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Modelling the two-dimensional growth and oriented attachment of goethite nanorods synthesized via oxidation of aqueous ferrous hydroxide slurries

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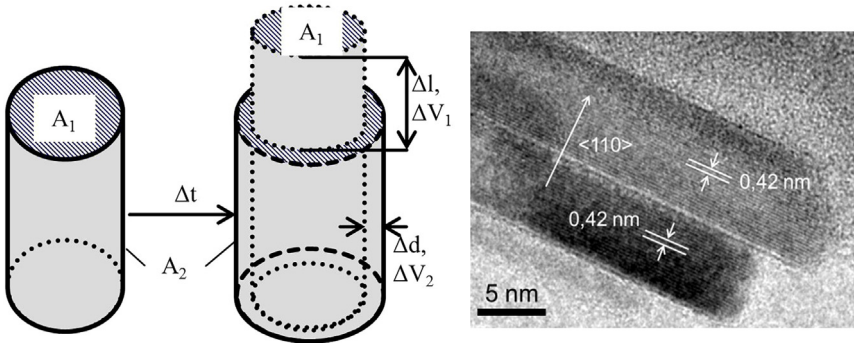
HIGHLIGHTS

- The 2D α-FeOOH crystal growth including aggregation by oriented attachment is modeled.
- O_2 mass transfer limits reaction rate in oxidation of ferrous hydroxide slurries.
- Oxidation of Fe(II) to Fe(III) occurs at constant rate.
- Excellent prediction of size and shape for various process conditions is obtained.

GRAPHICAL ABSTRACT



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ABSTRACT

Iron oxides and iron oxyhydroxides find wide applications as magnetic materials, adsorbents for wastewater treatment and pigments. This study addresses the formation of anisotropic α-FeOOH (goethite) nanorods during air oxidation of ferrous hydroxide slurries. The effects of concentration and aeration rate on reaction kinetics and particle size and shape have been studied. It could be shown that the gas-to-liquid oxygen mass transfer is the rate determining step for the reaction. We derive a rate equation for goethite formation which is coupled to a two-dimensional growth model. Aggregation is considered with an oriented attachment model based on Brownian motion of the nanorods. Simulated and experimental results agree very well for both the length and width distributions of the particles. In particular, the new model provides a predictive tool to study the effect of process conditions on the evolution of particle size and shape.

1. Introduction

Iron oxides belong to the most abundant minerals in nature and are of great importance for several industrial applications. The many existing different iron oxide and oxyhydroxide phases are typically synthesized by various wet chemical methods such as precipitation, electro-deposition, surfactant mediation etc. [1,2]. The α-FeOOH phase (goethite) is, for instance, applied in wastewater treatment as adsorbent for heavy metal ions and organic matter [3–5], as a visible-light-responsive photocatalyst [6] or as a pigment [7–9]. Synthetic goethite typically consists of acicular nanocrystals which are often bundled together in oriented aggregates [10]. Adjusting the size and shape of these nanoparticulate systems is essential to obtain the desired physical properties for the respective applications.

Goethite can either be synthesized from Fe(III) salts such as nitrates with ferrihydrite as metastable intermediate phase [11,12] or by

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oxidation of aqueous solutions/suspensions containing Fe(II) in gas-liquid-solid reactors [13]. The latter is the commonly applied process in industry [1] and therefore the focus of this work. Oxidation is typically achieved by bubbling air or pure oxygen through the suspensions. In several studies the impact of process parameters such as pH, reactant concentrations and aeration rate on goethite formation rate and particle size and shape was investigated. For neutral to slightly alkaline suspensions the reaction rate strongly depends on the pH, while in highly alkaline media the rate increases and is mostly determined by the oxygen transfer rate whereas the pH has only a small influence [14–18]. Olowe et al. described an increasing particle size with increasing iron concentration [19], whereas O'Connor et al. observed smaller particles for increasing reaction rates [20]. In addition to the reaction rate, aggregation by an oriented attachment (OA) mechanism can have an important impact on particle size and shape. It has been demonstrated that the growth of acicular goethite particles occurs by OA of goethite nanodots [10,21,22]. This process requires a preliminary phase transformation from ferrihydrate to goethite nanodots and is strongly influenced by the ionic strength [23] and the pH of the medium [24]. Yang et al. observed the presence of multi-twinned structures by high resolution transmission electron microscopy (HRTEM) supporting a side-by-side growth mechanism [22]. Vu et al. [25] and Burleson et al. [10] propose empirical growth equations based on OA kinetics. However, they use only one equivalent size parameter in their models. The development of a model containing two independent size parameters such as length and diameter is required for a more accurate description of both size and shape evolution and the prediction of the final particle properties. To the best of our knowledge such a model has not been reported so far.

In this work, we present a two-dimensional growth and aggregation model to predict the influence of the aeration rate and iron concentration on the size and shape evolution during goethite nanorod formation. Controlling these particle properties is of great importance, for instance for the application of goethite as a pigment, as particle size, shape and aggregation strongly influence the color effect and opacity of paint films [1]. The model builds upon the results of our previous study [26] where the synthesis of goethite particles by air oxidation of ferrous hydroxide suspensions at alkaline pH was studied. There, a notable influence of the aeration rate on the particle morphology was observed and an epitaxial growth mechanism of goethite on the edges of hexagonal $Fe(OH)_2$ intermediate nanoplatelets was ascertained. In the present work an analytical equation for the goethite formation rate is derived as a function of the aeration rate and used to model the anisotropic growth, whereas aggregation of the particles is considered with an OA model. The presented model predicts the effect of different process parameters on particle length, diameter and their respective distribution widths. Thus, it provides a better understanding of goethite nanorod formation through the underlying three-phase process and allows controlling and predicting the physical properties of the particles. The developed model is integrated in a generally applicable solver which can readily be transferred to other materials that follow similar anisotropic growth processes.

2. Material and methods

2.1. Chemicals

Chemicals of high purity grade have been used without any further purification. Sodium hydroxide (purity > 99.0%) was purchased from Carl Roth, and iron(II)sulfate heptahydrate (purity > 99.0%) was a Sigma Aldrich product. Ultrapure water (18.2 mΩ resistivity) was deoxygenated by bubbling N_2 (Linde, 5.0). For the oxidation, synthetic air (Linde) was used as oxygen source.

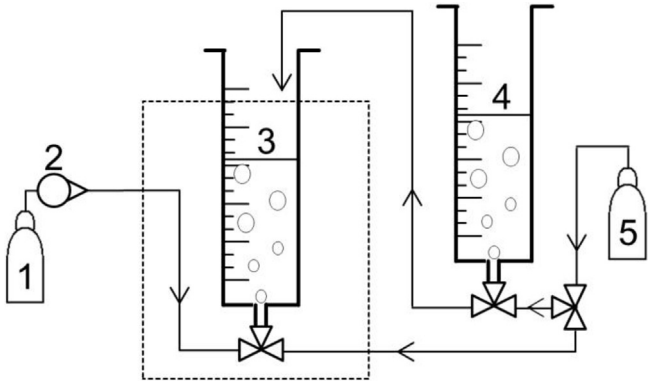

Fig. 1. Reaction setup: 1) synthetic air supply, 2) rotameter, 3) reactor syringe with $FeSO_4$, 4) syringe with NaOH (prior to mixing), 5) nitrogen supply; parts inside dashed lines are mounted inside water bath for temperature control.

2.2. Experimental setup

As reaction vessel, a 50 ml glass syringe (Luer Lock) was used. The syringe was installed vertically inside a water bath to keep the reaction temperature constant at 35 °C. To aerate the suspensions the respective gas was bubbled into the suspension through a three-way valve at the outlet of the syringe (see Fig. 1). The gas flow rates were controlled with a rotameter. To enhance the mixing effect of the bubbles the suspensions were additionally stirred with a magnetic stir bar.

2.3. Particle synthesis

Goethite samples were produced in two consecutive reaction steps. In a typical synthesis, an iron sulfate solution was mixed with a sodium hydroxide solution under constant bubbling with N_2 resulting in a white precipitate which can be attributed to the intermediate $Fe(OH)_2$ nanoplatelets. Both solutions were deoxygenated prior to mixing by bubbling N_2 through them until the oxygen sensor confirmed that no more dissolved oxygen was present. In the second step, the suspension was oxidized by bubbling synthetic air with rates between 50 and 500 ml/min. Iron concentrations in the mixed suspensions were varied between 0.075 and 0.225 mol/l while the NaOH concentration was adjusted so that the ratio $[OH^-]/[Fe]$ was always equal to 10. After the reactions, each sample was centrifuged, washed three times with ultrapure water and finally dried in an oven overnight at 60 °C. Finally, the dry solids were crushed to a fine powder with a mortar.

2.4. Analysis and characterization

For in situ reaction monitoring dip probes connected to a multichannel Mettler Toledo transmitter unit (M800) for either the oxygen concentration (LnPro6860i/12/420) or the pH (lnPro4260i/SG/425 pH/redox) were used. X-ray diffraction (XRD) patterns were measured from the dry powders with a D8 Advance (Bruker AXS GmbH, Germany) diffractometer using Cu Kα radiation in Bragg-Brentano geometry. Crystallite sizes were estimated with the Scherrer equation based on the (1 1 0) reflection around 21.1°. For size and shape analysis of the particles, images were taken by scanning electron microscopy (SEM) using an ULTRA 55 instrument (Carl Zeiss AG) at a voltage of 10 keV. Dilute suspensions of the received powders in water were sonicated for several minutes and deposited on Si/SiO_2 substrates via spin coating. For each sample, the length and width of at least 100 particles was determined using the software ImageJ to obtain a representative particle size and shape distribution. Transmission electron microscopy (TEM) analysis was performed using a CM 300 Ultra Twin microscope (Philips/FEI Company) with the particles being deposited onto standard copper grids.