

THE LINK BETWEEN CLAY MINERAL WEATHERING AND THE FORMATION OF NI SURFACE PRECIPITATES

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Spectroscopic and microscopic studies have shown that Ni and Co sorption by clay minerals may proceed via formation of surface precipitates, which may lead to a significant long-term stabilization of the metals within the soil profile. X-ray absorption fine structure (XAFS) studies suggested the formation of several mineral phases with distinct solubilities. While turbostratic α -type metal hydroxides may precipitate from pure metal solutions, the formation of layered double hydroxides (LDH) and of 1:1 or 2:1 phyllosilicates requires the release of Al and Si from clay minerals. Due to similar metal-metal distances in their hydroxide layers/sheets and due to the relatively weak backscattering from the light elements Al and Si, however, discrimination of these phases by XAFS is difficult.

In this paper we present a triplet approach to study the formation of surface-induced Ni precipitates over a period of up to one year at room temperature. First, we used various sorbents to investigate the role of different surfaces and elements released by them. Second, we employed multiple scattering analysis of XAFS spectra for an improved identification of sorption processes, and complement this technique by DRS and thermal analysis for a more precise distinction of solid phases. Third, we investigated a set of reference compounds with properties close to those of the potential surface-induced precipitates.

Our results confirm that in the presence of easily soluble Al hydroxide Ni-Al LDH is the initial precipitate under circum-neutral conditions, while α -type Ni hydroxide forms in the absence of Al hydroxide. Only solutions heavily oversaturated with respect to Ni hydroxides favor the initial formation of α -Ni hydroxide. However, this α -Ni hydroxide subsequently transforms into Ni-Al LDH in the presence of Al hydroxide. Furthermore, Si released by sorbent phases may cause a nitrate-by-silicate exchange in the hydrated anionic interlayer space of LDH. Such an exchange reaction followed by silicate polymerization transformed LDH into a Ni-Al phyllosilicate precursor. However, neither the further transformation of the precursor phase into a Ni-Al phyllosilicate, nor the direct formation of phyllosilicate from solution could be observed, even when Si concentration in solution was as high as 1.5 mmol/L.

The resistance of the precipitates against dissolution by protolysis and complexation with EDTA gradually increased from α -Ni hydroxide to Ni-Al LDH to the phyllosilicate precursor. Thus, the formation of surface-induced Ni precipitates and their subsequent aging may reduce the risk of Ni-polluted soils and sediments. We found, however, that organic ligands reduce or prevent the formation of such precipitates. Since organic ligands are present in many soils, the stabilization of metals by precipitation as LDH or related phases may be of lesser importance than was initially believed.

