DIVISION S-2—SOIL CHEMISTRY

Dissolution Kinetics of Nickel Surface Precipitates on Clay Mineral and Oxide Surfaces

Kirk G. Scheckel* and Donald L. Sparks

ABSTRACT

The formation of Ni surface precipitates on natural soil materials may occur during sorption under ambient environmental conditions. In this study, we examined proton- and ligand-promoted dissolution of Ni surface precipitates on pyrophyllite, talc, gibbsite, amorphous silica, and a mixture of gibbsite and amorphous silica aged from 1 h to 2 yr, by employing an array of dissolution agents (ethylenediaminetetraacetic acid [EDTA], oxalate, acetylacetone, and HNO_3). Ligand-promoted dissolution was more effective in removing Ni than the protolysis by HNO_3. In all cases, as residence time increased from 1 h to 2 yr, the amount of Ni released from the precipitates decreased from 98 to 0%, indicating an increase in stability with aging time regardless of sorbent and dissolution agent. For example, as residence time increased from 1 h to 2 yr, Ni release from pyrophyllite, as a percentage of total Ni sorption, decreased from 96 to 30% and 23 to 0%, respectively, when EDTA (pH 4.0) and HNO_3 (pH 6.0) were employed as dissolution agents for 14 d. Dissolution via oxalate of 1-yr-aged Ni–Al layered double hydroxide (LDH) on pyrophyllite saw 19% Ni removal, in comparison with 52% Ni release from α-$Ni(OH)_2$ precipitates on talc, suggesting that α-$Ni(OH)_2$ is less stable than Ni–Al LDH. The increase in stability of the Ni surface precipitates in this study with residence time was attributed to three aging mechanisms: (i) Al-for-Ni substitution in the octahedral sheets of the brucite-like hydroxide layers, (ii) Si-for-NO_3 exchange in the interlayers of the precipitates, and (iii) Ostwald ripening of the precipitate phases. It appeared that the second factor, Si-for-NO_3 exchange in the interlayers, was a major mechanism for the increase in stability of the precipitates.

Nickel is a heavy metal of concern in many parts of the world. The concentration of Ni in soil averages 5 to 500 mg Ni kg^{-1} soil, with a range up to 53 000 mg kg^{-1} Ni in contaminated soil near metal refineries and in dried sludges (USEPA, 1990). Agricultural soils contain approximately 3 to 1000 mg kg^{-1} Ni (WHO, 1991). Nickel sorption on soil minerals can result in both adsorbed (outer- and inner-sphere complexes) and precipitated phases (Scheidegger et al., 1997). With increasing awareness of the formation of metal surface precipitates on clay mineral and oxide surfaces (Chisholm-Brause et al., 1990; O'Day et al., 1994; Sheidegger et al., 1996; Towle et al., 1997), as well as soils and clay fractions (Roberts et al., 1999), understanding the potential long-term fate of the solid-state metal is necessary. The basic structure of these surface precipitates is a hydrotalcite-like structure $[(M^{2+})_6(M^{3+})_2A^-(OH)_{16}$, where M^{2+} and

M^{3+} are divalent and trivalent metal cations, respectively, and A^- is an interlayer anion that may include NO_3, silicate, or water] in which the metals are aligned in brucite-like octahedral sheets with anions in the interlayer for charge balance (O'Day et al., 1994; Scheinost et al., 1999; Scheinost and Sparks, 2000). If the sorbent possesses Al within its structure, the resulting precipitate phase is a mixed metal–Al LDH in which the Al has substituted into the octahedral sheet for the metal (d'Espinose de la Caillerie et al., 1995; Scheidegger et al., 1996, 1997, 1998; Scheidegger and Sparks, 1996; Towle et al., 1997; Scheinost et al., 1999; Thompson et al., 1999). Likewise, if Al is not available in solution during sorption, brucite-like metal hydroxide precipitates $[M^{2+}A^-(OH)_2]$ are formed (Scheinost et al., 1999).

Formation of surface precipitate phases drastically reduces metal concentration in soil and sediment solutions (Elzinga and Sparks, 1999). However, only a few investigations have assessed the stability of the surface precipitates. Scheidegger and Sparks examined the dissolution of short-aged Ni–Al LDH precipitates formed on pyrophyllite using HNO_3 at pH 4 and 6. Nickel detachment was initially rapid at both pH values (with <10% of total Ni released) and was attributable to desorption of specifically adsorbed, mononuclear Ni. Dissolution then slowed due to the gradual dissolution of the precipitates. In comparison with a β-$Ni(OH)_2$ reference compound, the Ni–Al LDH surface precipitates were much more stable.

Ford et al. investigated the dissolution of Ni–Al LDH surface precipitates on pyrophyllite using an EDTA solution at pH 7.5. Detachable Ni drastically decreased when the age of the precipitate increased from 1 h to 1 yr. By employing high-resolution thermogravimetric analysis (HRTGA), which is sensitive to changes in the interlayer composition of LDH, and by comparing the results of the surface precipitates with those of synthesized reference compounds, Ford et al. (1999) showed that a substantial part of the aging effect was due to replacement of interlayer NO_3 by silicate, which transformed the initial Ni–Al LDH into a Ni–Al phyllosilicate precursor. The source of the silicate was the dissolution of the pyrophyllite surface during Ni sorption.

Scheckel et al. (2000) and Scheckel and Sparks (2000), employing EDTA (pH 7.5) and HNO_3 (pH 4.0) for sorption aging times ranging from 1 h to 1 yr, investi-

Kirk G. Scheckel, National Risk Management Research Lab., US EPA, 5995 Center Hill Ave., Cincinnati, OH 45268; D.L. Sparks, Dep. of Plant and Soil Sciences, Univ. of Delaware, Newark, DE 19717-1303. Received 16 June 2000. *Corresponding author (Scheckel.Kirk@epamail.epa.gov).

Abbreviations: A, interlayer anion; DRS, diffuse reflectance spectroscopies; EDTA, ethylenediaminetetraacetic acid; HRTGA, high-resolution thermogravimetric analysis; LDH, layered double hydroxide; M, metal cation; XAFS, x-ray absorption fine structure; XRD, x-ray diffraction.

gated the dissolution of Ni–Al LDH phases on pyrophyllite and gibbsite and α-Ni(OH)$_2$ precipitates on talc and a mixture of gibbsite and amorphous silica. An array of analytical techniques was applied to examine the dissolution mechanisms of the Ni surface precipitates formed. The macroscopic dissolution studies demonstrated increased stability in Ni surface precipitates with aging. The differences in stability were ascribed to a combination of Al-for-Ni substitution in the hydroxide layers (for pyrophyllite and gibbsite) and silicate-for-NO$_3$ substitution in the interlayer (for pyrophyllite, talc, and the mixture). These substitutions resulted in the solid-state transformation of the precipitate phases (silication of Ni–Al LDH and α-Ni hydroxide), and possibly to crystal growth due to Ostwald ripening.

Previous studies have shown Ni surface precipitates form on the sorbents employed in this study. Scheidegger et al. (1996, 1997, 1998), Scheidegger and Sparks (1996), Scheinost et al. (1999), and Scheinost and Sparks (2000), using x-ray absorption fine structure (XAFS) and diffuse reflectance spectroscopies (DRS), observed the formation of a mixed Ni–Al LDH phase on pyrophyllite and gibbsite at sorption times of 15 min and 24 h, respectively. On talc and silica, α-Ni(OH)$_2$ precipitates form at sorption times of 1 and 12 h, respectively, as seen by Scheinost et al. (1999) and Scheinost and Sparks (2000), employing XAFS and DRS. Despite an Al source, α-Ni(OH)$_2$ precipitates, as determined by XAFS, DRS, and HRTGA, were observed on a mixture of gibbsite and silica (Scheckel and Sparks, 2000) within 1 h of reaction.

While the above studies definitively unraveled the mechanisms of metal surface precipitation–dissolution, limited dissolution agents were employed to examine stability of the neoformed precipitates. In this investigation, we used an array of dissolution agents at various pHs and sorption residence times to better understand Ni cycling in contaminated and sludge-amended soils and sediments where surface precipitates may readily form. Employing similar sorption reaction conditions as in the above previous studies, we conducted Ni sorption experiments from 1 h to 2 yr and examined the stability of surface precipitates using EDTA, HNO$_3$, oxalate, and acetylacetone as dissolution agents. The macroscopic dissolution behavior was interpreted in view of previous spectroscopic, microscopic, and thermogravimetric studies.

MATERIALS AND METHODS

Materials

The pyrophyllite (Ward's, Robbins, NC), talc (Excalibur, Cherokee Co., NC) and gibbsite (Arkansas, USA; Ward's) samples from natural clay deposits were prepared by grinding the clay in a ceramic ball mill for $\approx$14 d, centrifuging to collect the <2-μm fraction in the supernatant, Na$^+$ saturating the <2-μm fraction, and then removing excess salts by dialysis followed by freeze drying. The precipitated amorphous silica (SiO$_2$) (Zeofree 5112) was obtained from the Huber Corporation (Atlanta, GA). Pyrophyllite and talc show little deviation from the ideal chemical formula of dioctahedral and trioctahedral 2:1 phylliosilicate minerals, respectively, that are generally present in soils throughout the world. Metal oxides of Al and

Si are, individually, active sorbents for metals in the natural environment and, additionally, a mixture of the two (40% gibbsite and 60% silica by weight) was employed to more closely mimic heterogeneous systems. The sorbents were used for the following reasons: pyrophyllite and gibbsite–silica mixture to assess the combined role of Al and Si; talc and silica to assess the role of Si; and gibbsite to assess the role of Al. X-ray diffraction (XRD) showed minor impurities of kaolinite and quartz in pyrophyllite, and $\approx$10% bayerite in the gibbsite. Although the talc sample had $\approx$20% chlorite according to XRD, acid digestion resulted in an Al/Mg ratio of only 0.01. This small Al content was not sufficient in former experiments to induce the formation of detectable amounts of Ni–Al LDH. The N$_2$ Brunauer–Emmett–Teller surface areas of the sorbent phases were 95 m^2 g^{-1} for pyrophyllite, 75 m^2 g^{-1} for talc, 25 m^2 g^{-1} for gibbsite, 90 m^2 g^{-1} for amorphous silica, and 64 m^2 g^{-1} for the gibbsite–amorphous silica mixture.

The six dissolution agents employed in this study were HNO$_3$ at pH 4 and 6 to induce proton-promoted dissolution and 1 mM EDTA at pH 4 and 7.5, 3 mM oxalate at pH 4, and 3 mM acetylacetone at pH 6 to induce ligand-promoted dissolution. EDTA forms a stable Ni solution complex, and previous studies have shown that EDTA promotes desorption of Ni sorbed to oxide surfaces and the dissolution of poorly crystalline oxide phases (Borggaard, 1992; Bryce and Clark, 1996). Oxalate, a common root exudate that occurs in soils ranging in pH from 4 to 6 depending on plant species and soil conditions, illustrates ligand-catalyzed dissolution that naturally occurs in the soil environment (Taiz and Zeiger, 1991). Nickel acetylacetonate is readily formed from acetylacetone and Ni(OH)$_{2\,(s)}$ at near-neutral pH conditions, and acetylacetone is commonly used commercially to clean surfaces that have been in contact with metals (Lide, 2000). The pH values for this study and previous studies were chosen to simulate natural and industrial uses of these dissolution agents. EDTA at pH 7.5 was employed to observe dissolution under the same pH as the sorption conditions and to be relatively comparable to dissolution by HNO$_3$ and acetylacetone at pH 6.0. A pH of 4.0 was selected for the remaining dissolution agents—EDTA (industrial), oxalate (plant roots), and HNO$_3$ (industrial and acidic rain)—to compare the effectiveness of different agents at similar pH values and to allow comparison between similar agents at different pHs (EDTA: pH 4.0 vs. pH 7.5; HNO$_3$: pH 4.0 vs. pH 6.0).

Methods

To investigate the influence of aging on the stability of the precipitate phases, pyrophyllite, talc, gibbsite, silica, and the mixture were reacted with Ni for periods of 1 h to 2 yr. Experimental conditions were as described in Scheidegger and Sparks (1996) using an initial concentration of 3 mM Ni as Ni(NO$_3$)$_2$, 10 g L^{-1} sorbents and a background electrolyte of 0.1 M NaNO$_3$ at pH 7.5. The systems were purged with N$_2$ to eliminate CO$_2$, and the pH was maintained through addition of 0.1 M NaOH via a Radiometer pH-stat titrator (Westlake, OH). After 1 wk, the batch reaction vessel was removed from the pH-stat and placed in a 25°C incubation chamber. The pH was subsequently adjusted weekly with freshly prepared 0.1 M NaOH.

Dissolution was carried out by a replenishment technique using 1 mM EDTA at pH 4.0 or 7.5, 3 mM oxalate at pH 4.0, 3 mM acetylacetone at pH 6.0, and HNO$_3$ at pH 4.0 or 6.0. From the aging Ni–sorbent suspensions, 30 mL (corresponding to 300 mg of solid) were withdrawn. After centrifuging at 2 500 g for 5 min, the supernatant was decanted, and 30 mL of the dissolution agent was added to the remaining solids. The suspensions were then placed on a reciprocating shaker at 25°C for 24 h. The extraction steps were repeated either

10 times (=10 d) for short-term (aged <1 mo) or 14 d for long-term (aged ≥1 mo) Ni sorption samples. In total, 216 replenishment dissolution experiments were conducted. Inductively coupled plasma-atomic emission spectroscopy or atomic absorption spectroscopy was used to determine Ni concentrations in the supernatants. The maximum solution concentration of Ni after any given 24-h replenishment period was 0.46 mM, which is far below the saturation point for reprecipitation of Ni either back onto the sorbent or in bulk solution.

A disadvantage of the replenishment technique is that there will inevitably be some dissolved Ni entrained in the clay paste and one could argue the formation of Ni–ligand complexes on the surfaces. However, these account for a very small percentage of the overall Ni released (Scheidegger and Sparks, 1996). This is supported by the fact that the rate of dissociation for many metal–ligand complexes is slow relative to the residence time of the complexes in solution before the next replenishment period (Wilkins, 1974; Nuttall and Stalker, 1977; van den Berg and Nimmo, 1987; Hering and Morel, 1990). The conditional stability constant (K^{cond}) for Ni–EDTA complexes is ≈10^{20} M^{-1} and 10$^{9.5}$ M^{-1} for Ni-oxalate. Sorption of metal–ligand complexes is also unlikely under the reaction conditions of this study (Nowack and Sigg, 1996; Elliot and Huang, 1979; Elliot and Denney, 1982; Chang and Ku, 1994; Zachara et al., 1995; Bryce and Clark, 1996), suggesting the Ni–ligand complexes in this study thermodynamically prefer to remain in solution once formed. Additionally, metal–ligand complexes are less likely to sorb to surfaces than uncomplexed (non-metal bound) ligands if uncomplexed ligands are sufficiently present, as is the case for the dissolution agents involved with this study. For example, Gall and Farley (1994) noted that for Ni desorption from soil employing EDTA (10^{-3} M) at pH values of ≈5 and 7, EDTA adsorption on soil was 12 and 6%, while Ni desorption was 70 and 30%, respectively, after 20 h of reaction. However, a number of studies have shown that sorption of Ni–EDTA complexes is effectively common (Borggaard, 1992; Bryce et al., 1994; Zachara et al., 1995; Nowack and Sigg, 1996). These studies demonstrated that at lower pH values (<7) EDTA sorbed rapidly to surfaces but prevented the formation of ternary Ni–EDTA complexes on surfaces allowing the creation of strongly complexed Ni–EDTA solution molecules with excess solution EDTA. At pH values >7, Ni sorption tends to be kinetically faster than the formation of Ni–EDTA complexes, but with time the sorbed Ni is desorbed through the formation of solution Ni–EDTA complexes.

RESULTS AND DISCUSSION

The large-scale macroscopic dissolution data are presented in Fig. 1 through 5. Dissolution of Ni–Al LDH precipitates on pyrophyllite (Fig. 1) and gibbsite (Fig. 3) and α-Ni(OH)$_2$ precipitates on talc (Fig. 2), amorphous silica (Fig. 4), and the gibbsite–silica mixture (Fig. 5)

show that, regardless of the dissolution agent, as aging time increased, the amount of Ni remaining as a precipitate increased. The overall stability of the precipitates on the sorbents followed a general pattern of pyrophyllite (Ni–Al LDH) ≈ gibbsite–silica mixture (α-Ni(OH)$_2$) > silica (α-Ni(OH)$_2$) ≈ talc (α-Ni(OH)$_2$) > gibbsite (Ni–Al LDH). From Table 1, one can see that dissolution of 1-mo-aged Ni precipitates on pyrophyllite, gibbsite–silica mixture, silica, talc, and gibbsite with HNO$_3$ (pH 4.0) resulted in 91, 85, 77, 75, and 50% of the Ni remaining on the surface after 14 replenishment steps, respectively. Dissolution, employing EDTA at pH 7.5 and HNO$_3$ at pH 4.0, of Ni–Al LDH precipitates on pyrophyllite and gibbsite as well as α-Ni(OH)$_2$ precipitates on talc and the gibbsite–silica mixture, for which 1-mo-aged precipitates on these sorbents were examined by spectroscopic, microscopic, and thermogravimetric techniques, are published elsewhere with a brief detailed review of the analytical results presented below (Ford et al., 1999; Scheckel et al., 2000; Scheckel and Sparks, 2000). In the published studies, the Ni aging time ranged from 1 h to 1 yr. Based on these studies and the present investigation, the effectiveness of the dissolution agent in removing Ni from the surface, from greatest to least, followed the sequence: EDTA (pH 4.0) > EDTA (pH 7.5) ≈ oxalate (pH 4.0) > acetylacetone (pH 6.0) ≈ HNO$_3$ (pH 4.0) > HNO$_3$ (pH 6.0). This trend is seen in Table 1 for dissolution of 1-mo-aged sorption samples for each sorbent and dissolution agent after 14 replenishment steps. For example, dissolution of Ni–Al LDH precipitates from pyrophyllite resulted in 29, 41, 37, 88, 91, and 97% of the Ni remaining in the precipitate phase after 14 replenishments steps with EDTA (pH 4.0), EDTA (pH 7.5), oxalate, acetylacetone, HNO$_3$ (pH 4.0), and HNO$_3$ (pH 6.0), respectively. Similar trends were observed for dissolution of Ni precipitates on talc, gibbsite, silica, and the gibbsite–silica mixture (Table 1).

Typically, since transition metals, such as Ni, have empty valence orbitals, they can act as Lewis acids (electron-pair acceptors). Likewise, ligands have unshared pairs of electrons and can function as Lewis bases (electron-pair donors). The effectiveness of a ligand and the strength of a ligand–metal complex depend on the charge of the ligand and the number of donor atoms. Nickel is a favorable metal for chelates because of d^8 electron configuration and octahedral geometry (Shriver and Atkins, 1999). EDTA has six donor atoms (sexdentate ligand) and can encompass a metal ion using all six of these donor atoms. Oxalate and acetylacetone are

Table 1. Relative Ni remaining (%) on samples aged 1 mo after 14 dissolution replenishments (14 d of dissolution).

| | Ni remaining | | | | | |
	EDTA (pH 4.0)	EDTA (pH 7.5)	Oxalate	Acetylacetone	HNO$_3$ (pH 4.0)	HNO$_3$ (pH 6.0)
				%		
Pyrophyllite	29	41†	37	88	91†	97
Talc	11	17†	31	73	75†	97
Gibbsite	19	21†	20	56	50†	78
Silica	21	58	28	71	77	96
Gibbsite/silica	27	64‡	29	77	85‡	90

† From Scheckel et al. (2000).
‡ From Scheckel and Sparks (2000).
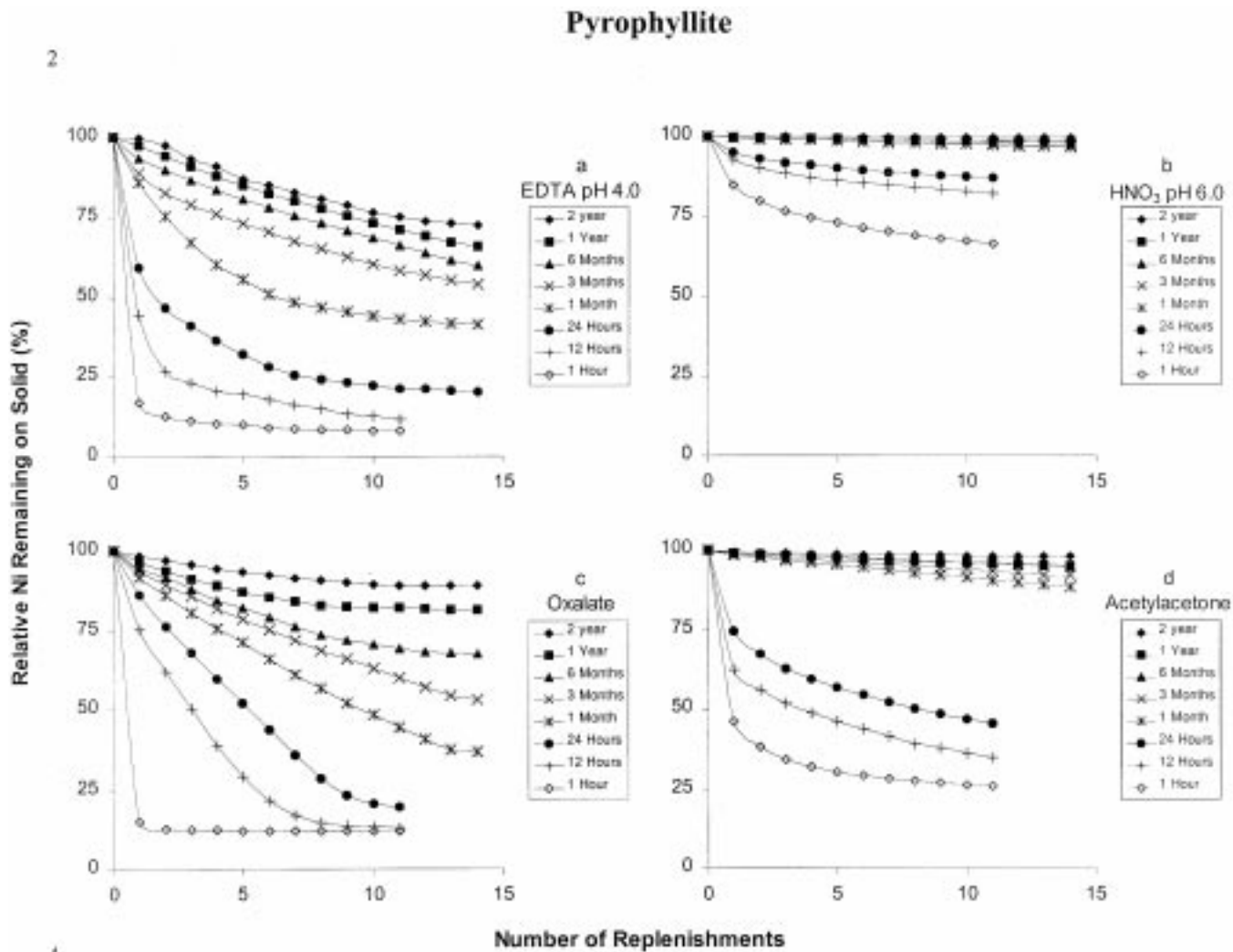
Pyrophyllite

Fig. 1. Macroscopic dissolution behavior of aged Ni precipitates on pyrophyllite showing the relative amount of Ni remaining on the surface following extraction with (a) 1 mM EDTA at pH 4.0, (b) HNO₃ at pH 6.0, (c) 3 mM oxalate at pH 4.0, and (d) 3 mM acetylacetone at pH 6.0 plotted against the total number of replenishments. The stability of the Ni precipitates increases with aging time.

bidentate ligands with two donor atoms. Based on ligand charge and number of donor atoms, one would expect EDTA to be more effective in complexing transition metal cations than oxalate and acetylacetone. According to crystal-field theory, the magnitude of the energy gap (Δ or $10Dq$) resulting from a metal chelating with a ligand determines the stability of the metal–ligand complex. As the energy gap increases, the metal–ligand formation constants decrease, indicating the creation of a weaker complex. In terms of the spectrochemical series, the ligands used in this study follow this order of increasing Δ: EDTA < oxalate < acetylacetone. This ranking supports the dissolution data in this study which shows that at pH 4.0, EDTA > oxalate > acetylacetone in forming stable ligand complexes and removing Ni from the surface precipitates.

Proton-promoted dissolution is generally slower kinetically than ligand-promoted dissolution (Stumm and Morgan, 1996). Surface protonation tends to be fast and results in polarization of the lattice sites around the metal center. Breaking of the metal-oxygen bond leading to detachment of the aqueous metal species is the

rate-determining step (Stumm and Morgan, 1996). The rate of proton-promoted dissolution increases as pH decreases ([H⁺] increases) as shown in this study for dissolution with HNO₃ at pH 4.0 vs. 6.0 (Table 1, Fig. 4).

Additionally, the pH of a ligand dissolution agent plays an important role in the rate of dissolution. EDTA at pH 4.0 released more Ni from the precipitates than EDTA at pH 7.5, suggesting that, at the higher pH, EDTA may be competing with OH⁻ ions for metal binding sites. EDTA adsorption to reaction sites is pH dependent, and the fraction of EDTA adsorbed increases with decreasing pH (anion sorption envelope), where the dissolution rate has been shown to be directly proportional to the surface concentration (Bondietti et al., 1993). With a higher concentration of a particular ligand at a surface interface with decreasing pH, one would expect an increase in the rate of dissolution as seen by comparing the results of EDTA at pH 4.0 vs. 7.5 (Table 1). This may explain the poor dissolution behavior of near-neutral acetylacetone at pH 6.0 in comparison with oxalate at pH 4.0.

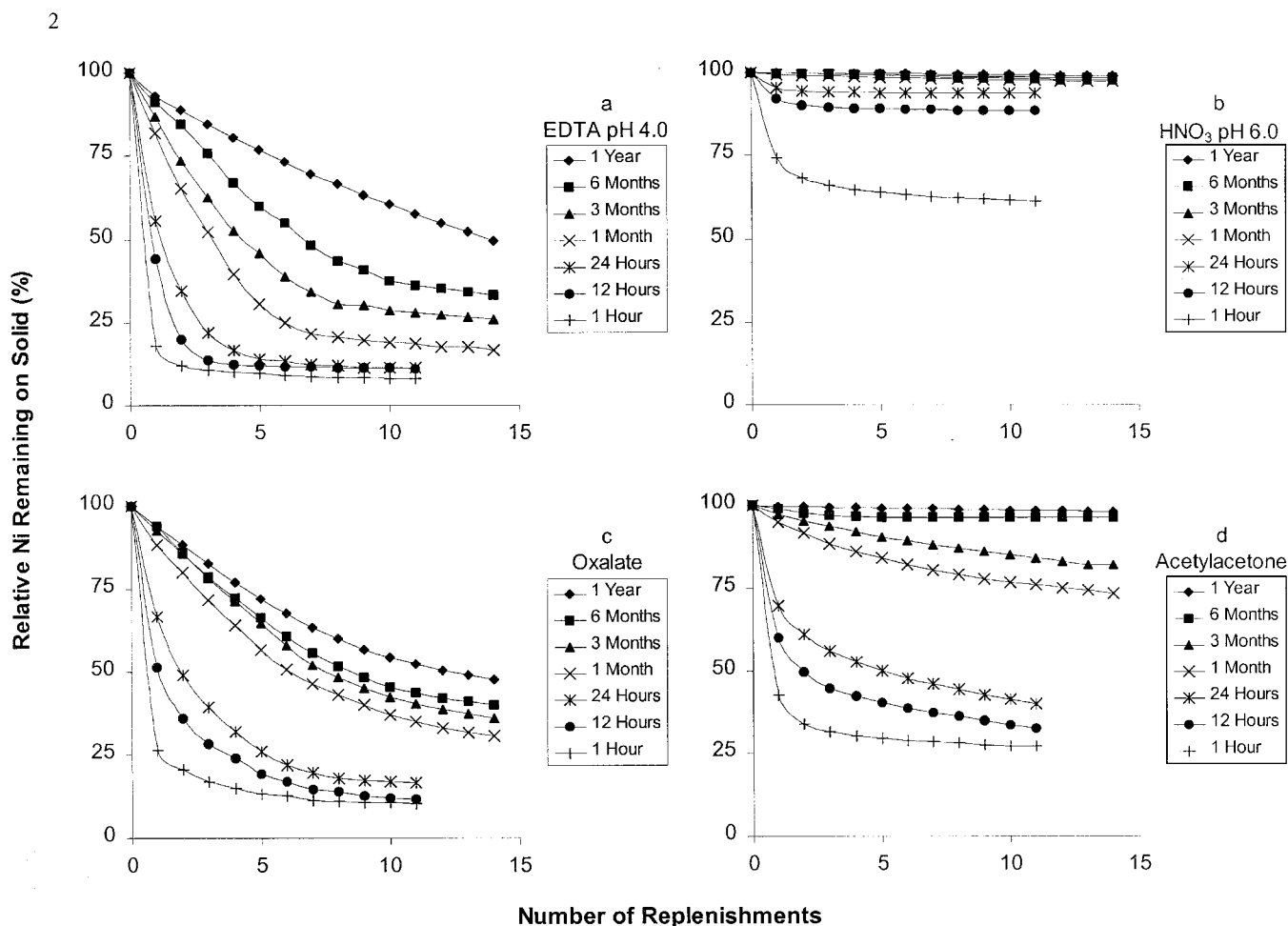The macroscopic data clearly show that (i) as aging

Talc

Fig. 2. Macroscopic dissolution behavior of aged Ni precipitates on talc showing the relative amount of Ni remaining on the surface following extraction with **(a)** 1 m*M* EDTA at pH 4.0, **(b)** HNO$_3$ at pH 6.0, **(c)** 3 m*M* oxalate at pH 4.0, and **(d)** 3 m*M* acetylacetone at pH 6.0 plotted against the total number of replenishments. The stability of the Ni precipitates increases with aging time.

time increases, the stability of the precipitates increase (Table 1, Fig. 1–5), (ii) ligand-promoted dissolution is more effective in removing Ni from the precipitate phases than proton-promoted dissolution (Table 1), and (iii) as the pH of a particular dissolution agent decreases, the rate of dissolution increases (EDTA pH 4.0 > EDTA pH 7.5; HNO$_3$ pH 4.0 > HNO$_3$ pH 6.0). However, an important issue to address and understand is the physical and chemical environment of the Ni precipitates during dissolution and the influence of residence time on the increase in precipitate stability. Recent studies employing molecular-level techniques have examined this subject in great detail for a few of the systems related to this study, and a brief review relating this literature to the current study is presented below.

Ford et al. (1999), Scheckel et al. (2000), and Scheckel and Sparks (2000) examined the dissolution of 1-mo-aged Ni–Al LDH precipitates on pyrophyllite and gibbsite and α-Ni(OH)$_2$ precipitates on talc and a mixture of gibbsite and silica with EDTA (pH 7.5) and HNO$_3$ (pH 4.0) via spectroscopic and thermogravimetric analyses. X-ray absorption fine structure studies showed that even after substantial dissolution of the precipitates with

EDTA and HNO$_3$, the local chemical environment of the Ni precipitates did not change. Employing DRS, decreases in the amount of Ni precipitates on the minerals were observed as indicated by decreases in the $\nu 2$ absorption band heights. However, as noted in the XAFS studies (Scheckel et al., 2000; Scheckel and Sparks, 2000), no changes were observed in the chemical composition of the precipitates. High-resolution thermogravimetric investigations also showed no changes in the chemical nature of the precipitates (Scheckel et al., 2000; Scheckel and Sparks, 2000), as confirmed by XAFS and DRS, but were able to detect changes in the amount of the precipitates remaining on the surfaces following dissolution as determined in the DRS experiments.

The macroscopic results (Fig. 1–5) suggest that the elemental compositions of the sorbents play a role in determining the long-term stability of sorbed Ni. Ford et al. (1999) and Scheckel and Sparks (2000) employed HRTGA to investigate Ni precipitate stability as a function of aging time on Si-bearing sorbents (pyrophyllite, talc, silica, and gibbsite–silica mixture), which resulted in the initial formation of Ni precipitate (NO$_3$-bearing
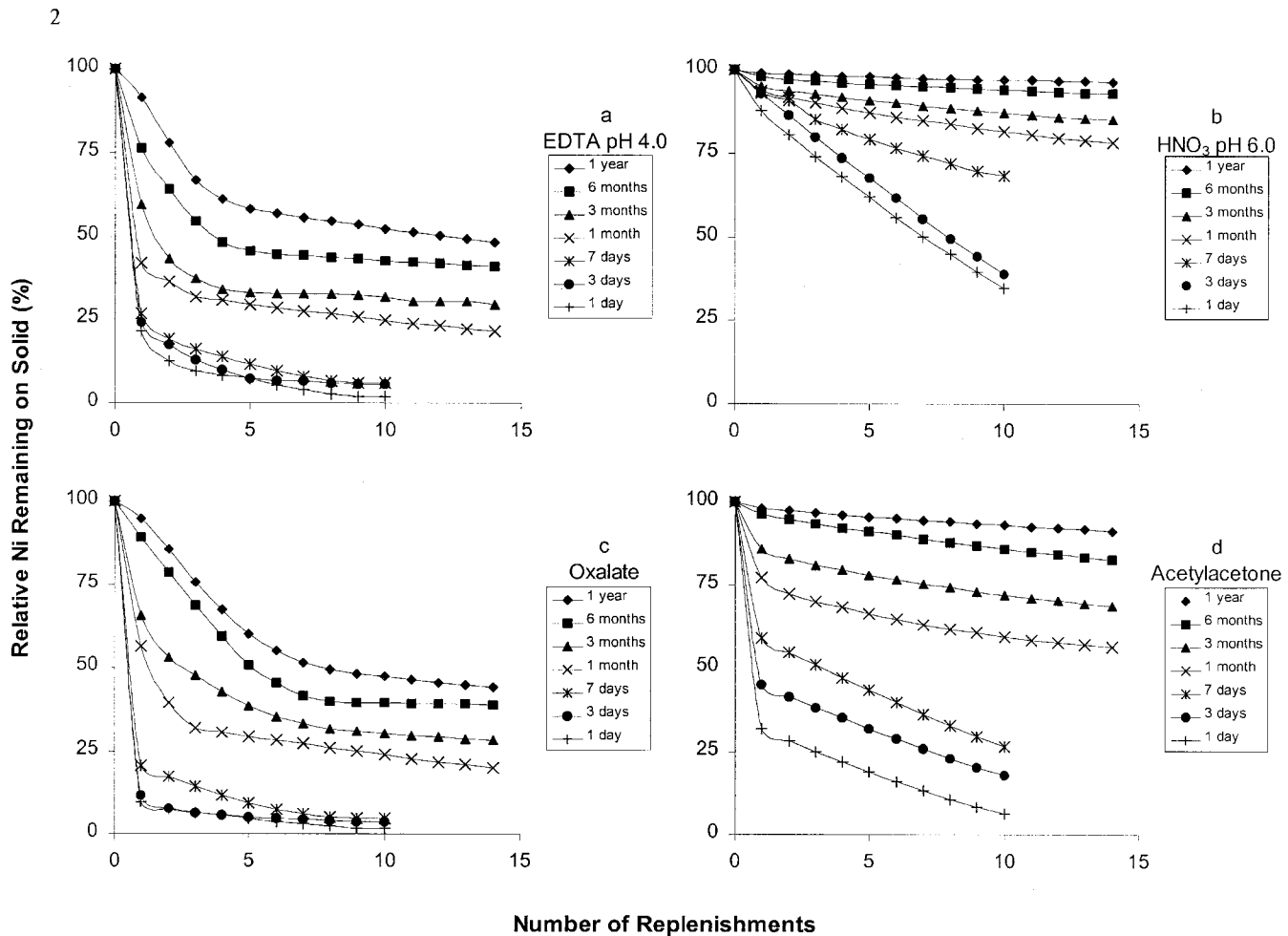
Gibbsite

2

Fig. 3. Macroscopic dissolution behavior of aged Ni precipitates on gibbsite showing the relative amount of Ni remaining on the surface following extraction with (a) 1 mM EDTA at pH 4.0, (b) HNO$_3$ at pH 6.0, (c) 3 mM oxalate at pH 4.0, and (d) 3 mM acetylacetone at pH 6.0 plotted against the total number of replenishments. The stability of the Ni precipitates increases with aging time.

interlayer) that transformed to a Si-exchanged interlayer precipitate and finally to a precursor Ni phyllosilicate in a 1-d to 1-yr reaction period. These perpetual interlayer changes of the Ni precipitates are believed to be part of the driving force for the observed increase in stability with aging time.

Table 2 lists the transformation sequence of the Ni precipitates associated with each sorbent for initial, short-term, and long-term reaction aging times. Initial product formation for pyrophyllite, talc, gibbsite, silica, and the mixture was determined from spectroscopic studies (Scheidegger et al., 1996, 1997; Scheidegger and Sparks, 1996; Scheidegger et al., 1998; Scheinost et al. 1999; Scheinost and Sparks, 2000; Scheckel and Sparks, 2000). The short-term reaction interval represents aging times up to ≈3 mo, and the long-term transition period denotes >3-mo aging times. The exact times for the short- and long-term transitions are not fully known since samples were collected at 1-, 3-, 6-, and 12-mo aging periods. The Al-for-Ni substitution in the octahedral sheet and/or Si-for-NO$_3$ substitution in the interlayer (Al and Si are derived from the sorbent, if present)

influence the mineral transformations (Ford et al., 1999; Scheckel et al., 2000; Scheckel and Sparks, 2000).

Table 2 can be supported and explained by referring to studies by Scheckel et al. (2000), who investigated the dissolution of Ni–Al LDH and α-Ni(OH)$_2$ synthetic reference compounds with NO$_3$ and Si-exchanged (confirmed by Fourier transform infrared) interlayers. Using HNO$_3$ at pH 4.0, α-Ni hydroxide dissolved more rapidly than Ni–Al LDH. However, Si exchange of both layered hydroxide phases drastically increased their stability. Scheckel et al. (2000) showed that the Si-exchanged α-Ni hydroxide was even more stable than the original NO$_3$-interlayer Ni–Al LDH. The observed ranking of the reference compound stabilities [Si-exchanged LDH > Si-exchanged α-Ni(OH)$_2$ > LDH > α-Ni(OH)$_2$] strongly supports the contention that the lower stability of Ni-gibbsite is due to Ni–Al LDH phases containing a NO$_3$ interlayer, while α-Ni hydroxide on talc, silica, and the mixture and the Ni–Al LDH phase on pyrophyllite have silicated interlayers that significantly enhanced Ni precipitate stability. The dissolution behavior for the Si-exchanged α-Ni(OH)$_2$ precipitates on talc, silica, and
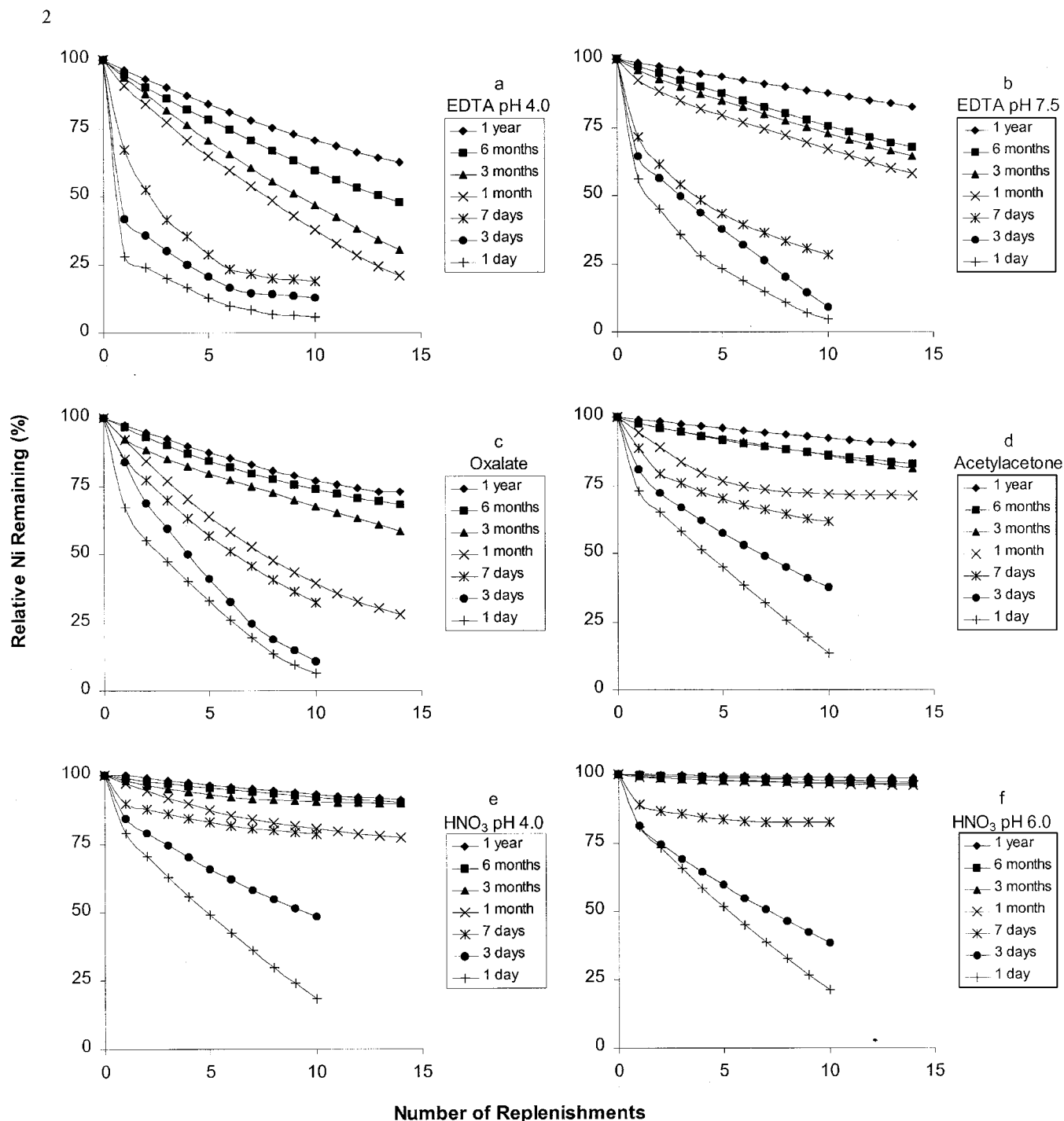
Silica

Fig. 4. Macroscopic dissolution behavior of aged Ni precipitates on silica showing the relative amount of Ni remaining on the surface following extraction with (a) 1 mM EDTA at pH 4.0, (b) 1 mM EDTA at pH 7.5, (c) 3 mM oxalate at pH 4.0, (d) 3 mM acetylacetone at pH 6.0, (e) HNO$_3$ at pH 4.0, and (f) HNO$_3$ at pH 6.0 plotted against the total number of replenishments. The stability of the Ni precipitates increases with aging time.

the mixture vary (Fig. 2, 4, and 5), probably as a result of the degree of silication of the interlayer (mixture > silica > talc).

Therefore, to summarize the data collected in this study, as aging time increased one observed the conversion of Ni–Al LDH to Ni–Al-phyllosilicate on pyrophyl-

lite and the transformation of α-Ni(OH)$_2$ to Ni-phyllosilicate on the gibbsite–silica mixture, talc, and silica. The exchange of Si for NO$_3$ substantially increased the stability of the Ni precipitates. However, with Si-free gibbsite, the increase in stability could be attributed to Ostwald ripening of the aged precipitates. The increase in stabil-
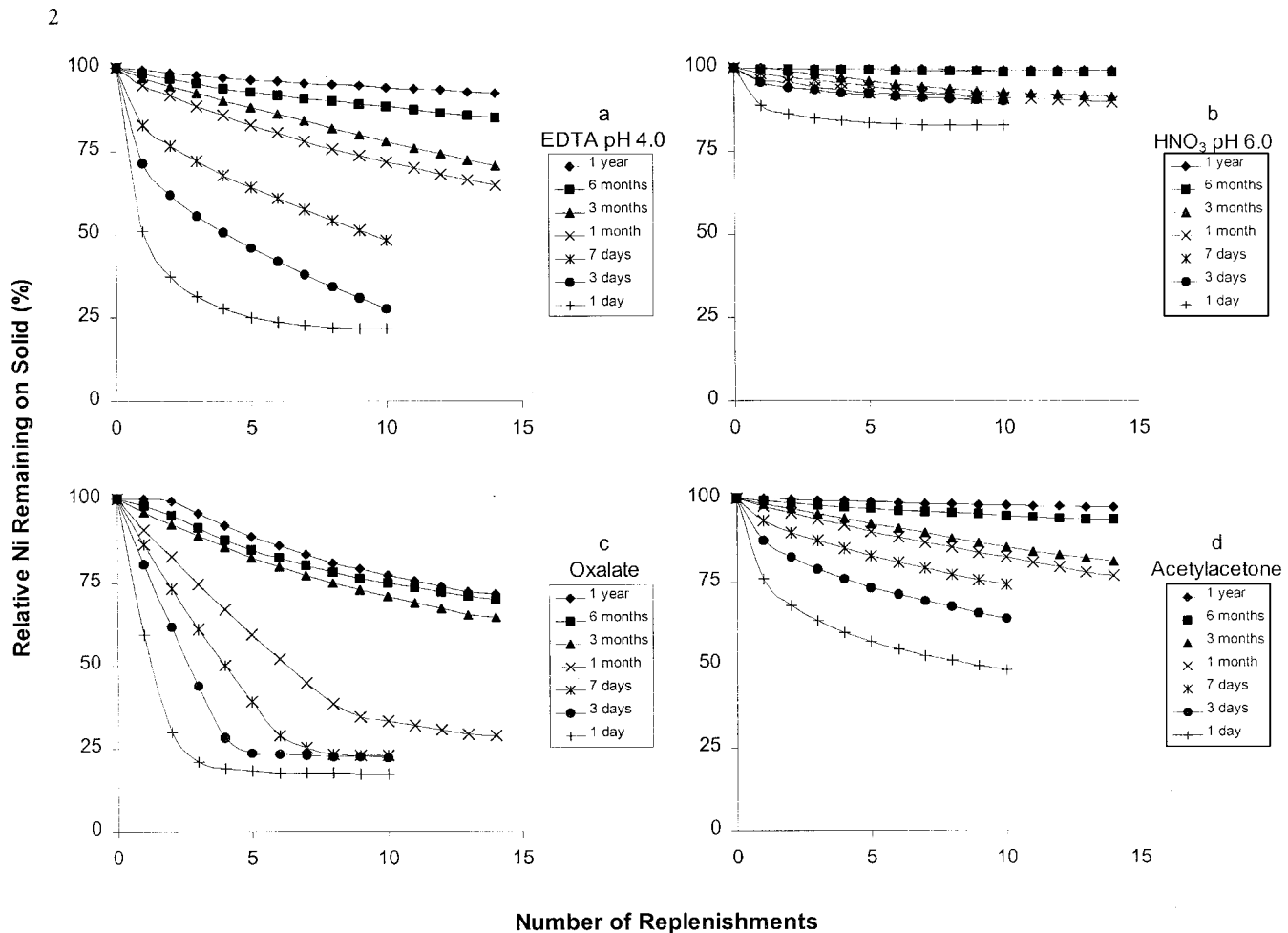
Gibbsite/Silica Mixture

Fig. 5. Macroscopic dissolution behavior of aged Ni precipitates in a gibbsite–silica mixture showing the relative amount of Ni remaining on the mixture surface following extraction with (a) 1 mM EDTA at pH 4.0, (b) HNO$_3$ at pH 6.0, (c) 3 mM oxalate at pH 4.0, and (d) 3 mM acetylacetone at pH 6.0 plotted against the total number of replenishments. The stability of the Ni precipitates increases with aging time.

ity was demonstrated macroscopically with all dissolution agents, by the decreasing amounts of Ni removed from the precipitates as residence time increased. The ligands employed in this study were more effective in releasing Ni from the aged precipitates than HNO$_3$, even when comparing EDTA at pH 7.5 to HNO$_3$ at pH 4.0. These results demonstrate that the formation of Ni precipitates and the influence of aging time may be an economical and practical way of remediating metals in natural environments via sequestration methods. This

could be as simple as maintaining a soil pH above 6, which in this study resulted in Ni release ranging from 0 to 2% under very active dissolution conditions (HNO$_3$, pH 6.0) for precipitates aged for 1 yr (Fig. 1–5).

CONCLUSIONS

While formation of metal surface precipitates has received much attention in the literature, it is incumbent that one examines the potential long-term release of the

Table 2. Solid-state transformation products of Ni precipitates with aging time.

Sorbent	Initial		Short-term		Long-term
			Precipitate transformation with time		
Pyrophyllite†‡	Ni-Al LDH	→	Si-exchanged Ni-Al LDH	→	Ni-Al phyllosilicate
Talc‡	α-Ni(OH)$_2$	→	Si-exchanged α-Ni(OH)$_2$	→	Ni phyllosilicate
Gibbsite‡	α-Ni(OH)$_2$	→	Ni-Al LDH	→	Ni-Al LDH
Silica§	α-Ni(OH)$_2$	→	Si-exchanged α-Ni(OH)$_2$	→	Ni phyllosilicate
Gibbsite/silica Mixture¶	α-Ni(OH)$_2$	→	Si-exchanged α-Ni(OH)$_2$	→	Ni phyllosilicate

† From Ford et al. (1999).
‡ From Scheckel et al. (2000).
§ From Scheckel (2000).
¶ From Scheckel and Sparks (2000).

metal back into the natural environment. This research compliments recent spectroscopic, microscopic and thermogravimetric studies (Ford et al., 1999; Scheckel et al., 2000; Scheckel and Sparks, 2000) that have examined in detail the mechanisms behind the increase in metal surface precipitate stability with residence time, by examining the effectiveness of two environmentally important dissolution agents in promoting ligand- and proton-enhanced dissolution of Ni surface precipitates from four sorbents. This study shows that with increasing residence time, all precipitate phases became more stable, as was documented by decreasing amounts of Ni released in the replenishment dissolution experiments. The effectiveness of the dissolution agents in removing Ni from the surface, from greatest to least, followed the sequence: EDTA (pH 4.0) > EDTA (pH 7.5) ≈ oxalate (pH 4.0) > acetylacetone (pH 6.0) ≈ HNO_3 (pH 4.0) > HNO_3 (pH 6.0). The stability of the precipitate phases decreased in the order: Ni–Al LDH on pyrophyllite > α-Ni hydroxide on the gibbsite–silica mixture, silica, and talc > Ni–Al LDH on gibbsite. This sequence could be explained by the greater stability of precipitates containing Al-for-Ni substituted hydroxide layers compared with pure Ni hydroxide layers, and by the greater stability of precipitates where silicate exchanged for NO_3 in the interlayer. During the first days of reaction between Ni and the mineral surfaces, there is silicate-for-NO_3 exchange in the interlayer of the metal hydroxides, followed by silicate polymerization and partial grafting onto the hydroxide layers (Ford et al., 1999). However, even precipitates formed on Si-free, Ni-reacted gibbsite exhibited a substantial aging effect, suggesting that factors other than interlayer silication may be equally important (e.g., crystal growth due to Ostwald ripening). Previous studies (Scheckel et al., 2000; Scheckel and Sparks, 2000) employing XAFS, DRS, and HRTGA showed that the chemistry of the Ni precipitates, which remained at the end of the dissolution experiments, were similar to the precipitates at the beginning of the dissolution. This indicated that no preferential dissolution of a structurally less stable phase occurred, and the precipitate phases seem to be structurally very homogeneous.

The influence of residence (aging) time on the stability of metal surface precipitates is an important area of study that warrants more investigation to truly understand the potential fate and mobility of metals in the natural environment. The conversion of metal precipitates to mineral-like precursor phases dramatically increases their stability, which in turn may mean that remediation is not necessary.

ACKNOWLEDGMENTS

REFERENCES

Bondietti, G., J. Sinniger, and W. Stumm. 1993. The reactivity of Fe(III)(hydr)oxides: Effects of ligands in inhibiting the dissolution. Colloids Surf. A 79:157–167.

Borggaard, O.K. 1992. Dissolution of poorly crystalline iron oxides in soils by EDTA and oxalate. Z. Pflanzenernaehr. Bodenkd. 155:431–436.

Bryce, A.L., and S.B. Clark. 1996. Nickel desorption kinetics from hydrous ferric oxide in the presence of EDTA. Colloids Surf. 107:123–130.

Bryce, A.L., W.A. Kornicker, A.W. Elzerman, and S.B. Clark. 1994. Nickel adsorption to hydrous ferric oxide in the presence of EDTA. Effects of component addition sequence. Environ. Sci. Technol. 28:2353–2359.

Chang, C., and Y. Ku. 1994. Adsorption-kinetics of cadmium chelates on activated carbon. J. Hazard. Mater. 38:439–451.

Chisholm-Brause, C.J., P.A. O'Day, G.E. Brown, Jr., and G.A. Parks. 1990. Evidence for multinuclear metal–ion complexes at solid/water interfaces from x-ray absorption spectroscopy. Nature 348:528–531.

d'Espinose de la Caillerie, J.B., M. Kermarec, and O. Clause. 1995. Impregnation of γ-alumina with Ni(II) and Co(II) ions at neutral pH: Hydrotalcite-type coprecipitate formation and characterization. J. Am. Chem. Soc. 117:11471–11481.

Elliott, H.A., and C.M. Denneny. 1982. Soil adsorption of cadmium from solutions containing organic-ligands. J. Environ. Qual. 11: 658–663.

Elliott, H.A., and C.P. Huang. 1979. Adsorption characteristics of Cu(II) in the presence of chelating-agents. J. Colloid Interface Sci. 70:29–44.

Elzinga, E.J., and D.L. Sparks. 1999. Nickel sorption mechanisms in a pyrophyllite–montmorillonite mixture. J. Colloid Interface Sci. 213:506–512.

Ford, R.G., A.C. Scheinost, K.G. Scheckel, and D.L. Sparks. 1999. The link between clay mineral weathering and structural transformation in Ni surface precipitates. Environ. Sci. Technol. 33: 3140–3144.

Gall, E.J., and K.J. Farley. 1994. Evaluation of nickel removal from Savannah River Site soil. p. 675–680. In Spectrum '94, Proc. Inter. Topic. Mtg. Nucl. Hazard. Waste Manage. Atlanta, GA. 14–18 Aug. 1994. Am. Nucl. Soc., LeGrange Park, IL.

Hering, J.G., and F.M.M. Morel. 1990. Kinetics of trace-metal complexation—Ligand-exchange reactions. Environ. Sci. Technol. 24: 242–252.

Lide, D.R. 2000. Handbook of chemistry and physics. 81st ed. CRC Press, Boca Raton, FL.

Nowack, B., and L.J. Sigg. 1996. Adsorption of EDTA and metal–EDTA complexes onto goethite. Colloid Interface Sci. 177: 106–121.

Nuttall, R.H., and D.M. Stalker. 1977. Tetradentate EDTA complexes of divalent nickel and zinc. J. Inorg. Nucl. Chem. 39:373–374.

O'Day, P.A., G.E. Brown, Jr., and G.A. Parks. 1994. X-ray absorption spectroscopy of cobalt(II) multinuclear surface complexes and surface precipitates on kaolinite. J. Colloid Interface Sci. 165:269–289.

Roberts, D.R., A.M. Scheidegger, and D.L. Sparks. 1999. Kinetics of mixed metal–aluminum precipitate formation on a soil clay fraction. Environ. Sci. Technol. 33:3749–3754.

Scheckel, K.G. 2000. Kinetics and mechanisms of the formation and dissolution of nickel(II) surface precipitates on clay minerals and metal oxides using macroscopic, spectroscopic, microscopic, and thermogravimetric techniques. Ph.D. diss. Univ. of Delaware, Newark, DE.

Scheckel, K.G., A.C. Scheinost, R.G. Ford, and D.L. Sparks. 2000. Stability of layered Ni hydroxide surface precipitates—A dissolution kinetics study. Geochim. Cosmochim. Acta 64:2727–2735.

Scheckel, K.G., and D.L. Sparks. 2000. Kinetics of the formation and dissolution of Ni precipitates in a gibbsite/amorphous silica mixture. J. Colloid Interface Sci. 229:222–229.

Scheidegger, A.M., M. Fendorf, and D.L. Sparks. 1996. Mechanisms of nickel sorption on pyrophyllite: Macroscopic and microscopic approaches. Soil Sci. Soc. Am. J. 60:1763–1772.

Scheidegger, A.M., G.M. Lamble, and D.L. Sparks. 1997. Spectroscopic evidence for the formation of mixed-cation hydroxide phases upon metal sorption on clays and aluminum oxides. J. Colloid Interface Sci. 186:118–128.

Scheidegger, A.M., and D.L. Sparks. 1996. Kinetics of the formation and the dissolution of nickel surface precipitates on pyrophyllite. Chem. Geol. 132:157–164.

Scheidegger, A.M., D.G. Strawn, G.M. Lamble, and D.L. Sparks. 1998. The kinetics of mixed Ni–Al hydroxide formation on clay and aluminum oxide minerals: A time-resolved XAFS study. Geochim. Cosmochim. Acta 62:2233–2245.

Scheinost, A.C., R.G. Ford, and D.L. Sparks. 1999. The role of Al in the formation of secondary Ni precipitates on pyrophyllite, gibbsite, talc, and amorphous silica: A DRS study. Geochim. Cosmochim. Acta 63(19/20):3193–3203.

Scheinost, A.C., and D.L. Sparks. 2000. Formation of layered single- and double-metal hydroxide precipitates at the mineral/water interface: A multiple-scattering XAFS analysis. J. Colloid Interface Sci. 223:167–178.

Shriver, D.F., and P.W. Atkins. 1999. Inorganic chemistry. W.H. Freeman, New York, NY.

Stumm, W., and J.J. Morgan. 1996. Aquatic chemistry. Wiley, New York, NY.

Taiz, L., and E. Zeiger. 1991. Plant physiology. Benjamin/Cummings Publ., Redwood City, CA.

Thompson, H.A., G.A. Parks, and G.E. Brown, Jr. 1999. Dynamic interactions of dissolution, surface adsorption, and precipitation in an aging cobalt(II)–clay–water system Geochim. Cosmochim. Acta 63:1767–1779.

Towle, S.N., J.R. Bargar, G.E. Brown, Jr., and G.A. Parks. 1997. Surface precipitation of Co(II)$_{(aq)}$ on Al$_2$O$_3$. J. Colloid Interface Sci. 187:62–68.

USEPA. 1990. Project summary health assessment document for nickel. EPA/600/S8-83/012. Office of Health and Environmental Assessment, Washington, DC.

van den Berg, C.M.G., and M. Nimmo. 1987. Determination of interactions of nickel with dissolved organic material in seawater using cathodic stripping voltammetry. Sci. Total Environ. 60:185–195.

Wilkins, R. 1974. The study of kinetics and mechanisms of reactions of transition metal complexes. Allyn and Bacon, Boston, MA.

World Health Organization. 1991. International programme on chemical safety. Environmental health criteria 108: Nickel. WHO, Geneva, Switzerland.

Zachara, J.M., P.L. Gassman, S.C. Smith, and D. Taylor. 1995. Oxidation and adsorption of Co(II)EDTA^{2-} complexes in subsurface materials with iron and manganese oxide grain coatings. Geochim. Cosmochim. Acta 59:4449–4463.

Adsorption Behavior of Cadmium, Zinc, and Lead on Hydroxyaluminum– and Hydroxyaluminosilicate–Montmorillonite Complexes

U. K. Saha,* S. Taniguchi, and K. Sakurai

ABSTRACT

The current imperfect understanding about the adsorption behavior of heavy metals on hydroxyaluminum (HyA)- and hydroxyaluminosilicate (HAS)-interlayered phyllosilicates led us to conduct this study. We examined the adsorption behavior of Cd, Zn, and Pb on synthetically prepared HyA– and HAS–montmorillonite (Mt) complexes in comparison with that on untreated Mt. A very dilute initial metal concentration of 10^{-6} M in 0.01 M NaClO$_4$ background was used in all the adsorption systems. The presence of HyA and HAS polymers on Mt greatly promoted the adsorption of all three metals. Such promoting effects of HyA and HAS polymers on the metal adsorption were, however, not very different from each other. The observed adsorption selectivity sequences of Pb > Zn > Cd on Mt as well as Pb $\gg$ Zn $\geq$ Cd on the complexes resemble the reported metal selectivity sequences on amorphous Fe and Al hydroxides. At different pHs, partitioning the adsorbed metals into strongly and weakly held fractions indicated that specific adsorption rather than nonspecific adsorption might have largely controlled the metal selectivity, particularly on the complexes. This led us to assume a predominant involvement of interlayered HyA or HAS polymers in metal adsorption from such dilute solutions. On Mt, the metals were predominantly adsorbed on the permanent charge sites in an easily replaceable state. However, a substantial involvement of the edge OH$^-$ groups of Mt in specific adsorption of the metals was also evident, especially at higher pH. Obviously, on Mt and on the complexes, the relative abundance of each type of site and their affinity to heavy metals were substantially different.

THE INTEREST IN HYA INTERLAYERS in 2:1 type silicate clays arises from their wide geographic distribution in acid to slightly acid soils. As a consequence, several attempts have been made to prepare HyA interlayers in smectites and vermiculites (Rich, 1960, 1968; Coulter, 1969; Barnhishel and Bertsch, 1989). The irreversible adsorption of HyA and HAS cations to the slicate surface causes a great reduction in permanent negative charge with a substantial increase in pH-dependent negative charge, a drastic reduction in internal surface area with a slight increase in external surface area (Inoue and Satoh, 1992, 1993). Recently, Saha and Inoue (1997a, 1998a) reported an abrupt modification of phosphate retention properties of Mt and vermiculite (Vt) as a result of interlayering with HyA and HAS cations. Interlayering also caused a great reduction in K and NH$_4$ fixation capacities of the clays, especially of Vt rendering the cations more exchangeable in the Vt interlayers (Saha and Inoue, 1997b, 1998b). Increased K/Ca and NH$_4$/Ca cation-exchange selectivities of the hydroxy-interlayered clays has been attributed to the "propping effect" allowing diffusion of K-sized cations, "preferential occupation" of Ca-selective sites by HyA cations, and/or steric effects retarding Ca^{2+} diffusion into the interlayer (Kozak and Huang, 1971; Saha et al., 1999).

In spite of wide geographic distribution of hydroxy-interlayered phyllosilicates and their importance in many soils, there has been little work conducted on the adsorption of metals by the interlayer components. It has been known that, compared with smectites, the cation adsorption sites on allophane, imogolite, and amor-

U.K. Saha and K. Sakurai, Faculty of Agriculture, Kochi Univ., B 200 Monobe, Nankoku 783-8502, Kochi, Japan; S. Taniguchi, United Graduate School of Agricultural Science, Ehime Univ., Matsuyama 790-8566, Japan. Received 20 June 2000. *Corresponding author (saha@cheerful.com).

Abbreviations: CEC, cation-exchange capacity; HAS, hydroxyaluminosilicate; HRTEM, high-resolution transmission electron microscopy; HSAB, hard–soft acid base; HyA, hydroxyaluminum; IAP, ion activity product; ICP-AES, inductively coupled plasma–atomic emission spectroscopy; M, metal; Mt, montmorillonite; SA, strongly adsorbed; TA, total adsorbed; Vt, vermiculite; WA, weakly adsorbed; XRD, x-ray diffraction.