

## Red mud as a substitute coloring agent for the hematite pigment

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### ABSTRACT

Red mud (RM), a highly alkaline iron oxide rich sludge obtained during the production of alumina, was treated to work as a coloring agent for ceramic glazes. The approach aims the valorization of this residue, adding environmental and economic value. RM was sintered at different temperatures (1100 °C, 1150 °C, 1200 °C, 1250 °C, 1300 °C and 1350 °C) to assess changes in its mineralogical composition. The obtained powders were characterized by XRD, UV–Vis and CIELab. The samples were added to glazes (transparent, opaque and matte) and their color stability analyzed by CIELab. RM sintered at 1300 °C was compared with commercial hematite producing lower coloring power but yielding better color stability on glazes for temperatures of 1100 °C ± 15 °C, thus presenting RM\_1300C as a suitable substitute for the hematite pigment.

### 1. Introduction

The valorization of residues has gained increasing momentum in the last decades due to environmental concerns and the recognition that natural resources are limited. The transformation of a residue from an industrial process into valuable raw material for another, besides the clear “green” concept behind it, also involves a potential economic gain. Companies, in most cases, have significant costs associated with waste disposal, costs that can be transformed into revenue if a waste-to-resource concept is applied. The increasing values of landfills fees together with the implementation or planned ban in some residues currently being deposited in landfills, are indicative of the pressing issue waste management have become in Europe [1]. This problematic is summed by the concept of circular economy [2], defined by M. Geissdoerfer and colleagues [3] as “a regenerative system in which resource input and waste, emission, and energy leakage are minimized by slowing, closing, and narrowing material and energy loops. This can be achieved through long-lasting design, maintenance, repair, reuse, remanufacturing, refurbishing, and recycling” [3].

Red mud (RM) or bauxite residue is originated from the production of alumina by the Bayer process. RM is a highly alkaline iron oxide rich sludge. In average, since the values vary with the source of bauxite, the production of 1 t of alumina yields 1–1.5 t of red mud [4]. This corresponds to an annual production near 120 Mt of waste. The accumulation of RM residues worldwide will reach ≈ 3.9 billion tons in 2017 [4,5]. This production is fueled by the world development as

demonstrated by the number of years that took the RM stockpile to achieve 1 billion tons: 93 years for the first, 15 years for the second and around 10 years for the third billion [4,5]. These values give a sense of urgency to the need to transform a material posing an environmental and economic problem into a valuable asset for the future.

The environmental impact nowadays is the most worrying aspect of RM management, with its disposal as the main issue, since RM has high alkalinity (pH = 10–13) and high salinity [6,7]. The RM disposal was done without much thought into the sea or in lagoons, the former have become obsolete and is only used in very isolated cases, the latter have suffered improvements with better designed lagoons and a progressive change from muds with high water contents to dry stacks [8]. However both the approaches still poses concerns, such as the leaching of hazardous components to the environment, the caustic nature of the lagoons or dust lift-off related problems of “dry” stacks [4].

Thus, different approaches have been attempted, over the time, to tackle the problem of RM recycling and valorization [8,9]. Literature reveals applications for RM in: environmental and agronomic [10–12]; construction and chemical industries [13–18]; and metallurgical [19–21]. The application of RM as colorant agent (pigments and dyes) is one of the most interesting approaches, due to the expected high added value of the final product. The literature is prolific in examples of colorant agent production from residues: steel waste [22,23], leather sludge [24], Al anodizing [25], Cr/Ni plating [25,26], and marble saw dust [26]. RM has been used as coloring agent in a variety of applications: ceramic glazes [15], heavy-clay ceramics [27], and glass-

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ceramics [16].

An example of the use of RM as a coloring agent was presented by Sglavo and colleagues [28], where the as-received RM was added to clay-based ceramics in percentages up to 50 wt%. The authors focus was not in the final appearance of the ceramic bodies, but in the amount of RM that could be added to the preparation of these materials without their mechanical properties being affected [28].

Another approaches make use of high temperature treatment that could enable the formation of stable structures while neutralizing and preventing the leaching of hazardous species. Yalçın and Sevinç [15] used different percentages of RM, as received and after calcination (500 °C), to coloring: porcelain (23 wt% of RM), sanitary ware (24 wt% of RM), tile (30 wt% of RM) and electroporcelain glazes (37 wt% of RM). The addition of RM produced color changes, such as cream, beige, yellow, mustard, green, red, brown and black [15]. The authors indicate the addition of RM as a possible pigment and glaze raw material. Nevertheless, the crystalline structure stability of the RM after addition to the glazes together with the color stability at different firing temperatures was not addressed by the authors.

Most of the literature shows RM being used, straightforward or after calcination at relatively low temperatures, as a pigment (dye) in the building material industry, without its structural and color stability being fully studied. In this work, Scheme 1, RM-based inorganic dyes were produced by calcination at high temperatures (1100–1350 °C). The obtained powders presented new crystalline structures and when added to commercial ceramic glazes as additives, 3 wt%, produced glazes with stable colors.

## 2. Experimental details

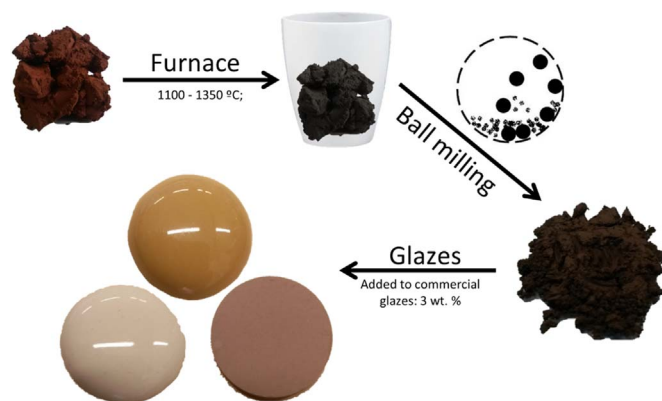
### 2.1. Materials

RM was kindly provided by Alcoa Spain. It contains about 31 wt% of moisture. The glazes were kindly provided by Esmalglass-Itaca group. Hematite was obtained from Sigma-Aldrich, ≥ 99% of ground substance, and used as received.

### 2.2. Dye preparation

RM was sintered in an electric furnace under a static air flow, according to the following cycle: i) 5 °C/min heating rate up to 100 °C to; ii) 30 min dwell to dry the sample; iii) 5 °C/min heating rate up to the maximum temperature (1100 °C, 1150 °C, 1200 °C, 1250 °C, 1300 °C and 1350 °C); iv) 3 h dwell time at the selected temperature; v) cooling (at 5 °C/min) until room temperature.

The obtained material was then ball milled (proportion of 1:4:1, sample: zirconia balls: water) for 1 h at 300 rpm. Afterwards the samples were dried in a ventilated oven at 80 °C and sieved through a 63 µm mesh.



Scheme 1. Process of transformation of RM from a residue to a coloring agent in glazes.

### 2.3. Test in glaze bodies

3 wt% of dye was added to three different commercial powdered glazes (transparent lead free, opaque bright and matte) and the homogenization process was conducted by wet-mixing, ball-milling for 30 min, and then drying at 80 °C. After disaggregation and sieving (63 µm), the powder was pressed into Ø2.5 cm pellets and fired at 1100 °C for 30 min. For assessing the color stability in the glazes a temperature variation of ± 15 °C (1085 °C and 1115 °C) was applied around 1100 °C. Heating/cooling rate of 10 °C/min was applied in an electric furnace under a static air flow. Exactly the same procedure was used to the study of hematite coloring power and color thermal stability.

### 2.4. Characterization methods

Fourier-transform infrared spectroscopy - Attenuated total reflection (FTIR-ATR) spectra were recorded with a Bruker IFS55 spectrometer equipped with a single horizontal Golden Gate ATR cell, with 256 scans using a 2 cm<sup>-1</sup> resolution. X-ray diffraction (XRD) analysis was performed using a PANalytical XPert PRO diffractometer (Ni-filtered CuK $\alpha$  radiation, PIXcel 1D detector, and the exposition corresponded to about 2 s per step of 0.02° 2 $\theta$  at room temperature). XRD data 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 $\alpha$  radiation, 5–80° 2 $\theta$ , step of 0.02° 2 $\theta$ , and time per step of 10 s. QPA was assessed on selected specimens, by way of the Rietveld method [29], as implemented in the GSAS-EXPGUI software package [30]. These parameters were refined: 15 terms of the shifted Chebyshev polynomial function to fit the background, scale factors, peak intensities, specimen displacement, and lattice parameters. The profile was modelled using the Thompson-Cox-Hasting formulation of the pseudo-Voigt function [31], refining two Lorentzian ( $L_x$  and  $L_y$ ) terms, together with an angle independent Gaussian term ( $G_w$ ); furthermore, peak correction for asymmetry, as well as sample displacement effects, were also refined.

The chemical composition was obtained by using X-ray fluorescence (Philips X'Pert PRO MPD spectrometer). The loss on ignition (LOI) at 1000 °C was also determined. The thermal behavior of the sieved (< 20 µm) powders was assessed by differential thermal/gravimetric (DTA/TG) analyses using a Netzsch STA 409 EP apparatus. The heating rate was 5 °C/min, from room temperature to 1200 °C, and runs were conducted in airflow.

Optical spectra of the specimens were recorded on a Shimadzu UV-3100 spectrometer in the UV–Vis–NIR range, 300–1500 nm, and their color was determined via the L\*a\*b\* chromatic coordinates on a Konica Minolta Chroma Meter CR-400, using D<sub>c</sub> illuminant and 10° standard observer (Y: 94.0, x: 0.3130, y: 0.3191) according to the Commission Internationale de l'Éclairage (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) [32]. The color stability was calculated using the value of  $\Delta E - \Delta E = \sqrt{(\Delta L)^2 + (\Delta a)^2 + (\Delta b)^2}$ . Values of  $\Delta E$  higher than 2, usually mean that the color change can be detected by the naked eye [33].

The particle size distribution was determined by laser diffraction on a Coulter LS particle size analyzer (LS230FM). SEM/EDS observations were performed using a Hitachi S-4100 microscope with electron beam energy of 25 kV.

## 3. Results and discussion

### 3.1. Red mud characterization

The chemical composition of RM is shown in Table 1. It tends to change according to the source of bauxite and processing variations,

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