Retention of Cobalt by Pure and Foreign-Element Associated Goethites

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Abstract: Retention studies of the cobalt-goethite system were carried out using synthetic, star-shaped and lath-shaped pure, Al-, Cd-, Cu- and Si-associated goethites. Aluminium and Si are commonly occurring foreign elements in natural goethites. The goethites were prepared by coprecipitating Fe and the foreign element under controlled conditions and characterized by X-ray diffraction, transmission electron microscopy, specific surface area determination and 2 M HCl extraction. The foreign-element associated goethites contained $\sim$3, $\sim$5 and $\sim$9 mole % Al, $\sim$4 mole % Cd and $\sim$3 mole % Cu incorporated by isomorphous substitution but only $\sim$0.4 mole % of probably occluded Si. Crystal size and shape but also number of defects and domains, and hence specific surface area, unit-cell dimensions and reactivity towards 2 M HCl, exhibited great variability among the goethites. Accordingly the amounts of Co sorbed from initially 10^{-7} M Co in 0.1 M $Ca(NO_3)_2$ in relation to pH (3 – 8) and reaction time (2 – 504 h) were very different for the eight goethites. The affinity of Co is highest for Cd- and lowest for Cu-goethite. These samples also form the extremes regarding time-dependent sorption with Cu-goethite showing the smallest and Cd-goethite the largest increase in sorption with increasing reaction time. The Co uptake was not caused by precipitation Co(III) oxides due to Co(II) oxidation, since oxygen exclusion during sorption had no effect on the amount of Co sorbed. The amounts of sorbed Co extracted by 2 M HCl decreased with increasing sorption time but 40 – 87% of sorbed Co remained unextracted after 48 h, most in Cu-goethite and least in lath-shaped pure goethite. The strong retention suggests Co uptake by diffusion into micropores and fissures resulting from structural defects and intergrowths. The diffusion coefficients range from $3 - 10^{-19}$ to $6 - 10^{-17}$ cm^2/s with the highest values for Al- and Si-associated goethites emphasizing the importance for Co immobilization, and hence availability, of foreign-element associations in goethite.

Key Words: Al-goethite • Cd-goethite • Co-extraction • Co-sorption • Cu-goethite • Micropore diffusion • Si-goethite

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