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Surface complex characteristics of synthetic maghemite and hematite in aqueous suspensions

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Abstract

The acid–base properties of the maghemite (γ-Fe_2O_3)/water and hematite (α-Fe_2O_3)/water interfaces have been studied by means of high precision potentiometric titrations and the experimental results are evaluated as surface complexation reactions. Synthetic maghemite and hematite were prepared and characterized using a combination of SEM, FT-IR and XRD. The specific surface area of the minerals was determined by the BET method. The titrations were performed at $25.0 \pm 0.2\,^{\circ}\mathrm{C}$ within the range $2.8 < \mathrm{pH} < 8.5$, $NaNO_3$ ionic medium giving total ionic strengths of 0.10 and 0.50 $\mathrm{mol\,dm^{-3}}$ in both systems. Experimental data were evaluated using the constant capacitance model. The total proton exchange capacities of the solids were determined by saturation of the surfaces with excess acid. The number of protonated surface sites per nm^2 was found to be 0.81 ± 0.05 and 1.03 ± 0.04 for maghemite, at $I = 0.10$ and $0.50\ \mathrm{mol\,dm^{-3}}$, respectively. The IEP for maghemite was determined from the ζ-potential using a Zetasizer 4 instrument.

Keywords: Maghemite; Hematite; Characterization; Potentiometric titrations; Surface complex modeling; Constant capacitance

1. Introduction

Magnetite (Fe_3O_4) is the main iron mineral in the ore deposits in the northernmost part of Sweden (LKAB, Kiruna). The ore is essentially free from impurities with the exception of some percent of gangue minerals, including apatite. Phosphorous, originating from the apatite is detrimental for most steel processes used today. It is therefore of great interest to achieve optimal conditions for the separation of apatite from magnetite as well as its oxidation products. The separation process involves comminution followed by magnetic separation and/or flotation, which gradually have evolved to a high level of efficiency. At the molecular level, however, many questions remain, such as the identity of the surface groups that are active in the flotation process and the stability of the surface species formed by the added flotation reagents.

This work forms a first step in an effort to model flotation systems including the oxidation products of magnetite, together with apatite and flotation reagents. The models used are based on the concept of surface complexation, involving the formation of surface complexes with charge-dependent formation constants. Surface complexation models provide an analogy to aqueous complexation by describing sorption processes as the formation of surface complexes [1]. In this work the constant capacitance model (CCM) has been used [2]. This is due to its capability to produce model systems at high and fixed ionic strengths, using few adjustable parameters. The aim of this study is to characterize the acid–base properties for aqueous suspensions of maghemite (γ-Fe_2O_3) and hematite (α-Fe_2O_3), which both are probable oxidation products of magnetite.

The acid–base characteristics of hematite have been studied in some recent publications [3,4] in which mineral surface areas between 6 and 19 $\mathrm{m^2\,g^{-1}}$ have been used and the experimental data were evaluated using the constant capacitance model. Maghemite has not been studied to the same

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extent. An earlier work [5] is found in which the triple-layer site-binding model was used to evaluate the experimental data. Synthetic maghemite samples with surface areas from 48.5 to 65.1 $m^2\,g^{-1}$ were studied having pH_{PZC} close to 6.6 in KNO_3, at the ionic strengths 0.1, 0.01 and 0.001 $mol\,dm^{-3}$.

To achieve products with large surface areas combined with a minimum of impurities, synthetically prepared maghemite and hematite were used in the present study.

2. Materials and methods

2.1. Maghemite

Synthetic maghemite was prepared according to Garcel et al. [5] and Marsart et al. [6] with a few modifications. 3.28 g $FeCl_2 \cdot 4H_2O$ and 8.92 g $FeCl_3 \cdot 6H_2O$ were dissolved in 50.0 ml MilliQ water to get a solution with the concentrations 0.33 $mol\,dm^{-3}$ Fe(II) and 0.66 $mol\,dm^{-3}$ Fe(III), respectively. A 1.0 $mol\,dm^{-3}$ NH_3 solution was prepared by diluting 33.7 ml of NH_3 (25%) to 450 ml, using degassed MilliQ water. This solution was then bubbled with N_2(g) for approximately 10 min to minimize the content of dissolved gases like oxygen and carbon dioxide. All chemicals were of pro analysis grade quality. The iron chloride solution was slowly added (taking approximately 5 min) to the NH_3 solution under continuous stirring and a black precipitate was immediately formed. When the precipitate had settled, the supernatant was decanted and replaced with fresh MilliQ filtrated water. The precipitate was stirred for a few minutes and then allowed to settle again. This washing procedure was repeated until the supernatant remained turbid. The suspension was then poured into dialysis tubes (spectrum spectra/por with MVCO 12-14000 D, 29 mm diameter). Dialysis was performed until the conductivity reached a stable value, about 1.7 $\mu S\,cm^{-1}$. The dialyzed synthesis product was then poured into crystallization beakers and allowed to dry overnight at 60 °C. After drying, the solid product was ground manually in a mortar to release the fine particles formed during the synthesis. The formed powder was then heated in an oven at 240 °C overnight to be oxidized in air to maghemite. After cooling, the final synthesis product was stored in a desiccator containing silica gel as a drying agent.

The synthetic maghemite was characterized with FT-IR using a Perkin–Elmer System 2000 FT-IR instrument (Fig. 1). The analysis was performed as DRIFT (diffuse reflectance infrared Fourier transform) measurements by mixing 0.2–0.3 mg maghemite together with 350 mg KBr. The resolution was set to ±4 cm^{-1}. The FT-IR spectra show good agreement with those presented in earlier published work [7,8]. Two broad bands with shoulders at 724, 694, 638, 584, 558, 442 and 396 cm^{-1} are characteristic for well-ordered maghemite [7]. The ν_1 band (580 cm^{-1}) is assigned to Fe–O deformation in the octahedral and tetrahedral sites, and the ν_2 band (420 cm^{-1}) to Fe–O deformation in the octahedral sites [8].

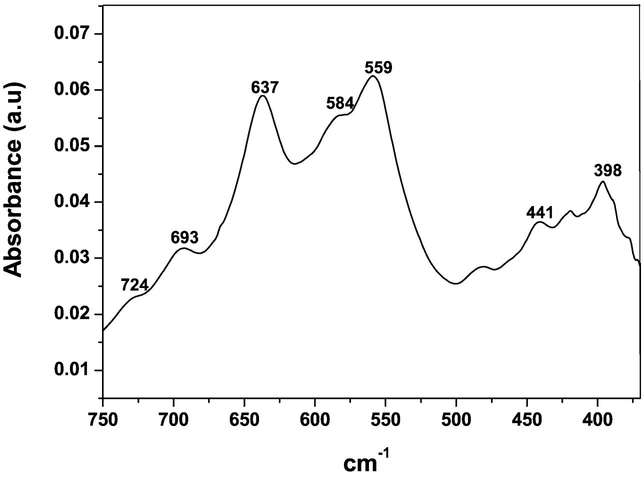

Fig. 1. FT-IR spectra of synthetic maghemite.

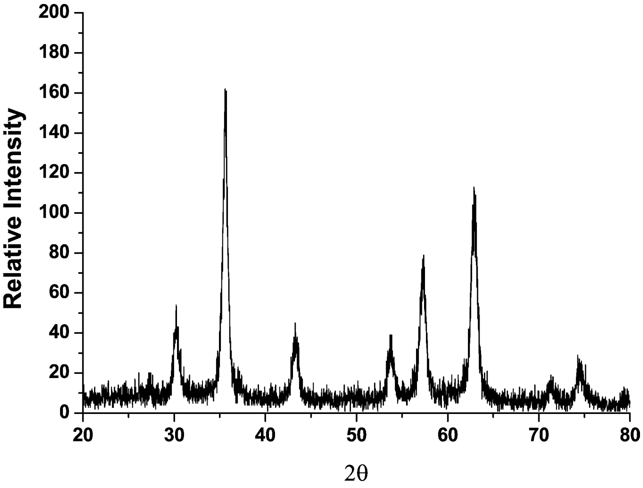

Fig. 2. XRD diffractogram of synthetic maghemite.

Further characterization, using XRD, were performed with a Siemens D5000 X-ray diffractometer (Fig. 2). The XRD diffraction pattern shows good agreement with the diffractograms presented in earlier publications [7–9]. The peak pattern is almost identical with the corresponding magnetite diffractograms, but the peaks are shifted to lower angles for magnetite [9].

The morphology and particle shapes were characterized using SEM (Fig. 3). Obviously the particles are approximately spherical. From a SEM image of the synthesized maghemite, a rough estimation of the particle diameters was performed. A calibration was made with reference to the scale on the SEM image and then the diameters of 20 randomly chosen particles were measured on the SEM image. The average diameter was found to be 32 ± 11 nm. The specific surface area was determined by the BET method (N_2 adsorption) [10] to 89.7 ± 6.3 $m^2\,g^{-1}$.