# Waste-based ceramic pigments prepared from: electroplating sludge, marble and granite sawing dust

J. Carneiro[1], D.M. Tobaldi[1], M.N. Capela[1], R.M. Novais[1], M.P. Seabra[1], J.A. Labrincha[1*]

[1]University of Aveiro, CICECO, Department of Materials and Ceramic Engineering, 3810-193, Aveiro, Portugal
Presenting author email: jal@ua.pt

## Introduction

The complexity of industrial wastes management has increased in the last decades, with the growing of environmental concerns and associated costs. The pressure applied by lawmakers, translated into restrictive environmental legislation and landfilling fees, together with the increasing of virgin raw-materials price lead to a new paradigm in terms of how the industrial wastes are viewed (Korhonen, 2018 and European Commission, 2015). The once looked as an annoying issue, taking space and money to be discarded, have become a potential source of income, as a raw material for another industry. The rise of these new interrelated industrial systems, embodied in the concept of circular economy, busted a new approach to how such wastes are treated, usually discarded into a landfill. Thus, the research of new applications for industrial wastes, in some cases hazardous, have been performed in the last years, trying to provide suitable alternatives to the industry problems with wastes (Esteves et al., 2010).

The synthesis of ceramic pigments based on industrial wastes embodies perfectly the concept of circular economy, bringing environmental and economic gains. A ceramic pigment must fulfill three main requirements: thermal stability (stable at high temperatures), chemical stability (stable when fired with glazes or ceramic bodies) and high coloring power (Monros, 2014). Several industrial wastes, due to their composition, have been studied as raw materials for the preparation of ceramic pigments, namely: electroplating sludge (ES) (Hajjaji et al., 2011), leather sludge (Chen et al., 2015), foundry sand (Esteves et al., 2010) and marble sawdust (Hajjaji et al., 2012).

In this work, wastes from several industries: a sludge from electroplating process (ES - rich in Cr and Ni), a sludge from the marble sawing (MS - rich in $CaCO_3$) and a sludge from the granite sawing (GS - rich in $SiO_2$), were used to produce ceramic pigments. Through the combination of these wastes in the right proportions is possible to synthetize ceramic pigments where the wastes hazards elements are inertized/immobilized since they are encapsulated inside the ceramic matrix. The economic value cannot be understated as well, since all the wastes used in this work represents an extra cost to the respective producers. The approach followed in this work focus the synthesis of ceramic pigments using only wastes, with no addition of virgin raw materials to enhance the pigments properties. The goal is to develop a material made only of wastes and whose production (scale-up) is simple to implement taking into account the existing industrial processes.

## Materials and methods

**Materials.** ES sludge and the transparent glaze were provided, respectively, by Grohe Portugal - Componentes Sanitários, Lda. and Esmalglass-Itaca group. MS was provided by - Centro Tecnológico para o Aproveitamento e Valorização das Rochas Ornamentais e Industriais Lda – Cevalor; Borba. GS was provided by Euro Granitos.

**Pigment preparation.** ES, MS and GS were mixed in different weight proportions: GS:ES (50:50, 25:75 and 75:25) and GS:MS:ES (30:20:50). The homogenization was done by wet ball milling. Afterwards, the mixtures were dried in a ventilated oven at 80 ºC. The mixtures were sintered in an electric furnace under a static air flow, using a 5 ºC/min heating rate until the maximum temperature (1100 ºC, 1200 ºC and 1300 ºC) with a dwell time of 3 hours. The cooling rate was also 5 ºC/min. The obtained pigments were then ball milled for 1 hour at 300 rpm. Afterwards, the pigments were dried in a ventilated oven at 80 ºC and sieved through a 63 µm mesh.

**Test in glaze bodies.** 3 wt.% of each pigment was added to a transparent commercial powdered glaze and the homogenization process was conducted by wet ball mixing. The mixtures were dried at 80 ºC, disaggregated and sieved (at 63 µm). The obtained powders were pressed into Ø2.5 cm pellets and fired in an electric furnace in air at 1100 ºC (30 min of dwell time and 10 ºC/min heating/cooling rate).

**Sample characterization.** The chemical composition of the input materials (MS, GS and ES) was obtained by X-ray fluorescence (XRF) in a Philips X'Pert PRO MPD spectrometer. The loss on ignition (LOI) at 1000 °C was also determined. The L*a*b* color coordinates were measured by means of a portable colorimeter – Konica Minolta Chroma Meter CR-400 – using DC illuminant and 10º standard observer (Y: 94.0, x: 0.3130, y: 0.3191) according to the Commission Internationale de l'Eclairage (CIE). CIE L*a*b* data are expressed as brightness L*, changing from 0 (black) to 100 (white), a* (+red, -green), and b* (+yellow, -blue) (CIE, 1978).

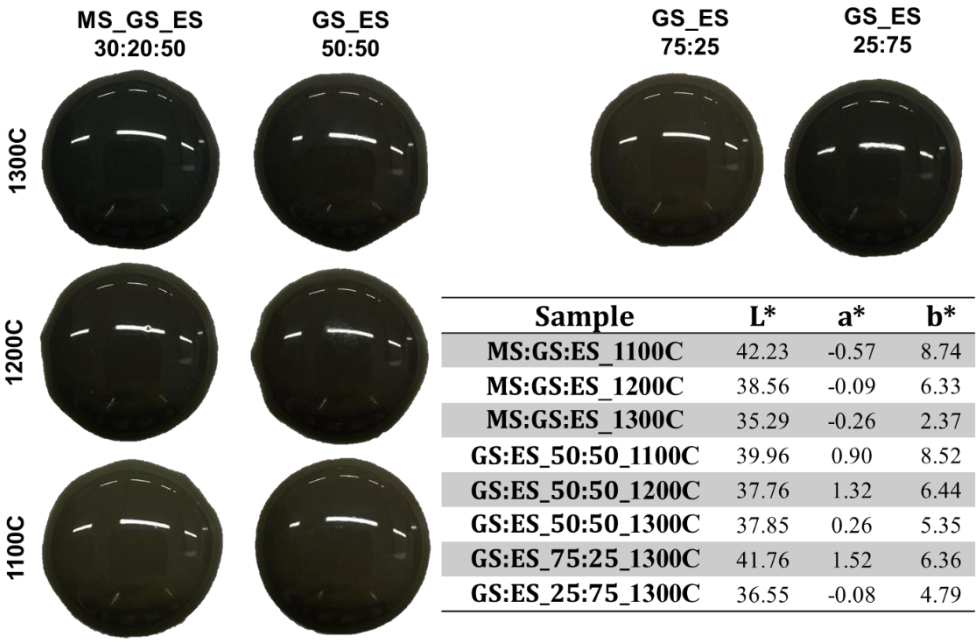
## Results and Discussion

The wastes composition was assessed by XRF, being ES sludge mainly composed by: nickel (25.86 wt.%), chromium (15.29 wt.%), sulfur trioxide (5.84 wt.%), silicon dioxide (5.63 wt.%), phosphorus pentoxide (4.45 wt.%) and a LOI of 34.30 wt.%. GS is composed by silicon dioxide (64.12 wt.%), aluminum oxide (17.94 wt.%),

potassium oxide (6.10 wt.%), iron oxide (3.38 wt.%) and a LOI of 1.50 wt.%. Lastly, MS has as main component calcium oxide (56.56 wt.%) and a LOI of 41.95 wt.%.

The ceramic pigments, after calcination, presented colours ranging from drack brown to black. Their tinting strength was tested by adding 3 wt.% to a bright transparent glaze [$SiO_2$ (51-53 wt.%); $Al_2O_3$ (41-43 wt.%); $ZrO_2$ (7-9 wt.%); and $P_2O_5$ (1-3 wt.%)], being the sample shown in Figure 1. The increase of the sintering temperature lead, for both mixtures, to a significant decrease in the values of lightness (L*) and yellow hue (b*). The values of L* decrease from 42.2 to 35.2 (MS_GS_ES) and 39.9 to 37.8 (GS_ES). The values of b* decrease in the case of MS_GS_ES, from 8.7 to 2.3, and remain fairly stable for GS_ES. In both mixtures, the values of the blue hue (*a), remained stable. The decrease in L* corresponds to an increase of the pigments tinting strength; the decrease in the b* values is associated to a decrease of the yellow component of the pigment.

The obtained results show excellent perspectives for the industrial application of waste-based pigments as colouring agents in transparent glazes. The pigments produced glazes with drack brown and black hues, without the presence of defects on their surface, such as pinholes.




| Sample | L* | a* | b* |
|---|---|---|---|
| MS:GS:ES_1100C | 42.23 | -0.57 | 8.74 |
| MS:GS:ES_1200C | 38.56 | -0.09 | 6.33 |
| MS:GS:ES_1300C | 35.29 | -0.26 | 2.37 |
| GS:ES_50:50_1100C | 39.96 | 0.90 | 8.52 |
| GS:ES_50:50_1200C | 37.76 | 1.32 | 6.44 |
| GS:ES_50:50_1300C | 37.85 | 0.26 | 5.35 |
| GS:ES_75:25_1300C | 41.76 | 1.52 | 6.36 |
| GS:ES_25:75_1300C | 36.55 | -0.08 | 4.79 |

**Figure 1:** Bright transparent glaze loaded with 3 wt.% of ceramic pigments obtained from different wastes mixtures (GS:MS:ES_30:20:50 and GS:ES_50:50; 25:75; 75:25), after sintering at several temperatures (1100 ºC, 1200 ºC and 1300 ºC). CIE L*a*b* coordinates of the colored glazes.

**References**

[1] E. Commission, Europe Closing the Loop - an EU Action Plan for the Circular Economy, in: t.E.E.a.S.C.a.t.C.o.t. Regions (Ed.), European Commission, Brussels, 2015.
[2] J. Korhonen, A. Honkasalo, J. Seppälä, Circular Economy: The Concept and its Limitations, Ecol. Econ., 143 (2018) 37-46.
[3] D. Esteves, W. Hajjaji, M.P. Seabra, J.A. Labrincha, Use of industrial wastes in the formulation of olivine green pigments, J. Eur. Ceram. Soc., 30 (2010) 3079-3085.
[4] G. Monros, Pigment, Ceramic, in: R. Luo (Ed.) Encyclopedia of Color Science and Technology, Springer New York, New York, NY, 2014, pp. 1-15.
[5] W. Hajjaji, C. Zanelli, M.P. Seabra, M. Dondi, J.A. Labrincha, Cr-doped perovskite and rutile pigments derived from industrial by-products, Chemical Engineering Journal, 171 (2011) 1178-1184.
[6] W. Hajjaji, G. Costa, C. Zanelli, M.J. Ribeiro, M.P. Seabra, M. Dondi, J.A. Labrincha, An overview of using solid wastes for pigment industry, J. Eur. Ceram. Soc., 32 (2012) 753-764.

**Acknowledgements**
This work was developed within the scope of the project CICECO-Aveiro Institute of Materials, FCT Ref. UID/CTM/50011/2019, financed by national funds through the FCT/MCTES.