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The preparation of magnetite, goethite, hematite and maghemite of pigment quality from mill scale iron waste

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Abstract

Mill scale iron waste has been used to prepare some iron oxide pigments via specific precursors. Magnetite and goethite were precipitated from their respective precursors in aqueous media. Various red shades of hematite were prepared by the calcinations of the precipitated goethite at temperatures ranging from 600 to 900 °C. Maghemite was obtained by thermal treatment of magnetite at 200 °C. The iron oxides were characterized by Raman spectroscopy, X-ray diffraction (XRD), surface area determination and scanning electron microscopy (SEM). They are generally composed of very small particles (mainly <0.1 μm) with high surface area. These particle properties suggest that the above pigments (prepared from mill scale) will show high tinting strength, quality hiding power and good oil absorption. Oil absorption is a property of the pigment that is closely related to the ease of dispersion.

Keywords: Mill scale; Raman; Iron oxides; Pigments; Precipitation

1. Introduction

Stainless steel finishing operations involve several cleaning processes, which eliminate dust, scale and metallic oxides [1]. Mill scale is a steel making by-product from steel hot rolling processes and is basically composed of iron oxides and metallic iron with variable oil and grease contents [2,3]. Its specific production is about 35–40 kg/t of hot rolled product [2]. The oil component in rolling mill scale makes the recycling difficult, and its direct re-use in sintering may lead to environmental pollution. Mill scale with high oil content is recycled after extracting the oil in a pretreatment stage. Coarse scale with a particle size of 0.5–5 mm and oil content of less than 1% can be returned to the sinter strand without any pretreatment. High oil content (>3%) results in increased emission of volatile organic compounds including dioxins and can lead to problems in waste gas purification systems, e.g. glow fires in electrostatic precipitators. Because of this mill scale needs to be pretreated before it can be re-used. Fine sludge mainly consists of very small-scale particles (0.1 mm). Since the fine particles adsorb oil to a very high degree (5–20%) this scale normally cannot be returned to the sinter strand without pretreatment [4]. The oil adsorption in the preceding line refers to the metallic mill scale and should not be confused with the oil absorption, pigment property, mentioned in the abstract and elsewhere in this paper. At MITTAL (former ISCOR), a steel manufacturing company in the Republic of South Africa, the bulk of mill scale waste is dumped in landfills. The continuous demand for more landfills and the leaching of some small percentages of heavy metals into soil and ground water, thus threatening the environment, highlight the need for more effective methods of waste disposal and productive utilisation of mill scale.

Production of iron oxide pigments is one of the possible ways of alleviating the problem facing the steel industry in RSA since mill scale has a high iron content in the form of oxides and metal. The use of iron waste in iron oxide preparations is vital because of the increasing demand for iron

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oxide pigments driven by the increases in construction activities, current economic needs [5] in emerging markets and growing concern over the use of heavy metal-based pigments. The increasing importance of iron oxide pigments is also based on their non-toxicity, chemical stability, durability [6], wide variety of colours and low costs.

There are many studies in the literature that deal with different methods for the preparation of magnetite [7–11], hematite [12–15], maghemite [16–20] and goethite [21–23]. These are the iron oxides commonly used as pigments giving black, red, brown and yellow colours, respectively. Steel pickling chemical waste (SPW) has been thermally decomposed at various temperatures to give red iron oxide (hematite) [9,24,25]. The formation of mill scale (mainly FeO and Fe) can also be accompanied by the precipitation of corrosion product mixture, viz. Fe_3O_4, FeOOH, Fe_2O_3, etc. [26]. FeO is usually closest to the metal surface while Fe_2O_3 forms the outer layer [27]. Since corrosion products occur in a mixture and the overall mill scale is hardened and of poor colour, it is not of pigment value. Oulsnam and Erasmus [28] have succeeded in preparing magnetite from ferrous mill scale using a dry oxidation step. However, the particles of their product were too large and had to be ground (wet and dry) to $<10\ \mu m$ to improve the pigment qualities (colour, tinting strength, hiding power and oil absorption) [24,25]. Hematite was prepared by calcination of the obtained magnetite and its particles also had to be ground to sizes $< 10\ \mu m$.

The present study was undertaken with the aim of preparing magnetite and goethite of pigment particle size $< 10\ \mu m$ via water-soluble mill scale-derived precursors. Furthermore, maghemite and hematite could then be prepared by thermal treatment of the obtained magnetite and goethite, respectively.

2. Experimental

2.1. Chemical preparation

2.1.1. Ferrous precursor

Conc. H_2SO_4 (analytical reagent, 300 ml) was added to 60 g of raw mill scale in a 600 ml glass beaker. The mixture when heated on a hot plate became turbid. The turbid mixture was further heated to dryness. The resulting muddy solid product was then used as the starting material for the preparation of magnetite and goethite. Preliminary investigations showed that the product was soluble in water (more readily in warm water) and a dark blue/green flaky sediment resulted when the aqueous solution was mixed with a base (e.g. NH_4OH or NaOH). This chemical behaviour is characteristic of the presence of $Fe(OH)_2$ in solution [21]. It indicates that the greater part of iron in the muddy solid product is in the Fe^{2+} form. The acidic environment was created in order to facilitate the conversion of iron oxides to ferrous or ferric ions in an aqueous solution [29].

2.1.2. Ferric precursor

Conc. H_2SO_4 (300 ml) was mixed with 30 g of raw mill scale in a 600 ml glass beaker. The mixture was then heated to dryness on a hot plate. The product, containing a fine white powder and dark solid particles, was cooled to room temperature and allowed to stand in open air for five days. During this time the product gradually turned into a yellowish fine white powder. No darker areas were observed. The fine powder was soluble in warm water and formed rust coloured sediment when a base, e.g. NH_4OH or NaOH, was added to its aqueous solution. This chemical behaviour is characteristic of the presence of $Fe(OH)_3$ [21]. Therefore, the greater part of iron in the fine yellowish white powder was in the form of Fe^{3+} [29].

Alternatively, 60 g of mill scale in 200 ml of conc. H_2SO_4 was digested on a hot plate at 100 °C for 30 min followed by the addition of 200 ml of 65% HNO_3. Further heating resulted in a cream white homogeneous solid substance, which was then heated to dryness. The cream white solid contained iron mainly in the Fe^{3+} form.

2.1.3. Magnetite (Fe_3O_4)

Magnetite was prepared by the method of Ueda et al. [8] with some modifications. Ferrous precursor (10 g) was dissolved in 120 ml of distilled water. To the filtered solution 130 ml of 25% NH_4OH solution was added, thus raising the pH to about 11–12. After ageing at room temperature for 20 h, the precipitate formed was collected by filtering. The precipitate was washed with 500 ml of distilled water and allowed to dry at room temperature. The black, magnetite product was qualitatively examined by Raman spectroscopy and confirmed by X-ray powder diffraction (XRD).

2.1.4. Maghemite (γ-Fe_2O_3)

The magnetite obtained above (Section 2.1.3) was heated in an oven at 200 °C for 3 h during which it turned light brown [30]. This product was identified by Raman spectroscopy and confirmed by XRD results to be maghemite.

2.1.5. Goethite (α-FeOOH)

This iron oxide polymorph was prepared using the method of Thiebeau et al. [23] with some modifications. Ferric precursor (20 g) was dissolved in 500 ml of distilled water. To the filtered solution 100 ml of 1 M $NaHCO_3$ solution was added which brought the pH to values between 5 and 7. The solution was held at 100 °C for 1 h and allowed to cool to room temperature. The resulting yellow precipitate was filtered off and washed with 300 ml of distilled water and allowed to dry in air. The product was identified by Raman spectroscopy and confirmed by XRD as goethite.

2.1.6. Hematite (α-Fe_2O_3)

The goethite obtained above, in Section 2.1.5, was calcined in the furnace at temperatures between 600 and 900 °C for 5 h. The colour of the resulting products gave the following shades of red as the temperature increased: orange-brown, brown-red, bright-red, maroon, purple and gray. The phase determination was carried out using Raman spectroscopy and XRD showed that the product was hematite.

The product particle characteristics (namely sizes, shapes and specific surface areas) were determined using scanning