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Determination of nanoparticulate magnetite stoichiometry by Mössbauer spectroscopy, acidic dissolution, and powder X-ray diffraction: A critical review

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Abstract

A solid solution can exist of magnetite (Fe_3O_4) and maghemite (γ-Fe_2O_3), which is commonly referred to as nonstoichiometric or partially oxidized magnetite. The degree of stoichiometry in magnetite is quantitatively measured by determining the ratio of Fe^{2+} to Fe^{3+}. Magnetite stoichiometry ($x = Fe^{2+}/Fe^{3+}$) strongly influences several physical properties, including the coercitivity, sorption capacity, reduction potential, and crystalline structure. Magnetite stoichiometry has been extensively studied, although very little work exists examining the stoichiometry of nanoparticulate samples (<<100 nm); when the stoichiometry was measured for nanoparticulate samples, it was not validated with a secondary technique. Here, we review the three most common techniques to determine magnetite stoichiometry: (1) acidic dissolution; (2) Mössbauer spectroscopy; and (3) powder X-ray diffraction (pXRD), specifically with nanoparticulate samples in mind. Eight samples of nonstoichiometric magnetite were synthesized with x ranging from 0 to 0.50 and with the particle size kept as similar as possible (BET specific surface area = 63 ± 7 m^2/g; particle size ≈ 20 nm). Our measurements indicate excellent agreement between stoichiometries determined from Mössbauer spectra and by acidic dissolution, suggesting that Mössbauer spectroscopy may be a useful means for estimating magnetite stoichiometry in nanoparticulate, multi-phases samples, such as those found in the environment. A significant linear correlation was also observed between the unit-cell length (a) of magnetite measured by pXRD and magnetite stoichiometry, indicating that pXRD may also be useful for determining particle stoichiometry, especially for mixed phased samples.

Keywords: Magnetite, maghemite, magnetite oxidation, nonstoichiometric magnetite, nanoparticle, Mössbauer spectroscopy, stoichiometry, X-ray diffraction