NOTES

GOETHITE MORPHOLOGIES INVESTIGATED VIA X-RAY DIFFRACTION OF ORIENTED SAMPLES

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INTRODUCTION

Synthetic and natural goethites display a variety of particle morphologies that are dependent on solution conditions during formation (Schwertmann 1990). Factors influencing goethite morphology include pH and the presence or absence of specifically adsorbing ions in solution. Particle morphology can affect goethite dissolution behavior and will govern the distribution of coordination sites available on the particle surface (Cornell et al. 1974; Colombo et al. 1994). Morphological information can be obtained via electron microscopic imaging (Schulze and Schwertmann 1984) or profile analysis of X-ray diffraction (XRD) patterns (Koch et al. 1986). These methods are essential for determination of absolute particle dimensions, but they may require a significant time commitment or advanced level of analysis. In order to facilitate rapid preliminary comparison of synthetic goethite samples, we have investigated the use of powder XRD to derive similar qualitative information via the influence of preferred orientation during sample preparation.

Materials and Methods

Prior to filtering onto a 25-mm, 0.2-µm membrane filter (Gelman Suprapore 200, polysulfone), 5–10 mL of a goethite slurry was dispersed in a sonication bath for 1 min at 43 kHz. The slurry concentration was adjusted prior to filtering to yield about 3–5 mg of goethite on the filter (0.15–0.25 mg cm⁻²). Corundum (25% w/w) from Baikowski International in Charlotte, North Carolina, and glass wool (2 mg) prepared by the procedure of Rich (1975) were included in the slurry as an internal peak position standard and a film binder, respectively. Corundum and processed glass wool

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Figure 1. Whole XRD pattern comparison for a synthetic goethite prepared to give a random particle orientation and a preferentially oriented film using the filter method. Select Bragg reflections are indicated with (hkl) indices.

were added from 0.6 g L\(^{-1}\) and 1.25 g L\(^{-1}\) stock suspensions. Volumetric additions were calibrated by weight after drying at 110 °C. The addition of glass wool was necessary to ensure film integrity after room temperature drying. Films were left attached to the membrane support for further analysis. The films were then characterized by XRD on a Scintag XDS 2000 diffractometer equipped with a vertical theta-theta goniometer employing CuK\(\alpha\) radiation and a solid state intrinsic germanium detector. Membrane-supported films were attached to circular glass cover slips by gluing along the outer edge. The rigid sample was then supported over petroleum jelly in a 25-mm circular cavity sample support provided by Scintag. Most samples were scanned over 10–70 °2θ at a rate of 0.5 °2θ min\(^{-1}\) and a 0.03 degree step size (3.6 s/step).

RESULTS AND DISCUSSION

We first examined a synthetic goethite prepared from an Fe(III) system which resulted in acicular crystals elongated along (001) (Schwertmann and Cornell 1991). Large differences in diffraction intensities between samples prepared either as a nearly-random or as an oriented mount were discernible (Figure 1). Most notable are the enhanced intensities for (hk0) reflections in the oriented sample. For the random mount, the ratio of integrated intensities (mixed Gaussian-Lorentzian profile) for (110) and (111) is 1.9 while for the oriented mount this ratio is 24. Both values differ from that predicted for a pattern produced by a theoretical random particle distribution (1.25, Brown 1980), and suggest that even careful loading procedures are insufficient to achieve a truly random distribution of particle orientations. However, duplicate preparations of a sample using our method resulted in a mean and standard error of 11.8 ± 2.8 in measured

Figure 2. Partial diffraction patterns for goethites synthesized in the presence of increasing amounts of aluminum. Bragg reflections for the minerals present are indicated with (hkl) indices; G = goethite, C = corundum and H = hematite. The legend includes intensity ratios calculated for the (110) and (111) goethite reflections.

results are consistent with morphological differences observed for these samples via scanning electron microscopy (SEM) in Figure 3. Goethite particles...
produced in the presence of high Al concentrations are more unidimensional and do not orient well using this procedure.

Similar to other work (Sugimoto et al. 1993), this method of sample preparation is quite simple and does not require specialized equipment. It clearly demonstrated morphological changes induced by variable synthesis conditions for synthetic goethites. Systematic changes in integrated intensity distributions were primarily related to particle orientation relative to the instrumental diffracting plane, thus the need to distinguish particle size- and disorder-induced broadening for morphological determinations via profile analysis is averted (Delhez et al. 1988). While the method appears suitable for preliminary characterization of synthetic mineral preparations, it may prove unreliable for natural samples where physical isolation of the mineral of interest may be required to achieve strong orientation effects.

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REFERENCES


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