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The surface state of hematite and its wetting characteristics

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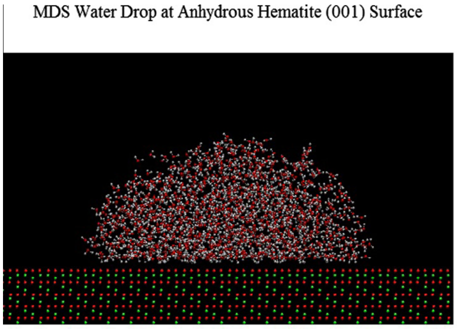
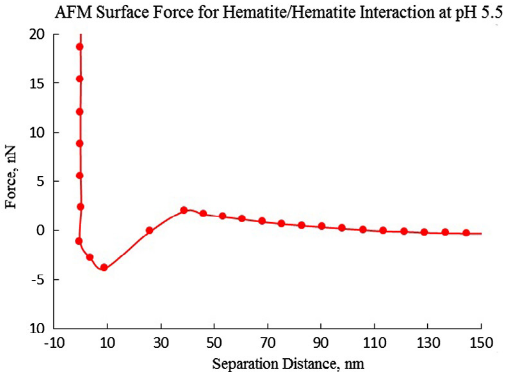
GRAPHICAL ABSTRACT


MDS Water Drop at Anhydrous Hematite (001) Surface


AFM Surface Force for Hematite/Hematite Interaction at pH 5.5

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ABSTRACT

Apart from being a resource for iron/steel production, the iron oxide minerals, goethite and hematite, are used in the paint, cosmetics, and other industries as pigments. Surface characteristics of these minerals have been studied extensively both in resource recovery by flotation and in the preparation of colloidal dispersions. In this current research, the wetting characteristics of goethite (FeOOH) and hematite (Fe_2O_3) have been analyzed by means of contact angle, bubble attachment time, and Atomic Force Microscopy (AFM) measurements as well as by Molecular Dynamics Simulation (MDS). Goethite is naturally hydroxylated and wetted by water at all pH values. In contrast, the anhydrous hematite surface (001) was found to be slightly hydrophobic at natural pH values with a contact angle of about 50°. At alkaline pH hydroxylation of the hematite surface occurs rapidly and the hematite becomes hydrophilic. The wetting characteristics of the hematite surface then vary between the hydrophobic anhydrous hematite and the completely hydrophilic hydroxylated hematite, similar to goethite. The hydrophobicity can be restored by heating of the hydroxylated hematite surface at 60 °C. The hydrophobic character of the anhydrous hematite (001) surface is confirmed by MDS which also reveals that after hydrolysis the hematite (001) surface can be wetted by water, similar to the goethite (001) surface.

1. Introduction

Iron oxide minerals are among the most abundant minerals in the earth's crust. Commonly available iron oxide minerals are magnetite (Fe_3O_4), hematite (Fe_2O_3), goethite (FeOOH), limonite

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($FeOOH \cdot nH_2O$) and siderite ($FeCO_3$). Magnetic separation is most frequently used for the processing of iron ores containing magnetite. However, flotation is used for most hematite/goethite ores requiring concentration to satisfy specifications for pelletization. Reverse flotation of silica from hematite is by far the most common route for the processing of iron ore containing silica gangue [1]. In reverse flotation of iron ore, quartz, the major impurity, is floated using ether amines and the iron oxide minerals are depressed, typically using polysaccharides such as starch, with the process carried out at pH 10.5. It is usually effective for feed varying from 10 μm to 150 μm in particle size. In Brazil more than 300 million tons of iron ore concentrate production per annum is achieved using polysaccharides in the reverse flotation process to remove silica gangue, while in the US the production is about 40 million tons annually.

According to authors' best knowledge, measurement of captive bubble contact angles for a natural hematite crystal have not been reported, but contact angle measurements on iron ore samples containing varying amounts of hematite, goethite, clay and quartz have been reported using the capillary method [2]. Even the effect of pH on the wettability of hematite and goethite has not been reported in the literature. Hydroxylation of the hematite surface at alkaline pH values has not been reported either, though it is reported that goethite is the thermodynamically stable form of ferric oxide in water [3].

In the present work, contact angle measurements were performed at different pH values for hematite and goethite to reveal the effect of pH on wettability. Molecular Dynamics Simulation (MDS) has been used to determine water sessile drop contact angles at various mineral surfaces [4] and was used in this research to determine contact angles for hematite, goethite and hydroxylated hematite surfaces. These contact angle measurements for hematite were complemented by bubble attachment time measurements. Atomic Force Microscopy (AFM) has been used extensively for surface force measurements [5–14], and in this work the wettability of hematite was also examined with in-situ surface force measurements at the hematite surface for different pH values. In these surface force measurements hematite particles were used as a colloidal probe and surface forces were measured between the hematite colloidal probe and the 001 hematite surface. This method is being reported for the first time.

Due to the marked increase in computational capabilities in recent years, MDS can be used to explore water/mineral interactions at the molecular-level [15,16]. Compared to quantum mechanical calculations, MDS has a greater capacity for studying a system with a large number of atoms. Because of this remarkable ability to simulate large systems, the contact angle of water nanodrops at solid surfaces can be determined by MDS [17]. In this study, MDS contact angles of the hematite (001) surface, the hydroxylated hematite (001) surface, and the goethite (001) surface were determined and the results compared to the experimental measurements.

The significance of the results is important in the understanding of existing flotation processes and in the design of new flotation separations [18]. In addition to the significance of these findings in the field of flotation chemistry, the results being reported are important to the pigment industry, since dispersion of hematite pigments will be influenced significantly by the wetting characteristics of hematite. Pigment powders used in the paint industry have to be properly dispersed in the aqueous solution, as dispersion of the suspension determines the quality of the paint. The final paint should be stable on storage and should not agglomerate or aggregate. Other applications include the preparation of composites and cosmetic products.

2. Experimental

2.1. Minerals and reagents

The specular hematite crystals for contact angle measurements and AFM surface force measurements were obtained from "The Iron Quadrangle," Brazil. The quality of the high purity single crystals was confirmed by XRD and EDAX analysis. Presence of peaks at 2θ angles of 84.48° and 39.26° signify that the crystal surface represents the (001) plane of hematite as described in the literature [19]. The (001) crystal surface of hematite was polished with a nylon polishing cloth purchased from Buehler using a DiaDuo-2 water based 1-μm diamond suspension obtained from Struers (Ballerup, Denmark). Natural smooth crystals obtained from the same source were used for AFM force measurements. The rms roughness of the 001 crystal surface used for force measurements was found to be around 2.69 nm.

Pulverized hematite samples used for bubble attachment time measurements were obtained from Orrisa, India, and the particle size used for bubble attachment time measurements was 106×75 μm.

Samples for zeta potential measurements were obtained by crushing and pulverizing the Brazilian crystals and the particle size used was minus 65 μm. Dry as well as wet screening was done to obtain the samples of 106×75 μm for bubble attachment time measurements and minus 65 μm for zeta potential measurements.

The goethite "needle ore" crystal sample used for contact angle measurements was obtained from Cary Mine, Ironwood, Gogebic County, Michigan. The crystal was polished by the same method used for hematite. The ground goethite samples for bubble attachment time measurements and zeta potential measurements were obtained by crushing and pulverization. The quality of the crystals was confirmed by XRD and EDAX analysis.

Sodium hydroxide (NaOH) and hydrochloric acid (HCl) obtained from Sigma-Aldrich were used to adjust the pH. Potassium chloride (KCl), also obtained from Sigma-Aldrich, was used as the electrolyte background in force measurements. DI water was obtained from a Millipore system in the laboratory with specific conductance of 18 MΩ cm.

2.2. Captive bubble contact angle

Both hematite and goethite samples were cleaned with acetone, ethanol, ample amounts of DI water and dried with ultra-pure nitrogen before measurements. The hematite sample was oven dried at 60 °C for 25 min and then cooled for half an hour open to the atmosphere before each contact angle measurement. The distance between the needle and the sample was kept constant for each captive bubble contact angle measurement. All the measurements were done in 0.001 M KCl solution and pH was adjusted by adding the desired amount of HCl or NaOH solution. Before every contact angle measurement, the sample was conditioned in respective pH solutions for 15 min and measurement was done in the same solution. At least 20 contact angle measurements were obtained for each pH at different locations and they were averaged to obtain the reported contact angle value for each pH. Variation in contact angle measurements was ±10°.

2.3. Bubble attachment time measurements

Bubble attachment time measurements were done using an MCT 100 electronic induction timer instrument. The particle bed was prepared in a cuvette of 1 cm × 1 cm × 2 cm and the particles were conditioned for 20 min in the same vial before taking each