Contents lists available at ScienceDirect

Ceramics International

journal homepage: www.elsevier.com/locate/ceramint

Green ceramic pigment based on chromium recovered from a plating waste

Griselda X. Gayo*, Araceli E. Lavat

CIFICEN (CONICET-UNCPBA-CICPBA), Facultad de Ingeniería, Universidad Nacional del Centro de la Provincia de Buenos Aires, Av. Del Valle 5737, B7400JWI Olavarría, Argentina

ABSTRACT

The development of pigments with new formulas, departing from lower-cost raw materials, is driven by market growth and competitiveness required by the ceramic sector. In this work, the application of a residue from a metallurgical plant, containing a high amount of chromium (III) in ceramics glazes was studied. Cr_2O_3 was successfully separated from chrome plating waste resulting in a suitable synthesize ceramic pigment, based on this chromophore. A washing treatment was applied to the residue followed by a calcination at 1000 °C prior to the usage as pigment. The adequate purity of Cr_2O_3 recovered from waste was confirmed by analytical techniques (XRF, XRD, DTA-TG, FTIR and SEM-EDX). The glasses, containing 5 wt% of recovered Cr_2O_3, were carried out using frits and transparent micronized glass for mono- and double firing processes. The materials were characterized by XRD and FTIR, and by the colorimetric parameters CIE*Lab*. The resulting glazes containing the waste are within the range of typical pigments based on Cr_2O_3 in silicate and aluminate glazes for single firing, showing dark green hues in comparison with the previous data obtained from commercial grade Cr(III) oxide. However the presence of small amounts of the other chromophores in the waste modifies the tonality, affecting the purity of the chroma by increasing darkness. The leaching tests performed on the glazes suggest that Cr(III) is stable in this ceramic matrix. This results show that glazing is a suitable process for the Solidification/Stabilization of this waste.

1. Introduction

Currently, one of the main requisites for sustainable industrial development is appropriate waste management. Therefore recycling and adding commercial value to end products have emerged as interesting strategies for many industries. The re-utilization of waste contributes, at the same time, to reduce final costs by replacing other raw materials, and the cost of disposal and environmental impact.

New products made out of recycled waste materials mainly involve the transformation of the waste into cementitious agglomerates, ceramics, glass and glass-ceramic. Among these, ordinary Portland Cement (OPC) provides an adequate matrix to immobilize many hazardous residues in a very easy way before its landfill deposit. However the durability of cement-based waste mixtures is still under discussion and the products cannot be used in the building industry. In this way, technological recovery procedures involving ceramic and glass seem to be more suitable for inertization of hazardous wastes because these are stable matrices with important volume reduction [1].

Some industries consume high amounts of raw materials and are able to receive waste which can then be reconverted. The construction and building industry is an example of this, since a large amount of

construction products are produced worldwide. A variety of waste materials, including construction rubble, tile rubber ash, blast furnace slag, silica fume, fly ash, and biological limestone have been successfully added in mortars, reducing the amount of Portland cement needed. The use of granite sludge wastes for the production of colored cement-based mortars has been previously investigated [2]. Moreover, ceramic waste tiles as a pozzolanic addition, have been reported elsewhere [3].

Some toxic elements which are dangerous for the health and the environment could be immobilized in vitreous matrix. In the case of glass ceramics the leaching tests performed demonstrated that the vitrified toxic elements are well stabilized in the formed phases [4].

Metallurgy in general, chrome plating and galvanizing or surface coating processes, generates large amounts of sludge, rich in metals such as Cr or Ni, which can be used in the formulation of ceramic pigments and other colored ceramic products. The production of green Ni-olivine pigment from such waste has been previously reported [5]. Heavy metals such as Cu, Zn, Pb and Co could be recovered from the large amount of copper slag production, as a benefit of sulfur mines. Brown and black pigments, which are in high demand by the ceramic industry, have been produced from copper slag [6]. Black ceramic

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* Corresponding author.
  E-mail address: xgayo@fio.unicen.edu.ar (G.X. Gayo).

pigments have been prepared using industrial wastes from Cr/Ni plating and Fe- based on the Cr-Fe-Ni black spinel (Ni,Fe)(Fe,Cr)$_2$O$_4$ (13-50-9 DCMA classification) [7]. The recycling of Zn-hydro-metallurgy in glass and glass-ceramic have been reported as being suitable for building products, such as tiles, glass fibers, and pigments for ceramics [1].

Fe-Mn wastes from the electrolytic production of MnO$_2$ were used in the manufacture of colored ceramic building products (e.g., bricks, tiles, etc.), ranging from light to dark green [8].

Other metals have been recovered from waste material. An important example is the production of Zn and oxide particles by pyrolysis of alkaline and Zn-C battery waste. Considering that battery waste generation has been increased worldwide, the huge amount of discarded batteries requires management. Normally, the waste management is regulated by complicated local and/or national laws and legislation. Submicron Zn particles can be used as catalyst, electrode material, or anticorrosive pigment. Recovered MnO particles have applications as a pigment or electrode material [9].

Cr-doped materials have been largely investigated as ceramic pigment. A wide variety of hues tonalities and colors are possible by Cr-chromophore. However Cr, such as other transition metals can adversely affect the environment and human health. Despite this facts, Cr (III) is an essential element with an insulin mimetic biological role; however, in higher doses it becomes toxic since it affects the body's immune system. Cr(VI) is even more toxic because it enters into cells and is carcinogenic. In addition, the oxidation of Cr(III) to Cr(VI) should be prevented because of its negative impact on the environment, since it is more soluble and will be segregated to the washing waters [10].

One of the earliest reports regarding the application of Cr- containing pigments recovered from waste proposes the preparation of Co-Cr green and Cr-Sn pink pigments from leather shavings produced as a waste product from the tanning industry [11]. Later, the preparation of other typical Cr-pigments using Al-rich sludge generated in an anodizing wastewater treatment unit from an industrial plant was also reported [12].

In the following paper, we present the application of a residue proceeding from a metallurgical plant, containing high amount of chromium (III), in ceramic glazes. The waste is studied thoroughly in order to design an optimization process prior to its technical use, and later incorporated in vitreous matrices as ceramic pigment. The potential environmental risks are also evaluated.

2. Experimental part

2.1. Recovery of Cr$_2$O$_3$ from waste

The industrial waste was collected and analyzed prior to be used as Cr$_2$O$_3$. The received residue (AR) consists of a powdered mixture of white and green particles. An 18% weight loss attributed to humidity was measured after drying for a few hours at 110 °C and a constant weight was achieved. With the aim to eliminate volatile and organic compounds present in the residue, two calcinations steps were carried out at 550 °C and 1000 °C. Mass losses of 41.37% and 46.82%, respectively, were determined. As detailed in Table 1, according to XRF technique, the main components of AR material expressed in oxides are SO$_3$, Na$_2$O and Cr$_2$O$_3$, representing around 90 wt%.

In view of these results, separation procedures were designed in the laboratory in order to get recovered Cr$_2$O$_3$ from the residue as pure as possible. The optimized residue was labeled OR.

The AR was washed with deionized water at ambient temperature, and stirred to favor the dissolution of salts. Later, it was filtered through a Whatman filter paper to separate the Cr-containing solid (WR). The procedure was repeated three times. Next, the slightly acid solution (pH = 6) was evaporated and the recovered crystals (RC) were analyzed by XRD and FTIR. Finally, in order to obtain OR, the dry solid residue (WR) was calcined in a muffle electrical furnace for 3 h at

Table 1
Chemical composition of Cr waste as received (AR), and optimized Cr residue (OR), in oxides (wt%).

Oxides	AR (wt%)	OR (wt%)
SO$_3$	35.62	–
Na$_2$O	25.49	–
Cr$_2$O$_3$	24.10	65.42
Al$_2$O$_3$	5.32	18.25
CaO	2.82	2.88
PbO	1.52	2.00
CuO	1.47	3.96
Fe$_2$O$_3$	1.20	3.42
Cl	1.04	–
P$_2$O$_5$	0.70	–
SiO$_2$	0.67	3.13
ZnO	0.05	0.14
SnO$_2$	–	0.39
MgO	–	0.30
I	–	0.09
SrO	–	0.01

Table 2
EDX elemental composition of OR.

Elements	C	O	Al	Si	Ca	Cr	Fe	Cu
Weight %	16.13	29.56	6.42	0.53	1.17	41.05	1.83	3.32
Elements %	30.86	42.47	5.46	0.43	0.67	18.15	0.75	1.20

1000 °C. The chemical composition of OR was also determined by XRF analysis (Table 1). In addition, the material was characterized by SEM, and the EDX elemental composition, as can be seen in Table 2.

2.2. Characterization of materials

The X-ray fluorescence analysis (XRF) of the materials was carried out by an energy dispersive spectrometer, Shimadzu, model EDX-800HS.

The thermal evolution of the washed residue (WR) was studied using a RIGAKU differential thermal analyzer, Thermo Plus Evo series, which has a differential TG-ATD horizontal high-temperature module. The tests were carried out in 100 ml/min air flow, with alumina as reference; using platinum crucibles and a heating rate of 10 °C/min, up to 1150 °C.

The materials were studied by x-ray diffraction (XRD) and Fourier Transformed Infrared Spectroscopy (FTIR). X-ray diffraction patterns were obtained using a Philips PW 3710 diffractometer equipped with graphite monochromator, using CuKa radiation, operating at 40 kV and 20 mA. The following x-ray data collection details were applied: step interval: 0.02° and step time: 0.5 (s). Unit cell parameters were obtained using a least-square procedure and refined with a locally modified version of the Werner PIRUM program [13]. The XRD measurements were calibrated using Si as the internal standard.

The infrared spectra were recorded on a Nicolet-Magna 550 FT-IR instrument, using the KBr pellet technique. The measurements were carried out in the 4000–250 cm^{-1} region.

The microstructure of the OR, on superficially polished gold-coated specimens, was obtained by a scanning electron microscopy (SEM) (Carl Zeiss, model MA10). The x-ray dispersive microanalysis was performed with EDS Orford equipment, model INCA energy.

The pigmenting aptitude of the optimized material, incorporated in glazes, was evaluated. For this purpose, suspensions of pigments with frits were prepared. The approximate composition of the transparent frits employed is detailed in Table 3. These glazes are representative of the double and single firing processes, currently applied in roof and floor tiles manufacturing.

Prior to enameling the pigment and ceramic frit test, specimens

Table 3
Composition of ceramic frits, in oxides, wt%.

Oxides	Frit A (wt%)	Frit C (wt%)	MD (wt%)
Na_2O	3	6	4.5
K_2O	2	2	4.5
CaO	4	4	5
MgO	–	–	5
PbO	30	–	–
B_2O_3	5	16	8
Al_2O_3	6	10	8
SiO_2	50	62	65

were prepared by thoroughly mixing. The mixtures were homogenized in an agate mortar with 5 wt% of powdered Cr_2O_3-OR. For comparison purposes, chromium oxide Cr_2O_3 (BDH 99 wt%) was used for all the preparations. Every batch was wet mixed and the slip was spread on porous ceramic tiles, then dried in air and finally subjected to thermal treatment. In some cases, particularly for leaching tests, cylindrical test specimens were formed by pressing the wet powder at 416 MPa. The resulting pellets were put onto ceramic biscuits and fired. The thermal cycles consisted in heating up to 1000 °C at 25 °C/min, holding this temperature for 15 min. A further step was made at 573 °C, holding for 30 min. The pure frit was also fired at different temperatures for comparative purposes. All the samples were milled and characterized by XRD and FTIR.

The technological performance of the glazes was evaluated through measuring the colorimetric behavior. $CIEL*a*b*$ color coordinates of coated tiles were obtained with a Braive Super Chroma 20 mm colorimeter and a white standard as reference. The chroma $c*$ and the tone $h*$ were calculated by means of the following equations. $C* = (a*^2 + b*^2)^{1/2}$ and $h* =$ arctan $(b*/a*)$. The color difference $\Delta E*$ between two samples was calculated as the Euclidean distance between each color stimulus in the $CIELAB$ space. Where $\Delta E* = (\Delta L*^2 + \Delta a*^2 + \Delta b*^2)^{1/2}$ (ISO 10545-16:1999).

2.3. Leaching tests

The efficiency of the solidification/stabilization process was examined by the leaching behavior of the glazes. To get a deeper insight about the leachate from glazes containing recovered Cr_2O_3, cylindrical test specimens, containing the powdered mixtures of frit C and 5 wt% Cr_2O_3-OR were formed and calcined to 1000 °C, as mentioned in the previous section.

The standard leaching test refers to a liquid/dry solid ratio with enough water to completely cover the solid, simulating conditions in landfill [14]. The samples were crushed and milled to a particle size of about or below 9.5 mm. The procedure consist of leaching by dispersing a fixed mass of dry solid with deionized water and shaking during 24 hs, at a constant temperature of 25 °C. The necessary volume of acetic acid 0.5 N was added to maintain the pH of the solution stable at 5 ± 0.2. The pH was controlled by a pH meter. Afterwards, elute was filtered and centrifuged to avoid the presence of fine particles and collected into flasks. The test was duplicated to validate the results.

Later, samples were taken for Cr(VI)-determination. Hexavalent chromium was measured according to the standard procedure formulated by NORM IRAM [15]. The Cr(VI) reacts quantitatively with the 1,5-diphenylcarbazide to form 1,5-diphenylcarbazone, which gives a red complex (0.01–0.50 mg/chrome). Then Cr(VI) was determined by colorimetric analysis. For this purpose, 25 ml of the sample is poured into a 50-ml Erlenmeyer flask, adding 2 ml of the diphenylcarbazide solution (0.25 g of diphenylcarbazide in a 50 ml solution of acetone and 50 ml of water) as reagent. The samples were introduced into a spectrophotometer at 540 nm. The calibration plot was obtained using a standard solution of chromium.
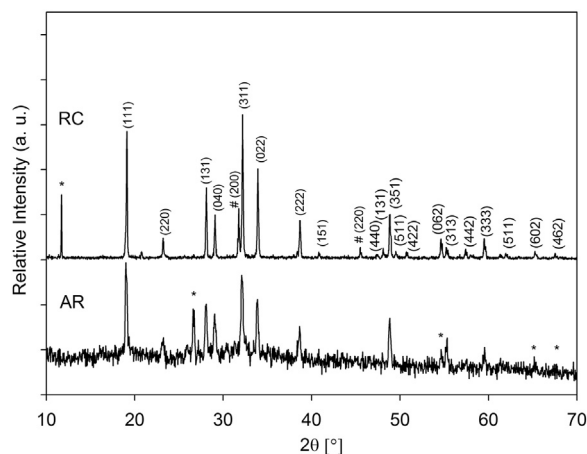

Fig. 1. XRD patterns of industrial residue AR, and of crystals recovered after washing RC (Na_2SO_4-Thenardite, (#) NaCl and (*) unidentified impurity).

3. Results and discussion

The industrial residue was subjected to washing and drying treatments, followed by calcination up to 1000 °C prior to use, as described previously. Subsequently, the colorimetric properties of the glazes were evaluated after the incorporation of the pigment and subjected to thermal treatment.

3.1. Characterization of waste AR and application as pigment

In order to obtain a pigment for glazing, with certain composition, it is necessary to determine the chemical composition of the residue prior to its incorporation in the formulation of pigments.

Usually Cr-plating sludge is mainly composed of water and soluble salts; accompanied by metallic species and processing additives that depends on the liquid effluents treatment applied. In general, the process involves a precipitation stage, starting with a reduction of Cr(VI) to (III), in acid media, by adding a reductant, such as $HNaSO_3$, followed by neutralization and coagulation-flocculation [16].

The comparison of the AR and RC XRD patterns shown in Fig. 1, suggest that the major soluble salts, accompanying the Cr- residue, are efficiently extracted by waste washing. The recovered crystalline solid (RC) was undoubtedly identified mainly as Na_2SO_4-thenardite and a secondary component of NaCl-halite. All the diagnostic peaks of the reference mineral are present, as can be concluded from Fig. 1.

The identification was confirmed by FTIR analysis. As can be seen in Fig. 2 the main bands observed in the spectrum are associated to the $SO_4^=$ group, constituent of the mineral thenardite. The spectra of the samples labeled AR and RC are identical. The two typical bands
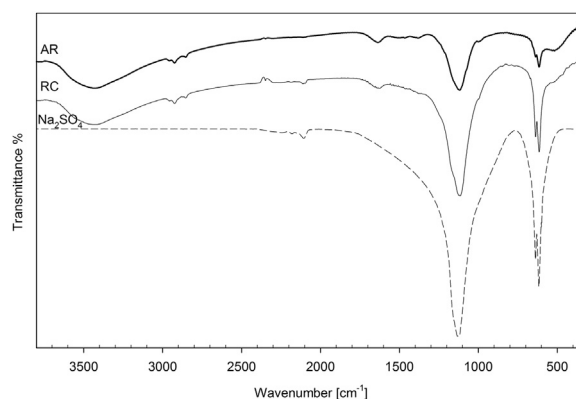

Fig. 2. FTIR spectra of AR, RC and Na_2SO_4-thenardite.

assigned to ν_3 antisymmetric stretching of S–O bonds and ν_4 deformations of O-S-O angles are observed at 1123 and 615 cm^{-1}, respectively, in total accordance with the reference spectrum of this mineral, available in the spectral library [17]. The presence of NaCl, detected by XRD, was not possible to confirm because this solid is transparent to IR radiation and therefore remains undetectable.

The other minor signals (in the high energy region of the IR spectrum), as the broad band lying at 3550–2000 cm^{-1} and at 1600 cm^{-1}, are due to OH- stretching and H-O-H deformation vibrations, respectively. These signals are attributed to the hydroxyl groups of the hydrated oxide surface and adsorbed water, which are highly sensitive to IR radiation [18].

In addition, other spurious signals observed in the range 2900–2800 cm^{-1}, are attributed to stretching motions of C–H aliphatic bonds and at 2100 cm^{-1} assignable to other functional group frequencies, present in organic compounds, from the additives used for Cr-plating, during manufacturing.

These results are compatible with the chemical composition, expressed in oxides, determined by XRF, and detailed in Table 1.

3.1.1. Characterization of recovered Cr_2O_3-OR

The optimized Cr-residue (OR) was characterized by DTA-TG thermal measurements, XRD, FTIR spectroscopy and SEM-EDX analysis, prior to being used in replacement of Cr_2O_3, in enamels.

The XRD pattern of the product obtained after washing and drying (WR) is shapeless, suggesting that it is amorphous (Fig. 3). When this sample is subjected to calcination from 100° to 1000 °C, in order to render the OR, the typical diffraction lines from crystalline Cr_2O_3 (JCPDF#381479) appear, as shown in the same figure [19].

The thermogram of non-crystalline WR was registered in order to study its thermal behavior and to interpret the changes that occurred during calcinations up to 1000 °C. The TG and DTA curves, shown in Fig. 4, are rather simple. Analyzing the TG curve, two thermal steps separated by the sharp signals around 300 °C appear. A continuous weight loss of 38.96%, is observed in the thermal range from ambient to 100 °C, followed by a drastic mass loss at 330 °C. It can be assigned to dehydration and relief of gases from thermal decomposition of organic matter, in presence of air in almost a single step. From 330–1000 °C a very slight weight loss is registered and no other thermal effects are observed, since the TG curve is almost featureless in this thermal interval. According to previous studies, the sharp exothermic signal at 330 °C has been interpreted to the crystallization of Cr_2O_3 from an amorphous phase departing from some precursor synthetic routes [20]. The mass loss seems to correspond mainly to the decomposition of the hydrated oxides forming Cr_2O_3 as the main component, followed by its crystallization. This thermal stage is accompanied by the release of light molecules, mainly H_2O and other volatile minor components, as
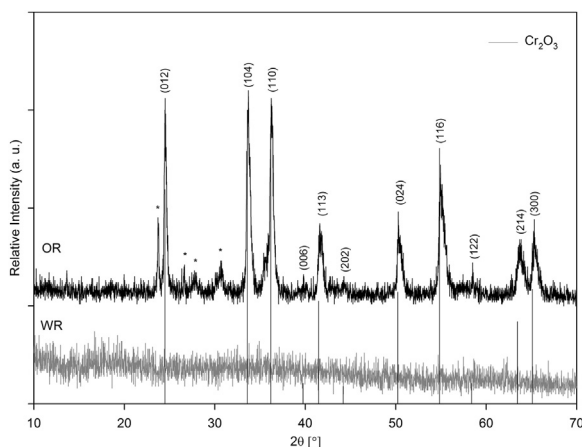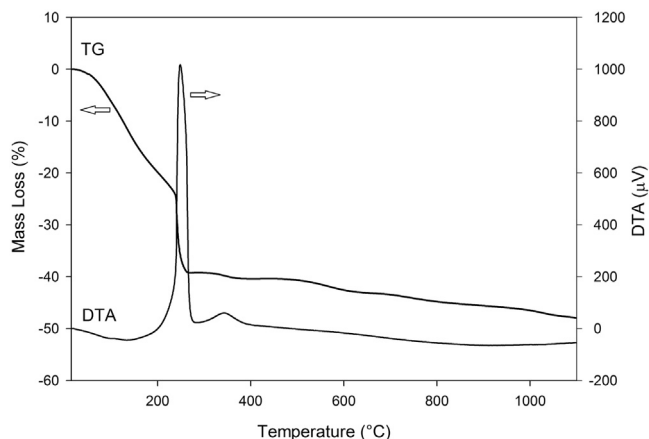

Fig. 4. TG-DTA curves of WR.

products of the destruction of the residual organic matter.

As will be shown below, the thermogravimetric assignment was confirmed by XRD and FTIR measurements. In accordance with previous reports [20], the crystallization was supported by the unambiguous change of the XRD pattern for the samples quenched before and after the sharp exothermic peak. The crystallinity of the sample calcined at 500 °C could be enhanced upon firing up to 1000 °C. As can be seen in Fig. 3, the XRD pattern displays the diffraction lines belonging to Cr_2O_3-eskolaite. The diffractogram could be indexed based on the corundum hexagonal structure, space group *R-3C*. The unit cell parameters calculated are a = b = 4.95(2) Å and c = 13.58(1) Å. These values are in good agreement with the reported values [19].

The structural characterization described is compatible with the chemical composition of OR, determined by XRF analysis. According to the data shown in Table 1, the solid consists mainly of ~ 65 wt% Cr_2O_3 and also includes ~ 18 wt% Al_2O_3. Due to the similarity in ionic radii between Cr(III) and Al(III), the oxides are isostructural, and the cells should have similar sizes, undistinguishable by their XRD patterns [21]. Moreover, the possibility of forming a solid solution between them should not be disregarded. Regarding the other oxides, present as minor components according to XRF data, these are not observed by XRD likely because these are under the detection limits. The potential presence of the spinel $CuFe_2O_4$, the product of reaction between Cu(II) and Fe(III), should not be disregarded.

The infrared spectra give additional support to DTA-TG, XRD and XRF results. FTIR spectroscopic characterization is a very useful tool to evaluate the chemical and structural changes during the processing of the AR sample, with the advantage that even poorly crystallized and amorphous compounds can be identified.

The IR spectral measurements of the samples, carried out after each treatment, are depicted in Fig. 5. The evolution of the IR spectra show predominance of $SO_4^=$ bands at 1200 cm^{-1} and 600 cm^{-1} in AR, with remarkable diminution after washing in WR sample until disappearance. In addition, a new absorption is developed in the low energy IR region; a broad poorly defined band centered at ~ 600 cm^{-1}. When the material is submitted to thermal treatment in order to achieve the OR, a drastic change in the spectral features is detected. Two well defined doublets with strong absorptions at 635–577 cm^{-1} and other weaker and less defined bands covering 400–360 cm^{-1} can be observed. As can be seen in Fig. 5, this spectral pattern is identical to the spectrum of Cr_2O_3 p.a., shown in the literature and the spectral libraries [17]. The doublet located at the higher wavenumber is assigned to the stretching vibration of Cr–O bonds in the CrO_6 condensed octahedrons forming the lattice of Cr_2O_3-eskolaite, and the lower energy bands belong to deformational modes of the same polyhedron [19]. On the other hand, the spurious broad shapeless band at around 1000 cm^{-1} is difficult to assign unambiguously and could be attributed to M-OH
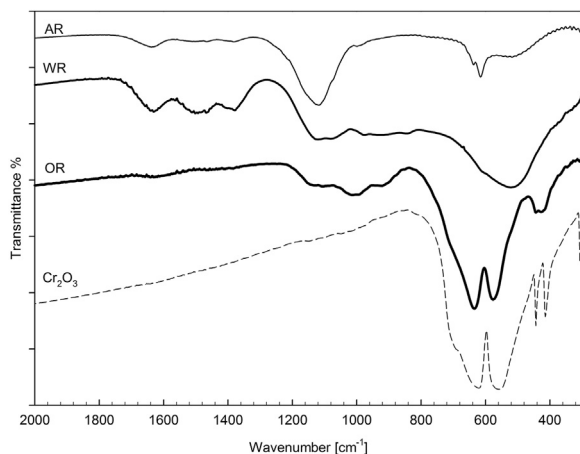

Fig. 3. XRD patterns of WR, OR and Cr_2O_3-eskolaite. (*) unidentified impurity.

Fig. 5. FTIR spectra of AR, WR, OR and Cr_2O_3.

stretching vibrations of the remaining impurities in the sample [18].

The SEM images of the OR, with different degrees of magnification, are illustrated in Fig. 6. The sample depicts homogeneous microstructure. The magnified pictures, shown in Figs. 6a, 6b and 6c, distinguish small micro particles of Cr_2O_3 ($< < 2\,\mu m$) forming agglomerates of bigger sizes.

Moreover, the EDX scanning confirmed that the global elemental composition detailed in Table 2 is compatible with the presence of Cr_2O_3, as the main component, in consistence with XRF quantitative analysis and previously used techniques. A significant amount of C, which appear as ashes after calcinations, was also detected which could be associated with carbonaceous residues departing from oils or other organic compounds used during the machinating of the pieces. The presence of the other elements, Al, Fe and Cu, is not surprising since these are components of the alloys commonly used in the industry.

In summary the simple optimization process applied to render OR, according to the analytical techniques XRF, XRD, DTA-TG, FTIR and SEM-EDX, seems to be appropriate in order to achieve Cr_2O_3 recovered from the residue of acceptable purity for the synthesis of pigments. Chromium oxide is accompanied by Al_2O_3 and other minor impurities, compatible with the composition of (white) ceramic raw materials. The effect of the presence of other chromospheres, such as Cu and Fe, as probably the mixed oxide $CuFe_2O_4$, was analyzed.

3.1.2. Frits characterization

The frits, forming transparent coatings, were provided by a local ceramic industry which manufactures floor and roof tiles. The approximate compositions are detailed in Table 3. The glazes were selected to be representative of the double and single firing procedures. In the case of frit A (FA), the high amount of PbO applies for a low softening point, commonly used in overglaze applications, carried out at around 850 °C in the so-called double firing processes. Frits C (FC) and micronized glaze (MD) both could be used in single firing schedules due to the higher softening and glazing temperatures, 1000 °C and 1100 °C, respectively. MD was received as micronized powder containing particles $< < 44\,\mu m$. Both frits A and C consist of flakes which were crushed and then submitted to grinding using a laboratory ball mill. The resulting powders were sieved through a 44 μm sieve (325 mesh).

The common feature of all frits is the absence of ZnO, which could react with Cr-pigments. In addition, frits C and MD contain a high amount of SiO_2, higher in MD, compatible with a higher melting point. In the case of frit C, it bears a significant amount of B_2O_3 as glass former; and also Al_2O_3.

The XRD patterns of all the frits are featureless due to their amorphousness, so the chemical characterization relies on the spectroscopic behavior, analyzed by FTIR vibrational spectroscopy. As can be seen from Fig. 7, the spectral patterns of FA and MD (and also FC) have been assigned in previous papers; the differences can be explained based on the chemical composition among the frits. In FA, only bands belonging to SiO_2, located in the 1070–1010 cm^{-1} and around 475–400 cm^{-1}, are present. These vibrations are typical of SiO_4^{3-}, belonging to stretching and deformational motions of tetrahedral units, respectively. In the case of FC and MD, besides these silicate spectral signals, the vibrations
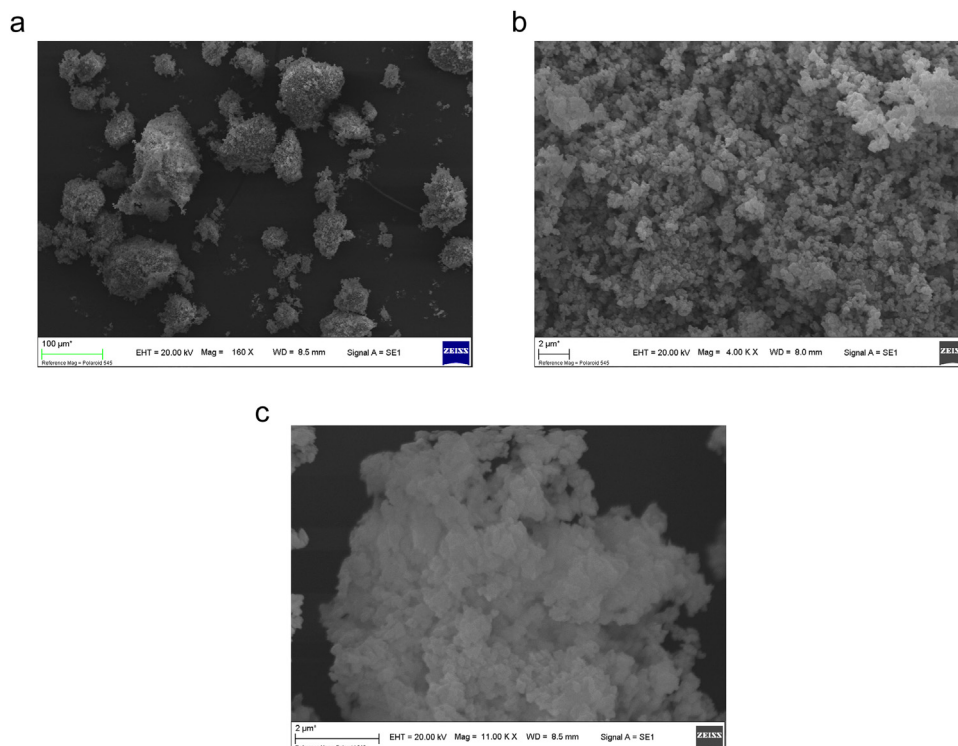
a

b

c

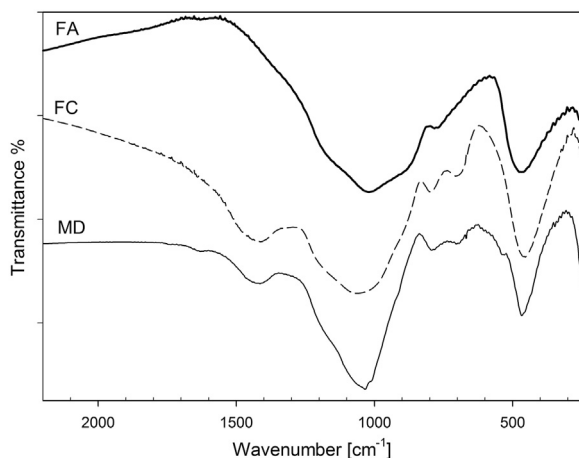**Fig. 6.** SEM micrograph of OR, a) 160×, b) 4.00 KX and c) 11.00 KX.

Fig. 7. FTIR plots of frits A and MD.

Fig. 8. CIE$L*a*b*$ chroma diagram of Cr_2O_3, reference numbers according to Table 4.

arising from B_2O_3 assigned to the extra bands at $1400 \, cm^{-1}$ and $700 \, cm^{-1}$, are observed [22].

3.1.3. Technological properties of glazes based on recovered Cr_2O_3-OR

Historically, in the ceramic industry, green pigmentation has been obtained with Cr_2O_3. This material is an important refractory with a high melting point ($2435 \, °C$). However the presence of ZnO or SnO_2, usually present as opacifiers in opaque frits, produces a deleterious effect on color stability because of the mutual reaction [23]. For this reason Cr_2O_3-OR recovered from the waste was submitted to testing by glazing with the three transparent frits, previously described. The colorimetric parameter measurements were made on white ceramic glaze tiles, at the stated temperatures of glazing of each frit.

The resulting CIE$L*a*b*$ coordinates of all the specimens, including the starting powders, are detailed in Table 4. The colorimetric parameters of glazes based on pure Cr_2O_3 are also included for comparison. As shown in the table, the colorizing behavior of the pigments prepared from the waste are within the range of the reference pigment in all the glazes investigated, in the same region of the chroma diagram. The color differences, evaluated by $\Delta E*$, the chroma $c*$ and the tone $h*$ can be seen in Table 4.

According to the data in Table 4, the maintenance of the green hue is dependent on the frit and thermal treatment. The coloring level of the starting powders is maintained when they are enameled with transparent frits. The negative value $–a*$, as measure of green, is observed for all the samples containing the transparent frits C and MD, for single firing obtained at $1000 \, °C$ and $1100 \, °C$, detailed in the Table 4. However when the pigments are enameled with double firing FA, the green chroma is lost and in its place a positive $+a*$ coordinate, with virage

Table 4

Color measurements of starting powders and glazes based on recovered Cr_2O_3 (-OR) and using the pure reagent. Chroma $c*$, hue $h*$ and difference of the color calculated as $\Delta E*$.

Cr source	Frit	Sample number	$L*$	$a*$	$b*$	$c*$	$h*$	$\Delta E*$
Cr_2O_3-OR	-	-	31.18	-2.03	15.59	15.72	97.42	22.20
Cr_2O_3	-	-	48.05	-15.92	19.53	25.20	129.18	
Cr_2O_3-OR	FC	1	25.83	− 2.35	14.68	14.86	99.10	19.47
Cr_2O_3	FC	1′	37.40	− 17.36	19.17	25.86	132.16	
Cr_2O_3-OR	MD	2	28.13	− 4.39	16.31	16.89	105.07	15.06
Cr_2O_3	MD	2′	34.09	− 17.74	19.92	26.64	131.69	
Cr_2O_3-OR	FA	3	25.88	6.07	27.13	27.80	77.39	10.56
Cr_2O_3	FA	3′	29.70	13.46	33.64	30.2	68.20	

Color difference $\Delta E* = (\Delta L*^2 + \Delta a*^2 + \Delta b*^2)^{1/2}$.
Chroma or color saturation: $c* = (a*^2 + b*^2)^{1/2}$.
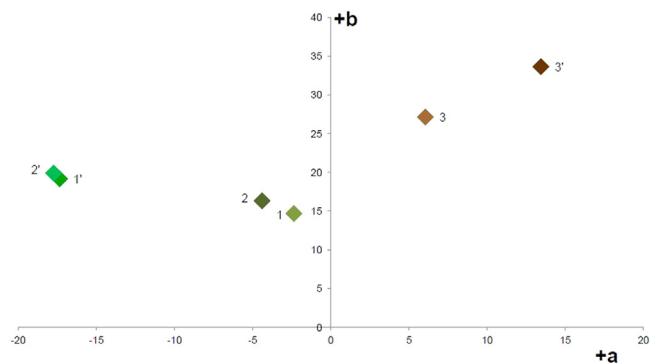Hue or tone of color: $h* = \arctan (b*/a*) + 180°$ (if the value is negative).

towards brown, is produced (Table 4). In comparison with the glazes prepared using pure Cr_2O_3 p.a., the green hue of glazes containing Cr_2O_3 from OR, labeled 1 and 2 in Table 4, are characterized by less negative $–a*$ values, lower $+b*$ values of yellow (1 and 2), and lower values of lightness.

Regarding the color difference $\Delta E*$, in all cases, it is higher than the established limit (< 0.75) by the International Standard ISO 10545-16:1999 for Ceramic Tiles. Therefore, the color difference obtained between Cr_2O_3 and Cr_2O_3-OR is detectable by human vision. Cr_2O_3-OR could not be used as a substitute for Cr_2O_3.

In the CIE$L*C*h*$ model, the green hue is between 120 and 190 degrees. In this study, only samples 1′ and 2′ can be described as green glazes. On the other hand, the lightness $L*$ is very low in all samples. In addition, the calculated chroma or saturation shows that the colors of Cr_2O_3-OR are low with respect to the reference and are seen as poor green.

The graph shown in Fig. 8 illustrates the purity of the color. According to the position of each sample in the CIE$L*a*b*$ chroma diagram, the distance from the origin is indicative of the purity of the pigment color. Consequently, in samples 1 and 2 the values closer to the origin, particularly $–a*$ coordinate is indicative of a less pure green shade, as expected. In addition, lower chroma values and lightness suggest darkening of these shades. These effects are due to the other accompanying metal chromophores in the waste, such as Cu and Fe, although these are present in low amounts. These cations could form brown $CuFe_2O_4$ spinel mixed oxide. Even colorless Al(III) cation has an effect since it could form $Cr_{2-x}Al_xO_3$ solid solution, belonging to corundum structure; producing a shift from shades of green to red, yielding the well-known red variety of corundum [21]. For this reason, the Cr_2O_3-OR is not suitable as a commercial source of Cr_2O_3. However this material could be proposed as a potential sustainable alternative of dark green tonality. The chromatic $L*, a*, b*$ parameters are within the chromatic domain of Cr-pigments, enlarging the palette of Cr-green shades, in silicate and aluminate glazes. To assure the invariability of the chemical composition, in order to obtain a pigment with the adequate composition it is necessary to control the waste received. In this way, the chemical analysis and XRD and FTIR measurements of WR and OR should be done before its incorporation to the frits.

On the other hand, in the matrices containing PbO, the positive combination of $+a*$ and $+b*$ values obtained, is responsible for the brown hues. The presence of corrosive PbO as flux causes the damage of the pigments power. The most remarkable feature is the change of green hues towards a brownish color and the darkening of the glazes. In this way, neither Cr_2O_3-OR nor pure Cr_2O_3 are stable as green Cr-pigments in this type of frit. Surely the virages detected are associated with the presence of $PbCrO_4$, the toxic pigment formed by the chemical reaction of PbO and Cr_2O_3, in alkaline media [24,25].

Table 5
Leaching test of glazes based on Cr-waste.

Composition of samples	Mass (g)	Absorbance mean values	Cr(VI) content ppm (µg/cm³)
Cr₂O₃-OR	0.5	0.054	0.007
Cr₂O₃-OR + Frit C	1.4	0.063	0.009
Cr₂O₃-OR + Frit C (duplicate)	1.4	0.090	0.012

Experimental conditions: in solution of pH = 5 (acetic acid), 24 hs shaking and at 25 °C.

3.1.4. Leaching tests and toxicity of Cr-enamels based on waste

The leaching availability was analyzed in order to evaluate the potential environmental risk of using the glazes based on Cr-residue. As well known, the release of Cr or other toxic elements from a given material depends mainly in their solubility in operative conditions, which is influenced by pH, presence of complex agents, permeability, porosity, contact time, and water/solid ratio [26].

The contamination of the water sources and soil due to solid waste leachate is of concern for health. In the case of chromium, ingestion can cause anemia and stomach cancer. Particularly Cr(VI) is more dangerous because of its negative environmental impact since it will be segregated to the waste washing waters [21]. Due to the lack of efficient industrial solid waste management, particularly in undeveloped countries, the uncontrolled dumping near towns or cities becomes an environmental problem due to the leachate of various toxic elements and ions. In addition, the leachates affect the water resources close to the dump sites.

If not adequately immobilized in the glaze/ceramic matrix, Cr(III) residue could be dissolved entering into the environment. Therefore, the evaluation of the removal of chromium from the glazes containing Cr-recovered is relevant.

The leaching behavior of the glazes containing OR are detailed in Table 5. The extraction procedures were described in the experimental section. Several samples of glazes containing recovered Cr₂O₃-OR from the chrome plating sludge were collected from the crushed and powdered specimen to provide a representative sampling. The leaching test standard refers to a liquid/dry solid ratio simulating conditions in landfill.

In Argentina, the national law for residual water establishes a maximum limit of 5 mgCr(VI)/l of liquids wastes (5.0 ppm of Cr(VI)) [27]. As can be seen in Table 5, all the values regarding µg of chrome/cm³ solution remain under the limit permitted by regulation. These results suggest that Cr(III) is stable in the glazes containing Cr recovered from the waste and that the enameling is a suitable process for the Solidification/Stabilization of this waste. Leaching tests performed on the enamels and Cr₂O₃-OR support the proposition that the vitrified hazardous chromium is well stabilized in the glassy matrices. In this way, ceramic technology contributes to inertization of this hazardous waste.

4. Conclusion

This study confirmed that the residues from a metallurgical industry, rich in Cr (III), can be used to synthesize ceramic pigments based on this chromophore. Cr₂O₃ was successfully separated from chrome plating waste by two simple steps: first, a washing procedure for extraction of soluble salts; and second, a pyrolisis up to 1000 °C, to decompose the hydrated oxides, eliminate volatiles and organic traces, to render finally the corresponding oxides.

The Cr(III) oxide is accompanied mainly by Al(III) oxide, and other minor impurities, compatible with the composition of white ceramic raw materials. In this way, the chemical composition achieved seems to be acceptable for the synthesis of ceramic pigments.

Recovered Cr₂O₃ from the optimized waste was used as raw

material for the synthesis of glazes for the manufacture of ceramic floor and roof tiles.

Batches containing 5 wt% were performed and fired according to cycles used for mono and double firing processes. The comparison with the reference tested from pure Cr₂O₃ was carried out. The color differences between the glazes prepared from the waste and the reference are noticeable. Therefore, Cr₂O₃-OR is not suitable as substitute of commercial Cr₂O₃. The presence of small amounts of the other chromophores, such as Cu(II) and Fe(III), modifies the purity of the reference shades. Notwithstanding, Cr₂O₃-OR could be proposed as a potential sustainable alternative of dark green hues, enlarging the palette of Cr-green shades in single firing glazes; and of brown tonality in the case of overglaze application. The coatings depict a homogeneous microstructure, free of surface defects.

Finally the leaching behavior of the glazes, simulating conditions typical of landfills, was evaluated and the amount of Cr(VI) lixiviated remains under the limit permitted by regulations.

Leaching tests performed on the enamels and Cr₂O₃-OR support the proposition that the vitrified hazardous chromium is well stabilized in the glassy matrices. In this way, ceramic technology contributes to inertization of this hazardous waste, destruction of the organic matter, reduction of the volume of wastes and its transformation into a useful material, with potential for commercial purposes.

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