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Blue cobalt doped-hibonite pigments prepared from industrial sludges: Formulation and characterization

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ABSTRACT

The structural stability of the pigment was investigated using X-ray diffraction coupled with SEM and UV–vis–IR analysis, as a function of the relative Co content and calcination temperature. A standard formulation prepared from commercial reagents was also prepared and characterized for the sake of comparison. The pigment was added to a transparent glaze and to a porcelain stoneware body. Since the relative amount of cobalt was low and the sintering temperature of the pigment was not too high (1350–1400 °C), the new pigment system offers an interesting alternative to spinel, olivine and willemite commercial blue pigments. Moreover, the use of several wastes in the pigment formulation does not diminish its colouring performance.

1. Introduction

With the exception of vanadium–zircon (14-42-2 DCMA), traditional blue inorganic pigments are based on cobalt-doped structures [1] namely, Co_2SiO_4 olivine (5-08-2 DCMA) $(Co,Zn)_2SiO_4$ willemite (7-10-2 DCMA), blue or blue green spinels, such as: $CoAl_2O_4$ (13-26-2 DCMA), Co_2SnO_4 (13-27-2 DCMA), $(Co,Zn)Al_2O_4$ (13-28-2 DCMA) and $Co(Al,Cr)_2O_4$ (13-29-2 DCMA). Cobalt aluminate is widely preferred to olivine, since a navy blue hue can be obtained using ~ 50% cobalt content (33.3% in $CoAl_2O_4$ against 56.1% in Co_2SiO_4), as well as differences in chroma [1,2]. In these formulations, the Co^{2+} ions are situated within non centrosymmetric sites (e.g. tetrahedronally) and offer the highest colouring efficiency among crystal-field transitions [2]. However, the above formulations contain relatively high amounts of cobalt which is not only expensive but also is a toxic component [3]. Hence, attention has foccussed on alternative pigmentary systems that contain lower amounts of cobalt [4,5].

Calcium hexaluminate ($CaAl_{12}O_{19}$ or $CaO\cdot 6Al_2O_3$), which occurs in nature as the mineral *hibonite*, possesses the magnetoplumbite-type structure (space group $P6_3/mmc$, $Z=2$) of general crystallochemical formula: A [12] M1 [6] $M2_2$ [5] $M3_2$ [4] $M4_2$ [6] $M5_6$ [6] O_{19}. Calcium occurs in 12-fold coordination (site A), whereas the Al^{3+} ions are distributed over five different coordination sites, including three distinct octahedra (M1, M4 and M5), one tetrahedron (M3) as well as an unusual trigonal bipyramid (M2) providing five-fold coordination by oxygen ions [6,7]. Of significance herein, is the tendency of the M^{2+} ions to be hosted at the M3 site, while M^{4+} and M^{5+} ions are preferentially accommodated at the M4 site [8]. Magnetoplumbite-group minerals may contain significant amounts of divalent as well as tetravalent and pentavalent cations occupying interstitial M sites [8]. The marked preference of divalent cations for the M3 site occurs because these substitutions are electrostatically more favourable than incorporation of highly charged cations. The ions of different charges tend to improve the local charge balance in the crystal structure. Therefore, the introduction of divalent ions is thought to be achieved by coupled incorporation of tetravalent or pentavalent cations which are mainly ordered over the octahedral sites in the face-sharing interlayer doublet [8].

This ability to accommodate such a wide variety of ions, with different valences and coordinations, makes the hibonite structure very interesting to be used as a pigment. The electroneutrality of the hibonite lattice was eased by making available a tetravalent ion in order to get a coupled substitution Co^{2+}–Al^{3+} and Ti^{4+}–Al^{3+}. Any excess of titanium oxide is not detrimental for the overall pigment performance, since it ensures increased brightness. However, the temperatures required for the synthesis make its application difficult [6]. To overcome kinetic hindrances, batch formulation might be adjusted introducing anorthite into the system, which contributes to lower the synthesis temperature of hibonite, allowing its application as pigment [9]. The use of wastes or by-products in the

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Table 1
Components and relative codes of synthesized pigments.

Pigment code	Alumina	AS	Calcite	MS	Silica	FS	Co_3O_4/TiO_2	n(Co) (mol)[a]
0.45Co/Ti-H_1400 °C	63.5		18.6		11.2		3.4	0.45
0.45Co/Ti-H_1350 °C								
0.3Co/Ti-H_1400 °C	65		19		11.4		2.3	0.3
0.3Co/Ti-H_1350 °C								
0.15Co/Ti-H_1400 °C	66.5		19.5		11.7		1.2	0.15
0.15Co/Ti-H_1350 °C								
0.45Co/Ti-H/3S_1400 °C		79.98		12.86		4.16	3.4	0.45
0.45Co/Ti-H/3S_1350 °C								
0.3Co/Ti-H/3S_1400 °C		80.8		13		4.2	2.3	0.3
0.3Co/Ti-H/3S_1350 °C								
0.15Co/Ti-H/3S_1400 °C		81.64		13.13		4.25	1.2	0.15
0.15Co/Ti-H/3S_1350 °C								

H: hibonite. 3S: with anodizing (LS) and marble (MS) sludges and foundry sand (FS).

[a] n_{Co} (Mol) = n_{Ti}(Mol).

formulation of hibonite might also improve the sintering process since they might contain mineralising/fluxing agents [10]. In fact, one of the current trends in pigments' production are the search for alternative and less expensive raw materials and wastes that might act either as colouring agents or as hosts for diverse colouring species, so they can be looked as supplementary raw materials for pigments' production [11–13].

2. Experimental

Hibonite-based pigments, doped with cobalt, were synthesized by the conventional ceramic route, designing a batch composition in the Al_2O_3–CaO–SiO_2–TiO_2 system (Table 1). The following precursors were used in batch formulations: calcite (Calcitec M1), silica sand (Sibelco P500), alumina (Alcoa, CT 3000), titanium dioxide (Kronos) and Co_3O_4 (Panreac). Alternative raw materials were used to formulate similar compositions.

(i) Aluminium anodising sludge (AS) of mass% composition: 36.36 Al_2O_3, 1.23 SiO_2, 3.08 CaO, 0.05 TiO_2, 40.0 (LOI) replacing the pure alumina above;
(ii) foundry sand (FS) of mass% composition: 0.20 Al_2O_3, 97.74 SiO_2, 0.20 CaO, 0.20 TiO_2, 0.2 (LOI) as the source of silica;
(iii) marble sawing sludge (MS) of mass% composition: 0.14 Al_2O_3, 0.64 SiO_2, 55.51 CaO, 0.02 TiO_2, 43.0 (LOI) replacing calcite.

Each was disintegrated or milled (<100 μm) and dried at 100 °C. Their full characterisation is given elsewhere [13].

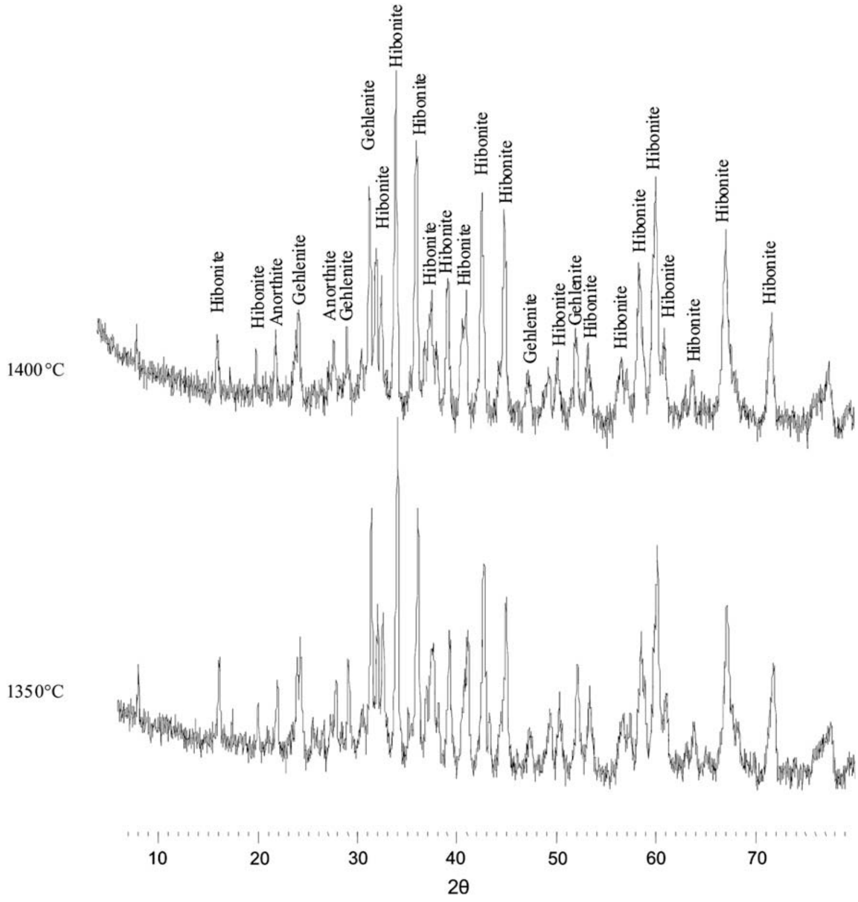

Fig. 1. X-ray diffraction patterns of 0.3Co/Ti-H/3S pigments calcined at 1350 °C and 1400 °C.

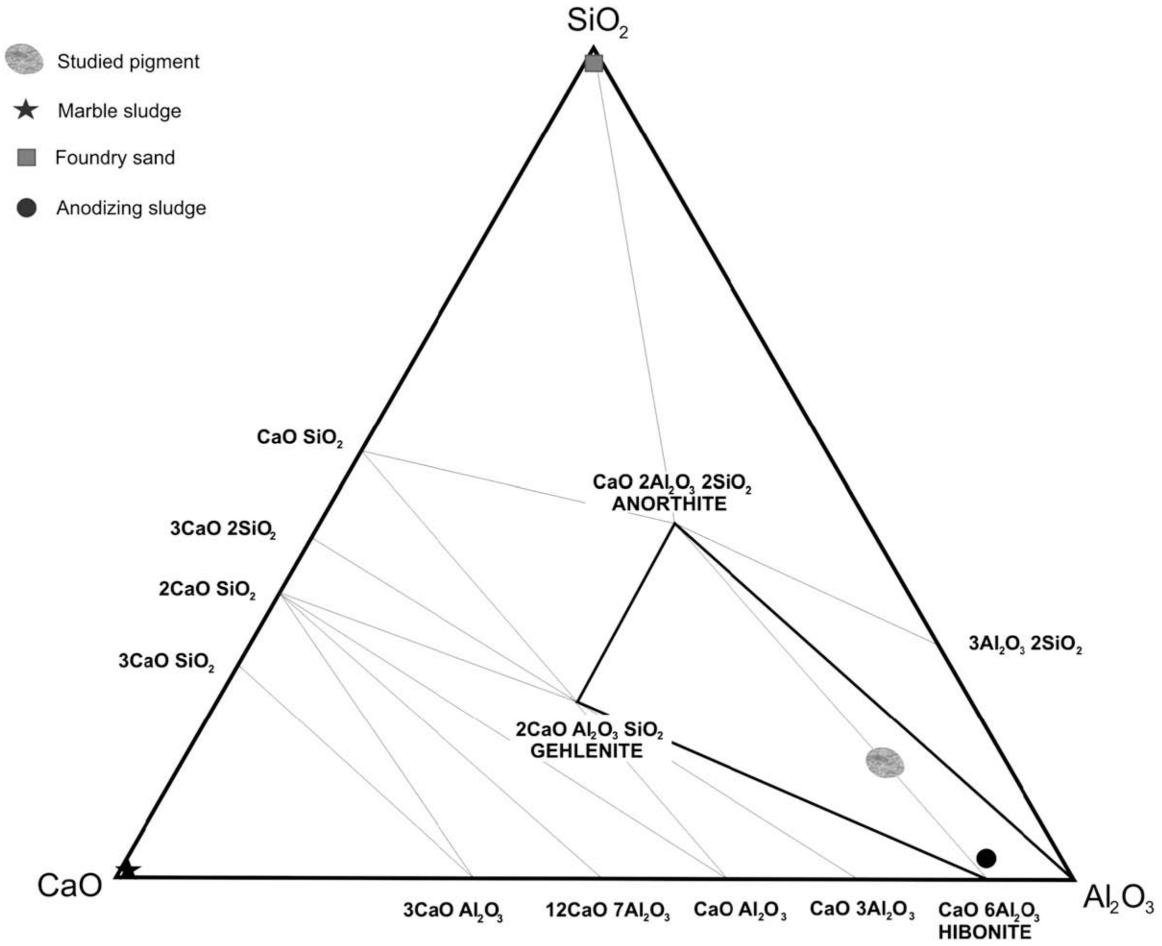

Fig. 2. SiO_2–Al_2O_3–CaO equilibrium phase diagram showing the location of the wastes and studied pigments' formulations.

In order to obtain fine, homogeneous slurries, the mixtures were wet ball-milled in ethanol for 1 h, dried at 110 °C and then calcined in an electric kiln at 1350 and 1400 °C (3 h dwell time and 5 °C/min heating rate). The calcined powders were manually disintegrated and characterized by X-ray diffraction (XRD) by using a Rigaku Geigerflex diffractometer (between 0 and 80°). The microstructure and chemical homogeneity of pigments were studied by scanning electron microscopy (SEM–Hitachi, SU 70) equipped with energy dispersion spectroscopy (EDS–EDAX with detector Bruker AXS, software: Quantax).

Colour measurement was carried out using a Shimadzu UV-3100 [14] for UV–vis–IR spectroscopy, a Konica Minolta colour reader CR-10 or chroma meter CR-400, using D_{65} and 10° standard observer.

Table 2
Unit cell parameters of selected pigments prepared from pure reagents.

Compound	0.15Co/Ti-H	0.3Co/Ti-H	0.45Co/Ti-H
Crystal system	Hexagonal	Hexagonal	Hexagonal
Space group	P_{63}/mmc	P_{63}/mmc	P_{63}/mmc
a (Å):	5.578(4)	5.575(3)	5.585(2)
b (Å):	5.578(4)	5.575(3)	5.585(2)
c (Å):	21.99(2)	21.97(1)	22.00(1)
a/*c*	0.254	0.254	0.254
Alpha (°):	90	90	90
Beta (°):	90	90	90
Gamma (°):	120	120	120
Volume of cell (Å^3) 1350 °C	592.33	591.27	594.33
Volume of cell (Å^3) 1400 °C	590.32	593.62	595.24

Finally, to evaluate the colour development in common products, each pigment was added to:

(i) at 5% to a commercial transparent, lead-free glaze (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) at 10% to porcelain stoneware bodies, to be fired at 1200 °C.

The mixtures were wet ball-milled for 30 min and dried at 110 °C. Pellets (2.5 cm diameter) were pressed which were fired using a 30 min dwell time and 5 °C/min heating rate in an electric furnace in air.

3. Results and discussion

3.1. Structural characterisation

The XRD patterns of calcined powders, at 1350 °C and 1400 °C, are depicted in Fig. 1. Strong diffraction peaks related to distorted hibonite ($CaAl_{12-2x}Ti_xCo_xO_{19}$) and anorthite ($CaAl_2Si_2O_8$) are visible. However, the presence of corundum (Al_2O_3) and gehlenite ($Ca_2Al_2SiO_7$) is detected, respectively, on formulations prepared from pure reagents and from waste mixtures. The first observation means incomplete formation of expected phases, while the presence of gehlenite on waste based formulations is predicted from the CaO–Al_2O_3–SiO_2 phase equilibrium diagram (Fig. 2). A similar result was observed in distinct works [15,16].

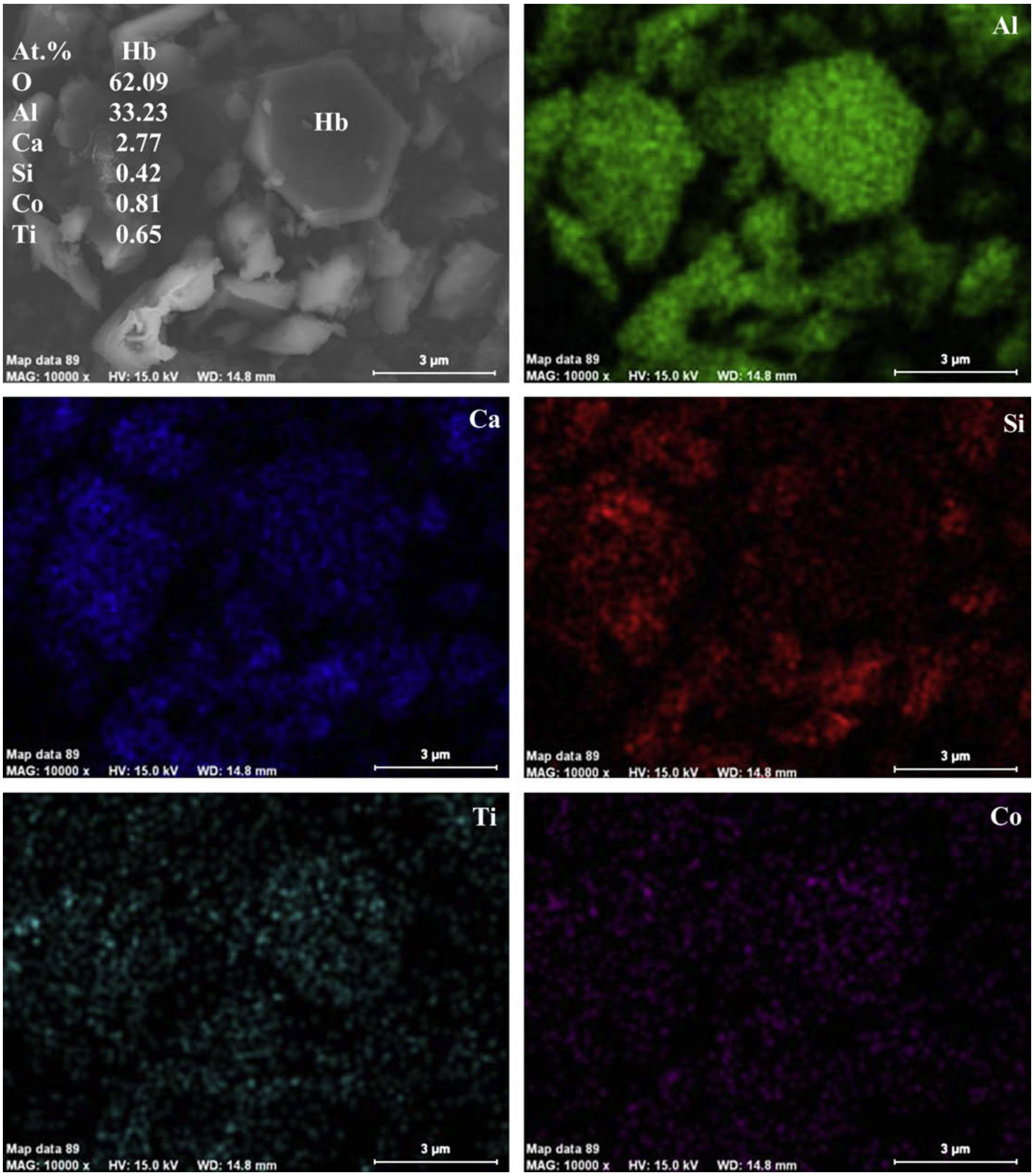

Fig. 3. Microstructure and EDS analysis of 0.3Co/Ti-H_1400 °C pigment. Mapping of relevant elements is also given.

In all cases, the most important observation is that cobalt seems to be incorporated in the structure. With the increase of calcination temperature, a very slight growing of peaks' intensity is perceptible associated to a crystallinity improvement of the formed phases. The superposition of the two diffractograms shows the relative constancy of the samples calcined at 1350 °C and 1400 °C and illustrates that the optimal firing temperature range was reached.

Table 2 gives the estimated unit cell parameters of selected pigments prepared from pure reagents. For sake of comparison, those of a naturally-occurring hibonite [17] are also given. The effect of cobalt and titanium addition is noticed by an increase of the hibonite cell volume. These slight variations on *a*, *b* and *c* fold axes are proportional to the radius of the ions incorporated in hosting site, raising the O–M3 bond distance. Obviously, the difference in this system is so ambiguous that is hardly attributable only to changes in the Al–O, Co–O, and Ti–O bonding (e.g. covalence degree, polarization, etc.), while this constitutes the most important variable in the system [8]. The preservation of the crystalline structure of hibonite in tested formulations is given by a fixed ratio $a/c \approx 0.254$ that is characteristic of the naturally occurring mineral specie [17]. A slight volume expansion is observed by increasing the firing temperature. The ions of distinct valences tend to improve the local charge balance in the crystal structure. Therefore, the introduction of divalent ions is thought to be achieved by coupled incorporation of Ti^{4+} cations which are mainly ordered over the octahedral sites in the face-sharing interlayer doublet [8].

3.2. Microstructure and microanalysis

The microstructural analysis of a selected pigment 0.3Co/Ti-H_1400 °C reveals the presence of hexagonal grains among others without a very well defined form. These grains (named Hb in Fig. 3) have a lamellar and their average molar ratios, estimated by EDS ($Al/Ca = 11.96$; $Ti/Al \approx Co/Al \approx 2.4 \times 10^{-2}$), are not too far from the theoretical hibonite composition ($Al/Ca = 11.6$; $Ti/Al = Co/Al = 2.58 \times 10^{-2}$). The anorthite, forming hypothetical elongated

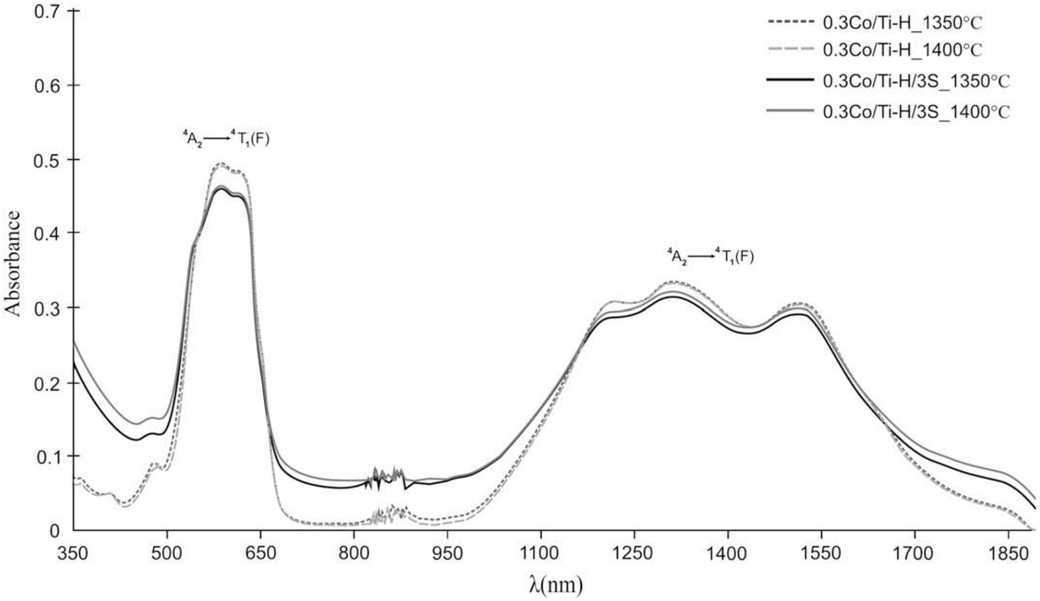

Fig. 4. Comparative vis–IR absorbance spectra of pigments prepared from pure and alternative raw materials.

grains, is not easily discernible even using the EDS mapping, because of the strong association between the existing phases and the spread/coverage of a vitreous phase. This connection explains the small amount of Si (0.42 at.%) found in the EDS quantification of the Hb grain. The mapping of all relevant elements (see Fig. 3) also illustrates the circumscription of titanium and cobalt in each Hb grain. Their relative amounts are lower in the surrounding areas, more rich in silica and, consequently, concentrating the anorthite phase. This observation suggests that anorthite acts mostly as a mineralising/fluxing agent in the actual conditions, contributing to lower the synthesis temperature of hibonite and then allowing its application as a viable pigment.

3.3. Vis–IR absorbance

As previously mentioned, Co^{2+} ions are in non-centrosymmetric sites (like tetrahedron) and assure the highest colouring efficiency known among crystal-field transitions [2,5]. When they assume octahedral coordination, the colour is pale red or purple, so a suitable hosting lattice should fix the chromophor ion in a tetrahedral coordination. Fig. 4 shows the absorbance spectra in the visible and IR regions. The energy-level for Co(II) ($3d^7$ configuration) excited by the light presents two transition zones. The first is noticed in the visible region and exhibits three strong bands, at 544, 580 and 609 nm, relative to the transition $^4A_2 \rightarrow {}^4T_1(F)$ in tetrahedral coordination. Generally, Co^{2+} in octahedral positions gives weaker absorption bands [5]. The absorption characteristics of tetrahedral Co^{2+} ions are confirmed by the multiple bands detected in the IR region (1200–1850 nm).

The comparative analysis of the absorbance spectra in the visible region between pure and waste-based formulations suggests that the first ones develop a slightly intense blue hue. This is a good indication about the potential use of those secondary raw materials in the preparation of cobalt containing pigments, since

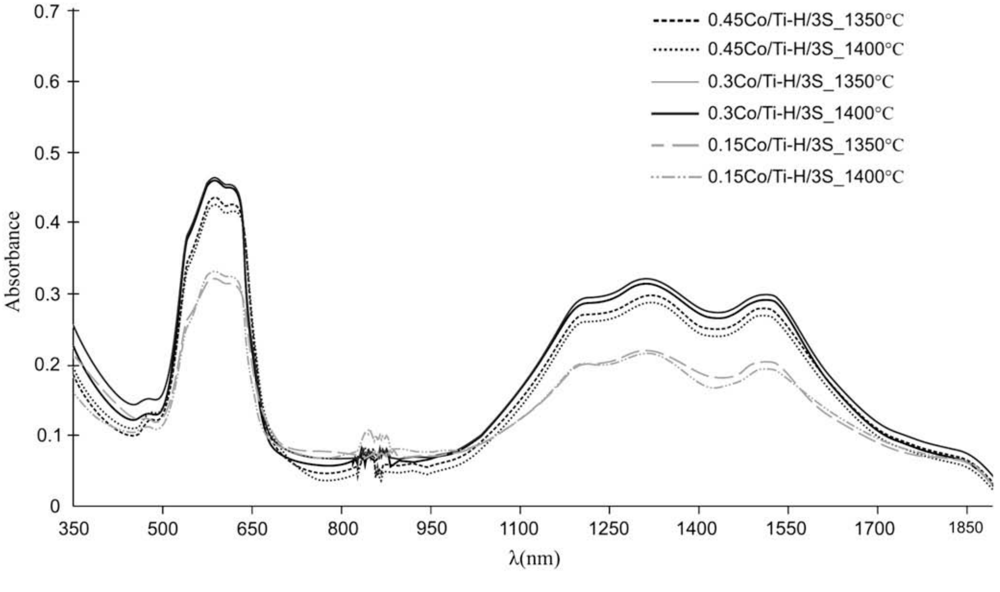

Fig. 5. Comparative vis–IR absorbance spectra of pigments prepared from wastes and containing distinct amounts of cobalt.

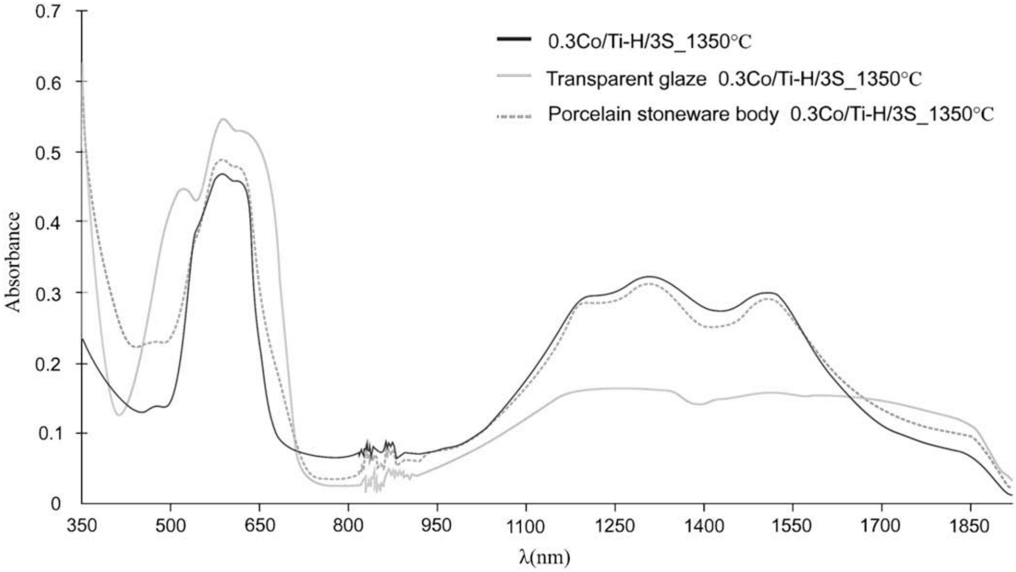

Fig. 6. Vis–IR absorbance spectra of the optimal pigment and of its application in selected supports.

the electronic configuration of the chromophor apparently is not affected by the presence of certain impurities in the hosting lattice that are introduced by the wastes.

Fig. 5 shows vis–IR absorbance spectra of distinct waste-based pigments, in which the relative amount of cobalt and the calcination temperature were tentatively optimised. A slightly higher intense hue is observed on pigments calcined at 1350 °C, being maximal when 0.3 mol cobalt is used. The further increase of cobalt concentration does not improve the blue colour while the use of 0.15 mol cobalt seems to be insufficient.

In sequence, the pigment 0.3Co/Ti-H/3S_1350 °C was selected to evaluate the colour development in common ceramic products, namely a porcelain stoneware body and a transparent and shining glaze. Fig. 6 shows the vis–IR absorbance spectra of the applications after being fired at the above mentioned suitable temperatures. The spectra of porcelain stoneware bodies are similar to those of the pure pigment, while changes are noticed in the pigment-containing transparent glaze, despite an intense blue colour is maintained. This suggests that Co(II) ions keep the tetrahedral coordination. Data of Co-doped hibonite are promising, but follow more or less the trend of the other cobalt pigments [5]. The critical point is the actual behaviour of cobalt is not adequately known: it is said that olivine in reality acts as a dye – being totally dissolved in the glaze [18] – but also spinel and willemite undergo a significant dissolution [1,5]. As a matter of fact, glazes containing the same amount of Co, supplied as different pigments, have similar colours.

3.4. Lab colour characterization

The chromatic coordinates *L*, *a* and *b* of the pigments and tested applications are given in Table 3. As expected, changes in the blue-yellow component (*b*) are stronger than in the red-green (*a*). Excluding the pigments containing only 0.15 mol cobalt, that reveal weak and distinct chromatic characteristics, a division in two groups can be assumed:

(i) the first one is composed by pigments obtained from pure reagents, apparently exhibiting the best bluish colour. The optimal formulation contains 0.3 mol cobalt and is calcined at 1350 °C. The gain observed by increasing either the calcination temperature (to 1400 °C) or the relative amount of cobalt does not compensate the cost increase;

(ii) the second group includes the pigments obtained from wastes, showing a slight decrease in the blue hue (−*b*) when compared with those of the first group. This degradation is also transmitted by the increase of brightness (*L*) and contradicts the previous comparative analysis of the absorbance spectra in the visible region (Fig. 4).

Table 3
CIE*Lab* parameters of pigments, porcelain stoneware bodies and transparent glazes.

Reference	Pigments			Porcelain stoneware body			Transparent glaze		
	L	*a*	*b*	*L*	*a*	*b*	*L*	*a*	*b*
0.45Co/Ti-H_1400	57.3	2.6	−34.4	50.6	−2.1	−14	30.3	6.8	−23.8
0.45Co/Ti-H_1350	55.6	3.3	−34.5	50.7	−2.1	−12.1	32.2	6.8	−23.4
0.3Co/Ti-H_1400	59.1	2.8	−34.2	56.7	−2.5	−7.9	35.1	6.2	−23.3
0.3Co/Ti-H_1350	56.8	2.6	−32.4	57.9	−2.3	−5.8	33	6.6	−23.3
0.15Co/Ti-H_1400	66.1	−1.5	−21.7	49.4	−2.3	−10.3	43.7	3.3	−19.8
0.15Co/Ti-H_1350	67.6	−1.9	−18.4	47.1	−2.2	−12.8	40.7	4.5	−21.5
0.45Co/Ti-H/3S_1400	63.2	−0.3	−26.2	48.9	−2.1	−14.6	35.5	5.2	−22.1
0.45Co/Ti-H/3S_1350	62.7	−0.1	−26.6	49.3	−2.6	−13.0	34.1	5.6	−22.2
0.3Co/Ti-H/3S_1400	60.8	−1.1	−25.1	49.4	−2.8	−19.5	36.4	3.8	−19.8
0.3Co/Ti-H/3S_1350	61.5	−0.2	−26.7	50.3	−2.8	−16.1	36.4	4.1	−20.5
0.15Co/Ti-H/3S_1400	66.3	−2.3	−18.6	56.3	−3.1	−10.4	47.0	0.8	−15.6
0.15Co/Ti-H/3S_1350	65.5	−3	−16	54.4	−3.2	−9.5	47.0	1.6	−17.2
Willemite (W)	–	–	–	58.7	−5.6	−16.9	47.9	11.3	−43.8
Cobalt spinel (Sp)	–	–	–	42.1	−7.9	−22.4	27.5	3.3	−14.2
Cobalt olivine (O)	–	–	–	39.7	−5.7	−9	29	11.2	−25.6

Since what really matters is the colour development of a pigment in a suitable application, Table 3 shows the CIE*Lab* parameters of coloured glazes and porcelain stoneware bodies. For sake of comparison, were also added the *L*, *a* and *b* values of some commercial Co-containing pigments, namely willemite, olivine and spinel [5].

The colour development of ceramic bodies significantly changed by using distinct hibonite pigments, namely if they are prepared with pure reagents or from wastes. A higher intense bluish hue is developed by pigments based on wastes and the colour coordinates are close to those reached by using the willemite commercial pigments, even better in the case of 0.3Co/Ti-H/3S. In the transparent glaze differences in colour are small, in accordance with previous comments that glazes containing the same amount of Co, supplied as different pigments, have similar colours, suggesting that they act as dyes.

4. Conclusions

This work reports the development of new blue solid solution pigment with Co(II) ions in tetrahedral coordination as chromophore element. This pigment consists of two structures: hibonite and anorthite. Gehlenite and rarely corundum might also be present. Cobalt is incorporated in the hibonite lattice, partially substituting the Al^{3+} ion. Although its ability to incorporate a variety of ions in different coordinations and valences is already recognized, the application of hibonite structure as pigment is novel, being the main hindrance the high temperatures required for its synthesis. However, when anorthite is included in the system, the temperature of hibonite crystallization is significantly reduced. The presence of tetravalent titanium ions is necessary to ensure the electrical neutrality of doped-hibonite by compensated the charge mismatch of Co^{2+}–Al^{3+} substitution with Ti^{4+}–Al^{3+}.

The pigments contain a relatively low cobalt amount (1.8 wt.%) and develop good chromatic properties in transparent glaze and in porcelain stoneware bodies, comparable to those assured by the commercial pigments. The most interesting formulation was designed to include 0.3 mol cobalt in the hibonite structure, and its recommended calcination temperature is 1350 °C. The use of wastes to compose the hosting hibonite structure for the chromophor ion is perfectly viable.

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