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Inorganic pigments made from the recycling of coal mine drainage treatment sludge

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Abstract

Continuous industrial development increases energy consumption and, consequently, the consumption of fossil fuels. Coal mineral has been used in Brazil as a solid fuel for thermoelectric generators for several years. However, coal exploitation affects the environment intensely, mainly because Brazilian coal contains excess ash and pyrite (iron disulfide). According to the local coal industry syndicate, the average annual coal run per mine is 6 million ton/year; 3.5 million ton/year are rejected and disposed of in landfills. Besides pyrite, Brazilian coal contains Mn, Fe, Cu, Pb, Zn, Ge, Se, and Co. Additionally, the water used for coal beneficiation causes pyrite oxidation, forming an acid mine drainage (AMD). This drainage solubilizes the metals, transporting them into the environment, making treatment a requirement. This work deals with the use of sedimented residue from treated coal mine drainage sludge to obtain inorganic pigments that could be used in the ceramic industry. The residue was dried, ground and calcined (~1250 °C). The calcined pigment was then micronized (D_{50}~2 μm). Chemical (XRF), thermal (DTA/TG), particle size (laser), and mineralogical (XRD) analyses were carried out on the residue. After calcination and micronization, mineralogical analyses (XRD) were used to determine the pigment structure at 1250 °C. Finally, the pigments were mixed with transparent glaze and fired in a laboratory roller kiln (1130 °C, 5 min). The results were promising, showing that brown colors can be obtained with pigments made by residues.

Keywords: Acid mine drainage; Pigments; Glazes; Ceramic tiles

1. Introduction

Acid mine drainage (AMD) continues to be an important water pollution problem in mining industry around the world (Bernardin et al., 2006; Pinetown et al., 2007; Zhao et al., 2007). AMD is produced when sulfide-bearing material is exposed to oxygen and water. In coal mines, the minerals pyrite and marcasite (FeS_2) are largely responsible for any AMD problems. The use of water during coal mining, in conjunction with atmospheric exposure, provides a suitable medium to supply sufficient oxygen for pyrite oxidation to occur. The oxidation of such sulfides exposed to atmospheric O_2 during or after mining activities generates acidic waters with high dissolved SO_4^{2-} and heavy metals (Al, Cu, Fe, Mg, Mn, and Zn) (Blodau, 2006; Devasahayam, 2006; Weber et al., 2006). Waters affected by these reactions are often strongly acidic, and may build up in significant quantities in underground workings and aquifers (Pinetown et al., 2007).

Various reactions between these waters and many other mineral phases may give rise to a complex combination of dissolved constituents, with numerous adverse effects on the surrounding environment. Iron hydroxide, iron sulfate, and sulfuric acid are formed as a result of a series of

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geochemical and microbial reactions on the pyrite (Blodau, 2006). An insidious feature of AMD is that its sources may remain active for decades or even centuries after mine closure. Both operating and abandoned polymetallic sulfide mining sites are often active sources of AMD (Devasahayam, 2006; Zhao et al., 2007).

The most environmentally effective techniques available for mitigating AMD are internal neutralization methods, water-covers and biological/natural degradation processes (Watten et al., 2005). A number of factors dictate the level of sophistication of the treatment system that is necessary to ensure that effluent standards will be met. These include the chemical characteristics of the AMD, the quantity of water in need of treatment, local climate, terrain, sludge characteristics, and the projected life of the plant.

The chemicals usually used for AMD treatment include limestone, hydrated lime, soda ash, caustic soda, ammonia, calcium peroxide, kiln dust, and fly ash (Watten et al., 2005).

Lime neutralization/precipitation, referred to in mining circles as the "chemical process", is often used to treat AMD in the mining industry (Canty and Everett, 2006). During lime treatment, the most commonly used process, AMD is discharged directly into a rapid mix chamber where hydrated lime is added in dry form or as slurry. Low ferrous iron concentrations (<50 mg/l) are treated to a pH of 6.5–8.0 and then diverted directly to a settling chamber. Higher concentrations have pH 8–10 and are passed through an aeration tank, where the ferrous hydroxide precipitate is converted to ferric hydroxide (Ackman, 1982; Skousen and Ziemkiewicz, 1995).

The water then flows to a settling chamber, where heavy metals are precipitated from the solution. Although limestone is generally an inexpensive reagent, and that its application produces a lower volume of sludge, it is not widely used, largely because carbon dioxide buffers the reaction, therefore making it difficult to raise the pH above 6. Limestone is also inefficient with high ferrous iron water, and the method of application is more complex than that involving lime.

Also, the chemical process results in the production of voluminous sludge (solids in this sludge is about 5%) and this sludge disposal represents a further environmental problem and additional cost. Thus, high cost of conventional clean up technologies has produced economic pressure and has caused engineers to search for creative, cost-effective and environmentally sound ways to treat AMD (Grady and Ackers, 1976; Simonyi et al., 1977; Gabr and Bowders, 2000; Zilberchmidt et al., 2004; Bulusu et al., 2007). As the coal mine drainage sludge contains a large amount of heavy metals, the residue obtained from the sedimented sludge can be used as an inorganic pigment (Kirby et al., 1999; Hedin, 2003; Xinchao et al., 2005; Wei and Viadero Jr., 2007).

Inorganic pigments are used in several applications: for paint, resin, polymer, and ceramic tile coloration. In ceramic tiles, they are used to cover tiles (added to glazes) or to color the entire body (porcelain tiles). The pigments used in the ceramics industry must be crystalline structures that are stable at high temperatures (Bondioli et al., 1998). 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 (López-Navarrete et al., 2003).

Inorganic pigments are formed by a host phase, where the compound responsible for pigmentation is contained, denominated a chromophore element (a transition cation). Modifying agents also exist that stabilize the structure and the material tonality (Muñoz et al., 2004). With few exceptions, inorganic pigments are oxides, sulfides, hydroxides, silicates, sulfates, or carbonates, consisting of particles with only one component and well-defined crystalline structures, such as red iron oxide (Bondioli et al., 1998).

The crystal structure where the chromophore element is to be lodged, can be simple, as in transition metal oxides and (Fe_2O_3, Cr_2O_3, V_2O_5, and CoO) rare earths or a complex structure (Pelino et al., 2000). Oxides formed by transition metals are mainly iron, chrome, and copper oxides, which form colored crystals that result in pigments with limited solubility in glass. These crystals are stable thermically after calcination, forming colored spinels (Ozel et al., 2006).

Spinels are $B^{2+}A_2^{3+}O_4$ structures, where B^{2+} present tetrahedral structures, like Cu^{2+}, Fe^{2+}, Zn^{2+} and Ca^{2+}, and A^{3+} present octahedral forms, like Al^{3+}, Fe^{3+}, and Cr^{3+}. In the spinel structures, oxygen is densily packed in planes parallel to the octahedron faces (Ricceri et al., 2002).

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, no reaction or release of gases in the glaze that could affect its surface or form bubbles; present an acceptable particle size, generally between 100 nm and 20 μm. The pigments must also be resistant to solar light, time, heat, and the atmosphere (López-Navarrete and Ocaña, 2002).

In the present work, the sedimented residue from coal AMD treatment sludge was used to produce ceramic pigments (Bernardin et al., 2006). The average annual coal run per mine in Brazil is 6 million ton/year; however, 3.5 million ton/year are rejected and disposed of in landfills due to excess pyrite. Besides pyrite, Brazilian coal contains Mn, Fe, Cu, Pb, Zn, Ge, Se, and Co. Additionally, the water used for coal beneficiation causes pyrite oxidation, forming an acid drainage. This drainage solubilizes the metals, and can cause their transportation into the environment, making treatment an essential requirement. The common AMD treatment used at Criciúma coal mines consists of alkalis neutralization (oxide or hydroxide), metallic precipitation, aggregate surface treatment by hydrophobic process and flotation.

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

Residue	SiO_2	Al_2O_3	Fe_2O_3	P_2O_5	CaO	MgO	MnO	Na_2O	LOI	Phases[a]
Drainage sludge	9.4	21.1	21.9	0.2	17.7	9.3	2.6	0.4	17.1	Gy, Go
Calcined at 1250 °C	11.4	25.6	26.5	0.2	21.4	11.2	3.1	0.5	–	A, M, H, Ge

[a] Gy, gypsum; Go, goethite; A, anhydrite; M, magnetite; H, hematite; and Ge, gehlenite.

2. Materials and methods

The raw material used in this work was a sedimented residue from acid drainage treated sludge collected at an effluent treatment station (Bernardin et al., 2006). The residue was dried (105 °C, 8 h), ground (250 μm) and analyzed. Chemical analysis was carried out by X-ray fluorescence (Phillips PW2400, molten sample) and phase analysis by X-ray diffraction (XRD) (Phillips PW1830, Cu Kα, 0–75°, 0.05°/s, analysis with X'Pert HighScore software). Particle size analysis was carried out by LASER diffraction (CILAS 1064, 60s ultrasound). Finally, thermal analysis was determined by differential thermal analysis (Netzsch STA 409 EP, 20–1200 °C, 10 °C/min, air).

As the residue chemical composition indicated that it did not contain all the transition metals needed to form spinels, commercial oxide pigments (ZnO and Cr_2O_3) were added to the residue. Two formulations were used: a blend formed by 33.3% ZnO, 33.3% Cr_2O_3 and 33.3% residue, and the pure residue acting as a pigment. The formulations were calcined at 1250 °C, grounded and micronized (below 10 μm).

After preparation, the pure residue and the mixed residue pigments were added in fractions of 3%, 5%, and 7% (weight basis) to a transparent glaze used as flux in ceramic tiles. The flux was mixed (eccentric mill, 5 min) and applied to ceramic tiles as a glaze covering. The tiles were fired in a laboratory roller kiln (1130 °C maximum temperature during 5 min) and the colors compared with a commercial brown pigment (Cr–Fe–Zn system).

3. Results and discussion

Table 1 shows the chemical and phase analysis of the residue (AMD sludge from the treatment station) sample in natura and calcined at 1250 °C. Iron oxide is a major phase indicating the residue was able to form a Fe–Zn–Cr spinel. The loss of ignition was very high due to the decomposition of calcium and iron sulfate, possibly iron hidroxides and organic matter and the elimination of water.

The particle size distribution of the residue in natura is shown in Fig. 1. Despite its small particle size (<23 μm), it would not be indicated for pigments (<10 μm). Fig. 1 shows also the particle size distribution of the calcined residue. It presented an adequate particle size (<10 μm).

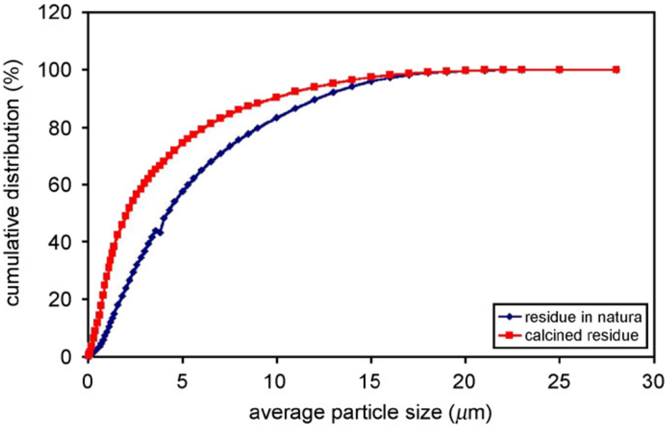

Fig. 1. Particle size distribution of the drainage residue in natura and calcined at 1250 °C.

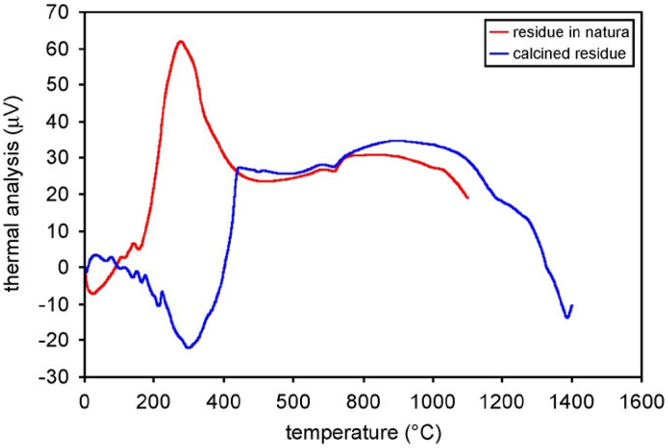

Fig. 2. Differential thermal analysis for the drainage residue in natura and after calcination at 1250 °C.

As the residue presented phase variation after calcination, thermal analysis was carried out (Fig. 2). At 285 °C, a sharp exothermic peak occurred, probably due the decomposition organic matter, coal remains or even breakdown of iron hydroxides. At 745 °C, an endothermic peak occurred, related to the decomposition of sulfates (calcium and iron), as indicated in the chemical analysis. Pyrite under oxidation condition shows an exothermal transformation of pyrite to hematite between 440 and 540 °C, but the reaction was not observed in the residue sample and pyrite was not identified in the XRD analysis.

After calcination, the pure and mixed residues were added (5% and 7%) to a transparent glaze and applied to ceramic tiles. The pure residue presented poor results at

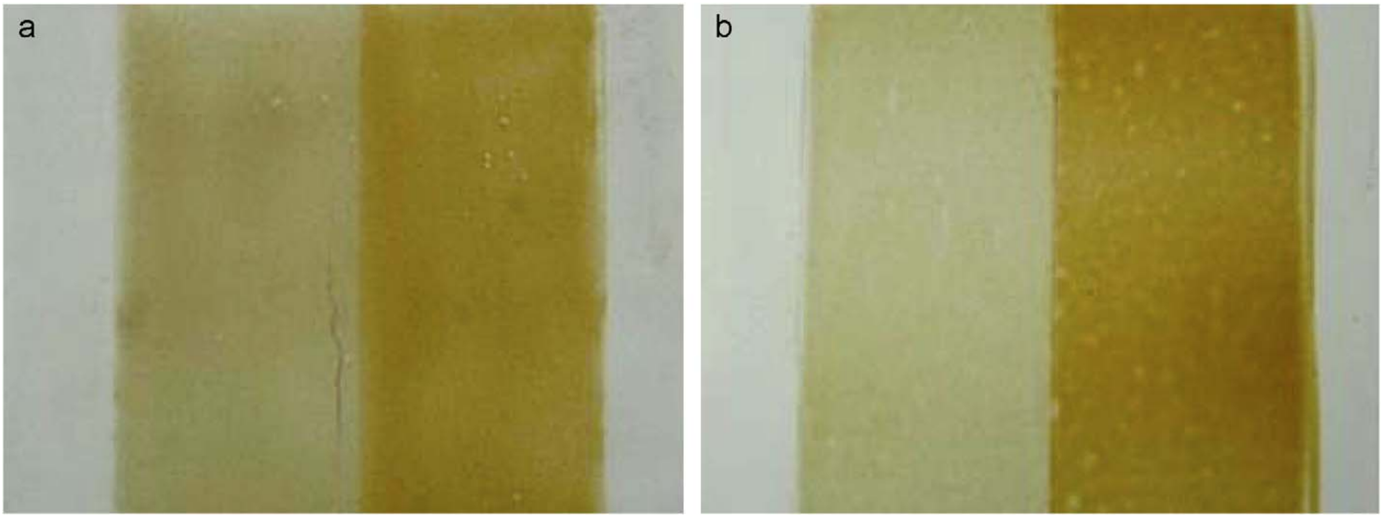

Fig. 3. Transparent glaze with standard and pure residue pigments applied to ceramic tiles with 5% (a) and 7% (b) pigment addition; the standard pigment is on the right side.

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

both concentrations, compared to a commercial brown pigment of the Cr–Fe–Zn system (Fig. 3). The color appeared faded in comparison with this standard pigment.

The mixed residue pigment presented better results than the pure residue pigment, but not as well defined as the standard Fe–Cr–Zn pigment (Fig. 4), appearing lighter than this standard. Three percent of the mixed residue pigment was added to the glaze in this case.

4. Conclusion

The residue from the active AMD treatment in this study can be used as a pigment only when mixed with pure oxides or as part of a commercial pigment. Used alone, the residue pigment presents a faded brown color, inadequate for ceramic glazes. When mixed, the residue presented better results, but still poor compared with a commercial pigment.

This study is preliminary. The residue from AMD treatment stations could be used in other ceramic applications, such as load for brick pastes and other ceramic products. The most important result was the elimination of this kind of residue from the environment.

Finally, it is important to emphasize that not all active treatment processes will produce the same sludge chemistry, mineralogy, and physical characteristics (Kirby et al., 1999). Also, passive treatment sludge has very different characteristics from active treatment sludge.

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