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 hydrotalcite, 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 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

<table>
<thead>
<tr>
<th>Soil</th>
<th>Type</th>
<th>Clay content</th>
<th>Organic matter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Matapeake</td>
<td>silt loam</td>
<td>12 %</td>
<td>1.5 %</td>
</tr>
<tr>
<td>Berryland</td>
<td>loamy sand</td>
<td>6 %</td>
<td>9.0 %</td>
</tr>
<tr>
<td>Fort Ellis</td>
<td>clay soil</td>
<td>34 %</td>
<td>5.4 %</td>
</tr>
</tbody>
</table>

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 NaNO₃ at 12 g/L in a polycarbonate bottle and hydrated overnight before the addition of 3 mM aqueous Ni as Ni(NO₃)₂. The slurries were continuously stirred and bubbled with N₂ before Ni addition and each time the bottle was opened to remove CO₂. 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 1st 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.

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...
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 χ-transformed signal at approximately 8 Å⁻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 Ni(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, but 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 Ni(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 Ni(OH)₂ formation occurs instead. The longer time for precipitate formation in this soil indicates that Ni(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.

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References