

## **Kinetics and mechanisms of nickel surface precipitation in multi-sorbent systems: a spectroscopic study**

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### **Abstract**

Contamination of soils with toxic metals derived from industrial, municipal, and agricultural sources is a worldwide concern. Recent metal sorption studies have shown that surface precipitates can form on clay minerals, particularly with metals such as Cr, Mn, Ni, and Zn. The surface products are either stable metal-aluminum layered double hydroxides when Al is present in the sorbent structure or metal hydroxides when Al is absent in the sorbent structure. Over time, the surface product evolves into a precursor metal phyllosilicate. However, in heterogeneous soil systems clay minerals are intimately associated with organic matter and metal oxides, which could mask the mineral surface from metals in solution and could compete with the clay mineral surface for metal uptake. Therefore, the objective of this study is to elucidate the effects of a Natural Humic Acid (NHA) and a goethite coating on the mechanisms of Ni and Zn surface precipitate formation and stabilization on a kaolinite surface.

The kinetics of Ni partitioning to kaolinite, coated with either goethite or NHA, were assessed in both batch and stirred-flow reaction chambers. Reaction conditions were pH = 7.0 - 7.5, I = 0.02 M, and an initial Ni concentration of 3 mM in the batch reactor and 0.05 mM in the stirred-flow reactor. Selected samples were retained for in-situ characterization of the sorption complex structure with extended x-ray adsorption fine structure spectroscopy (EXAFS) and thermogravimetric analysis (TGA).

Macroscopic sorption experiments show a fast initial Ni uptake followed by a slow continued Ni removal in all systems. The systems coated with NHA or goethite were more efficient in removing Ni from solution than kaolinite alone. Desorption experiments, using the background solution as a desorption agent, showed an increased stability of the Ni sorption complex with aging. EXAFS studies indicate the growth of a Ni containing precipitate over time in all systems. This Ni containing precipitate is similar in structure to brucite, with Ni and Al in the octahedral layer. Further evidence for the formation of a Ni containing precipitate phase is obtained from TGA studies which indicate sillication of the precipitate on the kaolinite surface. These findings suggest that the incorporation of Ni and other first row transition metals in stable surface precipitates might be an important way to sequester first row transition toxic metals in the environment such that they are less mobile and perhaps less bioavailable.

**Keywords:** surface precipitate, XAS, kinetics

### Introduction

Incorporation of first row transition metals into stable surface precipitates can play an important role in reducing the bioavailability of these metals in non-acidic soils. Research predominantly done in the last decade has shown that the availability of potential toxic metals such as Cr, Ni, Co, Cu and Zn is greatly reduced in the presence of clay minerals, quartz and aluminum oxides (Cheah *et al.*, 1998; Elzinga and Sparks, 1999; Fendorf *et al.*, 1994; Fendorf and Sparks, 1994; Fendorf and Zasoski, 1992; Ford and Sparks, 2000; Junta and Hochella Jr., 1994; Manceau *et al.*, 1999; O'Day *et al.*, 1994a; O'Day *et al.*, 1994b; O'Day *et al.*, 1994c; Scheidegger *et al.*, 1997; Scheidegger *et al.*, 1998; Scheinost *et al.*, 1999; Scheinost and Sparks, 2000; Schlegel *et al.*, 1999; Thompson *et al.*, 1999a; Thompson *et al.*, 1999b). In these studies numerous spectroscopic techniques, i.e. extended x-ray absorption spectroscopy (EXAFS), electron paramagnetic spectroscopy (EPR) and diffuse reflectance spectroscopy (DRS), to name a few, have been used to delineate the sorption complex. It is found that most metals are incorporated into surface precipitate phases. These surface precipitates show a dramatic stabilization with aging in the model systems studied (Ford *et al.*, 1999; Scheckel *et al.*, 2000) and thus might lead to a long-term removal of potentially hazardous metals from the soil solution.

The mechanism and stabilization of a Ni containing surface precipitate is understood to occur in the following sequence. In batch reactors, containing Al free sorbents, Ni is incorporated into a  $\beta$  NiOH<sub>2</sub> phase, well below super saturation conditions. In systems where Al is readily available, Al co-precipitation with Ni is thermodynamically preferred. This precipitation may be explained by the combination of several processes (Yamaguchi *et al.*, 2001). First, the electric field of the mineral surface attracts Ni ions through adsorption, leading to a local supersaturation at the mineral-water interface. Second, the solid phase may act as a nucleation center for polyhydroxy species and catalyze the precipitation process (McBride, 1994). Third, the physical properties of water molecules adsorbed at the mineral surface are different from those of free water (Sposito, 1989), potentially causing a lower solubility of metal hydroxides at the mineral-water interface.

Further stabilization of the precipitate can occur by diffusion of Si polymers in the interlayer space of the LDH, thereby replacing the anions. Polymerization and condensation of the interlayer Si polymers slowly transforms the LDH into a precursor Me-Al phyllosilicate. Which might further develop into a tri-octahedral clay. Stabilization also occurs in precipitates formed on Al-free substrates. This stabilization is contributed to Ostwald ripening (Scheckel and Sparks, 2001).

The incorporation of potential hazardous metals into surface precipitates and the subsequent stabilization might lead to an important long-term removal of the metal from the soil solution. However, in soils, clay minerals are intimately associated with organic matter and oxides, which will mask the mineral surface from the metals in solution. Free organic matter and oxides have been found to effectively compete with the clay mineral surface for metals. Therefore, the objective of this study is to elucidate the effects of Natural Humic Acids (NHA) on mechanisms of Ni surface precipitate formation and stabilization.

There are several ways in which NHA can potentially influence the formation and stabilization of metal surface precipitates. Formation of Ni and Al organic complexes

can effectively compete with Ni and Al uptake by precipitate phases and thus will prevent the formation and subsequent stabilization of precipitate phases. On the contrary, mineral dissolution by organic acids is considered to be far more effective than hydrolysis, which leads to a larger availability of Al and Si for the stabilization of the surface precipitate. In addition to their effects on weathering, organic substances have been found to retard or enhance the formation of secondary silicate minerals.

## Materials and Methods

### Materials and preparation

The kaolinite used in this study is a well-crystallized Georgia kaolinite obtained from the University of Missouri Source Clays Depository (KGa-1, Clay Minerals Society). The kaolinite was treated for the possible presence of carbonates, organic matter and manganese/iron oxides (Jackson, 1956). The resultant solids were washed twice with NaCl, and twice with DI water. The  $<0.2 \mu\text{m}$  fraction is separated by centrifugation, dialyzed against milli-Q H<sub>2</sub>O and freeze-dried.

The NHA used in this study was isolated from a bog-soil collected in the White Mountain National Forest in Rumney, New Hampshire. The isolation procedure and characterization of the NHA are outlined elsewhere (Davies *et al.*, 1997). Essentially the soil was treated with mild solvents (a benzene-methanol mixture) to remove trapped non-humic impurities such as chlorophyll, lipids and proteins. After the pre-extraction the humic substances are extracted with aqueous base. The supernatant is brought to pH 1.0 with concentrated HCl. The remaining HA gel was freeze-dried before any further use.

A high surface area Goethite was synthesized according to the method outlined in (Schwertmann and Taylor, 1989). Initially, ferrihydrite is precipitated by adding 50 ml of 1M ferric nitrate solution to 450 mL of 1 M KOH. The suspension of amorphous hydrous ferric oxide was aged for 21 days at 25°C. This suspension was then washed via centrifugation, where DI water is used to replace the supernatant in order to remove residual KOH. The rinsed solid was then resuspended in 0.4 M HCl and shaken for 2h using a mechanical shaker (Peak *et al.*, 1999). This treatment was used to remove any remaining ferrihydrite from the surface of the goethite. The acidified goethite suspension was washed with milli-Q H<sub>2</sub>O in order to remove the HCl, dialyzed against milli-Q H<sub>2</sub>O and freeze dried. The BET surface area of the obtained goethite is  $66.49 \text{ m}^2 \text{ g}^{-1}$ .

NHA coated kaolinite samples containing 1 and 5 wt% of organic matter (these percentages of organic matter include a representative range of organic matter contents found in mineral soils (Sparks, 1995)) were prepared using the following procedure: 0.01 g (1 wt%) and 0.05 g (5 wt%) of the freeze-dried NHA were dissolved in 50 mL of a 0.05 M NaOH solution. 1 g kaolinite is slowly added while stirring the solution, after which the pH of the solution was brought to pH 3.5. This mixture was shaken for 48 h and brought to 200 mL, pH=7.5 and I=0.02 prior to the sorption experiment. Details on the coating procedure employed here can be found in Ghabbour *et al.*, (1998). For all experiments the mass of kaolinite was maintained constant ( $5 \text{ g L}^{-1}$ ) while the fraction of organic matter was varied. The CEC and BET surface area of the mixtures and individual components are given in Table 1.

**Table 1** Physicochemical characteristics of the solids used in this study.

	CEC(cmol kg <sup>-1</sup> )	BET-surface area
Kaolinite:	9.37 (pH 6.0)	14.01 m <sup>2</sup> g <sup>-1</sup>
1-wt%	25.80 (pH 5.5)	13.42 m <sup>2</sup> g <sup>-1</sup>
5-wt%	29.62 (pH 5.5)	11.68 m <sup>2</sup> g <sup>-1</sup>
HA	83.83 (pH 3.6)	1.25 m <sup>2</sup> g <sup>-1</sup>

Goethite coated kaolinite samples, containing 1-5 wt% goethite, were prepared using the method of Scheidegger *et al.* (1992). They obtained maximum goethite coating on a quartz surface close to the pzc of goethite (7.8). Essentially, 130 mg of goethite was mixed with 2.5 g of kaolinite in a pH = 7.5 and I = 0.01 M NaNO<sub>3</sub> solution. This solution was shaken for 48 hour. After settling of the particles the suspension was re-suspended in a 1 M NaNO<sub>3</sub> solution (because goethite flocculates heavily when the pH is close to the pzc). The coated kaolinite particles will be washed several times with the background solution and finally with DI water. The coated kaolinite will be oven dried at 110<sup>o</sup>C for 24 h.

### Macroscopic sorption experiments

The kinetics of Ni partitioning to kaolinite, NHA, goethite and their mixtures were studied in batch sorption experiments. Experiments were carried out in a 0.02 NaNO<sub>3</sub> background solution and at pH = 7.5, since previous research (Scheidegger *et al.*, 1997; Scheinost and Sparks, 2000) indicated that Ni-Al precipitates will form at this pH in the absence of competing sorbent surfaces. The systems were purged with N<sub>2</sub> and boiled double deionized DI water was used throughout. All (polyethylene) glassware was acid washed for at least 48 h prior to use. After hydration of the solids in 200 mL background solution, Ni from a 0.1 M Ni(NO<sub>3</sub>)<sub>2</sub> stock solution was added in 1-mL aliquots to achieve initial conditions of [Ni]<sub>0</sub> of 3 mM. The solution was undersaturated with respect to homogeneous precipitation of Ni(OH)<sub>2</sub> (Mattigod *et al.*, 1997). The pH was kept constant at 7.5 using a Radiometer pH-stat titrator for the first 2 days and by weekly manual readjustments using 0.1 M NaOH. Samples (10 mL) were periodically collected from the suspension and filtered through a 0.2 µm membrane filter. Filtered supernatants were analyzed for dissolved Ni by inductively coupled plasma optical emission spectroscopy (ICP-OES).

Solid samples were collected periodically for characterization using EXAFS spectroscopy. Solids were isolated under vacuum filtration and the wet paste was transferred to a polyethylene holder. The wet paste was sealed into the holder with 0.0005-in. thick Kapton polyimide tape to avoid moisture loss during analysis.

### XAFS data collection and analyses

X-ray absorption spectra were recorded at beamline X-11A of the National Synchrotron Light Source, Brookhaven National Laboratory. The electron storage ring operated at 2.5 GeV with an average beam current of 180 mA. The monochromator consisted of two parallel Si (111) crystals with an entrance slit of 0.5mm. Higher order harmonics were suppressed by detuning 25% from the maximum beam intensity. The monochromator position was calibrated by assigning the first inflection point on the K-absorption edge of a nickel metal foil to 8333.0 eV. The spectra were collected in fluorescence mode using an Ar-filled Lytle detector. A Co-6 filter and soller slits were

placed between the sample and the detector to reduce elastically scattered X-rays entering the fluorescence detector. The incoming beam was measured with a N<sub>2</sub>-filled ion chamber. All spectra were collected at room temperature and at least three scans were collected per sample to improve the signal to noise ratio.

XAFS data reduction was performed using the WinXAS 2.1 software package. The  $\chi$  function is extracted from the raw data by fitting a linear function to the pre-edge region and a spline function to the post-edge region, and normalizing the edge jump to unity. The energy axis (eV) was converted to photoelectron wave vector units ( $\text{\AA}^{-1}$ ) by assigning the origin,  $E_0$ , to the first inflexion point of the absorption edge. The resulting  $\chi(k)$  functions were weighted by  $k^3$  to compensate for the dampening of the XAFS amplitude with increasing  $k$  and were Fourier-transformed to achieve radial structure functions (RSF). A Bessel window with a smoothing parameter of 4 was used to suppress artifacts due to the finite Fourier filtering range between  $\Delta k = 1.5\text{-}13.8 \text{\AA}^{-1}$ . Structural parameters are extracted with fits to the standard EXAFS equation. *Ab initio* Ni-O and Ni-Ni scattering paths were generated using the FEFF 7.02 code from the refinement of the structure of lizardite where Ni was substituted for Mg in octahedral positions (Mellini, 1982). Multishell fitting was done in R space over the range of the first two shells ( $\Delta R = 1.07\text{-}2.30$ ). To reduce the number of adjustable parameters, the amplitude reduction factor,  $(S_0)^2$ , was fixed at 0.85. A thorough discussion of the fitting procedure employed here is given in Scheinost and Sparks (Scheinost and Sparks, 2000).

### Results and Discussion

Kaolinite alone accounts for only 8% of initial Ni removal (data not shown), whereas 5 wt% of free NHA accounts for 40% of Ni removal from solution. NHA is a better sorbent of Ni when free in solution than combined with kaolinite. The more HA is coated onto the kaolinite surface, the greater Ni sorption. Similar trends were observed in a study on the influence of humic substances on Co sorption by a subsurface mineral separate and its mineralogic components (Zachara *et al.*, 1994). Zachara *et al.*, found an increasing Co sorption with increasing amounts of HA coated on the mineral surfaces and concluded that the presence of a humic acid coating augmented, rather than changed the intrinsic adsorption behavior of the mineral sorbents.

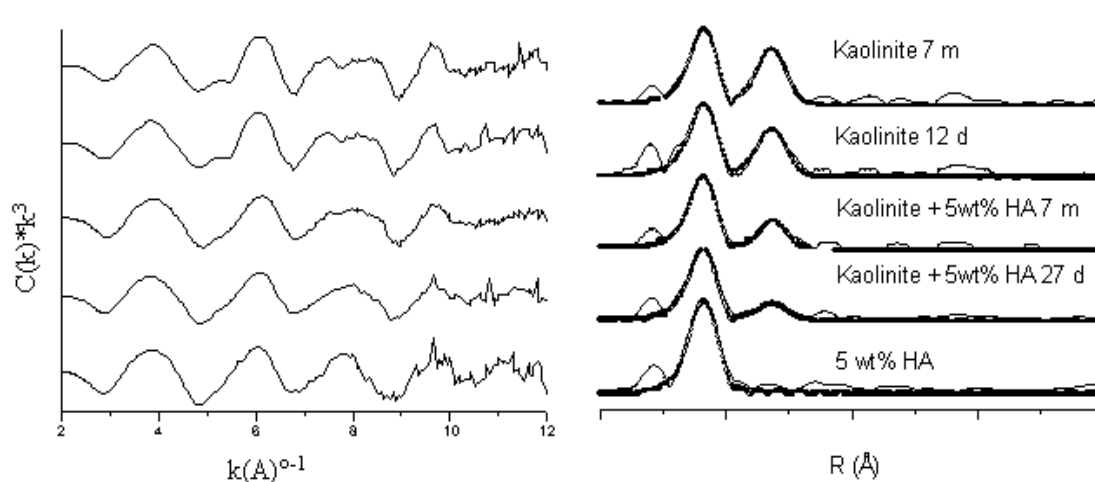
Ni sorption over the entire reaction range of the experiments show that in all kaolinite containing systems an initial fast sorption reaction is followed by a continued slow Ni uptake. This might be caused by a continuous growth of a surface precipitate away from the surface over time. The driving force for a continuous growth of the surface precipitate might be the low surface area of the kaolinite, where only a limited amount of Ni atoms can sorb and thus a relatively large amount of Ni will stay available in solution. The continued presence of Ni in solution is then a source for the growing precipitate. After an initial higher Ni sorption in the HA-kaolinite system, the HA-kaolinite systems show the same slow continued Ni removal trend, suggesting that similar removal processes are taking place.

The structure of the Ni sorption complex formed in the HA-kaolinite systems can be inferred from EXAFS analysis. Figure 1 shows the  $k^3$  weighted  $\chi$  functions (left) and radial structure functions (right) of the 5 wt% coated kaolinite systems which were

reacted with Ni for 27 days and 7 months respectively. The solid lines represent the Fourier transforms of the measured data, and the dotted lines those of the theoretical spectra derived with parameters for the fitting procedure. A good agreement between the fourier transformed EXAFS functions and theoretical fits is observed.

The first peak at 2.04 Å is indicative of backscattering from the first ligand shell, in this case O and the second peak indicates backscattering from the first Ni shell.

This second peak increases in intensity over time in both the kaolinite and the coated kaolinite systems, which indicates the growth of a Ni containing surface precipitate phase.



**Figure 1** Ni-K $\alpha$  EXAFS spectra of the kaolinite-HA systems, reacted with a 3mM Ni solution for 27 days and 7 months. The  $k^3$  weighted  $\chi$  functions are shown on the left side, and the measured (solid lines) and fitted (dotted lines) radial structure functions are shown on the right side (uncorrected for phase shifts).

The absence of a second Ni shell in the Ni-reacted HA sample indicates that these systems were not supersaturated with respect to precipitation of NiOH<sub>2</sub>. The fitted EXAFS spectra were obtained by including a Ni-O path for HA in the fitting procedure and a Ni-O and a Ni-Ni path for the other systems. Oxygen and nitrogen are both weak backscatters and thus cannot be distinguished from each other in EXAFS studies. Therefore, Ni is either bound to O or N containing functional groups of the HA. The absence of high frequency beating in the Ni-HA  $\chi$  function (Figure 1, left side) indicates the absence of higher order shells.

Since the partial replacement of Ni by Al in the octahedral layer leads to a stabilization of the precipitate, it is instructive at this point to see if any information on Al in the second shell can be obtained from the EXAFS data. Fitting of the data slightly improved by including a Ni-Al path, but lead to strange Ni-Al bond distances and coordination numbers. Since Al is a weak backscatterer, a better fit is expected since more fitting parameters are added.

Information on Al in the precipitate can be obtained from the  $\chi$  functions (Figure 1, left side). A characteristic beat pattern at 8-9 Å has been found by Scheinost and Sparks (Scheinost and Sparks, 2000) to be produced by the presence of second shell Al. This characteristic beat pattern is present in the kaolinite samples, indicating the formation of

a Ni-Al LDH, in line with former EXAFS studies (Eick and Fendorf, 1998; Scheidegger *et al.*, 1997). The absence of this peak in the HA coated kaolinite spectra indicates that the precipitate formed is more a pure NiOH<sub>2</sub> phase.

**Table 2** Best-Fit Structural Parameters Derived from XAFS Analysis.

Sample	Reaction time	Ni-O			Ni-Ni		
		CN	R(Å)	$\sigma^2(\text{Å}^2)$	CN	R(Å)	$\sigma^2(\text{Å}^2)$
HA	48h	5.8	2.06	0.004			
Kaolinite	12d	5.2	2.04	0.004	3.2	3.06	0.006
Kaolinite	7m	6.6	2.05	0.006	4.0	3.07	0.008
1wt% HA-kaolinite	1d	5.2	2.04	0.004	2.0	3.06	0.005
1wt% HA kaolinite	4d	5.0	2.04	0.005	3.0	3.05	0.006
5wt% HA-kaolinite	27d	5.7	2.04	0.005	1.0	3.06	0.005
5wt% HA-kaolinite	7m	5.4	2.04	0.006	1.6	3.06	0.006
Goethite-kaolinite	1w	5.8	2.04	0.006	3.7	3.08	0.009
$\alpha$ -Ni hydroxide <sup>a</sup>		5.5	2.04	0.005	5.6	3.09	0.006
LDH Ni/Al=1.3 <sup>a</sup>		5.4	2.05	0.004	2.8	3.06	0.004

CN = Coordination Number ( $\pm 20\%$ <sup>#</sup>)

R = Interatomic distance ( $\pm 0.02\text{Å}$ <sup>#</sup>)

$\sigma^2(\text{Å}^2)$  = Debye Waller factor

<sup>a</sup> = Adapted from Scheinost & Sparks 2000

<sup>#</sup> = Based on the results of theoretical fits to spectra of reference compounds of known structure (O'Day *et al.*, 1994c)

In Table 2 are the structural parameters, derived from EXAFS analysis, collected. The coordination number (CN) of the Ni-O shell is around 6 for all samples, indicating that Ni is surrounded by 6 O atoms in an octahedral environment. The Ni-O bond distance is the same in all samples, except for the HA samples where the Ni-O bond distance is slightly higher. The Ni-Ni bond distances are around 3.06 Å, which is significantly shorter than that of a pure Ni hydroxide phase ( $\alpha$ -NiOH<sub>2</sub>), 3.09 Å. An increase in the coordination number of the Ni-Ni shell over time indicates a growth of the precipitate with time. The low Ni-Ni coordination number in the 5 wt% HA-kaolinite mixture indicates that in these samples the development of a surface precipitate phase is still in an initial phase. The coordination number of the Ni shell should be 6 in a perfect octahedral coordination, but even in the pure kaolinite system, this is never reached. This is also an indication that partial substitution of Ni by Al in the octahedral layer took place.

Ni sorption experiments to kaolinite coated with goethite show similar nickel removal trends (data not shown). EXAFS data (Table 2) indicate the formation of a Ni/Fe LDH at the kaolinite surface, in the presence of goethite.

### Conclusions

These studies show that the incorporation of Ni and other first row transition metals in stable surface precipitates might be an important way to sequester first row transition toxic metals in the environment such that they are less mobile and perhaps less

bioavailable. This holds true even in the presence of strongly competing sorbents such as HA and goethite.

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