameters of the prepared pigments are presented in Table 4. Brightness values (L*) are mainly between 24 and 26, lower than the value exhibited by the commercial pigment (DCMA 13-50-9: L*a*b* = 33.0/1.0/0.0) [12]. On the other hand, samples GF and TF show larger a* (red) values than the SF compositions. The b* (yellow hue) values are similar for TF and SF pigments, while the GF pigment shows higher values. The brownish hue, accompanying the use of sludges G and T, can be explained by the presence of Zn. This element might form a spinel of the type (Fe_{1-2x}Mg_xZn_x)(Fe_xNi_{1-x}Cr_{1-x}Al_x)O₄ [12,20,23]. In addition, iron outward diffusion through the silica-rich glassy phase is known to give a reddish shadow [20,24]. The concentration of SiO₂ in sludges G and T is significant (13 and 6.5 wt.%, respectively), and hematite was only detected in sample TF3. These hypotheses could not be supported by the UV–vis spectra, since they do not really separate

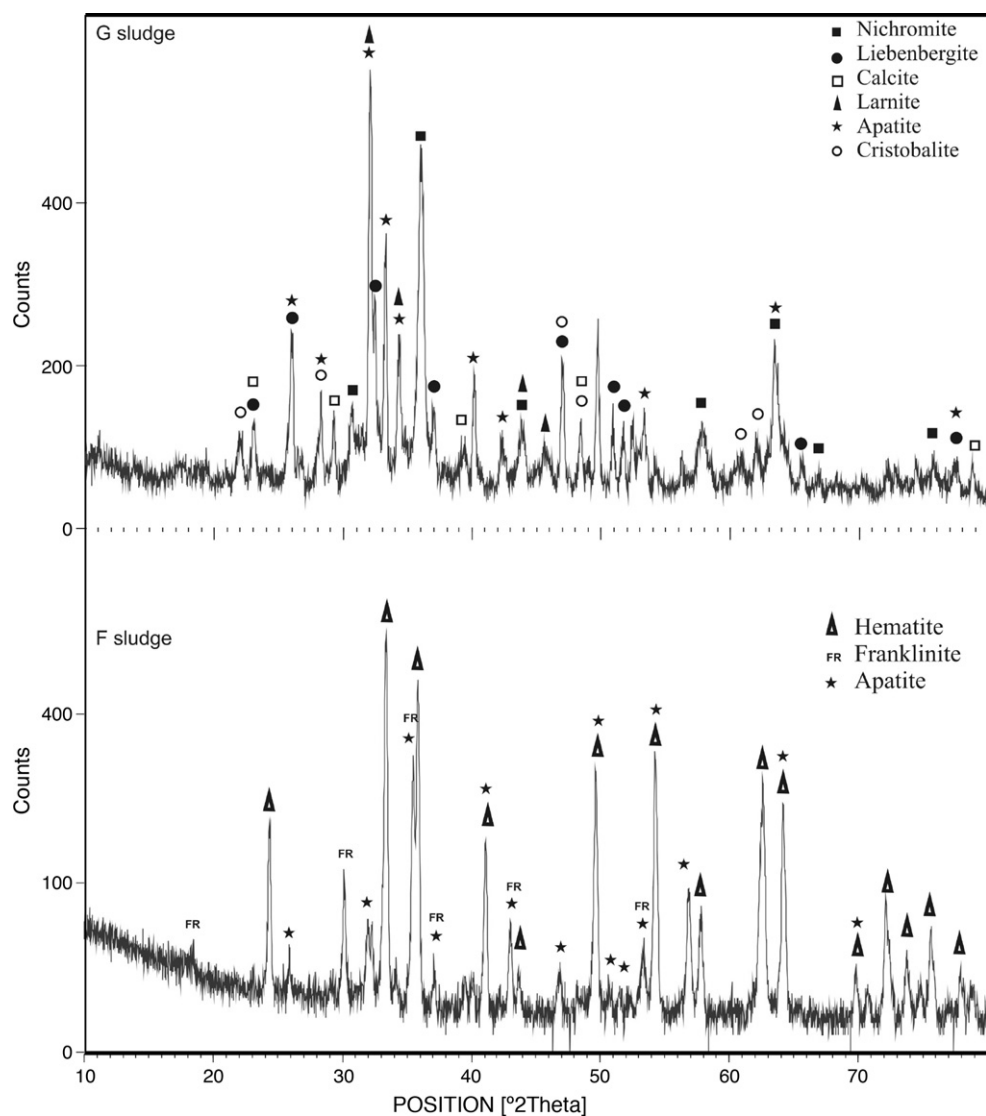


Fig. 1. XRD patterns of Ni/Cr plating (G-sludge) and Fe-rich sludges.

the absorption or reflectance bands of different reacting metal ions (Fe, Cr, Ni, Zn, Cu...). The spectra show a wide interval with band overlapping, as was observed in previous work [12]. The SF pigments are the more black ones, particularly the SF2 formulation, having the $L^*a^*b^*$ values 29.4/1.0/0.6 (Table 4). These coordinates are close to the ones exhibited by the tested commercial pigment ($L^*a^*b^* = 33.0/1.0/0.0$). In such SF formulations the amount of ZnO and silica is lower. At the same time, the copper introduced by sludge S can improve the black colour if properly combined with chromium and nickel in the spinel lattice [25–27].

3.3. Colour development on glazes and ceramic bodies

All prepared pigments were tested in the colouring of a transparent glaze, in lab-scale trials. The obtained colorimetric coordinates (Table 4) are in accordance with the behaviour observed for the pigments. GF samples present the greatest deviation from the expected black colour (highest a^* and b^* values), developing a clear brownish hue in the glaze. Transparent glazes coloured with TF pigments show an increase of the red component and a decrease of yellow, in comparison to the colour shown by the pigments alone. As observed for the powders, SF compositions develop the darkest coloration ($L^* = 26$) in the glaze. The hue is nearest to black (a^* and b^* inferior

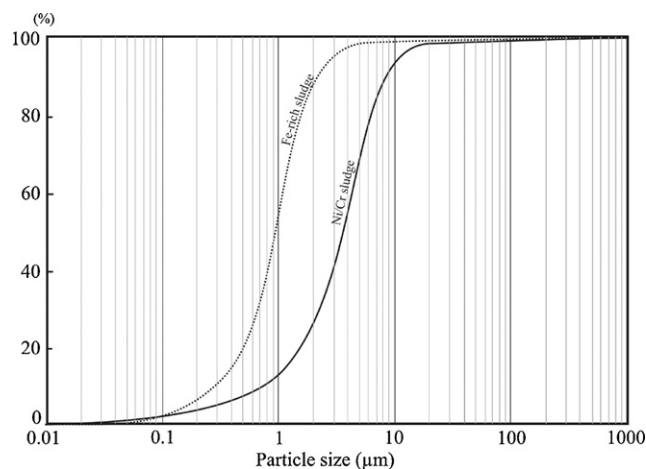


Fig. 2. Cumulative particle size distribution of Ni/Cr plating (average of the three tested samples) and Fe-rich sludges.

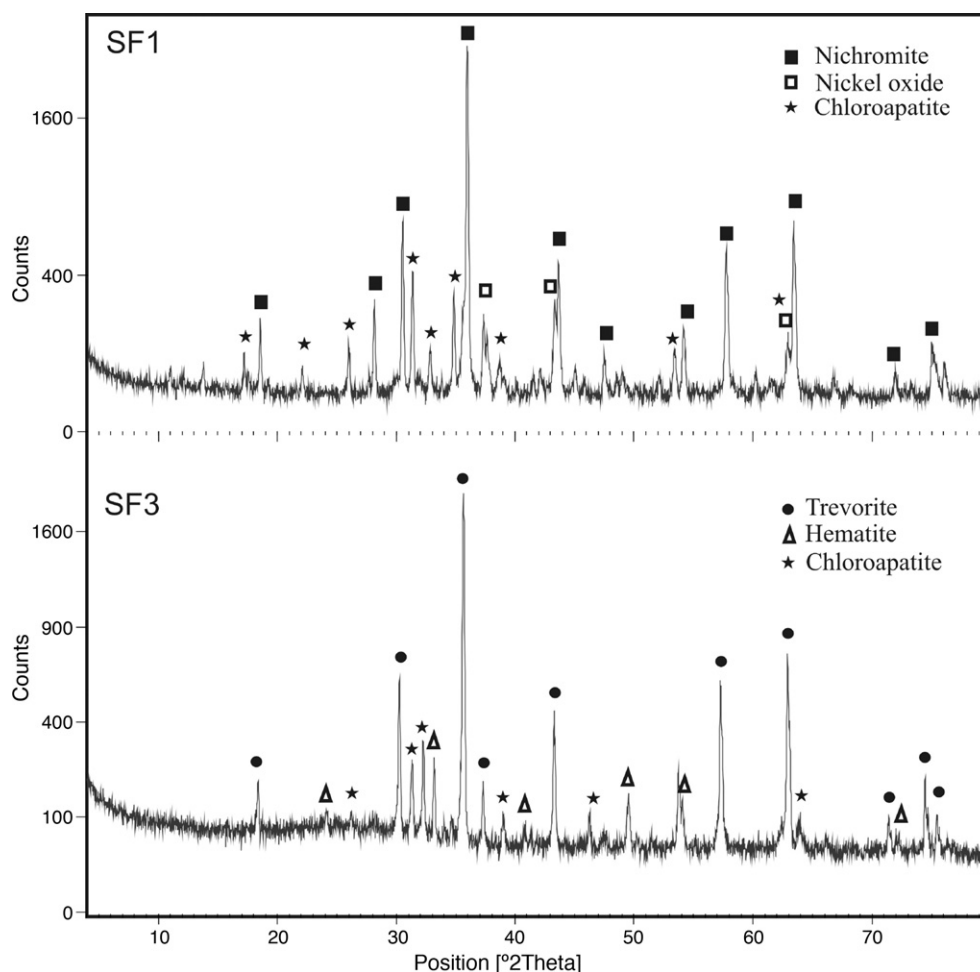


Fig. 3. Phase composition of two studied pigments (SF1 and SF3).

Table 4

Colorimetric coordinates of the pigments and their applications.

	GF1	GF2	GF3	TF1	TF2	TF3	SF1	SF2	SF3	GF5Co	GF5Mn	TF5Co	TF5Mn	SF2Co	SF2Mn
Pigments															
L*	24.3	25.9	21.4	25.3	24.0	25.1	24.2	29.4	24.5	18.6	17.3	16.2	19.2	24.1	23.7
a*	7.1	7.4	7.2	3.4	3.6	3.8	1.0	1.0	1.1	4.3	2.4	0.8	0.5	0.4	0.5
b*	10.9	9.0	6.4	1.1	1.4	1.5	1.6	0.6	2.0	6.1	3.9	0.5	0.3	0.1	0.2
Laboratory tests															
Transparent glaze															
L*	29.5	28.5	30.2	32.4	29.4	29.9	26.6	26.9	26.3	24.7	24.2	27.9	24.8	26.8	22.5
a*	2.6	2.4	2.8	1.1	0.8	1.1	0.4	0.6	0.6	0.9	1.4	1.9	0.5	0.7	0.2
b*	4.1	2.9	3.8	5.2	1.8	2.1	0.7	0.9	0.9	0.5	2.7	2.8	2.6	0.9	1.5
Industrial tests															
Transparent glaze															
L*		28.6			26.3		23.6	22.2	21.7						
a*		7.0			2.8		2.0	2.6	2.2						
b*		8.4			5.3		-5.0	0.6	-0.9						
Opaque glaze															
L*		59.5		61.0			47.5	52.9	51.5						
a*		5.1		1.0			1.4	1.9	1.4						
b*		11.3		8.1			1.9	4.6	2.5						
Porcelain stoneware body															
L*		38.9		37.4			38.5	35.9	37.3						
a*		3.1		1.2			1.9	1.1	0.9						
b*		7.5		3.4			5.2	2.8	3.2						

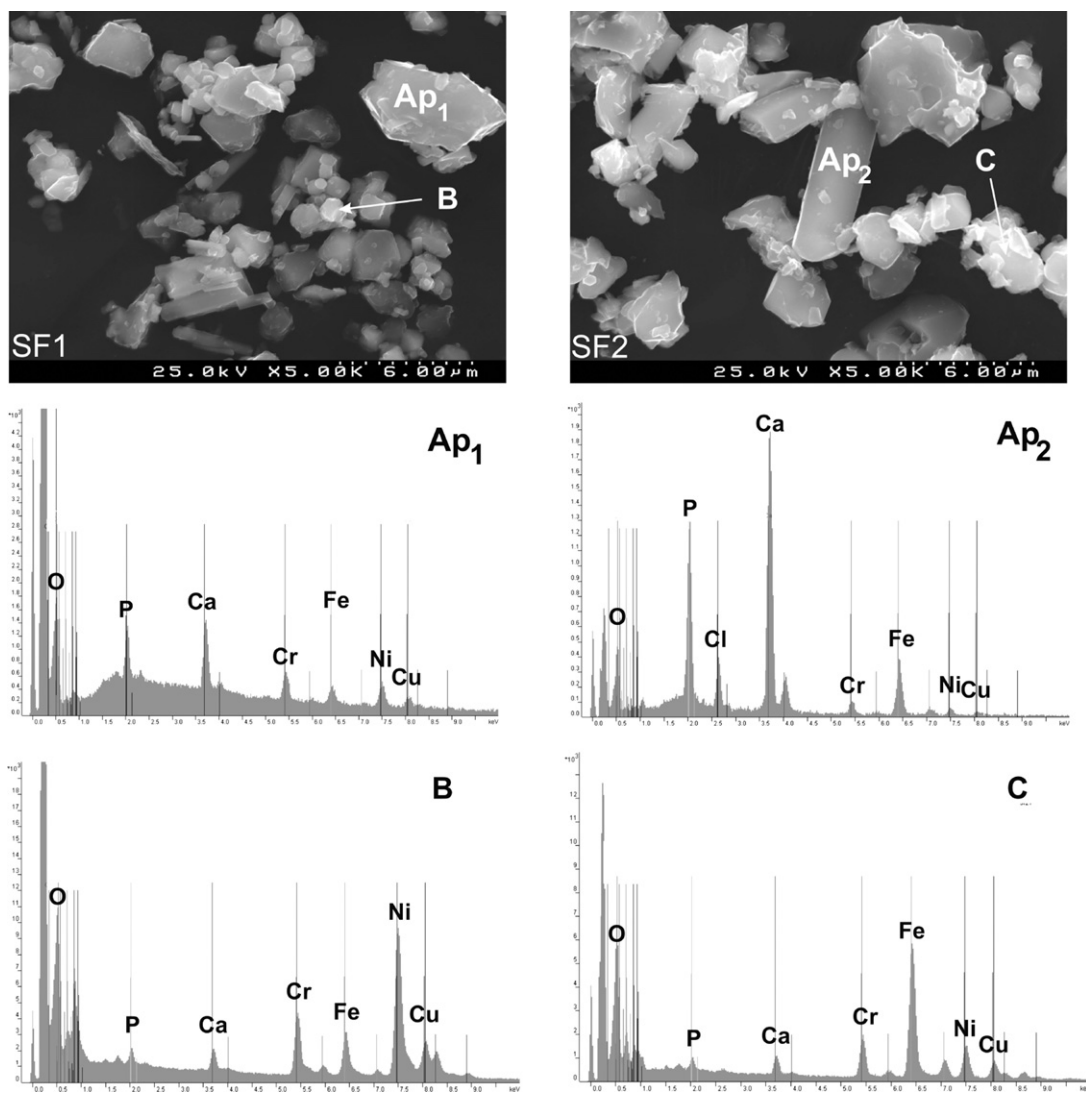


Fig. 4. Black pigment micrographs supported by EDS micropunctual analysis.

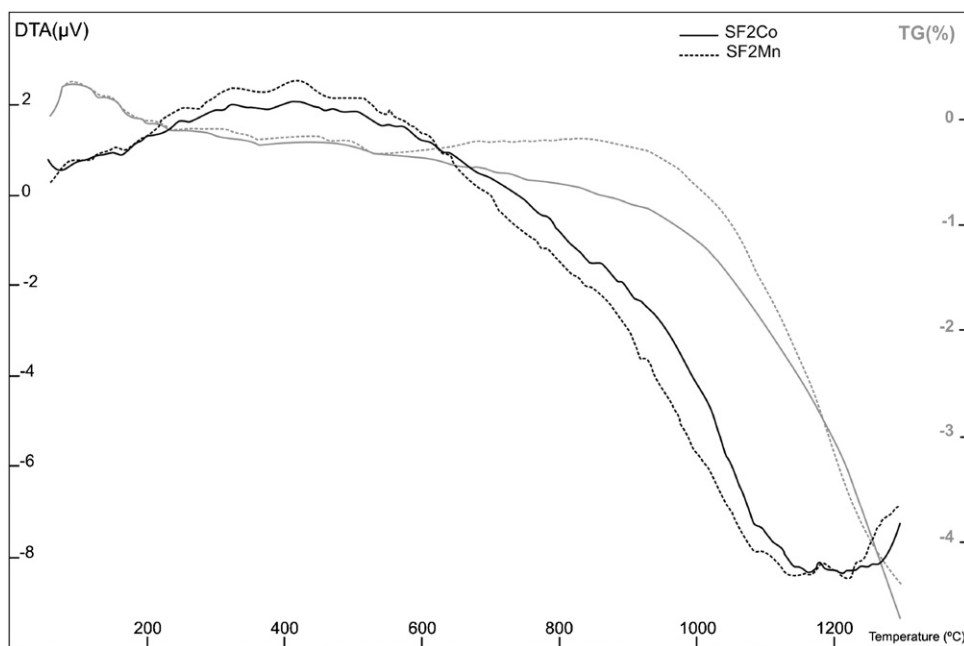


Fig. 5. Thermal behaviour of the SF2Co and SF2Mn pigments.

to 1), attesting the compositional stability of these pigments (SF1, SF2 and SF3).

Based on those indications, the most promising compositions SF1, SF2, SF3, GF2 and TF2, were selected to be industrially tested (Revigrés PT). In these trials, the pigments obtained from the combination of sludges T or G with sludge F (GF2 and TF2), develop an intense brown colour in all selected matrixes (transparent and opaque glazes, and porcelain stoneware body; see Table 4). This behaviour was somewhat predictable, and results from chemical interactions between glaze elements and the low stable pigment structure, since the sintering temperature is relatively low. The deepest black hue was revealed by SF2-containing transparent glaze, while the porcelain stoneware body shows the poorest colour development. The use of SF1 and SF3 pigments develops a higher blue component in the transparent glaze. This effect might result from Ni leaching from the pigment structure towards the reactive glassy matrix, again confirming the low thermal and chemical stability of the pigments. In the opaque glaze this interaction tends to neutralize the red component enhancing the darkest gray hue.

3.4. Colour optimization: effect of cobalt and manganese additions

Since the DCMA catalogue also lists $(\text{Fe},\text{Co})(\text{Fe},\text{Cr})_2\text{O}_4$ (DCMA 13-40-9) and $(\text{Fe},\text{Mn})(\text{Fe},\text{Mn})_2\text{O}_4$ (DCMA 13-41-9) as black spinel pigments, cobalt and manganese were separately added to GF2, TF2 and SF3 formulations (Table 1), attempting to optimize their colouring performance (intensity and stability). By looking to the $L^*a^*b^*$ coordinates (Table 4), we decided to add 5 wt.% Co_3O_4 or MnO_2 to the GF2 and TF2 compositions, and just 2 wt.% to the SF3 pigment. Results are also shown in Table 4.

In general, the addition of manganese oxide is more effective in improving the black colouration. Nevertheless, colour coordinates of GF pigments remain far from the commercial formulation, but when applied for colouring the transparent glaze it shows a good performance. In particular, the addition of cobalt assures an effective reduction of a^* and b^* coordinates (see Table 4). The use of TF pigments in colouring the transparent glaze is optimized by adding manganese oxide. The same happens with SF pigments, which reveal the best performance amongst the tested formulations. Cobalt additions seem to lower the a^* and b^* coordinates, while manganese mainly decreases the brightness (L^*). The thermal behaviour of these pigments (SF2Co and SF2Mn), investigated by thermo-differential and gravimetric analysis (Fig. 5), showed a relative stabilization upon the selected calcination temperature (1000 °C).

4. Conclusions

The aim of this work was testing industrial sludges as raw materials for ceramic black pigments having the $(\text{Ni},\text{Fe})(\text{Fe},\text{Cr})_2\text{O}_4$ spinel structure. The sludges were characterized in terms of toxicity, chemical and mineralogical composition. Nichromite, liebenbergite, apatite and calcite are the major phases detected on the galvanising sludges. The leaching test revealed their hazardous character, due to chromium and nickel solubility. The Fe-rich sludge, resulting from the steel wiredrawing process, has hematite, franklinite and apatite as crystalline phases. However, their use as raw materials of ceramic pigments neutralizes their harmful environmental effects, since the thermal treatment involved assures the desirable inertness. Therefore, this process would be doubly environmentally beneficial as it both removes hazardous wastes from the environment and reduces the use of raw materials.

Chemically balanced mixtures were then calcined at 1000 °C to generate the required pigment phases, namely nichromite or trevorite depending on the Ni/Fe ratio of the mixture. The varia-

tion of chromatic coordinates of pigments reveals oscillations that reflect the phase's development, being the differences enhanced in colouring transparent glazes, particularly those tested in the industrial environment. SF pigments show the best performance, while GF and TF formulations develop dark brown hues. The addition of minor amounts of cobalt or manganese oxides might improve the chromatic quality of the pigments, approaching their performance to that of the tested commercial formulation.

Acknowledgments

The work was supported by FCT (project PTDC/CTM/72318/2006). The support of Revigrés in performing the industrial trials should also be emphasized.

References

- [1] R.J. Hill, J.R. Craig, G.V. Gibbs, Systematics of the spinel structure type, *Phys. Chem. Miner.* 4 (1979) 317–339.
- [2] H.St.C. O'Neill, A. Navrotsky, Simple spinels: crystallographic parameters, cation radii, lattice energies, and cation distribution, *Am. Mineral.* 68 (1983) 181–194.
- [3] C.A. Harper, *Handbook of Ceramics, Glasses And Diamonds*, McGraw Hill, New York, 2001.
- [4] Ullman, *Pigments, inorganic Encyclopedia of Industrial Chemistry*, Vol. A20, 1992.
- [5] N. Wiberg, A. Holleman, E. Wilberg (Eds.), *Inorganic Chemistry*, Academic Press, San Diego, 2001.
- [6] U.V. Chhaya, B.S. Trivedi, R.G. Kulkarni, Magnetic properties of the mixed spinel $\text{NiAl}_{2x}\text{Cr}_x\text{Fe}_{2-3x}\text{O}_4$, *Phys. B* 262 (1999) 5–12.
- [7] S.H. Lee, S.J. Yoon, G.J. Lee, H.S. Kim, C.H. Yo, K. Ahn, D.H. Lee, K.H. Kim, Electrical and magnetic properties of $\text{NiCr}_x\text{Fe}_{2-x}\text{O}_4$ spinel ($0 \leq x \leq 0.6$), *Mater. Chem. Phys.* 61 (1999) 147–152.
- [8] G.N. Maslennikova, Pigments of the spinel type, *Glass Ceram.* 58 (2001) 216–220.
- [9] DCMA, Classification and chemical description of the mixed metal oxide inorganic coloured pigments, *Metal Oxides and Ceramics Colors Subcommittee*, 2nd ed. Dry Color Manufacturer's Association; Washington, DC, 1982.
- [10] R.A. Eppler, D.A. Eppler, *Glaze and Glass Coating*, vol.18, The American Ceramic Society, Ohio, 2000.
- [11] A. Kalendová, Application of spinel pigments in anticorrosive heat-resistant coatings, *Pigments Resin Technol.* 29 (2000) 164–172.
- [12] J. Calbo, S. Sorlí, M. Llusar, M.A. Tena, G. Monrós, Minimization of toxicity in nickel ferrite black pigment, *Br. Ceram. Trans.* 103 (2004) 3–9.
- [13] J.E. Croll, G.R. Wallwork, The design of iron–chromium–nickel alloys for use at high temperatures, *Oxid. Met.* 1 (1969) 55–71.
- [14] M.F. Gazulla, M.P. Gómez, A. Barba, M. Orduña, Chemical and phase characterization of ceramic Pigments, *X-Ray Spectrom.* 36 (2007) 82–91.
- [15] M.A. Legodi, D. de Waal, The preparation of magnetite, goethite, hematite and maghemite of pigment quality from mill scale iron waste, *Dyes Pigments* 74 (2007) 161–168.
- [16] R.R. Marcello, S. Galato, M. Peterson, H.G. Riella, A.M. Bernardin, Inorganic pigments made from the recycling of coal mine drainage treatment sludge, *J. Environ. Manage.* 88 (2008) 1280–1284.
- [17] G. Tchobanoglous, F.L. Burton, H.D. Stensel, *Wastewater Engineering: Treatment And Reuse*, 4th ed., Editorial Boston, McGraw-Hill, 2003.
- [18] J.M. Magalhães, J.E. Silva, F.P. Castro, J.A. Labrincha, Effect of experimental variables on the inertization of galvanic sludges in clay-based ceramics, *J. Hazard. Mater.* 106 (2004) 139–147.
- [19] J.M. Daniels, A. Rosencwaig, Mössbauer study of the Ni–Zn ferrite system, *Can. J. Phys.* 48 (1970) 381–396.
- [20] E. Ozel, S. Turan, Production and characterization of iron–chromium pigments and their interaction with transparent glazes, *J. Eur. Ceram. Soc.* 23 (2003) 97–104.
- [21] S.E. Ziemniak, A.R. Gaddipati, P.C. Sander, Immiscibility in the NiFe_2O_4 – NiCr_2O_4 spinel binary, *J. Phys. Chem. Solid* 66 (2005) 1112–1121.
- [22] B.H. Park, D.S. Kim, Thermodynamic properties of NiCr_2O_4 – NiFe_2O_4 spinel solid solution, *Bull. Korean Chem. Soc.* 20 (1999) 939–942.
- [23] F. Bondioli, L. Barbieri, T. Manfredini, Grey ceramic pigment $(\text{Fe},\text{Zn})\text{Cr}_2\text{O}_4$ obtained from industrial fly ash, *Tile Brick Int.* 16 (2000) 246–248.
- [24] M. Hosseini-Zori, F. Bondioli, T. Manfredini, E. Taheri-Nassaj, Effect of synthesis parameters on a hematite–silica red pigment obtained using a coprecipitation route, *Dyes Pigments* 77 (2008) 53–58.
- [25] P.M. Pimentel, A.E. Martinelli, D.C. Melo, A.M. Garrido Pedrosa, J.D. Cunha, N.S. Júnior, Pechini synthesis and microstructure of nickel-doped copper chromites, *Mater. Res.* 8 (2005) 221–224.
- [26] E. Özel, S. Turan, S. Çoruh, O.N. Ergun, Production of brown and black pigments by using flotation waste from copper slag, *Waste Manage. Res.* 24 (2006) 125–133.
- [27] P. Bělina, P. Sulcová, Utilization of DTA for two-step synthesis of Cu–Mn–Cr spinel, *J. Therm. Anal. Calorim.* 88 (2007) 107–110.