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# Use of industrial wastes in the formulation of olivine green pigments

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## Abstract

This work describes the formulation and synthesis of Ni-olivine green pigments from industrial wastes, namely foundry sand and a sludge resulting from the wastewater treatment of the Ni/Cr galvanising process. This second one is considered as hazardous waste since the leached levels of nickel and chromium are above legal concentrations. Pigments were prepared by the solid state reaction method and $Ni_2SiO_4$ is formed at only 1050 °C. $SiO_2$ (in excess) and $NiCr_2O_4$ are present as secondary phases. By using pure reagents and following similar processing conditions, the Ni-olivine phase is only observed at 1200 °C. The green colour of the pigments is due to spin-allowed transitions of $Ni^{2+}$ in octahedral M1 and M2 positions. The sample prepared from wastes shows a stronger and darker green hue. The colouring performance of ceramic glazes and bodies is also optimal, confirming the potential of the use of such wastes for ceramic pigments production.

*Keywords:* Ni-olivine; Green pigments; Galvanising waste; Foundry sand

## 1. Introduction

The commercial inorganic pigments are classified according to their chemical and structural characteristics in a list created by the DCMA (Dry Colour Manufactures Association) (DCMA, 1982).[1] According to it, several crystalline structures originate green pigments, namely, the green spinels of cobalt chromate [$CoCr_2O_4$ (DCMA 13-30-3)] and cobalt titanate [$Co_2TiO_4$ (DCMA 13-31-3)], the green victoria granate [$Ca_3Cr_2(SiO_4)_3$ (DCMA 4-07-3)] and the green olivine of nickel silicate [$Ni_2SiO_4$ (DCMA 5-45-3)].

The mineral liebenbergite, having the general formula $(Ni,Mg)_2SiO_4$, is the naturally occurring equivalent of Ni-olivine. The name was given by the discoverer W.R. Liebenberg (1973) in Mpumalanga Province, South Africa. Soon after, this term was proposed for the pure nickel olivine $Ni_2SiO_4$ and is still used for olivine where nickel mostly assumes an octahedral coordination.[2] Liebenbergite appears to have been formed at about 730 °C and at a pressure less than 2 kbar during thermal metamorphism, possibly of a Ni-rich meteorite. [2]

The olivine structure presents a hexagonal close-packed oxide lattice where one-eighth of the available interstitial tetrahedral sites are occupied by ions of the group IIIA or IVA and the transition metals occupy one-half of the available octahedral M1 and M2 sites.[3–6] In the case of $Ni_2SiO_4$, due to the strong tetrahedral site preference of $Si^{4+}$, such sites are completely occupied by this ion. The green coloration of the $Ni_2SiO_4$ olivine is due to the metal ion ($Ni^{2+}$) presence in the octahedral sites (six-fold coordination).[7–8]

The natural conditions for the synthesis of Ni-olivine (temperature, pressure, etc.) are difficult to simulate in laboratory trials, and it is difficult to obtain a single phase product. Sobolev et al.[7] prepared it from pure reagents; its formation only starts at 1400 °C and, after 1 h at this temperature, just 20 wt.% of the mixture was $Ni_2SiO_4$ olivine. The slow reaction was attributed to the formation of cristobalite and nickel oxide and to the absence of a liquid phase. Further tests also gave similar results.[9–10]

The industrial progress of countries inevitably results in the production of huge quantities of waste, such as galvanising sludge. In a complex hydrographical system like that in Portugal, these sub-materials containing hazardous contaminants constitute a threat to water, natural resources and human health due to their drainage and infiltration in the soils. This trial consists of industrial waste (galvanising sludge and foundry sands) being incorporated into ceramic pigments, both to neutralise

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their environmental effects and, at the same time, to limit the costs and damages of extraction and synthesis raw materials by furnishing convenient alternatives.

There has been a great interest in the development of inorganic pigments showing superior thermal and chemical stability, and efficient colouring power, but also complying with strict environmental and technological demands. There is always a demand for alternative and less expensive raw materials and wastes recycling.[11–13] Some industrial processes, such as galvanising or surface coating, generate large amounts of sludges that are rich in metallic species that should be treated or recovered somehow.[14–18] A recent estimate points out the existence of about 4,000 industrial units in EU countries, generating more than 150,000 tons/year of galvanic sludge.[18] Our approach utilises some of these wastes as secondary raw sources of metallic species, such as Ni and Cr, in the formulation of ceramic pigments. The use of relatively high sintering temperatures and the combination with suitable host matrices assures the desirable inertness of the final products.[19,20] Foundry sand, a by-product of industrial metal casting processes, is used as source of silica. In this actual paper, we describe the production of green Ni-olivine pigments from such waste products. The presence of impurities, in controlled amounts, in such secondary raw materials might act as mineralising/fluxing agents, helping to decrease the sintering temperature.[20]

## 2. Experimental procedure

The nickel silicate ($Ni_2SiO_4$) was prepared, from commercial reagents and from industrial wastes, by the conventional ceramic route. The raw materials used were nickel nitrate-6-hydrate ($Ni(NO_3)_2.6H_2O$; Riedel-de Haën) and silica ($SiO_2$; Sibelco P500). As an alternative, they were replaced by Cr/Ni galvanising sludge (GS) and foundry sand (FS), respectively.

The chemical and phase compositions of the wastes were determined by XRF (Philips X'UNIQUE II apparatus) and by XRD (Rigaku Geigerflex D/max), respectively. Toxicity levels of GS and pigments were evaluated by leaching tests performed according to the DIN-38414-S4 protocol to determine metals mobility under neutral conditions using 500 mL of distilled water for 50 g of sample. The DIN 38414-S4 test is a non-controlled extraction method where the sample is shaken in demineralised water (0.5 rpm) for 24 h. The solid fraction is separated from the eluate by filtration and the species concentration is determined by atomic absorption spectroscopy.

Pigment mixtures, reported in Table 1, were wet ball milled until reaching a particle size under 150 μm. The stoichiometric composition is named O_C or O_GS84, depending if it is prepared from pure/commercial raw materials or by using industrial wastes, respectively. As the chemical composition of the GS might change with time depending on processing and treatment conditions, and also to test the effect of Ni/Si ratio variation on pigment development and performance, another composition, having a lower relative amount of galvanising sludge, was prepared (O_GS50).

Mixtures were calcined in air at 1050, 1100 and 1200 °C (3 h dwell time and heating rate of 5 °C/min.). The resulting pigments were ball milled with water, dried (110 °C) and sieved bellow 75 μm. Their characterisation included (i) crystalline phase determination by XRD and using the X'Pert HighScore Plus software for ICDD pattern indexing, (ii) particle size distribution (laser, Coulter LS 230), (iii) microstructure and chemical elemental distribution by scanning electron microscopy (SEM–Hitachi, SU 70) equipped with energy dispersion spectroscopy (EDS–EDAX with detector Bruker AXS, software: Quantax) and (iv) the simultaneous differential thermal and thermogravimetric (DTA/TG) analysis on powders were carried out by using a Setaram apparatus with alumina crucible and a heating rate of 10 °C/min. The colour measurements were carried out using a Shimadzu UV-3100 for UV–Vis–NIR spectroscopy and a Konica Minolta Chroma Meter CR-400, using $D_{65}$ illuminant and 10° standard observer. This method, applied also to the tested ceramic applications described bellow, uses the reflectance data in the visible region to obtain the three relevant parameters: L*a*b* which measures the brightness, the red/green and yellow/blue hue intensities, respectively.[21]

The colouring potential of the pigments was tested by applying them in three common ceramic supports: (i) a transparent and bright lead free glaze (TB), (ii) an opaque and bright glaze (OB) and (iii) a porcelain stoneware ceramic body (PB). The weight ratio pigment/ceramic base was 1/20 and 1/10 for the glazes and for the porcelain stoneware body, respectively. After homogenisation, Ø 2.5 cm pellets were pressed and fired (30 min soaking

Table 1
Prepared pigment formulations and main crystalline phases (ordered by peak intensity) detected after calcination at distinct temperatures (1050, 1100, and 1200 °C).

| Pigment code | Used reagents (wt.%) | | | | Crystalline phases | | |
|---|---|---|---|---|---|---|---|
| | $Ni(NO_3)_2{\cdot}6H_2O$ | $SiO_2$ | GS | FS | 1050 °C | 1100 °C | 1200 °C |
| O_C | 90.6 | 9.4 | – | – | NiO<br>$SiO_2$(Q) | NiO<br>$SiO_2$(Q) | NiO<br>$SiO_2$(Q)<br>$Ni_2SiO_4$ |
| O_GS84 | – | – | 83.6 | 16.4 | $Ni_2SiO_4$<br>$SiO_2$(Q + Crt)<br>$NiCr_2O_4$ | $Ni_2SiO_4$<br>$SiO_2$(Q + Crt)<br>$NiCr_2O_4$ | $Ni_2SiO_4$<br>$SiO_2$(Q)<br>$NiCr_2O_4$ |
| O_GS50 | – | – | 50.0 | 50.0 | $SiO_2$(Q + Crt)<br>$Ni_2SiO_4$<br>$NiCr_2O_4$ | $SiO_2$(Q + Crt)<br>$Ni_2SiO_4$<br>$NiCr_2O_4$ | $SiO_2$(Q + Crt)<br>$Ni_2SiO_4$<br>$NiCr_2O_4$ |

GS, galvanising sludge; FS, foundry sand. $Ni_2SiO4$, Liebenbergite; $SiO_2$, (Q) = Quartz + (Crt) = Cristobalite; $NiCr_2O_4$: Nichromite

Table 2
Concentration of elements leached from the GS sludge (DIN-38414-S4 protocol). Legal limit of hazardousness is also given, as defined by European Council, Decision 2003/33/EC.

| Metal concentration (mg/L) | Cr (VI) | Cr (total) | Pb | Cu | Zn | Ni |
|---|---|---|---|---|---|---|
| Sludge | | | | | | |
| GS | <0.05 | **5.56** | <0.06 | 0.86 | <0.008 | **1.9** |
| Pigments | | | | | | |
| O_C (1200 °C) | – | – | – | – | – | 0.137 |
| O_GS84 (1200 °C) | – | 0.035 | – | – | – | 0.128 |
| O_GS50 (1200 °C) | – | – | – | – | – | 0.123 |
| Legal limit (mg/L) | 0.1 | 2 | 1 | 5 | 5 | 1 |

Bold means concentration over the legal limit.

time and 5 °C/min heating rate) in an electric furnace. The maximum temperature was 1050 °C for the glazes and 1200 °C for the porcelain stoneware body.

## 3. Results and discussion

### 3.1. Wastes characterisation

### 3.1.1. Chemical composition

As previously stated, GS is a sludge resulting from the physical–chemical treatment of the wastewaters generated by a Ni/Cr plating plant which needs careful sampling and homogenising procedures to ensure a reasonable constancy due to the possible chemical composition variability. According to the XRF results its average chemical composition is as follows (wt. %): 47.6 NiO; 8.96 CuO; 8.12 $Cr_2O_3$; 5.53 $SiO_2$; 3.65 $Na_2O$; 2.88 $P_2O_5$; 2.52 ZnO; 1.99 $SO_3$; 1.78 $Al_2O_3$; 0.53 $K_2O$; 0.40 $Fe_2O_3$; 0.36 MgO; 0.36 Cl; 0.32 CaO; 0.07 PbO; 0.05 $SnO_2$; 0.05 $CeO_2$; 0.03 BaO; 0.03 $Sb_2O_3$; 0.02 $MoO_3$ and 14.7 loss of ignition at 1000 °C. Nickel is the major element but other elements such as chromium, copper and silicon are also present in considerable amounts.

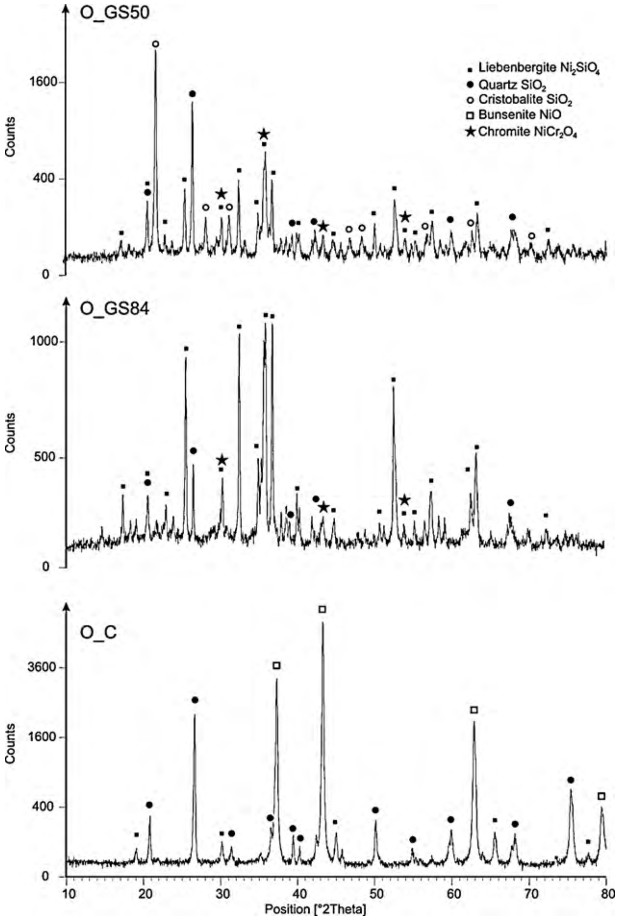

Fig. 1. X-ray diffraction patterns of the O_C, O_GS84, and O_GS50 pigments calcined at 1200 °C.

The average chemical composition of the foundry sand (FS) is much more constant (wt.%): 97.74 SiO2; 1.12 $Fe_2O_3$; 0.26 $K_2O$; 0.20 CaO; 0.20 $Al_2O_3$; 0.20 $TiO_2$; 0.20 $Cr_2O_3$; 0.03 MgO; 0.02 $Na_2O$; 0.02 ZnO and 0.2 ignition loss at 1000 °C. This material can be described as extra-siliceous, since XRD reveals high crystalline quartz as single component.[22] Nevertheless, the iron content could influence the pigments final colour.

### 3.1.2. Leaching test

The foundry sand is generally considered as inert waste and only the hazardous character of GS was investigated by leaching tests performed according to DIN-38414-S4 protocol to determine metals mobility under neutral conditions (using distilled water) (see Table 2). Concentration limits of leached elements adopted by the European Council, Decision 2003/33/EC are also given in Table 2. The concentration of chromium and nickel in the leachate (in bold) is above the legal limits, proving that Ni/Cr galvanising sludge is hazardous, so its recycling in the pigments development has enormous environmental benefits and, probably, also economic ones.

### 3.2. Pigments characterisation

### 3.2.1. Crystalline phases

The main phases detected in the pigments from XRD analysis are given in Table 1. The order of appearance reflects their diffraction intensities. Fig. 1 shows the spectra of pigments calcined at 1200 °C. For pigments prepared from commercial reagents (O_C), the calcination temperature exerts a noticeable effect on phase's development. NiO and $SiO_2$ (quartz) are still present in the powder calcined at 1200 °C, confirming the previously mentioned difficulties in sintering. This behaviour could be related to the preference of Ni for octahedral coordination rather than the tetrahedral sites.[23] $Ni_2SiO_4$ is observed at

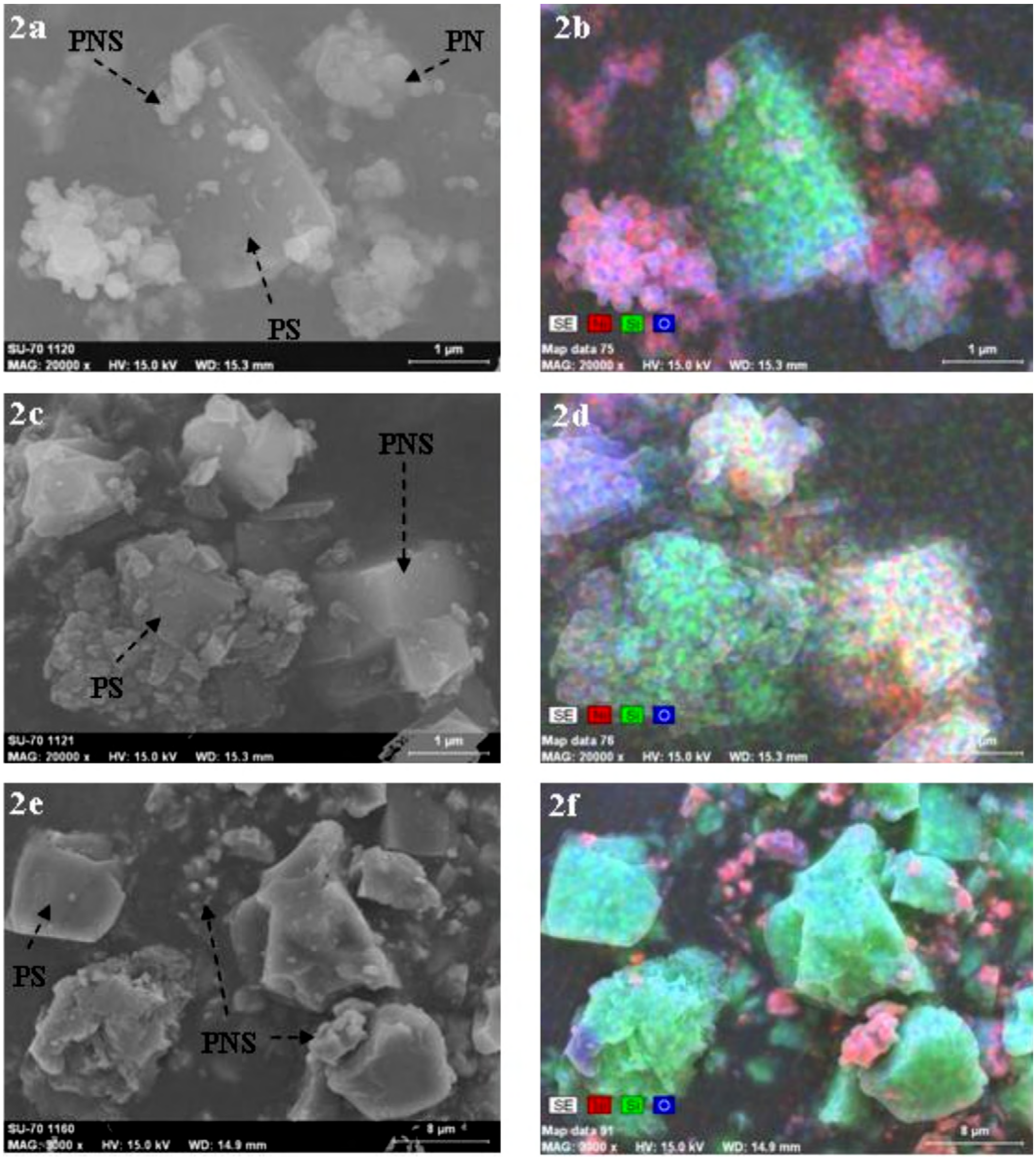

Fig. 2. SEM/EDS analysis of the pigments calcined at 1200 °C: (a and b) O_C; (c and d) O_GS84; (e and f) O_GS50. PS, PN and PNS are particles rich in silicon, nickel and nickel silicate, respectively.

1200 °C, a formation temperature considerably lower than that used by Sobolev et al.[7] These authors report the formation of Ni-olivine at 1400 °C, according to reaction (1).[23]

$$2\mathrm{NiO(s)} + \mathrm{SiO_2(s)} \rightarrow \mathrm{Ni_2SiO_4(s)} \qquad (1)$$

In our work, the premature appearance of $Ni_2SiO_4$ could be explained by differences in the calcination cycle used. The change in synthesis conditions, namely by using the sol–gel preparation route, leads to significant changes in the temperature of liebenbergite formation, crystallising at lower temperatures (800 °C).[24]

Pigments prepared from industrial wastes are notoriously more reactive and the desirable Ni-olivine is detected at 1050 °C. Some impurities in the wastes may act as mineralisers, anticipating the formation of $Ni_2SiO_4$. In both O_GS84 and O_GS50 pigments no free NiO is visible at 1050 °C, which is another sign of enhancement of the reactivity of the mixtures. However, silica in both forms, cristobalite and quartz, is omnipresent, being more prevalent (in excess) in the non-stoichiometric composition (O_GS50). In both cases, nichromite ($NiCr_2O_4$) is detected, certainly due to the sizeable concentration of chromium in the sludge.

### 3.2.2. SEM and EDS mapping

Fig. 2 shows the microstructure and the elemental distribution of the pigments calcined at 1200 °C. The SEM micrographs reveal the presence of three distinct compounds: Si-rich (PS), Ni-rich (PN), and one containing both Ni and Si elements (PNS). They could correspond to silica, nickel oxide and Ni-olivine, respectively. In agreement with XRD analysis, the main phases in the pigment prepared from pure reagents (O_C) are NiO and $SiO_2$ (see Fig. 2b in red and green, respectively). The crystal

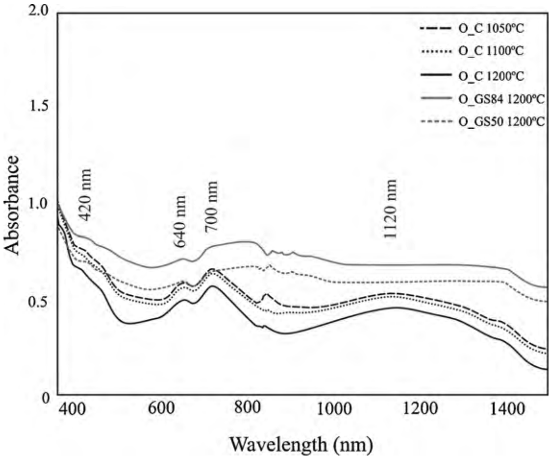

Fig. 3. UV–Vis absorbance spectra of the O_C, O_GS84 and O_GS50 pigments.

growth of $Ni_2SiO_4$ (PNS) is seen on the surface of quartz particles (PS), when these react at 1200 °C by contacting with nickel oxide and following reaction (1). (For interpretation of the references to colour in this sentence, the reader is referred to the web version of the article.)

The pigments prepared from industrial wastes have some areas richer in silicon, and others where exhibiting a combination of silicon and nickel. This second type of particles (PNS) is more abundant in the O_GS84 pigment, since it contains the desired stoichiometry. A quasi-homogeneous distribution of elements is visible in the mapping (Fig. 2d). As expected, the O_GS50 (50% GS + 50% FS) pigment shows an excess of $SiO_2$.

### 3.2.3. *Pigments toxicity*

The leaching tests performed to the pigments calcined at 1200 °C (Table 2) demonstrated that the hazard substances are stabilised. The nickel and chromium amounts in the eluate are considerable below the legal limits confirming its inertization and the non-hazard character of the obtained pigments.

### 3.2.4. *Optical spectroscopy*

The variation of chemical and phase compositions in the pigments should influence their exhibited colours. The UV–Vis–NIR spectra (see Fig. 3) show three intense absorption bands in the visible zone. The bands at 420 and 700 nm are assigned to the spin-allowed transitions of $Ni^{2+}$ in octahedral coordination from the ground state $^3A_2$ to the excited states $^3T_1(P)$ and $^3T_1(F)$, respectively. The third band at 640 nm results from the spin-forbidden transition $^3A_2(F)$ to $^1E(D)$.[25–27] Those bands can be assigned to nickel inserted in both M1 and M2 sites of olivine lattice.[26,28] In the near-infrared region a high-energy absorption band is measured at approximately 1120 nm, resulting from the transition $^3A_2 \rightarrow {}^3T_2(F)$ of $Ni^{2+}$ in octahedral field.[26,28] This band is larger for waste-based pigments, certainly due to the contribution of transition bands ascribed to other elements, such as chromium, copper and iron. These impurities could combine with residual or melted silica to form a coloured glass or they can be partially assimilated in the M1 site of the olivine structure.[29]

The O_GS84 samples have the maximum amount of Ni-olivine and display the higher absorbance. This is in accordance with our expectations that this compound is largely responsible for the green colour. In the visible zone, the increase of calcination temperature (from 1050 to 1200 °C) reduces the absorbance intensity of O_C pigments (Fig. 3), as a possible consequence of enhancing consumption of NiO and progressive formation of $Ni_2SiO_4$. On waste-based pigments the effect of calcination temperature is much less noticeable.

### 3.2.5. *Colour measurement and application*

The CIEL*a*b* chromatic coordinates of the pigments and tested applications (transparent, opaque bright glazes and porcelain stoneware body) are given in Table 3.

Firstly, all pigments display a dark olive green hue. The colour changes of waste-based formulations with calcination temperature are not significant, in agreement with less relevant variations in the main detected crystalline phases. This is a positive sign of colour stability, especially if it will be also observed in the applications. The higher green component (−a*) is registered for the O_C pigment calcined at 1200 °C but the brightness (L*) tends to be higher. By contrast, L* values of the waste-based formulations are lower, in accordance with measured high absorbance values. The O_GS84 samples shows the lowest L* and a* values, as a probable consequence of its greater relative $Ni_2SiO_4$ amount. In contrast, the superior values of b* coordinate measured on the O_C pigment can be explained by colorimetric effects of free nickel. This tendency is denoted by a yellow/brown hue that is ascribed to d–d electron transitions

Table 3
CIEL*a*b* parameters for the pigments and their applications: bright and transparent glaze (TB), opaque glaze (OB), and porcelain stoneware ceramic body (PB).

| Ref. | *T* (°C) | L*a*b* | | | |
|---|---|---|---|---|---|
| | | Pigments | TB | OB | PB |
| O_C | 1050 | 67.69/–8.66/15.97 | 68.67/–4.68/25.22 | 81.45/–3.73/19.44 | 44.35/–1.73/7.91 |
| | 1100 | 67.92/–6.9/14.24 | 64.31/–3.21/25.98 | 79.96/–2.14/20.99 | 42.48/–1.4/7.0 |
| | 1200 | 73.77/–13.43/14.44 | 53.75/0.21/15.16 | 81.36/–2.68/18.21 | 43.54/–1.82/6.97 |
| O_GS84 | 1050 | 58.35/–2.61/11.03 | 64.69/–2.33/25.44 | 78.92/–3.05/20.6 | 36.98/1.55/6.31 |
| | 1100 | 56.46/–2.17/9.72 | 43.34/–1.31/13.26 | 61.85/–1.77/11.26 | 37.32/1.72/7.13 |
| | 1200 | 55.2/–3.42/8.52 | 43.22/–1.5/12.04 | 61.77/–2.18/9.11 | 35.81/1.12/5.67 |
| O_GS50 | 1050 | 63.38/–3.14/10.69 | 49.34/–2.78/12.74 | 71.07/–2.9/9.09 | 37.05/2.81/8.9 |
| | 1100 | 61.21/–2.4/9.3 | 33.96/–1.87/7.88 | 70.60/–1.63/10.23 | 36.88/2.58/8.78 |
| | 1200 | 62.18/–3.58/7.89 | 32.9/–0.82/6.24 | 70.3/–2.85/8.52 | 40.83/2.3/9.97 |

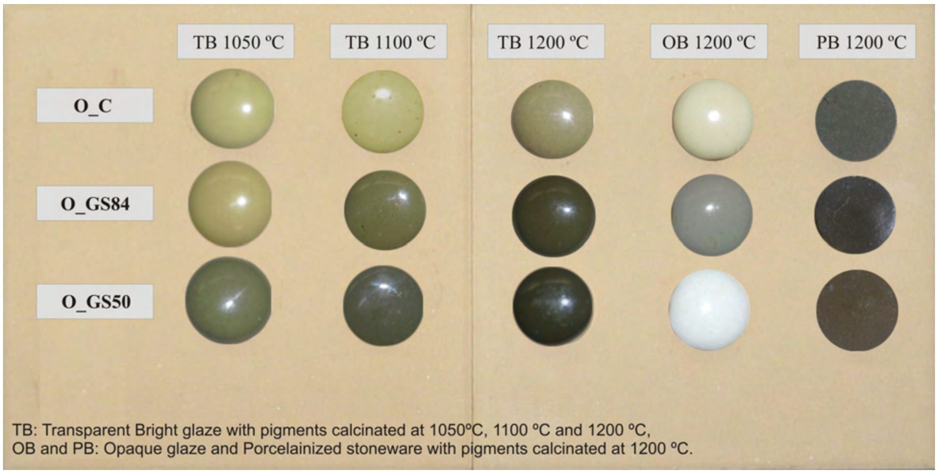

Fig. 4. Ceramic applications.

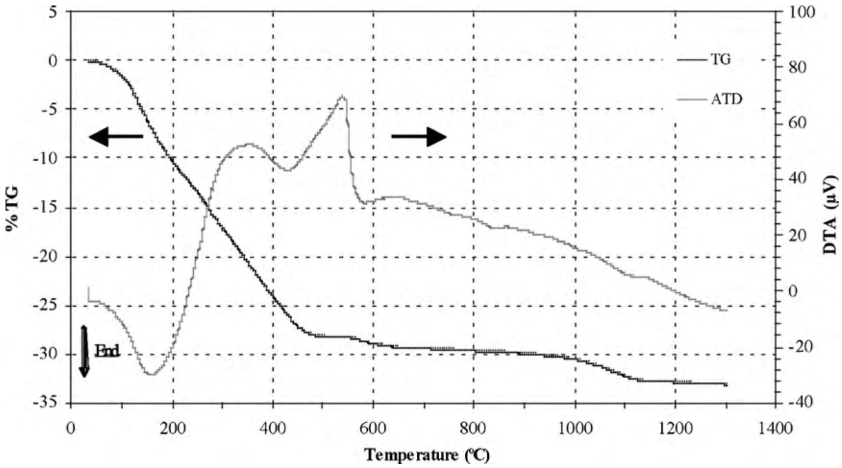

Fig. 5. DTA–TG curves of the waste-based pigment (O_GS84) before calcination.

of $Ni^{2+}$ ($3d^8$ configuration) ions in tetrahedral coordination.[4,29] The change from the desirable octahedral to tetrahedral configuration of $Ni^{2+}$ ions that dissolves into the melt existing in the pigment can also difficult the progression of Ni-olivine formation upon sintering.

Fig. 4 shows the colour evolution of the transparent, opaque glazes and the porcelain ceramic bodies. In general, the colour features discussed for pure pigments are maintained in the applications. The undesirable yellow/brownish colour tendency generated in the O_C pigments is more evident by their use in transparent glazes (see Fig. 4). Free Ni ions might be further inserted/dissolved in the glaze, accentuating the undesirable occurrence.

Better green colourations are observed for the waste-based pigments, particularly those calcined at 1200 °C. This is to be expected, since they contain higher amounts of $Ni_2SiO_4$, which also has improved crystallinity, so reinforcing the colouring power and its stability. This trend is supported by the thermal behaviour (before calcination) of the waste-based pigments (Fig. 5) for which was observed a relative stability in mass loss and DTA curves over 1100 °C indicating that the optimum calcination temperature was achieved. However, the dissolution of nichromite ($NiCr_2O_4$) in the glaze can induce the appearance of a brownish hue.[30]

Changes of L*a*b* values in opaque bright glaze (OB) and porcelain stoneware body (PB) applications are generally less important (see Fig. 4), as the opacity of those supports inhibits the colour development. In the case of porcelain stoneware body the observed behaviour can also indicate some reactivity of the pigment with the paste due to its composition and the higher sintering temperature.

## 4. Conclusions

The leaching test of the sludge generated from the Cr/Ni galvanising process (GS) revealed high concentrations of hazardous elements (nickel and chromium). The synthesis of Ni-olivine ($Ni_2SiO_4$) was investigated as a way to neutralise the hazardous effect of such species, by incorporating them in a suitable ceramic pigment structure. Pigments prepared from industrial wastes (GS + foundry sand) compare well with those obtained from pure/commercial reagents, once prepared in similar conditions, by solid state reaction. In particular, the presence of impurities in such secondary raw materials might enhance the mixture reactivity, causing the formation of Ni-olivine at much lower temperatures. The green hue of waste-based pigments is also stronger and darker, resulting from the increased presence of nickel in octahedral coordination sites. The transition bands of $Ni^{2+}$ from the ground state $^3A_2$ to the excited states $^3T_1(P)$ and $^3T_1(F)$ and at 640 nm $^3A_2(F)$ to $^1E(D)$ confirm this statement.

Once applied in common ceramic supports, the optimal pigment formulations conferred suitable and stable colouration. The presence of free Ni ions might give undesirable yellow-brown tonalities, especially after their incorporation in the glassy matrix. This aspect is less evident for pigments having maximal amount of well crystallized $Ni_2SiO_4$, so the waste-based ones.

## Acknowledgments

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