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DISSOLUTION KINETICS OF Ni(II) SURFACE PRECIPITATES ON KAOLINITE: RESIDENCE TIME EFFECTS

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INTRODUCTION

Understanding the kinetics and mechanisms of trace element sorption/desorption reactions are necessary to accurately predict their bioavailability and potential toxicity in the environment. With advances in surface spectroscopic and microscopic techniques we are able to probe the mineral/water interface and gain a more accurate understanding of the mechanisms of these reactions. For example, recent studies using extended X-ray absorption fine structure spectroscopy (EXAFS) have demonstrated that many trace metal cations form surface precipitates on clay and oxide surfaces similar to pure metal hydroxide phases. These precipitates occur at pH values and surface loadings that would preclude their formation based on thermodynamic solubility products (Chisholm-Brause et al., 1990; Charlet and Manceau, 1992; O'Day et al., 1994a,b; Fendorf et al., 1994; Scheidegger et al., 1996a; Scheidegger et al., 1997; Eick and Fendorf, 1998). This information is important from an environmental standpoint because one would expect that trace elements forming surface precipitates would be less bioavailable than those that are strictly chemisorbed or those sorbing via ion exchange (Scheidegger and Sparks, 1996b). However, the rate and extent of desorption/dissolution will ultimately depend on their structure, composition, and morphology (Fendorf et al., 1996).

Recently, a great deal of research has focused on understanding the mechanism of surface precipitate formation on soil constituent surfaces. Specifically, whether Ni(II) forms a pure $Ni(OH)_2$ surface precipitate or a co-precipitate similar to takovite (Ni-Al hydroxy-nitrate/carbonate) on phyllosilicate surfaces (Scheidegger et al., 1996; Scheidegger et al., 1997; Eick and Fendorf, 1998). While this information is important, data on dissolution kinetics is necessary for accurately predicting surface precipitate bioavailability in natural environments. However, there are relatively few studies examining the dissolution of trace metal surface precipitates (Fendorf et al., 1996; Scheidegger and Sparks, 1996). Furthermore, recent research has demonstrated that the desorption of many trace element cations becomes more recalcitrant with time (McKenzie 1970; McLaren et al. 1986 Ainsworth et al. 1994; Backes et al. 1995; McLaren et al. 1998: Eick et al., 1999). Several explanations have been proposed for these observed residence time effects including solid-state diffusion within oxide particles (Bruemmer et al. 1988), diffusion into micropores and intraparticle spaces (Backes et al. 1995), change in the type of surface complex (McBride 1994), incorporation into the mineral structure via recrystallization (Ainsworth et al. 1994), surface catalyzed oxidation and incorporation into the crystal matrix (McKenzie 1970; Backes et al. 1995), and surface catalyzed hydrolysis and precipitation (Backes et al. 1995).

Understanding surface sequestering processes in soils should better allow us to evaluate the bioavailability and potential toxicity of trace metals in the subsurface. Newly precipitated solids are often less ordered than those that have been allowed to age. Therefore, we hypothesize that the dissolution rate of an aged Ni(II) surface precipitate will be slower than a Ni(II) precipitate that has not been aged. Accordingly, the present study examines the dissolution kinetics of Ni surface precipitates on kaolinite and the effect of residence time. The dissolution kinetics of crystalline $Ni(OH)_2$ and a synthetic Ni-Al hydroxy-nitrate (takovite) were also examined as analogs for the Ni-surface precipitates. The Ni-kaolinite system was chosen because kaolinite is an abundant soil clay mineral and EXAFS has demonstrated that Ni has the ability to form surface precipitates on phyllosilicates at common soil pH ranges (Scheidegger et al., 1996; Eick and Fendorf, 1998).

MATERIALS AND METHODS

Kaolinite preparation and characterization

The sorbent used in this study was a well-crystallized Georgia kaolinite obtained from the University of Missouri Source Clays Depository. The bulk kaolinite was washed with doubly-deionized water until a stable conductivity resulted for 24 hours. The washed kaolinite was fractionated by standard procedures (Jackson, 1969), based on a gravimetric method, to an equivalent diameter of less than 2 μm. It was then dialyzed in doubly-deionized water until a stable conductivity resulted for 24 h and was subsequently freeze dried.

The <2 μm kaolinite fraction was characterized by X-ray diffraction (XRD) and diffuse reflectance infrared fourier transform (DRIFT) spectroscopy. X-ray diffraction and DRIFT analysis yielded results diagnostic for kaolinite with no impurities present. The cation-exchange capacity (CEC) of the Georgia kaolinite as determined by Ba-Ca exchange was 1.14 $\mathrm{cmol_c\ kg^{-1}}$. This value is in good agreement with published values for the well crystallized Georgia kaolinite and indicates the absence of significant amounts of 2:1 clay impurities (McBride, 1976; McBride, 1978). The specific surface area was 16.5 $\mathrm{m^2\ g^{-1}}$, as determined by a five point N_2 Brunauer-Emmett-Teller (B.E.T.) gas adsorption isotherm method.

Takovite Synthesis

A synthetic Ni-Al hydroxy-nitrate (takovite) was prepared for dissolution experiments as a comparison to Ni surface precipitates since it has been suggested that the Ni(II) surface precipitates formed on phyllosilicates are more like takovite than pure $Ni(OH)_2$ (Scheidegger et al., 1996). A modification of the method of Bish and Brindley (1977) was used as detailed below. A 100 ml solution of 0.75 M $Ni(NO_3)_2$ and 0.25 M $Al(NO_3)_3$ was dripped into a pH 10 solution of 0.10 M $NaNO_3$ at a rate of 0.40 ml min^{-1}. The suspension pH was kept constant and well-stirred with the aid of an automatic titrator (Brinkman, Metrohm 718 Stat Titrino) and mechanical stirrer (Caframo RZR-2000), respectively. The suspension was purged with N_2 to eliminate CO_2 and kept at a constant temperature of 298 ± 0.1 K. The precipitate was rinsed 6 times with doubly-deionized water and placed in an oven at 393 K for 24 hours. The dried sample was ground in an agate mortar an analyzed by X-ray diffraction (XRD) using a Scintag XDS-2000 diffractometer. The mounts were scanned at $2^\circ\ 2\theta\ min^{-1}$ using Cu Kα radiation and a graphite monochrometer. X-ray diffraction results were consistent with those presented by Bish and Brindley (1977).

Adsorption Experiments

Sorption experiments were conducted at various Ni surface coverages using a batch technique. Different surface coverages were achieved by varying sorptive concentrations (1×10^{-4}, 5×10^{-4}, and 7.5×10^{-4} M). All sorption experiments were conducted at a kaolinite suspension concentration of 25 g L^{-1} and a pH of 7.5. These conditions were selected because preliminary experiments indicated that > 99% sorption of Ni was achieved after 14 days while the suspensions were undersaturated with respect to $Ni(OH)_2(s)$. Samples of kaolinite were weighed into a 500 ml teflon lined flat-bottomed, water-jacketed reaction vessel (500 ml) covered with a removable glass lid containing entry ports for a mechanical stirrer, pH electrode, N_2 gas, burette tip, and pipette. The kaolinite was hydrated and N_2 sparged for 24 hours in 450 ml of 0.10 M $NaNO_3$ and adjusted to pH 7.5 using 0.10 M HNO_3. The Ni was dispensed in stepwise quantities from a 0.0515 M $Ni(NO_3)_2$ stock solution to minimize local oversaturation of the suspension. The suspension pH was kept constant and well-stirred with the aid of an automatic titrator (Brinkman, Metrohm 718 Stat Titrino) and mechanical stirrer (Caframo RZR-2000), respectively. All experiments were conducted at 298 ± 0.1 K at 1 atm pressure in a N_2 environment to eliminate CO_2 influences.

Sorption experiments were conducted for 14 days (short-term study) and 20 weeks (long-term study). Samples were taken until sorption reached > 99 % (14 days). An initial 2 mL aliquot was removed from the batch reactor and filtered through a 0.10 μm Gelman metrical membrane in order to "pre-saturate" the membrane. An additional 10 mL aliquot was removed from the batch reactor and filtered through the same "pre-saturated" membrane into previously acid-washed polypropylene test tubes. All suspension-samples were carefully removed from the batch reactor using an electronic pipet in order to avoid changes in the total surface area to solution ratio. The filtered samples were acidified to a pH < 2 with 8 M HNO_3, sealed and stored in a refrigerator prior to analysis. After 14 days all samples were removed from the pH-stat and placed in 500 ml acid-washed high-density polyethylene centrifuge bottles. The bottles were sealed with teflon tape to prevent evaporation and placed on an environmentally controlled rotating shaker (New Brunswick Scientific, Innova 4230) at 298 ± 0.1 K. The bottles were gently rotated at 130 rpm to avoid abrasion of the solid. The pH was maintained constant at 7.50 ± 0.10 through manual addition of 0.10 M HNO_3 or NaOH. All NaOH solutions were made from carbonate free doubly-deionized water and stored in bottles with sodium hydroxide coated silica sinks to absorb carbon dioxide.

Dissolution Studies

All dissolution studies were carried out using a pH-stat technique in the presence of 1 mM oxalate at pH 6. Oxalate was chosen because it is a common plant root exudate found at appreciable levels in natural soil environments (Stevenson, 1994). The kaolinite suspension from either the short- or long-term sorption experiments was carefully poured into a 500 mL teflon liner. The liner was placed into the flat-bottomed jacketed reaction vessel used in the sorption experiments. The pH was adjusted to pH 6 using an automatic titrator and an appropriate quantity of oxalate was dispensed from a 0.10 M sodium oxalate stock solution. All samples were carefully removed from the batch reactor using an electronic pipet in order to avoid changes in the total surface area to solution ratio. The samples were filtered and acidified to a pH < 2 with 8 M HNO_3, sealed and stored in a refrigerator prior to analysis. All experiments were conducted in the dark at 298 ± 0.1 K and 1 atm pressure in a N_2 environment to eliminate CO_2 influences. Nickel was analyzed using a Perkin Elmer 3300 atomic adsorption spectrometer. The detection limit for Ni is 0.06 ppm.

For comparison of dissolution rates crystalline $Ni(OH)_2$ and a synthetic takovite were measured using the same pH-stat technique and experimental conditions.

Takovite and crystalline $Ni(OH)_2$ samples were ground in an agate mortar. An appropriate mass was added to a 400 ml solution of 1mM oxalate (pH 6 and IS 0.10 M $NaNO_3$) to give final Ni concentrations of 0.10, 0.50, and 0.75 mM.

Infrared Analysis

Diffuse reflectance infrared fourier transform (DRIFT) spectroscopy was performed to examine changes in the crystallinity of the Ni(II) surface precipitates. DRIFT analysis was done using a Perkin-Elmer 1720x FTIR unit with a diffuse reflectance accessory. Sub-samples were taken from the batch samples prepared for the dissolution studies and were washed with approximately 100 mL of doubly-deionized water and freeze dried. The freeze dried material was diluted by 90% (by weight) with KBr to reduce spectral reflectance. The samples were placed in the DRIFT accessory which is continuously purged with CO_2 and H_2O free air. A DTGS detector was used, with 100 scans collected at $4 cm^{-1}$ resolution.

In addition to the short and long term Ni-Kaolinite samples, several reference materials were analyzed for comparison. Reference spectra were obtained from pure KGa-1 kaolinite, an aged $Ni(OH)_2$, and a freshly precipitated $Ni(OH)_2$. The $Ni(OH)_2$ precipitates were created by titrating 20 mM $Ni(NO_3)_2$ to pH 8.5 under an N_2 atmosphere. The precipitate was maintained at this pH for 24 hours and 15 weeks. After this time each precipitate was filtered and washed with approximately 100 mL of doubly-deionized water and freeze dried. This procedure is similar to that used by Fendorf et al., (1994) to create γ-CrOOH.

RESULTS AND DISCUSSION

Sorption Kinetics

The kinetics of Ni(II) sorption on kaolinite at three different loading rates and a pH of 7.5 is illustrated in Figure 1. Sorption is initially rapid with greater than 78% of the initial Ni sorbed in 24 hours. This initial rapid reaction is followed by a slower reaction which lasts approximately 14 days. For all initial solution concentrations > 99% of the initial Ni(II) added was sorbed on the kaolinite surface. An initial rapid reaction followed by a much slower reaction is characteristic of heavy metal sorption on clay and oxide surfaces (Benjamin and Leckie, 1981; Dzomback and Morel, 1986; Davis et al., 1987; Bruemmer et al., 1988; Scheidegger et al, 1996). Based on previous research the rapid sorption is attributed to chemisorption of Ni(II) on edge sites while the slow sorption is due to the nucleation and precipitation of $Ni(OH)_2$ on the kaolinite surface (Eick and Fendorf, 1998).

Dissolution Kinetics

The dissolution kinetics of Ni(II) surface precipitates for three different surface loadings as well as homogenous precipitates of $Ni(OH)_2$ and takovite are shown in figures 2-4. Similar to dissolution studies of other mineral surfaces, the release of Ni from all surfaces can be separated into a rapid phase (0 – 10 hours) followed by a slower stage (Ludwig and Casey, 1996; Ludwig et al., 1996; Eick et al., 1999). In the case of mineral surfaces that have been synthesized in the laboratory and not extensively pretreated, there is often a rapid release of a metal from the surface during the first 10 – 15 hours. This has been attributed to ultra-fine grains or other rapidly dissolving surfaces created during the grinding process (Stumm, 1992). This explains the rapid release of Ni observed for the homogeneous precipitates ($Ni(OH)_2$ and takovite) but not for the Ni surface precipitates. Examination of figures 2-4 indicate the rapid release of Ni from the surface precipitates is most pronounced at the lowest surface loading (Figure 2). Previous spectroscopic investigations of Ni sorbed to kaolinite and pyrophyllite have shown the presence of chemisorbed Ni surface complexes in addition to polynuclear surface precipitates (Scheidegger et al, 1996a; Eick and Fendorf, 1998). Therefore, the desorption of chemisorbed surface complexes may account for the rapid release of Ni. Furthermore, this would explain why at the lowest loading this rapid release is most pronounced since a greater proportion of the sorbed Ni would be present as chemisorbed surface complexes.

The dissolution rates for the four experiments are listed in Table 1. These rates were calculated from the linear regression of the slow linear stage of Ni release (> 20 hours). For all experiments dissolution rates decreased in the order $Ni(OH)_2$ > short-term Ni surface precipitate > takovite > long-term Ni surface precipitate. The dissolution rates for both short- and long-term surface precipitates were slower than for the pure homogeneous $Ni(OH)_2$. Scheidegger and Sparks (1996) observed similar results for the dissolution of Ni(II) surface precipitates on pyrophyllite. The slower dissolution rates for the Ni(II) surface precipitates compared to pure homogeneous $Ni(OH)_2$ may be due to the greater surface area of the homogeneous $Ni(OH)_2$ and/or co-precipitation of Al^{+3} with the Ni(II) surface precipitates. Since the Ni(II) surface precipitates are attached to the kaolinite surface the surface area exposed to the oxalate ligand would be less than the homogeneous $Ni(OH)_2$. Furthermore, whether the Ni(II) surface precipitate distributes evenly across the kaolinite surface or clusters will affect its exposed surface area and markedly influence its dissolution rate (Fendorf et al., 1996).

Previous research has demonstrated that the specific adsorption of Ni(II) on phyllosilicate surfaces accelerates mineral dissolution at near neutral pH values (Schiedigger et al., 1996a; Eick and Fendorf, 1998). Moreover, EXAFS results indicate that small quantities of Al^{+3} released from the phyllosilicate surface may co-precipitate with Ni (Eick and Fendorf, 1998). The solubility of many co-precipitated compounds can be lower than that of the pure compound (McBride, 1994). In the case of the Ni(II) surface precipitates it may be a combination of both factors that are responsible for the observed reduction in dissolution rates compared to the pure homogeneous $Ni(OH)_2$.

The dissolution rate of the mixed Ni-Al hydroxy-nitrate (Takovite) is between the dissolution rates of the short- and long-term Ni(II) surface precipitates. Previous research has suggested that incorporation of Al^{+3} released from phyllosilicate dissolution as well as nitrate used in the background electrolyte creates Ni(II) surface precipitates that are similar to pyroaurite-hydroxy minerals (e.g. takovite) (Schiedegger et al., 1997). It was suggested that this takovite-like structure was responsible for the contraction in metal-metal bond distances compared to pure hydroxide phases formed in the absence of the surface (O'Day et al., 1994a,b; O'Day et al., 1996: Scheidegger et al., 1996). However, in a recent study the validity of the mechanism for the formation of takovite-like surface precipitates on phyllosilicates was questioned due to differences in the rates of dissolution and precipitation and the driving force for precipitation/dissolution (Eick and Fendorf, 1998). Although the dissolution rates of takovite and the Ni(II) surface precipitates are similar, one cannot necessarily assume that their structures are the same. Dissolution of mineral surfaces will be related to a number of factors including composition, structure, degree of crystallinity, and morphology, and the similarity in dissolution rates between takovite and the Ni(II) surface precipitates may be fortuitous. Additional research is required for gaining detailed atomic compositional and structural information concerning the nature of Ni(II) surface precipitates which may ultimately resolve the question concerning the contracted metal-metal bond distances.

Residence Time effects

At all three surface loadings the dissolution rate and the total quantity if Ni released from the surface precipitates is greater for the short-term compared to the long-term experiments (Table 1 and Figures 2-4). This is in contrast to what Scheidegger and Sparks (1996) observed for the dissolution of Ni(II) surface precipitates on pyrophyllite at pH 4 and 6 that were aged between 1 and 8 weeks. This may be due to an insufficient aging time compared with the present study (20 weeks). There have been many explanations for observed residence time effects for trace metal desorption from mineral surfaces (see introduction). In this study we new a priori that Ni(II) would form surface precipitates on kaolinite similar to pure $Ni(OH)_2$ based on a previous EXAFS study (Eick and Fendorf, 1998). Our hypothesis for the observed residence time effect is that the Ni(II) surface precipitates become more crystalline with time. This is commonly observed for hydroxide precipitates of easily hydrolyzable metals (Schwertmann and Cornell, 1991). To test this hypothesis we conducted DRIFT spectroscopy on the short-and long-term Ni(II) surface precipitate samples as well as several reference samples. Unfortunately, absorbance bands from the kaolinite surface obscured the Ni-O vibrational mode characteristic of the crystalline structure of $Ni(OH)_2$. Insight into changes in crystallinity of Ni(II) surface precipitates may be obtained through a comparison of the freshly precipitated and aged homogeneous $Ni(OH)_2$ samples (Figure 5). The aged $Ni(OH)_2$ absorption spectrum shows bands characteristic of crystalline $Ni(OH)_2$: a narrow band at 3650 cm^{-1} which is characteristic of the valence vibration mode of ν-OH, a band at 520 cm^{-1} resulting from the plane deformation mode of δ-OH, and a band at 460 cm^{-1} resulting from the ν-NiO vibration mode (Figlarz and Le Bihan, 1971). In contrast the freshly precipitated $Ni(OH)_2$ shows a markedly different infrared spectrum (Figure 5). The freshly precipitated $Ni(OH)_2$ has a very wide band centered at 3500 cm^{-1} and a wide band at 1600 cm^{-1} which indicates the presence of "significant" quantities of water (Figlarz and Le Bihan, 1971). Furthermore, the δ-OH and ν-NiO a slightly displaced towards shorter wavelengths which is an indication of a less ordered structure (Figlarz and Le Bihan, 1971). Similar changes in crystallinity may be occurring for the Ni(II) surface precipitates which may be responsible for the observed residence time effect.

CONCLUSIONS

The kinetics of Ni(II) sorption on kaolinite is characterized by an initial rapid stage followed by a slower more gradual stage. Based on previous EXAFS experiments the rapid stage was attributed to the desorption of chemisorbed Ni while the slow stage was attributed to the dissolution of Ni(II) surface precipitates. For all experiments dissolution rates decreased in the order $Ni(OH)_2$ > short-term Ni surface precipitate > takovite > long-term Ni surface precipitate. Differences in dissolution rates between surface precipitates and pure homogeneous $Ni(OH)_2$ may be due to differences in exposed surface area or the co-precipitation of Al^{+3} with Ni on the kaolinite surface. The dissolution rates for both Ni(II) surface precipitates were similar to takovite, however, this may be fortuitous and is not necessarily an indication of a similar structure which has been previously proposed (Scheidegger et al., 1996). A pronounced residence time effect was observed between the short-term (14 day) and long-term (20 week) samples. It is suggested that an increase in crystallinity in the Ni(II) surface precipitate with time is responsible for the observed differences. Unfortunately, DRIFT results were inconclusive due to interference from the kaolinite surface. However, comparison of aged and freshly precipitated homogeneous $Ni(OH)_2$ solids indicated and increase in crystallinity with time. Previous investigations on metal surface precipitates have concentrated on determining their structure, composition, and morphology. While this information is extremely important for assessing the reactivity and hence bioavailability of surface precipitates, the present investigation demonstrates the importance of quantifying dissolution rates as well as examining residence time effects to accurately determine the bioavailability of metals in natural environments.

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List of Figures

Table 1: Dissolution rates of Ni(II) surface precipitates, takovite, and $Ni(OH)_2$ at pH 6 in the presence of 1 mM Oxalate (Ionic strength = 0.10 M $NaNO_3$)

0.10 mM Ni		**0.50 mM Ni**		**0.75 mM Ni**	
Treatment	**Rate (μM h^{-1})**	**Treatment**	**Rate (μM h^{-1})**	**Treatment**	**Rate (μM h^{-1})**
$Ni(OH)_2$	0.821	$Ni(OH)_2$	4.03	$Ni(OH)_2$	5.98
Short-term	0.313	Short-term	1.46	Short-term	2.04
Takovite	0.285	Takovite	1.38	Takovite	1.39
Long-term	0.257	Long-term	1.23	Long-term	1.21

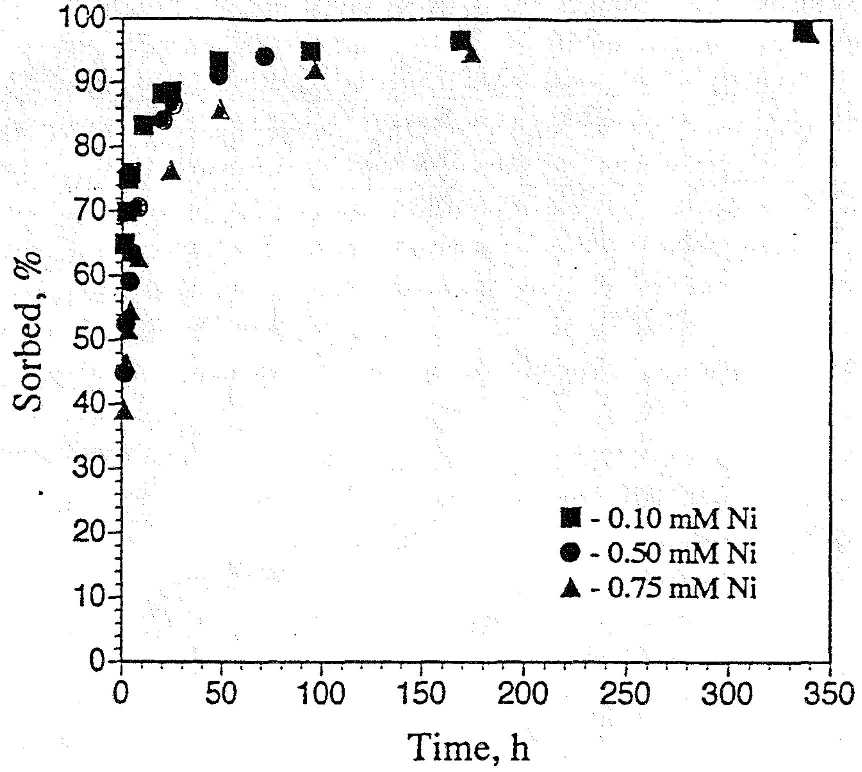
100
90
80
70
60
50
40
30
20
10
0
Sorbed, %
0
50
100
150
200
250
300
350
Time, h
■ - 0.10 mM Ni
● - 0.50 mM Ni
▲ - 0.75 mM Ni

Figure 1

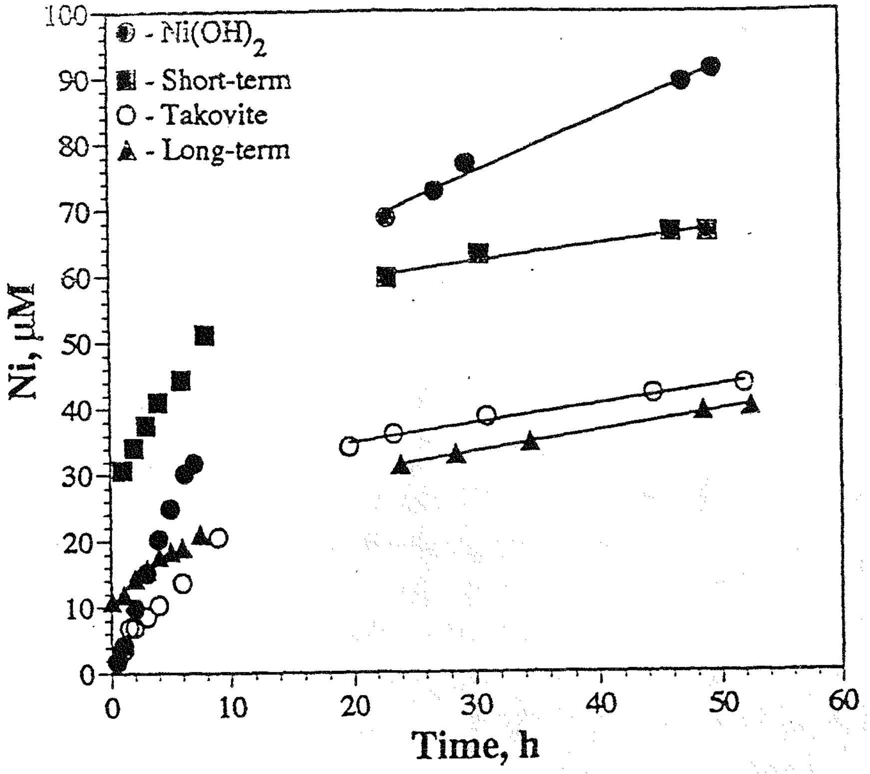

Figure 2 (0.10mM Ni)

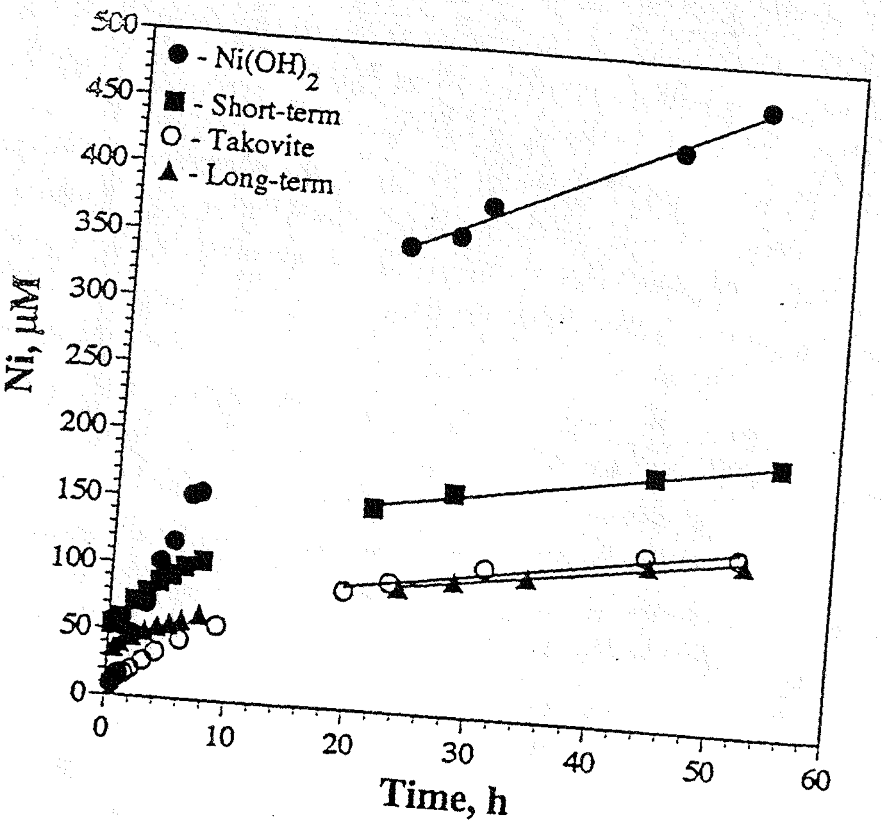

Figure 3 (0.50 mM Ni)

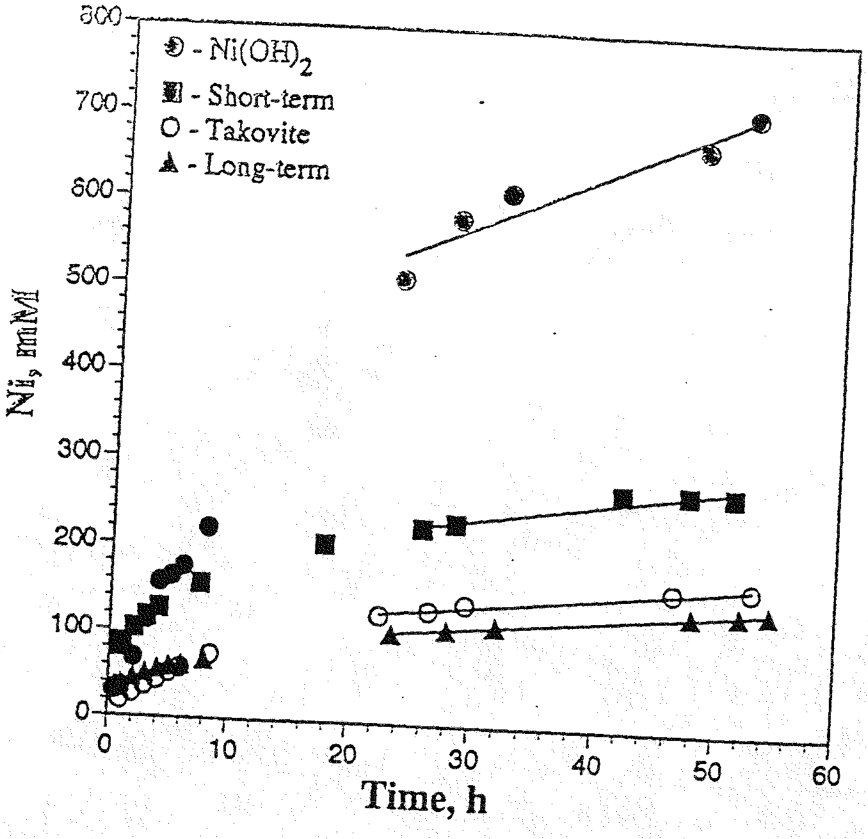

Figure 4 (0.75 mM Ni)

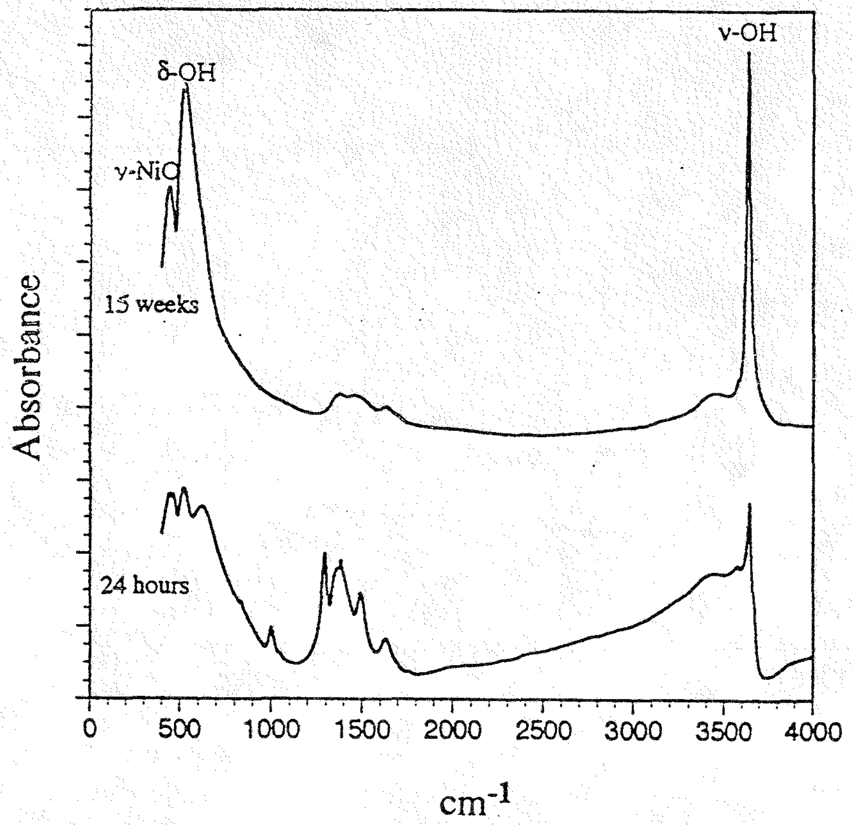
Absorbance
δ-OH
ν-OH
ν-NiO
15 weeks
24 hours
0
500
1000
1500
2000
2500
3000
3500
4000
cm-1

Figure 5