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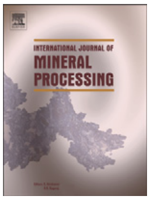

Acidic dissolution of hematite: Kinetic and thermodynamic investigations with oxalic acid

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ABSTRACT

Although extensively studied, consensus on the kinetics or thermodynamics of iron oxide dissolution has not yet been achieved among scientists. The aim of this study was to investigate the applicability of twelve different kinetic models in describing the dissolution of hematite (α-Fe_2O_3). In this study, hematite was dissolved in 0.6 mol/L oxalic acid at 50 °C to obtain kinetic data for modeling. In addition to the kinetic data, thermodynamic data were collected at 35 and 50 °C to discuss the dissolution mechanism. The Kabai equation and the first order rate law were found most suitable in describing the dissolution. The associated reaction rate constants were $2.0 \cdot 10^{-5}\ s^{-1}$ for both models.

1. Introduction

The dissolution of iron, *Fe*, from hematite has been described through various models. Cornell and Schwertmann (2003) have summarized 12 possible models describing dissolution reactions in general. In addition, a wide range of different experimental conditions have been covered in the dissolution of different Fe oxides. The kinetics of dissolution of hematite in oxalic acid have, however, not been presented by the authors.

Panias et al. (1996) have reviewed existing research and initially suggested a reaction mechanism for the dissolution of Fe oxides in organic acids. The mechanism comprises three processes: (1) adsorption of organic ligands from the solution to the solid Fe oxide surface, (2) non-reductive dissolution, and (3) reductive dissolution consisting of an induction and an autocatalytic period. The suggested mechanism indicates the participation of protons in the dissolution process. Although comprehensive in describing the reactions taking place during Fe oxide dissolution, pH was discussed only as a parameter affecting dissolution and, in this case, no additional experimental work was conducted to further verify the validity of the suggested reaction mechanism. The authors did conclude that non-reductive dissolution is not a viable reaction pathway at low temperatures.

Taxiarchou et al. (1997) investigated the dissolution kinetics of hematite in acidic oxalate solutions. The study indicated that the dissolution of Fe was significantly dependent on temperature and on the pH of the mother liqueur but was not affected by the oxalate concentration. The authors also concluded that increase in the solution acidity decreases the time necessary for the induction period, i.e. the lower the pH the shorter the induction period.

Lee et al. (2006) have studied the kinetics of dissolution of hematite in oxalic acid, too, and found that the dissolution was best described by a diffusion-controlled shrinking core model. The authors also concluded that the dissolution of Fe oxides in oxalic acid was very slow at temperatures of 25–60 °C and that, contrary to Taxiarchou et al. (1997), the dissolution of hematite could be correlated with the oxalate concentration of the mother liqueur. In addition, the authors found that the dissolution of hematite takes place through solid state reduction rather than a combination of non-reductive and reductive dissolution. Interestingly, signs of thermodynamic equilibrium were present in the data, as indicated by the steady state in the concentration of dissolved Fe although less than 40% of the initial Fe was dissolved. The authors reported deviations from linearity in their kinetic modeling but did not discuss the deviations further. The deviations were most likely caused by reaching an equilibrium state within the system. The framework of the study was, however, the dissolution of Fe oxides from clay and silica minerals, and the interpretation of the results and the selection of the suitable kinetic equation could have been based on that framework. In addition, it is unclear whether mixing was used in the studied system or not. Lee et al. (2007) have also suggested that the formation of an Fe oxalate product layer, at pH 1.6–3.2, can inhibit the dissolution of hematite in oxalic acid and that increase in the rate of dissolution can be observed with the addition of magnetite, Fe_3O_4, into the studied system. The addition of magnetite was roughly 10 wt.%. Mandal and Banerjee (2004) also studied the dissolution kinetics of Fe leaching from clay. Rate of dissolution was found to

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increase with increasing temperature. Mixing was done by shaking, where the shaking speed was not found significant in determining the outcome of the leaching.

Cornell and Schindler (1987) investigated the kinetics of photochemical dissolution of goethite in acidic oxalate solutions and suggested that both protons and oxalate ions participate in the dissolution reaction. The study reported a constantly increasing proton consumption, which could be seen as an increase in pH. To date, there appears to be no other published studies dealing with the behavior of pH in the dissolution of Fe oxides with oxalic acid.

Sidhu et al. (1981) studied the dissolution of several Fe oxides in hydrochloric and perchloric acids and found that the dissolution kinetics of hematite, among other Fe oxides, was described quite well by the cube root law suggesting that the dissolution was proportional to the surface area of the oxide. The mechanism of dissolution is not the same for hydrochloric and oxalic acids, but the authors suggested that complex formation played a role in the dissolution of hematite with hydrochloric acid thus bringing the dissolution processes of the two acids closer together.

Wells et al. (2001) studied the kinetics of acidic dissolution of aluminum substituted hematites in hydrochloric acid and found that the dissolution was well described by the Avrami–Erofe'ev equation, and that the cube root law and the Kabai equation were not applicable in this case.

The effect of temperature and acid concentration on the dissolution of magnetite has been investigated by Salmimies et al. (2011). The study concluded that temperature had no effect on the equilibrium concentration of Fe when dissolving magnetite in oxalic acid.

The objective of this study was to investigate the suitability of different kinetic models, also those discussed earlier in this chapter, in describing the dissolution of hematite in oxalic acid. In addition, thermodynamic data was collected to discuss the mechanisms of dissolution.

2. Materials and methods

2.1. Materials

A solid synthetic hematite powder, provided by Sigma-Aldrich (Schnelldorf, Germany) in 97% purity, was initially characterized with laser diffraction (Beckmann Coulter LS 13320) to obtain a particle size distribution for the powder (Fig. 1). The effects of particle size were not included in this study, although the particle size distribution plays a major role in the dissolution kinetics and possibly also in thermodynamics. The particle size distribution was determined mainly to characterize the used solid material comprehensively. In addition to the particle size measurement, X-ray diffraction (XRD, Bruker D8 Focus) was used to verify the chemical composition of the powder. According to the X-ray analysis, hematite was found to be the only mineralogical phase in the powder. In addition to XRD, scanning electron microscopy coupled with energy-dispersive X-ray spectrometry (SEM-EDS, JEOL JSM-5800) was employed to determine the elemental composition of any impurities. No impurities were found with SEM-EDS.

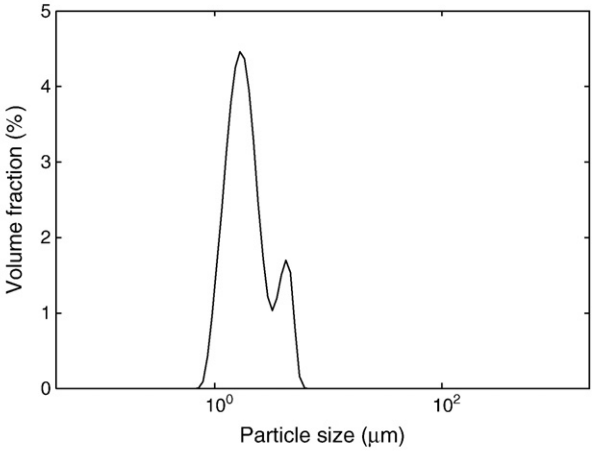

Fig. 1. Particle size distribution of the synthetic hematite powder.

Solutions of 0.6 mol/L oxalic acid were prepared using a solid oxalic acid dihydrate powder from BDH Prolabo (Leuven, Belgium). The purity of the solid powder was 99% with all solutions prepared in ultrapure water. The concentration of the acid was chosen so as to yield comparable results with previous studies conducted with synthetic magnetite (Salmimies et al., 2011).

2.2. Experimental

The dissolution experiments were conducted in a thermostated 1 L glass reactor. A pitched blade turbine and four baffles installed according to standard assembly (Tatterson, 1994) were used to induce sufficient mixing. To ensure that real kinetics would be observed and mass transfer in the bulk phase would not become a limiting factor with the stirred reactor, the effect of the stirrer speed was investigated with three different rotation speeds: 400, 800, and 1000 rpm. All experiments were conducted in 0.6 mol/L oxalic acid at a temperature of 50 °C. Solutions were prepared in ultrapure water and were thermostated in the reactor prior to adding the solids. A blank sample was drawn from the liquid phase by using a syringe, after which the solids were introduced into the reactor and mixing was commenced. Samples of the liquid phase were drawn at regular intervals. Solids were removed with a syringe filter after which the samples were diluted with 10 wt.% nitric acid and analyzed with inductively coupled plasma optical emission spectroscopy (ICP-OES, Thermo Electron Iris Intrepid II XDL) for dissolved Fe. The dilution factor varied between 0 and 300 depending on the experimental conditions. Measuring pH was done continuously from the liquid phase (WTW pH 401i, WTW SenTix 41 electrode). The initial mass of the hematite powder in the kinetic experiment was 12 g making the slurry density in this case 12 g/L.

The equilibrium data were collected in a similar way as the kinetic data but while initializing the experiments solids were added in excess to reach the equilibrium concentration, or solubility, without complete dissolution of the solids. Equilibrium data were collected at 35 and 50 °C. Initial pH in the experiments at 35 and 50 °C was 1.02 and 0.95, respectively.

The experimental error was estimated at roughly 2%. Quantifiable components included sampling and analysis errors.

2.3. Modeling

The models, summarized by Cornell and Schwertmann (2003), tested in this study have been presented in Eqs. (1)–(12).

$$\alpha^2 = kt \tag{1}$$

$$(1-\alpha)\ln(1-\alpha) + \alpha = kt \tag{2}$$

$$\left[1-\left(1-\alpha^{1/3}\right)\right]^2 = kt \tag{3}$$

$$\left(1-\frac{2}{3}\alpha\right)-(1-\alpha)^{2/3} = kt \tag{4}$$

$$-\ln(1-\alpha) = kt \tag{5}$$

$$[-\ln(1-\alpha)]^{1/2} = kt \tag{6}$$

$$[-\ln(1-\alpha)]^{1/3} = kt \tag{7}$$