NICKEL SPECIATION USING IN-SITU SPECTROSCOPIC AND MICROSCOPIC APPROACHES

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The speciation, mobility, bioavailability, reactivity, and fate of trace elements in soils and ground waters are controlled by equilibrium processes, as well as dynamic or kinetic pathways. The understanding of adsorption and desorption mechanisms is therefore of fundamental importance. Batch studies provide an efficient tool to determine partitioning coefficients of metal ions at the solid-water interface, but final conclusions on the mechanisms of the reactions are limited. An excellent way to glean mechanistic information and speciation about metal interactions on soil components is to apply surface spectroscopic and microscopic techniques (Charlet and Manceau, 1992, Fendorf et al., 1994).

Studies using surface analytical methods have shown that the adsorption of heavy metals on clay and oxide surfaces can result in the formation of multinuclear or polynuclear surface complexes (Charlet and Manceau, 1992, Fendorf et al., 1994, O'Day et al., 1994). Such surface complexes, or surface precipitates, have been observed at metal surface loadings far below a theoretical monolayer coverage and in a pH range well below the pH where the formation of metal hydroxide precipitates would be expected according to the thermodynamic solubility product (O'Day et al., 1994). Such precipitates could significantly affect the bioavailability, mobility, and the fate of metals in soil and water environments.

Pyrophyllite was chosen as a model system in order to elucidate adsorption and desorption mechanisms of transition and heavy metals on soil components. Prophyllite shows little deviation frome the ideal formula of the dioctahedral structure of 2:1 clays and has a negligible layer charge. The adsorption of metal ions on pyrophyllite can therefore be ascribed to edge surface sites only.

The adsorption of Ni on pyrophyllite was studied at various metal concentrations and ionic strengths. The adsorption behavior can be divided into two pH regions. In the lower pH region (pH<7) the relative nickel adsorption increased with decreasing ionic strength and initial nickel concentration. In the higher pH region (pH>7), but still well below the pH where the formation of Ni-hydroxide would be expected according to the thermodynamic solubility product, Ni removal from solution increased sharply up to 100% and did not exhibit any dependence on initial metal and salt concentrations. Nickel adsorption isotherms performed at pH=6 and pH=7.5 support these findings. Both data sets can be fitted well by a Freundlich isotherm, $y=Kx^\alpha$, where y is the amount of nickel adsorbed and x denotes the nickel concentration is solution. At pH=6 the nickel adsorption is nonlinear with a Freundlich exponent, α, of 0.67, while at pH=7.5 the adsorption appears to be linear with an exponent, α, of 0.98. One can hypothesize that there is a change in the adsorption mechanisms of nickel on pyrophyllite with increasing pH. Furthermore, the linear adsorption behavior in the higher pH region i. e., pH>7, can be interpreted as an indication that multinuclear or polynuclear surface complexes were formed.

The hypothesis that surface precipitates were formed is supported by kinetic measurements and desorption experiments. Nickel removal from a solution is fast at pH=6, whereas it becomes slow at pH=7.5. Desorption experiments resulted in pronounced hysteresis even in the case where the pH of the solution was lowered to pH=4. One can speculate that once surface precipitates are formed, the detachment of nickel ions from the surface precipitates is very slow, determining the overall rate of the desorption process and causing the observed hysteresis.

Surface analytical techniques such as high-resolution transmission electron microscopy (HRTEM), scanning force microscopy (SFM) and extended x-ray absorption fine structure (XAFS) spectroscopy were employed to find direct evidence for the presence of multinuclear Ni surface complexes. HRTEM images from Ni treated samples (pH=7.5) reveal that discrete crystalline particles were formed on the pyrophyllite surface. The interatomic distance, backscattering atom type and coordination number (N) for each atom derived from the analysis of XAFS spectra show that the first coordination shell consists of N≈6 O atoms at 2.02-2.04 Å, independent of the Ni sorption density. As Ni surface loading on pyrophyllite increased, the number of Ni second-neighbor atoms at a distance of 2.98-3.00 Å increases from N≈1 to N≈5. Compared to crystalline $Ni(OH)_2$ (s), Ni-Ni distances are shortened about 0.1 Å. At very low Ni sorption density on pyrophyllite, second-neighbor backscattering from Ni eventually disappears and second-neighbor backscattering is from Si or Al atoms only. XAFS data suggest the presence of approximately 1-2 second-neighbor atoms. With increasing Ni sorption density the number of second-neighbor backscattering from Si or Al atoms at about 3 Å remains almost constant.

The Debye-Waller factors were constrained to agree closely with reference compounds, good fits were obtained and a large data range (up to 14K) was used, though it must be mentioned that the solution of the second shell is not unique. Our most likely explanation for the observed data is the formation of mononuclear complexes at low surface coverage and the continuous formation of possibly oxy- or hydroxy-bridged multinuclear surface complexes in addition to mononuclear complexes with increasing Ni sorption density.

The results show that surface precipitates must be considered in modeling surface complexation reactions and in speciating metals in natural environments. The use of surface spectroscopic and microscopic techniques is an excellent way to obtain information on metal speciation and mechanisms.

References :

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