

Surface Induced Ni(II) Precipitation at the Palygorskite-Solution Interface Revealed by EXAFS, HRTEM, and DRS

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The sorption mechanisms of Ni at palygorskite/solution interfaces were investigated by a combination of macroscopic batch sorption studies, transmission electron microscopy (TEM), diffuse reflectance spectroscopy (DRS), and extended X-ray absorption fine structure (EXAFS) spectroscopy.

The results demonstrated that the mechanisms of Ni sequestration vary as a function of reaction time, pH, ionic strength, and temperature. Below pH 6, the sorption of Ni was dominated by outer-sphere and inner-sphere surface complexation. Above pH 7.5, the Ni-Ni distances ($R_{\text{Ni-Ni}}=3.09 \text{ \AA}$) determined by EXAFS suggested the formation of α -Ni(OH)₂ type of precipitates, which was different from those of Ni-Al LDH ($R_{\text{Ni-Ni}}=3.06 \text{ \AA}$) and β -Ni(OH)₂ ($R_{\text{Ni-Ni}}=3.13 \text{ \AA}$). Wavelet transform analysis of EXAFS data and DRS characterization further confirmed this result. Ni-rich surface precipitates formed with the initial Ni concentration as low as 0.07 mM, with the sorption density of $\Gamma=0.09 \text{ \mu mol m}^{-2}$, which corresponds to a 0.3% monolayer coverage for palygorskite. In contrast, at this low level of Ni concentration, surface precipitates have not form with γ -Al₂O₃.

We further tested the role of mineral surface in the Ni precipitates formation. The comparison of Ni sorption mechanisms on palygorskite, sepiolite, montmorillonite, and γ -Al₂O₃ revealed that for both the Ni/palygorskite and Ni/sepiolite systems, the sorption isotherms exhibited linear shape and the precipitate phases were determined to be α -Ni(OH)₂ precipitates and likely precursor Ni-rich phyllosilicates. This finding differed from the Ni/ γ -Al₂O₃ system, where DRS indicated a Ni-Al precipitate. The similar reactivity of the palygorskite-sepiolite minerals is reasonable because both minerals are chain-structure phyllosilicates. The findings presented in this study provide substantial novel and fundamental knowledge to improve the current understanding of Ni sorption and sequestration at the mineral/water interfaces. Adsorption and precipitation reactions described herein influence the fate and transport of Ni on larger scales in the environment.