

EFFECTS OF SORPTION AND SECONDARY PHASE PRECIPITATION ON OXIDATIVE DISSOLUTION OF CHROMIUM HYDROXIDE

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Dissolution of $\text{Cr}(\text{OH})_3(\text{s})$ was conducted in 0.01 M NaNO_3 suspension with/without a strong oxidant (HOCl/OCl^-) through batch experiments. In the presence of the oxidant, dissolution of the solid released toxic $\text{Cr}(\text{VI})$ and was substantially accelerated compared to non-oxidative dissolution under both basic (pH 9) and acidic conditions (pH 2 and 3). As expected from the thermodynamic driving forces, the acceleration of the dissolution by oxidation increased with increasing pH. The oxidative dissolution was linear at pH 9 and 3, consistent with pseudo zero-order kinetics for steady state dissolution. At pH 2 under oxidizing conditions, by contrast, the rate of Cr release decreased rapidly with time and the dissolution ceased in 2.5 h resulting from an inhibitory process. The product of the oxidative dissolution, $\text{Cr}(\text{VI})$, strongly sorbed to $\text{Cr}(\text{OH})_3(\text{s})$ under acidic conditions. The extent of $\text{Cr}(\text{VI})$ sorption increased with decreasing pH as is typical for anions and reached the maximum at pH 3. $\text{Cr}(\text{VI})$ sorption followed a Langmuir type isotherm and reached the maximum sorption densities at $307.8 \pm 8.3 \mu\text{mol/g}$ and $271.0 \pm 9.7 \mu\text{mol/g}$ at pH 3 and 2, respectively. The surface saturation of the solid with sorbed $\text{Cr}(\text{VI})$, however, did not result in the inhibition of the dissolution because (1) cessation of the dissolution was observed at only pH 2 and (2) the rate and the extent of the oxidative dissolution was independent upon the amount of sorbed $\text{Cr}(\text{VI})$ at both pH 2 and 3. Instead, the inhibited dissolution at pH 2 was attributed mainly to the secondary phase precipitation at a rate balancing that of the oxidative dissolution. A mixed $\text{Cr}(\text{III})/\text{Cr}(\text{VI})$ (hydr)oxide, which could be a $\text{Cr}(\text{III})$ end member of a solid solution with ferric hydroxy chromate phases reported elsewhere, was assumed to precipitate as a secondary phase.