

ACIDIC DISSOLUTION OF MAGNETITE: EXPERIMENTAL STUDY ON THE EFFECTS OF ACID CONCENTRATION AND TEMPERATURE

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Abstract—Magnetite (Fe_3O_4) is a key economically valuable component in iron ore and is extracted by dissolution processes, but among the Fe (oxyhydr)oxides its solubility behavior is one of the least understood. The objective of this study was to improve understanding of magnetite dissolution mechanisms leading to thermodynamic equilibrium by comparing the dissolution of two solid samples, one synthetic and one industrial, using oxalic, sulfuric, and nitric acids at varying concentrations and temperatures. Of the three solid-liquid systems investigated, only the system consisting of magnetite and oxalic acid reached an equilibrium state within the duration of an individual experiment (6 h). In this system, increasing the acid concentration resulted in a significant increase in the equilibrium concentration of dissolved Fe. When dissolving synthetic and industrial magnetite, increasing the temperature not only increased the rate of reaction but also affected the concentration of dissolved Fe. Significant effects were observed when increasing the temperature from 15 to 35°C, but only slight differences were seen on further increases in temperature. Observations regarding the equilibrium state of the sulfuric and nitric acid systems could not be made because equilibrium was not reached. The most important individual observation regarding the equilibrium state of the nitric- and sulfuric-acid systems seems to be that in future studies a much longer reaction time is necessary, due to slow kinetics of the dissolution mechanism. A proton-based mechanism has been hypothesized as the one governing the dissolution of magnetite by these two acids, but only the dissolution of the industrial sample yielded results that were similar for these two acids and consistent with that hypothesis.

Key Words—Dissolution, Iron Ore, Magnetite, Oxalic Acid, Nitric Acid, Sulfuric Acid, Particle Size, Temperature.

INTRODUCTION

Iron ore is one of the most widely mined minerals in the world, as indicated in a report of the British Geological Survey (2009). Iron oxides, key components in iron ore, are used in many areas of technology and are of interest to researchers in fields ranging from biology to mining and engineering.

Magnetite (Fe_3O_4) is one of the multifunctional oxides. Due to the stable nature of magnetite compared to its precursors, as characterized by a high standard free energy of formation ΔG_f^0 (Hemingway, 1990), its chemical dissolution requires a complete understanding of both the kinetics and thermodynamics of the dissolution process.

Although several dissolution models explaining the mechanisms for magnetite dissolution exist, as described by Brown *et al.* (1980), most of them pertain to complete dissolution of the solid compound, *i.e.* kinetics, rather than the reaching of an equilibrium state in the liquid phase. Houben (2003), Lee *et al.* (2007), and Reichard *et al.* (2007) studied the kinetics of dissolution of different Fe oxides in acidic or complexing conditions. The

removal of Fe, mainly magnetite, from kaolin with oxalic acid was studied by Arslan and Bayat (2009), who found that increasing temperature and pulp density increased the degree of Fe removal. Interestingly, increasing acid concentration was found to yield no increase in Fe removal. The kinetics of acidic dissolution of other Fe (oxyhydr)oxides has also been studied (Veglió *et al.*, 1998; Mandal and Banerjee, 2004). Hematite ($\alpha\text{-Fe}_2\text{O}_3$) and goethite ($\alpha\text{-FeOOH}$), as the most stable and sparingly soluble Fe oxides, have been studied to a much greater extent than magnetite. References to thermodynamic data for magnetite are rare, and only the study of Sweeton and Baes (1970) on the solubility product of magnetite measured in dilute acid and base media can be found in the literature.

When the particle size decreases, the surface area increases. In theory, this should yield faster kinetics due to the increased exposure of the mineral surfaces, which typically enhances dissolution of even the most poorly soluble solids. In particular, compounds with large surface free energies, such as the Fe oxides, should exhibit faster kinetics with decreasing particle size.

Langmuir and Whittemore (1971) derived equations to calculate the solubility products of goethite and hematite according to crystal dimensions, but the equations are only theoretical and no experimental evidence of increased solubility with decreased particle size exists for Fe oxides.

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A particle-size effect has been discovered for nanoparticles of other solid compounds, especially in the field of pharmaceuticals where many compounds are sparingly soluble. An attempt to predict the dissolution of an active pharmaceutical ingredient by means of particle-size distribution was made by Tinke *et al.* (2005), but they, too, adopted a kinetic approach by calculating the rate constant of dissolution, k , as a function of a single particle diameter, D . As a real solid has a particle-size distribution rather than having just a single particle size, an average rate constant, \bar{k} , was calculated. The model was generated using imaginary particle-size distributions and validated using *in vitro* dissolution data and real particle-size distributions measured with a Beckman Coulter LS320 laser-diffraction particle-size analyzer. A good correlation was found between the volume moment mean diameter, $D[4,3]$, and the dissolution rate constant, but for broader size distributions the distribution had to be split into smaller sections to achieve a better fit.

Demirkiran and Künkül (2007) dissolved ulexite, a boron ore, with perchloric acid and found that, even with micro-particles, the rate of dissolution increased with decreasing particle size. An increased dissolution rate was also observed as the perchloric acid concentration increased, as well as with increasing temperature.

A dissolution-enhancing temperature effect was also reported by Raschman and Fedorockova (2004) when dissolving Mg oxide (MgO) with hydrochloric acid. Interestingly, in this case an increase in the acid concentration failed to yield an increase in the dissolution rate. The effect of decreasing particle size was similar to the studies presented previously; a decrease in particle size resulted in an increase in the dissolution rate.

Hydrometallurgical studies (Chiarizia and Horwitz, 1991; Houben, 2003; Lee *et al.*, 2007) often focus on the kinetics of a single dissolution agent and use yield as a measure of performance. However, the mechanisms of dissolution for different dissolution agents, and also the concentration of functional groups in individual studies, can be very different and comparing the absolute performance of a chemical should not be based on kinetic studies alone but rather on mechanisms of dissolution, including the one state comparable for all systems, equilibrium.

Only a few studies exist which consider all three dissolution mechanisms of Fe oxides, *i.e.* protonation, complexation, and reduction (Zinder *et al.*, 1986;

Banwart *et al.*, 1989). Although commendable, the studies focus only on kinetics, leaving thermodynamic effects of the three different mechanisms undiscussed.

The objective of the present experimental study was not to investigate the kinetics of dissolution of magnetite, as this has already been covered by several authors, but to investigate the effects of temperature and acid concentration on the equilibrium state of magnetite dissolution. The dissolution experiments were conducted with synthetic and industrial magnetite, using oxalic, nitric, and sulfuric acid at different concentrations and temperatures as the dissolution agents.

MATERIALS AND METHODS

Design of experiments

A full factorial experimental design consisting of 54 experimental points, including the experimental sets for synthetic and industrial magnetite, was generated for data collection. Two variables, temperature and acid concentration, on three levels were considered. Temperature values of 15, 35, and 50°C were chosen. The values for acid concentration depended on the dissolving acid and were ultimately determined by the pH conditions applicable in industrial processes. Oxalic acid concentrations of 0.08, 0.33, and 0.60 mol/L (calculated as dihydrate) were chosen. The concentrations for sulfuric acid were 0.10, 0.26, and 0.41 mol/L, and for nitric acid 0.16, 0.72, and 1.30 mol/L. The pH of each solution was measured prior to the dissolution experiments (Table 1).

Experiments covering the set of variables were conducted with all three dissolution agents, dissolving both synthetic and industrial magnetite.

Chemicals

The dissolution experiments were conducted with a synthetic magnetite powder and a natural magnetite sample obtained from an industrial company. The synthetic powder with 97% purity, as reported by the manufacturer, was provided by Alfa Aesar (Karlsruhe, Germany) (Figure 1a).

An energy dispersive X-ray spectroscopy (EDS) analysis of the industrial sample, performed with a JEOL JSM-5800 scanning electron microscope (SEM), revealed that the solid consisted of 68.77 atomic % Fe and 29.25 atomic % O. Magnesium, Si, Ca, Al, and Ti were present as impurities. In addition, X-ray diffraction

Table 1. pH values of oxalic, sulfuric, and nitric acid at chosen concentrations.

C_{acid} (mol/L)	Oxalic acid			Sulfuric acid			Nitric acid		
	0.08	0.33	0.60	0.10	0.26	0.41	0.16	0.72	1.30
pH	1.34	0.95	0.79	1.06	0.70	0.41	1.36	1.01	0.88

(XRD), using a Bruker D8 Advance diffractometer, was also employed to determine the composition of the industrial sample. The XRD data ($\text{CuK}\alpha$ radiation) was recorded between 5 and $70^\circ 2\theta$ at a step size of $0.02^\circ 2\theta$ and a scanning speed of $0.02^\circ 2\theta \text{ s}^{-1}$. Magnetite was shown to be the primary component of the solid powder (Figure 1b). No other compounds were found in the spectrum, indicating the quantity of impurities to be minimal.

The initial particle-size distributions of the solids were measured using a Coulter LS 13320 laser diffraction particle-size analyzer (Figure 7a,b).

Oxalic acid, sulfuric acid, and nitric acid were chosen as dissolution agents. A solid oxalic acid dihydrate from BDH Prolabo (Leuven, Belgium) with a purity of 99% was used to formulate the oxalic acid solutions. Sulfuric acid and nitric acid from Merck, with purities of 95–97% and 65%, respectively, were used in the preparation of the other two acid solutions. For the sulfuric acid, 96% purity was chosen for calculation purposes. All solutions were prepared in reverse osmosis (RO) water.

Experimental set-up

The dissolution experiments were carried out in a 1 L glass reactor equipped with a thermostat to maintain constant temperature in the reacting mixture. A 4-blade, pitched blade turbine and four baffles were installed

according to standard assembly to keep the solids in motion, thus ensuring maximum surface area and eliminating mass transfer as a limiting step.

The liquid was held at constant temperature in the reactor and a blank sample was drawn from the solution adjacent to the mixing shaft with a syringe, after which solids were introduced into the reactor and mixing was commenced. A total reaction time of 360 min, estimated on the basis of previous studies by Cornell and Schindler (1987) and Lee *et al.* (2007), was employed to reach the equilibrium state. Samples were drawn from the mother liquor every 30 min until a reaction time of 120 min was attained, after which samples were taken every 60 min. A syringe equipped with a syringe filter of pore size $0.8 \mu\text{m}$ was used to draw the samples from the reactor, after which the samples were diluted with RO water ten times to avoid any precipitation caused by changes in the temperature. The dissolved Fe concentration of the mother liquor was analyzed with inductively coupled plasma optical emission spectrometry (ICP-OES) using a ThermoElectron Iris Intrepid II spectrometer.

To estimate the effects of the particle size of the solids on the dissolution process, the particle-size distribution was determined in RO water, incorporating three parallel runs to evaluate the particle-size distribution, before and after the dissolution experiments using a Beckman Coulter LS 13320 laser-diffraction particle-size analyzer. A separate optical model was created for

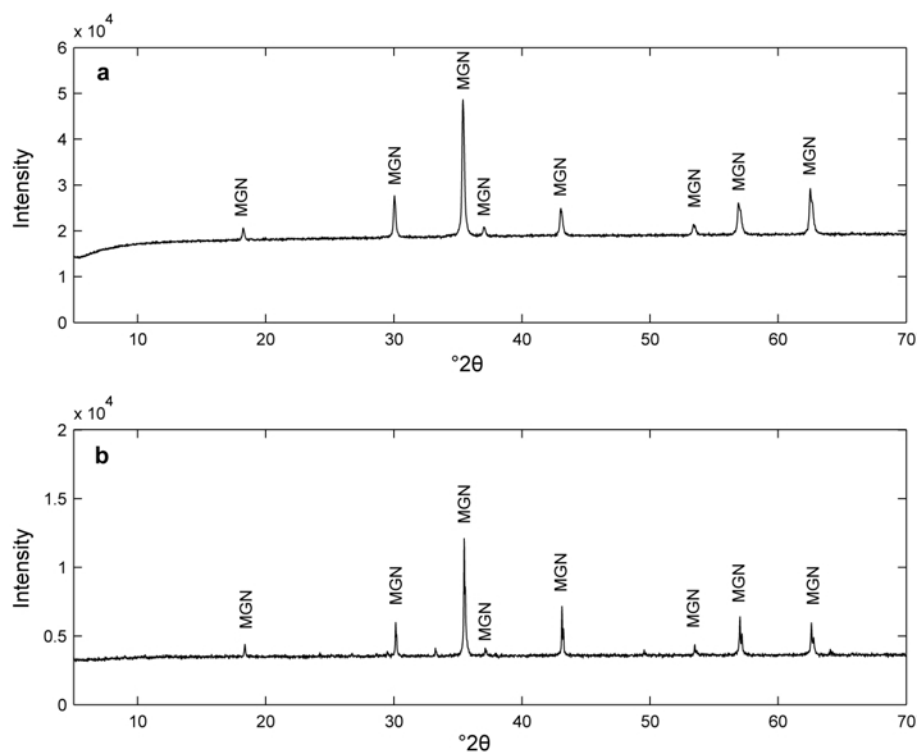


Figure 1. XRD patterns of magnetite powders: (a) synthetic; (b) industrial (MGN – magnetite).

the analysis of the magnetite powders using 2.42 as the real part of the refractive index (*Handbook of Chemistry and Physics*, 1998). The distribution was not determined for all the examined data points but by randomly selecting about half of the points in the experimental design.

RESULTS

Based on the dissolution experiments, the concentration of dissolved Fe increased with time under all conditions investigated but equilibrium was not always achieved.

Oxalic acid

In most cases, equilibrium was reached with oxalic acid after the first 2 h. A clear dependency for the dissolution of synthetic magnetite on temperature and acid concentration was observed (Figure 2a,b). Temperatures of 35 and 50°C resulted in the same equilibrium concentration of dissolved Fe, but, interest-

ingly, the reaction temperature of 15°C yielded a much lower equilibrium concentration. As with synthetic magnetite, no significant difference between the reaction temperatures of 35 and 50°C was observed when dissolving industrial magnetite, and a lower equilibrium concentration of Fe was once again observed at 15°C (Figure 2c). The temperature effects with oxalic acid were not in line with the other two acids during the initial stages of the dissolution, which may be due to different dissolution mechanisms and different temperature effects. The effect of temperature on equilibrium with nitric and sulfuric acid cannot be discussed as equilibrium was not reached.

The effect of acid concentration on the dissolution of magnetite was clearly seen with oxalic acid. Increased acid concentration yielded increased dissolution of Fe from magnetite. No noticeable difference in kinetics could be observed during the first 60 min when dissolving industrial magnetite and using oxalic acid with concentrations of 0.33 and 0.60 mol/L, indicating that an increase in the acid concentration yields no

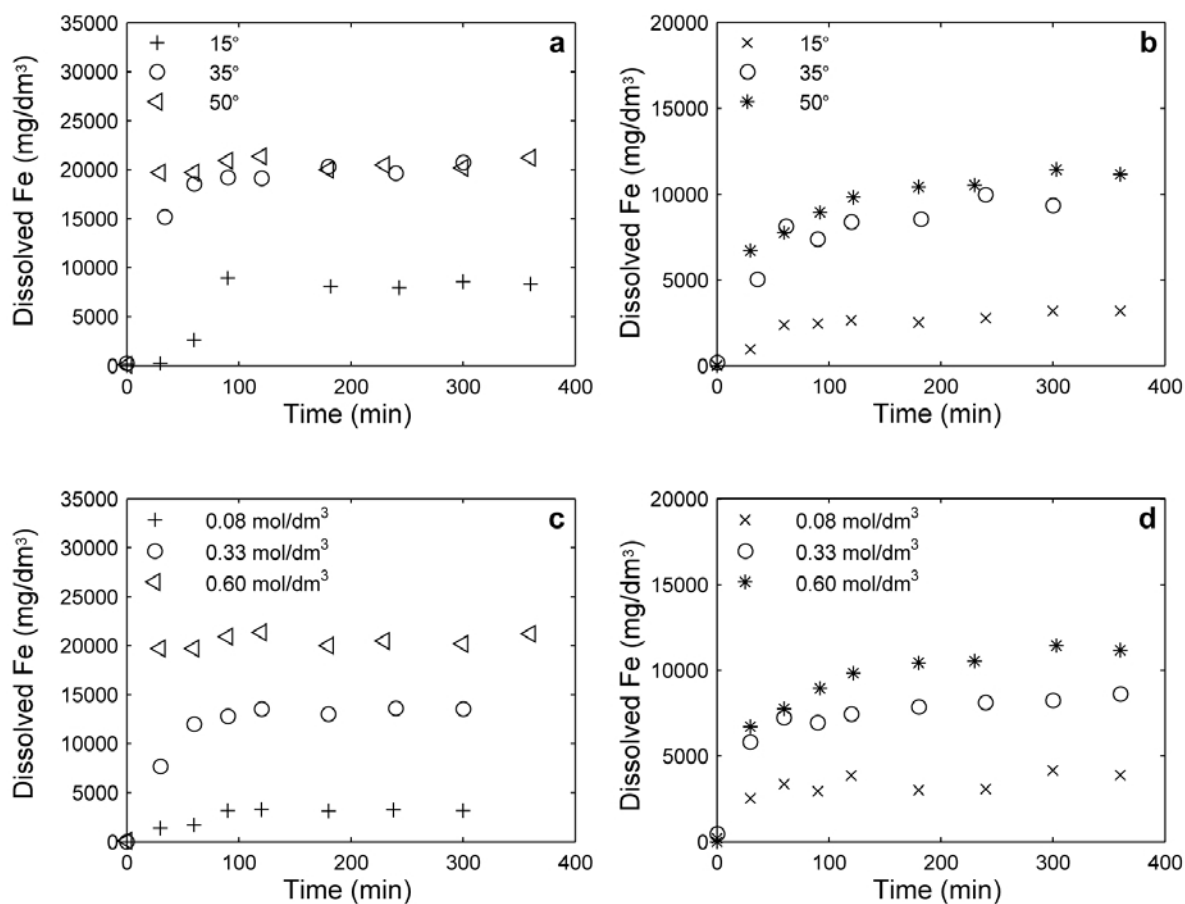


Figure 2. Dissolution of synthetic magnetite with oxalic acid at different (a) temperatures and (c) acid concentrations; and of industrial magnetite at different (b) temperatures and (d) acid concentrations. The concentration of sulfuric acid in (a) and (c) was 0.06 mol/L. The temperature in (c) and (d) was 50°C.

improvement in kinetics, although it increases the maximum dissolved Fe concentration (Figure 2d). While greater acid concentration yielded slightly faster kinetics with synthetic magnetite, *i.e.* equilibrium was reached more quickly, the opposite was observed for industrial magnetite; the lowest acid concentration yielded the shortest time needed to reach equilibrium.

Sulfuric acid

The dissolution experiments with sulfuric acid yielded kinetic data in addition to the effects of temperature and acid concentration on the equilibrium. Unlike in the case of oxalic acid, 6 h was insufficient to reach an equilibrium state with the sulfuric acid-magnetite system. Some indication that the equilibrium state could be reached by extending the reaction time by a few hours was, however, seen in the data set. The conclusion was based on visual observation of curving of the lines (Figure 3a–c).

When dissolving synthetic magnetite with sulfuric acid, the temperature had a greater effect on the dissolution than the acid concentration. By increasing

the temperature from 35 to 50°C, the dissolution of Fe could be increased twofold (Figure 3a). Acid concentration had only a slight effect on the kinetics in the early stages of dissolution, but as the dissolution proceeded, the effect became more evident (Figure 3c). Interestingly, the greatest acid concentration did not yield the largest quantity of dissolved Fe.

The effect of temperature on the dissolution of industrial magnetite was more straightforward than that of acid concentration. Increasing the temperature led to increased concentration of dissolved Fe (Figure 3b), whereas increasing the acid concentration from 0.26 to 0.41 mol/L yielded almost no difference (Figure 3d). An increase of more than threefold was, however, observed when increasing the acid concentration from 0.10 to 0.26 mol/L. The results for the two greatest acid concentrations could be explained by a limiting acid concentration beyond which no improvement in the dissolution of Fe can be achieved. Although the effective hydrogen ion concentrations are directly proportional to the acid concentrations, and are thus not equivalent, the quantities of dissolved iron are similar. A limiting acid

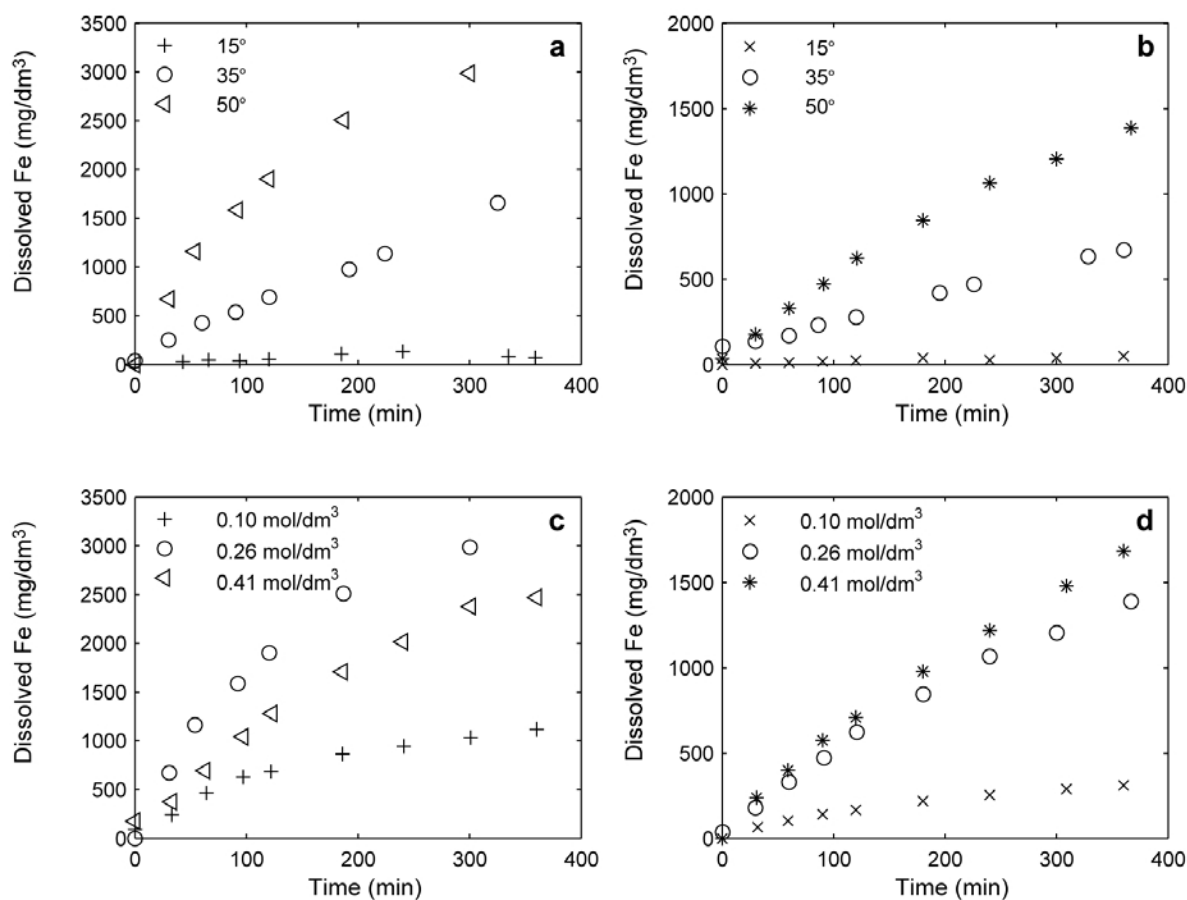


Figure 3. Dissolution of synthetic magnetite with sulfuric acid at different (a) temperatures and (c) acid concentrations, and of industrial magnetite at different (b) temperatures and (d) acid concentrations. The concentration of sulfuric acid in (a) and (b) was 0.26 mol/L. The temperature in (c) and (d) was 50°C.

concentration in this case means that increasing the effective hydrogen ion concentration results in no enhancement in dissolution. The inhibiting effect of increased anion adsorption could also have played a role here.

Nitric acid

Nitric acid was used as the third dissolution agent, in which case even slower kinetics were observed than with sulfuric acid. The nitric acid system also failed to reach equilibrium within 6 h.

As when dissolving synthetic magnetite with sulfuric acid, the dissolution of synthetic magnetite with nitric acid also exhibited a strong temperature dependency (Figure 4a). Increasing the temperature from 15 to 35°C increased the slope of the dissolution curve by a factor of more than ten. A more moderate increase, roughly threefold, was observed when further increasing the temperature to 50°C.

Increasing the acid concentration clearly had an effect on the dissolution of Fe from synthetic magnetite.

Increasing the acid concentration from 0.16 to 0.72 mol/L increased the slope more than twofold (Figure 4c). The same effect was observed when increasing the acid concentration from 0.72 to 1.30 mol/L.

The dissolution of industrial magnetite clearly depended on temperature (Figure 4b). Increasing the temperature increased the rate of dissolution and probably influenced the equilibrium concentration of Fe also.

Dissolution of industrial magnetite with nitric acid was similar to dissolution of industrial magnetite with sulfuric acid with respect to the effects of acid concentration. No difference between nitric acid concentrations of 0.72 and 1.30 mol/L was observed (Figure 4d) when dissolving the industrial magnetite. A significant difference was observed, however, between 0.16 and both 0.72 and 1.30 mol/L. As suggested for sulfuric acid, a limiting acid concentration could be the cause, as found also by Raschman and Fedorockova (2004).

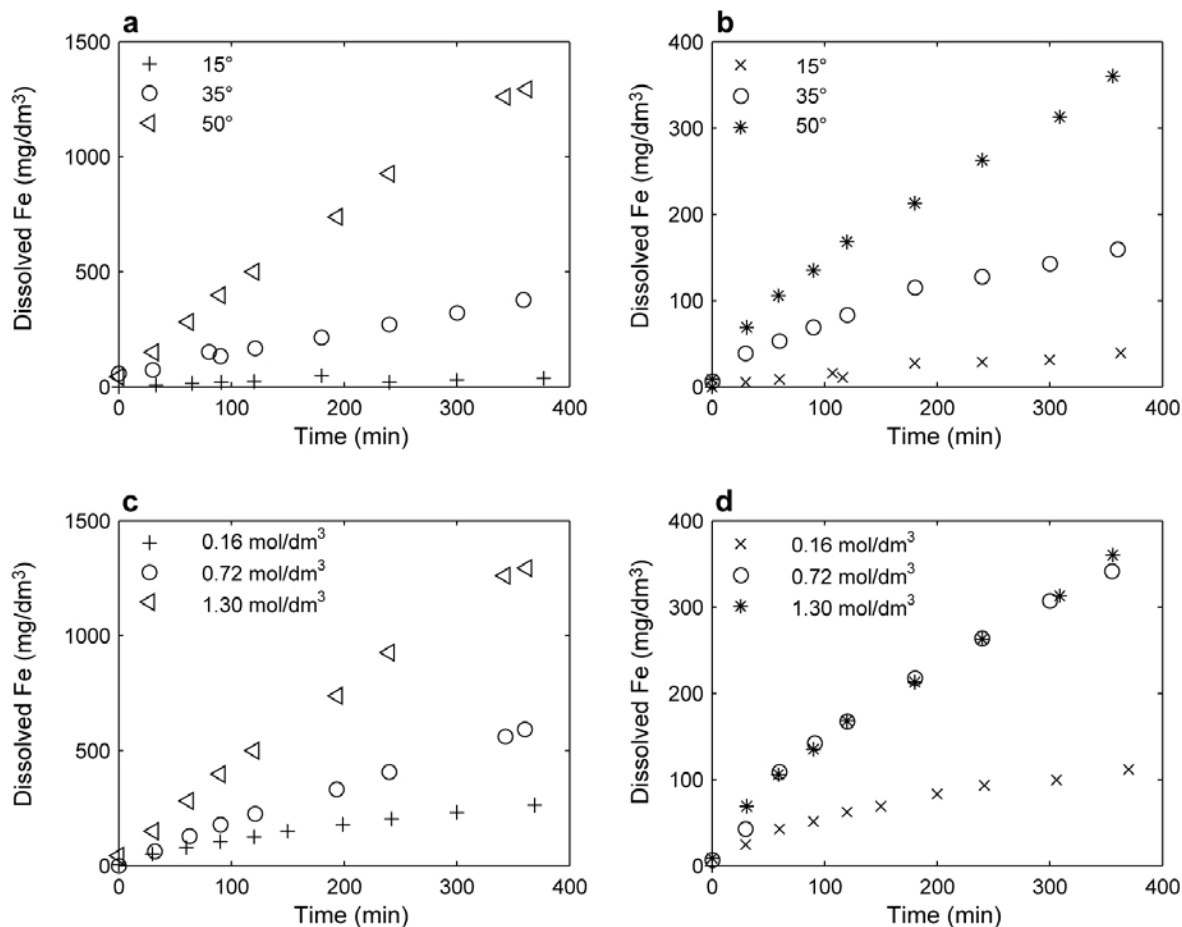


Figure 4. Dissolution of synthetic magnetite with nitric acid at different (a) temperatures and (c) acid concentrations, and of industrial magnetite at different (b) temperatures and (d) acid concentrations. The concentration of nitric acid in (a) and (b) was 1.30 mol/L. The temperature in (b) was 50°C and the acid concentration in (c) was 0.26 mol/L.

Comparison of the dissolution agents

All three dissolution agents were compared to establish the absolute performance of these chemicals in dissolving Fe from magnetite. As described above, the concentrations of the acids tested were chosen based on what could be applicable in real processes, and were ultimately determined by the pH conditions. Consequently, the minimum and maximum values of the acid concentrations of different dissolution agents are not readily comparable and any such comparison must be viewed with caution.

Nitric-acid dissociates almost completely, yielding an effective hydrogen ion concentration which is the same as the concentration of the actual acid. For oxalic and sulfuric acid, only the first proton represents a strong acid with complete dissociation. The second proton is a weak acid with incomplete dissociation, resulting in a less effective hydrogen ion or functional group concentration than could be calculated from the molecular formula of the acid. When comparing the different acids, pH was used as the basis for comparison instead of absolute acid concentration, as pH is considered to indicate the effective hydrogen ion concentration. Consequently, oxalic (0.33 mol/L, pH = 0.95), sulfuric (0.10 mol/L, pH = 1.06), and nitric (0.72 mol/L, pH = 1.01) acid were used to dissolve both synthetic and industrial magnetite at 50°C.

Oxalic acid was superior to sulfuric and nitric acid in dissolving Fe from magnetite independent of the type of magnetite (Figure 5a,b). The better performance

observed is probably due to the ability of oxalic acid (Zinder *et al.*, 1986) to dissolve Fe oxides by two mechanisms: complex formation and induced reduction (Stumm *et al.* 1985; Cornell and Schindler 1987; Blesa *et al.* 1987; Panias *et al.* 1996).

Sulfuric acid gave concentrations of dissolved Fe approximately twice those of nitric acid when dissolving synthetic magnetite (Figure 5a). When dissolving industrial magnetite, however, almost identical behavior was observed for sulfuric and nitric acids. Bruyere and Blesa (1985) suggested that sulfuric acid dissolves magnetite through protonation. Zinder *et al.* (1986) also suggested protonation as a mechanism of dissolution of hematite and goethite with nitric acid. One could speculate that these two acids act through the same dissolution mechanism, *i.e.* protonation, which would yield the same results for the two acids at the same proton concentration, but the results obtained in the present study fail to support that hypothesis. Although the results for industrial magnetite agree with the suggested mechanism, the results for synthetic magnetite do not. The discrepancy might be due to differences in the adsorption of the anions, as described by Sidhu *et al.* (1981) when comparing the dissolution of several Fe oxides and hydroxides with hydrochloric and perchloric acid, but differing anion adsorption does not explain why a difference is observed when dissolving synthetic but not industrial magnetite.

When dissolving synthetic magnetite, a dissolved Fe concentration of ~14,000 mg/L was reached with oxalic acid, whereas dissolution of industrial magnetite with

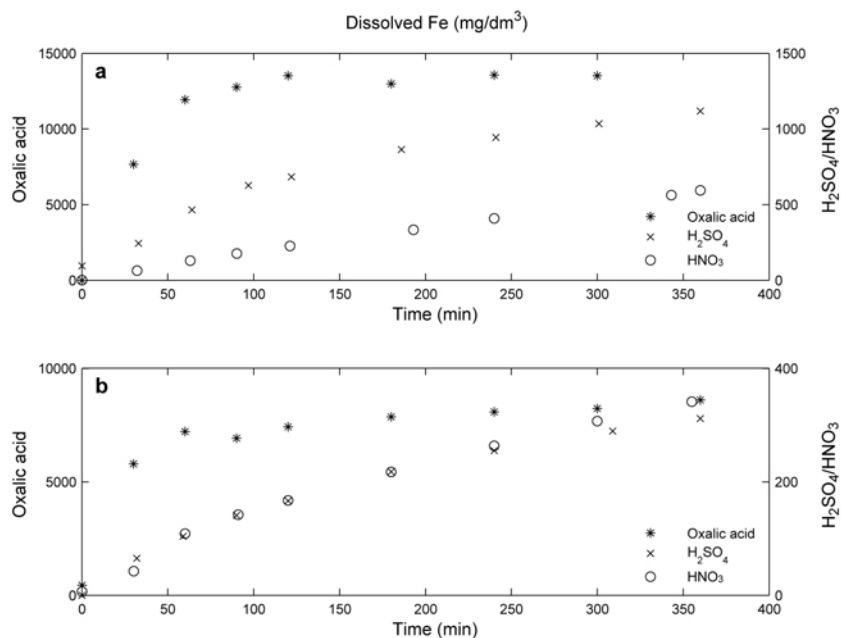


Figure 5. Dissolution of (a) synthetic and (b) industrial magnetite with different acids. The temperature in each experiment was 50°C. The concentrations of oxalic, sulfuric, and nitric acid were 0.33, 0.10, and 0.72 mol/L, respectively. The corresponding pH values were 0.95, 1.06, and 1.01, respectively.

oxalic acid yielded only 8000 mg/L. A similar decrease was observed with the other two acids, but here the difference could be explained by slower kinetics of dissolution of the industrial sample.

Two possible explanations for the different results for the two magnetite samples appear plausible: differences in particle-size distribution and impurities in the industrial sample. The synthetic magnetite powder had a smaller mean particle size and more fines (Figure 7a), and thus a larger specific surface area. Larger specific surface areas mean, in general, faster dissolution rates, and as discussed above, possibly greater solubility also, although particle size has not yet been shown explicitly to have an effect on the dissolution process of magnetite.

Impurities of other dissolved ions, *e.g.* Mg, Ca, Al, and Si, were reflected in the ICP analysis, indicating the dissolution of something other than Fe from the industrial sample. The impurities were those also found in the initial SEM-EDS analysis of the industrial material. Some traces of Ti were also present in the mother liquor. Dissolution

of the impurities exhibited similar behavior to dissolution of Fe from magnetite, *i.e.* in general, greater concentrations of dissolved species were observed with increasing acid concentration and temperature (Figure 6b,c). Calcium and Mg exhibited the greatest concentrations of dissolved impurities in the mother liquor (Figure 6a). Dissolution of Ca was rapid, reaching a maximum in the first 60 min even when dissolving with dilute nitric acid at 15°C. The concentrations of Ca were, however, not the same for each experiment, suggesting that an equilibrium state was observed rather than the dissolution of all the Ca in the industrial sample. Increasing the temperature greatly increased the dissolution of Mg from industrial magnetite. As was the case for Fe dissolution, increasing the acid concentration from 0.26 to 0.41 mol/L yielded almost the same response for the dissolution of Mg, *i.e.* no significant improvement was observed with increasing acid concentration. These impurities can diminish the dissolution capacity of the acid with respect to Fe by forming compounds with the dissolution agent, or even

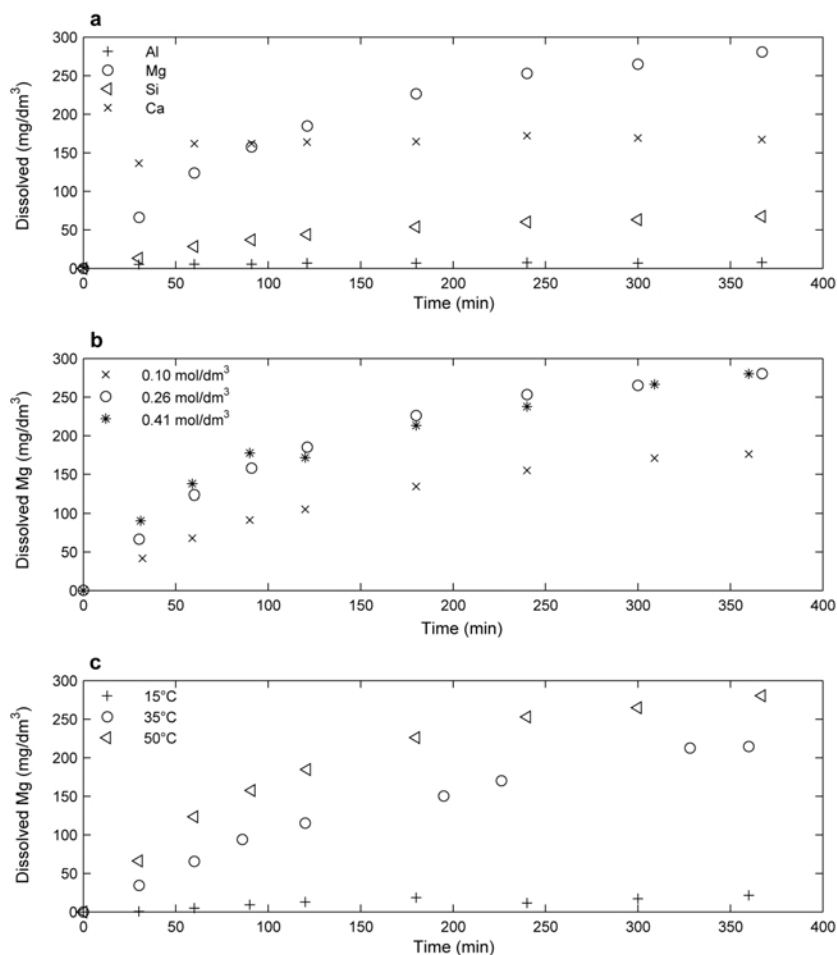


Figure 6. Dissolution of (a) impurities when dissolving industrial magnetite with 0.26 mol/L sulfuric acid at 50°C, and the effect of (b) temperature and (c) acid concentration on the dissolution of Mg from industrial magnetite. The acid concentration in (b) was 0.26 mol/L and the temperature in (c) was 50°C.

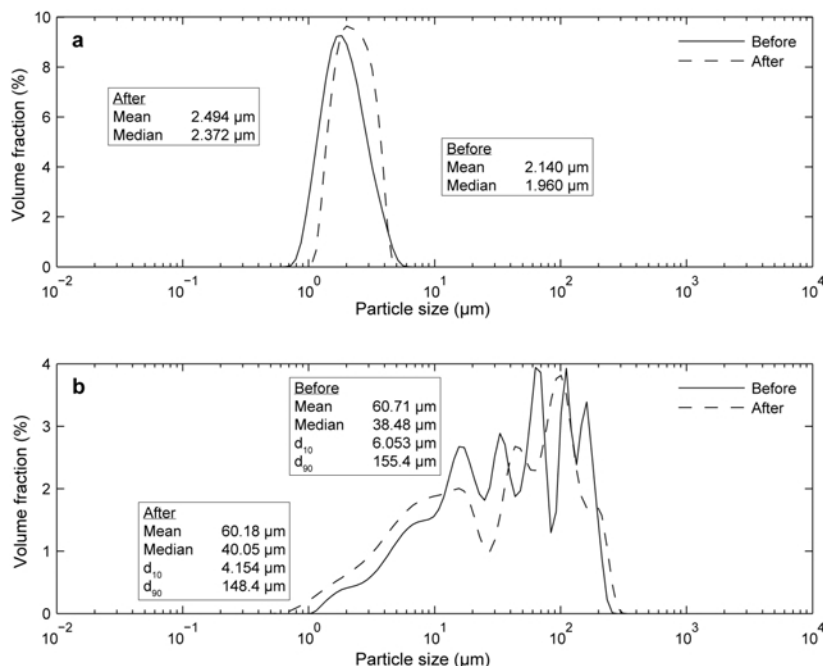


Figure 7. Particle-size distributions before and after dissolution experiments for (a) synthetic magnetite in sulfuric acid at a temperature of 15°C and acid concentration of 0.41 mol/L, and (b) industrial magnetite in oxalic acid at a temperature of 50°C and acid concentration of 0.33 mol/L.

inhibiting the dissolution of Fe from the solids. Due to greater dilution factors with oxalic acid (100-fold for ICP-OES), impurities were only observed in samples drawn from the sulfuric and nitric acid dissolutions (no dilution for ICP-OES). Although impurities were not seen in the analysis of the oxalic acid samples, a reasonable assumption would be that the same impurities were present but had just been diluted to a concentration below the detection limit.

No impurities were observed in the samples taken from the mother liquor used to dissolve synthetic magnetite, as would be expected due to the high purity of the synthetic powder.

Particle-size distribution

Particle-size distributions were determined for about half of the experimental points. As with the dissolution data, only a few examples characterizing the major trends in the data are presented here.

The original hypothesis concerning the particle-size distribution before and after the dissolution process was that the mean particle size should decrease and that the distribution itself should move to the left, indicating the dissolution of all particles to some extent. As reported by several authors (Langmuir and Whittemore, 1971; Raschman and Fedorockova, 2004; Demirkiran and Künkül, 2007), smaller particles dissolve faster and may even disappear completely, thereby increasing the fraction of larger particles.

In the present study, smaller particles disappeared, thus increasing the fraction of larger particles and

shifting the distribution to the right. This is also seen as an increasing mean particle size (Figure 7a). The results for the industrial sample, with the addition of the d_{10} and d_{90} values, gave a better indication of the changes which took place in the industrial sample as the result of dissolution (Figure 7b).

Due to the coarseness of the industrial sample, settling was a major problem in sampling, and greater deviation with regard to finding a repeating pattern in the particle-size analysis was observed. However, an increase in the fraction of small particles and merging of peaks was observed, indicating different dissolution rates for different particle sizes.

The differences in the mean and median particle sizes before and after the dissolution were small, although obvious changes in the particle-size distribution can be seen quantitatively in the d_{10} and d_{90} values (Figure 7b). The d_{10} value, in particular, suggests an increased fraction of smaller particles. Even the composition of different size fractions could lead to variation resulting in differences in the dissolution. Future work could usefully include dissolution experiments with fractionated industrial material.

CONCLUSIONS

Dissolution experiments with synthetic and industrial magnetite were conducted with oxalic, sulfuric, and nitric acid at different temperatures and acid concentrations in order to compare the effects of different acids on the dissolution mechanism for magnetite.

For each acid, an increase in the dissolution rate was, in general, observed with increased temperature and acid concentration. A few interesting exceptions, e.g. a limiting acid concentration with sulfuric and nitric acid, were observed. Equilibrium was reached only when dissolving magnetite with oxalic acid. Temperature affected the equilibrium but only when the temperature was increased from 15 to 30°C. Further increases in temperature yielded no significant increase in the equilibrium concentration of dissolved Fe independent of the type of magnetite used. Increasing the acid concentration yielded greater solubilities in both synthetic and industrial magnetite. The conclusion concerning sulfuric and nitric acid was that the mechanisms of dissolution are significantly slower than those affecting the dissolution of magnetite with oxalic acid. Protonation has been suggested as the mechanism involved in the dissolution of Fe oxides by sulfuric and nitric acid but, in this study, the results for the two acids differed, indicating that additional factors need to be considered. As equilibrium was not reached, valid comparison based on the dissolution mechanisms could not be made.

Oxalic acid exhibited the best capacity to dissolve Fe from magnetite, followed by sulfuric acid and nitric acid. The differences in dissolved Fe concentration between oxalic acid and the other two acids for both synthetic and industrial magnetite were over tenfold. In dissolving industrial magnetite, sulfuric and nitric acid exhibited similar behaviors, supporting the suggestion of protonation being the dissolution mechanism, but dissolution of synthetic magnetite with sulfuric and nitric acid yielded different results.

In general, synthetic magnetite gave greater concentrations of dissolved Fe in the dissolution experiments than industrial magnetite, as expected. Different particle-size distributions and impurities of the industrial sample are the most likely causes.

Further work on generating models, both empirical and theoretical, needs to be done. In addition, the time required to reach the equilibrium state with sulfuric and nitric acid should be further investigated.

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REFERENCES

- Arslan, V. and Bayat, O. (2009) Removal of Fe from kaolin by chemical leaching and bioleaching. *Clays and Clay Minerals*, **57**, 787–794.
- Banwart, S., Davies, S., and Stumm, W. (1989) The role of oxalate in accelerating the reductive dissolution of hematite (α -Fe₂O₃) by ascorbate. *Colloids and Surfaces*, **39**, 303–309.
- Blesa, M.A., Magaz, G., Salfity, J.A., and Weisz, A.D. (1987) Mechanism of dissolution of magnetite by oxalic acid-ferrous iron solutions. *Inorganic Chemistry*, **26**, 3713–3717.

- British Geological Survey (2009) *World Mineral Production 2003–07*. [Online] NERC. Available at: <http://www.bgs.ac.uk/mineralsUK/commodity/world/home.html> [Accessed 2 November 2009].
- Brown, W.E., Dollimore, D., and Galwey, A.K. (1980) Reactions in the solid state, Pp. 41–109 in: *Comprehensive Chemical Kinetics* (C.H. Bamford and C.F. Tipper, editors). Elsevier, Amsterdam.
- Bruyere, V.I.E. and Blesa, M.A. (1985) Acidic and reductive dissolution of magnetite in aqueous sulphuric acid. Site-binding model and experimental results. *Journal of Electroanalytical Chemistry*, **182**, 141–156.
- Chiarizia, R. and Horwitz, E. (1991) New formulations for iron oxides dissolution. *Hydrometallurgy*, **27**, 339–360.
- Cornell, R. M. and Schindler, R. W. (1987) Photochemical dissolution of goethite in acid/oxalate solution. *Clays and Clay Minerals*, **35**, 347–352.
- Demirkiran, N. and Künkül, A. (2007) Dissolution kinetics of ulexite in perchloric acid solutions. *International Journal of Mineral Processing*, **83**, 76–80.
- Handbook of Chemistry and Physics (1998) *Physical and Optical Properties of Minerals*. Pp. 4–140 (W. M. Haynes, editor). CRC Press Inc., Boca Raton, Florida, USA.
- Hemingway, B.S. (1990) Thermodynamic properties for bunsenite, NiO, magnetite, Fe₃O₄, and hematite, Fe₂O₃, with comments on selected oxygen buffer reactions. *American Mineralogist*, **75**, 781–790.
- Houben, G.J. (2003) Iron oxide incrustations in wells. Part 2: Chemical dissolution and modeling. *Applied Geochemistry*, **18**, 941–954.
- Langmuir, D. and Whittemore, D.O. (1971) Variations in the stability of precipitated ferric oxyhydroxides. Pp. 209–234 in: *Nonequilibrium Systems in Natural Water Chemistry* (R.F. Gould, editor). American Chemical Society, Washington D.C.
- Lee, S.O., Tran, T., Jung, B.H., Kim, S.J., and Kim, M.J. (2007) Dissolution of iron oxide using oxalic acid. *Hydrometallurgy*, **87**, 91–99.
- Mandal, S. and Banerjee, P. (2004) Iron leaching from China clay with oxalic acid: Effect of different physicochemical parameters. *International Journal of Mineral Processing*, **74**, 263–270.
- Panias, D., Taxiarchou, M., Paspaliaris, I., and Kontopoulos, A. (1996) Mechanism of dissolution of iron oxides in aqueous oxalic acid solutions. *Hydrometallurgy*, **42**, 257–265.
- Raschman, P. and Fedorocková, A. (2004) Study of inhibiting effect of acid concentration on the dissolution rate of magnesium oxide during the leaching of dead-burned magnesite. *Hydrometallurgy*, **71**, 403–412.
- Reichard, P.U., Kretschmar, R., and Kraemer, S.M. (2007) Rate laws of steady-state and non-steady-state ligand-controlled dissolution of goethite. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, **306**, 22–28.
- Sidhu, P., Gilkes, R., Cornell, R., Posner, A., and Quirk, J. (1981) Dissolution of iron oxides and oxyhydroxides in hydrochloric and perchloric acids. *Clays and Clay Minerals*, **29**, 269–276.
- Stumm, W., Furrer, G., Wieland, E., and Zinder, B. (1985) The effects of complex-forming ligands on the dissolution of oxides and aluminosilicates. Pp. 55–74 in: *The Chemistry of Weathering* (J.I. Drever, editor). D. Reidel, Dordrecht, The Netherlands.
- Sweeton, F.H. and Baes, C.F. (1970) The solubility of magnetite and hydrolysis of ferrous ion in aqueous solutions at elevated temperatures. *The Journal of Chemical Thermodynamics*, **2**, 479–500.
- Tinke, A.P., Vanhoutte, K., De Maesschalck, R., Verheyen, S., and De Winter, H. (2005) A new approach in the prediction

- of the dissolution behavior of suspended particles by means of their particle size distribution. *Journal of Pharmaceutical and Biomedical Analysis*, **39**, 900–907.
- Vegliò, F., Passariello, B., Barbaro, M., Plescia, P., and Marabini, A. (1998) Drum leaching tests in iron removal from quartz using oxalic acid and sulphuric acid. *International Journal of Mineral Processing*, **54**, 183–200
- Zinder, B., Furrer, G., and Stumm, W. (1986) The coordination chemistry of weathering: II. Dissolution of Fe(III) oxides. *Geochimica et Cosmochimica Acta*, **50**, 1861–1869.

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