Identification of Noncrystalline $(Fe,Cr)(OH)_3$ by Infrared Spectroscopy

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Abstract: Iron-chromium hydroxides are important solid phases governing the aqueous concentrations of Cr(III) in soils and fly ashes. Although direct identification of noncrystalline $(Fe,Cr)(OH)_3$ is difficult, the infrared spectra of noncrystalline $Fe(OH)_3$ and $Cr(OH)_3$, coprecipitated $(Fe,Cr)(OH)_3$, and physical mixtures of $Fe(OH)_3$ and $Cr(OH)_3$ can be distinguished on the basis of the asymmetric stretching doublet (ν_3) of structural carbonate anions. As the Cr mole fraction of the coprecipitated $(Fe,Cr)(OH)_3$ increases, the position of the low-frequency ν_3 peak (ν_3'') changes progressively to higher frequencies, and the carbonate ν_3 splitting decreases. No change in carbonate ν_3 splitting or ν_3'' location was observed for physical mixtures of $Fe(OH)_3$ and $Cr(OH)_3$. The changes in ν_3 splitting are believed to be caused by different degrees of polarization of the carbonate ligand by the Fe and Cr cations.

Pure $Cr(OH)_3$ exhibits a strong affinity for carbonate and H_2O and tends to remain noncrystalline even at very high pHs. In contrast, pure $Fe(OH)_3$ gradually converts to crystalline goethite at high pH, to the exclusion of much of the H_2O and carbonate. The presence of Cr in $(Fe,Cr)(OH)_3$ solid solutions seems to inhibit the transformation to crystalline goethite. The strong association of carbonate with Cr and the kinetic inertness of Cr(III) inner-sphere complexes in general may account for the maintenance of non-crystalline solid-solution materials in lieu of transformation to a crystalline end product.

Key Words: Chromium hydroxide • Goethite • Infrared spectroscopy • Iron hydroxide • Noncrystalline • Solid solution

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