

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

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Sorption reactions at the mineral/water interface control the fate and transport of trace metals on larger scale in aqueous geochemical environments. However, a good understanding of the structure-reactivity relationship at mineral/water interface is still not clearly established. While extensive studies have focused on layered structure clay minerals, we chose a chain-type clay mineral (palygorskite) as the adsorbent and investigated the mechanisms of Ni uptake with a combination of macroscopic batch studies, transmission electron microscopy (TEM), diffuse reflectance spectroscopy (DRS), and extended X-ray absorption fine structure (EXAFS) spectroscopy.

The results demonstrated that below pH 6, the sorption was dominated by outer-sphere and inner-sphere surface complexation. Above pH 7.5, the EXAFS data suggested the formation of α -Ni(OH)₂ type of precipitate, in agreement with its linear type sorption isotherm. A special finding is that the precipitates can form at a very low Ni concentration (~0.07 mM), with the sorption density of $\Gamma=0.09 \mu\text{mol m}^{-2}$, which corresponds to a 0.3% monolayer coverage for palygorskite. In contrast, at this low level of Ni concentration, surface precipitates have not formed with γ -Al₂O₃. We assume that Ni can be directly induced to precipitate on palygorskite surface (we call it “continuous nucleation”), differing from the traditional adsorption-to-polymerization process on γ -Al₂O₃ surface (we call it “staged nucleation”).

We further tested the role of mineral surface in the Ni precipitates formation. It was revealed that linear shape isotherm was also observed for Ni sorption on sepiolite, a clay with similar structure and chemical composition of palygorskite, indicating a similar reactivity of the both chain-structure phyllosilicates. The findings not only improved the current understanding of metal sequestration at the mineral/water interfaces, but also provided new insights into the surface reactivity of clay minerals.