INORGANIC PIGMENTS OBTAINED FROM COAL MINE DRAINAGE RESIDUES

Adriano Michael Bernardin(1,5), Reginaldo Rosso Marcello(1), Michael Peterson(1,5), Sérgio Galato(2), Giovano Izidoro(3), Vitorino Saulo(4), Humberto Gracher Riella(5)

(1) Engenharia de Materiais, Universidade do Extremo Sul Catarinense,
Criciúma, Santa Catarina, Brazil – adriano@unesc.net
(2) Instituto de Pesquisas Ambientais e Tecnológicas, Criciúma, Santa Catarina, Brazil
(3) Carbonífera Metropolitana S.A., Criciúma, Santa Catarina, Brazil
(4) Conselho Regional de Química, Florianópolis, Santa Catarina, Brazil
(5) Programa de Pós-Graduação em Engenharia Química, Universidade Federal de
Santa Catarina, Florianópolis, Santa Catarina, Brazil

ABSTRACT

The continuous industrial development increases energy consumption, also increasing the consumption of fossil fuels. Coal mineral has been used in Brazil as solid fuel for thermoelectric generators for several years. Although, coal exploitation affects intensively the environment, mainly because the Brazilian coal has an excess of ashes and pyrite (iron disulfide). According to the local coal industry syndicate, the annual coal run of mine average is 6 million ton/year, where 3,5 million ton/year are rejects, which are disposed of at landfills. Besides pyrite, the Brazilian coal presents Mn, Fe, Cu, Pb, Zn, Ge, Se and Co. Also, the water used for coal beneficiation causes the pyrite oxidation, forming an acid drainage. This drainage solubilizes the metals, transporting them to the environment, being necessary its treatment. So, this work deals with the use of coal mine drainage residues to obtain inorganic pigments that can be used in the ceramic industry. The drainage was dried, ground and calcined (~1,250°C). The calcined pigment was then micronized (D_{50}~2μm). Chemical (XRF), thermal (DTA/TG), particle size (laser) and mineralogical (XRD) analyses were carried out with the raw drainage. After calcination and micronization, mineralogical analyses (XRD) were used to determine the pigment structure at 1.250°C. Finally, the pigments were mixed with transparent glaze and fired in a laboratory roller kiln (1,130°C, 5min). The results are promising, showing that brown colours can be obtained with pigments made by residues.

1. INTRODUCTION

Inorganic pigments are used in several applications to colour paints, resins, polymers and ceramic tiles. In ceramic tiles they are used to coat tiles (added to glazes) or to colour the entire body (porcelain tiles). The pigments used in the ceramic industry must be crystalline structures stable at high temperatures [1]. They must be insoluble in the glaze matrix and must present adequate physical properties regarding the final product: good mechanical resistance to abrasion and to the environment [3].

The inorganic pigments are formed by a host phase where the compound responsible for pigmentation, named chromophore element (a transition cation), is contained. There are also modifying agents that stabilize the structure and the material tonality [4] With a few exceptions the inorganic pigments are oxides, sulphides, hydroxides, silicates, sulphates or carbonates, consisting of particles with only one component and well defined crystalline structures, as the red iron oxide [1].

The crystal structure where the chromophore element will be lodged could be simple, as in the transition metal oxides and rare earths (Fe_2O_3, Cr_2O_3, V_2O_5 or CoO) or complicated structures [6]. Oxides formed by transition metals are mainly iron, chrome and copper oxides that form coloured crystals resulting in pigments with limited solubility in glasses. These crystals are thermally stable after calcination, forming coloured spinels [5].

Spinels are $B^{2+}A_2^{3+}O^4$ structures where the B^{2+} are tetrahedral structures like Cu^{2+}, Fe^{2+}, Zn^{2+} and Ca^{2+} and the A^{3+} are octahedral like Al^{3+}, Fe^{3+} and Cr^{3+}. In the spinel structures the oxygen is densely packed in planes parallel to the octahedron faces [7].

The pigment properties are directly related to their crystal structures, chemical composition and particle size and shape. Glaze pigments must present low solubility in the glass phase; thermal stability, neither reacting nor releasing gases in the glaze that could affect its surface or form bubbles; present an acceptable particle size, generally between 100nm and 20μm. The pigments must be resistant to the solar light, time, heat and atmosphere [2].

In the present work the acid drainage of coal run of mine is used to produce ceramic pigments. The annual coal run of mine average in Brazil is 6 million ton/year, where 3,5 million ton/year are rejects. They are disposed on landfills. Besides pyrite, the Brazilian coal presents Mn, Fe, Cu, Pb, Zn, Ge, Se and Co. Also, the water used for coal beneficiation causes the pyrite oxidation, forming an acid drainage. This drainage solubilizes the metals, transporting them to the environment, being necessary its treatment.

2. MATERIALS AND METHODS

The raw material was an acid drainage collected at an effluent treatment station. The mud was dried (105°C, 8h), ground (250μm) and analysed. The chemical analysis was carried out by X-ray fluorescence (Phillips PW2400, molten sample) and the phase analysis by X-ray diffraction (Philips PW1830, CuKα, 0° to 75°, 0,05°/s, analysis with X'Pert HighScore software). The particle size analysis was carried out by LASER diffraction (CILAS 1064, 60s ultrasound). Finally, the thermal analysis was determined by differential thermal analysis (Netzsch STA 409 EP, 20°C to 1,200°C, 10°C/min, air).

As the mud chemical composition had indicated the residue did not contain all transition metals needed to form spinels, commercial pigments were added to the residue to form spinels. Two formulations were used: 33.3% ZnO, 33.3% Cr_2O_3 and 33.3% residue, and the pure residue was also used as a pigment. The formulations were calcined at 1,250°C, ground and micronized (below 10μm).

After preparation the pigments (pure and mixed) were added at 3%, 5% and 7% fractions (weight basis) to a transparent glaze used as flux in ceramic tiles. The flux was mixed (eccentric mill, 5min) and applied on ceramic tiles as a glaze. The tiles were fired in a laboratory roller kiln (1,130°C, 22min) and the colour compared with a standard brown pigment.

3. RESULTS AND DISCUSSION

Table 1 shows the chemical and phase analysis of the acid drainage sample for the residue in natura and calcined at 1,200°C. The iron oxide is a major phase indicating the residue could form a Fe-Zn-Cr spinel. The loss on ignition is very high due to decomposition of calcium and iron sulphate and organic matter and elimination of water.

Sample	SiO_2	Al_2O_3	Fe_2O_3	P_2O_5	CaO	MgO	MnO	Na_2O	LOI	Phases
Drainage mud	9.4	21.1	21.9	0.2	17.7	9.3	2.6	0.4	31.0	Gy, Go
Calcined at 1,250°C	11.4	25.6	26.5	0.2	21.4	11.2	3.1	0.5	-	A, M, H, Ge
Gy is gypsite, Go is goethite, A is anhydrite, M is magnetite, H is hematite and Ge is gehlenite										

Table 1. Chemical and phase analysis of the sample residues (% wt)

The particle size distribution of the residue in natura is in figure 1. Besides its small particle size (<23μm) it is not indicated for pigments (<10μm). Figure 1 shows also the particle size distribution of the calcined residue. It presents an adequate particle size (<10μm).

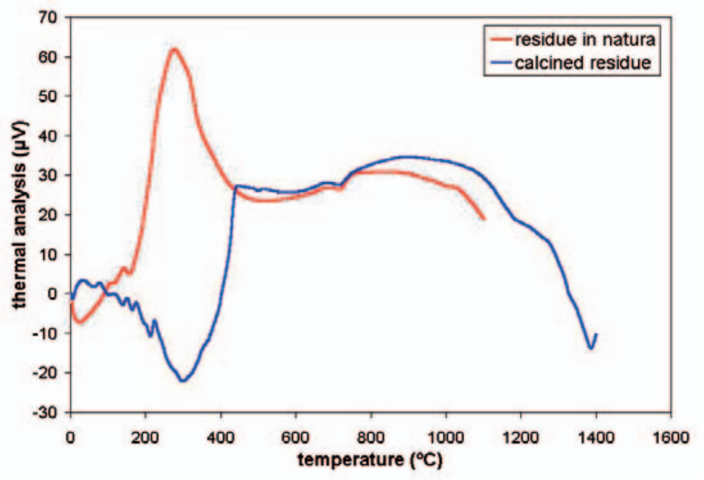

Figure 1. Particle size distribution of the drainage residue in natura and calcined at 1,250°C

As the residue presents phase variation after calcination, a thermal analysis was carried out, figure 2. At 285°C there is a sharp exothermic peak, probably due the decomposition of pyrite, organic matter or rests of coal. At 745°C there is an endothermic peak, related to the decomposition of sulphates (calcium and iron, as indicated in the chemical analysis).

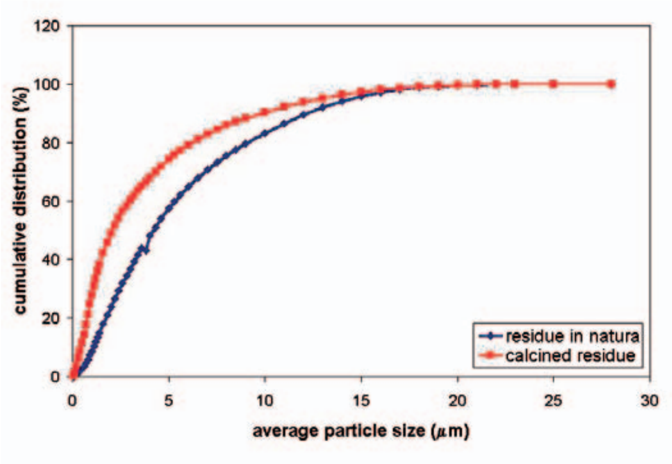

Figure 2. Differential thermal analysis for the drainage residue in natura and after calcination at 1250°C

After calcination the pure and mixed residues were added (5% and 7%) to a transparent glaze and applied on ceramic tiles. The pure residue (compared to a standard brown pigment) presents poor results for both concentrations, figure 3. The colour appeared faded in comparison with the standard pigment.

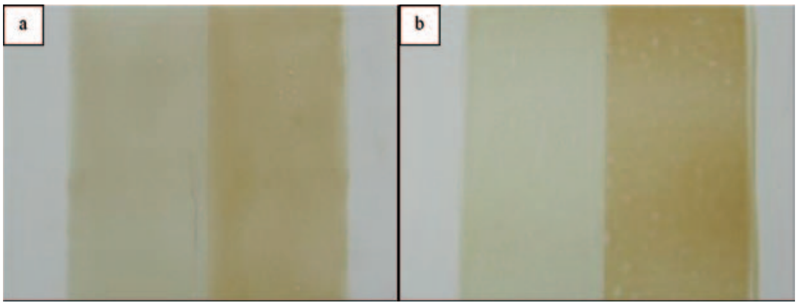

Figure 3. Transparent glaze with standard and pure residue pigments applied on ceramic tiles for 5% (a) and 7% (b) pigment addition; the standard pigment is on the left side

In turn, the mixed residue pigment has presented better results than the pure residue pigment, but far from the standard pigment (figure 4). It appeared lighter than the standard pigment. 3% of the mixed residue pigment was added to the glaze in this case.

Figure 4. Transparent glaze with standard and mixed residue pigments applied on ceramic tiles for 3% pigment addition; the standard pigment is on the left side

4. CONCLUSION

The drainage residue can be used as a pigment only mixed with pure oxides or as part of a commercial pigment. Used alone, the residue pigment presents a faded brown colour, inadequate for ceramic glazes. Mixed, the residue had better results, but poor regarding a commercial pigment.

This study is preliminary. The drainage residue could be used in other ceramic applications, as filler for brick pastes and other ceramic products. The most important result is the elimination of this kind of residue from the environment.

REFERENCES

[1] Bondioli, F. et al. Syntheses of Fe_2O_3/silica red inorganic inclusion pigments for ceramic applications. Materials Research Bulletin, v.33, n.5, pp.723-729, 1998.

[2] López-Navarrete, E. and Ocaña, M. A simple procedure for the preparation of Cr-doped tin sphene pigments in the absence of fluxes. Journal of the European Ceramic Society, v.22, n.3, pp.353-359, 2002.

[3] López-Navarrete, E. et al. Oxidation state and localization of chromium ions in Cr-doped cassiterite and Cr-doped malayaite. Acta Materialia, v.51, n.8, pp.2371-2381, 2003.

[4] Muñoz, R. et al. Environmental study of Cr_2O_3-Al_2O_3 green ceramic pigment synthesis. Journal of the European Ceramic Society, v.24, n.7, pp.2087-2094, 2004.

[5] Ozel, E. et al. Production of brown pigments for porcelain insulator applications. Journal of the European Ceramic Society, in press, 2005.

[6] Pelino, M. et al. Recycling of zinc-hydrometallurgy wastes in glass and glass ceramic materials. Waste Management, v.20, n.7, pp.561-568, 2000.

[7] Ricceri, R. et al. Ceramic pigments obtained by sol-gel techniques and by mechanochemical insertion of color centers in Al_2O_3 host matrix. Journal of the European Ceramic Society, v.22, n.5, pp.629-637, 2002.