



Development of waste-based ceramic pigments

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We report the preparation of ceramic pigments using industrial wastes as primary sources. In this context, the use of Al-rich sludge generated in the wastewater treatment unit of an anodising or surface coating industrial plant, and a galvanizing sludge from the Cr/Ni plating process, will be detailed. The ceramic pigments reported here were prepared using typical solid state reactions involving the metal rich sludge. The main focus will be on the synthesis of chrome-tin orchid cassiterite (Sn,Cr)O₂, chrome-tin red malayaite Ca(Cr,Sn)SiO₅, victoria green garnet Ca₃Cr₂Si₃O₁₂, and chrome alumina pink/green corundum (Cr,Al)₂O₃ pigments. The pigments were fully characterised and then were tested in a standard ceramic glaze after. Typical working conditions and colour development will be reported.

Keywords: industrial sludge; recycling; ceramic pigments.

Desarrollo de pigmentos cerámicos basados en residuos.

Se presenta la preparación de pigmentos cerámicos empleando residuos industriales como fuente de materias primas. Se detallan el uso de barros ricos en aluminio obtenidos en los tratamientos de depuración de aguas de plantas industriales de anodizado y barros de galvanizados de chapados de Cr/Ni. Los pigmentos cerámicos se prepararon empleando reacción en estados sólido a partir del barro rico en metal. Los principales pigmentos estudiados son orquídea casiterita de cromo-estaño (Sn,Cr)O₂, malayita rojo de cromo-estaño Ca(Cr,Sn)SiO₅, granate verde victoria Ca₃Cr₂Si₃O₁₂, y corindón rosa/verde de cromo alúmina (Cr,Al)₂O₃. Los pigmentos fueron caracterizados y ensayados después de ser vidriados en cerámicas estándares. Se presentan las condiciones de trabajo y el desarrollo de color.

Palabras clave: industriales, reciclado, pigmentos cerámicos.

1. INTRODUCTION

In the ceramic industry, natural and synthetic pigments find applications as colouring agents in glasses, enamels and unglazed bodies. Currently, synthetic ceramic inorganic pigments are prepared and widely used for the production of coloured glazed and unglazed tiles (1). There has been a great interest in the ceramic industry for developing high stable pigments that show intense tonalities and comply with technological and environmental demands (2). Due to these requirements, the concept of synthesis and classification of ceramic pigments keeps evolving. One of the current trends is the search for alternative and less expensive raw materials. Selected industrial wastes have been investigated for this purpose (3,4). In fact, industrial processes like aluminium anodizing and powder surface coating or Cr/Ni plating consume large amounts of water. It turns out that a huge flow of wastewater has to be treated yielding high amounts of sludge (5). Traditionally, waste products are disposed of as soil conditioners or in land filling. More recently, recycling methods of such waste products have emerged as interesting alternative procedures (6-10). This led us to investigate new ceramic pigments obtained by solid state reactions of mixtures composed of several industrial wastes, such as Al-anodising and galvanic sludge. Metal-rich sludge might act as colouring agents, or might be combined with other materials acting in

this case as the host for diverse colouring species.

Cr-doped materials have been widely investigated as ceramic pigments. Depending on the synthesis conditions, Cr ions might assume different oxidation states (II-IV) leading then different colours and variable stability degrees (11). Violet chromium-doped cassiterite (Sn,Cr)O₂ and pink chromium-doped malayaite Ca(Cr,Sn)O₅ are among the most important chromium pigments used in the ceramic industry for colouring glazes (12). Nowadays these pigments are the only alternative to cadmium-containing pigments in the pottery industry (13). However, some fundamental aspects associated to these pigments, such as the metal oxidation state, the localization and distribution of chromium species in the host matrices, are not well established (14).

Cr₂O₃ and Al₂O₃ (corundum) are sesquioxides with a similar crystal structure which consists in an hexagonal close-packed array of oxide ions with the Cr³⁺ (or Al³⁺) ions occupying two thirds of the octahedral sites (11). According to the Cr₂O₃-Al₂O₃ phase diagram, these two oxides can form a complete range of substitutional solid solution between the solidus temperature (~2100°C) and ~950°C, which can be formulated as Cr_{2-x}Al_xO₃ (0 ≤ x ≤ 2). An immiscibility region is present below 950°C, where two crystalline phases (alumina-rich and chromium rich solid solutions) are present, but the actual decomposition of a homogeneous solid solution into two phases takes place very

slowly. Depending on the chromium content, colouring varies from green to red; for example to produce a green pigment, the Cr_2O_3 content should exceed that one of Al_2O_3 (11). In general, Cr-green pigments are very dark. However, the combination with calcium and silica might give more bright hues, such as in the case of the "victoria green" or uvarovite pigment, that has a garnet ($\text{Ca}_3\text{Cr}_2\text{Si}_3\text{O}_{12}$) structure. This pigment is sintered between 700°C and 1350°C. Above this limit, the dissociation in to CaSiO_3 and Cr_2O_3 occurs, leading to the formation of typical dark-green hues (15).

The main focus of this work is on the synthesis of chrome-tin orchid cassiterite (Sn,Cr) O_2 , chrome-tin red malayaite $\text{Ca}(\text{Cr,Sn})\text{SiO}_5$, victoria green garnet $\text{Ca}_3\text{Cr}_2\text{Si}_3\text{O}_{12}$ and chrome alumina pink/green corundum $(\text{Cr,Al})_2\text{O}_3$ pigments, incorporating Al-anodising and Cr/Ni plating sludge as relevant components..

2. EXPERIMENTAL

2.1. Raw materials and formulations

Industrial wastes were collected and analysed to be used as the main components of the new pigments. The wastes consist on: i) Al-rich sludge (A-s) generated in the wastewater treatment unit of an anodising or surface coating industrial plant (as alumina matrix), and ii) a galvanizing sludge from the Cr/Ni plating process (G-s). Since the Al-sludge usually contains moisture levels in excess to 80%, we have used this sludge after calcination at 1400°C over 1 h. During this step, fully decomposition of hydroxides and sulphates occurs, remaining alumina as the stable component. All the other components were used as-received or after drying at 100°C. For comparison purposes, standard formulations (noted as St) obtained from commercial and chemical-grade reagents were prepared. Calcite (Calcitec M1), Silica sand (Sibelco P500), Cr_2O_3 (Merck, Selectipur) and SnO_2 (CCT, MP 989) were used.

The characterisation included determinations of chemical composition (XRF, Philips X'UNIQUE II), thermal behaviour (DTA and TGA, SETARAM – LabSys) and particle size distribution (Beckman Coulter LS 230 or SediGraph 5100). The crystalline phases in the samples were identified by X-ray diffraction (XRD, Rigaku Geigerflex D/max – Series).

The full characterization of G-sludge reveals its potential hazardous character (16). Suitable treatments were then proposed in order to minimise its dangerous character (17,18).

2.2. Preparation and characterisation of pigments

The starting batch formulations of pigments are shown in Table 1. In order to obtain fine and homogeneous slurries, the mixtures were prepared by a wet ball-milling method in ethanol for 1 hour. The as prepared suspensions were dried at 110°C and then calcined in an electric kiln at temperatures varying between 950-1550°C (3 hours dwell time and 5°C/min. heating rate). Calcined powders were manually disintegrated and sieved at 63 μm .

A preliminary characterisation of pigments involved the identification by powder XRD of the main crystalline phases formed, upon firing, and measurements of the CIELAB colour parameters. This method uses the reflectance data in the visible region to obtain the three relevant parameters, $L^*a^*b^*$, measuring the brightness, red/green and yellow/blue hue intensities, respectively (19). The visible diffuse reflectance spectra of the pigments were recorded on a Jasco V-560 UV-Vis spectrophotometer, using MgO as reference.

Finally, each pigment was added (5 wt-%) to a transparent and shining lead-free commercial glaze (SiO_2 , Al_2O_3 , B_2O_3 , CaO , as main constituents + >8 wt-%, 2-8% Na_2O , and <2% K_2O) and to an opaque and shining commercial glaze (SiO_2 , B_2O_3 , ZrO_2 , as main constituents + >8 wt-%, 2-8% Al_2O_3 , Na_2O , CaO , and <2% K_2O , MgO , ZnO and CoO). The mixtures were prepared by a wet ball-milling method in ethanol for 15 min. and were dried at 110°C. The powders were then used to press pellets or buttons ($\varnothing = 2.5$ cm) that were fired at 1050°C (30 min. dwell time and 5°C/min. heating rate) in an electric furnace and the final colour was evaluated.

3. RESULTS AND DISCUSSION

3.1. Wastes characterisation

Table 2 gives the average chemical composition of the wastes, while the fully characterization of some of them is detailed elsewhere (5,16). In A-s the relative concentration of alumina is over 85%, being silica, sodium and calcium oxides the relevant minor components. The persistence of sulphur based compounds in the calcined material means that the sulphate decomposition was incomplete. G-s is produced by the physico-chemical treatment of wastewaters generated by a Ni/Cr plating plant. This sludge is mostly composed of metal hydroxide gels, sulphate salts and occasionally chlorides. This chemical composition diversity implied careful sampling and homogenising procedures to assure reasonable

TABLE 1. PIGMENTS FORMULATIONS (WT-%) AND CORRESPONDING CODES (E.G. MA = MALAYAITE, GS = NI/CR SLUDGE). ST NOTATION CORRESPONDS TO PIGMENTS FULLY PREPARED FROM COMMERCIAL REAGENTS, ATTEMPTING TO REPRODUCE THE MOLAR % OF ONE WASTE-CONTAINING PIGMENT (E.G. GN-GS VS. GN-ST).

Pigment designation	Reference	Formulation (wt.%)					
		G-s	A-s	CaCO_3	SiO_2	SnO_2	Cr_2O_3
Chrome-tin pink malayaite $\text{Ca}(\text{Cr,Sn})\text{SiO}_5$	Ma-Gs/1	6.2	—	30.2	18.1	45.5	—
	Ma-Gs/2	5.2	—	30.5	18.3	46.0	—
	Ma-St/1	—	—	31.6	19.0	47.7	1.7
Chrome-tin orchid cassiterite (Sn,Cr) O_2	Ca-Gs	14.9	—	—	—	85.1	—
	Ca-St	—	—	—	—	95.6	4.4
Victoria green garnet $\text{Ca}_3\text{Cr}_2\text{Si}_3\text{O}_{12}$	Gn-Gs	57.0	—	28.2	14.8	—	—
	Gn-St	—	—	47.5	28.5	—	24.0
Green corundum (Cr,Al) O_3	Co-AsGs/1	84.3	15.7	—	—	—	—
	Co-AsGs/2	32.4	67.6	—	—	—	—

TABLE II. AVERAGE CHEMICAL COMPOSITION (WT-%) OF THE WASTES (OBTAINED BY XRF).

Component (wt.%)	G-s	A-s (calcined at 1400°C)
Al ₂ O ₃	0.06	87.2
Fe ₂ O ₃	0.83	0.72
NiO	38.7	-
Cr ₂ O ₃	28.1	0.36
SiO ₂	5.73	4.54
CaO	1.75	1.37
Na ₂ O	0.77	5.06
ZnO	3.44	-
SO ₃	11.7	0.79
Others	8.9	-

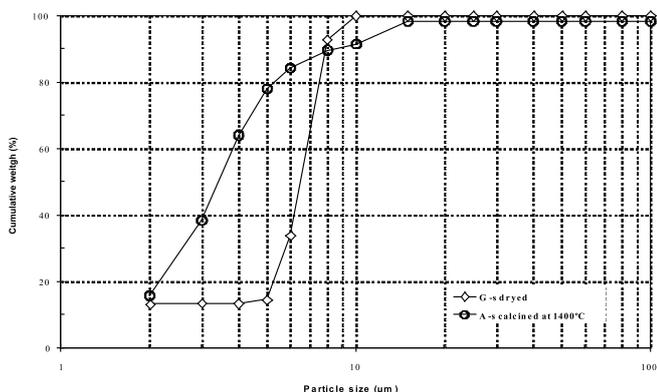
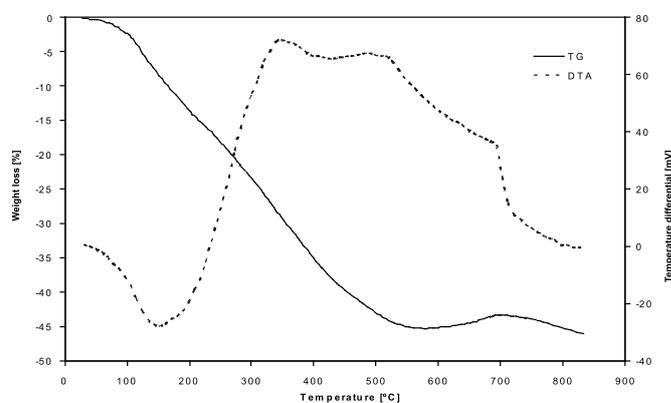


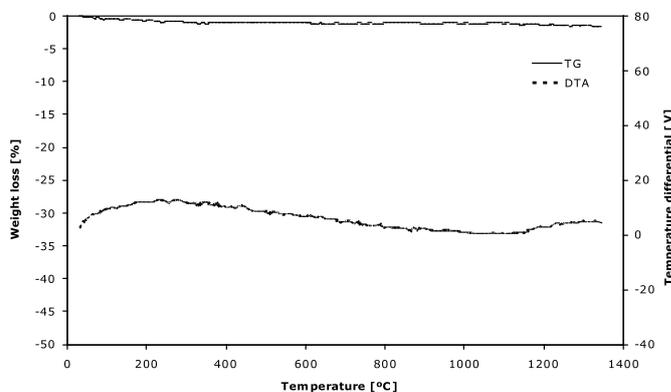
Fig. 1- Particle size distribution analyses of the as-prepared G-s dried and A-s calcined at 1400°C sludges.

Figure 2 shows the XRD patterns of G-s and A-s sludges after calcination at 950°C and 1400°C, respectively. A-s is mainly composed by α - and β -Al₂O₃, while G-s is much more complex in composition (nickel chromium oxide- NiCr₂O₄, nickel oxide- NiO, olivine- Ni₂(SiO₄), zincite- ZnO and quartz).

Figure 3 shows the DTA/TG curves for G-s and A-s materials. The first one is partially dried by exposure in open air conditions. The total weight loss reaches 45%, well below the value (over 80%) normally reported for As-collected sludges (5,16). Decomposition reactions for the earlier heating stages seem to be completed only at about 500°C (Figure 3a), confirming the presence of hydroxide gels in the starting samples. The changes at higher temperatures (650-700°C) are due to the decomposition of sulphates/chlorides. As expected, calcined A-s material is basically inert and no relevant reactions were detected (figure 3b).



(a)



(b)

Fig. 3- DTA/TG curves of G-s (a) and A-s (b) samples.

3.2. Pigments preparation and characterisation

The following pigment groups have been prepared (see Table 1): chrome-tin orchid cassiterite (Sn,Cr)O₂, chrome-tin red malayaite Ca(Cr,Sn)SiO₅, victoria green garnet Ca₃Cr₂Si₃O₁₂ and chrome-alumina pink/green corundum (Cr,Al)₂O₃. They will be now discussed separately.

Chrome-tin red malayaite Ca(Cr,Sn)SiO₅

A Cr₂O₃:SnO₂ molar ratio of 0.036 was used to prepare Ma-St/1 and Ma-Gs/1 pigments, following the work of Lopez-Navarrete et al. (14). In order to explore other hues

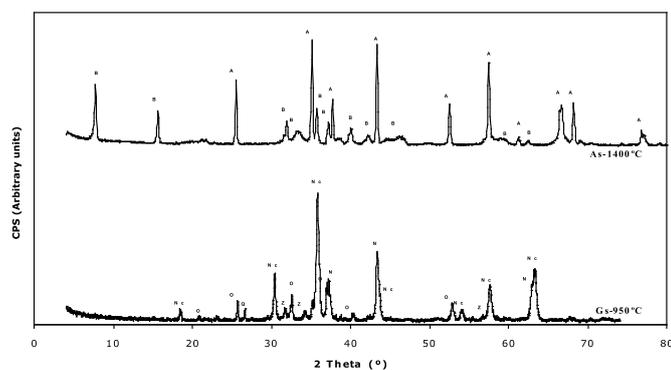


Fig. 2- XRD patterns for A-s and G-s powdered samples after calcination at 1400 and 950°C, respectively. The following phases were identified: Nickel-chromium spinel- NiCr₂O₄ = Nc; Olivine- Ni₂(SiO₄) = O; Nickel oxide- NiO = N; Zinc oxide- ZnO = Z; Quartz- SiO₂ = Q; α -Al₂O₃ = A; β -Al₂O₃ = B.

constancy (16). The main metal species are combined forming nitrogen, oxygen, hydrogen, sulphur and carbon-containing compounds. Figure 1 gives a representative cumulative particle-size distribution curve of both as-prepared sludges. The particles have sizes less than 10 μ m and the average diameter is about 6.5 μ m in the dried G-s sample and 3.5 μ m in the calcined (at 1400°C) A-s sample. However, some agglomeration has occurred during the calcination of A-s, and further milling + sieving (at 63 μ m) is required.

TABLE III. MAIN CRYSTALLINE PHASES DETECTED ON CALCINED WASTES AND PIGMENTS

Reference	Calcination Temp. (°C)	Main phases
G-s	950	NiCr ₂ O ₇ , NiO, Ni ₃ (SiO ₄)
A-s	1400	α and β-Al ₂ O ₃
Ma-St/1	1550	Ca(Cr,Sn)SiO ₅
Ma-St/1	1450	Ca(Cr,Sn)SiO ₅
Ma-Gs/1	1450	Ca(Cr,Sn)SiO ₅
Ma-Gs/2	1350	Ca(Cr,Sn)SiO ₅
Ca-St	1550	(Sn,Cr)O ₂
Ca-St	1450	(Sn,Cr)O ₂
Ca-Gs	1450	(Sn,Cr)O ₂
Gn-St	1000	CaSiO ₃ , SiO ₂ , Cr ₂ O ₃
Gn-Gs	1000	NiO, NiCr ₂ O ₄ , SiO ₂ , CaSiO ₃
Co-AsGs/1	1100	NiAl ₂ O ₄ , NiO
Co-AsGs/2	1250	Al _{1-x} Cr _x O _y , Ni ₂ SiO ₄

TABLE IV. L*A*B* VALUES FOR THE SINTERED PIGMENTS.

Reference	Parameter			Hue
	L*	a*	b*	
Ma-St/1-1450°C	35.2	+24.2	+4.8	Red wine
Ma-St/1-1550°C	28.7	+20.1	+3.1	Red wine
Ma-Gs/1-1450°C	31.3	+19.2	+2.4	Red wine
Ma-Gs/2-1400°C	39.6	+22.8	+4.1	Red wine
Ca-St-1450°C	41.3	+12.7	-7.6	Violet
Ca-St-1550°C	32.0	+12.8	-8.4	Violet
Ca-Gs-1450°C	34.5	+7.5	-6.0	Violet
Gn-St/1-1000°C	47.4	-11.5	+21.2	Light green
Gn-Gs/1-1000°C	36.4	-2.6	+8.3	Grey green
Co-AsGs/1-1100°C	27.2	-1.8	+5.0	Dark olive green
Co-AsGs/2-1250°C	40.6	+2.3	+9.0	Grey brownish

amount tends to diminish. In sludge containing samples, Ma-Gs/1 and Ma-Gs/2, traces of a pyroxene (CaNiSi₂O₆) were also detected, acting as host phase for Ni. In standard pigments traces of Cr₂O₃ are also detected by XRD and were clearly identified by SEM analysis as bright small grains (figure 5).

The Cr-doped malayaite has been considered for a long time as a solid solution pigment. Early works assumed that in this pigment, the Cr(III) cations are in an octahedral coordination geometry, whereas recent studies postulate that the chromium ions might also assume a tetrahedral coordination geometry. They seem to occupy octahedral Sn⁴⁺ sites although a very small amount might also substitute tetrahedral Si⁴⁺ sites (14).

Table 4 shows the L*a*b* values for the sintered pigments. Red-wine is the dominant hue and differences are small between all them. In standard formulations, the pigments brightness tends to decrease by improving the calcination temperature (from 1450 to 1550°C), due to the reduction of the chromophor oxidation state. Both values of red (a*) and yellow (b*) colour coordinates also tend to decrease with increasing temperatures. Sludge-containing pigments have similar properties, meaning that the presence of nickel does not cause significant (deleterious) changes in the colour development. As an example, the Ma-Gs/1 pigment calcined at 1450°C has a brightness value between the two St samples but a* and b* values that are closer to those of the Ma-St/1-1550°C. This means that a similar colour is developed at lower

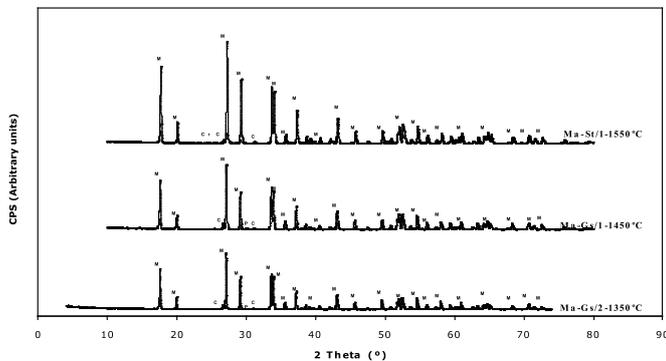


Fig. 4- XRD patterns of powdered pigments: Ma-St/1, Ma-Gs/1 and Ma-Gs/2 calcined at 1550°C, 1450°C and 1350°C, respectively. The following phases were identified: Malayaite = M; Cassiterite = C; Cr₂O₃ = Cr; pyroxene- CaNiSi₂O₆ = P.

Ma-Gs/2 pigment (Cr₂O₃:SnO₂ = 0.03) was also prepared. The XRD of those pigments (Table 3) shows malayaite as the major phase (Figure 4). However, traces of SnO₂ were detected in all formulations, denoting an incomplete reaction between the components. By increasing the firing temperature, their

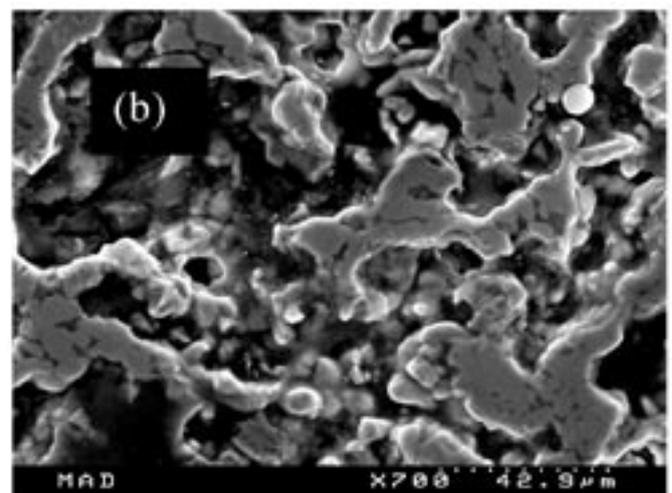
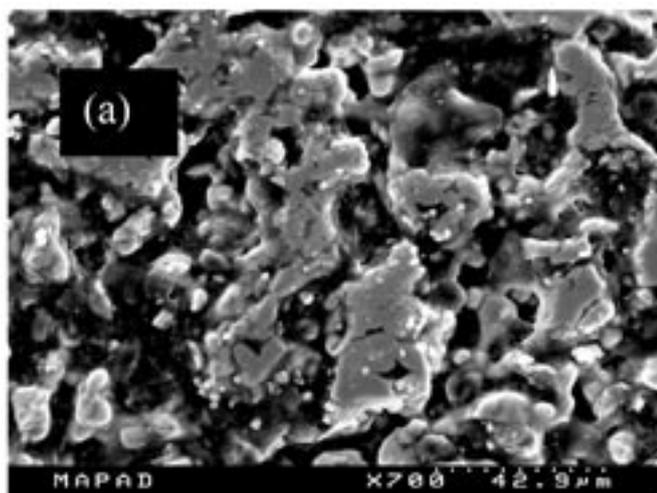


Fig. 5- SEM views (700X) of Ma-St/1 (a) and Ma-Gs/1 (b) buttons fired at 1550 and 1450°C, respectively.

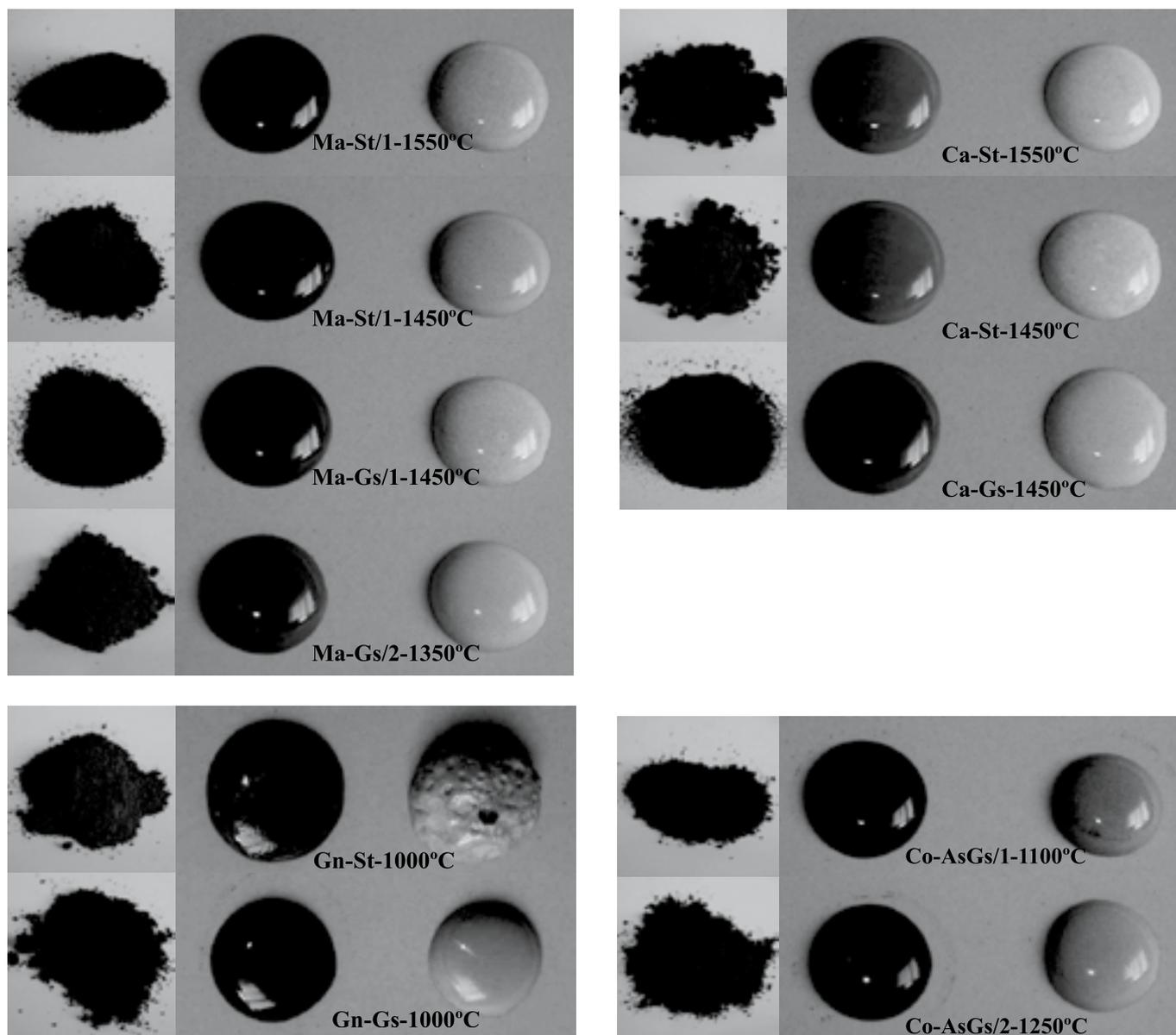


Fig. 6- Colours developed by the pure pigments (left) and colours of the transparent (center) and opaque (right) pigments: (a) malayaite-based compositions; (b) cassiterite-based pigments; (c) uvarovite-based pigments; (d) corundum-based pigments.

processing temperature with obvious economical benefits. This is even more evident in the case of the Ma-Gs/2 pigment that is calcined at only 1400°C. Figure 6a illustrates the colours obtained upon sintering of these pigments, and resulting hues after addition and firing (at 1050°C) in transparent and opaque glazes. The colour development in these two glazes by St and Gs pigments is also similar, as shown by the $L^*a^*b^*$ values of Table 5. Waste-containing pigments give slightly clean and bright colours (all coordinates are over those of the St). In the transparent glaze the colour development is easier to achieve (figure 6a).

Chrome-tin orchid cassiterite (Sn,CrO_2)

In this case the chosen $\text{Cr}_2\text{O}_3:\text{SnO}_2$ molar ratio was 0.044, as suggested in ref. (14). Figure 7 shows XRD spectra of the sintered pigments, while Table 3 lists the major crystalline phases. As expected, cassiterite is the dominant phase in all compositions. However, in standard formulations traces of Cr_2O_3 are detected, while waste-containing powders had

nichromite (NiCr_2O_4) as minor phase. This component was also observed in the single calcined sludge (figure 2).

The $L^*a^*b^*$ values of Table 4 correspond to the observed violet hue, due to the prevalence of red and blue primary colours. In the case of Cr-doped cassiterite, it was first postulated that the violet colour is given by the deposition of fine Cr(III) oxide particles on the surface of the tin oxide grains, but then Cr(III) for Sn(IV) substitution in the cassiterite lattice was proposed (20). The solid solution is possible due to the formation of anionic vacancies to compensate electric charge difference between the two ions. More recently, Ren et al. (21), reported that both mechanisms might act: the pigment might contain Cr(IV) in solid solution and Cr_2O_3 particles. In another work (14), three types of chromium species are assumed to be present in Cr-doped cassiterite pigments: Cr(III) oxide clusters, which represent the main phase, a very small amount of CrO_2 nanoparticles, and Cr(IV) ions in solid solution. The

TABLE V. L*a*b* VALUES OF BUTTONS (GLAZE + 5 WT-% OF PIGMENT) FIRED AT 1050°C

Reference	Parameter transparent glaze			Parameter opaque glaze		
	L*	a*	b*	L*	a*	b*
Ma-St/1-1450°C	35.3	+16.8	+3.5	66.0	+12.4	+0.4
Ma-St/1-1550°C	35.2	+14.5	+2.7	68.5	+9.8	+0.4
Ma-Gs/1-1450°C	38.5	+14.9	+4.4	71.3	+9.0	+0.5
Ma-Gs/2-1400°C	41.7	+19.5	+5.0	70.6	+12.1	+1.1
Ca-St-1450°C	51.7	-4.2	+6.8	76.9	+0.8	-1.0
Ca-St-1550°C	50.2	-2.2	+4.9	75.6	+2.3	-2.8
Ca-Gs-1450°C	44.5	+4.1	+5.0	72.6	+2.8	-1.1
Gn-St-1000°C	40.5	-11.1	+14.4	61.9	-9.2	+10.4
Gn-Gs-1000°C	32.5	-3.2	+6.1	62.5	-0.9	+11.1
Co-AsGs/1-1100°C	29.1	-1.5	+4.7	56.0	-0.8	+7.4
Co-AsGs/2-1250°C	32.3	-0.8	+6.8	63.8	+0.6	+11.8

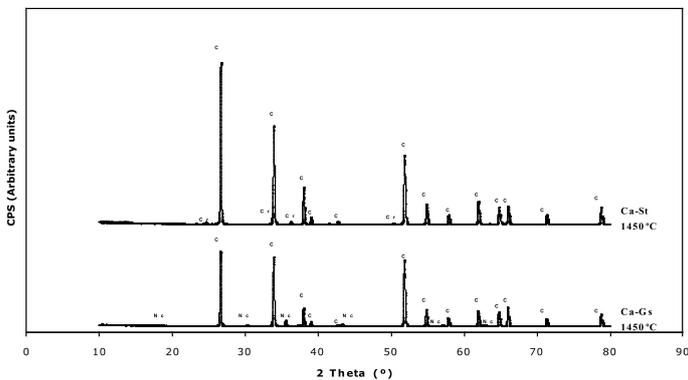


Fig. 7- XRD patterns of Ca-St and Ca-Gs powdered pigments calcined at 1450°C. The following phases were identified: Cassiterite = C; Cr_2O_3 = Cr; Nichromite- NiCr_2O_4 = NC.

colour development on glazes (transparent and opaque) fired at 1050°C is also visible in figure 6b and the corresponding L*a*b* values are given in table 5. The hues observed in the glazes are distinct from those generated by the respective pigments. This might be due to: (i) potential interaction with glaze constituents, changing the coordination environment of the chromophor (22); (ii) cassiterite dissolution and dominance of Cr_2O_3 or nichromite minor phases, since green hue is observed in the Ca-St containing transparent glaze. Further tests will be conducted to overcome this problem, namely by adding higher amounts of pigment to the opaque glaze, by refining the composition (lower amount of Cr_2O_3), by testing different glazes and by colouring unglazed bodies.

Victoria green garnet $\text{Ca}_3\text{Cr}_2\text{Si}_3\text{O}_{12}$

The pigment prepared from commercial chemicals shows CaSiO_3 , SiO_2 , Cr_2O_3 as the main phases. The waste-based formulation also presents some of those phases and Ni-containing components in addition (see table 3 and figure 8). Surprisingly the expected phase (uvarovite) is almost absent and was not detected in the Gn-Gs pigment. Uvarovite is detected on Gn-St pigments calcined at 1000°C but even so as a minor or a component with a low crystalline degree whose stability is dependent on the composition and temperature. In the Gn-Gs samples we never detect its formation.

Nevertheless, Gn-St pigments show an interesting bright green yellowish colour (see L*a*b* values on table 4), as can be seen in figure 6c. Gn-Gs pigment is not so bright and its colour

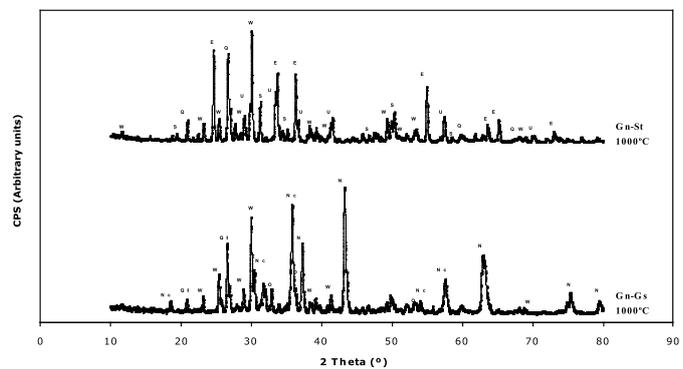


Fig. 8- XRD patterns of Gn-St and Gn-Gs powdered pigments calcined at 1000°C. The following phases were identified: Nickel oxide- NiO = N; Nickel-chromium oxide - NiCr_2O_4 = Nc; Wollastonite- CaSiO_3 = W; Quartz- SiO_2 = Q; Quartz low- SiO_2 = Ql; Eskolaite- Cr_2O_4 = E; Olivine- $\text{Ni}_2(\text{SiO}_4)$ = O; Uvarovite= U; Calcium chromium silicon oxide- $\text{Ca}_3\text{Cr}_2\text{SiO}_{12}$ = S

development is seriously determined by the presence of G-s.

Once applied in glazes the general colouring effects are similar to those obtained with the pure pigments (compare L*a*b* values of tables 4 and 5). However, the hue is not homogeneous (figure 6c) as a result of a strong undesirable interaction with the glaze. This is partially expected from the relatively low calcination temperature used to process the pigment. However, attempts to increase the calcination temperature were not successful since the amount of uvarovite diminished with increasing temperatures.

Chrome-alumina green corundum $(\text{Cr,Al})_2\text{O}_3$

Co-GsAs pigments use alumina as the host of the Cr chromophor. The pigment green hue originates from selective absorption in the visible region, which might result from optical transitions occurring in the Cr(III) ions located in octahedral sites of the host. However, there are other components in these formulations, such as nickel, that might have a determinant role in the colour development. Two different compositions were prepared, fully based on wastes. Cr-containing NiAl_2O_4 and NiO were the main phases detected in Co-AsGs/1 pigment calcined at 1100°C, while $\text{Al}_{1-x}\text{Cr}_x\text{O}_3$ and Ni_2SiO_4 were prevalent in the Co-AsGs/2. The second is closer to a desirable corundum-based formulation, since the relative amount of A-s is higher. The use of higher amounts of G-s in the mixture was explored based on a previous work where pure G-s powders

gave promising dark olive green hues (23). Now, Co-GsAs/1 also shows a similar hue, as can be seen in figure 6d and is confirmed by L^*, a^*, b^* values of table 4. Co-GsAs/2 shows grey brownish hue, as suggested by the changes observed in the a^* values (red appearance).

Once applied in a transparent glaze the brightness and hue are surprisingly similar, as denoted by values in table 5 and can be seen in figure 6d. Contrasting to this, there are marked differences for the brightness and hue in the opaque glaze which follow the colour differences observed in the starting pigments.

4. CONCLUSIONS

Pigments based on industrial wastes were prepared and preliminarily characterised. Four basic pigment groups were discussed in this work: chrome-tin red malayaite $\text{Ca}(\text{Cr},\text{Sn})\text{SiO}_7$, chrome-tin orchid cassiterite $(\text{Sn},\text{Cr})\text{O}_2$, victoria green garnet $\text{Ca}_3\text{Cr}_2\text{Si}_3\text{O}_{12}$, and chrome alumina green corundum $(\text{Cr},\text{Al})_2\text{O}_3$. In general, the hue developments for the pure pigments comply with standard expectations. In general, interesting colouring effects were observed for commercial transparent and opaque glazes containing such pigments. However, chrome-tin orchid cassiterite pigment develops unexpected colours in both glazes, and victoria green garnet did not assure an homogeneous hue. Further optimisation studies are then required. Although a complete evaluation of the stability limits is still required, it seems that the pigment hues remain fairly constant over a suitable temperature range.

ACKNOWLEDGEMENT

The work was supported by FCT (PhD grant of G. Costa).

REFERENCES

1. F. Bondioli, A.M. Ferrari, C. Leonelli, T. Manfredini, Syntheses of Fe_2O_3 /silica red inorganic inclusion pigments for ceramic applications, *Materials Research Bulletin*, 33, 5-11 (1998).
2. Y. Marinova, J.M. Hohemberger, E. Cordoncillo, P. Escribano, J.B. Carda, Study of solid solutions, with perovskite structure, for application in the field of ceramic pigments, *J. Eur. Ceram. Soc.*, 23, 213-220 (2003).
3. 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, 246-248 (2000).
4. V. Gomes, A. P. Novaes de Oliveira, J.A. Labrincha, Ceramic pigment based on mullite structure obtained from Al-sludge containing formulations, *Amer. Ceram. Soc. Bull.*, 84, 9501-9504 (2005).
5. M.J. Ribeiro, D.U. Tulyaganov, J.A. Labrincha, J.M.F. Ferreira, Production of Al-rich sludge-containing bodies by different shaping techniques, *J. Mat. Processing Techn.*, 148, 139-146 (2004).
6. M. Dondi, M. Marsigli, B. Fabbri, Recycling of industrial and urban wastes in brick production: a review, *Tile & Brick Int.*, 13, 302-308 (1997).
7. D.A. Pereira, J.A. Labrincha, Using of aluminum-rich salt slag in bauxitic-type refractories, *Amer. Ceram. Soc. Bull.*, 80, 61-63 (2000).
8. F. Raupp-Pereira, D. Hotza, A.M. Segadães, J.A. Labrincha, Ceramic formulations made of different wastes and natural sub-products, *Ceramics International*, 32, 173-179 (2006).
9. M.C. Granana, J.B. Vicent, M. Llusar, Recycling silica waste from support chromatography process in the synthesis sol-gel of ceramic pigments, *Bol. Soc. Esp. Ceram. V.*, 39, 237-242 (2000).
10. J. Calbo, M. Llusar, M. Tena, Environmental characterization of ceramic pigment industrial wastes, *Bol. Soc. Esp. Ceram. V.*, 41, 311-317 (2002).
11. R. Muñoz, N. Masó, B. Júlían, F. Márquez, H. Beltrán, P. Escribano, E. Cordoncillo, Environmental study of Cr_2O_3 - Al_2O_3 green ceramic pigment synthesis, *J. Eur. Ceram. Soc.*, 24, 2087-2094 (2004).
12. DCMA, Classification and Chemical Description of the Mixed Metal Oxide Inorganic Coloured Pigments, Metal Oxides and Ceramics Colors Subcommittee, 2^a ed. Dry Color Manufacturer's Ass, Washington DC (1982).
13. J.F. Papp, Chromite, *Am. Ceram. Soc. Bull.*, 74, 118-120 (1995).
14. E. Lopez-Navarrete, A. Caballero, V.M. Orera, F.J. Lázaro, M. Ocaña, Oxidation state and localization of chromium ions in Cr-doped cassiterite and Cr-doped malayaite, *Acta Materialia*, 51, 2371-2381 (2003).
15. V.P. Della, J.A. Junkes, I. Kuhn, H.G. Hiella, D. Hotza, By-product utilization of metallic recovering of stainless steel slags in the ceramic pigments synthesis; raw material characterization, *Cerâmica*, 51, 111-116 (2005).
16. J.M. Magalhães, J.E. Silva, F.P. Castro, J.A. Labrincha, Physical and chemical characterisation of metal finishing industrial wastes, *J. Environmental Management*, 75, 157-166 (2005).
17. J.E. Silva, D. Soares, A.P. Paiva, J.A. Labrincha, F. Castro, Leaching behaviour of a galvanic sludge in sulphuric acid and ammonical media, *J. Hazardous Mat.*, B121, 195-202 (2005).
18. J.E. Silva, D. Soares, A.P. Paiva, J.A. Labrincha, F. Castro, Solvent extraction applied to the recovery of heavy metals from galvanic sludge, *J. Hazardous Mat.*, B120, 113-118, (2005).
19. R. Tilley (Ed.), *Colour and the optical properties of materials*, John Wiley & Sons, England (2000).
20. J.W. Mellor, The chemistry of chrome-tin colours, *Trans. Brit. Ceram. Soc.*, 36, 720-721 (1936-1937).
21. F. Ren, S. Ishida, N. Takeuchi, and K. Fujiyoshi, Chromium-based ceramic colors, *Ceram. Bull.*, 71, 759-764 (1992).
22. H. Camacho, A. Garcia, L. Fuentes, Study of factor affecting colour in glaze ceramics, *Boletín Soc. Esp. Ceram. V.*, 44, 13-19 (2005).
23. G. Costa, M.J. Ribeiro, J.A. Labrincha, Waste-based new ceramic pigments, Proc. of V Int. Congress Valorisation and Recycling of Industrial Waste, June 28th – July 1st 2005, L'Aquila, Italy, (CD: poster-paper n°3).

Recibido: 29.11.05

Aceptado: 24.08.06

