Distinguishing between Surface and Bulk Dehydration-Dehydroxylation Reactions in Synthetic Goethites by High-Resolution Thermogravimetric Analysis

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Abstract: Synthetic goethites studied by high-resolution thermogravimetry (HRTGA) show variability in surface characteristics and structural stability as a function of aging conditions. Goethites were synthesized at either pH 6 or 11, at temperatures of 40 or 70 ° C, and in the presence or absence of sorbed Mn or Pb. Data from HRTGA analysis revealed at least four distinct weight-loss events near goethite dehydroxylation that relate to 1) three events involving the evolution of water associated with surface Fe-O functional groups and 2) bulk dehydroxylation of goethite during transformation to hematite. The relative mass of evolved surface and bulk structural water was related to the predominant particle morphology as determined by transmission electron microscopy (TEM). Differentiation of surface and bulk decomposition reactions allowed the identification of bulk structural dehydroxylation. Goethite crystallinity, estimated by the bulk dehydroxylation temperature, appeared to depend on the kinetics of crystallization. This trend was most evident for systems aged at pH 11 and 40 ° C. Greater concentrations of coprecipitated Mn or Pb dramatically improved goethite crystallinity as indicated by higher dehydroxylation temperatures and smaller widths of the (110) Bragg reflection. Comparison of bulk dehydroxylation temperatures for these samples to other preparations suggests that structural defects predominated over the effects of particle size and Mn/Pb substitution in determining goethite thermal stability. A conceptual model is proposed to account for the disparate dehydroxylation profiles displayed by goethites of varying crystallinity.

Key Words: Crystallinity • Dehydroxylation • Goethite • Thermogravimetry • Nonstoichiometric Water • TEM • XRD

Clays and Clay Minerals; June 1999 v. 47; no. 3; p. 329-337; DOI: 10.1346/CCMN.1999.0470309

Clay Minerals Society (www.clays.org)