Waste Management 80 (2018) 371–378

Contents lists available at ScienceDirect

Waste Management

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

Synthesis of ceramic pigments from industrial wastes: Red mud and electroplating sludge

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

University of Aveiro, CICECO, Department of Materials and Ceramic Engineering, 3810-193 Aveiro, Portugal

ARTICLE INFO

Article history:
Received 24 March 2018
Revised 18 August 2018
Accepted 18 September 2018

Keywords:
Bauxite residue
Electroplating sludge
Black pigment
Waste valorisation
Ceramic glaze

ABSTRACT

The perception of industrial waste has changed, in the last decades, from an economic and environmental problem to a potential raw material. In this work, the synthesis of a stable pigment was prepared by combining two hazardous and unexplored wastes: red mud (RM, rich in Fe) and electroplating sludge (ES, rich in Ni/Cr). The wastes were mixed in different proportions and calcined at 1200 °C. Black and brown pigments were obtained from the mixture of RM/ES in 1:3 and 1:1 wt proportions, respectively. The color was given by the chrome-iron-nickel spinels, based on Ni^{2+} $^3T_{1g}(^3F)$ transitions (≈13,000 cm^{-1}), Cr^{3+} $^4A_{2g} \rightarrow {}^4T_{1g}(^4F)$ transitions (≈24,400 cm^{-1}) and Fe^{3+} (≈15,000–≈22,500 cm^{-1}). The achieved coloring strength and thermal stability on various ceramic glazes render excellent prospects for the industrial application of such waste-based pigments.

1. Introduction

The production of ceramic pigments from industrial wastes have gained increasing interest in the last decades (Costa et al., 2007; Gargori et al., 2018; Hajjaji et al., 2012). The valorization of wastes, in most of the cases with a problematic disposal, is appealing in a modern world plagued by the overexploitation of natural resources and, consequently, environmental problems. The valorization of a waste, that will become the raw material for another product, falls in the concept of circular economy, where industrial production is based on regeneration, remanufacturing, refurbishing and recycling (Korhonen et al., 2018). An idea that gained relevance, as attested by the European Circular Economy package (European Commission, 2015).

A ceramic pigment is an organo-metal that 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). Industrial wastes, due to their composition, can be used as raw materials for the preparation of ceramic products, as proven by the examples found in literature: red mud (RM) (Yalçın and Sevinç, 2000), electroplating sludge (ES) (Gargori et al., 2018; Hajjaji et al., 2011), steel waste (Díaz et al., 2015), leather sludge (Chen et al., 2015), Al anodizing sludge (Costa et al., 2007), foundry sand (Esteves et al., 2010) and marble saw dust (Hajjaji et al., 2012). The preparation of ceramic pigments from waste-based materials besides the functional properties expected from a ceramic pigment (e.g. tinting strength, chemical and thermal stability) also allow the inertization of hazards elements, preventing their leaching to the environment (Esteves et al., 2010; Hajjaji et al., 2011).

Due to their composition RM (rich in Fe_2O_3) and ES (rich in Cr and Ni) are prime candidates for the synthesis of black pigments based on the chrome-iron-nickel $(Ni,Fe)(Fe,Cr)_2O_4$ structure (DCMA 13-50-9) (Hajjaji et al., 2011). RM and ES are wastes resulting from well-established industrial processes, respectively from the production of alumina by the Bayer process (Sahu and Patel, 2016) and from the galvanizing process of Cr/Ni (Pérez-Villarejo et al., 2015). The RM production worldwide reached ~120 Mt/year (Xue et al., 2016) while the amount stockpiled was over 3.9 Gt in 2017 (Xue et al., 2016). The electroplating sludges account for roughly 1 wt% of all the hazardous industrial wastes being produced (Cavaco et al., 2007; Wazeck, 2013), reaching values around 150 Mt/year in the EU countries (Magalhães et al., 2005).

The combination of electroplating sludge with an iron-rich waste has been reported in the literature. At this purpose, it is worth to mention the work by Hajjaji et al. (2011) combined a Ni/Cr sludge with another waste generated in the wiredrawing of steel to produce black pigments based on the $(Ni,Fe)(Fe,Cr)_2O_4$ spinel structure after calcination at 1100 °C (Hajjaji et al., 2011). Black pigments were also prepared combining vanadium tailing (iron-rich) with leather sludge (chromium-rich) (Du et al., 2017). Herein, the pigments based on the hematite $(Fe_xCr_{1-x})_2O_3$ structure, and were prepared by the common solid-state method with sintering at 1200 °C (Du et al., 2017).

* Corresponding author.
E-mail address: jcarneiro@ua.pt (J. Carneiro).

https://doi.org/10.1016/j.wasman.2018.09.032
0956-053X/

The waste-based ceramic pigments are a very competing alternative to traditional ones if, besides the obvious environmental gain, their final cost is smaller or similar to the existent pigments produced from virgin raw materials. The environmental advantages of using exclusively hazardous wastes as raw materials are the inertization of unexplored and highly hazardous wastes into ceramic products, mitigating their colossal environmental impact, and the reducing of the virgin raw materials consumption. Economically, these wastes (RM and ES) have currently no commercial value and their disposal has huge associated costs, landfill tax corresponding to an average of around 80 €/ton in the EU27 (Confederation of European Waste-to-Energy Plants, 2016). Based on this assumptions one can speculate that their cost would be lower than that of commercial virgin raw materials. The production costs of waste-based ceramic pigments can be similar or even lower than the traditional ones. The wastes can be used without any pre-treatment (e.g. milling, purification) which represents gains in time and costs. Afterwards most of the pigment preparation processes would be similar, no need for changes, such as the milling stage after sintering. The calcination could represent an additional gain for waste-based pigments since lower sintering temperatures are required (in this particular case between 1200 and 1300 °C) compared with the ones used in the production of commercial ceramic pigments (Gilabert et al., 2017). Overall, a waste-based approach is expected to be economically more favorable than the traditional one, besides the considerable environmentally advantages it brings. In this work we report the preparation by the solid state method of pigments based on a Ni $(Cr^{3+},Fe^{3+})_2O_4$ spinel structure by combining, RM and ES, in different proportions (1:1 and 1:3), and then fired at 1200 °C. The coloring capabilities of the newly formed pigments were tested in commercial glazes (3 wt% additions): transparent, opaque white and matte.

2. Experimental details

2.1. Materials

Red mud was provided by Alcoa Spain and contains about 31 wt % of moisture. Ni/Cr sludge and the glazes were provided, respectively, by Grohe Portugal – Componentes Sanitários, Lda. and Esmalglass-Itaca group. For comparison purposes the commercial pigments used by the ceramic industry, were supplied by Vitricer (pigment 5829-R, here named brown pigment), and Esmalglass-Itaca group (CE-5229 as black pigment).

2.2. Pigment preparation

RM and ES were mixed in different weight proportions (1:1, 1:3 and 3:1, RM:ES). The homogenization was done by wet ball milling (proportion of 1:4:1, sample: balls: water). Afterwards the mixture was dried in a ventilated oven at 80 °C. The mixtures were sintered in an electric furnace under a static air flow, using a 5 °C/min heating rate until the maximum temperature (1200 °C and 1300 °C) with a dwell time of 3 h. The cooling rate was also 5 °C/min. The obtained pigments were then ball milled (the same proportion of 1:4:1, sample: balls: water) for 1 h at 300 rpm. Afterwards the pigments were dried in a ventilated oven at 80 °C and sieved through a 63 μm mesh.

Both wastes were also sintered individually at 1200 °C using the same procedure as that for the mixtures. The reference is **ES_1200** and **RM_1200** for electroplating sludge and red mud, respectively.

2.3. Test in glaze bodies

3 wt% of each pigment was added to three different commercial powdered glazes (transparent, opaque and matte) and the homogenization process was conducted by wet ball mixing. The mixtures were dried at 80 °C, 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 °C (30 min of dwell time and 10 °C/min heating/cooling rate).

2.4. Sample characterization

The chemical composition of the input materials (RM 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. X-ray diffraction (XRD) analysis was performed using a PANalytical XPert PRO diffractometer (Ni-filtered CuKα radiation, PIXcel 1D detector, and the exposition corresponded to about 2 s per step of 0.02° 2θ at room temperature). XRD for quantitative phase analysis (QPA) were recorded on a Rigaku GeigerFlex D/Max-C series, equipped with a graphite monochromator on the diffracted beam, Cu k_α radiation, 10–80° 2θ, step of 0.02° 2θ, and time per step of 10 s. QPA was assessed on selected specimens, by way of the Rietveld method (Rietveld, 1969) on the XRD data; Rietveld analysis was performed *via* the GSAS-EXPGUI software package (Toby, 2001). Instrumental contribution was also taken into account in the refinements. This was evaluated recording the XRD pattern of NIST SRM 660b standard (LaB_6), using the same conditions as above. The particle size distribution was determined by laser diffraction on a Coulter LS particle size analyzer (LS230FM).

The optical properties were measured by absorption spectroscopy (Shimadzu UV-3100 UV–Vis–NIR spectrometer), whilst the $L^*a^*b^*$ color coordinates were determined by means of a portable colorimeter – Konica Minolta Chroma Meter CR-400 – using D_C illuminant and 10° 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). Color stability was obtained using the ΔE_{2000} formula [9]. $0 < \Delta E < 1$ means that differences in color cannot be perceived by the standard observer; $1 < \Delta E < 2$ only perceived by an experienced observer; $2 < \Delta E < 3.5$ an inexperienced observer can detect differences; $3.5 < \Delta E < 5$ everyone can see the differences; $5 < \Delta E$ two distinct color can be seen (Mokrzycki and Tatol, 2011; Rogowska, 2015).

3. Results and discussion

3.1. Wastes characterization

The chemical composition of RM and ES, obtained by XRF, is shown in Table 1. RM main components are iron oxide (52.25 wt%), aluminum oxide (14.63 wt%) and titanium oxide (9.41 wt%). These values are within the intervals reported by Liao and Shih (2016) for RM samples collected from different locations around the world: 6.75–64.2 wt% for iron oxide, 2.12–27.2 wt% for aluminium oxide and 2.55–16.4 wt% for titanium oxide.

Nickel (25.86 wt%), chromium (15.29 wt%), sulfur trioxide (5.84 wt%), silicon dioxide (5.63 wt%) and phosphorus pentoxide (4.45 wt%) are the main components of ES. Costa et al. (2008) measured 24.1 wt% of NiO and 9.57 wt% Cr_2O_3 in their Cr/Ni-rich sludge, while Hajjaji et al. (2011) reported values ranging from 7.32 to 15.1 wt% for Cr_2O_3, and between 13.8 and 42.9 wt% of NiO for three different galvanizing sludges resulting from Cr/Ni plating processes, thus in line with the values reported here.

The particle size distribution of RM and ES, after drying and manual disaggregation, is significantly different. RM presents an average particle size around 1.4 μm and a narrow size distribution