

**ADVANCES IN ENVIRONMENTAL REACTION  
KINETICS AND THERMODYNAMICS:  
LONG-TERM FATE OF ANTHROPOGENIC CONTAMINANTS**

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**FORMATION AND STABILITY OF NICKEL SOIL PRECIPITATES**

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**Introduction**

The fate of metal contaminants in polluted soils is primarily controlled by sorption and precipitation reactions at mineral surfaces. The formation of secondary precipitate phases in the soil can significantly reduce elemental toxicity and bioavailability, sequestering metals into relatively stable phases of low solubility. While most current models consider only sorption to solid surfaces and precipitation of single metal hydroxide phases when considering contaminant metal speciation in the environment, there is increasing evidence that mixed metal precipitate phases may be equally important in determining metal fate. At present, however, limited thermodynamic and kinetic data is available with regard to the formation of these mixed metal precipitate phases, making it difficult to assess the extent of their impact in natural systems.

Several laboratory studies have shown that the sorption of Ni, Zn, Co and other ions on Al-bearing clay minerals and metal oxides results in the formation of mixed metal-Al hydroxide precipitates with a layered double hydroxide (LDH) structure similar to that of hydrotalcite<sup>1-3</sup>. Nickel LDH phases have been observed on various substrates at low surface loadings and conditions undersaturated with respect to the formation of Ni(OH)<sub>2</sub>. Their formation on model substrates and soil clay fractions is rapid at pH values of 6.8 or above, with precipitate formation observable within 24 hours<sup>4,5</sup>. As the

surface precipitates age, metal release decreases substantially, indicating increased stability of the metal hydroxide phases<sup>6</sup>. However, few studies have attempted to determine the formation and stability of these phases in whole soils, where the presence of organic material and other solid phases may inhibit LDH formation either by competing for available Ni ions or by preventing Al release.

In this study, we have carried out laboratory studies of nickel sorption and desorption on several whole soils, monitoring nickel speciation in the soils for up to six months from the initial addition of aqueous nickel. Additionally, we have determined thermodynamic parameters for a number of model phases representing the various possible nickel surface precipitate phases for this system in order to assess their relative stability under equilibrium conditions. The combination of these approaches will begin to provide direct information on the extent of the role that Ni-Al hydroxide phases will play in determining nickel speciation and availability in contaminated soils under environmental conditions.

## Experimental

### Nickel sorption and desorption

Three soils were used for the sorption experiments (see Table 1). In the Matapeake and Berryland soils, kaolinite and vermiculite are the major clay mineral phases, while the Fort Ellis soil consists primarily of montmorillonite. Soils were added to a solution of 0.1 M NaNO<sub>3</sub> at 12 g/L and hydrated overnight before the addition of aqueous Ni at a concentration of 3 mM. Soil slurries were maintained at pH 6, 7 or 7.5 through the addition of 0.1 M NaOH. Samples were shaken for 1 month with periodic sampling for Ni, Al and Si and then stored for up to 6 months. Desorption studies were conducted at 1 month and 4 or 6 months using a HNO<sub>3</sub> solution at pH 4.0 and a 1 mM EDTA solution at pH 7.5. These experiments were carried out using a replenishment method with solutions changed every 24 hours for 2 weeks.

**Table 1.** Soil properties

Soil	Type	Clay content	Organic matter
Matapeake	silt loam	12 %	1.5 %
Berryland	loamy sand	6 %	9.0 %
Fort Ellis	reference clay soil	34 %	5.4 %

### Nickel speciation

Ni speciation on the solid phases was determined using Extended X-ray Absorption Fine Structure (EXAFS) analysis. During the first 30 days of the experiment, samples were collected by filtration onto a 0.2 µm filter, washed with 1-2 mL of deionized water to remove entrained solution and frozen until analysis could be conducted. At one month and again at six months, approximately 2 g of solids were separated from solution by centrifugation, washed with deionized water and freeze-dried for 24 hours. EXAFS spectra of the spiked soils were collected at NSLS beamline X-11A and APS beamline 5-BM-D from 200 eV below to 800 eV above the Ni K-edge. Data were collected either in fluorescence using a Lytle cell filled with flowing Ar gas or in transmission using an ion chamber filled with N<sub>2</sub>, depending on Ni loading.

EXAFS data were extracted from the raw spectra using the Sixpack suite of programs for background removal and  $\chi$  extraction. Sample spectra were compared to reference standards using linear combination fitting to spectra of reference Ni mineral and sorbed phases collected under identical conditions. The standards used in the linear combination fitting were determined using principal component analysis of the sample spectra followed by target transformation.

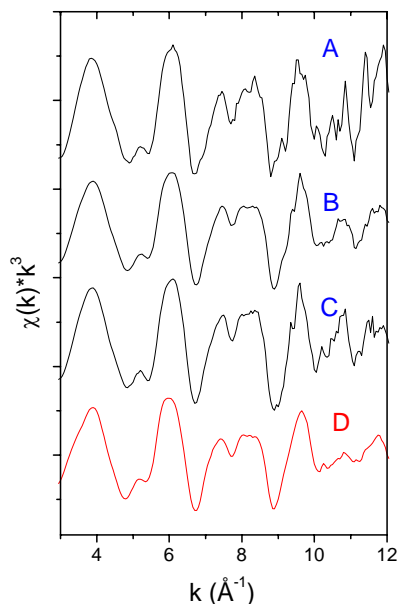
#### Thermodynamic analysis

Heats of formation were determined for a number of model nickel-aluminum LDH phases with varying Ni:Al ratios and anion interlayers. These phases were prepared by titration of a Ni-Al solution to pH 6.9 following the method described by Taylor<sup>7</sup> and their identities confirmed by both XRD and EXAFS analysis. Heats of formation were determined using high temperature oxide-melt calorimetry and acid-solution chemistry as described in Allada *et al.*<sup>8</sup>. Nickel hydroxide, carbonate and phyllosilicate phases ( $\text{Ni}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$ ) were also analyzed in a similar manner.

#### **Results**

Nickel uptake increases in all three soils as a function of pH. The Fort Ellis soil showed the greatest Ni loading after one month, at 16,000 mg/kg at pH 7.5, followed by the Berryland (13,000 mg/kg) and Matapeake (9,000 mg/kg) soils. Aluminum release to solutions was highest in the Berryland soil, while the Matapeake and Fort Ellis soils had similar release profiles. Al released to solution was 2-5 times higher in the Berryland and Matapeake soils when no Ni was added, but unchanged for the Fort Ellis soil.

EXAFS results indicate the presence of Ni-Al hydroxide phases in the Matapeake soil at pH 7 and 7.5 within 3 days (Figure 1). The Berryland soil also shows similar evidence at pH 7.5, but little precipitate formation at pH 7 even after a month. EXAFS results from the Fort Ellis soil do not seem to indicate the formation of Ni-AL hydroxide phases at any pH. Desorption experiments indicate much higher release of Ni in the EDTA solution, consistent with the formation of surface precipitate phases. At pH 7, longer aging times result in decreased release of Ni from the Matapeake and Berryland soils.



**Figure 1.** EXAFS spectra of pH 7.5 soils at 1 month. A) Fort Ellis B) Berryland C) Matapeake D) reference Ni-Al layered double hydroxide phase

These results suggest that the availability of Al for release from the mineral substrate plays a dominant factor in determining whether Ni-Al hydroxide phases form in soils. Organic matter also may inhibit formation of these phases, particularly at lower pH. Thermodynamic analysis indicates that in natural soils, these mixed hydroxide phases are likely to form with a carbonate interlayer. An evaluation of whether the increased long term stability of surface precipitates results from surface transformations to phyllosilicate type phases is ongoing.

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