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Production of magnetite by electrolytic reduction of ferric oxyhydroxide

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ABSTRACT

Magnetite (Fe_3O_4) particles were prepared by electrolytic synthesis without the use of a surfactant. Various techniques were used to evaluate the effect of two parameters, the current density and the separation between electrodes, in the formation process of ferrimagnetic magnetite particles. The crystallite sizes can be controlled by adjusting the current density. Particle formation was favored below a critical separation distance between the electrodes. Finally, a formation mechanism for magnetite was proposed based on the partial reduction of lepidocrocite.

1. Introduction

Magnetite is a divalent iron oxide with the spinel structure that is of great scientific and industrial interest [1]. Its electrical, chemical, magnetic and optical properties make it a suitable material for numerous technological applications (*e.g.*, industrial processes, environmental applications, and medical use) [2–5]. Because magnetite is naturally found in the form of an iron mineral that contains a number of impurities, including nonmagnetic forms of iron, it must be processed to obtain a greater degree of purity to be suitable for diverse applications [6].

Artificial methods to produce magnetite with higher purity (*e.g.*, chemical coprecipitation, the sol–gel process, hydrothermal synthesis, and the decomposition of organometallics) are limited by economic, environmental and safety constraints [7–9]. Therefore, alternative production methods, such as electrolytic synthesis, have been sought. This technique enables the production of magnetite from iron cations obtained from carbon–steel electrodes, and it produces particles with a large surface area, a narrow particle size distribution and high purity [10–15].

The electrolytic production of magnetite is still a subject of investigation, and knowledge gaps exist regarding the physicochemical, electrochemical and surface phenomena involved in this process. Consequently, a complete and detailed mechanism that can provide greater understanding and control of the process has not been defined [13].

The effect of parameters such as the iron concentration in solution, pH, proportion of Fe^{2+} and Fe^{3+} cations, current density, temperature, nature of the electrolytes present and distance between the electrodes is still unknown. As a result, it is difficult to exercise total, or even partial, control over the production of these particles, which would enable realization of the desired characteristics [16].

The lack of phenomenological knowledge of the process arises from the inherent complexity of the iron chemistry. Specifically, two complicating factors exist: the existence of two stable oxidation states within a wide range of pH, and the multiplicity of reactions that iron complexes can undergo [17,18].

Although studies have explored and discussed the effects of certain variables in the electrolytic synthesis of magnetite, no conclusions have allowed greater control over the characteristics of the final product [11,13,16]. In the present study, the synthesis of magnetite was investigated, using an electrolytic method and studying the effect of the separation between the electrodes and the current density on the nature and size of the particles obtained. Finally, a formation mechanism was proposed.

2. Experimental

The reactor used in the magnetite synthesis consisted of a monopolar arrangement of carbon–steel electrodes (dimensions: 9.2 cm × 6.2 cm × 1 mm; ASTM A36), which was completely immersed in 1000 cm^3 of a 0.04 M NaCl solution in deionized water and under constant magnetic agitation (not shown in figure) at 150 rpm during the entire experiment, Fig. 1.

Current density was varied from 2 to 20 $mA\,cm^{-2}$ using an

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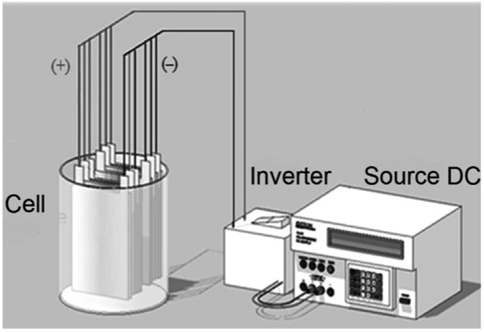

Fig. 1. Monopolar electrolytic cell.

EXTECH 382280 DC power source. All experiments were performed up to an electrical charge of 3000 C L^{-1}. The distance between the electrodes was varied from 0.3 to 8 cm. Room-temperature and room-pressure conditions were used in all experiments, and the products obtained were washed with distilled water and dried under the same conditions. The pH of the solution was monitored with an Orion 5 pH meter equipped with a glass electrode.

Structural characterization of the products was performed by X-ray diffraction using an X'Pert Pro PANalytical diffractometer. All measurements were performed at room temperature using Cu radiation ($\lambda_{K\alpha1} = 1.54056$ Å, $\lambda_{K\alpha2} = 1.54439$ Å) in a 2θ range of 15–90° at a step size of 1°/s. Analysis of the phases present in the samples was performed using the X'Pert High Score Plus software (PANalytical, Netherlands). Crystallographic analysis was performed by the Rietveld method using the computational package GSAS [19] and its graphic interface EXPGUI 3.0 [20].

The particle morphology and grain size were examined by scanning electron microscopy (SEM), using a JEOL JCM-6000 Benchtop scanning electron microscope. The samples were dispersed in alcohol and deposited onto a copper mesh (200 mesh) covered with carbon. The images were taken at a magnification of 96 kX and a voltage of 20 kV. Image analysis was performed by counting at least 1000 particles to obtain a representative statistical set.

The particle size distribution was determined by dynamic light scattering (DLS) using a Malvern Zetasizer S90 analyzer. The Stokes–Einstein equation [21] was used (Eq. (1)) to calculate the hydrodynamic diameter, d_H, of the particles from the values obtained of the translational diffusion coefficient, D:

$$d_H = \frac{\kappa T}{3\pi\eta D} \tag{1}$$

where κ is the Boltzmann constant, η the viscosity of the suspension medium and T is the absolute temperature of the measurement.

Mössbauer spectra were collected at room temperature (300 K) using a constant acceleration transmission spectrometer equipped with a source consisting of ^{57}Co incorporated into a Rh matrix. The isomeric shifts were reported relative to the centroids of the α-Fe spectrum at room temperature. The spectrum was fitted using the MOSFIT software [22].

IR spectra for lepidocrocite and magnetite samples were recorded on a JASCO FT/IR-4100, over the range 350–3000 cm^{-1}, using transmission mode and KBr pellet.

3. Results and discussion

3.1. Identification of phases

Under the conditions described above, a black precipitate was obtained, which was identified by X-ray diffraction as magnetite (black iron oxide, Fe_3O_4). Fig. 2 shows the diffraction patterns associated with magnetite for two representative samples. All samples obtained have characteristic diffraction peaks that are consistent with the magnetite standard pattern (Registry JCPDS number: 01-088-0315) [1].

This result was confirmed by Mössbauer spectroscopy. Fig. 3 shows the spectrum, which was analyzed using a model with two sextets (sextet 1: 57%; sextet 2: 43%) fitted to the experimental data, confirming the ferrimagnetic character of magnetite [23]. The first subspectrum presents a higher hyperfine magnetic field (48.5 T) associated with the tetrahedral sites occupied by the ferric and ferrous cations, and the second subspectrum presents a lower hyperfine field (45.9 T) assigned to octahedral sites occupied by ferrous cations. Values of 0.31 and 0.65 mm/s were obtained for the quadrupole splitting and isomeric shift, respectively, which are very similar to the magnetite bulk parameters of 48.8 T and 0.27 mm/s for tetrahedral sites and 45.7 T and 0.65 mm/s for octahedral sites [13,24].

4. Crystal and particle size

Rietveld refinement (pseudo-Voigt; $\chi^2 < 1.5$; $R(F^2) < 0.1$) of the X-ray patterns showed that all analyzed samples were cubic with space group Fd-3m, without the presence of additional phases. The crystallite size was estimated in the parallel and perpendicular directions to the growth anisotropy using the Scherrer equations [19]:

$$\phi_{\perp} = \frac{18,000k\lambda}{\pi L_x} \tag{2}$$

$$\phi_{\parallel} = \frac{18,000k\lambda}{\pi(L_x + ptec)} \tag{3}$$

where κ=0.9 is the Scherrer constant, λ=0.154056 nm is the wavelength of the Cu K$_{\alpha1}$ radiation, and L_x and $ptec$ are the isotropic and anisotropic Lorentzian broadenings, respectively, of the crystallite size [19]. For all samples analyzed, the ptec parameter was zero, which indicates that the crystallites were spherical.

Fig. 4 shows the dependence of the crystallite size on the current density used. At current densities between 10 and

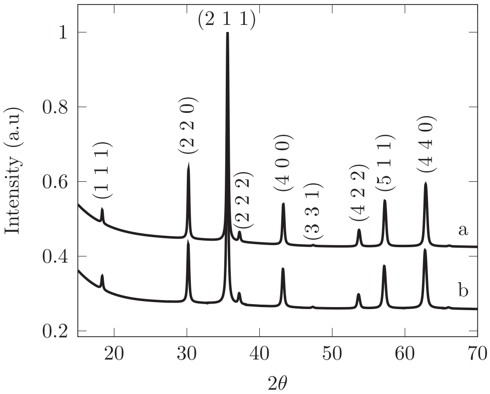

Fig. 2. XRD patterns of the particles obtained at 18 mA cm^{-2} and a distance between electrodes of (a) 0.3 cm and (b) 5 cm.