

Production of Iron Pigments (Goethite and Haematite) from Acid Mine Drainage

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Abstract Acid mine drainage (AMD) is recognized as one of the major sources of environmental damage in the coal mining industry. The treatment of AMD involves addition of alkaline reagents to raise the pH and precipitate dissolved metals as oxides/hydroxides. This treatment generates large volumes of sludge which requires further treatment and final disposal. Recent research has indicated the possibility of recovering the iron by selective precipitation. The aim of this work was to study the production of goethite and hematite from the iron present in AMD. The pigments were characterized in terms of physical-chemical and colorimetric properties and tested for paint production and colored concrete.

Key Words iron pigments, goethite, hematite, selective precipitation, acid mine drainage

Introduction

Acid mine drainage (AMD) continues to be an important water pollution problem in coal production. The active treatment of AMD involves the addition of alkaline reagents to increase the pH and precipitate dissolved metals as hydroxides. Although active treatment can provide effective remediation, it has the disadvantages of high operational costs and problems related to the disposal of the bulky sludge that is produced (Konopoulos 1998; Skousen et al, 1998).

The AMD treatment plants in Brazil mainly use sodium hydroxide or lime for neutralization. The precipitated metals are removed in settling ponds, conventional settling tanks, lamellar tanks, and dissolved air flotation units (Silveira et al, 2009). The sludge typically contains 2–5% solids and high concentrations of iron and aluminium along with minor concentrations of manganese, zinc, and other metals. Thus, it represents a major environmental problem (Marcello et al, 2008).

Recent studies have shown that it is possible to obtain some materials with high value from selective precipitation of AMD. The sludge obtained from AMD has been previously considered for the production of coagulants (Finch et al, 1992; Menezes et al, 2009), inorganic pigments (Marcello et al, 2008), and magnetic particles like ferrites (Wei and Viadero, 2005).

The aim of this study was to develop the process of selective precipitation to recover the iron present in AMD to obtain pigments. The pigments produced were goethite (yellow pigment) and hematite (red pigment).

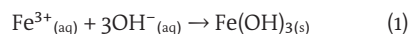
Reactions

The conventional synthesis of goethite and hematite by means of chemical precipitation includes the following steps (Schwertmann and

Murad 1983; Schwertmann et al, 2004; Cornell and Schwertmann, 1996):

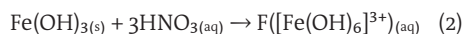
Step 1: Selective Precipitation of Iron

Hydrolysis of the soluble iron by addition of alkali to precipitate the metal as ferric hydroxide at pH 3.6. This allows the separation of iron from other metals present in the AMD. The process should be followed by successive washes with an aqueous solution at the same pH to remove the undesirable contaminants present in the interstitial water (Reaction 1):



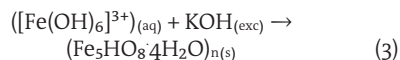
Step 2: Iron Dissolution

The iron hydroxide should be dissolved in water by the addition of nitric acid to form a complex called iron-hexa-aquo ion (Reaction 2).

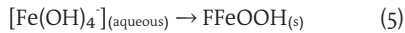
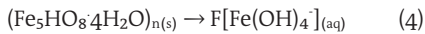


Step 3: Goethite Crystallization

The synthesis of goethite from Fe^{3+} can be obtained under alkaline conditions by the precipitation of the ferric nitrate solution (iron-hexa-aquo-ion), producing a precipitate called ferrihydrite ($\text{Fe}_5\text{HO}_8 \cdot 4 \text{H}_2\text{O}$) by the addition of potassium hydroxide at pH 12.0. (Reaction 3):

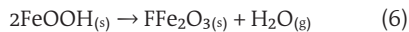


Under these conditions, the initially formed precipitate was dissolved and released an ionic species ($\text{Fe}(\text{OH})_4^-$) which will form crystalline goethite by nucleation, thus beginning the process of growth of goethite (FeOOH) (Reactions 4 and 5).



Step 4: Hematite Production

The goethite (FeOOH) can be converted into hematite (Fe_2O_3) by thermal dehydration (loss of water), dehydroxilation (loss of hydroxyl) or oxidation/reduction (by electron change). The most convenient method to convert goethite into hematite is thermal dehydration (Reaction 6), due to the reaction conditions and stability of the formed product.



Material and Methods

Sample Preparation

AMD was collected from a drainage channel near a tailings deposit in Santa Catarina State (Brazil) and sealed in high-density polyethylene bottles. At the laboratory, the solids and debris in the water samples were removed by settling and the remaining suspended solids were removed by filtration through a $0.45 \mu\text{m}$ filter. The AMD was analyzed for pH and concentrations of dissolved metals (total Fe, Fe^{2+} , Fe^{3+} , Al, Mn, Zn, Ca, Mg), and sulfate. All analyses followed the procedures described in the Standard Method for the Examination of Water and Wastewater (Eaton et al, 2005).

Iron Recovery and Solution Preparation

Iron recovery was achieved by the selective precipitation of 1 L of AMD at pH 3.6. The method applied for iron precipitation was the same as that applied by Wei *et al.* (2005) and Menezes *et al.* (2009). The pH of the AMD was increased to and maintained at 3.6 ± 0.1 , with the addition of a 4 N NaOH solution, to precipitate the iron as ferric hydroxide/oxyhydroxide. This was further separated from the AMD by centrifugation at 3,000 rpm. The supernatant was analyzed for the pH and the concentrations of dissolved metals and sulfate. Subsequently, the pH was adjusted to 7.0 to reach the standards for wastewater discharge. The precipitate obtained at pH 3.6 was washed with distilled water at $\text{pH } 3.6 \pm 0.1$, resuspended, and centrifuged; this cycle was repeated three times. The final precipitate was dissolved in nitric acid to achieve a clear iron solution for goethite production. The steps can be seen in Fig. 1.

Synthesis and characterization of yellow and red pigments

For the production of goethite (FeOOH) (yellow pigment), the ferric precipitated sludge was dissolved with nitric acid to form the iron-hexa-aqua-ion complex (Reaction 3). This solution was alkalinized with potassium hydroxide and the pH

adjusted at 12.0 to form the unstable compound with a red-orange color called ferrihydrite, according to Reaction 4. Immediately, the system was diluted with water and heated to 70°C for a period of 60 hours, for goethite crystallization (Reaction 5).

The hematite (Fe_2O_3) was produced by thermal treatment of the goethite particles in a muffle furnace at a temperature of about 350°C for 2 hours.

The goethite particles were prepared in two different forms: (a) as a paste – the goethite particles were centrifuged and prepared as water suspension containing about 50% solids; and (b) as a powder – the goethite particles were dried at 60°C . The hematite was prepared just as a powder. The materials were further analyzed for particle size (laser diffraction), crystalline compounds (X-ray diffraction – XRD), and elementary chemical analysis (atomic absorption spectroscopy – AA).

Paint and colored concrete production

Water based paints were produced with the goethite prepared as a paste and with the goethite prepared as a powder. Both paints were produced in a concentration of 2% solids. The colored concrete was produced with the hematite prepared as a powder in a ratio pigment: white cement of 1:10. The color measurements of the paints and colored concrete were recorded by reflectance spectra using a MINOLTA CM-2600D spectrophotometer with an integration sphere associated with an ultraviolet filter. As defined by the CIE (1964), the illuminant D_{65} , which simulates daylight and the standard observer at 10° were chosen. At the beginning of the experiment, the calibration was done with two reference points, the zero and the white standard. The color parameters corresponding to the uniform color space CIELAB (CIE, 1995) were obtained directly from the apparatus. Within the uniform space CIELAB, two color coordinates, a^* and b^* , as well as a psychometric index of lightness, L^* , are defined. a^* takes positive values for reddish colors and negative values for the greenish ones, whereas b^* takes positive values for yellowish colors and negative values for the bluish ones. L^* presents an approximate meas-

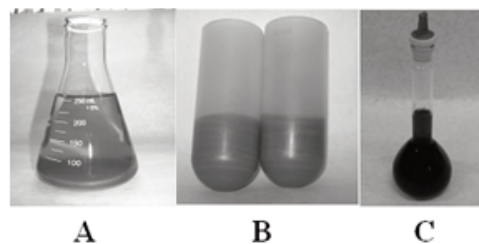


Figure 1 (A) Acid mine drainage; (B) Iron sludge purified; (C) Iron sludge solubilized.

Table 1 Chemical analysis of the raw AMD sample and after the metal precipitation at pH 3.6 and pH 7.0.

Parameters (mg/L)	Raw AMD	After pH adjustment at 3.6	After pH adjustment at 7.0	Brazilian Standards for Wastewater Discharge
pH	2.8	3.6	7.0	5-9
Fe _(total) (mg/L)	3,200.0	65.7	0.5	15.0
Fe ³⁺ (mg/L)	3,200.0	65.7	0.5	-
Fe ²⁺ (mg/L)	ND	ND	ND	-
Al (mg/L)	1,269.5	1,006.7	1.3	-
Mn (mg/L)	114.6	91.5	0.6	1.0
Zn (mg/L)	80.0	62.0	0.03	5.0
Ca (mg/L)	11.8	10.2	10.5	-
Mg (mg/L)	8.4	5.3	5.5	-
SO ₄ ²⁻ (mg/L)	12,600	10,470.0	9,236.7	-

ND – not detected

urement of luminosity; according to this property each color can be considered as equivalent to a member of the grey scale, ranging between black and white, taking values within the range of 0–100.

Results and Discussion

The dissolved metal concentrations in AMD obtained by the metal recovery process are presented in Tab. 1. It was found that the raw AMD waste was low in pH and contained elevated dissolved metals (Fe, Al, Mn, Zn, Ca, and Mg). When the pH was increased from 2.8 to 3.6, the dissolved iron concentration was found to drop from 3,200 mg/L to about 65.7 mg/L, thereby indicating that approximately 98% of the iron was recovered as iron hydroxide/oxyhydroxide. Moreover, at pH 3.6, the concentration of other metals remained nearly unchanged or dropped slightly, which ensured that the iron precipitate was of high purity. When the pH was adjusted to pH 7.0, most of the Fe and Al were precipitated. The water quality met the Brazilian Standards for Wastewater Discharge. Parameters (mg/L) Raw AMD After pH adjustment at 3.6 After pH adjustment at 7.0 Brazilian Standards for Wastewater Discharge.

The iron hydroxide/oxyhydroxide precipitate from AMD at pH 3.6 was resolubilized with nitric acid to obtain a ferric nitrate solution. The predominant metal was Fe (93.5%), present exclu-

Table 2 Elemental analysis of ferric nitrate solution, goethite and hematite particles.

Element	Goethite	Hematite
Fe (%)	60.3	51.4
Al (%)	0.8	0.1
Mn (%)	0.2	< 0.1
Ca (%)	0.1	0.1
Zn (%)	0.2	0.3

sively in the form of Fe³⁺, while other metals were present at very low concentrations. Consequently, ferric iron with relatively high purity was recovered successfully and used to synthesize the pigments. Tab. 2 presents metals concentration in the pigments. It is possible to observe that iron is the major element, although other metals (e.g. Al, Mn, Ca, and Zn) can be present in minor concentrations.

Fig. 2A presents the XRD patterns of the synthesized goethite powder. The result demonstrates that goethite is the main crystalline phase. Figure 2B presents the XRD patterns of the synthesized hematite powder. The result demonstrates that hematite is the main crystalline phase. However, in this case, other crystalline phases appeared, such as: goethite, calcite, and wüstite.

Fig. 3A presents the particle size analysis of the

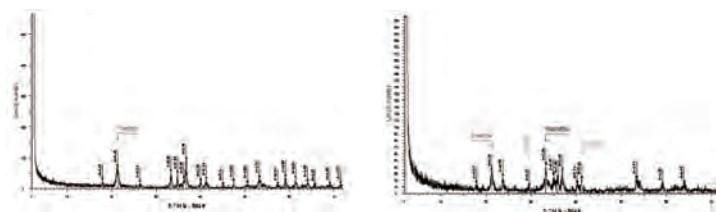


Figure 2 XRD patterns of goethite (A) and hematite (B) particles synthesized from AMD.

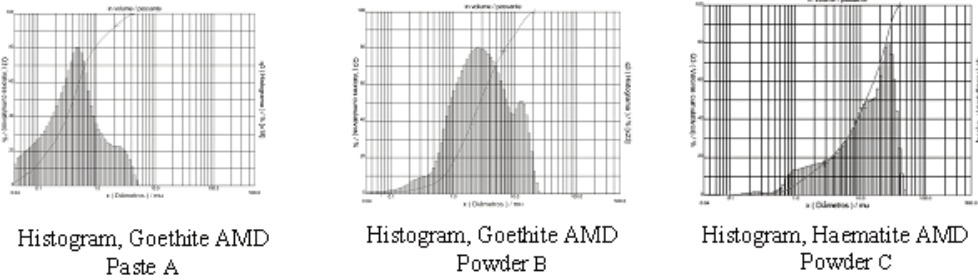


Figure 3 Particle size distribution of goethite as a paste (A), goethite as a powder, and (B) hematite as a powder (C).

Goethite Powder/Paste	Goethite DAM Po Goethite DAM Pasta	
	Powder	Paste
L*	89.5	89.9
a*	-0.4	-0.4
b*	27.8	27.5

Haematita Powder



Haematita Powder	Powder
	L*
a*	5,1
b*	41,8

Table 3 Colorimetric results of the paint produced with goethite (prepared as a powder and prepared as a paste) and concrete block produced with hematite (powder).

goethite particles prepared as a paste. It can be seen that the particles had a rather narrow size distribution, and the size of most goethite particles was in the range of 0.08 to 1.74 µm ($D_{50} = 0.41 \mu\text{m}$). Fig. 3B presents the particle size analysis of the goethite particles dried at 60 °C. In the previous case, the goethite particles agglomerated into clusters during the drying process, and the size of most goethite particles was in the range of 0.73 to 12.23 µm ($D_{50} = 4.37 \mu\text{m}$). Agglomeration while drying creates a problem in several particle systems (i.e. application as pigment for paint production). It is an advantage that drying of the particles is not necessary in the potential application of goethite particles for paint production. Fig. 3C presents the size analysis of the hematite. The size of most hematite particles was in the range of 1.56 and 29.43 µm ($D_{50} = 14.23 \mu\text{m}$).

The goethite particles prepared as a paste as well as those prepared as a powder were used for producing a yellow paint. It was observed that the paint prepared with the goethite as a paste showed satisfactory results whereas the paint prepared with the goethite as powder showed problems related to the dispersion of the goethite particles. The hematite particles were used to pro-

duce a colored concrete block. The colorimetric parameters are presented in Tab. 3

Conclusion

Iron was recovered from AMD treatment using a selective precipitation process based on the solubility characteristics of the iron hydroxide which can become an alternative source of iron with high purity. The process for production of the pigments goethite and hematite was successfully performed. The pigments can be potentially applied in paints and colored concretes.

Acknowledgments

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