

# Formation and Dissolution Kinetics of Mixed Metal Hydroxide Phases in Soils

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## Introduction

The formation of polynuclear metal hydroxide complexes and surface precipitates can play a significant role in reducing the toxicity and bioavailability of a wide range of metal contaminants in the soil environment. . In recent years, several studies have suggested that the formation of surface precipitate phases may occur at similar timescales to absorption reactions, and thus have the potential to play a significant role in removing metal ions from solution. In particular, the formation of mixed metal-Al hydroxide precipitates (often referred to as layered double hydroxide, or LDH, phases), has been indicated when metal ions are sorbed onto Al-bearing clay minerals for a number of metals of environmental interest, including Co, Cr, Cu, Ni and Zn. These precipitates have a structure similar to hydroxalite, with substrate derived aluminum substituting into the octahedral layer. Laboratory studies indicate a low solubility for these LDH phases under many typical soil conditions that decreases significantly as the precipitates age. For this reason, the presence of these phases in soils at contaminated sites could result in metal bioavailabilities much lower than would be predicted from the total metal concentration, potentially reducing or eliminating the need for costly remediation at these locations.

In order to assess the likelihood of LDH formation in a contaminated soil, it is first necessary to develop a better mechanistic model of how these precipitates form and change over time. At present, most of the work carried out on LDH phases has used model substrates, primarily clays and metal oxides. These studies have shown that formation of Ni LDHs on pyrophyllite and kaolinite materials at pH 7.5 is quite rapid, occurring within 4-24 hours of Ni addition to solution [1, 2]. Much less is known about the formation of these compounds in heterogeneous soils, where environmental conditions such as soil pH, organic matter content, and multiple mineral phases can all affect precipitate formation rates and stability. One study carried out on a whole Delaware soil did indicate the presence of LDH phases within 24 hours at pH 7.5 [3]. However, the soil used in this study had a low percentage of soil organic matter (SOM), which has been shown to inhibit LDH formation on clay substrates [4]. For this reason, more information is needed to determine whether LDH phases can play a significant role in Ni sequestration in contaminated soils. In this study, we analyzed the short term kinetics of Ni sorption and precipitate formation in three whole soils with varying clay fractions and soil organic matter content at pH 7. Wet chemical studies of Ni uptake over the first 48 hours after Ni addition were combined with XAS analysis of Ni speciation in the solid phase in order to assess the effects of changing soil physical and chemical parameters on Ni uptake and rates of precipitate formation.

## Methods and Materials

Three soils were used for the sorption experiments (see Table 1). The Matapeake and Berryland soils are common Delaware soil types. Since no Delaware soils contain high clay contents, the Fort Ellis reference soil from was also purchased

for use in these experiments. In the Matapeake and Berryland soils, kaolinite and vermiculite are the major clay mineral phases, while the Fort Ellis soil consists primarily of montmorillonite.

**Table 1: Soil properties**

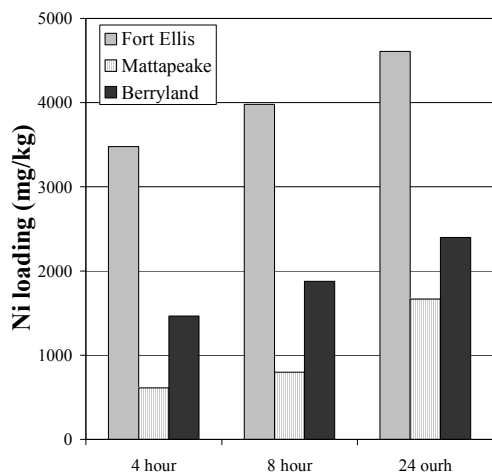
Soil	Type	Clay content	Organic matter
Matapeake	silt loam	12 %	1.5 %
Berryland	loamy sand	6 %	9.0 %
Fort Ellis	clay soil	34 %	5.4 %

Kinetic experiments were conducted at the Advanced Photon Source to remove the possibility of continued Ni reaction during storage. Soils were added to a solution of 0.1 M NaNO<sub>3</sub> at 12 g/L in a polycarbonate bottle and hydrated overnight before the addition of 3 mM aqueous Ni as Ni(NO<sub>3</sub>)<sub>2</sub>. The slurries were continuously stirred and bubbled with N<sub>2</sub> before Ni addition and each time the bottle was opened to remove CO<sub>2</sub>. A pH of 7 was maintained throughout the experiment by the addition of 0.1 M NaOH. To obtain precipitate samples for XAS analysis, 15 mL of slurry was removed from the reaction bottle and filtered through a 0.2 μm filter. The filter was then washed with 1 mL of de-ionized water to remove entrained aqueous Ni, and mounted between two pieces of Kapton tape.

The XAS experiments were performed in fluorescence mode at 5-BM-D. The incident beam was measured by an ion chamber and locked constant using a feedback mechanism, and the Ni fluorescence was measured using a Lytle detector. In order to obtain Ni-K edge spectra within 1.5-2 hours, quick-EXAFS scans were used. For each sample, 16 scans were collected from 200 eV below to 800 eV above the absorption edge at a rate of 5 mins/scan, and averaged to produce a single spectrum. EXAFS data were extracted from the raw spectra using the Sixpack suite of programs for background removal and χ 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.

## Results

Previous sorption experiments conducted under identical conditions showed that Ni sorption onto the three soils at pH 7 was much greater for the Fort Ellis soil than either of the two Delaware soils. Figure 1 shows calculated Ni loadings for each soil based on loss from solution various time intervals over the 1<sup>st</sup> 24 hours of the experiment. Ni sorption onto the Berryland soil was enhanced relative to the Matapeake soil, which has a similar clay composition, by the much higher concentration of SOM present.



**Figure 1: Calculated Ni loading on soils during reaction period.**

The formation of Ni precipitate phases can be observed in the EXAFS data by the growth in intensity of the second shell Ni-Ni interactions in the Fourier Transforms of the XAS spectrum for each soil. Figure 2 shows data for each soil at 24 hours after the addition of Ni to the soil slurry. Nickel precipitate formation begins in the Matapeake soil within 10 hours, based on the growth of Ni-Ni interactions in the Fourier Transformed EXAFS data. Growth of the precipitate phase continues through at least 48 hours (the longest time sampled in this experiment), while sorption data showing continued Ni uptake through 21 days suggests that the precipitate phase continues to increase long beyond this time. In the Berryland soil, precipitate formation is slower, beginning at 18 hours despite the higher overall Ni loadings on the soil. Precipitate growth between 24 and 48 hours is also retarded compared to the Matapeake soil. As with the Matapeake soil, Ni continues to be removed from solution at longer times, suggesting that precipitate formation likely continues beyond the times investigated here. While the Fort Ellis soil had the highest nickel loading at all times during the experiment, precipitate formation in this soil was much slower than in either of the Delaware soils. Little precipitate formation was observed during the first 24 hours, with significant Ni-Ni interactions not observed until 36 hours after Ni addition.

Analysis of the EXAFS data from the Matapeake and Berryland samples at longer times (36 to 48 hours) shows a dampening of the  $\chi$ -transformed signal at approximately  $8 \text{ \AA}^{-1}$  characteristic of LDH precipitates [5]. The identity of the precipitate phase in the Fort Ellis soil is harder to determine due to the lesser extent of Ni precipitation in this system at 48 hours. Experiments run for longer times (21 days) on these soils, however, suggest that the Ni precipitates on the Fort Ellis soil are not LDH phases, but  $\text{Ni}(\text{OH})_2$ . These results are consistent with earlier experiments using kaolinite and montmorillonite, suggesting that the composition of the clay fraction of the soil plays a dominant role in determining the type of Ni precipitate formed.

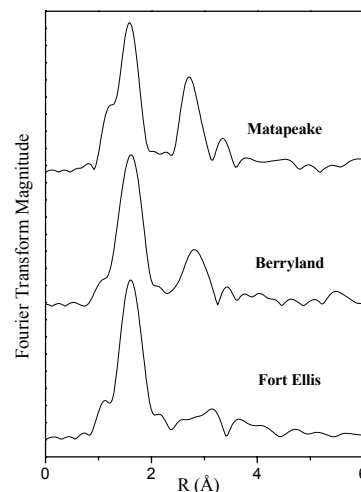
## Discussion

The nature of precipitate formation in the Matapeake soil is similar to that for previous experiments using a pure kaolinite substrate [2]. The apparent slower rate of precipitate formation in this soil compared to that for pure kaolinite (where

LDH formation was apparent within the first hour) may be due to the much lower overall Ni loading in this system, which results in a noisier and more reduced EXAFS signal. The much slower rate of precipitate formation in the Berryland soil is due to the much higher SOM content, which reacts with the aqueous Ni to form Ni-organic matter complexes and may also reduce Al release from the solid phase. However, the formation of Ni precipitates is only retarded, not blocked, by even this high concentration of soil organic matter, suggesting that, over the long term, Ni speciation in high SOM soils may still be determined primarily by the clay mineralogy of the soil.

The formation of  $\text{Ni}(\text{OH})_2$ , rather than Ni-LDH, in the Fort Ellis soil is also predicted by the clay mineralogy of the soil, as experiments with montmorillonite have not detected Ni LDH formation. Soluble Al concentrations measured in the Fort Ellis slurry are much lower than the Matapeake or Berryland soil, despite the higher clay content. Due to this lack of soluble Al, Ni-LDH phases never reach saturation conditions on the soil surface, and  $\text{Ni}(\text{OH})_2$  formation occurs instead. The longer time for precipitate formation in this soil indicates that  $\text{Ni}(\text{OH})_2$  formation kinetics are much slower, explaining why Ni-LDH phases are more likely to occur when soluble Al is present.

Based on these results, the formation of Ni-LDH phases is likely to occur in soils with neutral to basic pH that contain clays such as pyrophyllite and kaolinite that can provide a source of easily soluble Al. The retarding effect of organic matter on precipitate formation seen here may be reduced at higher pHs, as Ni sorption is likely to increase, suggesting that methods such as soil liming may be an effective means of inducing Ni precipitation in contaminated soils.



**Figure 2: Fourier Transformed EXAFS data for each soil at 24 hours after Ni addition**

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## References

1. Scheidegger, A.M., G. Lamble, and D.L. Sparks, J. Colloid Interface Sci. **186**, 118-128. (1997)
2. Scheidegger, A.M., D.G. Strawn, G. Lamble, and D.L. Sparks, Geochim. Cosmochim. Acta. **62**(13), 2233-2245. (1998)
3. Roberts, D.R., A.M. Scheidegger, and D.L. Sparks, Environ. Sci. Technol. **33**, 3749-3754. (1999)
4. Nachtegaal, M. and D.L. Sparks, Environ. Sci. Technol. **37**(3), 529-534. (2003)
5. Scheinost, A.C. and D.L. Sparks, J. Colloid Interface Sci. **223**, 167-178. (2000)