

Kinetics of the formation and the dissolution of nickel surface precipitates on pyrophyllite

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Abstract

The kinetics of the formation and the dissolution of Ni surface precipitates on pyrophyllite was studied in order to gain an understanding of the dynamics of heavy metal ion reactions in soils. Ni sorption at pH = 7.5 was initially fast. 25% of the initial Ni was removed within minutes. Thereafter, a gradual decrease in sorption was observed. Based on previous spectroscopic evidence, we attribute the fast reaction stage to adsorption phenomena and the slow reaction stage to nucleation processes on the pyrophyllite surface. The detachment of Ni from surface precipitates at pH = 4 and pH = 6 involves a small amount of Ni (< 10%) being desorbed relatively fast. The desorption of specifically adsorbed, mononuclear bound Ni may account for this rapid Ni release. Thereafter, Ni detachment was extremely slow, and the rate depended strongly on the experimental desorption method. Utilizing a conventional batch technique, further Ni release became negligible. The non-removal of reaction products may have caused the formation of secondary precipitates. Under steady-state conditions a constant Ni detachment rate was observed which we attribute to the dissolution of Ni surface precipitates. Compared to the dissolution of crystalline Ni(OH)₂, Ni detachment from pyrophyllite was slow. We hypothesize that the slow Ni detachment is due to the dissolution of mixed Ni–Al-hydroxides which formed prior to the desorption experiment and which have a lower solubility.

1. Introduction

Over the past several decades mechanistic interpretations and surface complexation models have been developed and applied to describe metal sorption reactions at the solid–water interface (Benjamin and Leckie, 1981; Hiemstra et al., 1989). The models are predominantly based on the idea that metal ions form complexes with surface functional groups in a manner similar to metal–ligand associations in the

solution phase. We will call this process adsorption. Few models have considered surface precipitation reactions (Farley et al., 1985). While adsorption is considered to be strictly a two-dimensional process, precipitation is three-dimensional (Corey, 1981; Sposito, 1986). According to the definition of Sposito (1986), a precipitation mechanism may be initiated by either homogeneous or heterogeneous nucleation, may involve the formation of a solid mixture either by inclusion or by coprecipitation, or may take place on the surface of a pre-existing solid phase. In the last case, the process is called surface precipitation. Interchangeably the terms multinuclear or polynuclear surface complexation are also commonly

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used since there is no defined line between multinuclear or polynuclear surface complexation and surface precipitation (Charlet and Manceau, 1993; O'Day et al., 1994). When we use the term sorption in this paper, it does not imply any particular mechanism.

Recent studies using surface spectroscopic and microscopic techniques such as X-ray absorption fine structure spectroscopy (XAFS), electron paramagnetic resonance spectroscopy (EPR), X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), scanning electron microscopy (SEM) and atomic force microscopy (AFM) have demonstrated that the formation of surface precipitates is a far more important process than previously thought (Charlet and Manceau, 1993; Fendorf et al., 1994a; Junta and Hochella, 1994; O'Day et al., 1994; Wersin et al., 1994). Using XAFS, the nucleation of heavy metals on clay and oxide surfaces has been observed at metal surface loadings far below a theoretical monolayer coverage and in a pH range well below where metal hydroxide precipitates would be expected to form according to the thermodynamic solubility product (Charlet and Manceau, 1992; Fendorf et al., 1994a; O'Day et al., 1994).

Kinetic data on the formation of surface precipitates have been primarily obtained in combination with heterogeneous nucleation reactions. The heterogeneous nucleation rate of CaF_2 on CeO_2 was enhanced only within the pH range where both Ca^{2+} and F^- were specifically bound to the pre-existing surface (Stumm et al., 1983). Similar results were observed for the nucleation of MgF_2 on TiO_2 (Stumm, 1992). On the other hand, even small concentrations of HPO_4^{2-} can inhibit nucleation of CaCO_3 (Morse and Berner, 1972; Dove and Hochella, 1993; Gratz and Hillner, 1993). The overall kinetics of heterogeneous precipitation reactions must consider that the process consists of a series of consecutive steps (Stumm, 1992): (1) adsorption; (2) surface nucleation; and (3) crystal growth. In simple cases, the slowest step is rate-determining.

Information on the dissolution of surface precipitates is scarce. One reason may be the lack of surface spectroscopic methods in the past. Without surface spectroscopic and microscopic methods it was not possible to provide direct atomic level evidence for the presence of surface precipitates. To the best of

our knowledge there are no studies on the kinetics of heavy metal detachment from surface precipitates. Information on the dissolution of surface precipitates, however, is of great importance in explaining the fate of heavy metals in soils.

The present study examines the kinetics of the formation and dissolution of polynuclear Ni complexes on the pyrophyllite surface. Ni^{2+} like many other heavy metal ions (e.g., Co^{2+} , Cd^{2+} , Pb^{2+} , Mn^{2+} , Cu^{2+} , Zn^{2+} and Cr^{3+}) has the tendency to adsorb specifically on clay and oxide surfaces and to hydrolyze within common environmental pH ranges (pH = 3–9). Pyrophyllite was chosen for these experiments because it shows little deviation from the ideal chemical formula $(\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2)$ of 2:1 clays. The dioctahedral structure of pyrophyllite consists of essentially neutral tetrahedral–octahedral–tetrahedral layers and is the prototype structure of the smectite and illite phyllosilicate groups which are very prominent in soils. The layer charge is negligible and the adsorption of ions on pyrophyllite can be ascribed to only edge surface sites (Keren et al., 1994). The edge site morphology of pyrophyllite consists of three types of edge sites: octahedral Al–OH, tetrahedral Si–OH, and transitional tetrahedral–octahedral Si–O–Al sites (White and Zelazny, 1988). In the pH range between pH = 4.5–9 the tetrahedral Si–OH sites are uncharged while the octahedral non-bridging Al–OH sites along the particle edge are negatively charged and considered to be the most reactive sites on pyrophyllite (White and Zelazny, 1988).

2. Experimental methods

2.1. Materials

Pyrophyllite ($\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2$) used in this study originated from North Carolina, U.S.A. (Ward Natural Science, 46E4630). The pyrophyllite was ground in a mortar to a size fraction of $< 125 \mu\text{m}$ and transferred to a porcelain ball mill which was one third filled with hard ball-shaped, wear-resistant media (Zirconia). The pyrophyllite was then ground dry for 30 h. The $< 2\text{-}\mu\text{m}$ clay fraction was obtained by centrifuging and decanting. The clay was saturated with Na by washing three times with 0.5 M NaNO_3 .

The clay was resuspended with distilled water and centrifuged. The clear supernatant was discarded and excess salts removed by dialysis until the electrical conductivity of the equilibrium solution was $< 10 \mu\text{S cm}^{-1}$. Thereafter, the white clay material was freeze-dried.

Pyrophyllite was characterized by X-ray diffraction (XRD; Philips, PW1729) and diffuse reflectance infrared Fourier transform spectroscopy (DRIFT; Perkin-Elmer 1720X spectrometer.) The IR spectra showed only characteristic peaks for pyrophyllite (Russel et al., 1970), while XRD spectra suggested the presence of a small amount of quartz ($< 5\%$) in addition to pyrophyllite. The specific surface area of pyrophyllite was determined by the BET method using N_2 adsorption and the ethylene glycol monoethyl ether (EGME) method (Carter et al., 1965). The variation between these two methods was small (BET = $96.3 \text{ m}^2/\text{g}$; EGME = $95 \text{ m}^2/\text{g}$) which demonstrates that no significant amount of swelling clay, such as montmorillonite, was present in the pyrophyllite. In this paper we will use the BET specific surface area value.

2.2. Kinetic studies

The kinetics of Ni adsorption on pyrophyllite were measured using a batch technique designed to maintain constant pH (pH-stat, Radiometer) and temperature (298 K) and to eliminate CO_2 by purging with N_2 . Pyrophyllite was hydrated in a 0.1 M NaNO_3 solution for 24 h prior to reaction. After hydration the pH of the suspension was adjusted to $\text{pH} = 7.5$ with 0.1 M NaOH and the mixture brought to a solid/liquid ratio of 10 g/l . Ni from a $0.1 \text{ M Ni(NO}_3)_2$ stock solution was dispensed in stepwise additions within $\sim 15 \text{ min}$ in order to avoid the formation of Ni precipitates due to local oversaturation of the suspension. The pH was automatically held constant ($\text{pH} = 7.5$) and the electrode recalibrated every 24 h. The initial Ni concentration (3 mM) and the reaction pH ($\text{pH} = 7.5$) were selected to achieve considerable Ni sorption under the experimental conditions (which are still clearly unsaturated with respect to Ni(OH)_2). Collected samples were passed through a $0.22\text{-}\mu\text{m}$ membrane filter. The clear solutions were analyzed by inductively coupled plasma emission (ICP) spectrometry for Ni. After a

reaction time of 200 h an apparent equilibrium was reached. The suspension was then poured into a vial. The vial was sealed and kept at 298 K in a desiccator containing granulated sodium hydroxide to adsorb CO_2 . The Ni-treated suspension was shaken from time to time and stored for 1–8 weeks prior to the desorption experiments.

Ni desorption experiments were performed at two different pH values using the pH-stat apparatus. The suspension pH was lowered from $\text{pH} = 7.5$ to $\text{pH} = 6$ and $\text{pH} = 4$ with 0.1 M HNO_3 and then held constant. Two different methods were employed. In the *conventional method* reaction products in the vessel (desorbed Ni and dissolved Al and Si) were not removed. In the *replenishment method* the solution was replaced every 24 h. The suspension was centrifuged and the supernatant removed and analyzed by ICP. The amount of trapped solution in the wet clay paste was determined, and the paste refilled with a 0.1 M NaNO_3 solution at $\text{pH} = 4$ and $\text{pH} = 6$ up to the initial volume. This method simulates a steady-state condition (see Section 3).

For comparison the dissolution rates of crystalline Ni(OH)_2 (Johnson Matthey Co., 90% of the particles pass through a $50\text{-}\mu\text{m}$ sieve) at $\text{pH} = 4$ and $\text{pH} = 6$ were measured at a constant ionic strength of 0.1 M NaNO_3 using the pH-stat apparatus. 140 mg Ni(OH)_2 were dissolved to give a final Ni concentration of 3 mM which corresponds to the Ni concentration used for the Ni sorption experiment described above.

3. Results and discussion

3.1. The kinetics of surface precipitate formation

The kinetics of Ni sorption on pyrophyllite was measured at $\text{pH} = 7.5$. The initial Ni solution concentration ($[\text{Ni}]_{\text{initial}} = 3 \text{ mM}$, ionic strength $I = 0.1 \text{ M NaNO}_3$) was undersaturated with respect to the thermodynamic solubility product of Ni(OH)_2 . Ni speciation was performed using a chemical equilibrium speciation program which is based on a thermodynamic database (Environmental Simulation Program, OLI Systems, Morristown, New Jersey, U.S.A.). Data reported by Glushko et al. (1972), Sverjensky (1987, and pers. commun. 1988), Shock

and Helgeson (1988), and Gurvich et al. (1993) were considered. The speciation reveals that Ni(II) is predominately present as $\text{Ni}^{2+}(\text{aq.})$ ($\sim 90\%$) and to a minor extent as $\text{NiNO}_3^-(\text{aq.})$ ($\sim 9\%$). The concentrations of hydrolysis products such as $\text{Ni}(\text{OH})^+$ and $\text{Ni}(\text{OH})_2^0$ are extremely low (Scheidegger et al., 1996). Fig. 1 illustrates the relative Ni removal as a function of the reaction time. The data suggest a rapid initial sorption reaction: 25% of the Ni is sorbed within the first 30 min. Thereafter the reaction slowed down considerably. After a reaction time of 24 h $\sim 90\%$ of the initial Ni was sorbed, and after 72 h Ni sorption was nearly complete (97% sorbed).

The observed sorption kinetics are common for heavy metal sorption on clay and oxide surfaces (Kinniburgh and Jackson, 1981; Brümmer et al., 1988). The sorption reactions are typically rapid initially, occurring on time scales of minutes or hours, then the rates diminish gradually, over time scales of days or weeks. The rapid stage is normally interpreted as an adsorption phenomenon (Kinniburgh and Jackson, 1981; Sparks, 1985). We suspect that this is the case also in our sorption experiment.

There are several interpretations of the slow reaction stage. Benjamin and Leckie (1981) and Dzombak and Morel (1986) attribute the slow sorption kinetics on mineral surfaces to adsorption onto sites

of lower reactivity. The decline in reaction rate is regarded as nonhomogeneous and has been explained by diffusion of the adsorbate into the adsorbent (Brümmer et al., 1988) or by a precipitation reaction (Davis et al., 1987). However, it is not possible to discriminate among the suggested sorption mechanisms without spectroscopic evidence (Sposito, 1986).

Wersin et al. (1989) studied the kinetics of Mn(II) sorption on FeCO_3 . At high Mn(II) concentrations, the sorption decreased considerably after a rapid initial reaction, and required several days to reach equilibrium. Electron spin resonance (ESR) spectroscopy provided evidence that the slow sorption kinetics were the result of the precipitation of a mixed MnCO_3 and FeCO_3 solid phase. Similar results were obtained studying uranium(VI) sorption on pyrite (Wersin et al., 1994).

We employed XAFS spectroscopy to discern the local atomic structure of Ni(II) sorbed onto pyrophyllite. In this paper we will briefly summarize the main results of an XAFS study by Scheidegger et al. (1996). General discussions on XAFS are given elsewhere (Charlet and Manceau, 1993; Fendorf et al., 1994b). The XAFS spectra of pyrophyllite samples treated with Ni at $\text{pH} = 7.5$ suggested the presence of surface precipitates on the pyrophyllite surface. This can be clearly demonstrated in Fig. 2. This figure illustrates radial structure functions (RSFs) of Ni-treated pyrophyllite spectra compared to the spectrum of the crystalline $\text{Ni}(\text{OH})_2(\text{s})$ model compound. With increasing surface loading ($\Gamma = 0.51 \mu\text{mol m}^{-2}$) a peak appeared at $R \approx 2.7 \text{ \AA}$ and increased in intensity with further increased Ni uptake (Fig. 2b–d). This peak, also present in $\text{Ni}(\text{OH})_2$, represents the second Ni shell and reflects backscattering among multinuclear Ni complexes. Data analysis revealed the presence of oxy- or hydroxy-bridged multinuclear surface complexes in addition to mononuclear complexes. As Ni surface loading on pyrophyllite increased, the number of Ni second-neighbor atoms increased from approximately 1 to 5, which indicates an increase in the average size of multinuclear Ni clusters. The presence of multinuclear surface complexes was depicted at low surface loading and at reaction conditions undersaturated with respect to the formation of $\text{Ni}(\text{OH})_2(\text{s})$. Spectrum b in Fig. 2 represents a sample we collected at the end of the kinetic

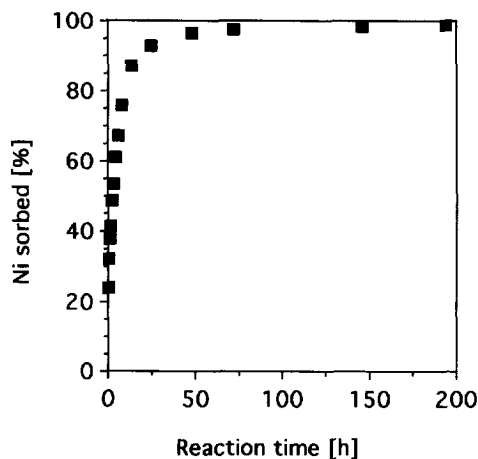


Fig. 1. Kinetics of Ni sorption on pyrophyllite from a 3 mM Ni solution at $\text{pH} = 7.5$ and an ionic strength $I = 0.1 \text{ M}$ (NaNO_3); ■ denotes the relative amount of sorbed Ni (%). The last sample of the experiment (98% sorbed, surface loading, $\Gamma = 3.1 \mu\text{mol m}^{-2}$) was collected and analyzed by XAFS.

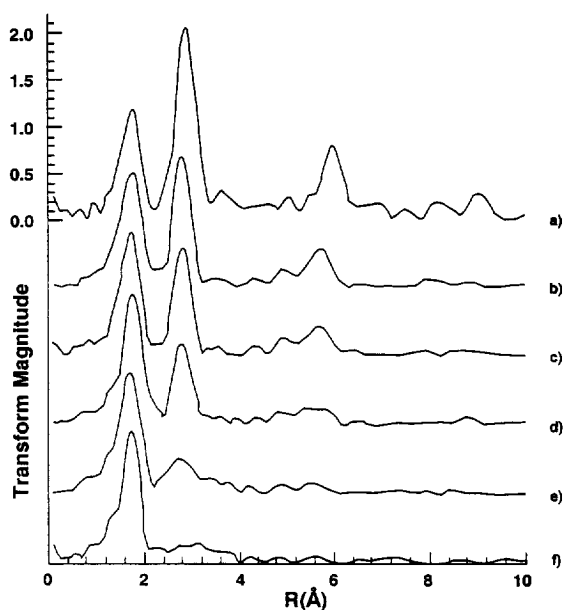


Fig. 2. Radial structure functions (RSFs) of Ni-treated pyrophyllite samples at surface sorption densities, Γ ($\mu\text{mol m}^{-2}$), of 3.1 (b), 2.0 (c), 1.0 (d), 0.49 (e), and 0.27 (f) compared to the spectrum of the crystalline $\text{Ni}(\text{OH})_2(\text{s})$ model compound (a). The spectra are uncorrected for phase shift. Note the appearance of a peak at a R of ~ 2.7 Å with increasing sorption density. (After Scheidegger et al., 1996.)

experiment (see Fig. 1). The peak at $R \approx 2.7$ Å is pronounced and the number of Ni second-neighbor atoms derived from data analysis is ~ 5 . Based on this finding, we propose that surface precipitation is the reason for the slow Ni sorption reactions on pyrophyllite.

3.2. The kinetics of Ni detachment from surface precipitates

The detachment of Ni from the pyrophyllite surface was studied using the *conventional* and *replenishment methods* (see Section 2). The results of the kinetic study at pH = 6 and pH = 4 are shown in Figs. 3 and 4, respectively. The kinetics of crystalline $\text{Ni}(\text{OH})_2$ dissolution at the corresponding pH are also illustrated for comparison.

The kinetics of Ni detachment from the pyrophyllite surface can be separated into two time stages: a primary stage which lasted a few hours, and a slower secondary stage. During the primary stage a small

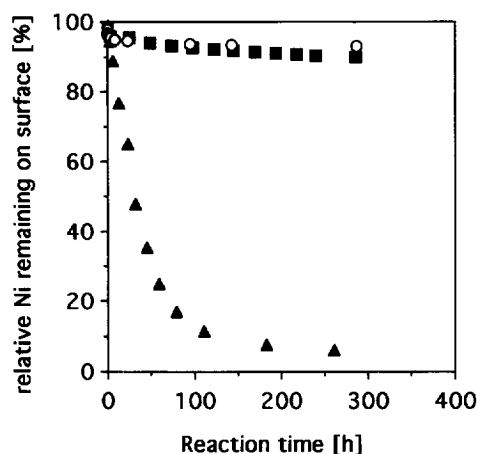


Fig. 3. Kinetics of Ni detachment from surface precipitates at pH = 6. Relative Ni remaining on the surface (%) is shown for the *conventional method* (○) and the *replenishment method* (■) as a function of the reaction time. 98% of the initial Ni was sorbed in the beginning of the detachment experiment. The dissolution of an equivalent amount of crystalline $\text{Ni}(\text{OH})_2$ (in mol) at pH = 6 is given for comparison (▲).

amount of Ni was desorbed relatively fast. The amount of sorbed Ni decreased within the first 2–3 h from 98% to $\sim 95\%$ at pH = 6 (Fig. 3), and from 98% to $\sim 90\%$ at pH = 4 (Fig. 4). The desorption of specifically adsorbed, mononuclear bound Ni may account for this rapid Ni release. The presence of

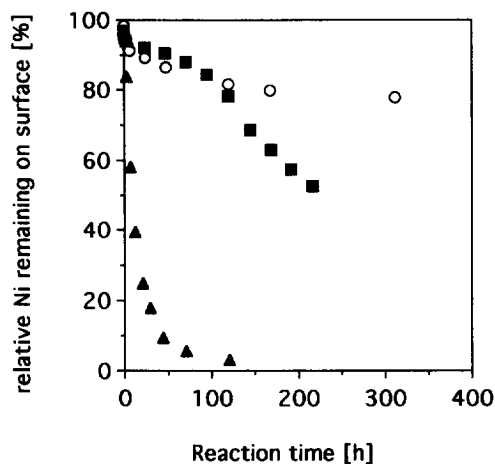


Fig. 4. Kinetics of Ni detachment from surface precipitates at pH = 4. Relative Ni remaining on the surface (%) is shown for the *conventional method* (○) and the *replenishment method* (■) as a function of the reaction time. 98% of the initial Ni was sorbed in the beginning of the detachment experiment. The dissolution of an equivalent amount of crystalline $\text{Ni}(\text{OH})_2$ (in mol) at pH = 4 is given for comparison (▲).

mononuclear Ni complexes in addition to polynuclear surface complexes has been previously detected on the pyrophyllite surface by XAFS measurements (Scheidegger et al., 1996). Decreasing the suspension pH from 7.5 to 4 resulted in complete Ni desorption of specifically adsorbed, mononuclear bound Ni, while decreasing the pH from 7.5 to 6 only resulted in a partial desorption. This may explain why the amount of detached Ni that was released rapidly at pH = 4 (~ 8%) was roughly twice the amount at pH = 6 (~ 3%) (see Figs. 3 and 4). However, the amount of readily desorbed Ni at pH = 4 and 6 is much smaller than the amount of rapidly adsorbed Ni. It appears that the formation of mononuclear bound Ni complexes on the pyrophyllite surface is faster than their desorption.

The secondary time stage was characterized by much slower Ni detachment. The detachment kinetics, however, depended strongly on the experimental method. The data obtained with the *conventional method* showed only a small release of Ni after the primary rapid stage. The release of sorbed Ni seemed to level off at ~ 75% (pH = 4) and 92% (pH = 6).

In the *conventional method* reaction products were not removed, and their concentrations increased during the experiment. Hence, this could have caused readsorption or the formation of secondary precipitates. It is not clear in what way secondary precipitates affect dissolution rates; however, they appear to depress the rate and cause parabolic kinetics (Aagaard and Helgeson, 1982).

Dissolution studies of pure pyrophyllite have shown that the release of Si and Al is more or less constant within the first few days after hydration. The dissolution rates were comparable to dissolution rates of kaolinite at similar conditions (Wieland and Stumm, 1992; Scheidegger et al., 1996). After a reaction time of 24 h Si and Al concentrations were low and far from saturation. Steady-state dissolution is the main process controlling many weathering reactions in soil and aquatic environments. Only if the residence time of the solution in contact with the mineral surface is sufficiently long, will the concentration of the dissolved elements reach oversaturation values high enough to induce secondary precipitation (Chou and Wollast, 1984). Therefore, daily replenishment would simulate a steady-state condition and Ni detachment from surface precipitates could be

studied without risking formation of secondary precipitates.

The data obtained using the *replenishment* method suggest a constant rate of Ni detachment from the pyrophyllite surface. Assuming a constant Ni detachment rate, complete "reversibility" and a daily exchange of the solution, one can estimate the time needed for complete Ni detachment. At pH = 6, the detachment process could last between 200 and 250 days, while at pH = 4 the process could last between 15 and 20 days. The difference in the Ni detachment kinetics can be explained by the fact that both the dissolution of pyrophyllite and the dissolution of Ni(OH)₂ are faster in the acidic pH range (see Figs. 3 and 4).

We doubt that the second stage is due to the slow release of metal ions diffused into the adsorbent as suggested by Brümmer et al. (1988). Instead, we ascribe the slow release to the dissolution of oxy- or hydroxy-bridged surface precipitates. The presence of polynuclear Ni complexes on the pyrophyllite surface has been clearly demonstrated (see spectrum b in Fig. 2). As illustrated in Figs. 3 and 4 the release of Ni into solution is much slower than the dissolution of crystalline Ni(OH)₂. Based on XAFS results the structure of the surface precipitates is similar, but not identical to the structure of Ni(OH)₂ (Scheidegger et al., 1996). XAFS data suggest Ni–Ni distances of ~ 3 Å, which are distinctly shorter than in Ni(OH)₂ (3.09 Å). Furthermore a single Ni–Al/Si distance (2.96–3.03 Å) was observed. Such a bond distance indicates edge sharing of Ni and Al octahedra and the presence of mixed Ni–Al-hydroxides, while it excludes the presence of a new hydrous Ni silicate phase (Scheidegger et al., 1996).

Therefore, we hypothesize that the dissolution of mixed Ni–Al-hydroxides is the reason for the slow Ni detachment from the pyrophyllite surface. Such compounds could have formed during Ni sorption or during storage of the pyrophyllite suspension prior to the desorption experiment, even though we did not observe a correlation between the Ni detachment rate and the storage time. The existence of mixed-cation hydroxide phases has been reported in the literature (Allmann, 1970; Taylor, 1984). However, their compositions are extremely variable and their solubilities are not known. Furthermore, the addition of a small amount of aluminum retards the development of the

original hexagonal Ni(OH)₂ plates, and results in the formation of spheroidal particles (Milligan and Richardson, 1955). It is not clear how such a difference in structure would influence the dissolution rate.

Further studies must be performed which include the measurements of all involved components (Ni, Si, Al). The utility of composite surface analysis techniques such as high resolution transmission electron microscopy (HRTEM) and atomic force microscopy (AFM), in addition to XAFS, offers the best hope for gaining detailed atomic and morphological information about the nature of the multinuclear Ni complexes on the pyrophyllite surface.

4. Conclusions

The kinetics of Ni sorption on pyrophyllite at pH = 7.5 was fast initially and gradually diminished. Slow nucleation processes resulted in the formation of polynuclear surface complexes, even though the suspension was undersaturated with respect to Ni(OH)₂. We suspect that the slow formation of surface precipitates is a far more important sorption mode for many heavy metals than previously thought. Adsorption experiments in the literature, however, are normally performed for only 24 h. Therefore, distribution coefficients often underestimate the long-term removal of heavy metals from the bulk solution of a real soil system.

Nickel detachment from the pyrophyllite surface was extremely slow. The detachment rate depended strongly on the pH and the experimental method. Under steady-state conditions, a constant Ni detachment rate was observed which could be ascribed to the dissolution of Ni surface precipitates. Ni detachment was much slower than the dissolution of a crystalline Ni(OH)₂ reference compound. We hypothesize that the dissolution of mixed Ni–Al-hydroxides with a low solubility is the reason for the slow Ni detachment from the pyrophyllite surface.

Slow detachment processes from surface precipitates will have a major impact on the bioavailability, mobility, and the fate of metals in soil and water environments. One can speculate that these processes are the reason for the “hysteresis” observed in many heavy metal sorption experiments. Therefore,

we suggest that the formation of surface precipitates be considered in metal surface complexation modeling, in metal speciation, and in risk assessments of the migration of contaminants in polluted sites.

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