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Reaction of nickel with soils and goethite: Equilibrium and kinetic studies

Mehadi, Ahmed Ali, Ph.D.

University of New Hampshire, 1993

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**REACTION OF NICKEL WITH SOILS AND GOETHITE:
EQUILIBRIUM AND KINETIC STUDIES**

BY

**AHMED ALI MEHADI
BS, Addis Ababa University, 1980
MS, Alabama A&M University, 1988**

DISSERTATION

**Submitted to the University of New Hampshire
in Partial Fulfillment of
the Requirements for the Degree of**

Doctor of Philosophy

in

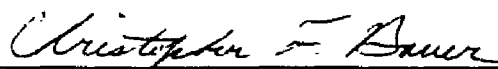
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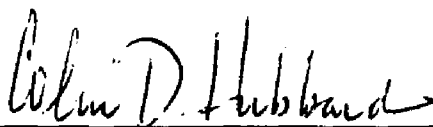
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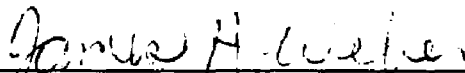
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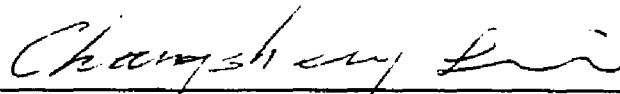
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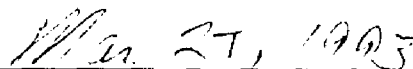
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Biogeochemistry



Date

DEDICATION

To my parents

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I am especially thankful to my major advisor Dr. Robert D. Harter for his support, guidance and friendship over the past few years. His optimism has been a constant source of inspiration.

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ABSTRACT

REACTION OF NICKEL WITH SOILS AND GOETHITE: EQUILIBRIUM AND KINETIC STUDIES

BY

AHMED ALI MEHADI
University of New Hampshire, May, 1993

Reaction of nickel with soil B horizons under various ionic strengths, pH and temperature conditions was conducted using a batch kinetics method. The forward and reverse apparent rate constants were determined using computer simulation techniques. Thermodynamic parameters were calculated from the rate constants. Increase in soil pH and temperature increased the sorption of nickel, while increase in ionic strength decreased nickel sorption. The reactions were all spontaneous with negative standard free energies (ΔG°); soils having higher nickel sorption capacity were more negative. The free energy decreased with increase in pH. The enthalpy (ΔH°) and entropy (ΔS°) for the reactions were positive and higher for higher nickel sorbing soils, both ΔH° and ΔS° increased with increase in surface coverage. The large positive ΔS° indicated a certain degree of nickel dehydration when sorbed by soils particles, greater dehydration is observed with increase in surface coverage.

Nickel sorption sites on soil surfaces were evaluated using nickel sorption isotherms and Wavelength Dispersive Spectroscopy (WDS). No specific soil component explained the relative nickel sorption capacities of the soils. WDS

indicated that nickel sorption is related to iron in soils, but neither total, citrate-dithionite-bicarbonate (CDB) nor ammonium oxalate (NH_4OX) extractable iron were able to explain this trend.

The reaction of nickel at the goethite/water interface was studied using kinetics by means of pressure-jump (p-jump) relaxation. Two step relaxations were observed for nickel adsorption at 25°C . The fast and slow relaxations decreased with decrease in pH. Both relaxations were attributed to simultaneous adsorption/desorption of Ni^{2+} on sites with different bonding energies. A modified triple layer model (TLM) was used to analyze the effect of ionic strength on nickel adsorption at the goethite/water interface. An inner-sphere complexation model fitted the experimental data well. Results of zeta potential also supported the specific adsorption of nickel at the interface.

INTRODUCTION

With growing population and industrialization, the production of waste containing toxic heavy metals is increasing at alarming rate. In the U.S., disposal of sludges is currently accomplished by five methods: land spreading, incinerating, landfilling, ocean dumping and lagooning (Baker, et al., 1985). Land application has become increasingly popular because of environmental and economic concern, and as means of recovering N, P, and organic matter in the sludge (Epstien et al., 1976).

The nickel content of representative northeastern U.S. soils varies from 10 to 65 $\mu\text{g g}^{-1}$ (Johnson and Chu, 1983), while the mean nickel content of sludges varies from 300 to 400 $\mu\text{g g}^{-1}$ (Sommers, 1977). The dominant form of nickel in aqueous solution and taken up by plants is Ni^{2+} (Tinker, 1986). Ni^{2+} can be toxic to plants, causing decrease in growth and brown interveinal growth (Mishra and Kar, 1974; King and Morris, 1972). It is not so strongly adsorbed by soil organic matter and clays as is Cu^{2+} , and is comparable to Cd^{2+} in susceptibility to leaching through acid soils (Tyler and McBride, 1982). Activities related to mining and smelting can result in high Ni^{2+} content of surface water and sediments, with associated toxicity to aquatic biota and higher animals. Toxicity in higher animals and humans is manifested by Ni^{2+} interference with iron metabolism (NRCC, 1981).

Increasing pH by liming has been found to increase nickel sorption

(Harter, 1979), reducing the solubility and mobility of Ni^{2+} in acid soils. High soil pH does not, however, appear to prevent Ni^{2+} uptake by plants (Berrow and Burridge, 1981; Lepow et al., 1975). In monitoring diethylenetriaminepentaacetic acid (DTPA)-extractable Zn, Cu, Cd and Ni for 2.4 years after composted-sludge containing these metals were added to sandy soils, Korcak et al. (1979) reported that extractable Cd, Zn and Cu decreased with time, indicating increased retention, while Ni extractability tended to increase. The retention of Ni^{2+} by soils is decreased by the presence of other heavy metals (Harter, 1992; Kinniburgh, et al., 1976) and alkaline earth metals (Petruzzelli et al., 1988) thus enhancing Ni^{2+} mobility in soils (Petruzzelli and Lubrano, 1981).

Proper monitoring of Ni^{2+} mobility and retention in soil systems require understanding the various factors affecting the retention of Ni^{2+} by solid phases, and the energetics of the reactions. It requires modeling of Ni^{2+} reactions at soils/water interfaces and predicting of reaction mechanisms. To date, the thermodynamics of Ni^{2+} sorption by whole soils has not been studied. The few studies conducted involve the use of specific soil minerals. The effect of ionic strength, pH and surface coverage on Ni^{2+} sorption by soils are lacking. Knowledge of soils components responsible for the variability in the amount of Ni^{2+} sorbed by different soils is needed. Moreover, neither the triple layer model (TLM) nor chemical kinetics has been used to study the reaction of Ni^{2+} with

important soil minerals. It is, therefore, the objectives of this study to: 1) study the reaction of Ni^{2+} with soils in relation to the effect of time, temperature, pH and ionic strength; 2) determine apparent thermodynamic parameters and identify the driving force for the reactions; 3) identify the important component(s) of the soils that is most responsible for nickel sorption; and 4) study the reaction of nickel with goethite to a) establish surface complexation reaction by using the modified TLM, b) evaluate the chemical kinetics of Ni^{2+} sorption at the goethite/water interface using the pressure-jump (p-jump) technique, and c) suggest possible reaction mechanism(s).

CHAPTER I

LITERATURE REVIEW

Environmental problems arising from nickel contamination of ground water and soil systems have long been recognized. Nickel added in high concentrations to soils within sludge or other forms has been found to make its way into the food chain or leached into the ground water. Because of its toxicity to plants and animals, there is a growing need to understand nickel reaction with soils.

The essentiality of nickel as plant nutrient in soybeans (Eskew et al., 1983, 1984), chickpeas (Eskew et al. 1984), and temperate cereals (Brown, et al., 1987) has been illustrated. Nickel is a necessary constituent of the enzyme urease in legumes. Leaf urease, which reduces accumulation of urea, is higher in plants supplied with nickel than those not receiving this element (Eskew et al. 1983). The essentiality of Ni to higher plants other than legumes is yet to be established (Brown et al., 1990). On the other hand, the phytotoxicity of Ni has been known for a long time (Mishra and Kar, 1974). Toxicity symptoms include decrease in growth, chlorosis, stunted root growth and brown interveinal necrosis.

The primary source of Ni²⁺ in soils is parent materials (Tiller, 1989; Uren, 1992). The actual content in soils depend on the parent material (Uren, 1992), and pedogenic processes of soil formation as well as anthropogenic sources

(Tiller 1989). Contamination of agricultural soils by metal containing substances can result from agricultural sprays, fertilizers, sewage sludge, emission from motor vehicles, and others. Fertilizers usually contain up to $30 \mu\text{g g}^{-1}$ Ni although some phosphatic rocks have higher concentration (Swain, 1962). Emission from nickeliferous diesel oil account for high accumulation of Ni near roads and high amount of Ni in the atmosphere (Niragu, 1979).

The spreading of sewage sludge on land as a means of disposal, a source of nutrients, and a soil conditioner contributes to significant increase in soil nickel content. Sludges vary greatly in nickel content, ranging from 2 to 3,500 $\mu\text{g g}^{-1}$ with a mean of 300 to 400 $\mu\text{g g}^{-1}$ (Sommers, 1977). The total nickel content of northeaster U.S. soils vary from 10 to 65 ppm (Johnson and Chu, 1983).

Nickel, which is a member of the group VIII first transition series, readily yields 4s electrons to give the divalent Ni^{2+} ion. Ni^{2+} is octahedrally coordinated in aqueous system occurring as $\text{Ni}(\text{H}_2\text{O})_6^{2+}$. This form dominates in natural pH range of soils. The dominance of the hydrated form decreases in presence of ligands like OH^- , SO_4^{2-} , Cl^- , and NH_3 (Theis and Richter, 1980). The ligands can form inner-sphere complexes with metal ions, as in the case of NiOH^+ , or outer-sphere complex or ion-pair formation, as in case of NiSO_4 . All complexes are labile (Cotton and Wilkson, 1988) in that they form instantaneously, rapidly establishing reversible equilibrium (Mattigod et al., 1981). The main form of

nickel taken up by plants is Ni^{2+} , with the uptake mechanism being similar to that of Zn^{2+} , Mn^{2+} and Cu^{2+} (Tinker, 1986).

The quantity and nature of sorption or interaction at the soil or soil mineral interfaces is determined by the factors that govern solid-solution interfacial interactions. Studying factors that govern these reactions and predicting the reaction mechanism will aid in providing the means of dealing with the problem of leaching into the ground water and accumulation in the soil system.

Sorption of nickel by soils and soil minerals is affected by mineralogical composition of soils (or type of clay minerals present), pH, ionic strength, concentration, temperature, type of ligands and reaction time. These factors will be discussed in order.

Mineralogy

The secondary minerals in the clay fraction that are most likely to accommodate nickel are hydrous oxides of iron and manganese (and possibly Ti and Al) (Anderson and Christensen, 1988), and the trioctahedral species of layer silicates such as vermiculite and chlorite (Uren, 1992). Concretionary forms of iron and manganese oxides sometimes have high concentration of nickel (McKenzie, 1975), as much as 20 times higher than in the bulk soil (Dawson, et al. 1985).

Electron microprobe analysis has demonstrated a close association of nickel and cobalt with manganese in lateritic soils (Norrish, 1975); and nickel with manganese and iron in nodule-free soils (McKenzie, 1975). Higher concentrations of nickel was associated with iron than with manganese (McKenzie, 1975).

The primary enrichment process for Co^{2+} , Ni^{2+} and Zn^{2+} is sorption by iron and manganese oxy-hydroxy phases, presumably as the oxides form, rather than by ionic replacement after the oxide is formed (Dawson, 1985). Solid-state diffusion and subsequent ionic replacement must, however, be considered a strong possibility when the oxide phase is stable and the reaction times extend over hundreds of years or more (Uren, 1992). Sorption of Co^{2+} , Cd^{2+} , Ni^{2+} and Zn^{2+} was shown by Anderson and Christinsen (1988) to be positively related to iron and manganese oxides, and Tiller et al. (1984) related sorption of Cd^{2+} , Ni^{2+} and Zn^{2+} with iron oxides or with more iron rich clay fractions.

In contrast to iron oxides or iron oxide rich minerals, soils dominated by 2:1 type layer silicates have lower sensitivity to pH and relatively higher sorption of Cd^{2+} , Ni^{2+} and Zn^{2+} at low pH (Tiller et al. 1984). Within the layer silicates, montmorillonite has higher affinity for Ni^{2+} than Co^{2+} and the reverse is true for hectorite (Davison et al. 1991). The sorption of Ni^{2+} at pH 6 and Cu^{2+} at pH 5 has been found to occur in the order chlorite > illite > kaolinite (Koppelman and Dillard, 1977). Relative conditional equilibrium constants for

cadmium adsorption by soils and soil components decreased in the following order; clay > whole soil > soils without iron and manganese oxides > silt > sand (Kim and Fergusson, 1992). Theis and Ritcher (1980) also found that goethite adsorbed greater amount of nickel at lower pH values than did silica. The dominant species for maximum adsorption by goethite and silica are Ni^{2+} and NiOH^+ respectively.

Over a wide pH range, manganese oxide adsorbed more Cu, Co, Ni and Pb than did iron oxides. Among iron oxides, goethite adsorbed more than hematite while the converse is true for Pb. When the adsorbed metals were extracted with 2.5% acetic acid, significantly higher percentage of the adsorbed metals were non-extractable from hematite compared to goethite (McKenzie, 1980). This implies that iron oxides which constitutes higher proportion of oxides than manganese oxide in soils serve as a sink for heavy metals retention in soils.

pH

Increase in pH increases sorption of Ni^{2+} , Cu^{2+} , Pb^{2+} , and Zn^{2+} (Harter, 1979; Kurdi and Donner, 1983; Srivastava and Srivastava, 1990; Shuman, 1975). The adsorption of nickel is strongly pH dependent for hydrous oxides and organic matter, but much less so for illite and kaolinite, and virtually absent for montmorillonite (Andersson, 1977) The latter may be due to limited pH

dependent sites for layer silicates. Adsorption of Cd^{2+} and Pb^{2+} (Hayes, 1987), Zn^{2+} , Cd^{2+} and Ni^{2+} (Barrow et al., 1989), Cd^{2+} (Johnson, 1990), Ni^{2+} (Benjamin and Leckie, 1981; Tiller et al., 1984) by goethite and Pb^{2+} , Cu^{2+} , Cd^{2+} (Hachiya et al. 1984) and Pb^{2+} (Hohl and Stumm, 1979) by aluminum oxides increased from 0 to 100% in a pH range of 4 to 7 which is well below the pK for the dissociation of hydrogen ion from the hydration shell of these cations.

Using pH_{50} , the pH at which 50% of metal ions is adsorbed, Kinniburgh et al. (1976) reported metal adsorption selectivity for iron and aluminum hydroxides to be, respectively, Cu (pH 4.4) > Zn (5.4) > Ni (5.6) > Co (6.0) and Cu (4.8) > Zn (5.6) > Ni (6.3) > Co (6.5). Likewise, sequences for kaolinite, Cd (4.5) > Zn (5.4) > Ni (5.8) and montmorillonite, Cd (4.7) > Zn (4.8) > Ni (5.3) (Pulse and Bohn, 1988); goethite, Zn (4.9) > Ni (5.6) > Cd (5.8) (Gerth and Brummer, 1983) were reported. In solution of mixed metals, pH was found to be the most influential factor in determining the distribution of Cd , Co , Ni and Zn in soils (Anderson and Christensen, 1988). The order of adsorption of Zn , Ni , and Cd by goethite follows the order the hydrolysis constant, pK, for the equation $\text{M}^{2+} + \text{H}_2\text{O} = \text{MOH}^+ + \text{OH}^-$ (8.96, 9.86 and 10.08 respectively). Similar results were reported by Tiller et al., (1984). A lower pH_{50} indicates greater selectivity of the surface for the metal (Uren, 1992).

The effect of pH on metal adsorption by soils and soil minerals can be explained by considering the effect of pH on hydrolysis of cations and surface charge density or electrical potential at the interface. When the pH of the suspension is below the pK for the dissociation of the metals (M^{2+}), as for example Cd^{2+} (pK 10.08), Ni^{2+} (9.86) and Zn^{2+} (8.96) (Baes and Mesmer, 1976), the concentration of MOH^+ in a solution with pH below 7 is cannot explain the sharp increase in the amount of metal adsorbed. Direct relationship between surface charge distribution and pH for hydrous oxides (Atkinson et al., 1967) and TiO_2 have been reported, as has the increase in metal adsorption with increase in pH (Hayes, 1987; Benjamin and Leckie, 1981; Barrow et al., 1989). It is known that surface potential is related to surface charge density through double layer theory. These observations suggest that increase in metal adsorption with increase in pH can be explained by the pH effect on the electrical potential at the interface (Barrow et al. 1989; Fokkink et al., 1990).

Ionic Strength

Increase in ionic strength (adjusted using calcium salt) has been shown to decrease nickel sorption by soils (Petruzzelli et al., 1988) and kaolinite (Mattigod et al. 1979) due to competition of calcium and nickel for the same sorption sites. The adsorption was greater where the anion was NO_3^- compared to SO_4^{2-} . In layer silicates, the dominant fraction of metals are adsorbed non-

specifically (McBride, 1989); both Ca^{2+} and Ni^{2+} compete for the same site. Moreover, decrease in the activity of Ni^{2+} with increase in ionic strength will occur as a result of ion-pair formation; for example NiSO_4° and NiNO_3^+ with association constant $10^{2.33}$ and $10^{0.40}$ respectively (Nair and Nancollas, 1957; Fedorov et al., 1973). Ion-pair formation explains the decrease in the adsorption of Ni^{2+} and why there is less sorption in SO_4^{2-} systems than in NO_3^- systems. On the other hand, when the ionic strength is adjusted using NaNO_3 salt, adsorption of Ni^{2+} by iron oxides (Gerth and Brummer, 1983; Barrow et al., 1989) was found to be independent of ionic strength. The reason being Na^+ and NO_3^- , which are known to form outer-sphere complexes do not compete with Ni^{2+} for adsorption sites. Actually the effect of ionic strength variation, using an indifferent electrolyte like NaNO_3 , has been used to determine specific adsorption of metal by metal oxides (Hayes and Leckie, 1986; Barrow et al. 1989).

In natural systems, metallic cations do not occur as single solutes but are more often found in combination with other heavy metals and alkaline earth cations such as Ca^{2+} and Mg^{2+} . Therefore, accurate prediction of metal sorption onto oxides and soils in the presence of other metals is necessary as is providing the selectivity sequence in the adsorption process.

In a single -element experiment involving Ca^{2+} and Cd^{2+} , changing the metal concentration (between 0.005 and 0.50 M) did not influence Cd^{2+}

adsorption but did influence the adsorption of Ca^{2+} by $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ (am). This implies that some of the Ca^{2+} surface complexes are outer-sphere (Cowan et al., 1991). In binary metal-Ca adsorption onto calcium saturated soils Harter (1992) reported a sorption sequence of $\text{Cu}^{2+} > \text{Ni}^{2+} \approx \text{Co}^{2+}$. Nickel sorption was equivalent to Ca^{2+} release. In the system, neither Co^{2+} nor $0.016 \text{ mmol L}^{-1} \text{ Cu}^{2+}$ caused a significant decrease in Ni^{2+} sorption. At higher Cu^{2+} concentration ($0.079 \text{ mmol L}^{-1}$) the sorption of nickel was decreased. Nickel sorption affected Co^{2+} but not Cu^{2+} sorption.

Selectivity sequence of metals for amorphous iron hydroxides has been reported to follow $\text{Pb}^{2+} > \text{Cu}^{2+} > \text{Zn}^{2+} > \text{Ni}^{2+} > \text{Cd}^{2+}$ whereas for aluminum hydroxide the sequence was $\text{Cu}^{2+} > \text{Pb}^{2+} > \text{Zn}^{2+} > \text{Ni}^{2+}$ (Kinniburgh et al. 1976). Metal affinity for the silanol group of silica follow $\text{Pb}^{2+} > \text{Cu}^{2+} > \text{Co}^{2+} > \text{Zn}^{2+} > \text{Ni}^{2+}$ (Drugger et al. 1964; Schindler et al. 1976); for soils $\text{Cu}^{2+} > \text{Zn}^{2+} > \text{Ni}^{2+}$ (Harter, 1983); for montmorillonite $\text{Cd}^{2+} > \text{Zn}^{2+} > \text{Ni}^{2+}$ (Puls and Bohn, 1988) and $\text{Pb}^{2+} > \text{Zn}^{2+} > \text{Ni}^{2+} > \text{Cd}^{2+}$ (Schulthess and Huang 1990).

Temperature

In an environment where the soil temperature varies dramatically between winter and summer, studying the influence of temperature on heavy metal sorption by soil and soil minerals is very important. Temperature affects the partitioning of metal ions between the solid and liquid phases. Studying the

temperature-dependence of adsorption enables one to separate entropic and enthalpic contributions to the process and therefore provide important information on the driving forces involved. The latter is necessary in model interpretations. The effect of temperature on the measured cation exchange capacity (CEC) (Wada and Harada, 1971) and metal adsorption on iron oxides (Brummer et al., 1988; Srivastava and Srivastava, 1990; Johnson, 1990; Jurinak and Bauer, 1956) has been studied.

Increase in temperature increased the adsorption of Zn^{2+} , Ni^{2+} , Cd^{2+} , Cu^{2+} and Co^{2+} by precipitated silica (Baye et al., 1983), Cd^{2+} by rutile and hematite (Fokkink et al., 1990), Cd^{2+} by goethite (Johnson, 1990), Zn^{2+} by dolomite and Ca-magnesite (Jurinak and Bauer, 1956) and, at pH 5.5 and 6.85, Zn^{2+} by iron hydroxide (Srivastava and Srivastava, 1990). Effects of temperature on cation adsorption by solids have been attributed to its effect on a) the rates of reactions that follow adsorption b) solution equilibrium or activity, c) pH of pzc or surface potential and d) binding constant (Bowden et al., 1977; Barrow, 1992; Machesky, 1990).

Using the effect of temperature on metal adsorption, a few efforts have been made to determine various thermodynamic parameters for sorption metals on dolomite, Ca-magnesite and hematite (Jurinak and Bauer, 1956; Machesky, 1990). These indicate endothermic reactions with negative free energies, positive ΔH° , and large and positive entropies. Entropy was felt to be driving

force of the reactions. The large and positive entropies were explained as resulting from dehydration of adsorbed ions (Jurinak and Bauer, 1956; Machesky, 1990). How this varies with the surface coverage is not known (Barrow, 1992).

Complexing Ligands

The effects of complexing ligands on the interaction between metal and adsorbent surface may be divided into two groups based on the origin and strength of the interaction: a) formation of soluble complexes which compete with adsorption reactions by forming surface complexes and b) indirect or direct interaction of the ligand to enhance adsorption reactions by attaching the complex to the sorption sites (Benjamin and Leckie, 1981; Davis and Leckie, 1978).

Goethite and silica oxides both adsorb Ni specifically (McBride 1989) with goethite adsorbing more Ni at lower pH values in which Ni^{2+} is the dominant species (Theis and Richter, 1980). Maximum adsorption of Ni by silica occurs at higher pH where NiOH^+ is the dominant species.

Addition of excess SO_4^{2-} (10^{-3} M) or citrate (10^{-3} M) with respect to Ni^{2+} ($10^{-4.77}$ M) shifted the adsorption edge for goethite and silica to the higher pH, thus reducing Ni^{2+} adsorption at lower pH. A portion of this reduction is attributed to Ni^{2+} complexation by SO_4^{2-} (50%) and formation of a tridentate

chelate with citrate (Theis and Richter, 1980). Silica adsorbs Ni once the pH become high enough to produce NiOH^+ . It has been suggested that at a higher pH precipitation of Ni(OH)_2 plays a greater role, using the oxide surface as a nucleation site. Metal Complexing ligands like ethylenediaminetetraacetate (EDTA) was found to suppress metal adsorption (Bourg and Schindler, 1979). In the study of Cl^- effect on the mobility of Ni^{2+} , Cu^{2+} and Cd^{2+} in soils, Donner (1978) reported much higher mobility of Cd^{2+} , and, to a lesser extent, Ni^{2+} and Cu^{2+} in Cl^- solution than in ClO_4^- . This was attributed to metal-chloro complex formation. Christensen (1985) reported that the Cd distribution coefficient (Cd-soil/Cd-solution) determined in waste leachates were lower by almost two orders of magnitude than those determined in unpolluted soil solution. This was attributed to complexation, cation competition and ionic strength effects.

The ligands such as ethylenediamine and glycine are capable of complexing the metal ions while allowing simultaneous coordination of metal to the surface. Copper ion and glycine bound to crystal steps of gibbsite can enhance or inhibit metal adsorption, depending on metal/ligand ratio (McBride, 1989). If the metal end of the complex is surface bound, as in the case of Cd(Cl)_x and $\text{Cd(SO}_4)_x$ complexes, adsorption decreases for a given pH. If the ligand end of the complex is surface bound, as in the case of $\text{Cd(S}_2\text{O}_3)_x$ complex, as the ligand concentration increases metal adsorption increases in low pH range and decrease in higher pH range (Benjamin and Leckie, 1982).

Concentration

Increase in the initial metal ion concentrations, in Zn^{2+} sorption by iron hydroxide (Kinniburgh and Jackson, 1982), and Cd^{2+} , Ni^{2+} and Zn^{2+} adsorption by goethite (Bruemmer, et al., 1988), shifted the pH_{50} to a higher pH. At constant pH, relative adsorption decreases with increasing initial metal ion concentration, indicating gradual saturation of sorption sites. A similar effect was reported when initial metal concentrations was constant and solid/solution ratio was decreased (Benjamin and Leckie, 1981). The decrease in pH_{50} at low concentrations of metals in solution is limited by a value below which fractional adsorption of metals becomes independent of initial concentration (Benjamin and Leckie, 1981; Kinniburgh and Jackson, 1982).

In their review of distribution coefficient (metal-soil/metal-solution) data for several trace metals-soil systems, Hendrickson and Corey, (1981) observed that the coefficients increased dramatically as metal concentration decreased relative to the other competing cations. They concluded that this dependence upon relative metal concentration was due to the heterogeneous nature of the soil surface and a competition among various cations for the binding sites on the surface. The existence of sites with a range of binding energies has been discussed by several authors (Shuman, 1975; Benjamin and Leckie, 1981).

Time

Reaction time is another important component in the sorption and transformation of Ni^{2+} in the solid phase. Most studies of the reactions of Ni^{2+} with soils and soil minerals were carried out at relatively short reaction times of a few hours or less (Forbes et al., 1976; Harter, 1979, 1983). With increasing reaction time the bound metals become more immobilized through crystallization of the reaction products (Kuo and Mikkelsen, 1980; McKenzie, 1980). With increasing reaction time from 2 h to 42 days sorption of nickel by goethite at pH 6 increased by 58%, which is much higher than Zn (33%) and Cd (21%). The continuous increase in the amount adsorbed with prolonged reaction time was reflected by decreasing pH_{50} . The pH_{50} levels off after 42 days, suggesting that the kinetics of heavy metals adsorption by goethite are characterized by slow reactions rates, hence require long reaction time to reach equilibrium. The time-dependent reaction was described as a) initial adsorption of metals by external surface and b) solid state diffusion of metals from external surface to internal binding sites (Brummer et al., 1988; Gerth, 1985; Barrow, 1986).

Adsorption of metals by soils or soil minerals is a fast process (Hachiya et al. 1984; Hayes, 1987). During short reaction periods, metals will be adsorbed on the external part of the solid surfaces (Brummer et al., 1988). Understanding the relative proximity of the adsorbed metals to solids at the

solid/water interface is important for the understanding the mobility and accumulation of the metals in the soil system.

The nature of ion adsorption at oxide/water interfaces have been studies using several approaches and techniques. These can be classified as providing direct and indirect evidence. Example of indirect evidence for specific adsorption include the release of H^+ for each metal ion adsorbed (Forbes et al., 1976) and change in surface charge properties of oxides as a result of metal adsorption (Stumm and Morgan, 1981). The later can be detected as a change on the electrophoretic mobility of suspended oxide particles (Bleam and McBride, 1985; Hong and Xiao-Nian, 1991; Vordonis et al., 1992). The indirect approach also includes the use of surface complexation models such as adsorption/desorption by coordinate binding and the modified triple layer model (TLM). The TLM allows the placement of the adsorbed ions either in the inner- or outer-sphere planes and can be used over a wide ionic strength range (Hayes and Leckie, 1986). With the availability of computer programs like FITEQL it is versatile and easy to use.

Reaction of heavy metals with permanent sites of layer silicates is via non-specific electrostatic force. Thus the strength of metal binding depend on the charge and hydration properties of the metal. Nickel and other heavy metal ions retains its water of hydration and a high degree of rotational mobility upon sorption on smectite (McBride, 1976; McBride, 1980; Schoonheydt, 1982),

and shows typical ion exchange behavior. Thus, strength of bonding should depend only on the charge and hydration properties of the cations. However, in the case of vermiculite, where interlayer spacing is limited to one or two molecular layers of water molecules a high degree of motional restriction of the hydrated metal ion is observed. The ion exchange selectivity coefficient for ion exchange at permanent charge sites of layer silicates obeys concentration-charge effects (Mcbride, 1989).

Using x-ray photoelectron spectroscopy to evaluate adsorption of Ni^{2+} and Cu^{2+} by chlorite, Koppelman and Dillard (1977) indicate that Ni^{2+} is probably adsorbed as hexaquo and copper as CuOH^+ . Using the same technique, Davison, et al.(1991) found that Co^{2+} and Ni^{2+} adsorbed onto hectorite and montmorillonite retained their waters of hydration. However, there is evidence of specific adsorption of heavy metals such as Co^{2+} , Zn^{2+} and Cd^{2+} (Tiller and Hodgson, 1962; Garcia-Miragaya and Page, 1976, 1977) at low adsorption levels on layer silicate clays. This might be explained by the presence of a few sites capable of specific metals adsorption on the edges, ie. $-\text{AlOH}$ or $-\text{SiOH}$ (Inskeep and Baham, 1983). Two sorption sites have been identified for metal ions, namely clay-ion-exchange sites and broken bond sites (Egozy, 1980; Peigneur, et al. 1975). Maes and Cremers, (1975), have indicated that Co^{2+} and Zn^{2+} sorption by montmorillonite at pH 6 or below can be fully explained by reversible ion exchange processes. At higher pH, greater

specificity of clays for heavy metals (Farrah and Pickering, 1977; Tiller et al., 1984) is explained by formation of hydrolysis products.

The reaction of heavy metals with metal oxides and hydroxides as well as amorphous aluminum silicates is via specific adsorption. The adsorption of Mg^{2+} by goethite (Bleam and McBride, 1985), and Co^{2+} and Ni^{2+} by $\gamma-Al_2O_3$ (Vordonis et al. 1992) prevents the oxides from developing negative charge at a higher pH, thus shifting the zero point of charge to higher pH. This suggests that the interaction at the interface is inner-sphere complexation.

Using surface complexation models, adsorption of Cu^{2+} , Mn^{2+} , Zn^{2+} , Co^{2+} and Pb^{2+} by $\gamma-Al_2O_3$ (Hachiya et al. 1984), Ca^{2+} and Mg^{2+} by oxisols (Charlet, 1986), and Pb^{2+} and Cd^{2+} by goethite (Hayes 1987) was found to be inner-sphere or specific. Some of these findings have been supported by means of spectroscopic studies.

Direct evidence for metal bonding at interfaces have been provided by the use of instruments such as electron spin resonance (ESR) and x-ray absorption fine structure (EXAFS). The adsorption of Cu^{2+} by aluminum hydroxide (McBride, 1982), Pb^{2+} by goethite (Chisholm-Brause et al. 1990), Cu^{2+} by silica (McBride, 1989), Cu^{2+} , Co^{2+} , Ni^{2+} and Pb^{2+} by manganese oxides (Murray et al., 1968; Gadde and Laitinen, 1974; Murray, 1975; McKenzie, 1980; Golden et al., 1986), and Cu^{2+} by titanium dioxide (Bleam and McBride, 1986) is indicated to be via inner-sphere complexation.

Kinetics

As a result of plant uptake, fertilizer addition and other factors, agricultural soils are rarely in state of equilibrium with regard to ion transport. Therefore, to assess the rate of ions transport in the soil system and to predict the reaction mechanism, extensive study of reaction and chemical kinetics is important.

Kinetic studies involve both complex theoretical and experimental treatments. These complexities are exacerbated when the kinetic studies are extended from homogenous solution to highly heterogeneous soil system. In spite of the complexities, however, recently kinetic approaches to study adsorption reactions in soils is getting more attention (Aringheri and Paradini, 1989; Caski and Sparks, 1985; Elkatib and Hems, 1988; Harter and Lehmann, 1983).

The type of reaction kinetic data obtained depends on the method employed. At present there are two major types of reaction kinetic methods: batch and flow techniques. The others employed so far involves the combination of the two techniques in one way or another. However, it is important to note that the techniques currently used are limited to measuring diffusion-controlled kinetics hence, can not be used to predict reaction mechanism(s) (Sparks, 1989).

Recently a pressure-jump (p-jump) technique in conjunction with surface

complexation models has been used to determine mechanism of ion adsorption at the solid/liquid interface (Astumiam et al., 1981; Hachiya et al., 1979; Hachiya et al., 1984; Ikeda et al., 1982; Sasaki et al., 1985; Zhang and Sparks, 1989, 1990).

Two step relaxations on the order of micro- and milli-seconds were observed in γ -Al₂O₃/aqueous suspension containing Pb²⁺ (Hachiya et al., 1979), Cu²⁺ Mn²⁺, Zn²⁺, Co²⁺ and Pb²⁺ (Hachiya et al., 1984) and in goethite/aqueous suspension containing Pb²⁺ (Hayes, 1987). In all above mentioned relaxations, the inverse of the reaction time constant increased with increasing metal adsorption and pH.

From the kinetic results, the fast relaxations were attributed to the adsorption/desorption processes of metal ions on the hydrous oxide surface group of Al-OH and the slow relaxations to the deprotonation/protonation process induced by the adsorption of metals (Hachiya et al., 1979; Hachiya et al., 1984). For the adsorption/desorption of Pb²⁺ at the goethite/aqueous interface, Hayes (1987) suggested two step reaction: a) adsorption/desorption of Pb²⁺ in the inner-sphere by surface complexation and b) adsorption/desorption of inner-sphere surface complexation which form an ion-pair with an interfacial nitrate ion.

CHAPTER II

REACTION OF NICKEL WITH SOME NORTHEASTERN U.S. SOILS

MATERIALS AND METHODS

B horizons from Christiana (Typic Paleudult), Dekalb (Typic Dystrochrept), Evesboro (Typic Quartzipsamment) and Hagerstown (Typic Hapudalf) soils were used for this study. The chemical and physical properties of the soils are given in Table 2.1. The pH of the soils was measured in 1:1 soil-water and soil-CaCl₂-solutions using glass and saturated calomel electrodes. Free iron oxide was extracted using citrate-dithionite extractant (Olson and Ellis, 1982) and the concentration of iron in the extract was measured using atomic absorption spectrophotometry. Organic carbon content was determined by the method of Walkley and Black (Nelson and Sommers, 1982); and cation exchange capacity was determined by using the neutral 1 M NH₄OAc saturation method. For pH adjustment, one-hundred gram subsamples of the soils were placed in a twin shell dry blender along with varying amounts of Ca(OH)₂ and allowed to mix for at least 0.5 h. After mixing, an appropriate amount of water to approximate field capacity was added to each sample. The soils were allowed to air dry and were then rewet for a total of five wetting and drying cycles. At the end of this time, the samples were ground to pass a 2-mm sieve, and were stored in glass

Soil	pH	pH	O.C	Clay	Silt	Sand	Fe	CEC	MnO ₂
	H ₂ O	CaCl ₂	-----		%	-----		cmol _c kg ⁻¹	μg g ⁻¹
Christiana	4.5	3.7	0.05	28.4	52.1	19.5	4.7	5.3	28.6
Dekalb	4.4	4.1	0.94	20.7	43.7	35.6	1.1	10.1	30.6
Evesboro	5.3	4.8	0.12	3.2	7.7	89.1	0.3	1.3	6.4
Hagerstown	5.0	4.2	0.16	42.4	43.2	13.9	3.6	13.9	145.6

Table 2.1 Physical and chemical characteristics of the B-horizon soils.

bottles. The pH was measured in 1:1 soil-to-water suspensions.

The kinetics of nickel chloride hexahydrate reaction with these soils were conducted using batch kinetics method at temperatures of 288, 298, and 308 K. The effect of pH on the reaction kinetics was obtained by using the limed and unlimed soils. The effect of ionic strength was studied by adjusting soil suspension concentration with CaCl_2 and allowed to equilibrate for two days. The detail of this procedure is as follows.

Twenty-gram soil samples were placed in a water-jacketed linear polyethylene reaction vessel, and 2 L of distilled deionized water were added to provide a 1:100 soil-to-solution ratio. The suspension was allowed to stand 2 d for complete wetting and to attain equilibrium. Prior to initiation of the kinetics measurements, an immersion stirrer was activated and the temperature of the reaction vessel was adjusted to the required value. CO_2 -free nitrogen gas was bubbled through the solution to purge the solution of CO_2 , and an atmosphere of nitrogen gas was maintained over the suspension to provide an inert environment during the reaction. The initial pH of the of the suspension was maintained during the reaction by using the titrimeter set for pH-stat titration. Metal was added at time = 0, and a strip chart recorder recorded both hydroxide demand to maintain pH, and sampling time; the former continuously, the latter by activation of an event marker.

Samples of the suspension were obtained in the following manner: 10-ml syringes were filled with nitrogen, and the gas was used to purge the sampling

tube, then approximately 5-ml sample was drawn into the syringe. The phase were separated by forcing the syringe contents through a Swinney filter equipped with 0.45- μm membrane. (The time required for phase separation varies from 8 s to 12 s) Upon separation of the phases, an event marker on the chart recorder was activated to record the time. After separation, solutions were acidified by adding 0.1-mL of concentrated HCl. The concentration of added nickel remaining as well as concentration of Ca, and Mg in solution were determined by atomic absorption spectrophotometry. The difference between nickel added and nickel remaining in solution were assumed to be sorbed.

A simulation program developed by Harter (1989), was used for modeling purposes. Equation [2-1] can be used to describe one or two simultaneous first-order reversible reaction(s). It is of the form:

$$C/C_0 = \left\{ \left(\frac{1}{k_f} \right) \left[(k_f - k_r A) \exp(-k_f t) + k_r A \right] \right\}_1 + \left\{ \left(\frac{1}{k_r} \right) \left[(k_f - k_r A) \exp(-k_f t) + k_r A \right] \right\}_2 \quad [2-1]$$

where C/C_0 is the fraction of solute remaining in solution at time, t , k_f and k_r are the forward and reverse apparent rate constants, respectively, and A is fraction of solute lost from solution ($1 - C/C_0$); 1 & 2 represent the first and second simultaneous reversible first order reactions (Harter, 1989). Once the apparent rate constants were determined, thermodynamic parameters were calculated according to the following equations:

$$K = k_f / k_r \quad [2-2]$$

$$\Delta G^\circ = -RT \ln K \quad [2-3]$$

$$\log (K_2 / K_1) = \frac{\Delta H_r^\circ}{2.303R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \quad [2-4]$$

the integrated form of van't Hoff equation with reaction enthalpy (ΔH_r°) taken to be independent of temperature, and

$$\Delta S^\circ = \frac{(\Delta H_r^\circ - \Delta G^\circ)}{T} \quad [2-5]$$

K_1 and K_2 are equilibrium constants at temperature T_1 and T_2 respectively; R is the gas constant.

RESULTS AND DISCUSSIONS

The apparent equilibrium constants for the sorption of nickel by soils are given in Table 2.2. The order of sorption and equilibrium (K) values at any given temperature was Hagerstown > Christiana > Evesboro > Dekalb. The Hagerstown soil has the highest cation exchange capacity (CEC) and clay content and sorbed more nickel than the others. The relative difference in the amount of nickel sorbed by the soils cannot, however, be explained on the basis of any single soil property (Table 2.1). A similar case was reported for the reaction of copper, nickel, and zinc with soils using equilibration method (Harter, 1983). On-going experimental work indicates that the goethite content of the soils might explain the relative sorption capacities.

pH Effect

Increase in soil pH increased the sorption of nickel by all soils (Table 2.3). The effect of pH on nickel sorption by soils can be explained by its effect on surface charge (cation exchange capacity), hydrolysis of the hydrated nickel and, possibly, precipitation reactions.

The pK_a for the reaction of $Ni^{2+} + H_2O = NiOH^+ + H^+$ is 9.86 (Baes and Mesmer, 1976). This value is sufficiently high that within the pH range used (Table 2.3) nickel ion exists in solution as hydrated nickel(II). If hydrolysis is responsible for the increase in sorption with increase in pH, as described by

Soil	T (°C)	Keq ₁	Keq ₂	ΔG°_1	ΔG°_2	ΔH_1	ΔH_2	ΔS_1	ΔS_2
				----- KJ mol ⁻¹ -----				---- J (K mol) ⁻¹ ----	
Christiana	15	1.30	---	-0.63	---				
	25	1.35	1.40	-0.74	-0.83	11.72 ± 2.5	17.55	41.1 ± 8.6	61.7
	35	1.70	1.80	-1.36	-1.51				
Dekalb	15	0.38	---	2.40	---				
	25	0.43	---	2.10	---	12.0 ± 3.16	---	33.9 ± 10.8	---
	35	0.51	---	1.72	---				
Evesboro	15	0.65	---	1.03	---				
	25	0.80	---	0.55	---	12.7 ± 4.0	---	40.7 ± 13.4	---
	35	0.91	---	0.24	---				
Hagerstown	15	2.46	2.55	-1.41	-2.24				
	25	3.33	3.33	-2.10	-2.98	13.33 ± 1.65	19.32	38.0 ± 5.5	54.4
	35	4.28	4.30	-2.44	-3.78				

Table 2.2 Effect of temperature and soils on equilibrium constant (Keq), standard free energy (ΔG), enthalpy (ΔH) and entropy (ΔS). Subscripts 1 & 2 represent the first- and second-reversible first-order reactions.

Soil	pH	Keq ₁	Keq ₂	ΔG_1 ---KJ mol ⁻¹ ---	ΔG_2
Dekalb	4.52	0.43	---	2.10	---
	5.37	1.20	0.88	-0.45	0.33
	7.37	1.80	9.00	-1.46	-5.45
Evesboro	5.68	0.80	---	0.55	---
	6.63	1.21	---	-0.47	---
Hagerstown	5.15	1.71	2.00	-1.34	-1.72
	6.43	2.67	2.10	-2.43	-1.84
	7.55	2.75	6.00	-2.51	-4.40

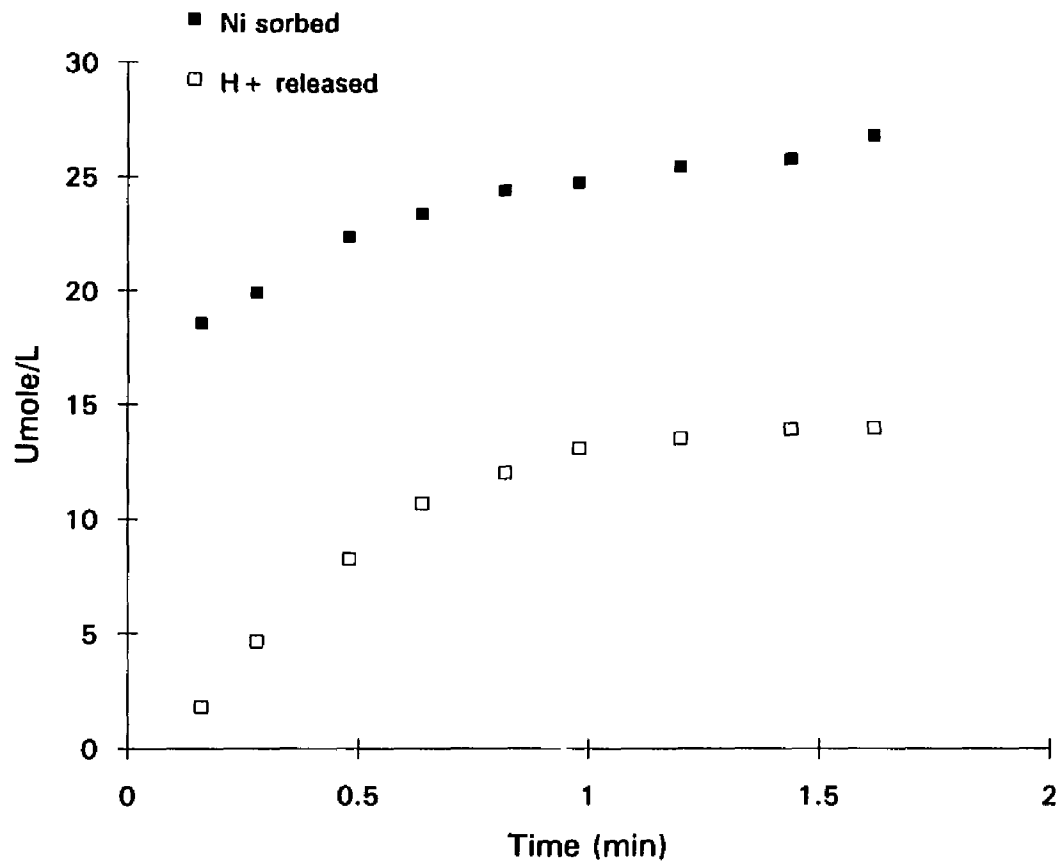
Table 2.3 Effect of pH on equilibrium constant (Keq) and free energy (ΔG).

Barrow (1986) for sorption of zinc by soils, the amount of H^+ released should be twice that of the amount of metal sorbed. This is according to the reaction $SOH + M^{2+} + H_2O = SO-MOH + 2H^+$, where SOH and M^{2+} represent the surface and the divalent metal, respectively. The relationship between the amount of nickel sorbed and H^+ released to solution is given in Fig. 2.1 for Hagerstown soil at pH 7.55. The amount of hydrogen ion released is determined from the hydroxide added to maintain the pH constant during the first two minutes of the reaction. The overall ratio of H^+ released to nickel sorbed is generally lower than 50%. At any given pH, any succeeding increase of nickel sorption with time is larger than the associated H^+ release.

In aqueous systems, the most probable solid form of nickel is $Ni(OH)_2$. The ionic strength of these systems, however, is so low that formation of solid precipitate is improbable. A study of nickel adsorption by chlorite at pH 6.69 suggest that nickel ion is adsorbed as hydrated Ni^{+2} , not as $Ni-OH^+$, nor it is precipitated as $Ni(OH)_2$ or NiO (Koppelane and Dillard, 1977). This indicates that in the pH range used neither hydrolysis nor precipitation reactions are responsible for increased sorption of nickel with increased in pH.

The pH of the soils in water and $CaCl_2$ solution are given in Table 2.1. The pH in $CaCl_2$ is lower than in water, indicating that the soils carry net negative charge. Obviously, pH_o , the pH values of the hydroxylated surfaces at net zero charge, must be lower than the original soils pH. The net surface charge is directly proportional to $pH_o - pH$ (Singh and Uehara, 1986). With

Fig. 2-1. Relationship between the amount of nickel sorbed and hydrogen ion released for Hagerstown soil at pH = 7.55.



increase in soil pH due to liming, $pH_0 - pH$ becomes larger and more negative, and soil negative surface charge density increases. Therefore, the significant contribution of increased nickel sorption with pH can be attributed to increase negative surface charge developed at high pH.

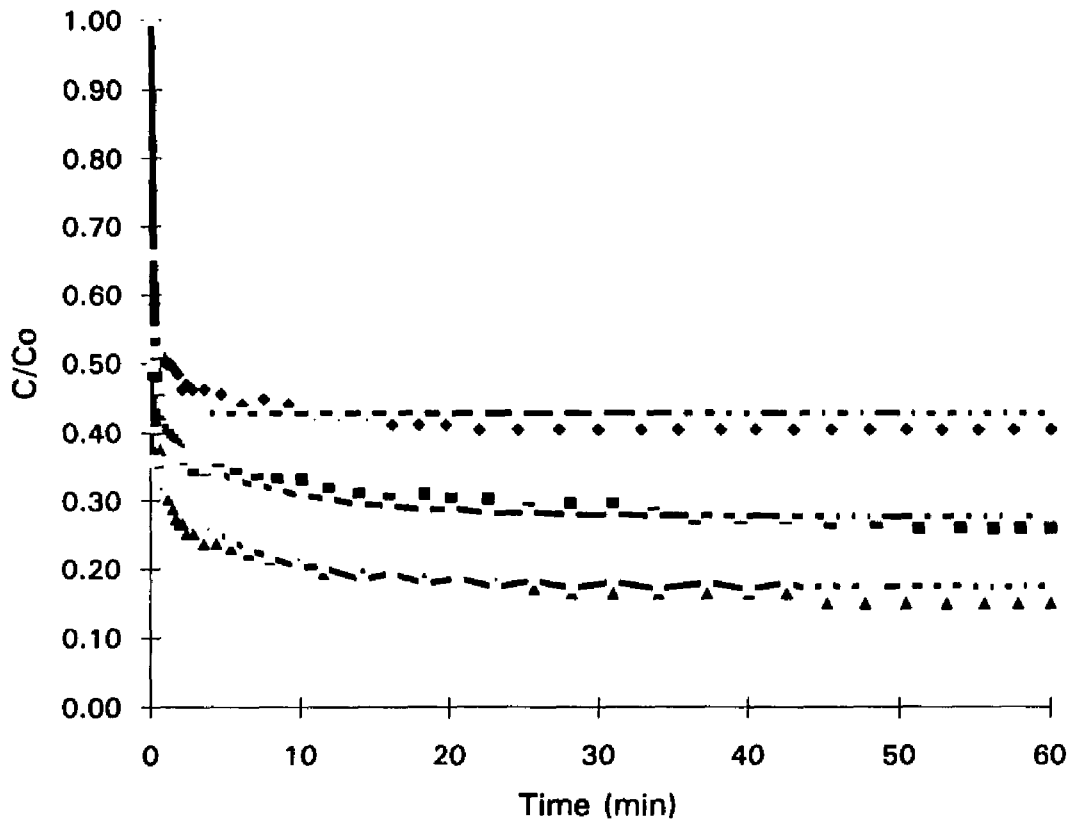
Ionic strength (Calcium) Effect

When adjusted with $CaCl_2$, increase in ionic strength decreases the K for nickel retention by Christiana and Hagerstown soils (Table 2.4). Others have reported similar results when ionic strength was adjusted with $Ca(NO_3)_2$. For example increase in ionic strength decreased sorption of nickel on kaolinite (Mattigod et al. 1979), zinc on soils (Barrow and Ellis, 1986), copper, cadmium, and lead on kaolinite (Schindler et al. 1987), and copper and cadmium on soils (Petruzzelli et al. 1985). Competition of calcium with nickel for the same site at the solid-liquid interface can account for the decreased nickel sorption. Besides competition, increase in ionic strength can reduce the activity of nickel in solution by Ni-Cl complex formation (Doner, 1978), hence contributing to the decrease in nickel sorption. Mattigod et al. (1979), have reported higher adsorption of nickel by kaolinite when the anion was nitrate than when anion was sulfate. Thus, pH, ionic strength and the type of cations and anions present are all important when considering the capacity of soils to sorb nickel.

Soil	[CaCl ₂] M	Keq1	Keq2	ΔG_1 ----KJ mol ⁻¹ ----	ΔG_2
Christiana	0.0	1.35	1.40	-0.74	-0.83
	0.005	0.12	---	5.24	---
Hagerstown	0.0	2.23	3.33	-2.00	-2.98
	0.0005	0.74	---	0.75	---
	0.001	0.32	---	2.79	---
	0.01	0.13	---	5.02	---

Table 2.4 Effect of ionic strength on equilibrium constant (Keq) and free energy (ΔG).

Fig. 2.2 Effect of temperature on nickel sorption by Christiana soil. The points are experimental data and the lines are simulation model.



Temperature Effect

Increase in temperature decreased the concentration of nickel in solution (Fig. 2.2), indicating an endothermic reaction. The increase in temperature increased both the forward and reverse apparent rate constants, with higher increase in the forward rate constant. This resulted in increase of the apparent equilibrium constant (Table 2.2). Copper, cadmium, cobalt, nickel and zinc adsorption by precipitated silica (Bye et al. 1983) and cadmium adsorption by rutile and hematite (Fokkink et al. 1990) were also reported to increase with temperature. Lowering the point of zero charge (Tewari and McLean, 1972; Balesa et al., 1984; Akrapopulu et al., 1986) and increasing adsorbed nickel diffusion into the solid phase (Bruemmer et al. 1988) with increase in temperature have been suggested as an explanation for increased sorption of metals by a solid phase. However, the change in pzc is not sufficient to account for the effect of temperature on metal sorption (Machesky, 1990). Similarly, Bruemmer et al.(1988) have noted that with reaction time of a few hours or less the sorption of nickel by soils is predominantly a surface reaction. Therefore, the effect of temperature on sorption processes can not be explained by increased diffusion.

As seen from the Table 2.2, the standard free energies of Christiana and Hagerstown soils are negative, indicating a spontaneous reaction. The greater the sorption of nickel with pH increase, the more negative the value of the standard free energy. The positive standard free energy of Dekalb and Evesboro

does not mean that the reaction is not spontaneous. It is not ΔG° , but ΔG that determines whether the reaction is spontaneous (Rock, 1983).

The calculated standard enthalpies are all positive (Table 2.2) indicating an endothermic reaction. The wide range of ΔH° calculated are within the same range as the calculated and measured ΔH° of nickel sorption by hematite (Machesky, 1990) and zinc sorption by calcium-magnesite (Jurinak and Bauer, 1956).

Chemical adsorption, if it to proceed spontaneously, must be exothermic. When an ion is adsorbed onto a solid surface, its translational freedom is reduced so the process is accompanied by decrease in entropy which is also negative. For ΔG° to be negative, ΔH° must be negative (Atkins, 1979). On the contrary, this and others findings indicate adsorption of metals is endothermic (Positive ΔH°), ΔS° is positive, and the reaction proceeds spontaneously. This suggests that the adsorption free energy is dominated by a positive and large entropy contribution. To explain this, the hydrated nature of the adsorbed ions must be considered (Jurinak and Bauer, 1956; Machesky, 1990).

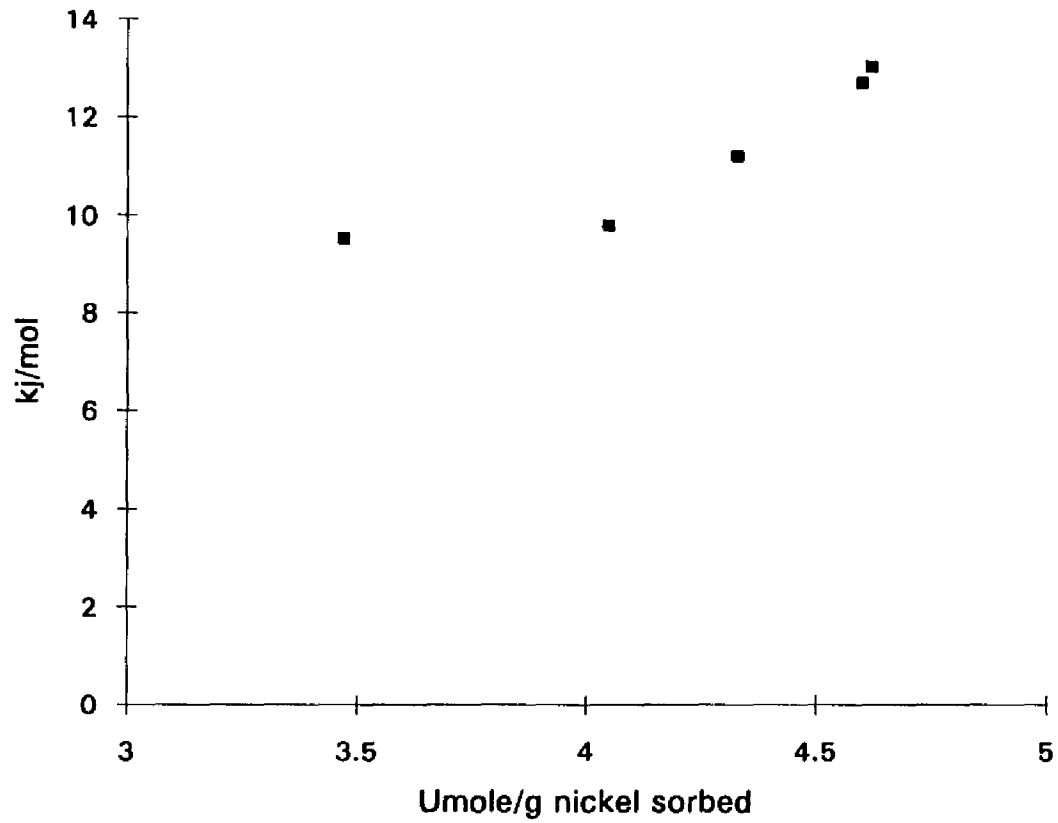
To be strongly adsorbed by the soil (i.e, inner sphere coordination), a hydrated nickel must be partially dehydrated. The absolute entropy of nickel ion hydration is $-173.3 \text{ KJ mole K}^{-1}$ (Marcus, 1985). The calculated ΔS° for the soils are high, but lower than that of ΔS° for complete dehydration. The large entropy calculated can be understood by partial dehydration of nickel ion upon adsorption. Thus, the effect of temperature can be considered as enhancing

entropy by desolvation of water from the primary hydration sheath of adsorbed nickel-ions.

The effect of increasing sorption or surface coverage on ΔH° is illustrated by determining the ΔH° using Clausius-Clapeyron equation, taking into account the time dependent decrease in solution nickel concentration at two temperatures (Fig. 2.3). Increase in sorption for the reaction time of less than three minutes is considered to be related to increase in surface coverage. The change in ΔH° with surface coverage varies among soils, but, the general tendency is increase in ΔH° with increase in sorption. Johnson (1990), has reported decreasing ΔH° with increasing cadmium surface coverage of goethite. This result was obtained for longer reaction time. The result presented in this paper is based on the reaction time of less than three minutes. As more nickel is sorbed, the reaction became more endothermic and the entropy is larger, implying that increasing fraction of water is shed from the primary hydration sheath of the sorbed nickel.

It therefore appears that the large positive entropy is the result of sorbed nickel ion dehydration. Increase in surface coverage increased the entropy, hence, dehydration processes. When nickel is sorbed by the soils, calcium, magnesium and hydrogen ions are released (data not shown). The hydrogen ion released have been suggested to come from oxide and/or the functional group of organic matter, or from the hydration sheath of the adsorbed ion (Quirk and Posner, 1975). However, under the pH conditions used the possibility of H^+

Fig. 2-3. Effect of surface coverage on enthalpy of reaction for reaction time of three minutes for Evesboro soil.



release from the primary hydration sheath is unlikely. Charlet (1986), found a good fit of the triple-layer model to calcium and magnesium adsorption on an oxisol, using inner-sphere surface complexes. For the ion to form an inner-sphere complex, it must lose at least one water of hydration (Grahame, 1947). The suggested dehydration of nickel upon sorption and the resulting release of calcium and magnesium, which were suggested to form inner-sphere complexes, indicates that nickel forms inner-sphere complexes upon sorption. Plant availability and mobility of nickel in soils is a major concern after sludge containing nickel is added to the landscape. Nickel sorption is enhanced by increase in pH, temperature and reaction time, while increase in ionic strength decreased sorption. Therefore, minimizing the mobility and plant availability of nickel added to soils requires the proper consideration of climatic factors, time, soil pH and ionic strength or the competition between metals.

CHAPTER III

IDENTIFICATION OF NICKEL SORBING SITE(S) IN SOILS

MATERIALS AND METHODS

The methods of determination of pH, O.C, and CEC has been mentioned in the materials and methods section of chapter II. The methods of analysis of total Fe, CDB-Fe, and NH_4OX -Fe were as follows:

Citrate-dithionite-bicarbonate (CDB) extraction. This extracts primarily crystalline and amorphous oxides of iron, including goethite. According to this procedure, 4-g of soil was placed into a 100-ml centrifuge tube and 40-ml of 0.3 M Na-citrate + 5-ml of 1 M NaHCO_3 were added. The temperature was brought to 80°C in water bath. One gram of solid $\text{Na}_2\text{S}_2\text{O}_4$ was added with stirring constantly for one min then occasionally for another 15 min. To promote flocculation, 10 ml of acetone and 10 ml of saturated NaCl solution were added. The mixture was mixed, warmed in water bath, and centrifuged. The supernatant was decanted into 500 ml volumetric flask and brought to volume. The concentration of iron in solution was determined using an atomic absorption spectrophotometry (AAS) (Mehra and Jackson, 1960).

Ammonium oxalate (NH_4OX) extraction. This extractant primarily removes the amorphous iron oxides. The detail of this procedure was presented by Schwertman (1973). In this procedure 2 g of soil was placed in 250 ml polypropylene centrifuge bottle. Two-hundred ml of 0.2 M $(\text{NH}_4)_2\text{C}_2\text{O}_4$ solution

was added and shaken immediately in the dark for 4 hrs. About 5 drops of 0.4 % superfloc was added, shaken, and centrifuged. The supernatant was separated and the content of iron in solution was determined using an AAS.

Determination of total iron the soils was performed using HF, H₂SO₄, and HClO₄ digestion method as described by Olsen and Ellis (1982). Half a gram soil sample of finely ground soil was placed in a 30-ml Pt crucible. The sample was wetted with a few drops of H₂SO₄, and added 5 ml of HF and 0.5 ml of HClO₄. The sample mixture was heated on a hot plate until fumes of HClO₄ appeared. The mixture was then allowed to cool and 5 ml of HF was added. The crucible was placed in a sand bath, covered about nine tenths of the crucible top with a Pt lid. The crucible heated to 200 to 225°C, until it evaporate to dryness. The crucible was allowed to cool after which 2 ml of water and a few drops of HClO₄ was added. This was followed by placing the crucible in the sand bath and evaporated the content to dryness. The crucible was removed from the sand bath and allowed to cool followed by addition of 5 ml of 6 N HCl and about 5 ml of water. The mixture was again heated on a hot plate until the solution boiled gently. Once the residue dissolved in HCl, the sample was transferred into 50-ml volumetric flask and the volume was brought to the mark. Similarly, reagent blank was carried through the same procedure. The content of iron in the solution was determined by using an AAS.

Sorption Studies

In nickel sorption experiment, soils were sieved to pass through 0.5-mm sieve. Known weight of these soils were placed into polyethylene centrifuge tubes and known concentration of $\text{Ni}(\text{Cl})_2$ solution was added and allowed to equilibrate by shaking them on end-to-end shaker for 24 h at room temperature. At the end of the shaking the samples were centrifuged and filtered. The concentration of nickel in solution were measured. The soils were spread on plastic dishes and placed in vacuum desiccator for drying. The dried samples were crushed for the purpose of mounting on the slides.

Wavelength Dispersive X-ray Spectrophotometer (WDS)

The sample mounting was similar to the one mentioned above. The model of the instrument used was electron probe micro analyzer, super probe 733. The experimental conditions for WDS setup were: voltage, 20 kv; current, 150 nA; and exposure time of 10 min.

RESULTS AND DISCUSSION

The characteristics of fifteen A-horizons and fifteen B-horizons of some northeastern U.S. soils and the correlation of these characteristics vs the nickel sorption capacities of these soils are given in Tables 3.1 and 3.2 respectively. For both horizons soil pH provided the only good correlation with nickel sorption. Similar results were reported by Harter (1983), and others. No soil component was able to explain the variability in the amount of nickel sorbed by these soils. Harter (1979) reported the failure to quantify the nickel sorption capacities of the soils in terms of soil properties.

The result of WDS for Christiana and Hagerstown B-horizon soils are given in Fig. 3.1 to 3.3. For both soils the x-ray microprobe image of nickel sorbed was closely related to the iron image. Using an electron microprobe technique McKenzie (1975) found that nickel was closely associated with Mn and Fe oxides.

Christiana soil has higher iron content than Hagerstown soil (Table 3.2). However, there is higher sorption of nickel by Hagerstown soil than Christiana (Table 3.2) and there is better association of nickel with iron in Hagerstown soil than in Christiana (Fig. 3.2 and 3.3). On the other hand, there is poor correlation between total- CDB- NH_4OX - extractable iron forms (Table 3.1 and 3.2). Increase in nickel sorption with increase in pH (Table 2.3) indicates a significant contribution of pH dependent sites to sorption. The good correlation

Soil	Sorbed Ni ($\mu\text{g g}^{-1}$)	pH	OC %	CEC $\text{cmol}_c \text{ kg}^{-1}$	% Fe -----			% Al -----		
					Total	NH ₄ OX	CDB	Total	NH ₄ OX	CDB
Caribou	12.3	5.1	1.90	12.3	1.92	0.70	1.28	3.44	0.28	0.59
Christiana	11.6	5.0	0.98	4.0	1.53	0.11	1.28	2.71	0.02	0.14
Dekalb	6.5	4.0	2.19	17.4	1.74	0.36	1.24	4.44	0.15	0.53
Evesboro	4.1	5.1	0.67	2.4	0.26	0.06	0.19	0.65	0.03	0.08
Fauquier	39.5	---	---	---	3.47	0.39	2.45	4.03	0.08	0.37
Gilpin	35.4	6.2	1.61	11.3	1.69	0.22	1.16	3.17	0.11	0.37
Grovton	39.5	6.2	4.25	23.2	2.09	1.26	2.04	2.00	0.42	0.76
Hagerstown	27.6	5.5	1.37	11.7	1.75	0.26	1.45	4.37	0.15	0.43
Lima	51.4	7.3	1.41	11.2	1.87	0.23	1.26	3.45	0.11	0.29
Mardin	23.5	5.1	1.54	11.7	1.97	0.65	1.25	4.06	0.13	0.35
Marlton	22.8	4.3	1.55	16.1	5.46	0.38	0.54	2.30	0.09	0.19
Paxton	28.6	5.5	3.81	16.4	1.47	0.40	1.16	3.35	0.51	0.79
Pocomoke	4.8	4.2	2.05	7.2	0.16	0.06	0.07	1.26	0.09	0.13
Sassafras	4.8	5.0	0.63	3.6	0.58	0.07	0.47	1.56	0.06	0.14
Vergennes	44.3	6.0	2.83	20.3	2.57	0.43	1.13	5.70	0.13	0.29
R ²		0.72	0.20	0.36	0.20	0.16	0.39	0.10	0.07	0.38

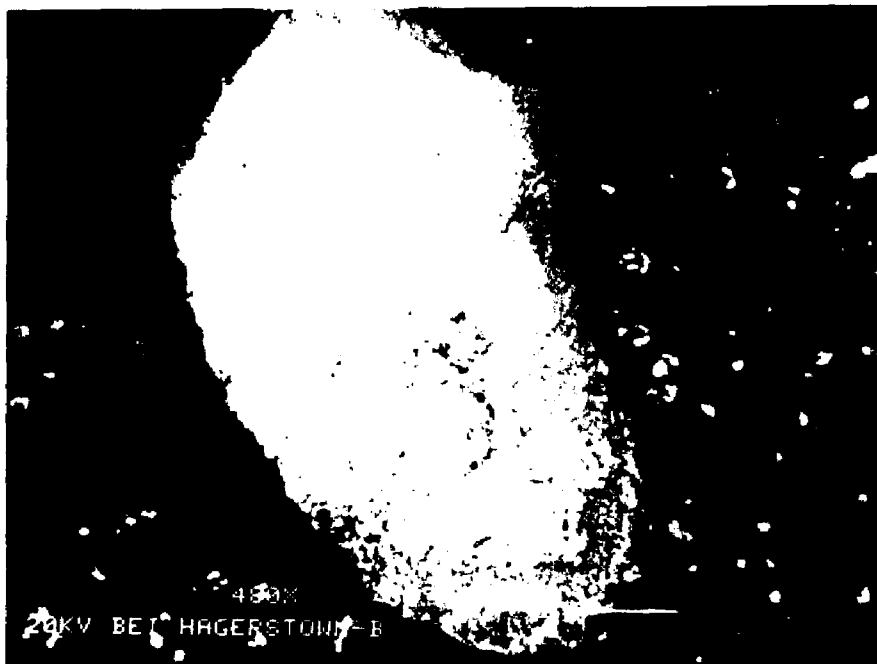
Table 3.1 The chemical characteristics of A-horizon soils and their relationship to the amount of nickel sorbed. Chemical characteristics data were taken from "Mineralogical characteristics of selected soils from northeastern U.S." Bulletin 847, 1983.

Soil	Sorbed Ni ($\mu\text{g g}^{-1}$)	pH	OC %	CEC $\text{cmol}_c \text{ kg}^{-1}$	% Fe			% Al		
					Total	NH ₄ OX	CDB	Total	NH ₄ OX	CDB
Caribou	52.5	7.7	0.20	11.7	2.60	0.18	1.17	5.10	0.08	0.24
Christiana	8.0	4.5	0.05	5.3	5.57	0.17	4.73	7.26	0.03	0.32
Dekalb	3.1	4.4	0.91	10.1	1.91	0.09	1.34	5.32	0.11	0.63
Evesboro	3.1	5.3	0.12	1.3	0.29	0.02	0.22	0.78	0.02	0.08
Fauquier	63.0	---	---	---	3.84	0.33	2.78	4.56	0.07	0.33
Gilpin	41.2	6.2	0.34	10.5	2.79	0.23	1.81	5.63	0.02	0.38
Grovton	19.4	6.1	1.68	11.9	1.82	0.92	1.71	2.14	0.50	0.84
Hagerstown	27.3	???	0.16	13.9	3.92	0.24	2.76	10.4	0.12	0.60
Lima	47.7	7.8	0.59	10.3	2.80	0.29	1.84	4.93	0.12	0.41
Mardin	17.7	5.1	0.24	7.2	1.78	0.22	0.87	3.90	0.06	0.20
Marlton	24.5	4.3	0.25	20.5	16.36	0.83	1.11	6.16	0.49	0.28
Paxton	11.2	5.2	1.51	8.9	1.12	0.14	0.46	0.97	0.16	0.21
Pocomoke	1.7	4.5	0.15	2.7	0.20	0.01	0.03	2.02	0.04	0.08
Sassafras	15.0	4.9	0.25	4.7	2.07	0.18	2.00	4.19	0.10	0.52
Vergennes	54.2	6.6	0.57	24.0	5.60	1.04	2.24	11.7	0.31	0.47
R ²		0.69	0.00	0.43	0.04	0.16	0.08	0.21	0.01	0.01

Table 3.2 The chemical characteristics of B-horizon soils and their relationship to the amount of nickel sorbed. Chemical characteristics data were taken from "Mineralogical characteristics of selected soils from northeastern U.S." Bulletin 847, 1983.



a)

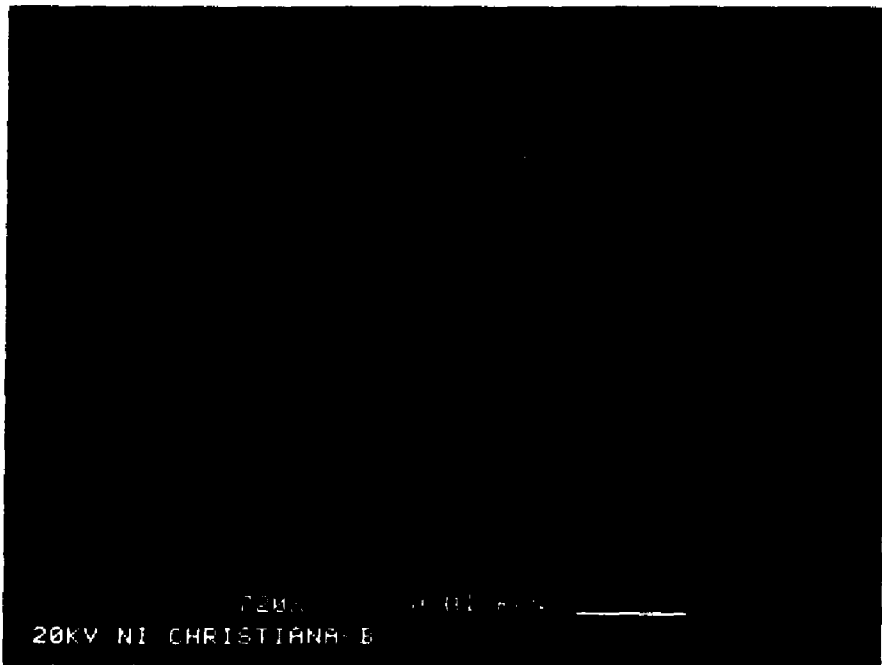


b)

Fig. 3.1 Wavelength dispersive spectroscopic (WDS) images of background particles of a) Christiana and b) Hagerstown soils.



a)



b)

Fig. 3.2 WDS images of iron and nickel on background particle, a) iron and b) nickel for Christiana soil.

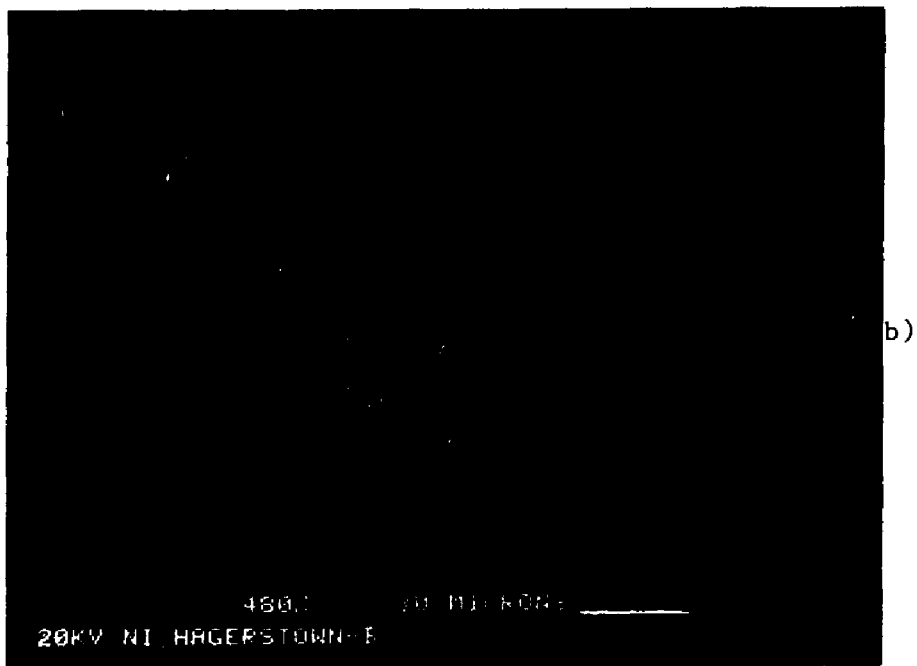
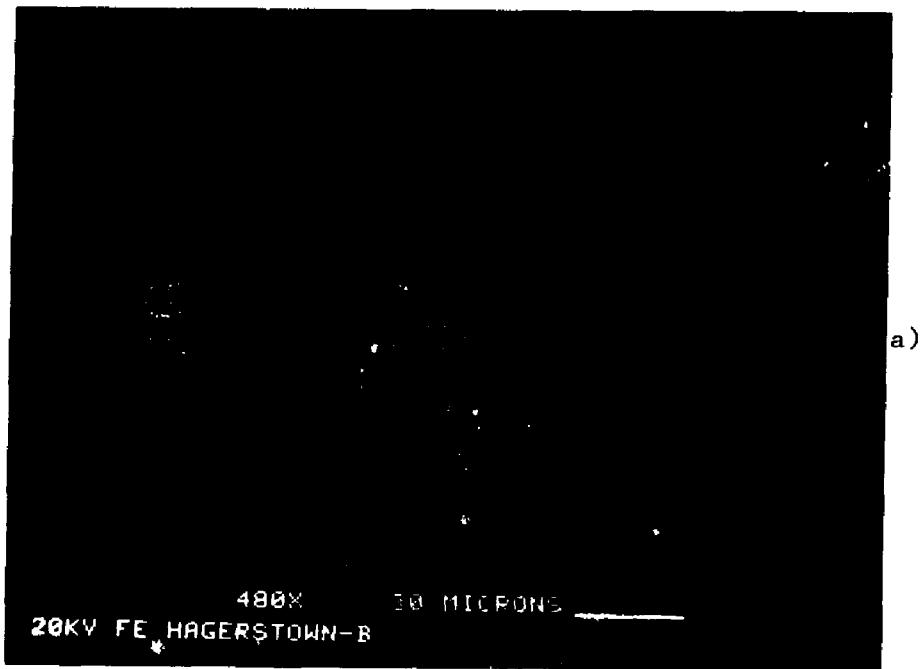


Fig. 3.3 WDS images of iron and nickel on background particle, a) iron and b) nickel for Hagerstown soil.

(0.7) between nickel sorption and soil pH can be explained in the same manner.

The increase in nickel sorption with pH (Table 2.3), significant correlation of nickel sorption capacities with soil pH (Table 3.1 and 3.2) and close association of nickel sorbed with iron oxide (Fig. 3.3 and 3.3) suggest that some mineralogical form of iron oxide may explain the variability in the nickel sorption capacities of the soils. Soil color (dry, 2.5YR 5/8) indicates that the iron oxide in Christiana is probably in the hematite form, which is known to be a poor adsorber of metals. Soil Color of the Hagerstown soil indicates that the iron oxide may be in the goethite form, which is a strong adsorber of metals.

CHAPTER IV

REACTION OF NICKEL WITH GOETHITE: EQUILIBRIUM AND KINETIC STUDIES

MATERIALS AND METHODS

The goethite used in this study was prepared according to the procedure described by Atkinson et al. (1967). Following stabilization, the goethite was placed in dialysis tubing and dialyzed in deionized water by changing the water four times each day until the conductivity of the water equaled that of deionized water. The dialyzed goethite was transferred into a polyethylene container and dispersed using ultrasonic dispersor. The particle size of the goethite was less than 2 μm . A portion of the goethite was freeze dried and examined using x-ray diffraction; the diagnostic 0.418 nm goethite peak was observed (Fig. 4.1). The specific surface area of the goethite was determined using the ethylene glycol monoethyl ether (EGME) method of Carter et al. (1986) and was found to be 69.7 $\text{m}^2 \text{g}^{-1}$.

A potentiometric titration technique was used to determine the surface site density. This technique was also used to determine the pH at point of zero salt effect (pzse), as well as the intrinsic constant for protonation (K_{a1}^i) and deprotonation (K_{a2}^i). The intrinsic constants which are defined in equations

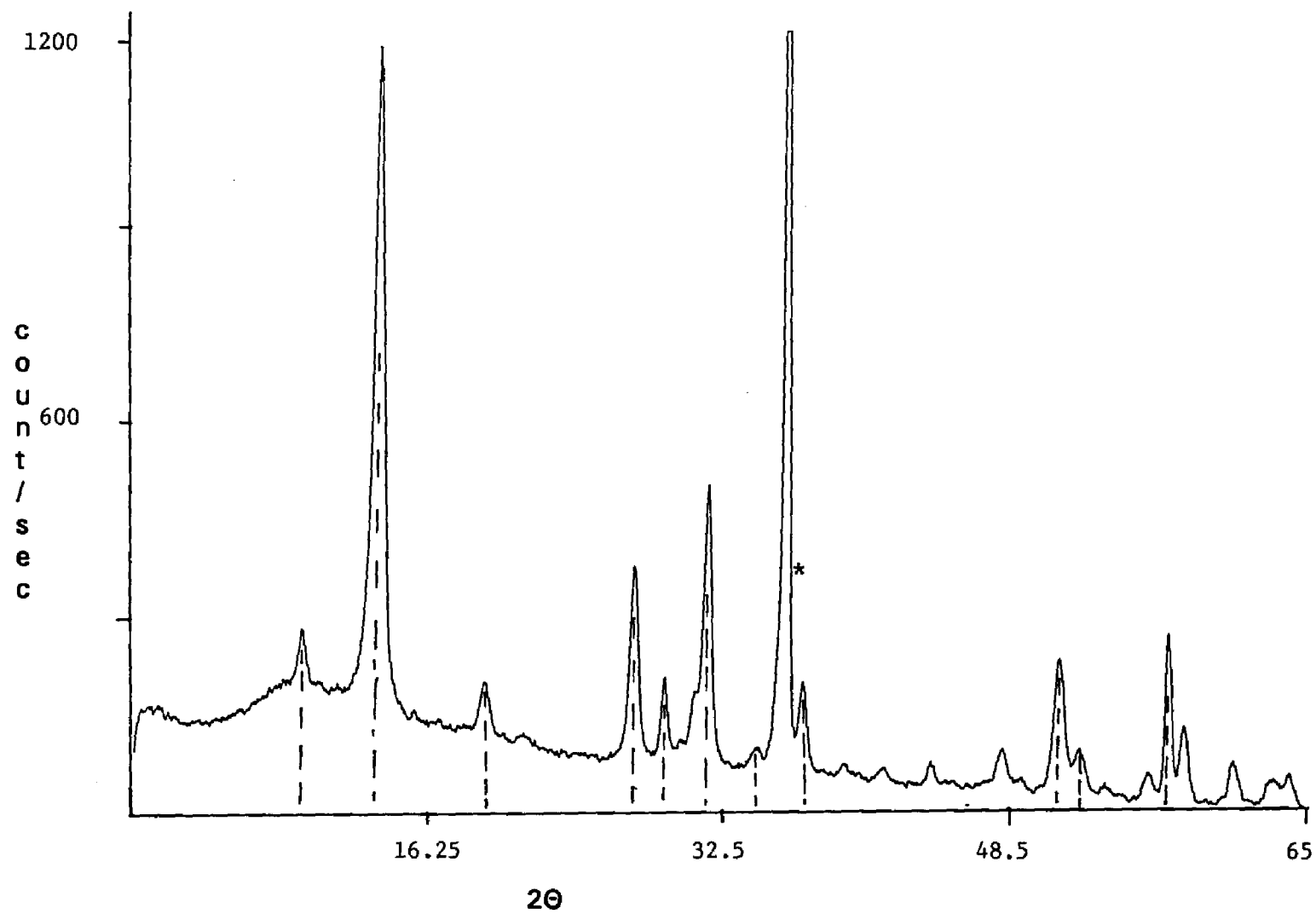


Fig. 4.1. X-ray diffraction spectrum of synthesized goethite. Vertical strikes indicate goethite spectrum, *, indicate tungsten x-ray standard.

[4-1], [4-2], [4-5], and [4-6] were determined using the non-linear least square optimization program, FITEQL (Westall, 1982). The intrinsic constants for the background electrolytes (K_{Na}^i and $K_{NO_3}^i$) were taken from Hayes and Leckie, (1986). The value of surface hydroxyl concentration ($[FeOH]$) was determined using the procedure described by Hohl and Stumm (1976) and was found to be 1.18×10^{-2} M. All the reagents used were analytical grade and no further purification was done.

Titration Experiments

The potentiometric titrations were performed in 125-ml Nalgene bottles maintained at 25°C by inserting the bottle into a water-jacketed plastic reaction vessel. The concentration of goethite suspension was 15 g L^{-1} with the ionic strengths adjusted to 0.01, 0.02, 0.10 and 0.50 M using $NaNO_3$. A teflon coated magnetic stir bar was used to mix the suspension. Nitrogen gas was bubbled through the suspension to purge out CO_2 , and an atmosphere of nitrogen gas was maintained over the suspension to provide an inert environment during the titration.

Acid and base additions were made using burette/dispenser (Fisher, model 395) to which the end was connected to a narrow teflon tube submersed in the suspension. A small incremental amount of 0.1 M HNO_3 and $NaOH$ were added to prevent significant increase in the total volume of the

mixture so that the ionic strength is not affected. Ten minutes were allowed for equilibration after each addition of acid or base before the pH was recorded. The pH was measured using Orion combination electrode.

Adsorption Experiments

The adsorption of $\text{Ni}(\text{NO}_3)_2$ on goethite was studied using 15 g L^{-1} suspensions adjusted to varying pH. Initial nickel concentration was $1.02 \times 10^{-3} \text{ M}$, and three ionic strengths of 0.01, 0.1 and 0.5 M NaNO_3 were used. Ionic strength, pH and metal ion concentrations were adjusted using NaNO_3 , HNO_3 , NaOH , and $\text{Ni}(\text{NO}_3)_2$. After adjusting the ionic strength the goethite-nickel suspensions were placed in polyethylene centrifuge tubes and shaken for 24 h at room temperature using an end-to-end shaker. The phase separation was performed by first centrifuging at 27,000 RCF for 30 min, then filtering through a $0.2\text{-}\mu\text{m}$ membrane filter. The pH of the filtrate was determined and the concentration of nickel in solution was measured using an atomic absorption spectrophotometer.

Zeta Potentials

Zeta-potentials of the goethite- H^+ and goethite- Ni^{2+} in 0.01 M NaNO_3 background electrolyte were measured using model 501 Lazer Zee Meter (PenKem, Inc.). Initial nickel concentration was $1.02 \times 10^{-3} \text{ M}$ and temperature maintained at 25°C .

Kinetic experiments

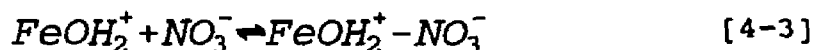
In the kinetic studies, the relaxation times (τ) were measured for the nickel-goethite suspension in 0.01 M NaNO₃ using a Dia-Log p-jump apparatus (Dia-RPC) and conductivity detector (Dia-RPM, Dia-Log Co.). Before conducting kinetic measurements, part of the suspensions were filtered and analyzed for pH and Ni²⁺. During the p-jump relaxation measurements, 10 MPa of pressure was established on a cell containing the goethite-nickel suspension. The pressure was released within 70 μ s by bursting a brass membrane of 0.08 mm thickness. A digitizer (Dia-RRC, Dia-Log Co.) was triggered, and the change in suspension conductivity was recorded. The signals were digitized and sent to computer. The results of the relaxation could be read from the computer print out and displayed on an oscilloscope. Detailed information about the p-jump equipment used and method of measurement have been published elsewhere (Zhang and Sparks, 1989).

Upon p-jump the amplitude rise signifies increase in conductivity. To attribute this increase in conductivity to the shift in the direction of reaction [4-6], an experiment was conducted as follows. Into six plastic bottles, equal amount of goethite suspension from the same source were measured. Small incremental amounts of Ni(NO₃)₂ solution were added. The total ionic strength was adjusted using NaNO₃ solution, and the mixture was allowed to equilibrate for two days. At the end of two days, the suspensions were filtered, conductivity, pH, and concentration of Ni²⁺ in the filtrate measured. A series

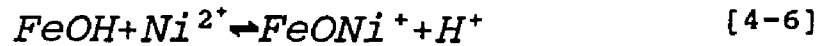
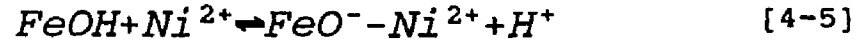
of goethite-free blanks were evaluated in a similar way to investigate the effect of the small incremental amount of nickel added. No significant change in conductivity of the blanks was observed.

The Triple Layer Model (TLM)

In this study Hayes and Leckie's (1986) modified version of the TLM has been used. They modified the model by a) allowing the metal ions to form surface complexes at either the inner- (α -) or outer-sphere (β -) plane instead of the β -plane only, and b) modifying the thermodynamic basis of the TLM, leading to different relationship between activity coefficients and interfacial potentials. Based on the modification, the following chemical reactions are defined to account for reactions of goethite in a NaNO_3 solution.



When nickel is added to the system it may form either the outer-sphere or inner-sphere complexes which can be expressed, respectively, as:



where FeOH represents 1 mole of reactive OH group bounded to Fe in goethite. The intrinsic equilibrium constants (K^i) for the above reactions can be written as:

$$K_{a_1}^i = \frac{[FeOH] [H^+] \exp(-F\psi_o/RT)}{[FeOH_2^+]} \quad [4-7]$$

$$K_{a_2}^i = \frac{[FeO^-] [H^+] \exp(-F\psi_o/RT)}{[FeOH]} \quad [4-8]$$

$$K_{NO_3}^i = \frac{[FeOH_2^+ - NO_3^-] \exp(F(\psi_o - \psi_\beta)/RT)}{[FeOH_2^+] [NO_3^-]} \quad [4-9]$$

$$K_{Na}^i = \frac{[FeO^- - Na^+] \exp(-F(\psi_o - \psi_\beta) / RT)}{[FeO^-] [Na^+]} \quad [4-10]$$

$$K_{Nios}^i = \frac{[FeO^- - Ni^{2+}] [H^+] \exp(-F(\psi_o - 2\psi_\beta) / RT)}{[FeOH] [Ni^{2+}]} \quad [4-11]$$

$$K_{Niis}^i = \frac{[FeONi^+] [H^+] \exp(F\psi_o / RT)}{[FeOH] [Ni^{2+}]} \quad [4-12]$$

where ψ_o and ψ_β are inner- and outer-sphere potentials respectively, F is the Faraday constant, R is the universal gas constant, and T is the absolute temperature. Square brackets indicate concentration and the exponential terms represent the activity coefficients for charged surfaces.

The inner- (σ_o) and outer-sphere (σ_β) charge balance equations when nickel ion is placed in the outer-sphere complex are:

$$\sigma_o = B ([FeOH_2^+] + [FeOH_2^+ - NO_3^-] - [FeO^-] - [FeO^- - Na^+] - [FeO^- - Ni^{2+}]) \quad [4-13]$$

$$\sigma_\beta = B ([FeO^- - Na^+] + 2 [FeO^- - Ni^{2+}] - [FeOH_2^+ - NO_3^-]) \quad [4-14]$$

Where B is $10^3 \times F/A$, and A is surface area in $m^2 g^{-1}$.

When nickel ion is placed in the inner-sphere plane, the charge balance is:

$$\sigma_o = B ([FeOH_2^+] + [FeOH_2^+ - NO_3^-] + [FeONi^+] - [FeO^-] - [FeO^- - Na^+]) \quad [4-15]$$

$$\sigma_\beta = B ([FeO^- - Na^+] - [FeOH_2^+ - NO_3^-]) \quad [4-16]$$

From the electroneutrality condition,

$$\sigma_o + \sigma_\beta + \sigma_d = 0 \quad [4-17]$$

The charge at the diffuse layer (σ_d) can be calculated from Gouy-Chapman-Stern-Grahame theory as follows.

$$\sigma_d = -11.74 C_s^{1/2} \sinh(F\psi_d/2RT) \quad [4-18]$$

Where C_s is the concentration of a symmetrical monovalent electrolyte. The relationship between charge and potential can be derived by assuming that the planes can be treated as plates of two parallel plates in series with,

$$\sigma_o = C_1 (\psi_o - \psi_\beta) \quad [4-19]$$

$$-\sigma_d = C_2 (\psi_\beta - \psi_d) \quad [4-20]$$

where C_1 and C_2 are the capacitance for the inner- and outer-plane surfaces.

RESULTS AND DISCUSSION

Equilibrium Results

Variation of the ionic strength between 0.01 and 0.5 M (NaNO_3) has little effect on nickel adsorption by goethite (Fig. 4.2), indicating little or no competition between supporting electrolyte and nickel ion for adsorption sites. The ionic strength dependence of nickel ion adsorption at the goethite/water interface was modeled using the modified TLM. The parameters used in the model are given in Table 4.1. All the values except for the capacitance were obtained experimentally. Various values of capacitance were checked by TLM modeling of the experimentally obtained surface charge densities. The values of C_1 and C_2 that best fitted the experimental data (Fig. 4.3) as reported in Table 4.1 were used in the subsequent TLM modeling of Ni^{2+} adsorption by goethite. Outer-sphere and inner-sphere models for the three ionic strengths are shown in Fig. 4.4a and 4.4b, respectively. Both the inner- and outer-sphere models assumed one proton released per nickel ion adsorbed as described in Eqs. [4-5] and [4-6].

As indicated by Fig. 4.4a, modeling simulations assuming outer-sphere coordination do not fit the observed data. The TLM model assuming an inner-sphere surface complex (Fig. 4.4b) agrees well with the experimental results; ionic strength has little or no effect on inner-sphere adsorption of nickel ion at the goethite/water interface. Several other reactions given in Table 4.2 along

Fig. 4.2 Adsorption of nickel on goethite at various ionic strengths as a function of pH.

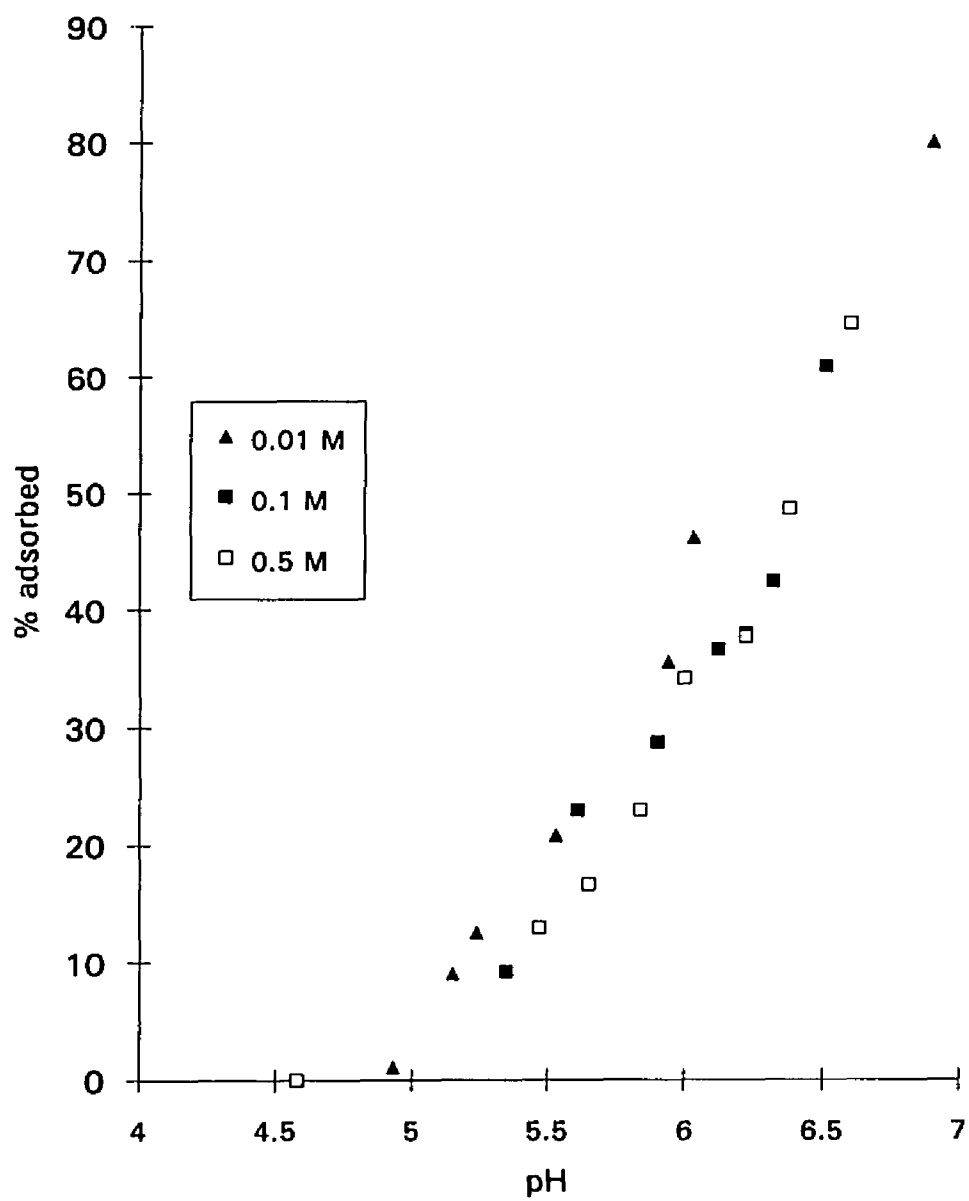


Table 4.1 Triple layer model parameters and values

Surface area	=	69.8 m ² /g
Site density	=	6.8 sites/nm ²
Capacitance: C ₁	=	120 μF/cm ²
C ₂	=	20 μF/cm ²
LogK _{a1} ⁱ	=	-4.16
LogK _{a2} ⁱ	=	-9.12
LogK _{Na} ⁱ	=	-8.80
LogK _{NO3} ⁱ	=	7.60

Table 4.2 Surface complexation reactions stoichiometries considered for TLM calculations.

<u>Surface complexes</u>	<u>Stoichiometric coefficients</u>						
	<u>FeOH</u>	<u>Ni²⁺</u>	<u>H⁺</u>	<u>NO₃⁻</u>	<u>Na⁺</u>	<u>Ψ_o</u>	<u>Ψ_p</u>
Nickel adsorption (inner-sphere)							
1. FeOH + Ni ²⁺ ⇌ FeONi ⁺ + H ⁺	1	1	-1	0	0	1	0
2. FeOH + Ni ²⁺ + H ₂ O ⇌ FeONiOH + 2H ⁺	1	1	-2	0	0	0	0
3. FeOH + Ni ²⁺ + NO ₃ ⁻ ⇌ FeONi ⁺ -NO ₃ ⁻ + H ⁺	1	1	-1	1	0	1	-1
Nickel adsorption (outer-sphere)							
4. FeOH + Ni ²⁺ ⇌ FeO ⁻ -Ni ²⁺ + H ⁺	1	1	-1	0	0	-1	-2
5. FeOH + Ni ²⁺ + H ₂ O ⇌ FeO ⁻ -NiOH ⁺ + 2H ⁺	1	1	-2	0	0	-1	1
Proton adsorption (inner-sphere)							
6. FeOH + H ⁺ ⇌ FeOH ₂ ⁺	1	0	1	0	0	1	0
7. FeOH ⇌ FeO ⁻ + H ⁺	1	0	-1	0	0	-1	0
Sodium adsorption (outer-sphere)							
8. FeOH + Na ⁺ ⇌ FeO ⁻ -Na ⁺ + H ⁺	1	0	-1	0	1	-1	1
Nitrate adsorption (outer-sphere)							
9. FeOH + NO ₃ ⁻ + H ⁺ ⇌ FeOH ₂ ⁺ -NO ₃ ⁻	1	0	1	1	0	1	-1

Table 4.3 Surface complex reactions and equilibrium constants

<u>Reactions</u>	<u>logK</u>
$\text{FeOH} + \text{Ni}^{2+} \leftrightarrow \text{FeONi}^+ + \text{H}^+$	-2.458
$\text{FeOH} + \text{Ni}^{2+} + \text{NO}_3^- \leftrightarrow \text{FeONi}^+ \text{-NO}_3^- + \text{H}^+$	-0.989
$\text{FeOH} + \text{Ni}^{2+} + \text{H}_2\text{O} \leftrightarrow \text{FeO}^- \text{-NiOH}^+ + 2\text{H}^+$	0.500
$\text{FeOH} + \text{Ni}^{2+} \leftrightarrow \text{FeO}^- \text{-Ni}^{2+} + \text{H}^+$	-5.230

Fig. 4.3 Surface charge density as a function of pH. The points are experimental data and the lines represent TLM modeling.

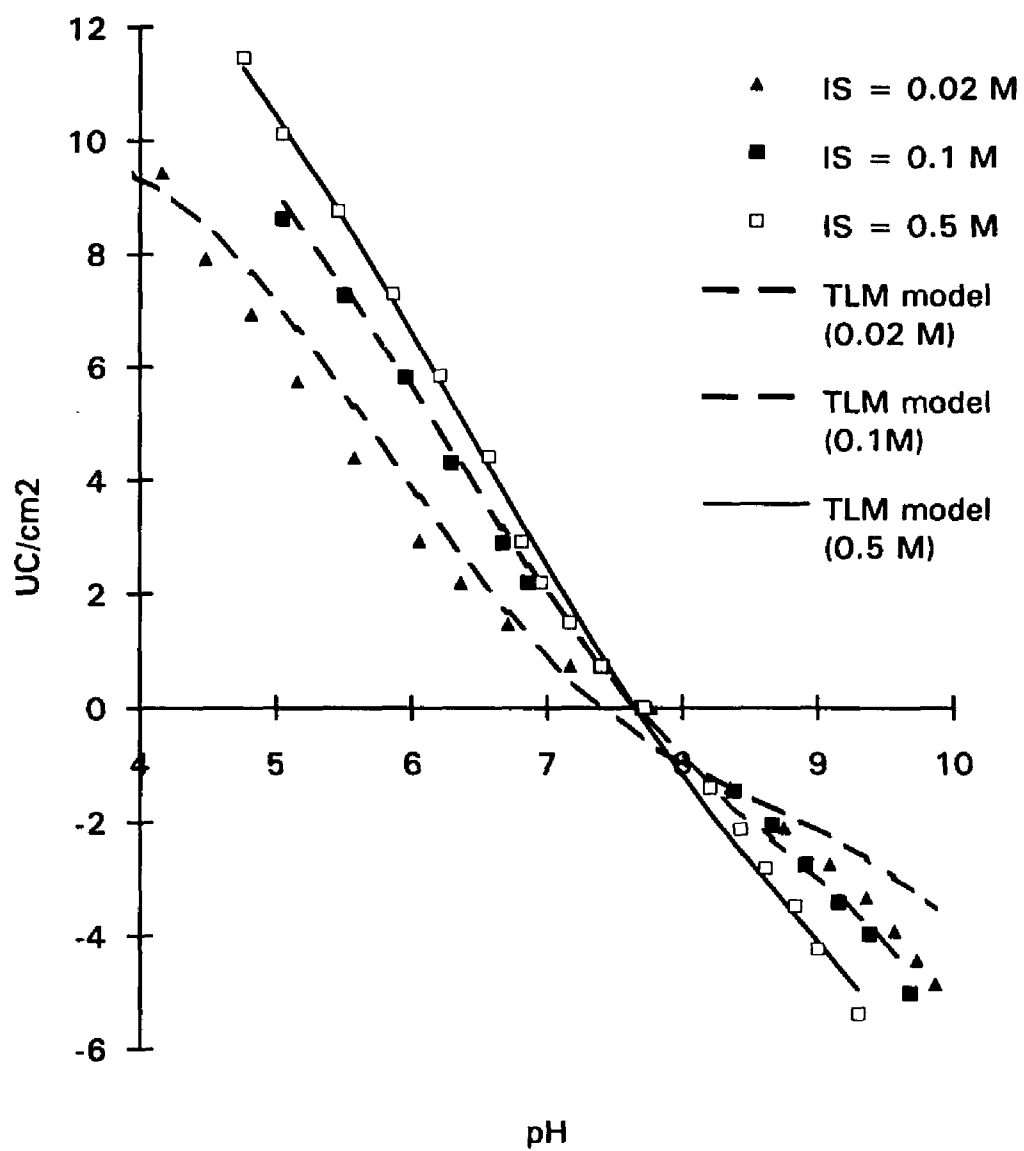


Fig. 4.4a TLM calculation for outer-sphere complexes at three ionic strengths.

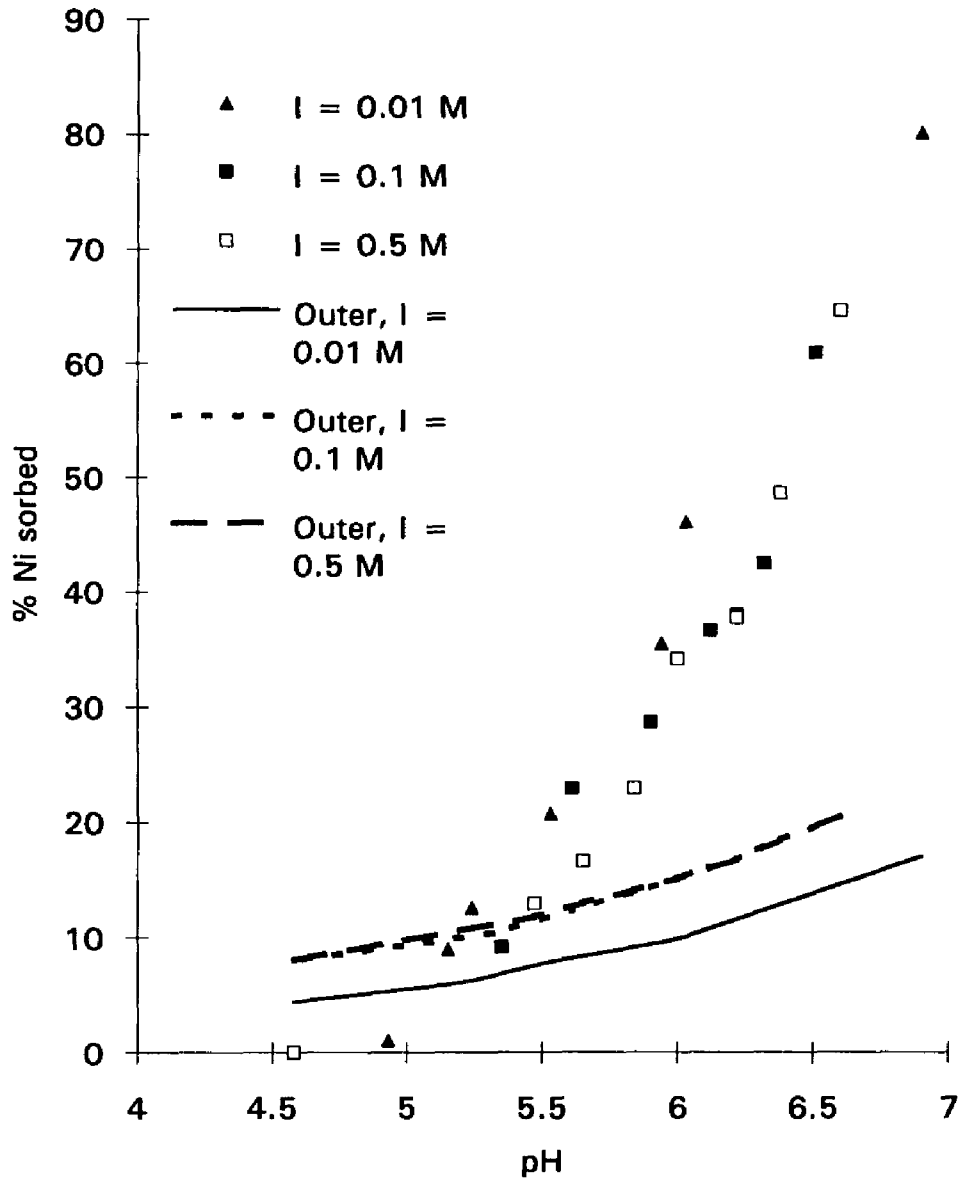
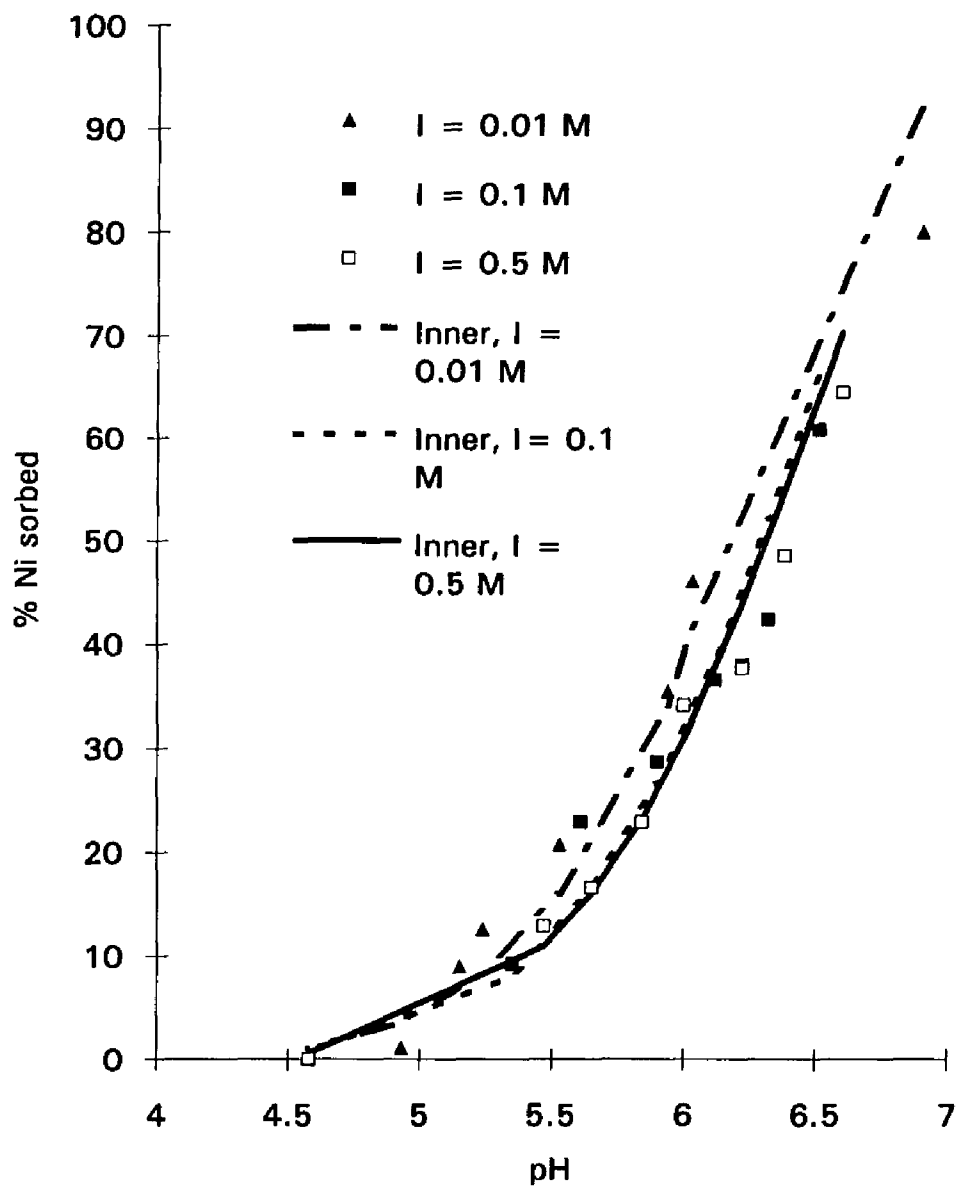


Fig. 4.4b TLM calculation for inner-sphere complexes at three ionic strengths.

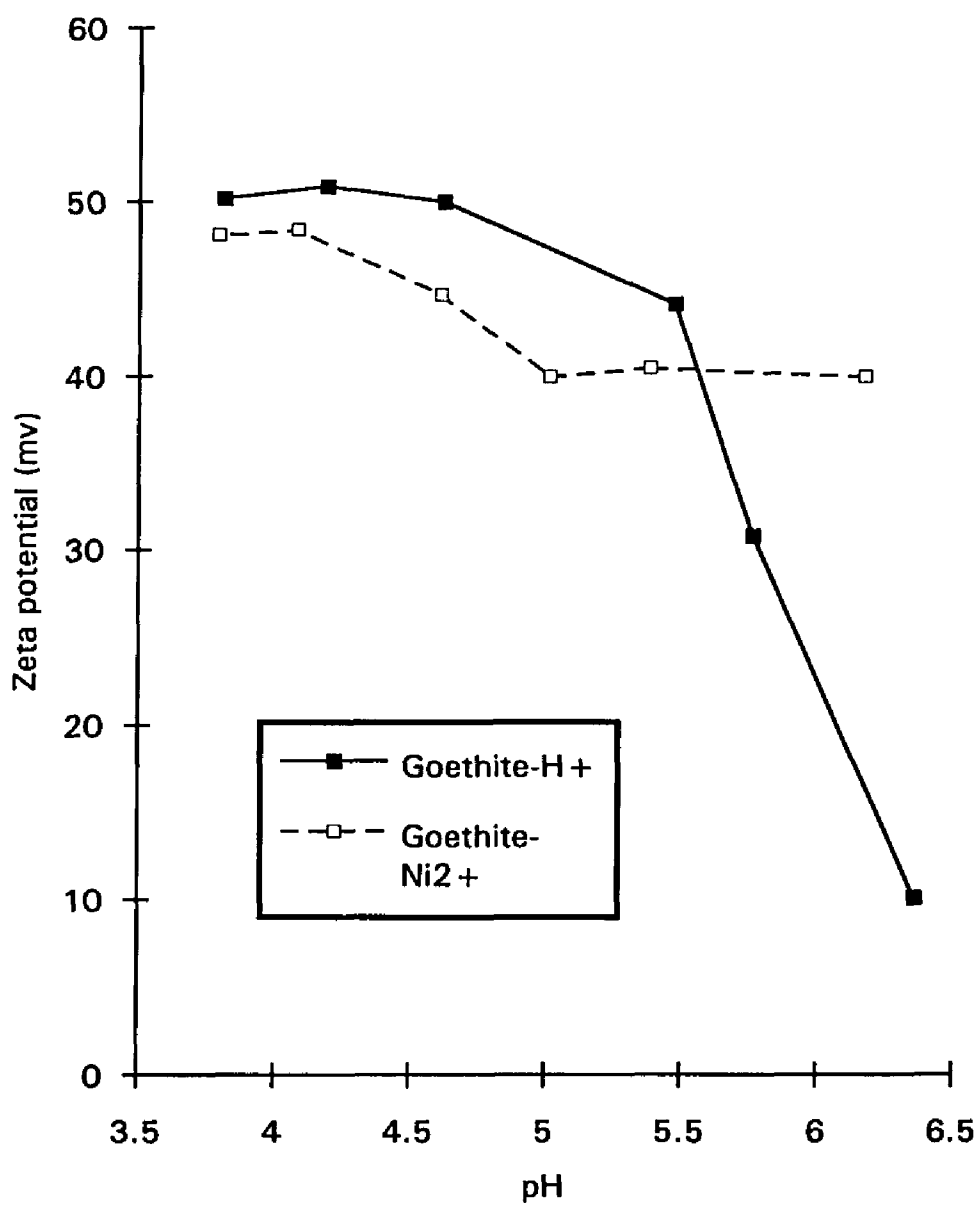


with their stoichiometric coefficients were tested. The values of the equilibrium constants are given in Table 4-3. However, only Eq. [4-6] was able to adequately describe the experimental data. Incorporation of hydrolyzed Ni^{2+} into the model for the outer- and inner-sphere complexes did not change the value of K_{Ni}^i for the reaction. This was expected, because of the high pK_a for NiOH^+ formation ($\text{pK}_a = 9.86$) and the comparatively low pH range in which the reactions were conducted. Therefore, the possibility of nickel ion hydrolysis in the adsorption processes was ruled out.

The zeta potential for goethite- H^+ and goethite- Ni^{2+} system as a function of pH is given in Fig. 4.5. The zeta potential of goethite- H^+ is higher at lower pH, while that of goethite- Ni^{2+} is higher at higher pH. The higher zeta potential of clay-metal compared to clay- H^+ at higher pH has been attributed to specific adsorption (Hong and Xia-Nian, 1991). This is in agreement with the results of TLM modeling, above.

The modified TLM used in this study equate α -plane to the inner Helmholtz plane and β -plane to outer Helmholtz plane (Hayes and Leckie, 1986). For the ion to be in the inner-sphere plane it must lose at least one water molecule from the primary hydration sheath on the side facing the surface (Grahame, 1947). In the study of nickel reaction kinetics with some northeastern U.S. soils, the entropy of nickel sorption was found to be positive and larger for higher nickel sorbing soils. This was interpreted as loss of nickel hydration shell water molecules upon sorption by the surface (Chapter II).

Fig. 4.5 Zeta potential of goethite-H⁺ and goethite-Ni²⁺ as a function of pH.



Kinetic Model

The electrical double layer not only affects the equilibrium partitioning between solid and liquid phases, but also the reaction at the interfaces. Therefore, describing the kinetic results using the TLM model is necessary. This can be performed as follows for equation [4-6].

$$K_1^i = \frac{k_1^i}{k_{-1}^i} = \frac{k_1}{k_{-1}} \exp(F\psi_o/RT) \quad [4-21]$$

Where k_1 and k_{-1} are forward and reverse rate constants; k_1^i and k_{-1}^i are intrinsic forward and reverse rate constants respectively.

Relating surface potential to activation potential for adsorption/ desorption, let the activation potential be ψ_1^* and ψ_{-1}^* , for the activation required to overcome the EDL potential for adsorption and desorption steps, respectively. This allows the intrinsic rate constants to be related to rate constants k_1 and k_{-1} . For a small perturbation of equilibrium, surface potential is relatively unchanged during the course of the reaction. Thus, assuming the magnitude of the activation potential for the processes of adsorption and desorption are equal and opposite, $\psi_1^* = \psi_{-1}^* = \psi_o/2$ (Hayes and Leckie, 1986).

Therefore,

$$k_1^i = k_1 \exp(F\psi_o/2RT) \quad [4-22]$$

Rearranging to express k_1 in terms of k_1^i

$$k_1 = k_1^i \exp(-F\psi_0/2RT) \quad [4-23]$$

and

$$k_{-1}^i = k_{-1} \exp(-F\psi_0/2RT) \quad [4-24]$$

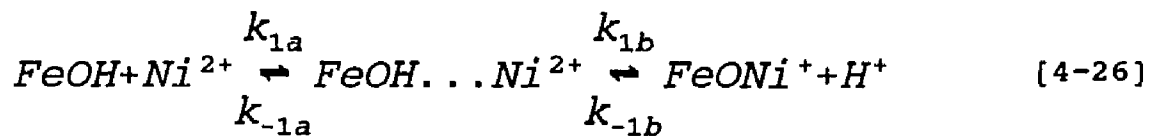
or

$$k_{-1} = k_{-1}^i \exp(F\psi_0/2RT) \quad [4-25]$$

Determination of Reaction Mechanism

Changes in the reciprocals of the relaxation time constants (τ^{-1}) with the amount of nickel sorbed are used to test proposed mechanisms of the reaction.

The derivation of τ_i^{-1} concentration dependence for the mechanism



(step 1a, K_{1a})

|

(step 1b, K_{1b})

is as follows. In terms of $[FeOH]$ the rate equation can be given as:

$$r = \frac{d[FeOH]}{dt} = -k_{1a}[FeOH][Ni^{2+}] + k_{-1a}[FeOH \dots Ni^{2+}] \quad [4-27]$$

and the mass balance equations are:

$$H_T = [FeOH] + [FeOH \dots Ni^{2+}] + [H^+] \quad [4-28]$$

$$Ni_T = [Ni^{2+}] + [FeOH \dots Ni^{2+}] + [FeONi^+] \quad [4-29]$$

$$FeOH_T = [FeOH] + [FeOH \dots Ni^{2+}] + [FeONi^+] \quad [4-30]$$

leads to

$$\Delta [FeOH] = \Delta [Ni^{2+}] \quad [4-31]$$

$$\Delta [H^+] = -\Delta [FeOH \dots Ni^{2+}] - \Delta [FeOH] \quad [4-32]$$

$$\Delta [H^+] = \Delta [FeONi^+] \quad [4-33]$$

and

$$\frac{d(\Delta [FeOH])}{dt} = -k_{1a} ([FeOH] + [Ni^{2+}]) \Delta [FeOH] + k_{-1a} \Delta [FeOH \dots Ni^{2+}] \quad [4-34]$$

Defining the rate in terms of $[FeOH \dots Ni^{2+}]$,

$$r = \frac{d[FeOH \dots Ni^{2+}]}{dt} = k_{1a} [FeOH] [Ni^{2+}] - k_{-1a} [FeOH \dots Ni^{2+}] + k_{-1b} [FeONi^+] [H^+] - k_{1b} [FeOH \dots Ni^{2+}] \quad [4-35]$$

and assuming species I is steady-state intermediate

$$0 = k_{1a} ([FeOH] + [Ni^{2+}]) \Delta [FeOH] - (k_{-1a} + k_{1b}) \Delta [FeOH \dots Ni^{2+}] + k_{-1b} ([FeONi^+] + [H^+]) \Delta [FeONi^+] \quad [4-36]$$

Under steady-state conditions

$$\Delta [FeOH] = -\Delta [FeONi^+] \quad [4-37]$$

$$\Delta [FeOH \dots Ni^{2+}] \ll \Delta [FeOH]$$

so that

$$\begin{aligned}
0 = & k_{1a} ([FeOH] + [Ni^{2+}]) \Delta [FeOH] \\
& - (k_{-1a} + k_{1b}) \Delta [FeOH \dots Ni^{2+}] \\
& + k_{-1b} ([FeONi^+] + [H^+]) \Delta [FeOH]
\end{aligned}
\tag{4-38}$$

or

$$\begin{aligned}
\Delta [FeOH \dots Ni^{2+}] = & (k_{-1a} + k_{1b})^{-1} \{ k_{1a} ([FeOH] + [Ni^{2+}]) \\
& - k_{-1b} ([FeONi^+] + [H^+]) \} \Delta [FeOH]
\end{aligned}
\tag{4-39}$$

$$\begin{aligned}
\frac{d\Delta [FeOH]}{dt} = & -k_{1a} ([FeOH] + [Ni^{2+}]) \Delta [FeOH] \\
& + k_{-1a} \Delta [FeOH \dots Ni^{2+}]
\end{aligned}
\tag{4-40}$$

Substituting for $\Delta[FeOH \dots Ni^{2+}]$

$$\begin{aligned}
\frac{d\Delta [FeOH]}{dt} = & (k_{-1a} + k_{1b})^{-1} \{ k_{1a} k_{1b} ([FeOH] + [Ni^{2+}]) \\
& + k_{-1a} k_{-1b} ([FeONi^+] + [H^+]) \} \Delta [FeOH]
\end{aligned}
\tag{4-41}$$

Integrating

$$\Delta [FeOH] = \Delta [FeOH] \exp(-t/\tau_f)
\tag{4-42}$$

with

$$\tau_f^{-1} = (k_{-1a} + k_{1b})^{-1} \{ k_{1a} k_{1b} ([FeOH] + [Ni^{2+}]) + k_{-1a} k_{-1b} ([FeONi^+] + [H^+]) \} \quad [4-43]$$

Assuming $k_{1b} \gg k_{1a}$

$$\tau_f^{-1} = k_{1a} ([FeOH] + [Ni^{2+}]) + k_{-1a} (K_{1b}^{-1} ([FeONi^+] + [H^+])) \quad [4-44]$$

Based on Eqs. [4-23] and [4-25] since

$$\begin{aligned} K_{1a} &= k_{1a}^i \exp(-2F\psi_0/RT) \\ k_{1a} &= k_{1a}^i \exp(-F\psi_0/RT) \\ k_{-1a}^i &= k_{-1a}^i \exp(F\psi_0/RT) \\ K_{1b} &= K_{1b}^i \exp(F\psi_0/RT) \\ k_{1b} &= k_{1b}^i \exp(F\psi_0/RT) \\ k_{-1b} &= k_{-1b}^i \exp(-F\psi_0/RT) \end{aligned} \quad [4-45]$$

then

$$\tau_f^{-1} = k_{1a}^i \exp(-F\psi_0/RT) ([FeOH] + [Ni^{2+}]) + k_{-1a}^i (K_{1b}^i)^{-1} ([FeONi^+] + [H^+]) \quad [4-46]$$

or

$$\tau_f^{-1} = k_{-1}^{i'} \{ K_1^{i'} \exp(-F\psi_0/RT) \times ([FeOH] + [Ni^{2+}]) + ([FeONi^+] + [H^+]) \} \quad [4-47]$$

with

$$k_{-1}^{i'} = k_{-1a}^i (K_{1b}^i)^{-1} \quad [4-48]$$

$$K_1^{i'} = K_{1a}^i K_{1b}^i$$

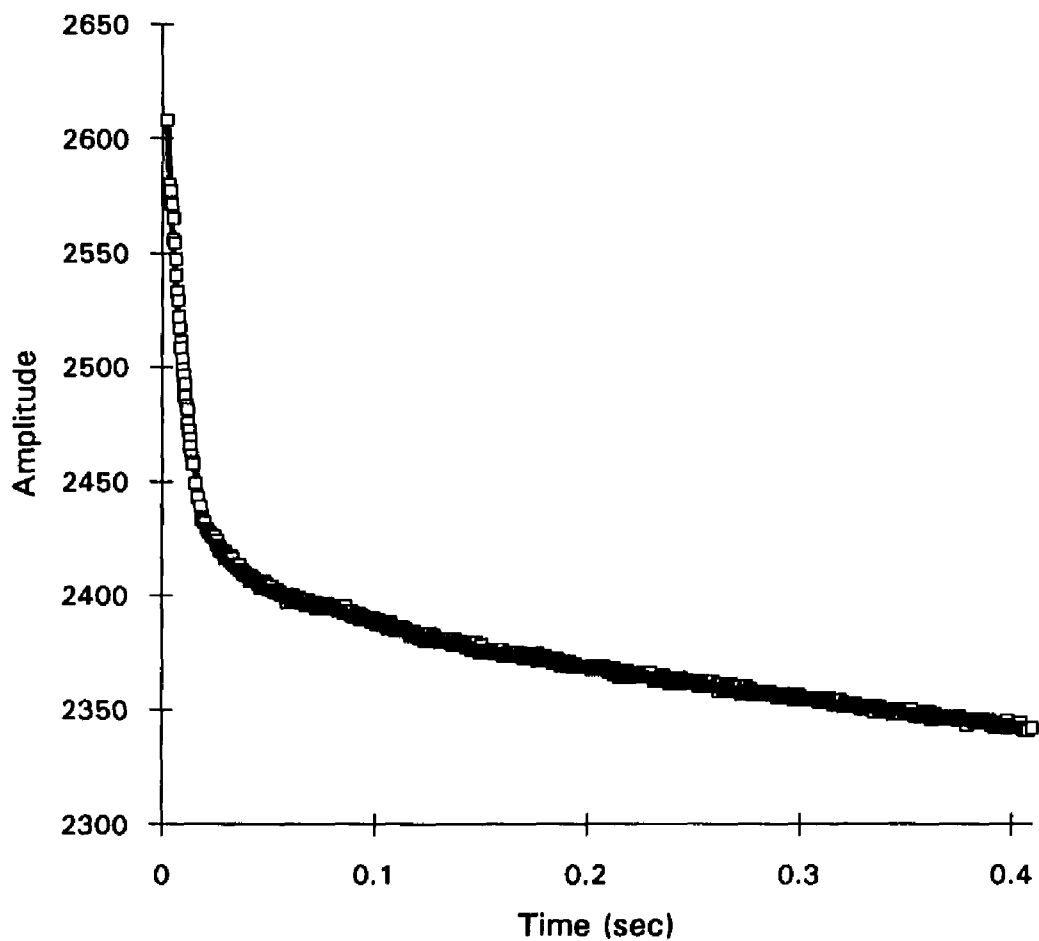
If adsorption/desorption reaction of Eq. [4-26] represents plausible reaction mechanism, then the plot of τ^{-1} versus the terms in the bracket of Eq. [4-47] will give a straight line passing through the origin with the slope equal to $k_{-1}^{i'}$.

Kinetic Results

Kinetics of nickel adsorption on goethite using the p-jump technique exhibited two steps relaxation (Fig. 4.6). No relaxation was observed in goethite- $NaNO_3$, filtrate of goethite- Ni^{2+} , filtrate of goethite- $NaNO_3$, or goethite itself. From the static study we already know that nickel is specifically adsorbed on the surface of goethite. Therefore, relaxations obtained for goethite- Ni^{2+} system is attributed to adsorption/desorption of nickel at the interface.

Relaxation for goethite- Ni^{2+} was observed only when the surface coverage was high, or more nickel was adsorbed. For the cases when

Fig. 4.6 Typical pressure-jump relaxation curve for Ni(II) adsorption on goethite. Amplitude versus time.



suspension pH and the amount of nickel adsorbed were low the relaxations were not consistent. The reason(s) for the inconsistency of relaxation time constants at lower pH values are not understood at this moment. Therefore, only those relaxation data at higher pH and higher adsorption were considered. The relaxation time constants were determined from the relaxation curves using computer simulation (Fig. 4.6). The fast relaxation time constants (τ_f) values are about 30 times shorter than slow relaxation time constants (τ_s). Both decreased with decrease in pH (Fig. 4.7). Upon p-jump, the amplitude rise (Fig. 4.6) signifies increase in conductivity. This increase in conductivity was related to increase in sorption of nickel, with concomitant release of H^+ (Fig. 4.8). This means that increase in pressure shifted the equilibrium reaction of equation [4-6] to the right thus producing more H^+ , which is responsible for the increase in conductivity.

Using the relaxation data, various mechanisms of nickel adsorption /desorption at the interface were considered. Some of them (adsorption /desorption by electrostatic binding and adsorption/desorption of hydrolyzable metal ion) were ruled out based upon the information from the equilibrium results. Adsorption/desorption by coordinate binding as described in equation [4-6] and steady-state model in adsorption/ desorption were investigated.

Adsorption/desorption by coordinate binding was checked as a possible reaction mechanism by using the Eq. [4A-20] given in Appendix 4A. The plot failed to give a straight line that passes through the origin, thus excluding the

Fig. 4.7 Effect of pH on fast (τ_4') and slow (τ_3') relaxation times.

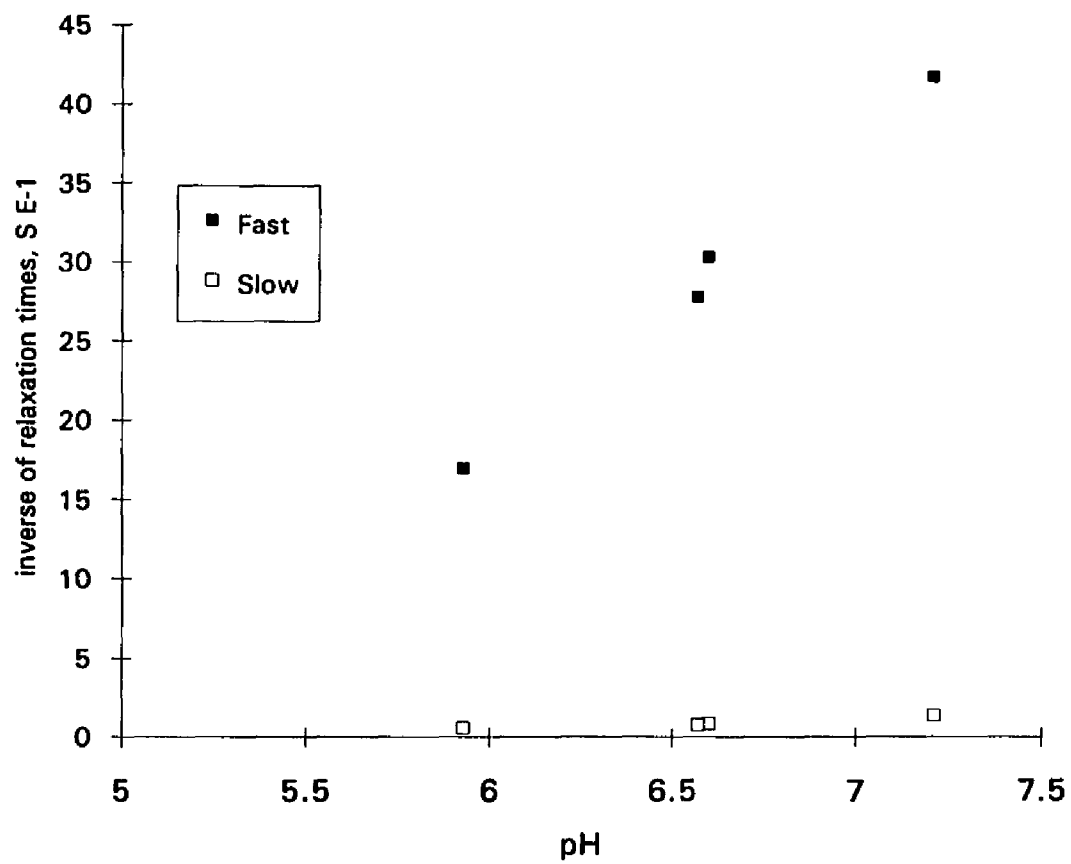
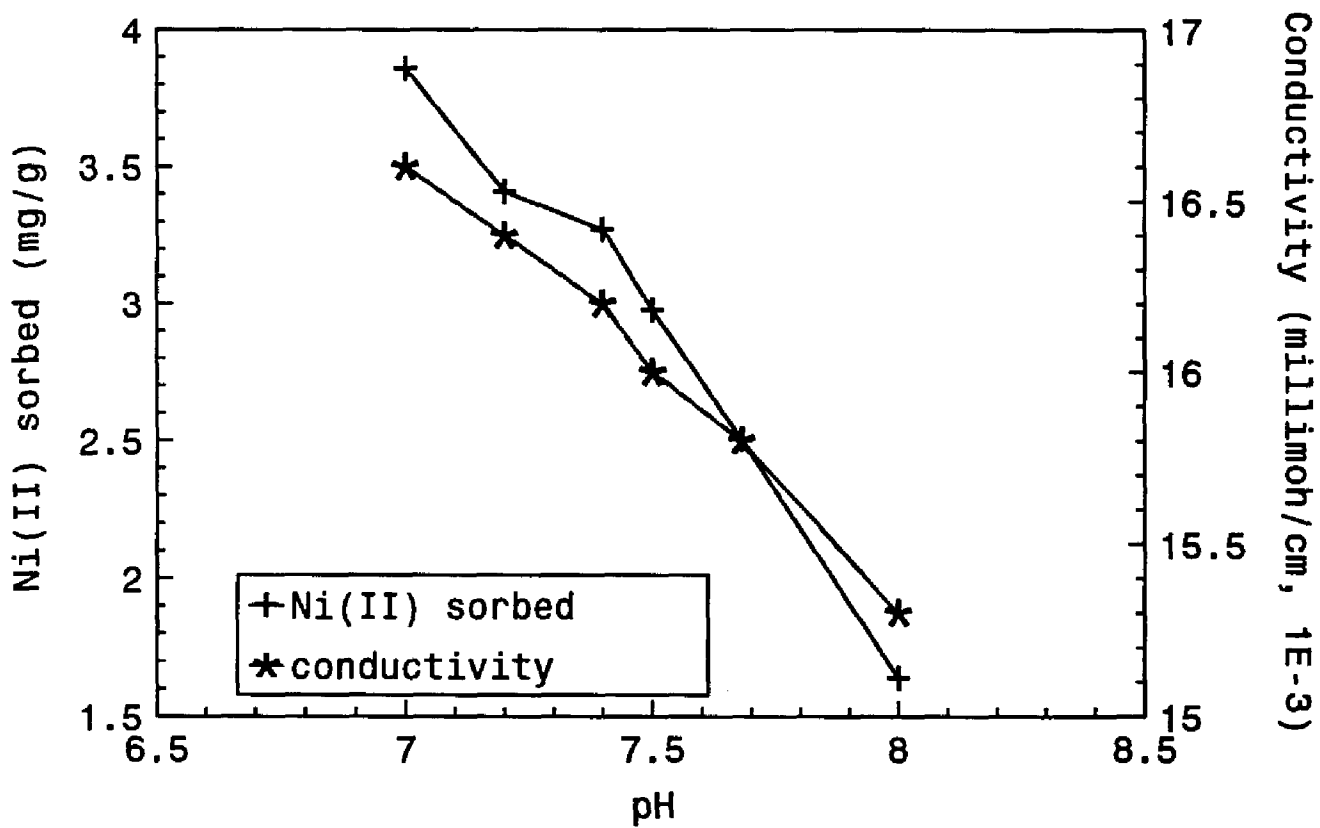


Fig. 4.8 Effect of pH on the amount of Ni(II) sorbed and conductivity

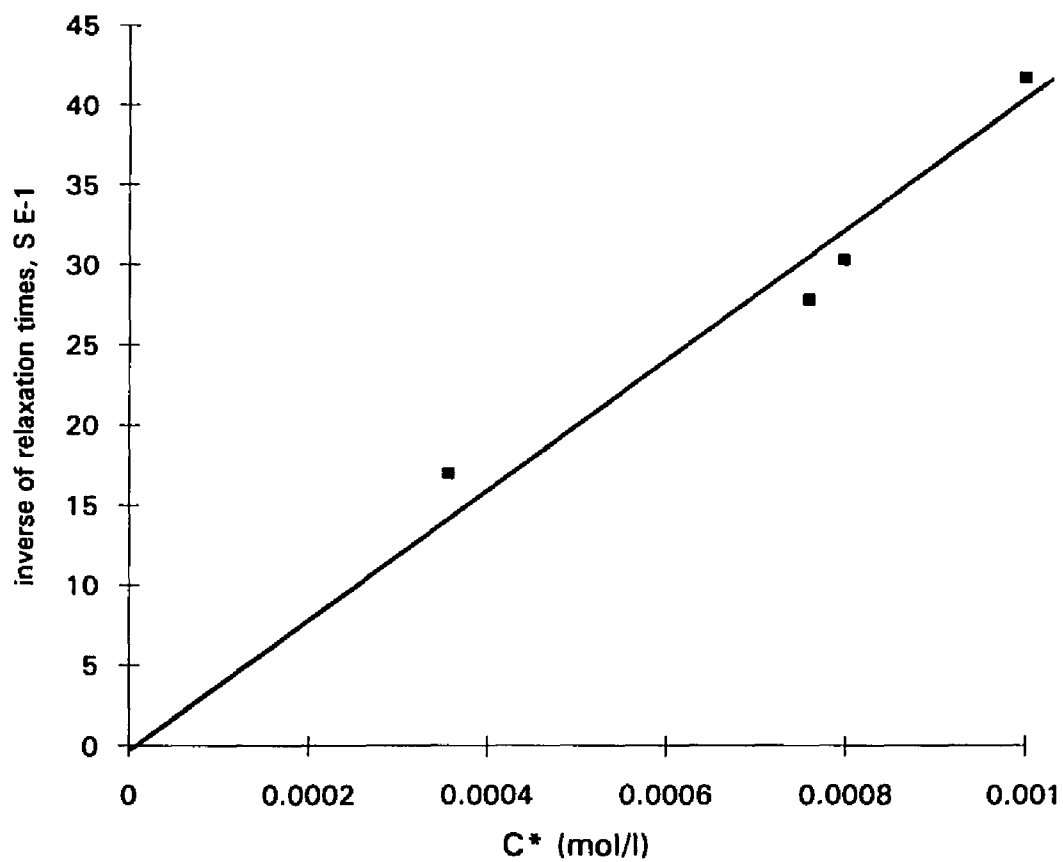


possibility of this mechanism.

The equation describing steady-state model for adsorption /desorption is described using Eq. [4-26] where I is an intermediate complex. In this system, the concentration of the intermediate species is extremely small as can be seen from the static results. Providing the intermediate species is a steady-state intermediate and step 1a is the rate determining one ($k_{-1a} \ll k_{1b}$), the equation for inverse of relaxation time (τ^{-1}) is described using Eq. [4-47]. The plot of the term on the right hand side of Eq. [4-47], defined as C^* , against τ_1^{-1} is shown in Fig. 4.9. The values of the reactant and product concentrations, and K^i , input into the equation are from equilibrium modeling results calculated at each pH. As can be seen (Fig. 4.9), the plot gave a straight line that passes through the origin, which suggests that the fast relaxation is attributed to step 1a and 1b in Eq. [4-26]. The slope of the line is the value of k_{-1}^i , which is $3.89 \times 10^4 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$, and using K^i from static result (3.48×10^{-3}) the calculated value of k_{1}^i is found to be $1.36 \times 10^2 \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$. This is the rate limiting step. The mechanism illustrated in Eq. [4-26] seems to be the most plausible to describe for adsorption/desorption of nickel at the goethite/water interface.

Hayes and Leckie (1986) have reported that changing the pressure-jump magnitude changes the τ_a . Consequently, the forward and reverse rate constants. Increasing perturbation decreased the rate constants. They attributed this observation to the presence of different energy sites on the surface. Previously, using equilibrium studies Benjamin and Leckie (1981)

Fig. 4.9 Plot of τ_f^{-1} versus the term in the bracket on the right-hand side of eq. [4-47] denoted by C^* .



reported the presence of sites with different binding energies for metal adsorption on oxides. The τ_s obtained in this study is attributed to the same reaction Eq. [4-26] but with sites that have different energies. Hachiya et al. (1984), attributed the fast and slow relaxations of divalent metal ions to simultaneous adsorption/desorption of ions on the surface. The fast relaxation was attributed to the large fraction of the surface site with relatively uniform energy, while the slow relaxation was attributed to site with small fraction of the total sites and with different energies. However, they could not statistically confirm the existence of small fraction sites because the adsorption/desorption processes at the largest fraction is overwhelmingly predominant.

In summary, the combination of the static and kinetic approaches provided better insight into nickel reactions at the goethite/aqueous interface chemistry. Based on equilibrium results, nickel forms inner-sphere complexes at the goethite/water interface. Fast and slow relaxations are observed and can be attributed to simultaneous adsorption/desorption of nickel at the interface at sites with different energies. All observations were consistent with adsorption/desorption mechanism suggested by Hachiya et al. (1984).

SUMMARY AND CONCLUSIONS

SUMMARY

Chapter II involves studies of nickel sorption by Christiana, Dekalb, Evesboro and Hagerstown soils using kinetic batch reaction method. Effect of ionic strength, pH and temperature on nickel sorption by soils were investigated. Thermodynamic parameters K_{eq} , ΔG , ΔH and ΔS were calculated. Temperature and pH increased nickel sorption, while increase in calcium ion concentration decreased nickel sorption. The reaction were all endothermic with positive entropy.

Chapter III involves investigation of nickel sorption sites using sorption isotherm, WDS, and XRD techniques. Correlation coefficients nickel sorption capacities of fifteen A and fifteen B-horizon soils vs soil chemical characteristics were calculated. No significant correlation was obtained between nickel sorption capacities and OM, CEC and various iron and aluminum forms. The only significant correlation obtained was with soil pH. The results of WDS indicate association of nickel sorption sites with that of iron for Christiana and Hagerstown soil.

Results of reaction of nickel with goethite was reported in chapter IV. Reaction of nickel with goethite was studied at three ionic strength and wide pH range. The reaction was modeled using the modified triple layer model (TLM). The zeta potentials of Ni^{2+} -goethite and H^+ -goethite were measured.

The chemical kinetics of nickel adsorption at goethite/water interface was determined using p-jump method. Change in sorption of nickel from 0 to 100% occurred over a narrow pH range. There was no effect of ionic strength on nickel adsorption by goethite. Adsorption of nickel onto goethite maintained positive surface charge over a wide pH range. Modeling using inner-sphere complexation fitted the experimental data well. Both the results of zeta potential and TLM suggest that nickel forms inner-sphere complex at goethite/water interface. Kinetic results indicate that adsorption of nickel at the interface is faster than release of H⁺ ion from the surface.

CONCLUSIONS

1. Increase in pH and temperature increased sorption of nickel by the soils. On the other hand increase in calcium ion decreased nickel sorption.
2. Sorption of nickel by soils was found to be endothermic with positive ΔH and ΔS for all soils.
3. Positive entropy suggests the partial dehydration of nickel ion upon sorption thus forming inner-sphere complex.
4. The higher correlation of nickel sorption with pH and association of nickel sorption site with iron indicate that the goethite content of the soils might explain the variability nickel sorption capacities of the soils.
5. Nickel forms inner-sphere complex at goethite/water interface.
6. Adsorption of nickel at the interface follows two step mechanism, in which nickel adsorption is faster than H^+ release.

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APPENDICES

Appendix 2-A
Concentration of nickel in solution at any given time at
various temperatures, pH and ionic strengths, for four
soils using the method of batch kinetics

Christiana, B-horizon pH = 4.96					
T = 15C		T = 25C		T = 35C	
Time (min)	Ni ppm	Time (min)	Ni ppm	Time (min)	Ni ppm
0	2.50	0	2.5	0	2.50
0	2.50	0	2.5	0	2.50
0.2	1.47	0.17	1.21	0.16	1.23
0.41	1.30	0.38	1.16	0.36	1.05
0.61	1.28	0.58	1.07	0.58	0.94
0.8	1.27	0.76	1.01	0.74	0.87
1.04	1.25	0.98	0.99	0.97	0.81
1.28	1.25	1.18	0.99	1.18	0.78
1.54	1.23	1.4	0.98	1.45	0.72
1.8	1.21	1.62	0.96	1.68	0.68
2.05	1.16	1.84	0.94	1.94	0.67
2.36	1.18	2.06	0.92	2.14	0.67
2.76	1.16	2.34	0.90	2.38	0.63
3.58	1.16	2.9	0.87	2.84	0.63
4.68	1.14	3.68	0.87	3.52	0.59
6.1	1.10	4.54	0.87	4.38	0.59
7.52	1.12	5.7	0.85	5.36	0.57
9.2	1.10	7.12	0.83	6.54	0.56
10.98	1.07	8.46	0.83	7.96	0.54
12.6	1.07	10.14	0.83	9.84	0.52
14.46	1.07	11.88	0.79	11.58	0.48
16.2	1.03	13.92	0.77	14.2	0.48
17.9	1.03	15.98	0.76	16.2	0.48
19.76	1.03	18.28	0.77	18.32	0.47
22	1.01	20.12	0.76	20.56	0.47
24.56	1.01	22.6	0.76	23.04	0.45
27.36	1.01	25.32	0.72	25.65	0.43
29.92	1.01	28.14	0.74	28.2	0.41
32.86	1.01	30.94	0.74	30.96	0.41
35.3	1.01	33.7	0.70	34.02	0.41
36.7		36.42	0.68	37.22	0.41
38.12	1.01	38		40.04	0.41
39.3		39.53	0.68	42.52	0.41
40.48	1.01	42.5	0.68	44	
42.96	1.01	44		45.24	0.37
44.5		45.44	0.67	46.5	
45.5	1.01	46.5		47.74	0.37
47		47.5		48.6	
48	1.01	48.49	0.67	50.44	0.37
50.4	1.01	51.3	0.65	51.9	
51.4		52.5		53.13	0.37
52.8	1.01	54.04	0.65	54.5	
54.2		55.2		55.6	0.37
55.18	1.01	56.2	0.65	56.6	
56.5		57.2		57.84	0.37
57.56	1.01	58.02	0.65	58.8	
58.8		59.2		60	0.37
60	1.01	60	0.65		

Christiana, B-horizon

pH = 4.96

T = 25C

Ca =	0.0 M		0.005 M
Time	Ni	Time	Ni
(min)	ppm	(min)	ppm
0	2.5	0	2.75
0	2.5	0	2.75
0.17	1.21	0.14	2.44
0.38	1.16	0.3	2.44
0.58	1.07	0.44	2.44
0.76	1.01	0.62	2.46
0.98	0.99	0.76	2.44
1.18	0.99	0.98	2.46
1.4	0.98	1.16	2.47
1.62	0.96	1.34	2.47
1.84	0.94	1.52	2.46
2.06	0.92	1.72	2.44
2.34	0.90	1.9	2.49
2.9	0.87	2.1	2.44
3.68	0.87	2.34	2.44
4.54	0.87	2.76	2.47
5.7	0.85	3.26	2.44
7.12	0.83	3.8	2.46
8.46	0.83	4.42	2.46
10.14	0.83	5.16	2.46
11.88	0.79	5.94	2.47
13.92	0.77	6.9	2.47
15.98	0.76	7.94	2.44
18.28	0.77	9.02	2.46
20.12	0.76	10.22	2.46
22.6	0.76	11.52	2.46
25.32	0.72	12.84	2.46
28.14	0.74	14.16	2.43
30.94	0.74	15.56	2.44
33.7	0.70	17.02	2.46
36.42	0.68	18.44	2.46
38		19.52	2.46
39.53	0.68	21.3	2.43
42.5	0.68	22.68	2.44
44		24.04	2.44
45.44	0.67	25.5	2.46
46.5		26.98	2.46
47.5		28.5	2.43
48.49	0.67	29.96	2.43
51.3	0.65	31.38	2.43
52.5		32.84	2.44
54.04	0.65	34.34	2.44
55.2		35.74	2.44
56.2	0.65	37	2.43
57.2		38.32	2.41
58.02	0.65	39.66	2.43
59.2		41.22	2.41
60	0.65	42.5	2.43

T = 15C		Dekalb, B-horizon T = 25C		T = 35C	
Time (min)	Ni ppm	Time (min)	Ni ppm	Time (min)	Ni ppm
0	1.00	0	1	0	1.00
0	1.00	0	1	0	1.00
0.18	0.88	0.16	0.79	0.16	0.72
0.44	0.87	0.33	0.78	0.38	0.71
0.6	0.85	0.5	0.76	0.56	0.69
0.8	0.84	0.68	0.76	0.77	0.69
0.98	0.84	0.88	0.75	0.98	0.68
1.4	0.82	1.06	0.74	1.21	0.68
1.42	0.82	1.25	0.74	1.41	0.66
1.6	0.82	1.42	0.72	1.6	0.65
1.82	0.82	1.6	0.72	1.85	0.65
2	0.82	1.8	0.72	2.06	0.65
2.32	0.81	1.98	0.72	2.48	0.63
3.2	0.81	2.2	0.71	3.06	0.63
4.1	0.81	2.6	0.69	3.86	0.62
5	0.81	3.14	0.69	4.94	0.63
6.08	0.81	3.88	0.71	6.18	0.62
7.28	0.79	4.9	0.69	7.85	0.62
8.28	0.79	6.32	0.68	9.42	0.62
9.62	0.78	7.68	0.68	11.32	0.62
10.92	0.79	9.88	0.66	13.26	0.62
12.18	0.79	12.09	0.65	15.35	0.62
13.87	0.79	14.18	0.66	17.68	0.62
15.6	0.79	16.12	0.66	20.06	0.62
17.68	0.79	18.12	0.66	22.36	0.62
19.68	0.79	20.1	0.66	24.72	0.62
21.8	0.78	22.5	0.65	27.19	0.62
24.24	0.78	24.42	0.65	29.52	0.62
26.84	0.78	26.92	0.65	31.76	0.62
29.24	0.78	29.3	0.65	34.24	0.62
31.92	0.78	30.5		36.78	0.62
35.08	0.76	31.93	0.65	39.12	0.62
38.14	0.76	33.5		41.62	0.62
41.42	0.76	34.32	0.65	44.36	0.62
44.72	0.76	36		46.78	0.62
47.96	0.76	37.3	0.65	49.38	0.62
50.96	0.76	38.5		51.98	0.62
54.46	0.76	40.4	0.65	54.72	0.62
57.92	0.76	41.9		57.36	0.62
60	0.76	43.5	0.65	60	0.62
		45			
		46.92	0.65		
		48			
		50.4	0.65		
		51.5			
		53.72	0.65		

Dekalb, B-horizon
T = 25

pH = 4.52		pH = 5.37		pH = 7.37	
Time (min)	Ni ppm	Time (min)	Ni ppm	Time (min)	Ni ppm
0	2	0	2.00	0	2.00
0	2	0	2.00	0	2.00
0.14	1.79	0.16	1.17	0.16	0.91
0.32	1.77	0.36	1.07	0.28	0.83
0.48	1.77	0.54	1.01	0.48	0.69
0.68	1.71	0.7	0.97	0.64	0.63
0.84	1.63	0.9	0.95	0.82	0.57
1.04	1.63	1.16	0.93	0.98	0.55
1.24	1.63	1.36	0.87	1.2	0.51
1.42	1.61	1.56	0.85	1.44	0.49
1.6	1.61	1.8	0.83	1.62	0.43
1.82	1.65	2	0.85	1.88	0.43
2.04	1.61	2.22	0.81	2.06	0.43
2.2	1.61	2.52	0.79	2.4	0.43
2.58	1.61	3.34	0.79	3.04	0.39
3.32	1.61	4.5	0.73	4.1	0.37
4.64	1.61	5.96	0.75	5.32	0.37
6.08	1.57	7.72	0.73	6.56	0.33
7.44	1.57	9.6	0.75	7.78	0.29
8.96	1.59	11.28	0.71	9.1	0.29
10.8	1.59	13.3	0.65	10.54	0.29
12.74	1.59	15.38	0.61	12.12	0.31
14.62	1.59	17.38	0.71	13.82	0.27
16.72	1.59	19.68	0.69	15.52	0.25
18.92	1.59	22	0.67	17.24	0.21
21.02	1.59	24.54	0.75	19.16	0.21
23.26	1.59	26.98	0.65	21.2	0.21
25.72	1.59	29.62	0.67	23.12	0.21
28.36	1.59	32.02	0.63	25.28	0.19
31.4	1.59	34.38	0.65	27.24	0.19
34.6	1.59	36.84	0.57	29.58	0.19
37.7	1.59	38		31.94	0.17
40.46	1.59	39.32	0.59	34.5	0.17
43.34	1.59	41.1		37	0.17
44.8		42	0.61	39.64	0.17
46.16	1.59	43.2		42.62	0.17
47.6		44.5	0.59	45.5	0.17
48.88	1.59	45.8		49.12	0.17
49.8		47.18	0.59	54.04	0.17
51.76	1.59	48.3		59.56	0.17
53.2		49.56	0.59		
54.58	1.59	51			
55.5		52	0.59		
56.5		53.2			
57.6	1.59	54.42	0.59		

Evesboro, B-horizon
pH = 5.68

T = 15C		T = 25C		T = 35C	
Time (min)	Ni ppm	Time (min)	Ni ppm	Time (min)	Ni ppm
0	1.5	0	1.5	0	1.5
0	1.5	0	1.5	0	1.5
0.14	1.12	0.12	1.00	0.18	0.97
0.3	1.05	0.28	1.05	0.36	0.93
0.48	1.03	0.44	1.00	0.54	0.92
0.68	1.01	0.6	0.99	0.68	0.92
0.86	1.01	0.76	0.92	0.84	0.90
1.04	0.98	0.92	0.99	1	0.89
1.22	0.98	1.1	0.93	1.16	0.88
1.42	0.98	1.24	0.96	1.34	0.86
1.66	0.94	1.42	0.96	1.48	0.82
1.86	0.94	1.6	0.93	1.64	0.84
2.04	0.97	1.8	0.88	1.88	0.82
2.26	0.90	2.04	0.93	2.04	0.84
2.84	0.94	2.32	0.92	2.3	0.84
3.92	0.88	3.3	0.91	3.3	0.81
6.18	0.93	5.26	0.87	6.12	0.80
8.8	0.94	7.7	0.88	8.78	0.80
11.76	0.94	10.24	0.88	11.38	0.79
14.86	0.94	12.86	0.83	14.46	0.81
17.52	0.92	15.42	0.85	17.48	0.81
20.58	0.90	18.1	0.85	19.96	0.77
23.34	0.94	20.72	0.83	22.46	0.77
26.12	0.94	23.26	0.83	25.42	0.81
28.6	0.93	26.6	0.87	27.9	0.82
30.7	0.92	29.44	0.87	30.52	0.79
33.6	0.88	32.26	0.87	33.06	0.80
36.64	0.89	35.16	0.67	36.3	0.77
39.62	0.90	37.62	0.85	38.04	0.77
41.72	0.90	39.74	0.83	40.06	0.79
43.84	0.89	41.78	0.83	42.02	0.79
45.88	0.88	43.58	0.83	44.12	0.76
47.84	0.88	45.68	0.83	48.28	0.80
50.2	0.85	47.6	0.83	50.6	0.76
52.02	0.85	49.6	0.83	53.32	0.76
53.88	0.85	51.62	0.83	55.74	0.73
55.78	0.84	53.72	0.83	57.02	0.75
57.4	0.84	55.64	0.83	58.3	0.75
58.4	0.84	57.44	0.83	60	0.76
60	0.81	59.54	0.83		

Evesboro, B-horizon

T = 25C

pH = 5.68		pH = 6.63	
Time (min)	Ni ppm	Time (min)	Ni ppm
0	1.5	0	1.50
0	1.5	0	1.50
0.12	1.00	0.14	0.90
0.28	1.05	0.34	0.82
0.44	1.00	0.54	0.78
0.6	0.99	0.8	0.78
0.76	0.92	1.02	0.76
0.92	0.99	1.26	0.75
1.1	0.93	1.5	0.72
1.24	0.96	1.74	0.75
1.42	0.96	1.94	0.69
1.6	0.93	2.2	0.71
1.8	0.88	2.42	0.72
2.04	0.93	3.22	0.71
2.32	0.92	3.86	0.71
3.3	0.91	4.92	0.67
5.26	0.87	5.84	0.67
7.7	0.88	7.12	0.65
10.24	0.88	8.8	0.68
12.86	0.83	10.62	0.65
15.42	0.85	12.66	0.65
18.1	0.85	14.44	0.65
20.72	0.83	16.24	0.65
23.26	0.83	18.2	0.65
26.6	0.87	20.2	0.64
29.44	0.87	22.6	0.65
32.26	0.87	25.28	0.65
35.16	0.67	27.78	0.64
37.62	0.85	28.76	0.65
39.74	0.83	31.6	0.64
41.78	0.83	34.48	0.61
43.58	0.83	37.32	0.61
45.68	0.83	40.08	0.63
47.6	0.83	42.96	0.63
49.6	0.83	45.8	0.64
51.62	0.83	48.88	0.65
53.72	0.83	51.54	0.63
55.64	0.83	54.48	0.64
57.44	0.83	57.24	0.64
59.54	0.83	60	0.64

Hagerstown
 B -horizon
 pH = 5.1

T = 15C		T = 25C		T = 35C	
Time (min)	N ppm	Time (min)	N ppm	Time (min)	Ni ppm
0	3.50	0	3.5	0	3.50
0	3.50	0	3.5	0	3.50
0.16	1.89	0.2	1.59	0.14	1.46
0.32	1.60	0.44	1.28	0.32	1.12
0.52	1.46	0.66	1.16	0.52	1.12
0.7	1.34	0.88	1.02	0.76	0.95
0.88	1.29	1.14	1.00	0.96	0.87
1.06	1.25	1.37	0.95	1.2	0.83
1.26	1.23	1.64	0.92	1.38	0.81
1.44	1.15	1.89	0.89	1.6	0.78
1.64	1.10	2.09	0.87	1.8	0.81
1.86	1.12	2.38	0.84	2.28	0.79
2.08	1.10	2.88	0.79	2.92	0.76
2.26	1.07	3.56	0.79	3.92	0.68
2.58	1.02	4.16	0.74	5.28	0.65
2.92	1.00	5.48	0.71	6.82	0.60
3.66	0.91	6.56	0.68	8.72	0.57
4.64	0.91	7.92	0.68	10.52	0.55
5.4	0.89	9.54	0.65	12.54	0.53
6.36	0.86	11.06	0.61	14.32	0.50
7.58	0.81	12.72	0.61	16.53	0.49
8.98	0.78	14.48	0.61	18.6	0.49
10.58	0.74	16.16	0.58	20.86	0.49
12.16	0.76	17.84	0.55	23.3	0.49
13.8	0.73	19.78	0.55	25.74	0.47
15.4	0.71	22.38	0.53	28.16	0.47
17.24	0.71	25.01	0.53	30.56	0.47
19.32	0.70	28.12	0.52	33.2	0.47
21.4	0.68	30.94	0.52	35.66	0.47
23.68	0.70	34.06	0.52	38.52	0.47
27.48	0.68	36.92	0.52	40.8	0.44
30.66	0.68	39.88	0.53	43.26	0.44
34.08	0.68	42.58	0.53	45.76	0.44
37.42	0.68	45.36	0.53	48.12	0.44
41.12	0.68	48.32	0.53	50.28	0.44
44.61	0.68	50.6	0.53	52.48	0.44
48.04	0.68	53.34	0.53	54.8	0.44
52.06	0.68	56.12	0.53	56.98	0.44
56	0.68	58.04	0.53	58.88	0.42
60	0.68	60	0.52	60	0.42

Hagerstown
B-horizon
T = 25C

pH = 5.15		pH = 6.43		pH = 7.55	
Time (min)	N ppm	Time (min)	N ppm	Time (min)	Ni ppm
0	5	0	5.00	0	5.00
0	5	0	5.00	0	5.00
0.14	2.70	0.16	2.26	0.18	2.17
0.3	2.40	0.34	1.74	0.4	1.62
0.46	2.19	0.54	1.50	0.58	1.39
0.61	2.04	0.72	1.41	0.78	1.25
0.76	1.94	0.92	1.34	1	1.20
0.92	1.87	1.08	1.27	1.18	1.07
1.08	1.78	1.38	1.22	1.4	1.02
1.24	1.69	1.44	1.22	1.58	1.00
1.41	1.66	1.64	1.16	1.78	1.00
1.59	1.64	1.84	1.14	1.98	0.97
1.78	1.57	2.08	1.11	2.2	0.93
2	1.55	2.4	1.11	2.48	0.92
2.42	1.52	2.84	1.07	3.3	0.85
3.04	1.44	3.3	1.04	4.12	0.81
3.61	1.39	4.06	1.02	5.26	0.76
4.34	1.36	5.42	1.00	7.06	0.74
5.1	1.32	6.76	1.02	8.76	0.70
5.96	1.27	8.38	0.99	10.72	0.67
7.14	1.25	10.32	0.95	12.5	0.67
8.62	1.18	12.22	0.95	14.36	0.62
10.19	1.14	14.66	0.93	16.18	0.62
12.03	1.14	16.9	0.92	18	0.60
14.27	1.11	19.08	0.92	20.22	0.58
16.38	1.09	21.5	0.92	23.12	0.58
18.58	1.04	23.96	0.92	25.72	0.56
20.96	1.04	26.48	0.92	27.76	0.56
23.22	1.04	28.62	0.92	30.78	0.55
25.62	1.02	31.32	0.92	33.8	0.55
27.9	1.02	34.16	0.90	36.48	0.55
30.15	1.02	36.86	0.90	39.48	0.53
32.7	1.00	39.74	0.88	42.32	0.53
35.64	1.00	42.88	0.90	45.68	0.53
39.4	1.00	43.5		48.52	0.53
42.9	1.00	45.78	0.88	50.84	0.49
46.5	1.00	47.5		53.24	0.49
49.94	1.00	49	0.90	55.82	0.51
54.8	0.97	50.1		58	0.51
60	0.93	52.2	0.88	60	0.51

Hagerstown
B-horizon
T = 25C

Ca =	0.0005 M		0.001 M		0.01 M
Time	N	Time	N	Time	Ni
(min)	ppm	(min)	ppm	(min)	ppm
0	3.50	0	3.50	0	3.5
0	3.50	0	3.50	0	3.5
0.14	2.38	0.12	2.92	0.07	
0.36	2.21	0.3	2.81	0.15	
0.56	2.16	0.5	2.82	0.24	2.96
0.74	2.13	0.7	2.72	0.36	3.14
0.94	2.05	0.88	2.69	0.56	3.11
1.26	2.06	1.08	2.70	0.72	3.09
1.44	2.03	1.28	2.69	0.9	3.09
1.64	2.01	1.48	2.72	1.08	3.03
1.84	2.03	1.7	2.65	1.28	3.06
2.06	2.03	1.96	2.69	1.48	3.11
2.36	1.99	2.3	2.65	1.72	3.08
2.88	2.01	2.9	2.67	1.92	3.06
3.74	2.01	3.68	2.65	2.16	3.08
4.62	2.01	4.66	2.62	2.42	3.08
5.64	2.01	5.7	2.62	3.08	3.09
6.92	2.01	7	2.60	4	3.09
8.7	2.01	8.48	2.62	5.28	3.08
10	2.01	10.16	2.62	6.8	3.08
11.76	1.98	11.48	2.62	8.52	3.08
13.44	1.98	14.2	2.62	10.74	3.08
15.3	1.98	16.2	2.62	13	3.08
17.72	1.98	18.2	2.62	15.3	3.08
20.04	1.99	20.44	2.64	17.26	3.08
22.04	1.99	23.05	2.64	20.1	3.08
24.38	1.99	25.64	2.64	22.72	3.08
25.5		27.96	2.64	25.36	3.08
27.18	1.99	29.2		27.84	3.08
29.12	1.99	30.76	2.64	31.1	3.08
31.76	1.99	32.9	2.64	33.6	3.08
33.2		34.1		35.88	3.08
34.52	1.99	35.66	2.60	38.46	3.08
35.8		37		40.82	3.08
37.06	1.99	38.1	2.62	43.28	3.08
38.5		39.2		45.62	3.08
39.64	1.99	40.74	2.60	47.86	3.08
42.84	1.99	43.28	2.60	50.12	3.08
44.2		44.4		52.4	3.08
45.3	1.99	45.84	2.60	54.44	3.08
46.5		46.9		56.94	3.08
47.86	1.99	48.42	2.60	59.78	3.08

APPENDIX 2B

THE AMOUNT OF NICKEL SORBED AND HYDROGEN RELEASED AT ANY GIVEN TIME

Soil: Dekalb
:pH = 5.37

Time (min)	Ni ²⁺ sorbed <u>μmol/l</u>	H ⁺ released <u>μmol/l</u>
0.16	14.14	2.7
0.36	15.84	4.15
0.54	16.86	4.8
0.70	17.54	5.30
0.90	17.88	5.60
1.16	18.22	6.65
1.36	19.24	7.05
1.56	19.58	7.50
1.80	19.93	7.95

Soil: Dekalb
:pH = 7.73

Time (min)	Ni ²⁺ sorbed <u>μmol/l</u>	H ⁺ released <u>μmol/l</u>
0.16	18.56	1.8
0.28	19.92	4.65
0.48	22.31	8.25
0.64	23.33	10.65
0.82	24.36	12.00
0.98	24.70	13.05
1.20	25.38	13.50
1.44	25.72	13.90
1.62	26.74	13.96

Soil: Hagerstown
: pH = 6.63

Time (min)	Ni ²⁺ sorbed <u>μmol/l</u>	H ⁺ released <u>μmol/l</u>
0.16	46.67	6.5
0.34	55.53	12.15
0.54	59.61	15.30
0.72	61.15	16.90
0.92	62.34	17.55
1.08	63.53	17.85
1.28	64.38	18.00
1.44	64.38	18.00
1.64	65.41	18.05
1.84	65.74	18.15

Soil: Hagerstown
: pH = 7.55

Time (min)	Ni ²⁺ sorbed <u>μmol/l</u>	H ⁺ released <u>μmol/l</u>
0.18	48.20	8.45
0.40	57.57	15.75
0.58	61.48	18.75
0.78	63.87	19.95
1.00	64.72	20.55
1.18	65.07	20.90
1.40	67.97	21.15
1.58	68.13	21.45
1.78	68.13	21.75
1.98	68.64	22.20

APPENDIX 2C

EFFECT OF SURFACE COVERAGE ON HEAT OF SORPTION (ΔH)

Soil: Christiana

Ni sorbed <u>$\mu\text{mol/g}$</u>	ΔH <u>kJ/mol</u>
0.0	0.0
2.16	6.59
2.47	7.88
2.65	11.38
2.77	13.95
2.87	16.00

Soil: Dekalb

Ni sorbed <u>$\mu\text{mol/g}$</u>	ΔH <u>kJ/mol</u>
0.0	0.0
0.48	7.4
0.57	8.0
0.60	8.56
0.63	9.70

Soil: Hagerstown

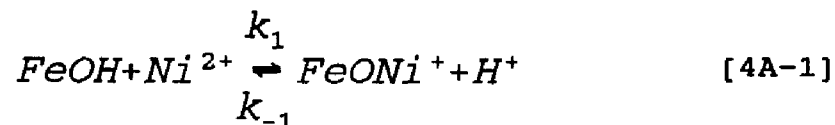
Ni sorbed <u>$\mu\text{mol/g}$</u>	ΔH <u>kJ/mol</u>
0.0	0.0
3.47	9.52
4.05	9.77
4.33	12.68
4.60	11.18
4.62	13.01

Soil: Evesboro

Ni sorbed <u>$\mu\text{mol/kg}$</u>	ΔH <u>kJ/mol</u>
0.0	0.0
0.99	3.44
1.04	3.55
1.12	4.14
1.16	5.03
1.19	5.55

APPENDIX 4A

The following derivation is for the relationship between the inverse of the relaxation time constant and the concentration of the reacting species for inner-sphere complexation, i.e:



The rate equation, r , can be given as:

$$r = \frac{-d[FeOH]}{dt} = \frac{-d[Ni^{2+}]}{dt} = \frac{d[FeONi^+]}{dt} = \frac{d[H^+]}{dt} \quad [4A-2]$$

$$r = -k_1 [FeOH] [Ni^{2+}] + k_{-1} [FeONi^+] [H^+] \quad [4A-3]$$

where k_1 and k_{-1} represent the forward and reverse rate constants respectively.

At equilibrium, $r = 0$, or

$$0 = -k_1 [\overline{FeOH}] [\overline{Ni^{2+}}] + k_{-1} [\overline{FeONi^+}] [\overline{H^+}] \quad [4A-4]$$

where overline indicate equilibrium concentration.

Rearranging [4A-4]

$$\frac{k_1}{k_{-1}} = \frac{[\overline{FeONi^+}] [\overline{H^+}]}{[\overline{FeOH}] [\overline{Ni^{2+}}]} = K \quad [4A-5]$$

Following small perturbation (pressure-jump), the equilibrium concentration are shifted by small amount, Δ , and the new time dependent concentrations are given by

$$[FeOH] = [\overline{FeOH}] + (\Delta [FeOH]) \quad [4A-6]$$

$$[Ni^{2+}] = [\overline{Ni^{2+}}] + (\Delta [Ni^{2+}]) \quad [4A-7]$$

$$[FeONi^+] = [\overline{FeONi^+}] + (\Delta [FeONi^+]) \quad [4A-8]$$

$$[H^+] = [\overline{H^+}] + (\Delta [H^+]) \quad [4A-9]$$

Based on the law of mass conservation:

$$\begin{aligned} (\Delta [FeOH]) &= (\Delta [Ni^{2+}]) = \\ &- (\Delta [FeONi^+]) = - (\Delta [H^+]) \end{aligned} \quad [4A-10]$$

allowing this quantity to be x , we can rewrite [4A-5] through [4A-8] to the form:

$$[FeOH] = [\overline{FeOH}] + x \quad [4A-11]$$

$$[Ni^{2+}] = [\overline{Ni^{2+}}] + x \quad [4A-12]$$

$$[FeONi^+] = [\overline{FeONi^+}] - x \quad [4A-13]$$

$$[H^+] = [\overline{H^+}] - x \quad [4A-14]$$

Substituting [4A-10] through [4A-13] into [4A-3] gives:

$$r = \frac{dx}{dt} = -k_1 ([\overline{FeOH}] + x) ([\overline{Ni^{2+}}] + x) + k_{-1} ([\overline{FeONi^+}] - x) ([\overline{H^+}] - x) \quad [4A-15]$$

$$\frac{dx}{dt} = -k_1 [\overline{FeOH}] [\overline{Ni^{2+}}] + k_{-1} [\overline{FeONi^+}] [\overline{H^+}] - \{k_1 ([\overline{FeOH}] + [\overline{Ni^{2+}}]) + k_{-1} ([\overline{FeONi^+}] + [\overline{H^+}])\}x - k_1 x^2 + k_{-1} x^2 \quad [4A-16]$$

The first two terms reduces to 0 according to [4A-4]. For a small perturbation x is small, hence x^2 is very small. Therefore, [4A-16] reduces to

$$\frac{dx}{dt} = -\{k_1 ([\overline{FeOH}] + [\overline{Ni^{2+}}]) + k_{-1} ([\overline{FeONi^+}] + [\overline{H^+}])\}x \quad [4A-17]$$

Now

$$\frac{dx}{dt} = -\frac{1}{\tau}x \quad [4A-18]$$

where τ is relaxation time constant.

So we can write

$$\tau^{-1} = k_1 ([\overline{FeOH}] + [\overline{Ni^{2+}}]) + k_{-1} ([\overline{FeONi^+}] + [\overline{H^+}]) \quad [4A-19]$$

Replacing the values of k_1 and k_{-1} with that of [4-23] and [4-25], respectively and rearranging gives

$$\tau^{-1} = k_1 \{ ([\overline{FeOH}] + [\overline{Ni^{2+}}]) + (K^i)^{-1} ([\overline{FeONi^+}] + [\overline{H^+}]) \} \quad [4A-20]$$

APPENDIX 4B
PERCENT NICKEL ADSORBED VERSUS pH

Goethite : 15g/L
 [Ni²⁺] : 1.02x10⁻³ M
 Temperature: 25°C

I = 0.01 M (NaNO₃)

pH	%
4.68	0.00
4.93	1.09
5.09	4.90
5.15	9.01
5.24	12.56
5.53	20.76
5.94	35.53
6.03	46.12
6.90	80.10
7.00	81.46

I = 0.1 M (NaNO₃)

pH	%
5.35	9.22
5.61	22.94
5.90	28.68
6.12	36.60
6.22	37.98
6.31	42.43
6.51	60.88

I = 0.5 M (NaNO₃)

pH	%
5.47	12.91
5.65	16.60
5.84	22.95
5.96	29.29
6.00	34.14
6.22	37.70
6.36	40.15
6.38	46.62
6.60	64.57

APPENDIX 4C

TITRATION DATA FOR AQUEOUS SUSPENSION OF GOETHITE AT DIFFERENT IONIC STRENGTHS USED TO CALCULATE SURFACE CHARGE DENSITY (Fig.3-3)

Goethite: 15 g/l
I = 0.02 M (NaNO₃)

<u>pH</u>	<u>Equivalence bases added (M)</u>
3.92	-1.28x10 ⁻³
4.16	-1.12x10 ⁻³
4.48	-9.60x10 ⁻⁴
4.82	-8.00x10 ⁻⁴
5.16	-6.40x10 ⁻⁴
5.58	-4.80x10 ⁻⁴
6.05	-3.20x10 ⁻⁴
6.36	-2.40x10 ⁻⁴
6.71	-1.60x10 ⁻⁴
7.17	-8.00x10 ⁻⁵
7.76	0.00000
8.35	1.60x10 ⁻⁴
8.75	2.40x10 ⁻⁴
9.09	3.20x10 ⁻⁴
9.36	4.00x10 ⁻⁴
9.57	4.80x10 ⁻⁴
9.73	5.60x10 ⁻⁴
9.87	6.40x10 ⁻⁴

I = 0.1 M (NaNO₃)

pH	<u>Equivalence base added (M)</u>
5.05	-9.60x10 ⁻⁴
5.50	-8.00x10 ⁻⁴
5.95	-6.40x10 ⁻⁴
6.29	-4.80x10 ⁻⁴
6.48	-4.00x10 ⁻⁴
6.67	-3.20x10 ⁻⁴
6.86	-2.40x10 ⁻⁴
7.10	-1.60x10 ⁻⁴
7.40	-8.00x10 ⁻⁵
7.70	0.0000
8.17	8.00x10 ⁻⁵
8.38	1.60x10 ⁻⁴
8.66	2.40x10 ⁻⁴
8.91	3.20x10 ⁻⁴
9.15	4.00x10 ⁻⁴
9.38	4.80x10 ⁻⁴
9.68	6.40x10 ⁻⁴
9.91	8.00x10 ⁻⁴

I = 0.5 M (NaNO₃)

pH	Equivalence base <u>added (M)</u>
5.46	-9.60x10 ⁻⁴
5.86	-8.00x10 ⁻⁴
6.21	-6.40x10 ⁻⁴
6.57	-4.80x10 ⁻⁴
6.72	-4.00x10 ⁻⁴
6.81	-3.20x10 ⁻⁴
6.96	-2.40x10 ⁻⁴
7.17	-1.60x10 ⁻⁴
7.40	-8.00x10 ⁻⁵
7.72	0.0000
7.98	8.00x10 ⁻⁵
8.20	1.60x10 ⁻⁴
8.43	2.40x10 ⁻⁴
8.61	3.20x10 ⁻⁴
8.83	4.00x10 ⁻⁴
9.00	4.80x10 ⁻⁴
9.30	6.40x10 ⁻⁴
9.55	8.00x10 ⁻⁴

APPENDIX 4D

MEASUREMENTS OF ZETA POTENTIALS

Goethite: 428 $\mu\text{g/ml}$

I = 0.01 M (NaNO_3)

Goethite- H^+

<u>pH</u>	<u>zeta potential</u> <u>mv</u>
6.36	10.1
5.76	30.8
5.47	44.2
4.62	50.0
4.19	50.9
3.81	50.2

Goethite- Ni^{2+}

<u>pH</u>	<u>zeta potential</u> <u>mv</u>
6.17	40.0
5.38	40.5
5.01	40.0
4.61	44.7
4.08	48.4
3.79	48.1

APPENDIX 4E

MEASUREMENTS OF RELAXATION TIME CONSTANTS

<u>pH</u>	<u>τ_f</u>	<u>τ_s</u>	<u>C^*</u>
7.21	0.024	0.74	1.00×10^{-3}
6.60	0.033	1.22	7.98×10^{-4}
6.57	0.036	1.30	7.59×10^{-4}
5.93	0.059	1.76	3.56×10^{-4}

where τ_f and τ_s represent fast and slow relaxation times respectively. C^* is the calculation of the terms on the right-hand side of equation x for steady-state model with the values of the components as follows.

<u>pH</u>	<u>$-\log[\text{FeOH}]$</u>	<u>$-\log[\text{FeONi}^+]$</u>	<u>$-\log[\text{Ni}^{2+}]$</u>	<u>$\psi_0(\text{v})$</u>
7.21	2.12	3.00	4.60	0.063
6.60	2.08	3.12	3.24	0.088
6.57	2.08	3.10	3.23	0.086
5.93	2.06	3.45	3.15	0.1008

where the log terms are in mol/l.

APPENDIX 4F

CONDUCTIVITY MEASUREMENTS

Goethite: 15 g/l
Ionic strength: 0.1 M (NaNO_3)

<u>Ni²⁺ adsorbed</u>	<u>pH</u>	<u>EC</u>
<u>mg/g</u>		<u>$\mu\text{mohs/cm}$</u>
1.640	8.00	15.3
2.504	7.68	15.8
2.979	7.50	16.0
3.272	7.40	16.2
3.409	7.20	16.4
3.860	7.00	16.6

where EC = electrical conductivity