8623878

Puls, Robert William

ADSORPTION OF HEAVY METALS ON SOIL CLAYS

The University of Arizona PH.D. 1986

University
Microfilms
International 300 N. Zeeb Road, Ann Arbor, MI 48106

ADSORPTION OF HEAVY METALS

ON SOIL CLAYS

by

Robert William Puls

A Dissertation Submitted to the Faculty of the

DEPARTMENT OF SOIL AND WATER SCIENCE

in Partial Fulfillment of the Requirements
For the Degree of

DOCTOR OF PHILOSOPHY

In the Graduate College

THE UNIVERSITY OF ARIZONA

1 9 8 6

THE UNIVERSITY OF ARIZONA
GRADUATE COLLEGE

As members of the Final Examination Committee, we certify that we have read

the dissertation prepared by Robert William Puls

entitled ADSORPTION OF HEAVY METALS ON SOIL CLAYS

and recommend that it be accepted as fulfilling the dissertation requirement

for the Degree of DOCTOR OF PHILOSOPHY.

Hinrich Bohn	28 July 86 Date
W B Denton	7-28-86 Date
David M. Hendricks	7-28-86 Date
J C Tucker	28 July 86 Date
	Date

Final approval and acceptance of this dissertation is contingent upon the candidate's submission of the final copy of the dissertation to the Graduate College.

I hereby certify that I have read this dissertation prepared under my direction and recommend that it be accepted as fulfilling the dissertation requirement.

Hinrich Bohn
Dissertation Director

22 July 86
Date

STATEMENT BY THE AUTHOR

This dissertation has been submitted in partial fulfillment of the requirements for an advanced degree at the University of Arizona and is deposited in the University Library to be made available to borrowers under the rules of the Library.

Brief quotations from this dissertation are allowable without special permission, provided that accurate acknowledgement of the source is made. Requests for permisssion for extended quotation from or reproduction of this manuscript in whole or in part may be granted by the head of the major department or the Dean of the Graduate College when in his or her judgement the proposed use of the material is in the interests of scholarship. In all other instances, however, permission must be obtained from the author.

SIGNED: Robert William Lide

ACKNOWLEDGEMENTS

I wish to acknowledge the support and direction provided by my advisor, Dr. Hinrich L. Bohn. His concern for and devotion to his field of study inspired my own interest in Soil Chemistry. I also thank him for the hospitality and friendship his entire family extended to mine.

I would also like to thank Dr. Thomas Tucker, Dr. David Hendricks, Dr. Bonner Denton and Dr. Quintus Fernando for serving on the dissertation committee and for their valuable suggestions and guidance. Additionally I am indebted to Dr. Oliver Chadwick and Dr. Gregory Ferguson for their helpful suggestions and support.

Finally, I would like to recognize my wife, Jan, for without her love and belief in me this would never have been possible. For the many years of sacrifice and devotion I thank her, as well as my two wonderful children, Andrea and Erin.

TABLE OF CONTENTS

TABLE OF CONTENTS--Continued

LIST OF TABLES

LIST OF ILLUSTRATIONS

ABSTRACT

Metal cation adsorption is the predominant chemical mechanism governing the attenuation of toxic metal movement in soils. Clay minerals are the primary adsorbent surfaces in soils due to their ubiquitous nature and large reactive surface area. This study examined the the relative affinity of the metals cadmium, nickel and zinc for the clay minerals kaolinite and montmorillonite. The influence which different mineral adsorbents and different complexing ligands in solution have on the adsorption of metal ions was assessed using the Hard-Soft Acid-Base Principle as a theoretical framework for predicting the maximum extent of adsorption and rate of adsorption. The HSAB principle is that hard bases prefer to complex hard acids and soft bases prefer to complex soft acids.

The hypothesis that initiated these investigations was that the hard-soft character of mineral surfaces is due to their surface functional groups and can be measured using metal cation adsorption selectivity experiments where pH and complex ion formation are controlled.

When complex ion formation in aqueous solution was minimized (i.e. in $Ca(ClO_4)_2$), adsorption decreased in the order of decreasing softness: Cd > Zn > Ni for both clay minerals.

Montmorillonite behaved as a slightly harder Lewis base than kaolinite, sorbing the harder Ni and Zn ions to a greater extent than Cd, although both minerals behaved as soft Lewis bases.

In the presence of chloride and sulfate ligands, adsorption sequences changed and reflected results from typical soil solution studies. In some cases the adsorption sequences can be explained using the HSAB principle together with computer speciation data and this approach merits further consideration and research.

Adsorption over time and calculated adsorption rate constants were generally consistent with equilibrium selectivity data. Adsorption rates decreased in the order Cd > Zn > Ni in $Ca(ClO_4)_2$ for both clay minerals. The adsorption curves reflect a two-step adsorption process involving a rapid exchange-type reaction followed by a much slower adsorption involving diffusion into the crystal or alteration of the surface through the formation of a new solid phase involving the adsorbed ions.

CHAPTER 1

INTRODUCTION

The adsorption of metal cations on natural materials has been of interest to researchers for years as environmental pollution concerns among the general public continue to grow. The selection of suitable sites for nuclear waste isolation, industrial discharge to streams, landfill leachate movement, fallout and precipitation from air and the direct application of toxic elements to soils as sewage sludge and wastewaters are ever increasing. To estimate the magnitude of the hazard posed by these elements, it is important to study the processes and factors which control their movement from the soil surface through the soil profile and underlying geologic material to groundwater and surface water supplies.

The soil is a complex and dynamic system involving complex physical, biological and chemical reactions. Soils are variable both areally and vertically. It is this variability, coupled with the complexity of the above reactions which complicates the prediction of the fate of heavy metals in soils. It should be noted that soils themselves contain natural levels of toxic trace metals and these native levels may or may not contribute to groundwater or surface water pollution depending on the natural physical, geologic and chemical cycling processes which take place in a particular soil. Disturbances by man, while not necessarily adding additional toxic metals to the system, may accelerate the leaching and cycling of elements thus promoting the pollution of water supplies. Time is also a factor which must be considered in any predictive modelling scheme. Ions exchanged or adsorbed on soil colloids may desorb or re-exchange as the soil-water environment changes. These changes can occur via unnatural additions to the soil, such as waste disposal, or via natural changes such as weathering.

Attenuation and mobility are two terms commonly used to describe cation movement in soils. Attenuation is described as "the soil's capacity for retaining a solute and the rate at which the solute is immobilized by the soil" (Fuller,1977). Related to this concept is that of mobility which is "the ease with which a specific element becomes distributed vertically in soil and/or weathered geologic parent materials as a function of the rate and direction of movement of soil solution or leachates from waste deposited in or on the soil" (Fuller,1977). The mobility of a solute is determined by the soil's attenuation capacity which is determined by many factors. These factors are: physical factors such as texture or particle size distribution, structure and pore size distribution, temperature and the soil water status; biological factors such as microbial processes involving oxidation-reduction reactions, and the mineralization and immobilization of elements; and chemical factors such as the hydrogen ion activity (pH), concentration of metal cations, complexing ligands and solid sorbent surfaces in solution, and sorption reactions which include precipitation, adsorption, and ion exchange. Of these three factors, this research is primarily concerned with the chemical factors which contribute to metal ion mobility.

The predominant chemical mechanism governing the attenuation of metal ions in soils is adsorption on mineral and organic surfaces. Adsorption may be defined as the "adhesion, in an extremely thin layer of gas molecules, dissolved substances or liquids, to the surface of solids with which they are in contact" (Ellis and Knezek,1972). Specific adsorption is the case which, upon adsorption, less than equivalent amounts of other cations are released. This has been shown to occur for many metal ions (Forbes et al,1976). The difference between specific adsorption and precipitation is mainly that adsorption is a two dimensional process whereas precipitation is three dimensional. Precipitation forms well defined solid phases, whereas adsorption can have a number of reaction products. These are: crystal growth and/or diffusion into the solid phase, the formation of a stable surface compound or the heterogeneous nucleation of a new solid phase. In general, adsorption reactions are considered in terms of a stable surface compound in equilibria with the solution. Hydrous oxides of iron, manganese and aluminum demonstrate specific adsorption capacities for metal ions due to large surface areas and the postulated presence of specific distinct types of surface sites with varying affinity for adsorbed ions (Benjamin,1980).

A significant influence to the adsorption of metal ions is complex ion formation in solution. Both inorganic and organic complexing ligands are present in soil solutions and can significantly affect metal cation adsorption and the surface properties of adsorbents. Metal-ligand complexes can form in solution and not sorb, decreasing the potential adsorption compared to a ligand-free system, or the metal-ligand complex may adsorb and contribute to greater removal of the metal from solution. Another possibility is that the ligand may adsorb to the surface and alter the electrical properties of the surface and as a result either enhance or retard adsorption of the metal cation. These differences are experimentally hard to distinguish but are important considerations in assessing relative affinities and kinetic differences in adsorption reactions. It is also possible to treat the adsorbent surface as a complexing ligand. The adsorption of free metals thus creates a metal-ligand complex and the adsorption of a metal-ligand complex creates a mixed metal-ligand complex. Finally, even the terms "free" and "complexed" are open to interpretation as metals are usually present in solution as aquo complexes.

This study examined the relative affinity of the metals cadmium, nickel and zinc for the clay minerals kaolinite and montmorillonite. The influence which different mineral adsorbents and different complexing ligands in solution have on the selectivity sequence is assessed utilizing the Hard-Soft Acid Base Principle as a theoretical framework for predicting the maximum extent of adsorption and the rate of adsorption. A computer model, MINEQL, is used to describe the metal distribution between the solid and solution phases and speciation of chemical components of the clay-metal equilibrium.

The HSAB principle simply stated is that hard acids prefer to complex hard bases and soft acids prefer to complex soft bases.

$$A_s + B_s \text{ -- } A_sB_s$$

$$A_h + B_h \text{ -- } A_hB_h$$

The hypothesis of this research is that the hard-soft character of mineral surfaces is due to their surface functional groups and can be measured using metal cation adsorption selectivity experiments where pH and complex ion formation are controlled.

CHAPTER 2

LITERATURE REVIEW

Hard-Soft Acid-Base Theory

The Principle of Hard and Soft Lewis Acids and Bases (HSAB) was first proposed by Ralph G. Pearson at Northwestern University in 1963. The HSAB principle simply stated is that hard acids prefer to complex hard bases and soft acids prefer to complex soft bases (Pearson,1963). According to G. N. Lewis, a base is an atom, molecule or ion which has at least one pair of valence electrons which are not already shared and an acid is a similar unit which has a vacant orbital in which a pair of electrons can be accomodated (Pearson,1968). Most cations are acids and most anions are bases. When the two react, an acid-base complex can be formed. All metal atoms or ions are Lewis acids and are usually coordinated to several bases or ligands. The formation product may be a complex ion or an inorganic compound. Inorganic and organic compounds as solid, liquid, gas or in solution are examples of acid-base complexes and the hard-soft character of the acid and base components has been qualitatively determined.

Hard acids are generally small in size, have high electronegativity, low polarizability and do not contain unshared pairs of electrons in their valence shell. Soft acids are generally large in size, have low electronegativity, high polarizability and contain unshared pairs of electrons in their valence shell. Polarizability is the ability of a species' electron cloud to become distorted in the presence of an eletric field. The polarizability of acid and base units is used to correlate hard and soft character with whether bonds formed between those units will be ionic or covalent. The term hard describes graphically those cases where the electrons or orbitals remain localized on the reacting species (low polarizability) and the acid and base tend to form ionic bonds, whereas the term soft graphically describes those cases where the orbitals on the reactants are easily distorted and mixed together and the species form covalent bonds (Jensen,1974). Obviously the above criteria are extremes and a continuum is actually formed by the many acids and bases. Table 1. is a partial listing of hard, borderline and soft Lewis acids and bases (Pearson,1968). Many cations important to plant nutrition are in the hard acid category while many of the environmentally hazardous metal cations are in the borderline and soft categories. Even within categories there is a continuum with some harder or softer than others. Misono (1967) proposed a numerical scale for evaluating the relative hardness or softness based primarily on charge, size and ionization potential. Table 2 lists some acids and bases along with their Misono "softness"

Table 1.

Classification of Hard and Soft Acids and Bases

Hard Acids	Hard Bases
H^+, Li^+, Na^+, K^+, Cs^+	H_2O, OH^-, O^{2-}
Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}	CO_3^{2-}, NO_3^-
Cr^{3+}, Mn^{2+}, Fe^{3+}, Al^{3+}	PO_4^{3-}, SO_4^{2-}
Co^{3+}, Si^{4+}	ClO_4^-, F^-
Borderline Acids	**Borderline Bases**
Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}	NO_2^-, SO_3^{2-}
Zn^{2+}, Sn^{2+}, Pb^{2+}	Br^-, Cl^-
Soft Acids	**Soft Bases**
Cu^+, Cd^{2+}, Hg^+, Hg^{2+}	$S_2O_3^-$, S^{2-}, I^-

Table 2.

Misono Softness Values
for Lewis Acids in Aqueous Solution

Oxidation State					
+1		+2		+3	
Li	0.36	Mg	0.87	Al	0.70
K	0.92	Ca	1.62	Fe	2.37
Na	0.93	Sr	2.08	La	2.45
Rb	2.27	Zn	2.34	Co	2.56
Cs	2.73	Ba	2.62	Cr	2.70
Cu	3.45	Ni	2.82	Ti	3.23
Tl	3.78	Cu	2.89	Au	3.90
Ag	3.99	Mn	3.03		
Au	5.95	Cd	3.04		
		Fe	3.09		
		Sn	3.17		
		Hg	4.25		

values. These values are derived from the following equation:

$$Y = 10\ (I_n/I_{n+1})(r_i/n^{1/2})$$

where r_i is the ionic radius of the metal ion, n its formal charge, and I the ionization potential with Y being the "softness" value. A second attempt to predict hardness and softness by Klopman (1968) uses a quantum mechanical approach. Both have inconsistencies when compared with experimental data and are not totally reliable.

The principle's importance is that it can be used to understand a large array of chemical phenomena including solubility relationships, solution equilibria, charge tranfer complexes and metal atom and metal surface behavior (Pearson,1968). The possibility of HSAB theory as a predictive tool for adsorption selectivity in soil solutions comes from the awareness of different mineral adsorbents having varying preferences for metal cations. When these studies are analyzed from the perspective of HSAB theory, there are some indications that some mineral surfaces behave as soft or hard bases relative to other surfaces or even water molecules in solution. Evans (1980) concluded that goethite is "hard" from experiments comparing the surface charge density/pH functions of CO_2-free goethite suspended in NaI and NaCl solutions. Chloride ion was more surface active and more specifically adsorbed than the softer iodide. This approach of using acids or bases with distinctly different hard-soft character is utilized in the present study. By measuring adsorption and determining whether the mineral surface reacts more favorably with the hard or soft species, one can assign a relative "softness" strength to the mineral as well as postulate which surface functional groups are the most selective sites for adsorption. Sullivan's (1977) review article showed that soil exchange surfaces in general behave as soft bases relative to water which is a very hard base. This is consistent with the Hofmeister series where adsorption selectivity decreases in the order

$$Cs > K > Na > Li$$

for monovalent cations, and for divalent cations the order is

$$Ba > Sr > Ca > Mg$$

when reacted with soil clays (Stumm and Morgan,1981). This is the order of decreasing softness. The suggestion then is that with soil clays classified as relatively soft bases, the HSAB principle would predict that softer cations will replace harder cations. Data indicates that this may only be true of metals in the same oxidation state and even then there are discrepencies, most notably with the transition elements, such as the Cd, Ni and Zn ions studied here.

Selectivity Sequences of Metal Adsorption

Many researchers have reported "selectivity sequences" for metal ions or "replaceability series" based on experimental adsorption data. Forbes et al (1974) assigned the following order to adsorption by goethite (FeOOH): Cd < Co < Zn < Pb < Cu with adsorption increasing with increasing pH. Here, the softer Cd has less afinity than the harder cations Cu and Zn. Benjamin and Leckie (1980) found adsorption to increase in the order Cd < Zn < Cu < Pb on amorphous iron oxyhydroxide (Fe_2O_3 * H_2O(am)). Again the harder cations show preference for the iron oxide surface. Biddappa et al (1981) found selectivity in the order Ni < Cd <Zn < Cu < Pb for soils dominated by volcanic parent material in Japan. Here no clear trends are observable with respect to softness character, but of course the adsorbent material is mixed and variable. Tiller and Brummer (1984) found a relative sorption affinity sequence of Cd < Ni < Zn for soils dominated by iron oxide parent material. For soils dominated by 2:1 clay minerals the sequence was Cd = Ni << Zn. McKenzie (1980) found selectivity to follow the order Ni < Co < Zn < Cu < Pb for hematite (Fe_2O_3) and for goethite the same except for Cu having greater preference than Pb. This is similar to the order found by others for iron oxides. In silicates, Stuanes (1976) found the selectivity order for albite and labradorite to be Hg < Mn < Cd < Zn. For kaolinite , montmorillonite and vermiculite, the order was Hg < Cd < Mn <

Zn. This is the order of increasing hardness with the exception of Mn. Table 3 summarizes the studies where selectivity sequences are proposed based on experimental evidence. Although there are inconsistencies among the studies, the harder metal cations reflect an adsorption preference indicating that iron oxides may be classified as relatively hard bases. Unfortunately many studies neglect to study the effects of complex ion formation in aqueous solution on adsorption. This is obviously a concern in adsorption studies using soils as the adsorbents or where the background electrolyte used may complex with the metals under study.

The experimental factors which influence selectivity order are metal cation concentration, solution pH, presence and concentration of complexing ligands, cation charge and solid concentration. The factors of the reactants are electronegativity, hydration radius and energy, polarizability, surface charge density of adsorbent and the physical and chemical nature of the clay surface.

Bivalent metal cation adsorption data obtained over a range of pH values, where initial metal molar concentrations are equal and the same amount of adsorbent is suspended in the same

Table 3.

Selectivity Sequences for adsorption of heavy metals on various mineral adsorbents.

Sequence	Adsorbent	Reference
Pb > Zn > Cd	Fe gel	Gadde,'74
Zn > Cd > Hg	Fe gel	Bruninx,'75
Cu > Pb > Zn > Co > Cd	FeOOH	Forbes,'76
Cu > Pb > Zn > Co > Ni	FeOOH	McKenzie,'80
Pb > Cu > Zn > Co > Ni	Fe_2O_3	McKenzie,'80
Pb > Cu > Zn > Cd	Fe_2O_3	Benjamin,'80
Pb > Zn > Cd	MnO_2	Gadde,'74
Zn > Cu > Co > Mn > Ni	Si gel	Vydra,'79
Cu > Zn > Ni > Co > Cd	Al gel	Kinniburgh,'76
Zn > Cd > Mn > Hg	albite	Stuanes,'76
Zn > Cd > Mn > Hg	labradorite	Stuanes,'76
Zn > Mn > Cd > Hg	kaolinite	Stuanes,'76
Zn > Mn > Cd > Hg	montmorillonite	Stuanes,'7[illegible]

background electrolyte and concentration, has been shown to be empirically described by the following equation (Kinniburgh et al, 1982):

$$\ln D = a + bpH$$

where a and b are constant parameters determined experimentally, and D is a distribution ratio of fraction of metal sorbed to fraction of metal in solution. A plot of lnD versus pH is called a Kurbatov plot. The pH at which D =1 is where 50% of the metal is sorbed and 50% remains in solution and is designated pH_{50}, and from the above equation $pH_{50} = -a/b$ (Kinniburgh and Jackson, 1981). The pH_{50} values determined experimentally in the above manner are a relative measure of the selectivity of an adsobent for a particular series of bivalent metal cations, the smaller the pH_{50} the more selective the adsorbent for the metal cation (Sposito, 1984).

Table 4 lists several studies where pH_{50} values were used to assess the relative selectivity of an adsorbent for a series of metal cations. In the case of the iron oxides, there is again evidence of these surfaces behaving as "hard" Lewis bases, with affinity decreasing from the borderline acids Zn and Co to the softer Cd. In the case of the clays, the series is opposite to what would be expected from studies of monovalent cation selectivity (Heald et al,1964;Shainberg and Kemper,1967). The selectivity of monovalent cations for montmorillonite and other

Table 4.

Comparison of specific adsorption of heavy metals by means of pH_{50} values.

Selectivity	Adsorbent	pH_{50} values	Reference
Zn >> Cd > Ni	2:1 clays *	4.5,6.0,6.8	Tiller,'84
Zn >> Ni = Cd	2:1 clays *	4.5,6.7,6.9	Tiller,'84
Zn > Ni > Cd	FeOOH *	5.3,6.0,6.2	Tiller,'84
Cu > Zn > Co > Cd	FeOOH @	5.2,7.0,7.4,7.7	Forbes,'76
Cu > Zn > Co > Ni	FeOOH #	4.5,5.4,5.8,6.0	McKenzie,'80
Pb > Cu > Zn > Cd	Fe_2O_3 ~	4.0,5.2,6.3,6.5	Benjamin,'81

* [M] = 5 x 10^{-6}M and in 0.01M $Ca(NO_3)_2$.
@ [M] = 3.2 x 10^{-5}M and in 0.075M $NaNO_3$.
# [M] = 1.0 x 10^{-4}M and in 0.1M KNO_3.
~ [M] = 5.0 x 10^{-7}M and in 0.1M $NaNO_3$.

clay minerals increases with increasing ionic radii and polarizability which follows the order of increasing softness. Stuanes (1976) postulated that the stability of chloride and hydroxide complexes in the suspensions affected the selectivity. Hg and Cd form chloro complexes to a signifigant extent, while Zn occurs mainly as the aquated divalent ion under the conditions studied.

Complex Ion Formation/Effects on Adsorption

The amount of metal sorbed by a clay depends on several factors, in particular pH and the nature and concentration of ligands present in solution (Farrah and Pickering,1977; Cavallaro and McBride,1978; Hahne and Kroontje,1973; Egozy,1980; Barrow et al,1981). Adsorption increases with increasing pH regardless of solution composition, indicating pH to be the dominant controlling mechanism.

Complexing ligands can effect the extent of adsorption either positively or negatively depending on the particular ligand and metal. For cadmium, $CdCl^+$ and $CdSO_4$ species are less strongly sorbed than Cd^{2+} (Garcia-Miragaya and Page,1976; Egozy,1980; Benjamin and Leckie,1982). Mattigod et al (1979) showed less nickel adsorption in $CaSO_4$ versus $Ca(NO_3)_2$ solutions. Bolland (1970) showed that zinc adsorption was greater from chloride solutions than from perchlorate and Forbes (1973) and Forbes et al (1976) showed zinc adsorption to be greater from chloride than

nitrate solutions. Figure 1, adapted from Sposito (1984) outlines the possible interactions between metal, ligand and adsorbent in a soil system. The diagram emphasizes the competition between adsorbent and complexing ligand for the metal and in this way gives credence to the idea of the adsorbent surface functioning as a ligand itself complexing with the metal
in solution.

Adsorbent Effects

All the above indicate not only the importance of the particular background electrolyte used in experiments, but also the complexity of factors affecting adsorption of metal ions in soil solutions where many different complexing ligands are present and in varying amounts. Adding to the complexity is the presence of numerous different adsorbents. These include the many clay minerals such as kaolinite, montmorillonite, and chlorite as well as iron, manganese and aluminum oxides. All offer different chemical and physical environments for adsorption of metal ions.

Two properties of the adsorbent in particular which may affect adsorption are surface area and the isoelectric point (IEP) of the solid. The IEP is defined as the solution pH at which the solid/solution interface has a net zero charge. At pH values above the IEP, the surface has a net negative charge, while at pH values below the IEP, the surface has a net positive charge. Thus at solution pH values below the IEP, adsorption of positively

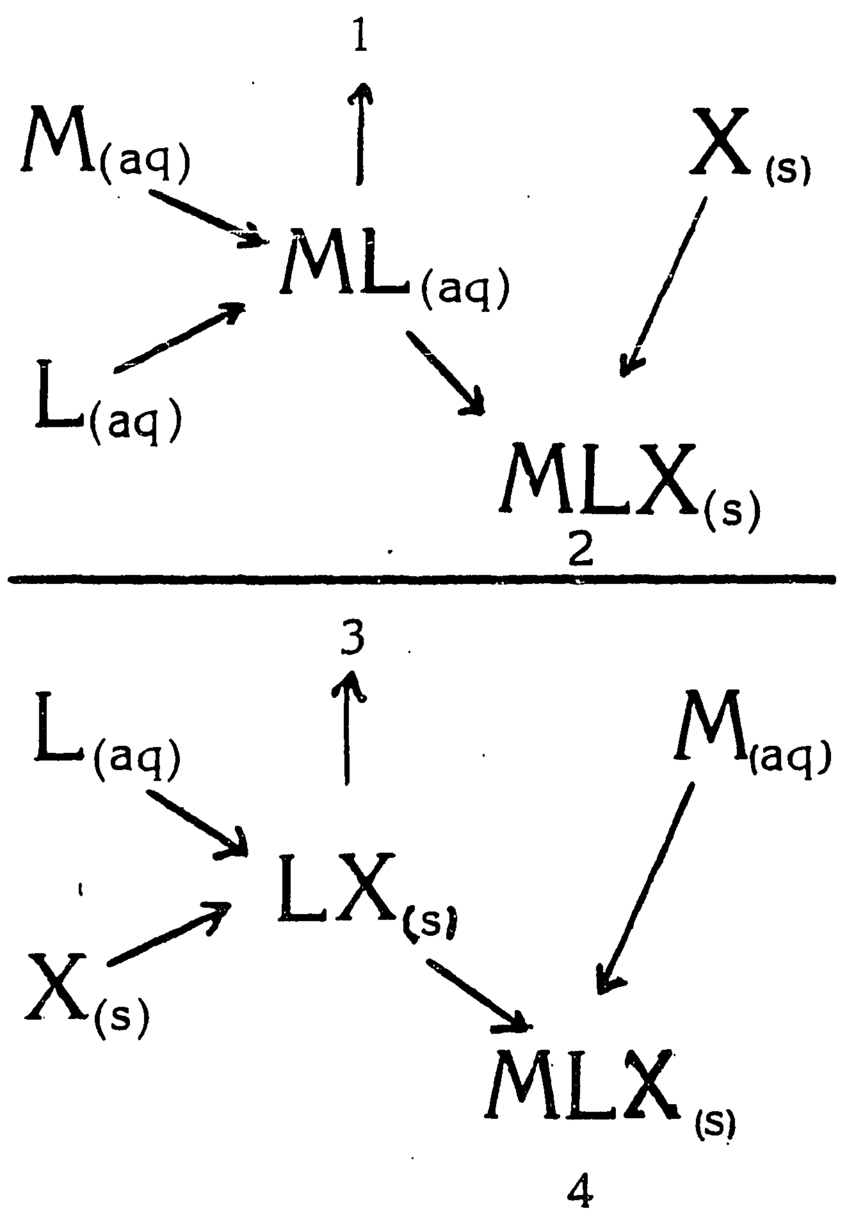

Figure 1. Interactions in an aqueous metal-ligand-surface system.

charged metal ions is significantly less because most metal adsorbate species are positively charged. Table 5 lists the IEP values and surface areas of selected mineral substrates (Harding and Healy,1979).

Surface area is also important in determining the effect of different adsorbents on adsorption of metal cations.
It is, however, difficult to distinguish the physical effect of surface area from electro-chemical differences in adsorbing sites from one adsorbent to another. In dealing with a specific adsorbent however, as surface area increases, adsorption increases in a manner similar to that of increasing pH. Vuceta and Morgan (1978) demonstrated the effect of surface area on metal adsorption using SiO_2 as the adsorbent. As surface area increased, adsorption increased. Likewise, increasing pH increased metal adsorption on SiO_2 (Harding and Healy, 1979). When surface area or the availability of surface sites for adsorption is limiting, adsorption density approached a maximum which in turn depends on the pH of the solution and adsorbent present (Benjamin and Leckie,1982).

Heavy metals also show specificity of adsorption for particular adsorbents. Brummer et al (1983) showed adsorption capacities for Zn increased in the order $CaCO_3$ << bentonite << humic acid < Fe-oxide = Al-oxide < MnO_2 . Differences in surface area were determined to be of minor importance due to experimental

Table 5.

Isoelectric points and surface area of selected mineral adsorbents.

Adsorbent	Isoelectric point	Surface area
Titanium dioxide	5.8	16.0
Copper oxide		31.6
Manganese oxide	7.2	4.1
Iron oxide	8.7	41.7
Silica	2.1	5.0
Kaolinite	2.8	6.1 *
Montmorillonite	4.0	305.0 *

Expressed as m^2/g.
* As determined in this study.

design; chemical and mineralogical composition were the determining factors. Tiller et al (1984) showed Ni to have a greater relative affinity for kaolinite dominated soils as opposed to soils dominated by 2:1 clay minerals. Reid and McDuffie (1980) showed Cd adsorption preference in the following order: kaolinite < illite < montmorillonite. Garcia-Miragaya and Page (1985), using signifigantly lower metal concentrations than Reid and McDuffie, showed Cd preferred kaolinite over montmorillonite. This indicates that metals not only have different affinities for different mineral adsorbents, but that the metal concentration also affects the affinity sequences.

Identification of Adsorption Sites

Egozy (1980) concluded in a study of Cd and Co adsorption that montmorillonite has two distinct types of adsorption sites. One exhibited simple ion-exchange equilibria and the other adsorption behavior similar to that on hydrous aluminum and iron oxides where pH has a great effect and adsorbability is high even from concentrated (1M) electrolyte solution. Farrah and Pickering (1976) also postulated a dual site theory based on Cu adsorption on kaolinite. One site is the positive site of the kaolin edges which sorb hydroxyl ions and coordinate Cu ions. The other site is the negatively charged sites on the mineral faces where divalent Cu is directly sorbed. If one considers the clay as a ligand, then the two sites represent a mixed metal-ligand complex and simple metal-ligand complex. Davis and Leckie (1978) proposed that adsorption occurs as a monohydroxo complex on the mineral surface or by the formation of a bidentate surface complex. They measured Pb adsorption on amorphous iron oxyhydroxide. They concluded that the primary mechanism was the formation of surface complexes with hydrolyzed metal ions rather than the adsorption of Pb^{2+} to two adjacent ligand groups on the surface. Kalbasi et al (1977) in studying Zn adsorption on iron and aluminum oxides postulated specific and nonspecific adsorption. Specific adsorption was the adsorption of Zn^{2+} and release of two H^+ ions for each mole of Zn adsorbed and nonspecific adsorption was the adsorption of $ZnCl^+$ or other univalent Zn complex ions and the release of one H^+ ion for each mole of Zn adsorbed.

Kinetic Approach to Metal Cation Adsorption

A thermodynamic equilibrium approach to the study of metal adsorption provides information about the final state of a system in comparison to an initial nonequilibrium state (Zasoski,1978). It is difficult to propose how that equilibrium or quasi-equilibrium state was reached. With a kinetic approach, details of ongoing changes to the system are available and conclusions may be drawn concerning reaction pathways and mechanisms. Reaction order and rate constants can provide information about reaction mechanisms and the nature of the adsorbent surface and its properties (Aringhieri,1985). Finally it is of interest to compare equilibrium and kinetic data. Since the two approaches are theoretically complementary, results should also provide complementary information about reaction mechanisms and the nature of the adsorbing surface.

Bunzyl et al (1976), found adsorption selectivity in the order $Pb^{2+} > Cd^{2+} > Zn^{2+} > Ca^{2+}$ on peat. This is the order of decreasing softness. They also concluded that half times of adsorption or the time at which half of the equilibrium is attained, decreased with increasing amount of metal added. This is characteristic for all ion-exchange processes controlled by film diffusion and thus they determined that film diffusion was the rate-limiting step in the adsorption reaction. Salim and Cooksey (1980) also concluded that film diffusion was the rate-limiting step in the adsorption of lead on river-mud. Film diffusion is the transport of a cation through a thin film of external solution surrounding an adsorbent particle driven by a concentration gradient. They concluded that adsorption proceeded from this step to the diffusion of the adsorbate into pores of the adsorbent or 'intraparticle diffusion'; with the subsequent actual adsorption onto surfaces of the adsorbent. If film diffusion is rate-limiting, agitation of the suspension should increase the rate of adsorption and this was also found to be the case for the adsorption of lead on river-mud.

Characteristics and Properties of Metals

Cadmium

Cadmium is a toxic heavy metal which is used in a variety of products. Almost all cadmium is obtained as a by-product from the treatment of zinc, copper and lead ores. Most exposure is of an occupational nature, involving workers in battery manufacturing, electroplating, metal fabrication, photographic, rubber and aircraft industries. It is used in many types of solder, in phosphors for TV tubes, and as a barrier to control atomic fission. Cadmium is released into the air during the smelting of other metals and from incineration of cadmium-containing products such as rubber tires.

Drinking water, foods grown on high cadmium soils, seafood and the inhalation of cadmium fumes are the chief sources of human cadmium intake. Appreciable quantities are found in coffee, tea, peanuts, and cigarette tobacco (Burgess,1973). It produces acute health effects when inhaled or ingested at high concentrations. From epidemiological and experimental studies, kidneys are the organ most affected by long-term low-level exposure to cadmium. In addition to kidney damage, cadmium also contributes to cardio-vascular disease, chronic renal disease and lung disease. In Japan, a chronic form of cadmium poisoning called "itai-itai" or ouch ouch disease was caused by the pollution of river water by a cadmium mine. In addition to kidney damage , individuals developed extreme pain in their joints and bones and softening of bones leading to spontaneous multiple fractures (Burgess,1973).

Nickel

Almost 30% of all nickel is obtained from pentlandite and pyrrhotite of the Sudbury region of Ontario, Canada. It is used in the production of stainless steel and various alloys and in making nickel steel for armor plate and burglar-proof vaults. Nickel plating is often used as a protective coating for other metals and nickel is also a catalyst for hydrogenating vegetable oils. The most toxic form of nickel is nickel carbonyl, formed by reactions of nickel with hot carbon monoxide. Workers in nickel refineries, are prone to developing lung cancer and cancer of the nose and sinus (Burgess,1973). The presence of nickel in tobacco, possibly released as nickel carbonyl, may signifigantly contribute to the carcinogenic potential of cigarette smoke. Found in coal and petroleum, it is present in air in varying quantities from combustion of these products.

Zinc

The principal ores of zinc are sphalerite or blende (sulfide), smithsonite (carbonate), calamine (silicate), and franklinite (zinc, manganese, iron oxide). The metal is used to form numerous alloys with other metals such as brass, nickel silver, bronze, soft solder and aluminum solder. Large amounts of zinc are used to produce die castings for the automotive, electrical and hardware industries. Zinc is also used to galvanize other metals to prevent corrosion. Zinc oxide is widely used in the manufacture of paints, rubber products, cosmetics, pharmaceuticals, plastics, batteries and electrical equipment. Zinc sulfide is used in making luminous dials, x-ray and TV screens, and fluorescent lights. It is an essential element in the growth and development of animals and humans, but can be toxic in large amounts. Inhalation of ZnO can cause a disorder known as the oxide shakes.

Table 6 is a partial list of chemical and physical properties of Cd, Ni and Zn.

Table 6.

Properties of Cd, Ni and Zn (arranged according to decreasing softness).

Element	Electro-negativity	Polar-izability	Ionic Radii	Atomic Weight	Ionization Potential
Cd	1.46	1.15	92	112.40	8.99
Zn	1.66	0.50	74	65.37	9.39
Ni	1.75		69	58.71	7.64

Electronegativity is according to Allred and Rochow (1958).
Polarizability is in units of 10^{-24} cm^3 (Phillips and Williams,1965).
Ionic radii for Cd^{2+}, Ni^{2+} and Zn^{2+} is in units of pm (Huheey,1978).
Atomic weights are those adopted by the International Union of Pure and Applied Chemistry at its 1969 meeting and are based on a relative atomic mass of $C^{12} = 12$.
Ionization potential are in units of electron volts (Weast,1985).

CHAPTER 3

MATERIAL AND METHODS

Materials

All glassware and polyethylene bottles were acid rinsed with 0.1M nitric acid made from double distilled concentrated nitric acid. A kaolinite sample was obtained from the Georgia Kaolin Company and a montmorillonite (Texas bentonite) sample from the Clay Minerals Society at the University of Missouri. The water used was distilled-deionized water.

Preparation of Clay Suspensions

The < 2 um fraction of kaolinite and montmorillonite were separated by sedimentation (Day,1965). The clay samples were oven-dried and 50.0 g weighed into 250 ml polyethylene wide-mouth bottles. To these was added 150 ml of 0.5M $CaNO_3$. These were thouroughly shaken on a mechanical shaker to suspend and mix the clays. The samples were then centrifuged, decanted and the supernatent discarded. This was repeated 5 times and then finally mixed with 150 ml distilled-deionized water, centrifuged and the supernatent discarded. The samples were weighed to determine the moisture content of the samples. The moist clay was then added to 1 liter Pyrex distilling flasks made to 0.01M in $CaClO_4$, $CaCl_2$, or

$CaSO_4$. The pH of the suspensions was adjusted to 5.5, 6.5, or 7.5 with 1M NaOH or 1M HNO_3 over a period of 48 hours. This was determined to be the time required for stabilization of suspension pH. The pH of the suspensions was determined by a Beckman Electromate pH meter equipped with a Beckman glass/calomel electrode pair. The suspension was continuously stirred with a Teflon-coated stirring rod driven by a magnetic stirring unit. The reaction vessel was kept in a water bath at 25C plus or minus 1C throughout the experiment. The suspensions were continuously purged with nitrogen gas to exclude carbon dioxide.

Equilibrium Sorption Experiment

After the 48 hour suspension pH stabilization period, 10 ml of 10^{-4}M metal as $Cd(NO_3)_2$,$Ni(NO_3)_2$, or $Zn(NO_3)_2$ was added bringing solution volume to 1000 ml and the time noted. The pH was continually adjusted to remain stable at 5.5, 6.5, or 7.5 through addition of 1M NaOH via buret. During this time temperature remained constant and carbon dioxide was excluded as previously described. Preliminary experiments indicated that sorption equilibrium was attained within 24 to 48 hours, so 48 hours was decided upon as the appropriate reaction time period. At 48 hours, 10 ml of suspension was extracted with a minipet glass syringe and transferred to a 50 ml polyethylene centrifuge tube and centrifuged at 15,000 RPM (Sorvall Model SS-3) for 20 minutes to separate the solid phase. The supernatent was then decanted and stored for analysis to determine by difference the amount of metal sorbed. Triplicate samples were taken for all metals at 48 hours after metal addition and reported results are the average.

Kinetics of Cation Sorption

Metal addition, pH and temperature adjustment, and carbon dioxide exclusion were performed as for equilibrium experiments. Upon addition of the Cd^{2+},Ni^{2+} and Zn^{2+} ion, 10 ml was taken at 1,3,10,30 and 90 minutes and at 5,24 and 48 hours with a minipet glass syringe. For the first 3 time intervals the 10 ml suspension extracts were filtered through # 44 Whatman filter paper and the filtrate saved for analysis. Weighing of filter paper upon drying showed an average of 490.8 mg of clay collected on the filter paper or a solution/clay ratio of 20.37 in the extracts. This indicated that this method of sampling removed a good sample of the suspension and that the filtrate was free of clay. The latter 5 time intervals (30 minutes to 48 hours), samples were centrifuged as described above. The amount of clay remaining in the centrifuge tubes was 493.4 mg or a solution/clay ratio of 20.26. A ratio greater than 20/1 is expected due to adsorption and entrapment of clay in the extraction syringe, as well as minute amounts in the filtrate or decanted solution. All runs were duplicated and reported results are the average.

Chemical/Instrumental Analysis

Atomic Absorption Analysis of Metals Remaining in Solution

Concentrations of Cd, Ni and Zn were determined using a model 503 Perkin-Elmer Atomic Absorption Spectrophotometer equipped with graphite furnace. All analytical solutions contained 0.5% double distilled HNO_3. Standards were made with 1000 ppm Baker Chemical Company reagents for Atomic Absorption Analysis.

Total Metal Analysis of Prepared Clay Samples

The $CaNO_3$ saturated clay samples were analyzed for total metal analysis as follows:

1. Clay was dried at 105 C until moisture-free, weighed to 1.0000 g on analytical balance using triplicate samples, and placed in 150 ml teflon beakers.
2. 20 ml freshly made aqua regia (3:1 $HCl:HNO_3$) and 6 ml HFwere added. The beaker was covered with teflon watchglass and heated to 80-90 C to near dryness.
3. Teflon watchglass and beaker washed with 0.20 M HNO_3 and heated gently to 70-80 C to near dryness.
4. 25 ml of 0.10M HNO_3 was added and the solution heated gently to dissolve all residue.
5. The beaker contents were filtered through a 0.45 um pore size filter while scrubbing the sides of the beaker with a clean policeman and washing the sides with 0.10M HNO_3.

The solution was made up to 50 ml volume with 0.10M HNO_3 and analyzed as above.

This measured the native amounts of Cd, Ni and Zn in the clays before metal addition.

Clay Surface Area

The surface area of the Ca-saturated kaolinite was 6.05 m^2/g and that of the montmorillonite 304.98 m^2/g from water absorption at 19 percent relative humidity (Quirk, 1955). The procedure was:

1. A sample of clay was dried at 105 C overnight and triplicate samples of 1.0000 g weighed on an analytical balance.
2. The sample was placed in a dessicator over saturated $CaBr_2$ solution at 19 % relative humidity and evacuated.
3. After 1 week at 20 C the clay + weighing can was weighed with the area of a water molecule taken to be 0.108 nm^2.

Metal Speciation in Solution

The amount of metal sorbed was determined by difference from the amount added and the amount analyzed in the filtrate or supernatent solution. That amount analyzed by the atomic absorption spectrophotometer was total metal and includes species, which before acidifying may have included ion pairs and complex ions. Some of these species were also presumably sorbed as well as present in solution. A computer speciation program, MICROQL, was used to determine the speciation of Cd, Ni, and Zn at the various pH's and in the presence of the complexing ligands in solution.

CHAPTER 4

PHYSICAL/CHEMICAL CHARACTERIZATION OF CLAYS

Kaolinite

The kaolinite used in this study was a well crystallized kaolinite from the contact of the Coastal Plain and Piedmont in Georgia. Designated KGa-1 by the Clay Mineral Society, it was collected and provided by Georgia Kaolin Company. The well crystalized sample occurs at a depth of 12 meters overlain by sand. The kaolin bed was about 7.2 meters thick (Van Olphen and Fripiat, 1980).

Kaolinite is a 1:1 clay mineral composed of a tetrahedral and octahedral sheet. The tetrahedral sheet consists of polymerized silica tetrahedra (SiO_4^-), formed from the sharing of corners occupied by oxygen ions. The octahedral sheet consists of a polymerized octahedral complex composed of a central metal ion surrounded by six anions (eg.oxygens,hydroxyls;Figure 2). This central metal ion is aluminum in kaolinite and it occupies 2 out of 3 octahedral positions with the third vacant. This arrangement is termed dioctahedral. When all central metal positions are occupied the structure is termed trioctahedral and these are the serpentine minerals (amesite,cronstedite). When magnesium is in the octahedral position, the mineral is antigorite. The two

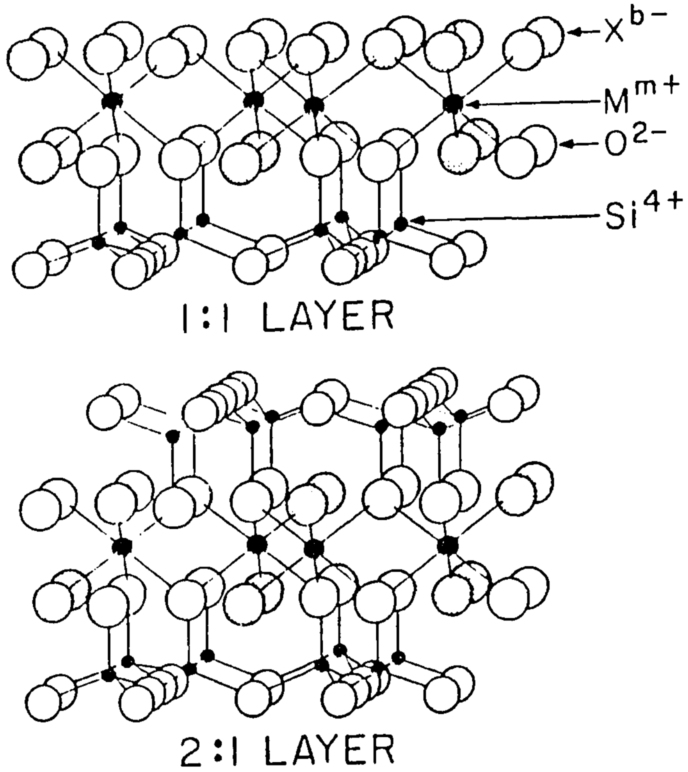

Figure 2. 1:1 and 2:1 layer type clay minerals.

sheets are held together by hydrogen bonding between the oxygen ions of the tetrahedral sheet and hydroxyls of the octahedral sheet. The thickness of the two sheets (z direction) is 0.7 nm.

The chemical analysis of the kaolinite sample is from Van Olphen and Fripiat,1980 and is listed in Table 7. Also included in the table are the amounts of native Cd, Ni and Zn in the clay from total metal analysis as described in Chapter 3.

Infrared spectrophotometry involves the twisting, bending rotating and vibrational motions of atoms. When exposed to infrared radiation, portions of the incident radiation are absorbed at wavelengths unique for the particular substance. This produces a highly complex 'blueprint' or absorption spectrum reflecting the functional groups and overall atomic arrangement of the material. Infrared spectral analysis is from Van Olphen and Fripiat and is summarized in Figure 3 and Table 8.

Differential thermal analysis (DTA) is another analytical means of identifying clay materials and is supportive of IR analysis. DTA involves the heating of a sample and an inert reference material together and monitoring temperature changes of the sample which result from liberation or absorption of energy compared with the inert material. The differential temperature tells wether the transition is exothermic (gives off energy-temperature increases) or endothermic (absorbs

Table 7.

Chemical Analysis of Clay Mineral Society Clays (as %).

	Kaolinite (KGa-1)	Montmorillonite (STx-1)
SiO_2	44.2	70.1
Al_2O_3	39.7	16.0
TiO_2	1.39	0.22
Fe_2O_3	0.13	0.65
FeO	0.08	0.15
MnO	0.002	0.009
MgO	0.03	3.69
CaO	0.02	1.59
Na_2O	0.013	0.27
K_2O	0.050	0.078
P_2O_5	0.034	0.026
Total	99.40	99.37

Trace Elements of Interest (ppm = ug/g clay).

	Kaolinite (KGa-1)	Montmorillonite (STx-1)
Cd_T	1.8	0.9
Ni_T	10.5	6.6
Zn_T	16.6	10.5

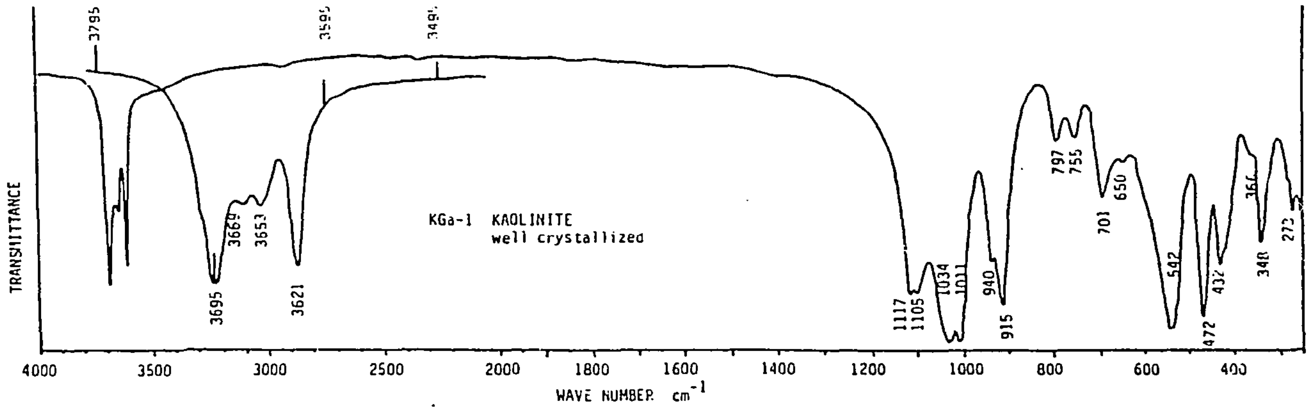

Figure 3. Infrared Spectral Analysis of Kaolinite (KGa-1).

Table 8.

Infrared Spectroscopy Analysis Data--KGa-1 Kaolinite.

peak-maxima (cm^{-1})	Assignments
3695, 3669, 3653	OH stretching, hydroxyl sheet
3621	OH stretching inner OH
1117, 1105, 1034, 1011	SiO stretching
940, 915	OH deformation
797, 650, 542, 472, 432, 366, 348, 273	mixed SiO deformations and octahedral sheet vibrations

sample 0.5 mg heated at 200 C. in 0.5 inch KBr disk

energy-temperature decreases). Endothermic and exothermic peaks have been identified and are summarized for the kaolinite sample by Van Olphen and Fripiat, 1980 in Figure 4 and Table 9.

Montmorillonite

The montmorillonite in this study was from an extremely white bentonite deposit in south central Texas. It is widely used in the tile industry as a binder owing to its white-firing nature. It was designated STx-1 by the Clay Mineral Society.

Montmorillonite is a 2:1 clay mineral composed of an octahedral sheet sandwiched between two tetrahedral sheets (Figure 2). Dioctahedral forms result from weathering, whereas the trioctahedral forms are inherited from parent material and are much less common in soils. Cationic substitution occurs in the octahedral sheet. Iron and magnesium are the predominant cations which substitute for aluminum in the octahedral sheet, leaving a positive charge defecit, which must be balanced by other cations either inside or outside the crystal.

Three clay mineral groups are defined in the 2:1 clay minerals. These are micas, vermiculites and smectites. They are differentiated by their layer charge which is the number of moles of net electron charge per unit cell produced by isomorphic substitutions. Table 10, adapted from Bohn, 1979 lists the layer charge for these groups as well as where the substitutions occur and the names of the resulting clay minerals.

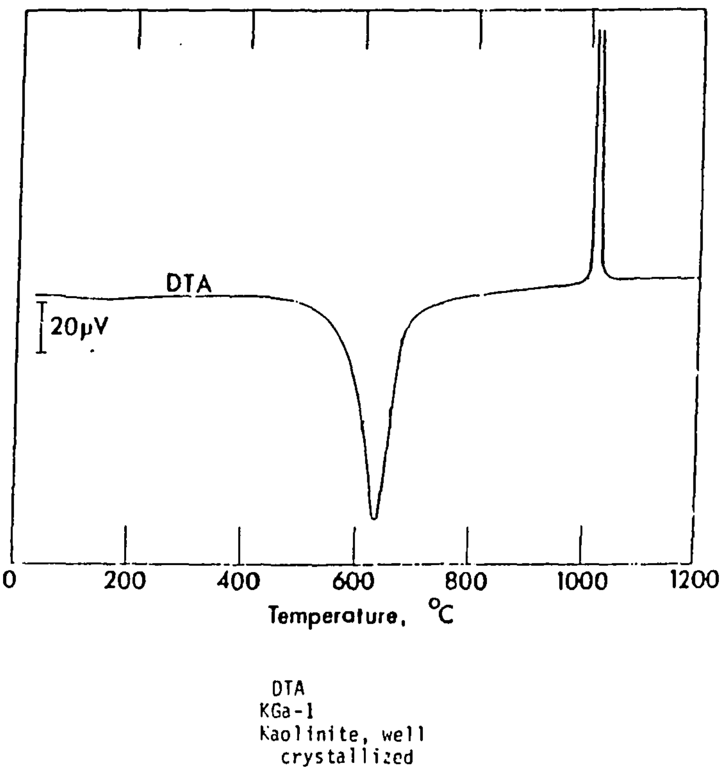

Figure 4. Differential Thermal Analysis of Kaolinite (KGa-1)

Table 9.

Differential Thermal Analysis Data--Clay Mineral Society Clays.

Sample		DTA peak temperatures (C)
KGa-1	Kaolinite	630- @, 1015+ #
STx-1	Montmorillonite	185- ^, 240- ^ (sh), 720- @, 1055+ #, 1090+ #, 1135+ #

(@) dehydroxylation; (#) formation of thermal decomposition products; (^) desorption of water; (sh) shoulder; (-) endothermic peaks; (+) exothermic peaks.

TABLE 10.

2:1 Layer Silicate Minerals.

Mineral Group	Layer charge per formula unit in Tetrahedral Sheet	Octahedral Sheet	Predominant Octahedral Cation Al^{3+} (dioc)	Mg^{2+} (trioc)
Smectites	0.25-0.6	0	Beidellite	Saponite
	0	0.25-0.6	Montmorillonite	Hectorite
Vermiculites	0.6-0.9	0	Vermiculite	
Micas	1	0	Muscovite	Biotite @

@ Mg^{2+} and Fe^{2+} in octahedral coordination, K in the interlayer position.
From Bohn, 1979.

The degree of swelling in clay minerals is inversely relatea to the magnitude of the layer charge. The smectite group, of which montmorillonite is the best known example, has the greatest tendency to expand when wet, exposing much greater surface area than that of the mica and vermiculite groups. Kaolinite, a 1:1 clay mineral, is nonexpanding and exhibits only external surface area.

The chemical analysis of the montmorillonite sample is from Van Olphen and Fripiat,1980 and is listed in Table 7. Also included in the table are the native amounts of Cd, Ni and Zn as determined from the total metal analysis described in Chapter 2.

Differential thermal analysis and infrared spectral analysis data from the same source is also included in Figures 5 and 6 and Tables 9 and 11.

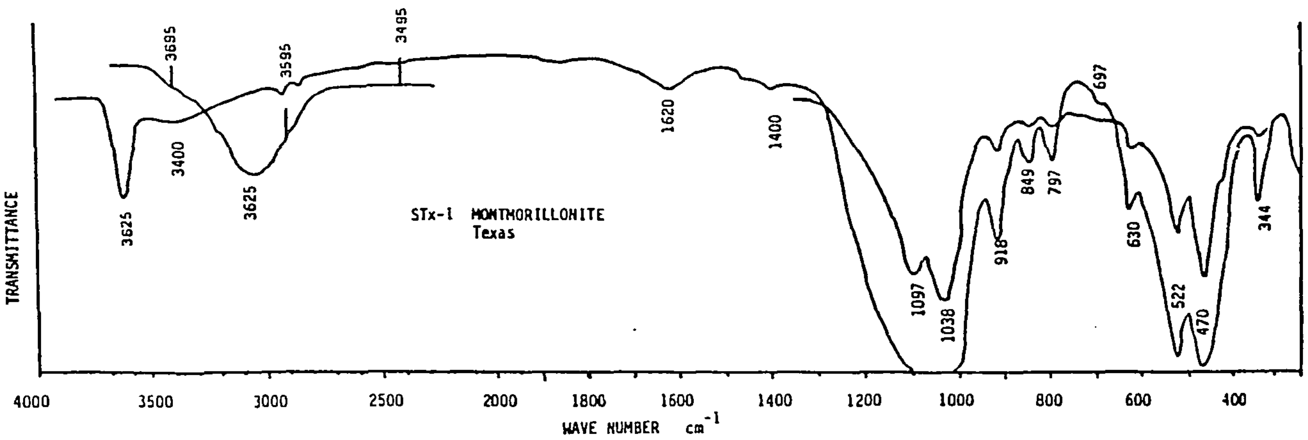

Figure 5. Infrared Spectral Analysis of Montmorillonite (STx-1).

Table 11.

Infrared Spectroscopy Analysis--STx-1 Montmorillonite.

peak maxima (cm^{-1})	Assignments
3625	OH stretching
3400	hydration, OH stretching
1620	hydration, HOH deformation
1400	carbonate
1097, 1038	SiO stretching
918	OH deformation, linked to 2 Al^{3+}
849	OH deformation, linked to $Al^{3+}Mg^{2+}$
797	silica
697	quartz
630, 522, 470, 344	SiO deformation and AlO stretching

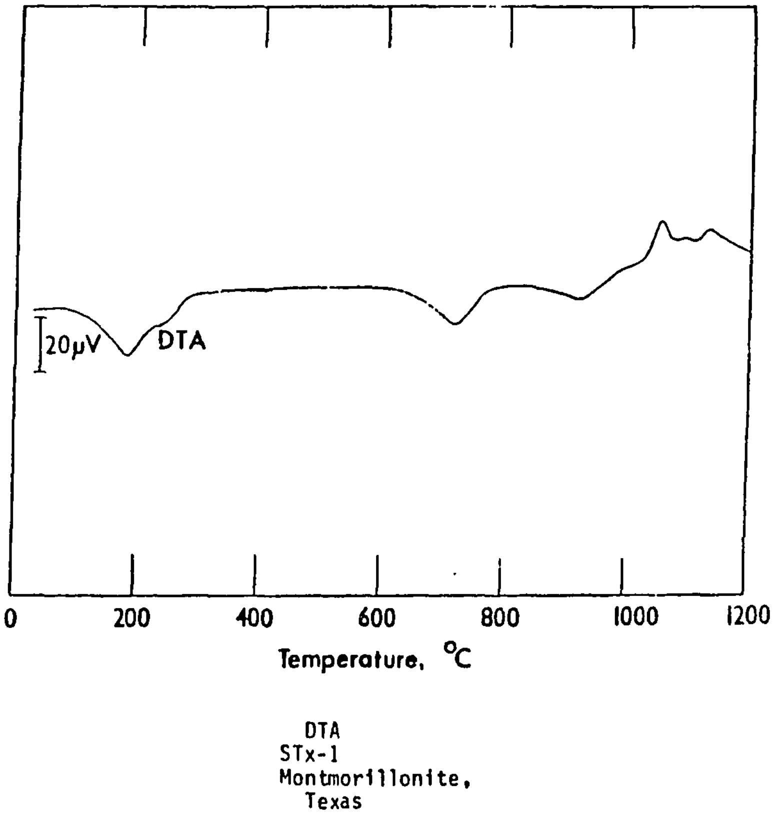

Figure 6. Differential Thermal Analysis of Montmorillonite (STx-1).

CHAPTER 5

RESULTS AND DISCUSSIONS-I. EQUILIBRIUM SORPTION OF CD, NI AND ZN.

Sorption in $Ca(ClO_4)_2$ by kaolinite.

The selectivity of Cd, Ni and Zn by kaolinite was measured using Kurbatov plots as described in Chapter 2. Adsorption selectivity decreased in the order Cd > Zn > Ni when reactions were carried out in 0.01M $Ca(ClO_4)_2$ over a range of pH from 5.5 to 7.5 as shown in Figure 7. The pH_{50} values were 4.49, 5.37 and 5.80 for Cd, Ni and Zn respectively. The standard deviation of pH_{50} values was 0.1 pH units. The Cd > Zn > Ni order follows the order of decreasing ionic radii and increasing electronegativity, or decreasing softness as shown in Table 12. Kaolinite has a marked preference for the softer metal Cd compared to the relatively hard Ni. Kaolinite follows the same trend found in univalent cation adsorption and suggests from the HSAB principle that the kaolinite surface behaves as a soft Lewis base. As discussed in Chapter 2, 'hard' and 'soft' are relative terms. In this case the surface functional groups of kaolinite are softer than the hard solvating water molecules. Table 13 lists the percent metal sorbed after 48 hours at pH 5.5, 6.5 and 7.5 as well as the ln D values (see Chapter 2). In all cases adsorption increases with increasing pH. The hydroxyl ligand affects

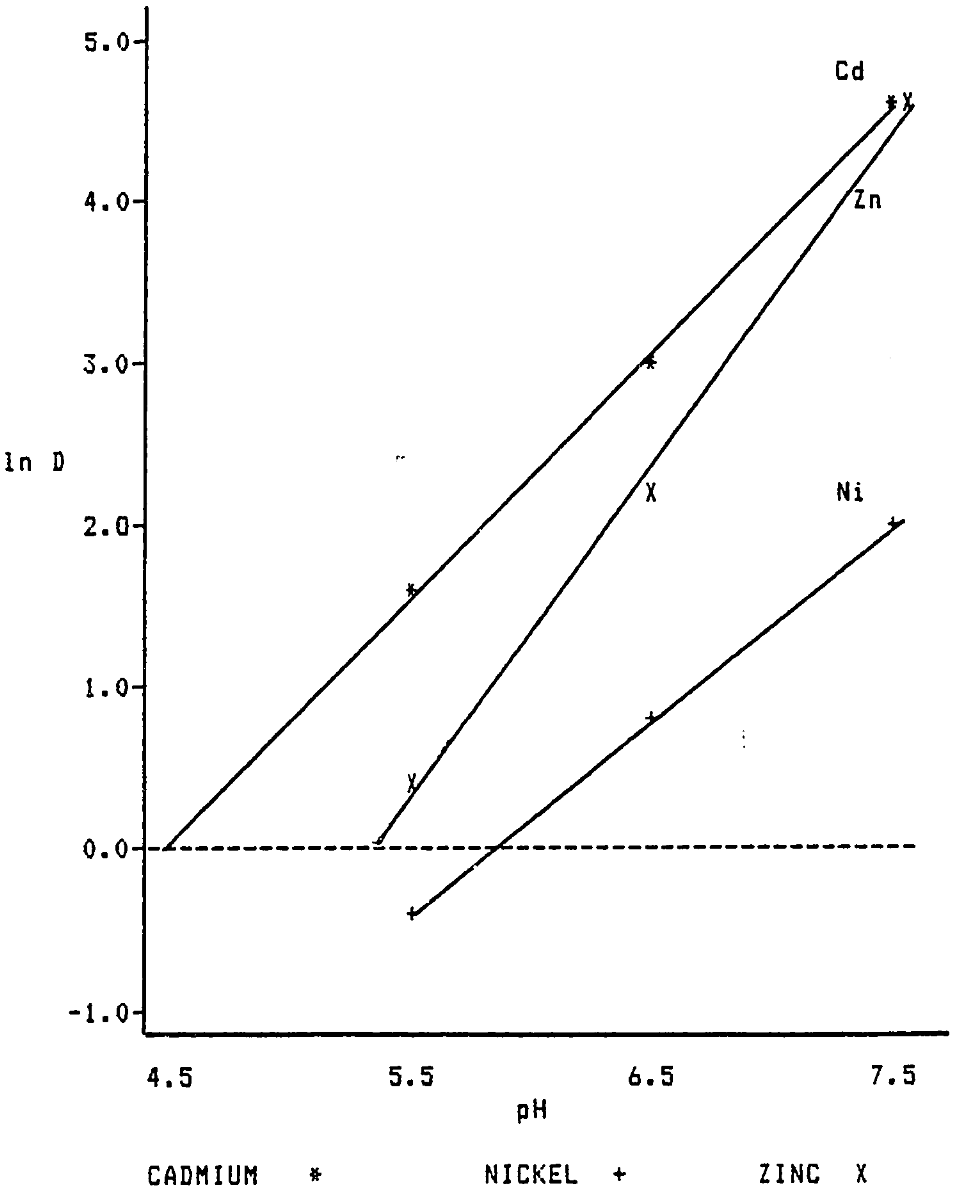

Figure 7. Adsorption of Cd, Ni and Zn on kaolinite
(in 0.01M calcium perchlorate).

Table 12.

Comparison of pH_{50} values and physical constants for metal adsorption on kaolinite in 0.01M $Ca(ClO_4)_2$.

Metal	pH_{50}	Radii(pm)	Electronegativity
Cd	4.49	97	1.46
Zn	5.37	74	1.66
Ni	5.80	69	1.75

Selectivity: Cd > Zn > Ni

Table 13.

Adsorption of Cd, Ni and Zn by kaolinite in 0.01M $Ca(ClO_4)_2$.

Metal	pH	% ads	ln D
Cd	7.5	99	4.60
	6.5	95	2.94
	5.5	83	1.59
Zn	7.5	99	4.60
	6.5	89	2.09
	5.5	64	0.58
Ni	7.5	82	2.09
	6.5	61	0.71
	5.5	48	-0.08

adsorption according to pathway 2 or 4 in Figure 1. MOH^+ species exhibit a high affinity for surface functional groups or OH^- is adsorbed and functions as a bridge between the surface and the metal cation.

From computer speciation data, the only adsorbate species present in these solutions are M^{2+} and MOH^+. With perchlorate as the background electrolyte anion and carbonate excluded, the only complex ion formation in solution involved is the hydroxide anion. Adsorption on the clay minerals was the predominant means of metal removal from solution. Precipitation was precluded with the concentrations of metals and other species used and the exclusion of carbonate from the reactions.

<u>Sorption in $Ca(ClO_4)_2$ by montmorillonite.</u>

Selectivity for the clay mineral, montmorillonite, was also measured by Kurbatov plots. As with kaolinite the order of selectivity was Cd > Zn > Ni in 0.01M $Ca(ClO_4)_2$ from pH 5.5 to 7.5 as shown in Figure 8. One notable difference was the closeness of the pH_{50} values for Cd and Zn (Table 14). The difference was 0.10 pH unit which is within one standard deviation (0.10 unit) and hence the difference was not significant. The difference between Cd ,with the greatest affinity, and Ni, the least preferred, was 0.62 units as compared with a range of 1.31 in the case of kaolinite. The pH_{50} value for Cd increased compared to kaolinite, while the values for Zn and Ni decreased. This indicated that the

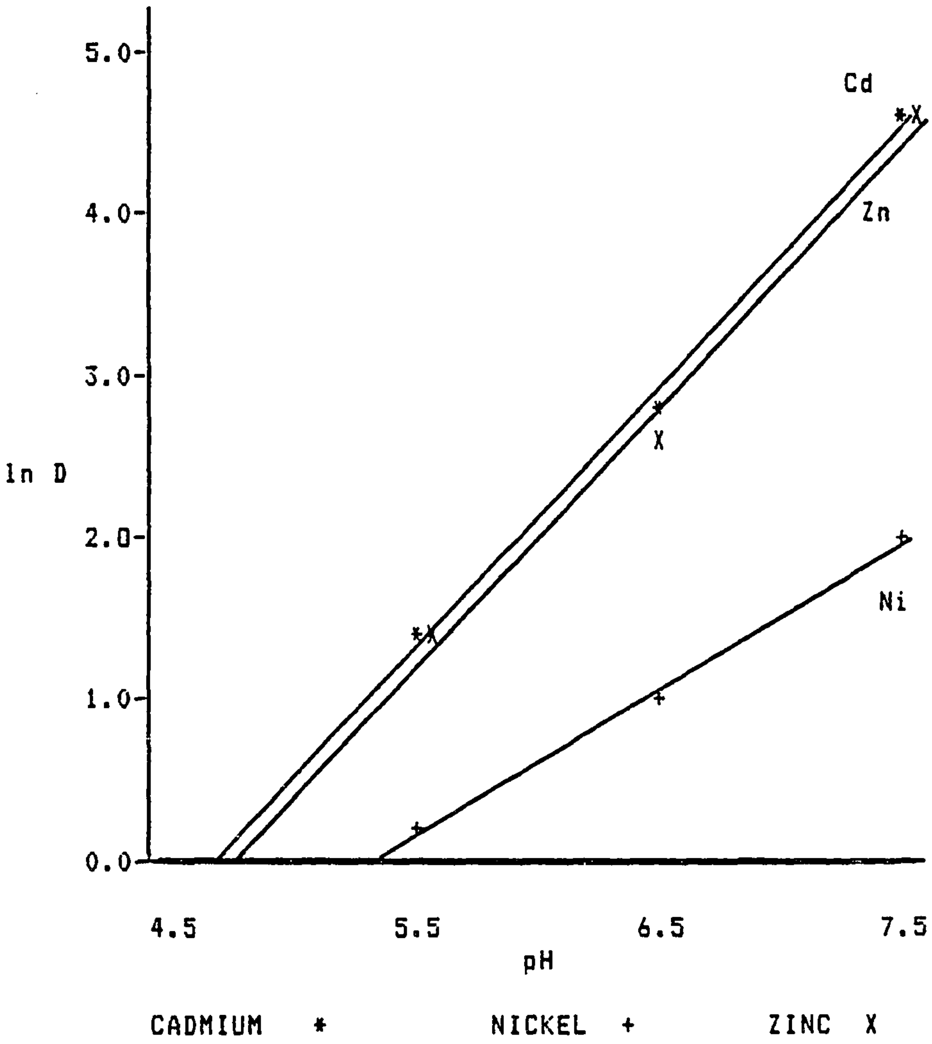

Figure 8. Adsorption of Cd, Ni and Zn on montmorillonite (in 0.01M calcium perchlorate).

Table 14.

Comparison of pH_{50} values and physical constants for metal adsorption on montmorillonite in 0.01M $Ca(ClO_4)_2$.

Metal	pH_{50}	Crystal Radii(pm)	Electronegativity
Cd	4.66	97	1.46
Zn	4.76	74	1.66
Ni	5.28	69	1.75

Selectivity: Cd > Zn > Ni

mineral surface of montmorillonite behaved as a 'harder' base than kaolinite, but was still relatively soft compared to the water molecules which solvate the metal ions in solution.

Adsorption increased with pH as with kaolinite. This is illustrated in Table 15. Hydroxyl groups facilitated adsorption by acting as bridges between the surface and the metal cation as well as by hydrolyzing metal ions in solution for adsorption as univalent complexes. The sorption equilibrium and metal speciation was the same as with kaolinite, with M^{2+} and MOH^{+} the predominant adsorbing species.

The differences between kaolinite and montmorillonite which contribute to adsorption differences are basically twofold. In addition to the greater percentage of hydroxyl edge sites on kaolinite, the ditrigonal cavity formed by six corner-sharing silica tetrahedra associated with the siloxane surface functions as a relatively hard Lewis base when isomorphic substitution has occurred in the crystal structure of montmorillonite. Where isomorphic substitution has occurred in the octahedral sheet (Fe^{2+} or Mg^{2+} for Al^{3+}), the resulting excess negative charge can distribute itself over the oxygen atoms of the silica tetrahedra associated through their apices with the octahedral layer (Sposito,1985). This is a greater distribution of the net negative charge than is the case for substitution in the tetrahedral layer (Al^{3+} for Si^{4+}), where the excess charge is only

Table 15.

Adsorption of Cd, Ni and Zn by montmorillonite in 0.01M $Ca(ClO_4)_2$.

Metal	pH	% ads	ln D
Cd	7.5	99	4.60
	6.5	94	2.75
	5.5	81	1.45
Zn	7.5	99	4.60
	6.5	93	2.59
	5.5	80	1.39
Ni	7.5	88	1.99
	6.5	75	1.10
	5.5	55	0.20

distributed among the three surface oxygen atoms of one tetrahedra; and it being more localized on the surface can form stronger surface complexes. These would be inner-sphere surface complexes as opposed to outer sphere complexes. Inner-sphere complexes have no water molecules interposed between the metal (bound species) and the surface site. Outer-sphere complexes have water molecules separating the metal ion and the surface site. Outer-sphere complexes are characterized by long-range electrostatic bonds, whereas inner-sphere complexes are short range and stronger, that is, more stable. Generally, inner-sphere complexes are more covalent in their acid-base bonding mechanisms.

Pearson (1968) equates ionic bonding with hardness and covalent bonding with softness. Sposito (1981) also makes this point and further equates hard with ionic bonding and outer sphere complexes, and soft with covalent bonding and inner sphere complex formation:

> Because ionic size and charge are the dominant properties of hard Lewis acids and bases, it is expected that their complexes will involve ionic chemical bonds and, therefore, will tend to form outer-sphere complexes. Because a high polarizability is their (bivalent transition metal cations) dominant property as Lewis acids, these cations are expected to engage in more covalent bonding to ligands and, therefore, to form inner-sphere complexes.

The data suggest that the surface functional group, the siloxane ditrigonal cavity, acts as a harder site than the edge hydroxyls, decreasing the overall softness of the mineral sorbent.

This is consistent with the above, when isomorphous substitution takes place in the octahedral layer of the montmorillonite. This creates excess negative charge, which is spread out between the tetrahedral and octahedral contact within the crystal, and leads to the formation of relatively hard outer-sphere complexes with metal ions in solution.

<u>Sorption in $CaCl_2$ by kaolinite.</u>

When the adsorption reaction was carried out in 0.01M $CaCl_2$, the selectivity order was changed to the order Zn > Ni > Cd over the pH range 5.5 to 7.5, Figure 9. The only change from the experiment above was that $CaCl_2$ was the electrolyte as opposed to $Ca(ClO_4)_2$. The extent of complex ion formation in solution is shown in Apppendix B, Tables B2, B3 and B6. $CdCl^+$ accounts for almost 39% of metal species in solution whereas $ZnCl^+$ and $NiCl^+$ account for only about 2% and 1% respectively. Table 16 lists the pH_{50} values for this case as well as those where perchlorate was the major anion. Also listed is the percentage of divalent metal in solution when chloride was present from MICROQL data. In comparison to the case (0.01M $Ca(ClO_4)_2$) where virtually all of the metal is present as M^{2+}, the decrease in Cd adsorption was due to $CdCl^+$ having a low affinity for adsorption sites. This also appeared to be the case for Ni, where the pH_{50} value decreased by about the same percentage as the amount of divalent species in solution; but because of the large extent of chloro-cadmium

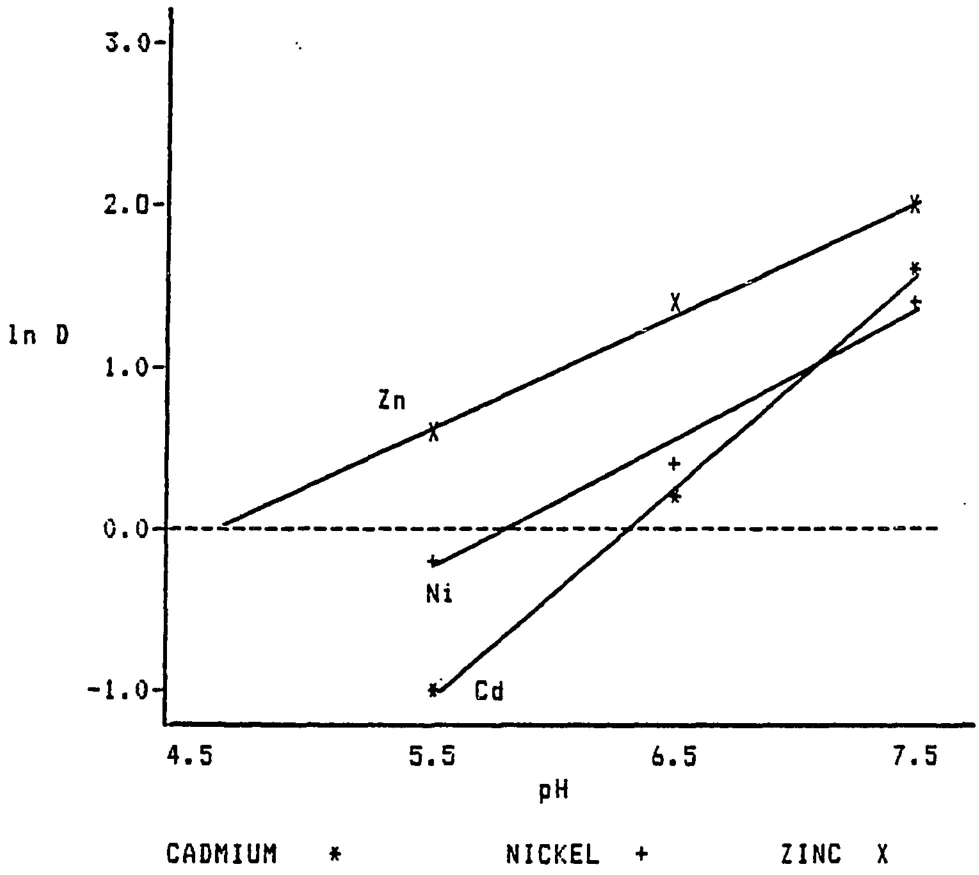

Figure 9. Adsorption of Cd, Ni and Zn on kaolinite (in 0.01M calcium chloride).

Table 16.

Comparison of pH_{50} values and metal speciation for metal adsorption on kaolinite.

Metal	ClO_4^-	Cl^-	% M^{2+}
Cd	4.49	6.20	58
Zn	5.37	5.12	96-98
Ni	5.80	5.82	91-99

Selectivity in 0.01M $CaCl_2$: Zn > Ni > Cd complex ion formation, adsorption by cadmium was depressed most. The Zn adsorption was enhanced by the presence of chloride with the pH_{50} value the lowest for all cases and lower than with $Ca(ClO_4)_2$ as the background electrolyte. This is consistent with studies by Bolland (1970) and Forbes (1973), where zinc adsorption was greater from chloride solutions than from perchlorate and nitrate solutions.

The soft acid, cadmium, is strongly attracted to the relatively soft base, chloride, competing with the mineral surface for cadmium; and as a result more of the cadmium remains in solution. The relatively hard acid, zinc, is increasingly sorbed from chloride solution, presumably as chloro-zinc complexes or from favorable alteration of the negatively charged mineral surface, when chloride is present in solution.

The adsorption increased with increasing pH as before, but the range was much wider. In particular, at pH 5.5 only 30% of Cd was adsorbed (Table 17), compared with 83% where complex ion formation was minimized using $Ca(ClO_4)_2$. This wider range of adsorption differences over a narrow pH range is typical of soil adsorption isotherms where a wide array of complexing ligands are present in solution.

Table 17.

Adsorption of Cd, Ni and Zn by kaolinite in 0.01M $CaCl_2$.

Metal	pH	% ads	ln D
Zn	7.5	98	3.89
	6.5	92	2.44
	5.5	64	0.58
Ni	7.5	81	1.45
	6.5	59	0.36
	5.5	47	-0.12
Cd	7.5	86	1.82
	6.5	56	0.24
	5.5	30	-0.85

Sorption in $CaCl_2$ by montmorillonite.

The adsorption selectivity on montmorillonite, with chloride as the complexing species, was the same as for kaolinite with chloride: Zn > Ni > Cd (Figure 10). The effects of complex ion formation were once again the most significant factor affecting the adsorption sequence. Table 18 lists the pH_{50} values and extent of adsorption at equilibrium. Once again the $CdCl^+$ species had a low affinity for the clay surface, the Ni was little affected, and Zn adsorption was increased over that in perchlorate solutions. The pH_{50} value for Zn^{2+} was very low, 4.13. This was due to the combined effect of the chloride ion and the montmorillonite surface. Where perchlorate was used and the mineral surface varied, montmorillonite adsorbed more Zn. Likewise when the variable was the ligand, chloride resulted in increased adsorption of Zn. The combination of both a favorable surface and chloride present in solution led to optimum adsorption of Zn.

Increasing pH in the range of 4.5 to 5.5 increased adsorption reflecting the significant effect of the hydroxide ligand in the adsorption of metal ions. The range of equilibrium adsorption for Cd im Table 19 is further proof that the surface of montmorillonite was less preferred by the Cd adsorbing species compared to kaolinite (Table 17). Ranges in adsorption of Ni from the above two tables indicate little difference in adsorption

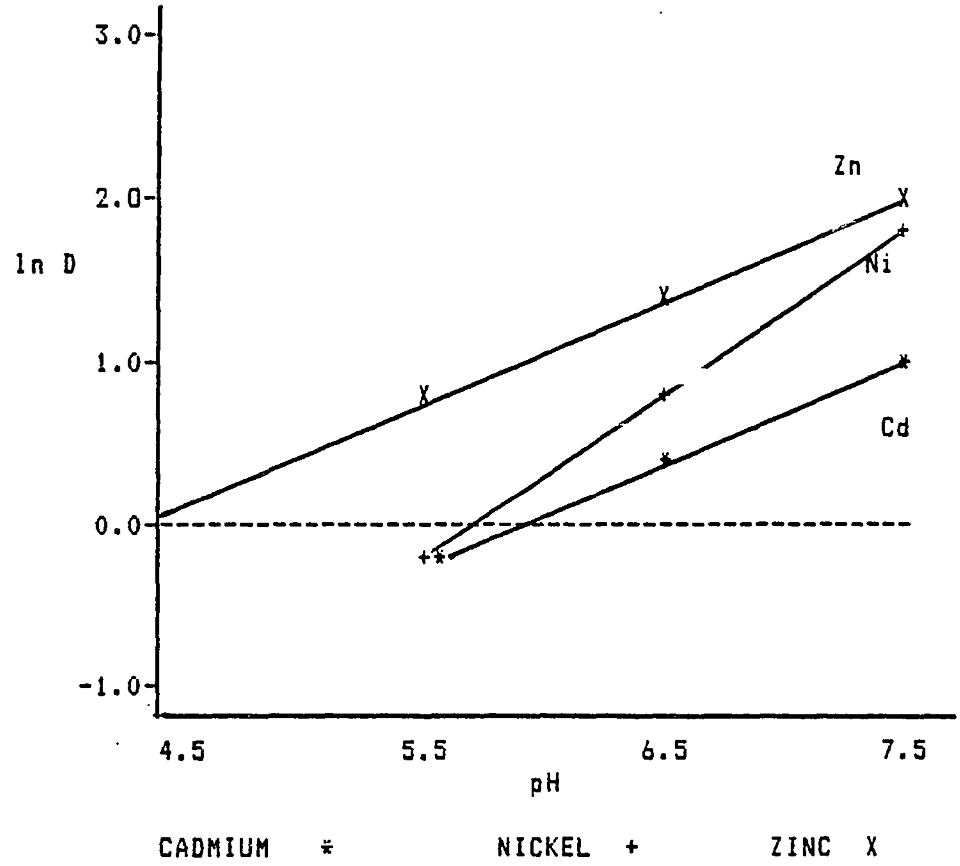

Figure 10. Adsorption of Cd, Ni and Zn on montmorillonite (in 0.01M calcium chloride).

Table 18.

Comparison of pH_{50} values and metal speciation for metal adsorption on montmorillonite.

Metal	ClO_4^-	Cl^-%	% M^{2+}
Cd	4.66	5.70	58
Zn	4.76	4.13	96-98
Ni	5.28	5.65	91-99

Selectivity in 0.01M $CaCl_2$: Zn > Ni > Cd

Table 19.

Adsorption of Cd, Ni and Zn by montmorillonite in $CaCl_2$.

Metal	pH	% ads	ln D
Zn	7.5	88	1.99
	6.5	81	1.45
	5.5	69	0.80
Ni	7.5	85	1.73
	6.5	70	0.85
	5.5	46	-0.16
Cd	7.5	71	0.90
	6.5	56	0.24
	5.5	50	0.00

preference by the two mineral surfaces.

Sorption in $CaSO_4$ by kaolinite.

In the case of metal adsorption on kaolinite with $CaSO_4$ as the background electrolyte, adsorption differed slightly from the chloride solutions. The sequence was Zn > Cd > Ni, Figure 11. Zn was the most preferred, but Cd was adsorbed to a greater extent than Ni. The difference between pH_{50} values, Table 20, was less than in the Cl^- and ClO^{4-} solutions. Data from the MICROQL speciation program (Appendix B, Tables B1,B4,B5) shows the percentages of M^{2+} and MSO_4 species for the metals under these conditions. Extent of complexation was aproximately the same for Cd, Ni and Zn. The adsorption sequence was a function of the adsorbent and its preference for the metal ions present in solution. Without a complexing ligand, as was the case for the ClO^{4-} solutions, the sequence for kaolinite was Cd > Zn > Ni. Least affected by sulfate was Zn. The pH_{50} value was 5.39 as opposed to 5.37 for adsorption on kaolinite in ClO^{4-} (Table 20). Cd and Zn both had higher values in sulfate compared with perchlorate solutions. Sulfate is a relatively hard Lewis base and associates strongly with Zn. The data suggest that sulfate aids or has little effect on Zn adsorption, but depresses the adsorption of the other metals when the adsorbent is kaolinite. Zinc sulfate complexes may sorb or the sulfate anion may act as a bridge for Zn adsorption on kaolinite.

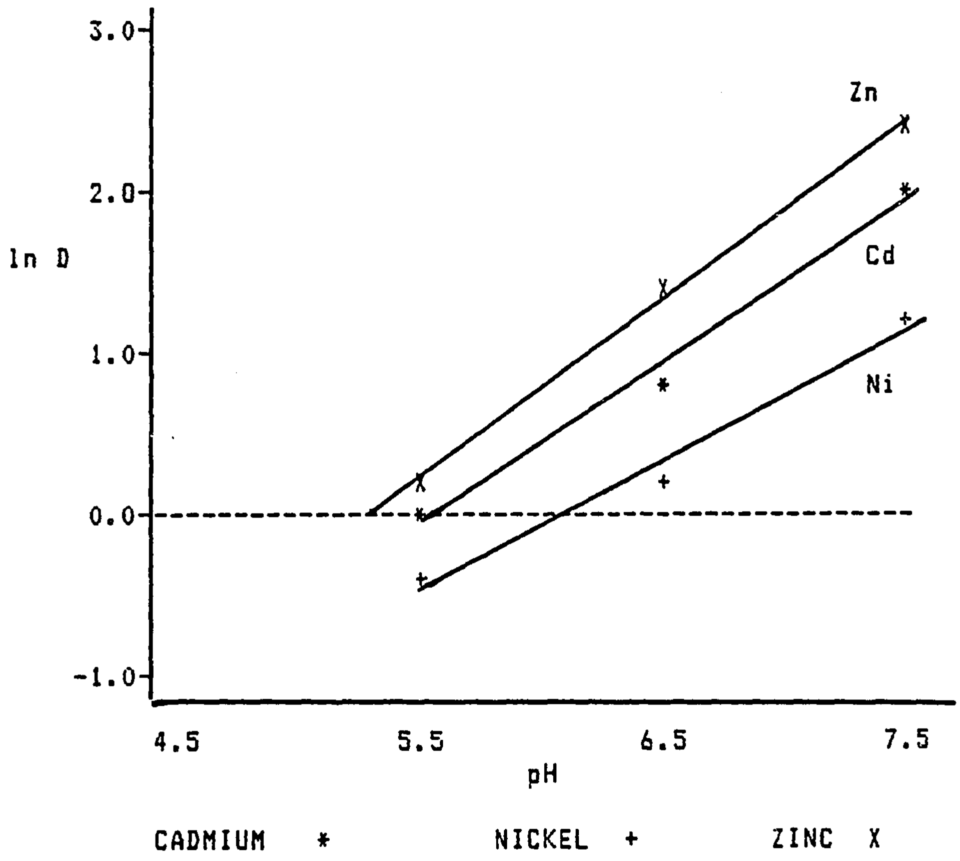

Figure 11. Adsorption of Cd, Ni and Zn on kaolinite (in 0.01M calcium sulfate).

Table 20.

Comparison of pH_{50} values and metal speciation for metal adsorption on kaolinite.

Metal	ClO_4^-	SO_4^{2-}	% M^{2+}
Cd	4.49	5.62	58
Zn	5.37	5.39	62
Ni	5.80	6.02	60-63

Selectivity in 0.01M $CaSO_4$: Zn > Cd > Ni

Table 21.

Adsorption of Cd, Ni and Zn by kaolinite in 0.01M $CaSO_4$.

Metal	pH	% ads	ln D
Cd	7.5	93	2.59
	6.5	80	1.39
	5.5	64	0.12
Zn	7.5	89	2.09
	6.5	69	0.80
	5.5	49	-0.04
Ni	7.5	77	1.20
	6.5	55	0.20
	5.5	43	-0.28

As pH increased, adsorption increased for all metals. Adsorption in sulfate by kaolinite represented the lowest range of Ni adsorption in the study (Table 21), and further explains the position of Ni in the above sequence. The relatively hard Lewis acid, Ni, complexes the hard Lewis base, SO_4^{2-}. The sulfate anion competes with the kaolinite surface for the Ni and more Ni remains in solution.

Sorption in $CaSO_4$ by montmorillonite.

With montmorillonite as the adsorbent, the order of selectivity in $CaSO_4$ solutions is Zn > Ni > Cd, Figure 12, the same as in Cl^- solutions. The only difference from the $CaSO_4$-kaolinite case was the adsorbent. This is further evidence of the preference of Cd for the kaolinite surface as was seen in the adsorption of metals on kaolinite and montmorillonite in $Ca(ClO_4)_2$. The high affinity of Cd for the kaolinite is responsible for the transposition of Ni and Cd in the sulphate solutions. Figure 12 also demonstates the selectivity of the harder Ni and Zn ions for montmorillonite as was the case with the perchlorate experiments. Table 22 shows the lowest Zn pH_{50} value in the entire study. This is reflected in the equilibrium sorption data in Table 23, where maximum extent of Zn sorption is higher than when $CaCl_2$ is the background electrolyte; and adsorption, even at pH 5.5, is relatively high (72%).

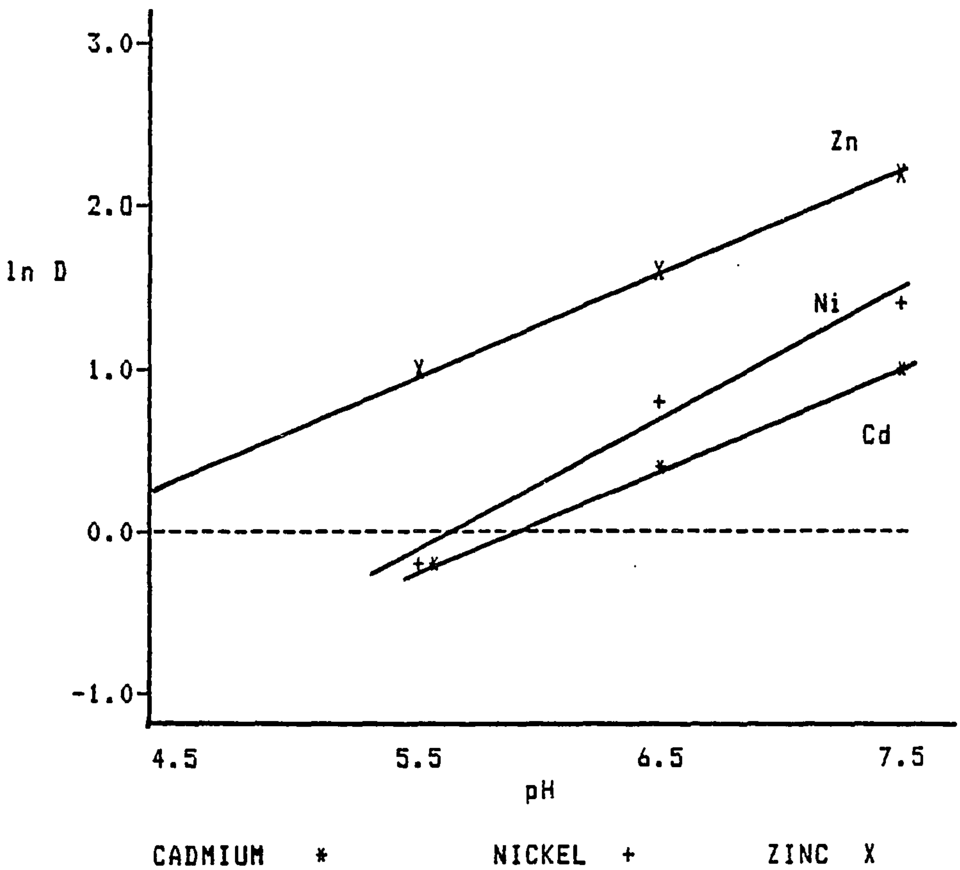

Figure 12. Adsorption of Cd, Ni and Zn on montmorillonite (in 0.01M calcium sulfate).

Table 22.

Comparison of pH_{50} values and metal speciation for metal adsorption on montmorillonite.

Metal	ClO_4^-	SO_4^{2-}	% M^{2+}
Cd	4.66	5.95	58
Zn	4.76	4.00	62
Ni	5.28	5.81	60-63

Selectivity in 0.01M $CaSO_4$: Zn > Ni > Cd

Table 23.

Adsorption of Cd, Ni and Zn by montmorillonite in 0.01M $CaSO_4$.

Metal	pH	% ads	ln D
Zn	7.5	90	2.20
	6.5	83	1.59
	5.5	72	0.94
Ni	7.5	80	1.39
	6.5	68	0.75
	5.5	42	-0.32
Cd	7.5	71	0.90
	6.5	61	0.24
	5.5	42	-0.32

A comparison of Tables 20 and 22 show the same pH_{50} trends as were seen in the perchlorate data. The pH_{50} value for Cd on kaolinite is smaller (greater affinity) than for montmorillonite, while the values for Ni and Zn are larger for kaolinite than montmorillonite. Cd apparently has a high affinity for the hydroxyl edge sites characterized by the kaolinite mineral. While montmorillonite also has these sites, it has a much lower proportion than does kaolinite. Kaolinite tends to stack in the vertical direction (c plane), while in montmorillonite particle dimensions are 10 to 20 times greater in the horizontal (ab plane) direction (Garcia-Miragaya et al,1985). Ni and Zn on the other hand prefer the relatively harder sites created by the siloxane ditrigonal cavities on the surface of the montmorillonite mineral.

Table 23 also shows increasing adsorption with increasing pH. As the concentration of OH^- increases, the solid/solution interfacial region becomes a more favorable environment for metal adsorption for both clay minerals and all complexing ligands studied.

Proposed Adsorption Mechanisms

A comparison of Figures 7-12 shows a marked difference in the slopes, between those in a relatively non-complexing solution environment ($Ca(ClO_4)_2$) as opposed to those where extensive complex ion formation occurred ($CaCl_2$, $CaSO_4$). The slope is a measure of the steepness of the adsorption edge and that steepness

Table 24.

Kurbatov Plot Slopes--A Measure of the 'Adsorption Edge'.

Metal	Ligand	Adsorbent	Slope	% M^{2+}
Cd	ClO_4^-	kaolinite	1.4	99
Ni	"	"	1.3	99
Zn	"	"	1.7	99
Cd	"	montmoril.	1.4	99
Ni	"	"	0.9	99
Zn	"	"	1.4	99
Cd	Cl^-	kaolinite	1.3	61
Ni	"	"	0.9	98
Zn	"	"	0.8	99
Cd	"	montmoril.	0.7	61
Ni	"	"	1.0	98
Zn	"	"	0.7	99
Cd	SO_4^{2-}	kaolinite	0.9	58
Ni	"	"	0.8	63
Zn	"	"	1.0	62
Cd	"	montmoril.	0.6	58
N	"	"	0.7	63
n	"	"	0.6	62

is a reflection of the amount of H^+ ions released upon metal adsorption (Sposito,1984). The slopes were steepest in the cases where M^{2+} species were the predominant adsorbing species, and averaged about 1.4 compared to 0.7 and 0.9 for the sulfate and chloride suspensions, Table 24. The slope steepened with decreasing complexation in solution. One hypothesis is that the slopes are steeper because more H^+ ions are released with M^{2+} as the adsorbing species than when MOH^+ or ML is the adsorbing species. This is consistent with the models proposed by Kalbasi (1977) and Benjamin and Leckie (1980).

The proposed mechanisms of adsorption are illustrated in Figure 13. In cases a and b, the cations adsorb from solutions in which complex ion formation by chloride and sulphate ions is insignificant. If mechanism a were predominant, the change in slope would be less when complexing ions were added to solution and the slopes would be much closer to 1.0. If case b alone were predominant, the slopes would be higher than 1.4. Mechanism a therefore cannot be completely discounted.

In cases c and d, two mechanisms are proposed when species such as sulphate and chloride are present. In case c, the metal and ligand either complex in solution and are adsorbed or the adsorption occurs sequentially with the same net result, the displacement of one H^+ ion. In this case the metal-ligand complex behaves as a metal-like complex. This would result in the overall

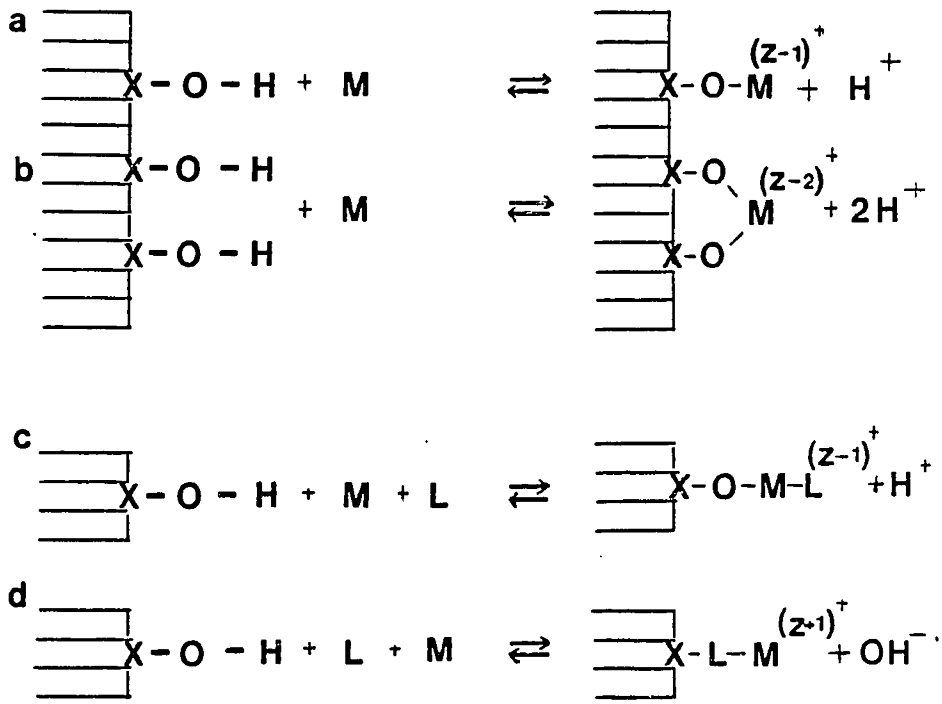

Figure 13. Diagram of adsorption mechanisms for an aqueous metal-surface and metal-ligand-surface system.

decrease in pH of the solution initially as was observed for all cases or experimental additions. In case d, the ligand (Cl^- or SO_4^{2-}) exchanges for an OH^- on the mineral surface and then acts as a bridge for the metal ion with the release of an OH^- to solution. This would result in an immediate increase in solution pH, which never occurred. In case d the metal-ligand complex would behave as an anion. Thus, mechanisms b and c appear to be the predominant mechanisms responsible for Cd, Ni and Zn adsorption by kaolinite and montmorillonite in the suspensions studied.

CHAPTER 6

RESULTS AND DISCUSSION--II. KINETICS OF CD, NI AND ZN SORPTION.

Sorption on Montmorillonite and Kaolinite in $Ca(ClO_4)_2$.

The adsorption of Cd, Ni and Zn on kaolinite and montmorillonite surfaces was found to best fit a second order rate equation of the form $1/[M] - 1/[M]_o = kt$, where [M] is the molar concentration of metal in solution at a given time during the reaction, $[M]_o$ is the initial molar concentration in solution, t is time and k is the reaction rate constant in units of $dm^3mol^{-1}min^{-1}$. Strength of adsorption or affinity of the metal ion for the adsorbent is reflected in the magnitude of the rate of the reaction.

Table 25 lists the pk (-log rate constant) values for the adsorption of Cd, Ni and Zn on kaolinite and montmorillonite at pH 5.5, 6.5, and 7.5 and the correlation coefficients for the respective second order equations. The equations have high correlation coefficients for the pH 6.5 and 7.5 cases, but were considerably lower for pH 5.5. This was true for all cases studied. Adsorption was depressed at the lower pH and the characteristic inverted 'L' shaped curve was flattened out in many cases. Kinetic adsorption curves are found in Appendix C for all cases. The curves for pH 5.5 were fitted for first order reaction

Table 25.

Kinetic Adsorption Data for Cd, Ni and Zn in $Ca(ClO_4)_2$.

METAL	ADSORBENT	pH	pK	R SQ
Cd	kaolinite	7.5	3.50	.9893
		6.5	4.54	.8802
		5.5	5.41	.5715
Zn	kaolinite	7.5	4.08	.9353
		6.5	5.53	.8230
		5.5	6.34	.8242
Ni	kaolinite	7.5	4.53	.9607
		6.5	5.19	.9178
		5.5	5.84	.6582
Cd	montmorillonite	7.5	3.53	.9839
		6.5	4.51	.9522
		5.5	5.74	.7500
Zn	montmorillonite	7.5	3.82	.9837
		6.5	4.60	.8640
		5.5	5.07	.4711
Ni	montmorillonite	7.5	4.49	.9815
		6.5	**	
		5.5	5.20	.8231

** no value--produced negative number.

equations with similar results (i.e., poorly correlated). For this reason the analysis of results was limited to the pH 6.5 and 7.5 cases.

Data from Table 26 shows rate of adsorption in the order Cd > Zn > Ni, or the same observed for adsorption selectivity in the equilibrium study. The fastest reaction rate was for the adsorption of Cd on kaolinite, although the difference between that and Cd adsorption on montmorilonite was not significant. The sequence was the same for montmorillonite. The kinetic rate constants follow the same order as the pH_{50} values in the equilibrium study. Rates were faster for Zn and Ni adsorption on montmorillonite compared with kaolinite, while the opposite was true for Cd adsorption. Table 26 compares the equilibrium and kinetic data for the adsorption of Cd, Ni and Zn on kaolinite and montmorillonite. Both approaches show kaolinite to have a high affinity for Cd. At pH 7.5 the correlation between pk and pH_{50} values was very high.

The adsorption curves over time (Appendix C) show a two-step process. Adsorption is extremely fast in the first few minutes with the majority of the adsorption taking place in this time interval. A limitation of the study was that filtration took about 15 minutes and presumably some adsorption continued to occur during the filtration process. This was most critical at the initial time periods and became less so as the experiment

Table 26.

Comparison of rate constants (pk) versus pH_{50} values for metal adsorption in 0.01M $Ca(ClO_4)_2$ at pH 7.5.

Metal	Adsorbent	pk	pH_{50}
Cd	kaolinite	3.50	4.49
Zn	kaolinite	4.08	5.37
Ni	kaolinite	4.53	5.80
Cd	montmorillonite	3.53	4.66
Zn	montmorillonite	3.82	4.76
Ni	montmorillonite	4.49	5.28

Correlation coefficient, pk vs. pH_{50} = 0.9924 (kaol.)
0.9905 (mont.)

k in units of $dm^3mol^{-1}min^{-1}$

proceeded. Nonetheless, an immediate adsorption occurred with pH of solution dropping immediately, requiring additions of 0.01M NaOH to stabilize pH at one of the 3 levels. As the reaction proceeded, continued additions of NaOH were necessary but the amount required became progressively less and reflected the gradual flattening out of the adsorption curves. The initial step was postulated to be a rapid exchange-type reaction with the adsorbent surface. These types of reactions have been shown to be first order reactions (Salim,1976; Sparks,1980). If more accurate data was possible for the initial time period, it is possible this would fit a first order rate equation. In the case where the background electrolyte was $Ca(ClO_4)_2$, this involved adsorption of the divalent metal and release of 1 or 2 H^+ ions to solution as depicted below.

$$]X\text{-}O\text{-}H + M^{2+} \quad \text{--->} \quad]X\text{-}O\text{-}M^{+} + H^{+}$$

and/or

$$\begin{array}{l}]X\text{-}O\text{-}H \\ | \\ ]X\text{-}O\text{-}H \end{array} + M^{2+} \quad \text{--->} \quad \begin{array}{l}]X\text{-}O\text{-} \\ | \\ ]X\text{-}O\text{-} \end{array} M + 2\,H^{+}$$

The much slower rate of adsorption approaching equilibrium accounts for making the overall reaction rate second order and this portion of the curves represent a slower diffusion into the crystal matrix.

Film diffusion was the initial rate limiting step for all reactions (Bunzyl,1976 and Salim and Cooksey,1980). To negate this effect all reactions were carried out in stirred suspensions at equal speed, and reaction rates reflected the varying affinities of the metals for the adsorbents.

<u>Sorption on Montmorillonite and Kaolinite in $CaCl_2$.</u> The adsorption of Cd, Ni and Zn on kaolinite and montmorillonite with chloride present, was found to best fit a second order rate equation as described above. The correlation coefficients for the reaction at pH 5.5 were also low. Table 27 lists the pk values for adsorption in $CaCl_2$. For kaolinite, the sequence of rate of adsorption was Zn > Ni > Cd as was the order of selectivity in the equilibrium study. Rates were lower in all cases compared to the above where $Ca(ClO_4)_2$ minimized complex ion formation in aqueous solution. The conclusion is that the adsorption of the chloro complex ions is slower. This may be due to prior complex formation in solution or on the surface of the clay.

$$\begin{array}{l}]X\text{-}O\text{-}H \\ \vert \\ ]X\text{-}O\text{-}H \end{array} + M^{2+} + Cl^{-} \longrightarrow \begin{array}{l}]X\text{-}O\text{-} \\ \vert \\ ]X\text{-}O\text{-} \end{array} MCl^{-} + 2\ H^{+}$$

or

$$\begin{array}{l}]X\text{-}O\text{-}H \\ \vert \\ ]X\text{-}O\text{-}H \end{array} + MCl^{+} \longrightarrow \begin{array}{l}]X\text{-}O\text{-} \\ \vert \\ ]X\text{-}O\text{-} \end{array} MCl^{-} + 2\ H^{+}$$

Table 27.

Kinetic Adsorption Data for Cd, Ni and Zn in $CaCl_2$.

METAL	ADSORBENT	pH	pK	R SQ
Zn	kaolinite	7.5	4.43	.8119
		6.5	5.06	.8786
		5.5	6.49	.5413
Ni	kaolinite	7.5	4.75	.9554
		6.5	5.25	.7930
		5.5	5.39	.6937
Cd	kaolinite	7.5	5.03	.5805
		6.5	5.73	.9878
		5.5	**	
Zn	montmorillonite	7.5	4.94	.8274
		6.5	5.35	.7868
		5.5	5.70	.5625
Ni	montmorillonite	7.5	4.72	.9893
		6.5	5.13	.9207
		5.5	5.66	.8231
Cd	montmorillonite	7.5	5.01	.8023
		6.5	5.73	.9681
		5.5	6.05	.6506

** no value--produced negative number

When montmorillonite was the adsorbent, the sequence was Ni > Zn > Cd rather than Zn > Ni > Cd, the sequence observed in the equilibrium study. Equilibrium studies showed high adsorption for Zn in $CaCl_2$ compared with the other metals, and much of this occurred immediately. This information is hidden in the adsorption experiments.

In general the adsorption vs. time curves were similar to those previously described with the exception of Ni. When montmorillonite was the adsorbent, the Ni curves are almost linear with time. This indicates that the number of available adsorption sites remained constant (Mattigod et al,1979), and that an adsorption maxima was not reached.

Sorption on Montmorillonite and Kaolinite in $CaSO_4$.

The adsorption of Cd, Ni and Zn on kaolinite and montmorillonite with sulfate present, was found to fit a second order rate equation better than a first order equation; but they had the lowest correlation of the background electrolytes studied. In no case was the correlation coefficient higher than 0.9. Table 28 lists the pk values and correlation coefficients for adsorption in $CaSO_4$. The rate constants were the lowest for all cases studied. The adsorption rate sequence for kaolinite was Cd > Ni > Zn. The equilibrium adsorption sequence for this system was Zn > Cd > Ni. The marked preference of Cd for kaolinite as mentioned in the equilibrium study may be responsible for this sequence,

Table 28.

Kinetic Adsorption Data for Cd, Ni and Zn in $CaSO_4$.

METAL	ADSORBENT	pH	pK	R SQ
Zn	kaolinite	7.5	5.21	.7073
		6.5	5.66	.7198
		5.5	6.51	.5523
Cd	kaolinite	7.5	4.77	.8239
		6.5	5.47	.7110
		5.5	6.23	.6480
Ni	kaolinite	7.5	5.10	.6794
		6.5	5.64	.7612
		5.5	6.25	.6267
Zn	montmorillonite	7.5	4.80	.8993
		6.5	5.35	.5966
		5.5	5.61	.6493
Ni	montmorillonite	7.5	4.95	.8468
		6.5	5.19	.8951
		5.5	5.96	.5619
Cd	montmorillonite	7.5	5.38	.7980
		6.5	5.62	.8991
		5.5	6.36	.5273

however the low correlation values preclude making this statement with any reliability in the kinetic study.

For montmorillonite, the adsorption rate sequence was the same as for the equilibrium study or Zn > Ni > Cd. Although the correlation coefficients are higher for the montmorillonite than the kaolinite, they were still below 0.9 in all cases. The greatest difference in adsorption sequences for both studies occurred in the same system; that is, the adsorption on kaolinite in $CaSO_4$. That Cd has a marked preference for the kaolinite surface compared with montmorillonite is clear from both the kinetic and equilibrium studies.

CHAPTER 7

SUMMARY AND CONCLUSIONS

Kaolinite may be classified as a relatively soft Lewis base due to the hydroxyl surface functional groups which characterize this clay mineral. Adsorption of the relatively soft Cd was most preferred over the harder Ni and Zn ions, and adsorption of Cd was always greater on kaolinite than on montmorillonite. When complex ion formation in aqueous solution was minimized (i.e. in $Ca(ClO_4)_2$), adsorption decreased in the order of decreasing softness, Cd > Zn > Ni, for both clay minerals.

Montmorillonite behaved as a slightly harder Lewis base than kaolinite, sorbing the harder Ni and Zn ions to a greater extent than Cd. The charge exhibited by the siloxane ditrigonal surface due to isomorphic substitution in the octahedral layer of the montmorillonite is non-localized and leads to the formation of relatively hard outer sphere complexes with metal ions in solution. While montmorillonite also possesses surface hydroxyl groups, it has a much lower proportion than kaolinite.

The presence of complex ions in soil solutions complicates the application of the Hard-Soft Lewis Acid-Base Theory to the adsorption of metal ions in solution. Suspensions which were free of complexing ligands reflected predictable results. In the presence of chloride and sulfate ligands, adsorption sequences changed and reflected results from typical soil solution studies. In some cases the adsorption sequences can be explained from chemical speciation data. When Cl^- is present in solution, Cd adsorption decreased significantly due to competition from the relatively soft Lewis base Cl^-, with the mineral surface, for the soft acid Cd. The chloride ion effectively competed with the surface functional groups of the clay mineral and more of the Cd remained in solution as chloro-cadmium complexes. For the harder acid Zn, this was not the case and Zn adsorption was actually increased in $CaCl_2$. For Ni, the hardest Lewis acid, adsorption was low in all cases reflecting the relative softness of the clay minerals studied. When a hard Lewis base, SO^{4-}, was present in solution, adsorption decreased further as the sulfate anion competed with the mineral surface leaving more of the Ni in solution as a complex ion.

Adsorption over time and calculated adsorption rate constants were consistent with equilibrium selectivity data. Adsorption rates decreased in the order Cd > Zn > Ni in $Ca(ClO_4)_2$ for both clay minerals. The adsorption curves over time reflect a two-step adsorption process involving a rapid exchange-type reaction followed by a much slower adsorption involving diffusion into the crystal matrix and/or alteration of the surface through formation of a new solid phase involving adsorbed ions.

Adsorption of divalent metal ions involves the release of 1 or 2 H^+ ions to solution while the adsorption of metal-ligand complexes of the form, ML^+, results in the release of only 1 H^+ ion to solution.

Both kinetic and equilibrium approaches to the study of adsorption reactions in aqueous systems provide complementary information on system behavior and support the use of HSAB as a limited predictive tool for metal adsorption in environmental studies.

APPENDIX A: SORPTION DATA

Table A1.

Sorption data for Cd on kaolinite in $Ca(ClO_4)_2$.

System	Ligand	pH	time	conc.(ppb)	%ads	mmol/g
Cd/kaol	perch	5.5	1	32	72	14.3
			2	26	77	15.4
			3	23	80	16.0
			4	22	81	16.1
			5	22	80	16.0
			6	19	83	16.6
			7	21	82	16.3
			8	19	83	16.6
		6.5	1	14	88	17.6
			2	13	89	17.7
			3	12	89	17.9
			4	8	93	18.6
			5	9	92	18.4
			6	8	93	18.6
			7	7	94	18.8
			8	6	95	19.0
		7.5	1	17	85	17.0
			2	13	89	17.7
			3	12	90	17.9
			4	10	91	18.1
			5	6	95	18.9
			6	3	97	19.4
			7	2	98	19.6
			8	1	99	19.8

Table A2.

Sorption data for Cd on kaolinite in $CaCl_2$.

System	Ligand	pH	time	conc.(ppb)	%ads	mmol/g
Cd/kaol	chloride	5.5	1	78	31	6.1
			2	77	31	6.3
			3	77	31	6.3
			4	79	30	5.9
			5	79	30	5.9
			6	79	30	5.9
			7	79	30	5.9
			8	79	30	5.9
		6.5	1	67	40	8.1
			2	67	40	8.1
			3	66	41	8.3
			4	67	40	8.1
			5	67	40	8.1
			6	61	46	9.1
			7	56	50	10.0
			8	49	56	11.3
		7.5	1	66	41	8.3
			2	33	71	14.1
			3	31	72	14.5
			4	21	81	16.3
			5	20	82	16.4
			6	16	86	17.2
			7	19	83	16.6
			8	16	86	17.2

Table A3.

Sorption data for Cd on kaolinite in $CaSO_4$.

System	Ligand	pH	time	conc.(ppb)	%ads	mmol/g
Cd/kaol	sulphate	5.5	1	67	40	8.1
			2	64	43	8.6
			3	58	48	9.6
			4	62	45	9.0
			5	66	41	8.3
			6	64	43	8.6
			7	61	46	9.1
			8	57	49	9.9
		6.5	1	69	39	7.7
			2	56	50	10.0
			3	57	49	9.9
			4	41	64	12.7
			5	41	64	12.7
			6	40	64	12.9
			7	40	64	12.9
			8	35	69	13.8
		7.5	1	54	52	10.4
			2	41	64	12.7
			3	25	78	15.6
			4	21	81	16.3
			5	22	80	16.1
			6	21	81	16.3
			7	16	86	17.2
			8	12	89	17.9

Table A4.

Sorption data for Cd on montmorillonite in $Ca(ClO_4)_2$.

System	Ligand	pH	time	conc.(ppb)	%ads	mmol/g
Cd/mont	perch	5.5	1	25	78	16
			2	23	80	16
			3	23	80	16
			4	23	80	16
			5	22	80	16
			6	21	81	16
			7	21	81	16
			8	21	81	16
		6.5	1	27	76	15
			2	20	82	16
			3	17	85	17
			4	19	83	17
			5	14	88	18
			6	13	88	18
			7	10	91	18
			8	7	94	19
		7.5	1	23	80	16
			2	9	92	18
			3	8	93	19
			4	7	94	19
			5	4	96	19
			6	6	95	19
			7	3	97	19
			8	1	99	20

Table A5.

Sorption data for Cd on montmorillonite in $CaCl_2$.

System	Ligand	pH	time	conc.(ppb)	%ads	mmol/g
Cd/mont	chloride	5.5	1	70	38	8
			2	68	40	8
			3	67	40	8
			4	60	47	9
			5	60	47	9
			6	57	49	10
			7	57	49	10
			8	56	50	10
		6.5	1	66	41	8
			2	66	41	8
			3	64	43	9
			4	64	43	9
			5	63	44	9
			6	61	46	9
			7	52	54	11
			8	49	56	11
		7.5	1	79	30	6
			2	72	36	7
			3	60	47	9
			4	48	57	11
			5	46	59	12
			6	39	65	13
			7	33	71	14
			8	33	71	14

Table A6.

Sorption data for Cd on montmorillonite in $CaSO_4$.

System	Ligand	pH	time	conc.(ppb)	%ads	mmol/g
Cd/mont	sulphate	5.5	1	78	31	6
			2	69	39	8
			3	68	40	8
			4	72	36	7
			5	68	40	8
			6	65	42	8
			7	65	42	8
			8	65	42	8
		6.5	1	72	36	7
			2	64	43	9
			3	64	43	9
			4	58	48	10
			5	58	48	10
			6	54	52	10
			7	50	56	11
			8	44	61	12
		7.5	1	72	36	7
			2	49	56	11
			3	42	63	13
			4	42	63	13
			5	43	62	12
			6	42	63	13
			7	34	70	14
			8	33	71	14

Table A7.

Sorption data for Ni on kaolinite in $Ca(ClO_4)_2$.

System	Ligand	pH	time	conc.(ppb)	%ads	mmol/g
Ni/kaol.	perchl	5.5	1	62	22	5.8
			2	60	24	6.5
			3	55	30	8.2
			4	54	32	8.5
			5	46	42	11.2
			6	45	43	11.6
			7	46	42	11.2
		6.5	8	45	43	11.6
			1	57	28	7.6
			2	54	32	8.5
			3	51	35	9.5
			4	51	35	9.5
			5	43	46	12.3
			6	35	56	15.0
			7	32	59	16.0
			8	26	67	17.9
		7.5	1	62	22	5.8
			2	48	39	10.6
			3	42	47	12.6
			4	30	62	16.7
			5	24	70	18.7
			6	16	80	21.5
			7	14	82	22.1
			8	9	89	23.9

Table A8.

Sorption data for Ni on kaolinite in $CaCl_2$.

System	Ligand	pH	Time	conc.(ppb)	%ads.	mmol/g
Ni/kaol	chloride	5.5	1	57	23	6.0
			2	55	26	6.6
			3	48	36	9.0
			4	49	34	8.7
			5	43	42	10.7
			6	41	45	11.4
			7	39	48	12.1
			8	40	47	11.9
		6.5	1	44	41	10.4
			2	40	46	11.8
			3	38	49	12.4
			4	39	48	12.1
			5	35	53	13.5
			6	32	57	14.5
			7	30	60	15.2
			8	30	59	15.1
		7.5	1	55	26	6.7
			2	51	32	8.0
			3	54	28	7.0
			4	46	38	9.7
			5	46	38	9.7
			6	25	66	16.9
			7	19	74	18.9
			8	14	81	20.6

Table A9.

Sorption data for Ni on kaolinite in $CaSO_4$.

System	Ligand	pH	Time	conc.(ppb)	%ads.	mmol/g
Ni/kaol	sulphate	5.5	1	46	36	9.2
			2	43	40	10.2
			3	44	39	9.9
			4	43	40	10.2
			5	46	36	9.2
			6	41	43	10.9
			7	42	42	10.6
			8	41	43	10.9
		6.5	1	45	38	9.5
			2	40	44	11.3
			3	42	42	10.6
			4	37	49	12.3
			5	35	51	13.0
			6	33	54	13.7
			7	33	54	13.7
			8	32	55	14.0
		7.5	1	35	51	13.0
			2	33	54	13.7
			3	26	64	16.2
			4	24	67	16.9
			5	22	69	17.6
			6	17	76	19.4
			7	18	75	19.0
			8	17	77	19.5

Table A10.

Sorption data for Ni on montmorillonite in $Ca(ClO_4)_2$.

System	Ligand	pH	Time	conc.(ppb)	%ads.	mmol/g
Ni/mont.	perchl.	5.5	1	50	28	6.5
			2	45	35	8.2
			3	42	39	9.2
			4	40	42	9.9
			5	36	48	11.2
			6	32	54	12.6
			7	31	55	12.9
			8	31	55	12.9
		6.5	1	46	33	7.8
			2	41	41	9.5
			3	40	42	9.9
			4	38	45	10.6
			5	33	52	12.3
			6	30	57	13.3
			7	22	68	16.0
			8	17	75	17.7
		7.5	1	45	35	8.2
			2	37	46	10.9
			3	36	48	11.2
			4	34	51	11.9
			5	27	61	14.3
			6	20	71	16.7
			7	14	80	18.7
			8	8	88	20.8

Table A11.

Sorption data for Ni on montmorillonite in $CaCl_2$.

System	Ligand	pH	Time	conc.(ppb)	%ads.	mmol/g
Ni/mont	chloride	5.5	1	62	22	5.8
			2	60	24	6.5
			3	56	29	7.8
			4	55	30	8.2
			5	51	35	9.5
			6	48	39	10.6
			7	43	46	12.3
			8	43	46	12.3
		6.5	1	54	32	8.5
			2	46	42	11.2
			3	43	46	12.3
			4	41	48	12.9
			5	39	51	13.6
			6	37	53	14.3
			7	25	68	18.4
			8	24	70	18.7
		7.5	1	37	53	14.3
			2	39	51	13.6
			3	37	53	14.3
			4	34	57	15.3
			5	36	54	14.7
			6	34	57	15.3
			7	16	80	21.5
			8	12	85	23.0

Table A12.

Sorption data for Ni on montmorillonite in $CaSO_4$.

System	Ligand	pH	Time	conc.(ppb)	%ads.	mmol/g
Ni/mont	sulphate	5.5	1	55	25	6.1
			2	56	23	5.8
			3	46	37	9.2
			4	45	38	9.5
			5	46	37	9.2
			6	42	42	10.6
			7	43	41	10.2
			8	42	42	10.6
		6.5	1	40	45	11.2
			2	37	49	12.3
			3	31	58	14.3
			4	37	49	12.3
			5	35	52	12.9
			6	30	59	14.7
			7	23	68	17.0
			8	23	68	17.0
		7.5	1	38	48	11.9
			2	29	60	15.0
			3	21	71	17.7
			4	21	71	17.7
			5	22	70	17.4
			6	22	70	17.4
			7	23	68	17.0
			8	14	80	19.9

Table A13.

Sorption data for Zn on kaolinite in $Ca(ClO_4)_2$.

System	Ligand	pH	Time	conc.(ppb)	%ads.	mmol/g
Zn/kaol.	perchl	5.5	1	336	46	86.3
			2	338	45	85.7
			3	290	53	100.3
			4	294	52	99.1
			5	287	54	101.3
			6	245	60	114.1
			7	235	62	117.2
			8	222	64	121.1
		6.5	1	220	64	121.7
			2	198	68	128.5
			3	119	81	152.6
			4	116	81	153.6
			5	111	82	155.1
			6	93	85	160.6
			7	70	89	167.6
			8	68	89	168.2
		7.5	1	124	80	151.1
			2	62	90	170.1
			3	35	94	178.3
			4	19	97	183.2
			5	6	99	187.2
			6	6	99	187.2
			7	5	99	187.5
			8	4	99	187.8

Table A14.

Sorption data for Zn on kaolinite in $CaCl_2$.

System	Ligand	pH	Time	conc.(ppb)	%ads.	mmol/g
Zn/kaol	chloride	5.5	1	373	40	74.9
			2	278	55	104.0
			3	249	60	112.9
			4	230	63	118.7
			5	234	62	117.5
			6	231	63	118.4
			7	224	64	120.5
			8	222	64	121.1
		6.5	1	270	40	54.8
			2	259	42	58.1
			3	211	53	72.8
			4	201	55	75.9
			5	82	82	112.3
			6	65	86	117.5
			7	36	92	126.3
			8	36	92	126.3
		7.5	1	121	73	100.3
			2	95	79	108.3
			3	80	82	112.9
			4	41	91	124.8
			5	15	97	132.8
			6	11	98	134.0
			7	9	98	134.6
			8	8	98	134.9

Table A15.

Sorption data for Zn on kaolinite in $CaSO_4$.

System	Ligand	pH	Time	conc.(ppb)	%ads.	mmol/g
Zn/kaol	sulphate	5.5	1	325	28	37.9
			2	240	47	63.9
			3	224	50	68.8
			4	228	49	67.6
			5	230	49	67.0
			6	210	53	73.1
			7	211	53	72.8
			8	209	53	73.4
		6.5	1	307	32	43.4
			2	306	32	43.7
			3	145	68	93.0
			4	200	55	76.2
			5	101	78	106.5
			6	90	80	109.8
			7	93	79	108.9
			8	90	80	109.8
		7.5	1	135	73	108.9
			2	89	82	123.0
			3	77	84	126.6
			4	62	87	131.2
			5	47	90	135.8
			6	36	93	139.2
			7	37	92	138.9
			8	34	93	139.8

Table A16.

Sorption data for Zn on montmorillonite in $Ca(ClO_4)_2$.

System	Ligand	pH	Time	conc.(ppb)	%ads.	mmol/g
Zn/mont.	perchl	5.5	1	112	21	9.2
			2	52	63	27.5
			3	34	76	33.0
			4	31	78	34.0
			5	30	79	34.3
			6	29	80	34.6
			7	28	80	34.9
			8	29	80	34.6
		6.5	1	62	56	24.5
			2	39	73	31.5
			3	29	80	34.6
			4	25	82	35.8
			5	19	87	37.6
			6	15	89	38.8
			7	11	92	40.1
			8	10	93	40.4
		7.5	1	55	61	26.6
			2	29	80	34.6
			3	24	83	36.1
			4	24	83	36.1
			5	19	87	37.6
			6	13	91	39.5
			7	7	95	41.3
			8	2	99	42.8

Table A17.

Sorption data for Zn on montmorillonite in $CaCl_2$.

System	Ligand	pH	Time	conc.(ppb)	%ads.	mmol/g
Zn/mont	chloride	5.5	1	116	28	14.1
			2	69	57	28.4
			3	68	58	28.8
			4	62	62	30.6
			5	58	64	31.8
			6	51	69	34.0
			7	52	68	33.6
			8	51	69	34.0
		6.5	1	59	64	31.5
			2	57	65	32.1
			3	59	64	31.5
			4	41	75	37.0
			5	43	73	36.4
			6	36	78	38.5
			7	32	80	39.8
			8	31	81	40.1
		7.5	1	69	57	28.4
			2	55	66	32.7
			3	52	68	33.6
			4	44	73	36.1
			5	29	82	40.7
			6	25	85	41.9
			7	21	87	43.1
			8	19	88	43.7

Table A18.

Sorption data for Zn on montmorillonite in $CaSO_4$.

System	Ligand	pH	Time	conc.(ppb)	%ads.	mmol/g
Zn/mont	sulphate	5.5	1	67	53	22.9
			2	59	58	25.4
			3	60	58	25.1
			4	49	65	28.4
			5	41	71	30.9
			6	39	73	31.5
			7	40	72	31.2
			8	40	72	31.2
		6.5	1	55	61	26.6
			2	48	66	28.8
			3	27	81	35.2
			4	28	80	34.9
			5	25	82	35.8
			6	26	82	35.5
			7	24	83	36.1
			8	24	83	36.1
		7.5	1	57	60	26.0
			2	37	74	32.1
			3	38	73	31.8
			4	26	82	35.5
			5	25	82	35.8
			6	16	89	38.5
			7	16	89	38.5
			8	14	90	39.2

APPENDIX B: COMPUTER SPECIATION DATA

TABLE B1.

CDSO4
03-03-1986

pH= 5.5

Species	Concentration	% total metal	% total metal	%ligand
Ca2+	5.891937E-03	65.46	0	0
CaOH+	7.785169E-10	0	0	0
CaSO4	3.108167E-03	34.54	0	34.54
CdSO4	4.213604E-07	0	42.14	0
CdOH+	9.625375E-12	0	0	0
SO4	5.891415E-03	0	0	65.46
Cd2+	5.786292E-07	0	57.86	0
CdOH2	1.562877E-16	0	0	0
H+	3.162281E-06	0	0	0
OH-	3.162277E-09	0	0	0

pH= 6.5

Species	Concentration	% total metal	% total metal	%ligand
Ca2+	5.891831E-03	65.46	0	0
CaOH+	7.785169E-09	0	0	0
CaSO4	3.108167E-03	34.54	0	34.54
CdSO4	4.213253E-07	0	42.13	0
CdOH+	9.624522E-11	0	.01	0
SO4	5.891418E-03	0	0	65.46
Cd2+	5.785795E-07	0	57.86	0
CdOH2	1.562749E-14	0	0	0
H+	3.162277E-07	0	0	0
OH-	3.162281E-08	0	0	0

pH= 7.5

Species	Concentration	% total metal	% total metal	%ligand
Ca2+	5.891777E-03	65.46	0	0
CaOH+	7.785107E-08	0	0	0
CaSO4	3.108144E-03	34.53	0	34.53
CdSO4	4.2096E-07	0	42.1	0
CdOH+	9.616166E-10	0	.1	0
SO4	5.891434E-03	0	0	65.46
Cd2+	5.780764E-07	0	57.81	0
CdOH2	1.56139E-12	0	0	0
H+	3.162281E-08	0	0	0
OH	3.162277E-07	0	0	0

Table B2.

Speciation Data

CdCl
03-03-1986

pH= 5.5

Species	Concentration	% total metal	% total metal	%ligand
Ca2+	9.993382E-03	99.93	0	0
CaOH+	1.320473E-09	0	0	0
CaCl+	6.613423E-06	.07	0	.07
CdCl+	3.872504E-07	0	38.73	0
CdOH+	1.019287E-11	0	0	0
SO4	9.993002E-03	0	0	99.93
Cd2+	6.127441E-07	0	61.27	0
CdOH2	1.65503E-16	0	0	0
H+	3.162281E-06	0	0	0
OH-	3.162277E-09	0	0	0

pH= 6.5

Species	Concentration	% total metal	% total metal	%ligand
Ca2+	9.993372E-03	99.93	0	0
CaOH+	1.320473E-08	0	0	0
CaCl+	6.613399E-06	.07	0	.07
CdCl+	3.87213E-07	0	38.72	0
CdOH+	1.019188E-10	0	.01	0
SO4	9.993002E-03	0	0	99.93
Cd2+	6.126849E-07	0	61.27	0
CdOH2	1.654868E-14	0	0	0
H+	3.162277E-07	0	0	0
OH-	3.162281E-08	0	0	0

pH= 7.5

Species	Concentration	% total metal	% total metal	%ligand
Ca2+	9.993254E-03	99.93	0	0
CaOH+	1.320459E-07	0	0	0
CaCl+	6.613329E-06	.07	0	.07
CdCl+	3.868579E-07	0	38.69	0
CdOH+	1.018254E-09	0	.1	0
SO4	9.993002E-03	0	0	99.93
Cd2+	6.12123E-07	0	61.21	0
CdOH2	1.65335E-12	0	0	0
H+	3.162281E-08	0	0	0
OH-	3.162277E-07	0	0	0

Table B3.

Speciation Data

*** MICROQL ***

ZnCl
03-03-1986

pH= 5.5

Species	Concentration	% total metal	% total metal	%ligand
Ca2+	9.993382E-03	99.93	0	0
CaOH+	1.320473E-09	0	0	0
CaCl+	6.613652E-06	.07	0	.07
ZnCl+	1.749731E-08	0	1.75	0
ZnOH+	2.057116E-10	0	.02	0
Cl-	9.993367E-03	0	0	99.93
Zn2+	9.822963E-07	0	98.23001	0
ZnOH2	8.390136E-13	0	0	0
H+	3.162291E-06	0	0	0
OH-	3.162277E-09	0	0	0

pH= 6.5

Species	Concentration	% total metal	% total metal	%ligand
Ca2+	9.993372E-03	99.93	0	0
CaOH+	1.320473E-08	0	0	0
CaCl+	6.613652E-06	.07	0	.07
ZnCl+	1.746353E-08	0	1.75	0
ZnOH+	2.053147E-09	0	.21	0
Cl-	9.993367E-03	0	0	99.93
Zn2+	9.803996E-07	0	98.04	0
ZnOH2	8.373933E-11	0	.01	0
H+	3.162277E-07	0	0	0
OH-	3.162281E-08	0	0	0

pH= 7.5

Species	Concentration	% total metal	% total metal	%ligand
Ca2+	9.993254E-03	99.93	0	0
CaOH+	1.320459E-07	0	0	0
CaCl+	6.613582E-06	.07	0	.07
ZnCl+	1.700827E-08	0	1.7	0
ZnOH+	1.999623E-08	0	2	0
Cl-	9.99337E-03	0	0	99.93
Zn2+	9.548413E-07	0	95.48001	0
ZnOH2	8.155631E-09	0	.82	0
H+	3.162281E-08	0	0	0
OH-	3.162277E-07	0	0	0

Table B4.

Speciation Data

*** MICROQL ***

ZnSO4
03-03-1986

pH= 5.5

Species	Concentration	% total metal	% total metal	%ligand
Ca2+	5.891825E-03	65.46	0	0
CaOH+	7.785169E-10	0	0	0
CaSO4	3.108177E-03	34.54	0	34.54
ZnSO4	3.825925E-07	0	38.26	0
ZnOH+	1.292701E-10	0	.01	0
SO4	5.891443E-03	0	0	65.46
Zn2+	6.172778E-07	0	61.73	0
ZnOH2	5.272385E-13	0	0	0
H+	3.162281E-06	0	0	0
OH-	3.162277E-09	0	0	0

pH= 6.5

Species	Concentration	% total metal	% total metal	%ligand
Ca2+	5.891819E-03	65.46	0	0
CaOH+	7.785158E-09	0	0	0
CaSO4	3.108173E-03	34.54	0	34.54
ZnSO4	3.821285E-07	0	38.21	0
ZnOH+	1.29113E-09	0	.13	0
SO4	5.891443E-03	0	0	65.46
Zn2+	6.165282E-07	0	61.65	0
ZnOH2	5.265989E-11	0	.01	0
H+	3.162277E-07	0	0	0
OH-	3.162281E-08	0	0	0

pH= 7.5

Species	Concentration	% total metal	% total metal	%ligand
Ca2+	5.891769E-03	65.46	0	0
CaOH+	7.785086E-08	0	0	0
CaSO4	3.108158E-03	34.54	0	34.54
ZnSO4	3.758033E-07	0	37.58	0
ZnOH+	1.269753E-08	0	1.27	0
SO4	5.891471E-03	0	0	65.46
Zn2+	6.063207E-07	0	60.63	0
ZnOH2	5.178795E-09	0	.52	0
H+	3.162281E-08	0	0	0
OH-	3.162277E-07	0	0	0

Table B5.

Speciation Data

*** MICROQL ***

NiSO4
03-03-1986

pH= 5.5

Species	Concentration	% total metal	% total metal	%ligand
Ca2+	6.36851E-03	63.69	0	0
CaOH+	8.415029E-10	0	0	0
CaSO4	3.63149E-03	36.31	0	36.31
NiSO4	3.684811E-07	0	36.85	0
NiOH+	2.29818E-11	0	0	0
SO4	6.368146E-03	0	0	63.68
Ni2+	6.314912E-07	0	63.15	0
NiOH2	5.393785E-12	0	0	0
H+	3.162281E-06	0	0	0
OH-	3.162277E-09	0	0	0

pH= 6.5

Species	Concentration	% total metal	% total metal	%ligand
Ca2+	6.368509E-03	63.69	0	0
CaOH+	8.415017E-09	0	0	0
CaSO4	3.631485E-03	36.31	0	36.31
NiSO4	3.682074E-07	0	36.82	0
NiOH+	2.296476E-10	0	.02	0
SO4	6.368146E-03	0	0	63.68
Ni2+	6.31023E-07	0	63.1	0
NiOH2	5.389779E-10	0	.05	0
H+	3.162277E-07	0	0	0
OH-	3.162281E-08	0	0	0

pH= 7.5

Species	Concentration	% total metal	% total metal	%ligand
Ca2+	6.368447E-03	63.68	0	0
CaOH+	8.414939E-08	0	0	0
CaSO4	3.631473E-03	36.31	0	36.31
NiSO4	3.488722E-07	0	34.89	0
NiOH+	2.175876E-09	0	.22	0
SO4	6.368182E-03	0	0	63.68
Ni2+	5.978838E-07	0	59.79	0
NiOH2	5.106732E-08	0	5.11	0
H+	3.162281E-08	0	0	0
OH-	3.162277E-07	0	0	0

Table B6.

Speciation Data

*** MICROQL ***

NiCl
03-03-1986

pH= 5.5

Species	Concentration	% total metal	% total metal	%ligand
Ca2+	9.993382E-03	99.93	0	0
CaOH+	1.320473E-09	0	0	0
CaCl-	6.613669E-06	.07	0	.07
NiCl-	1.111362E-08	0	1.11	0
NiOH+	3.598691E-11	0	0	0
Cl-	9.993372E-03	0	0	99.93
Ni2+	9.889413E-07	0	98.88	0
NiOH2	8.446038E-12	0	0	0
H+	3.162281E-06	0	0	0
OH-	3.162277E-09	0	0	0

pH= 6.5

Species	Concentration	% total metal	% total metal	%ligand
Ca2+	9.993372E-03	99.93	0	0
CaOH+	1.320473E-08	0	0	0
CaCl-	6.613652E-06	.07	0	.07
NiCl-	1.110074E-08	0	1.11	0
NiOH+	3.594511E-10	0	.04	0
Cl-	9.993372E-03	0	0	99.93
Ni2+	9.876954E-07	0	98.76999	0
NiOH2	8.436238E-10	0	.08	0
H+	3.162277E-07	0	0	0
OH	3.162281E-08	0	0	0

pH= 7.5

Species	Concentration	% total metal	% total metal	%ligand
Ca2+	9.993254E-03	99.93	0	0
CaOH+	1.320459E-07	0	0	0
CaCl-	6.613592E-06	.07	0	.07
NiCl-	1.021464E-08	0	1.02	0
NiOH+	3.307579E-09	0	.33	0
Cl	9.993382E-03	0	0	99.93
Ni2+	9.088502E-07	0	90.89	0
NiOH2	7.762805E-09	0	7.76	0
H+	3.162281E-08	0	0	0
OH-	3.162277E-07	0	0	0

APPENDIX C: KINETICS OF METAL ADSORPTION

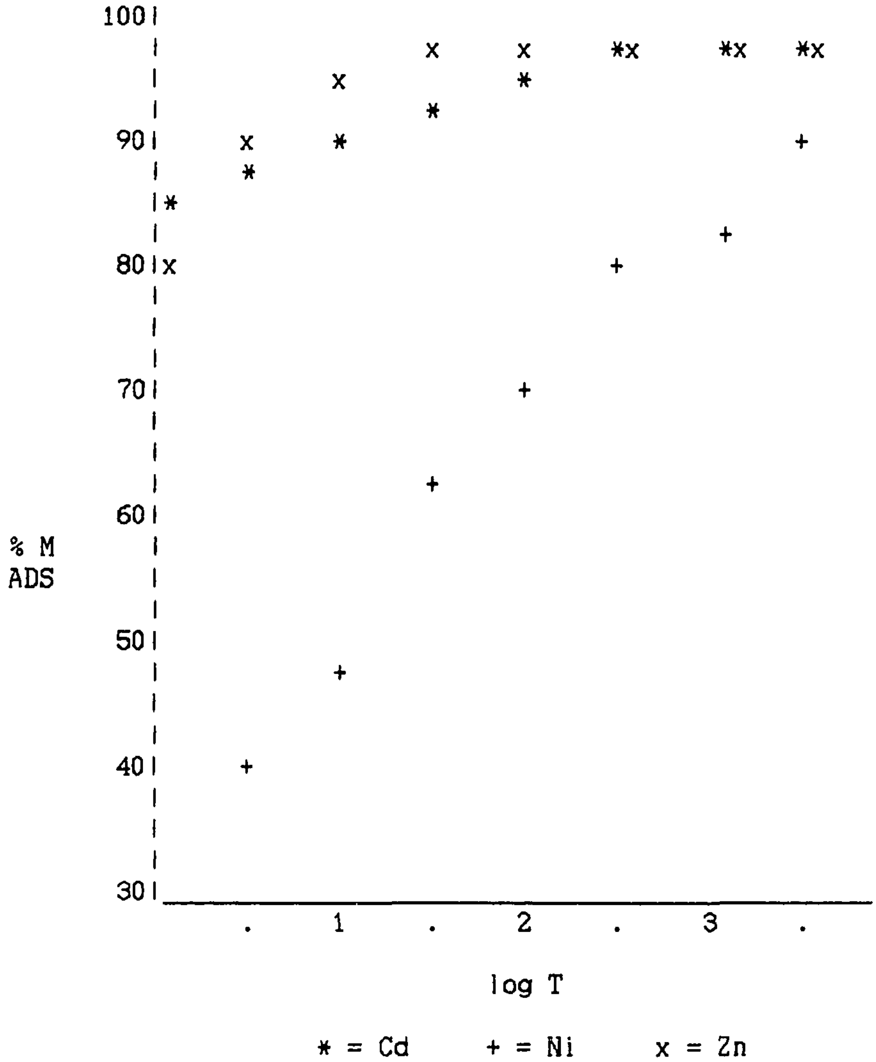

Figure C1.

Kinetics of Cd, Ni and Zn adsorption in perchlorate (pH 7.5) on kaolinite.

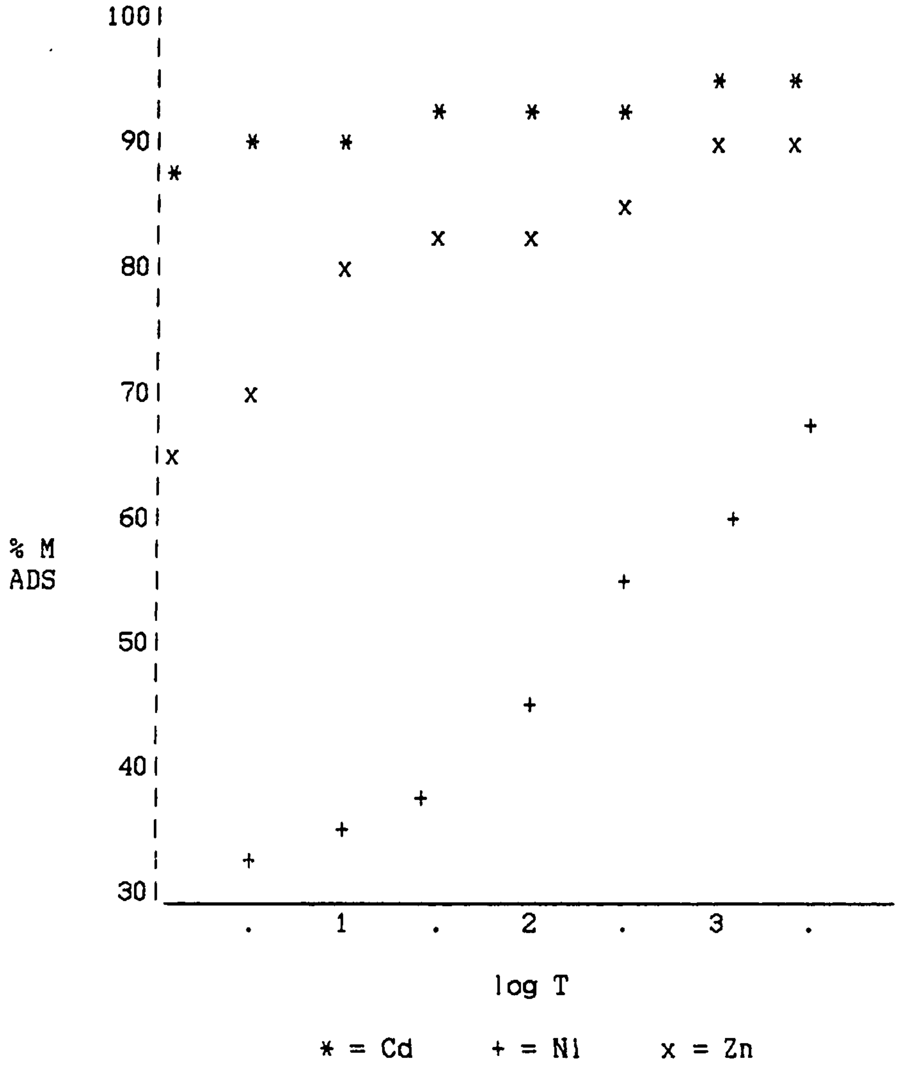

Figure C2.

Kinetics of Cd, Ni and Zn adsorption in perchlorate (pH 6.5) on kaolinite.

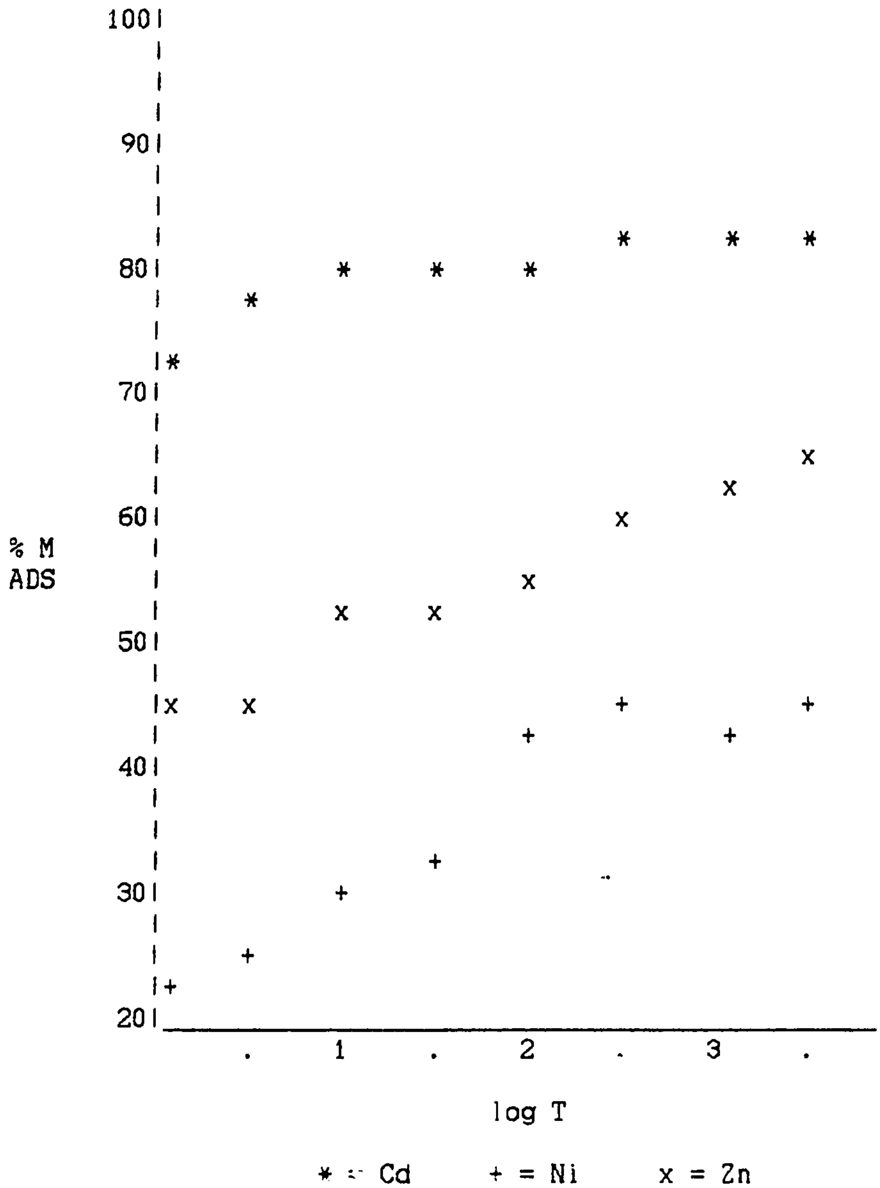

Figure C3.

Kinetics of Cd, Ni and Zn adsorption in perchlorate (pH 5.5) on kaolinite.

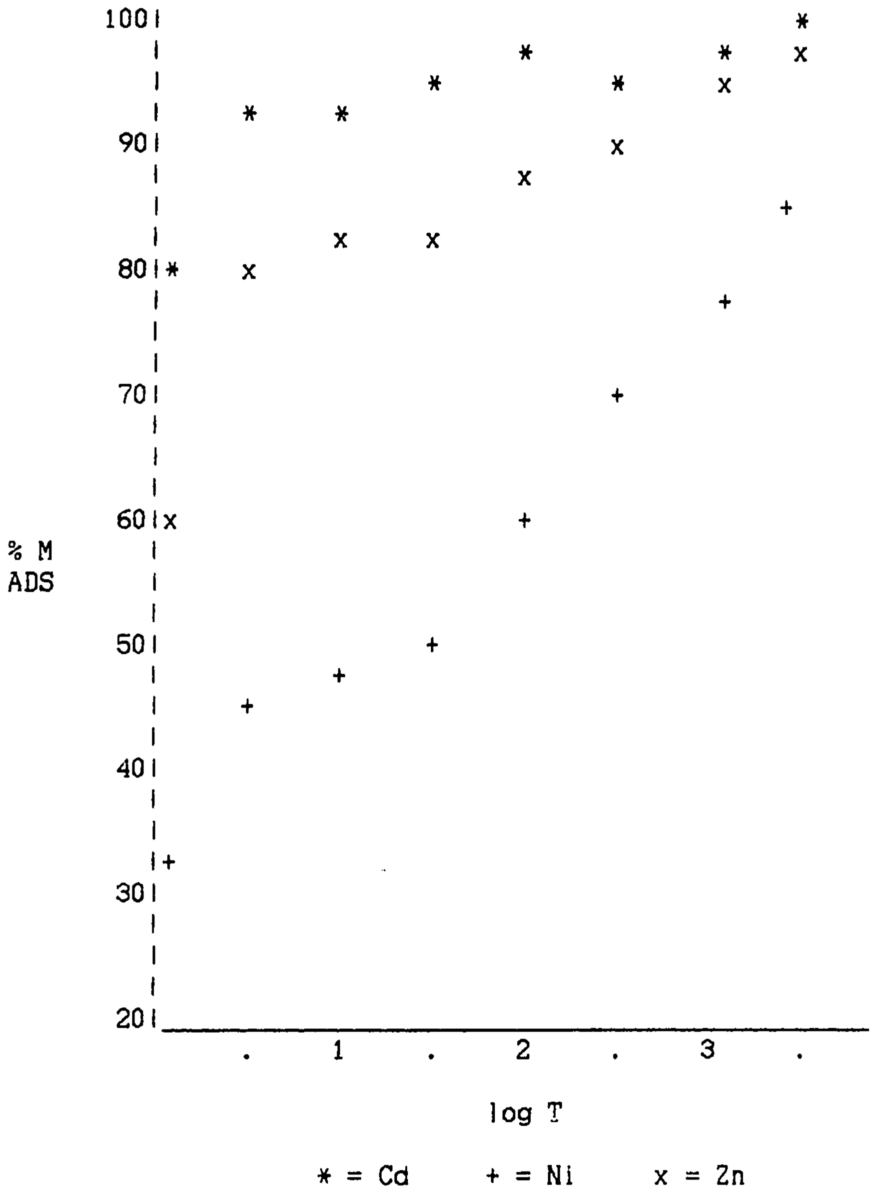

Figure C4.

Kinetics of Cd, Ni and Zn adsorption in perchlorate (pH 7.5) on montmorillonite.

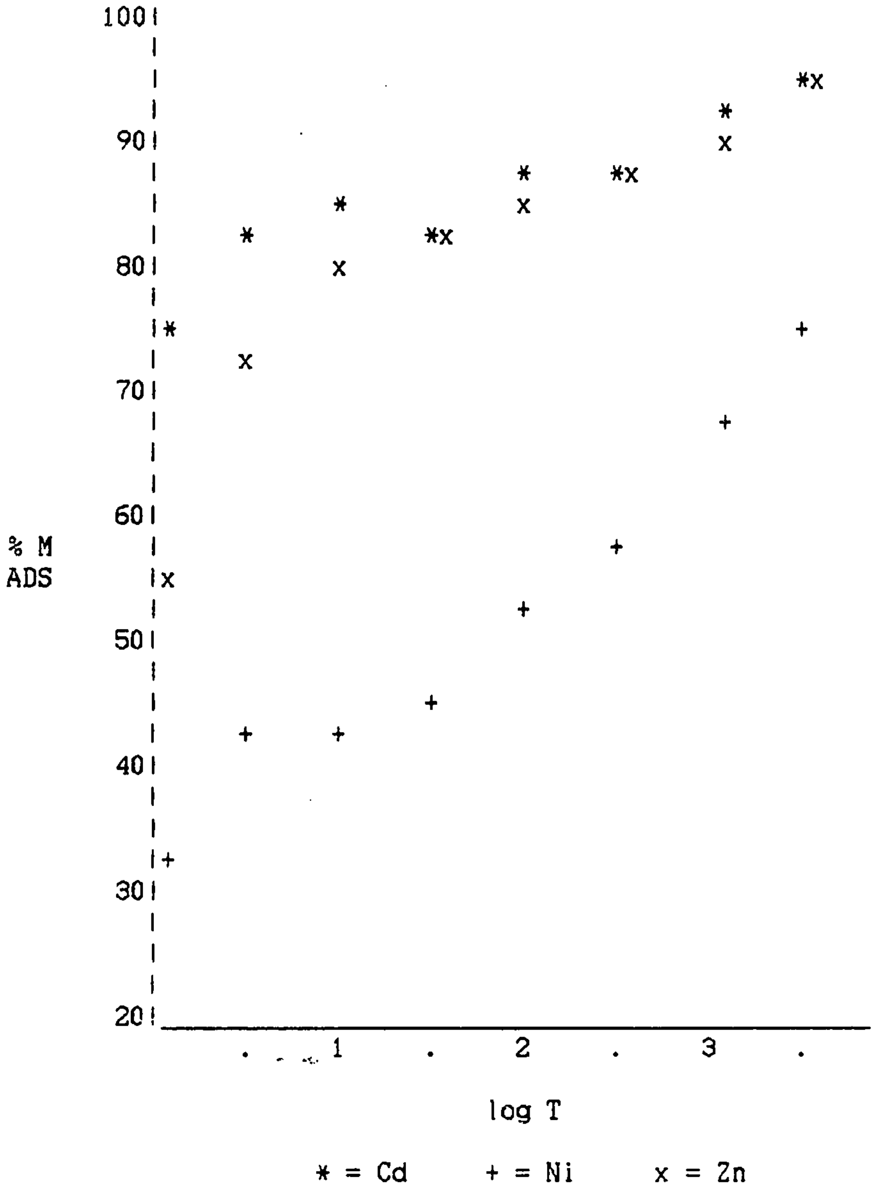

Figure C5.

Kinetics of Cd, Ni and Zn adsorption in perchlorate (pH 6.5) on montmorillonite.

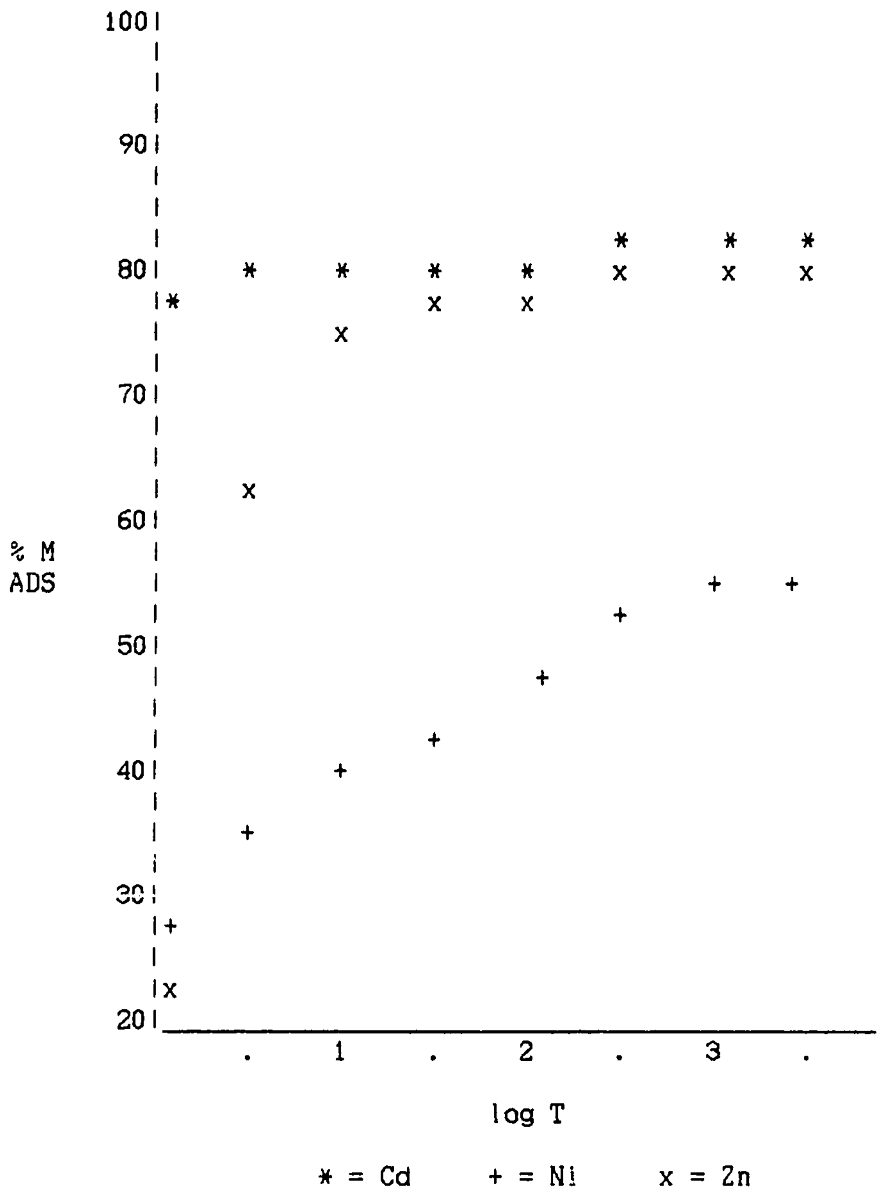

Figure C6.

Kinetics of Cd, Ni and Zn adsorption in perchlorate (pH 5.5) on montmorillonite.

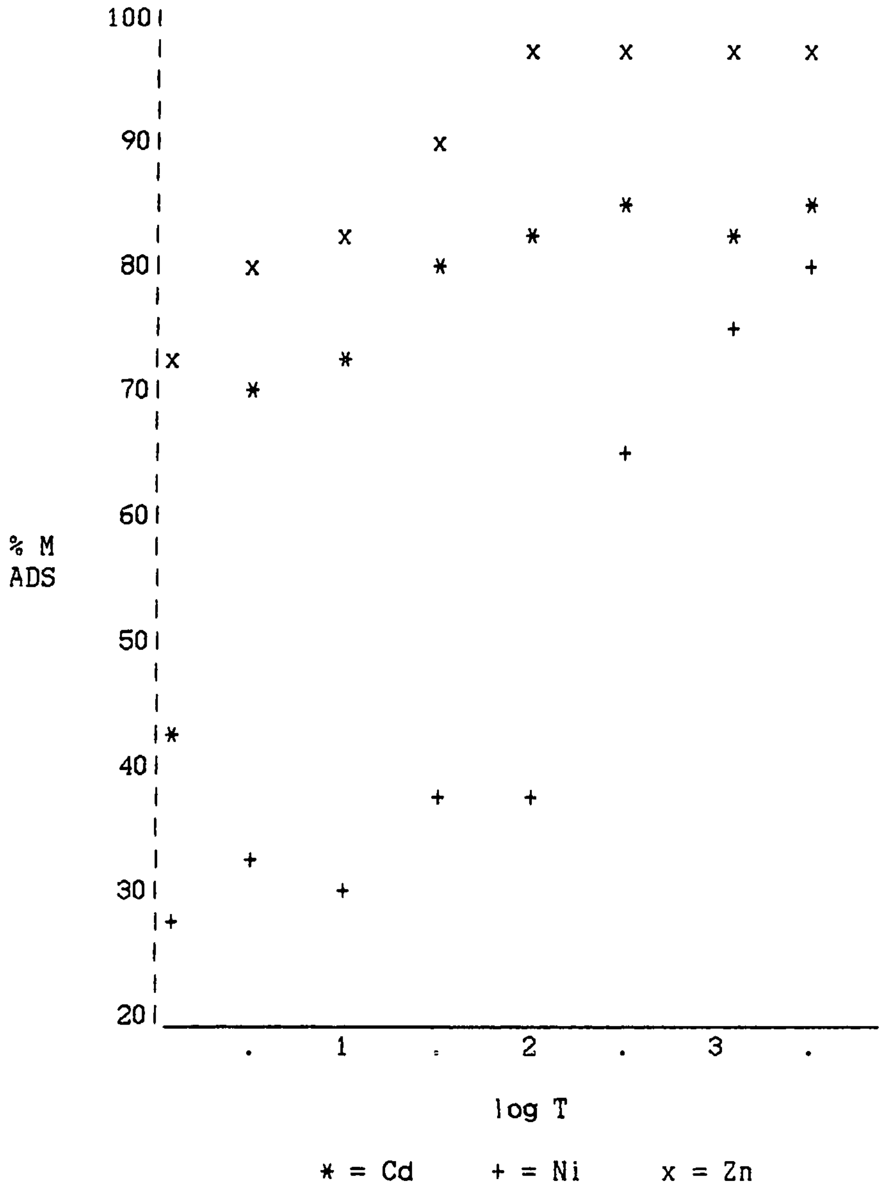

Figure C7.

Kinetics of Cd, Ni and Zn adsorption in chloride (pH 7.5) on kaolinite.

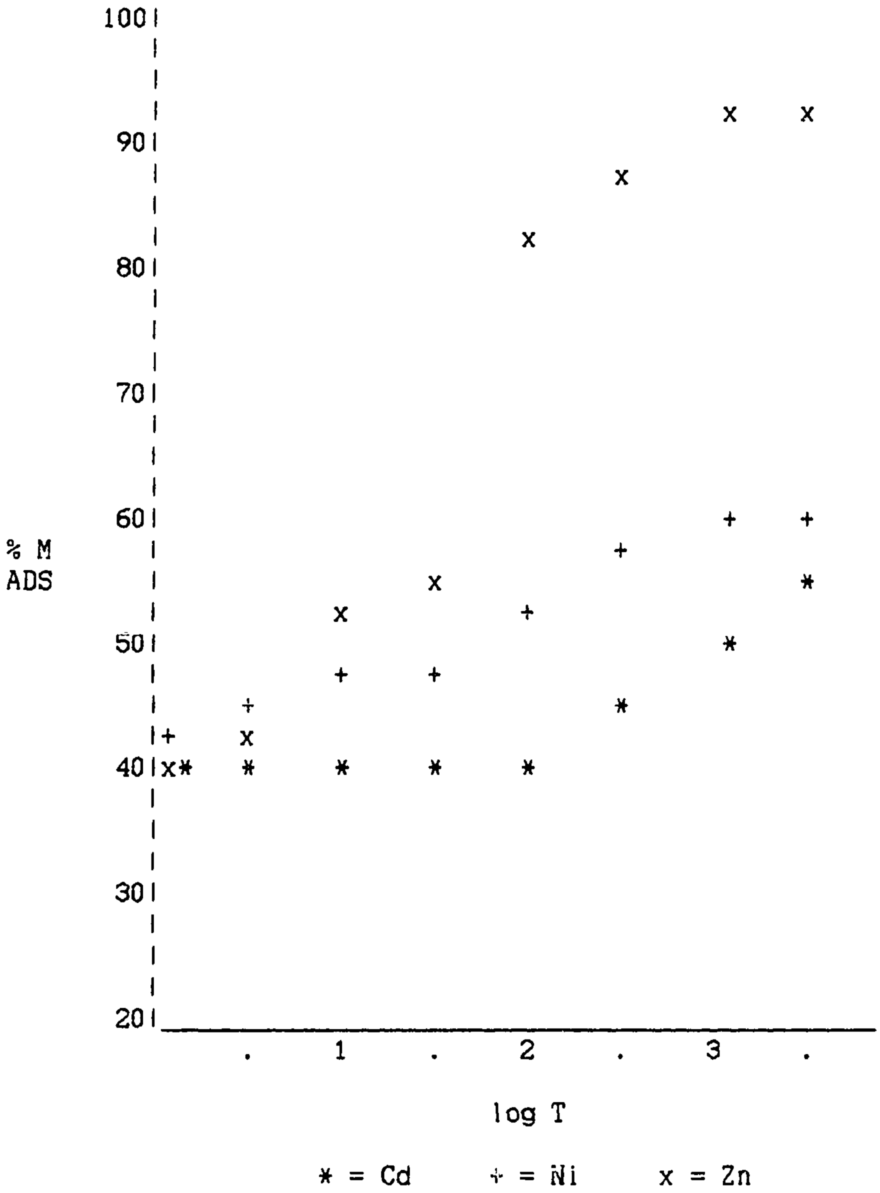

Figure C8.

Kinetics of Cd, Ni and Zn adsorption in chloride (pH 6.5) on kaolinite.

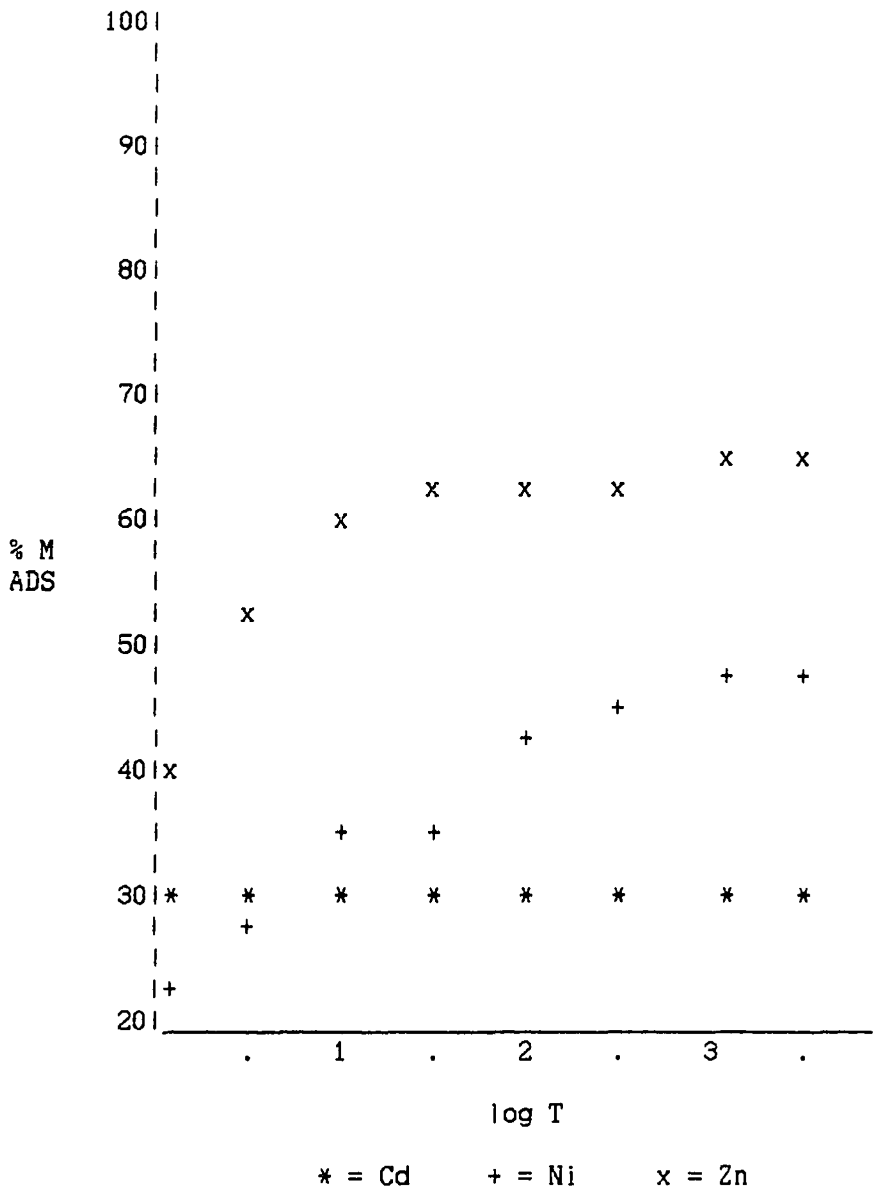

Figure C9.

Kinetics of Cd, Ni and Zn adsorption in chloride (pH 5.5) on kaolinite.

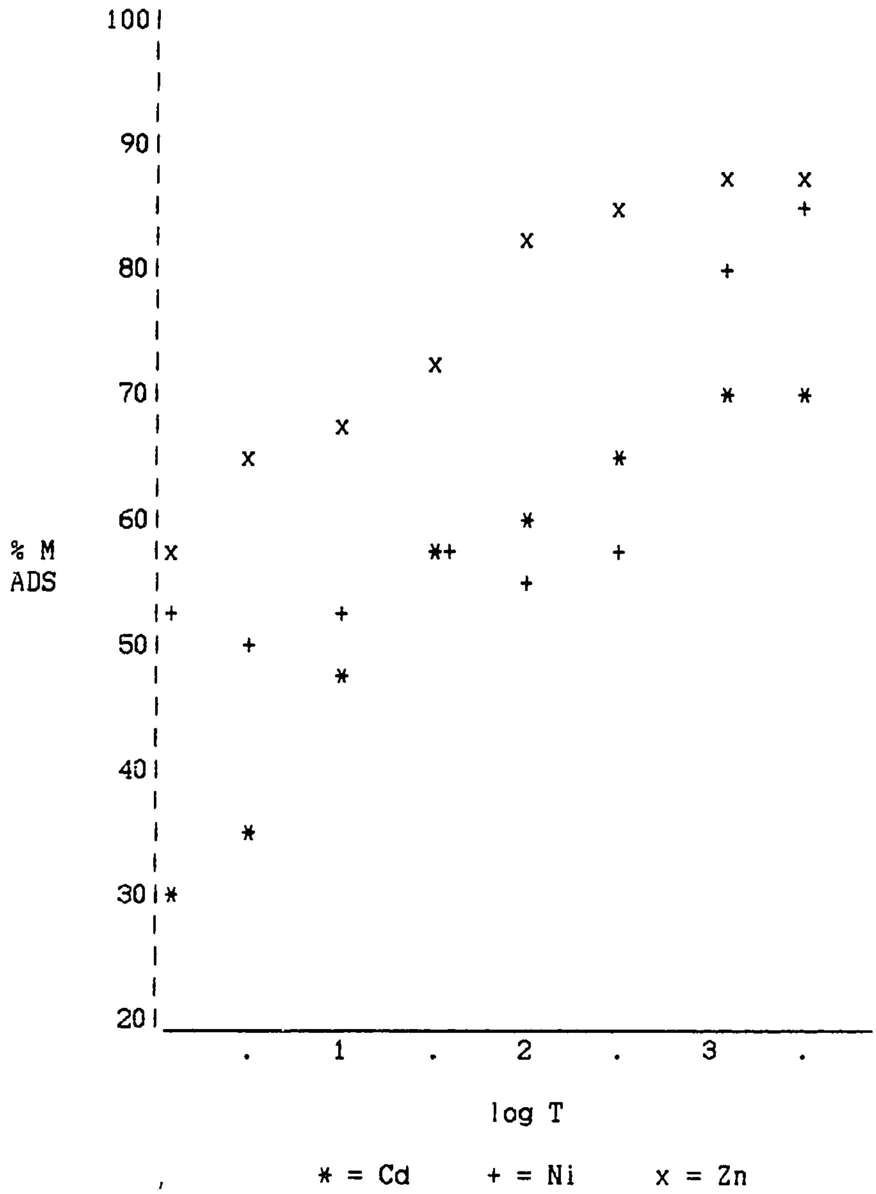

Figure C10.

Kinetics of Cd, Ni and Zn adsorption in chloride (pH 7.5) on montmorillonite.

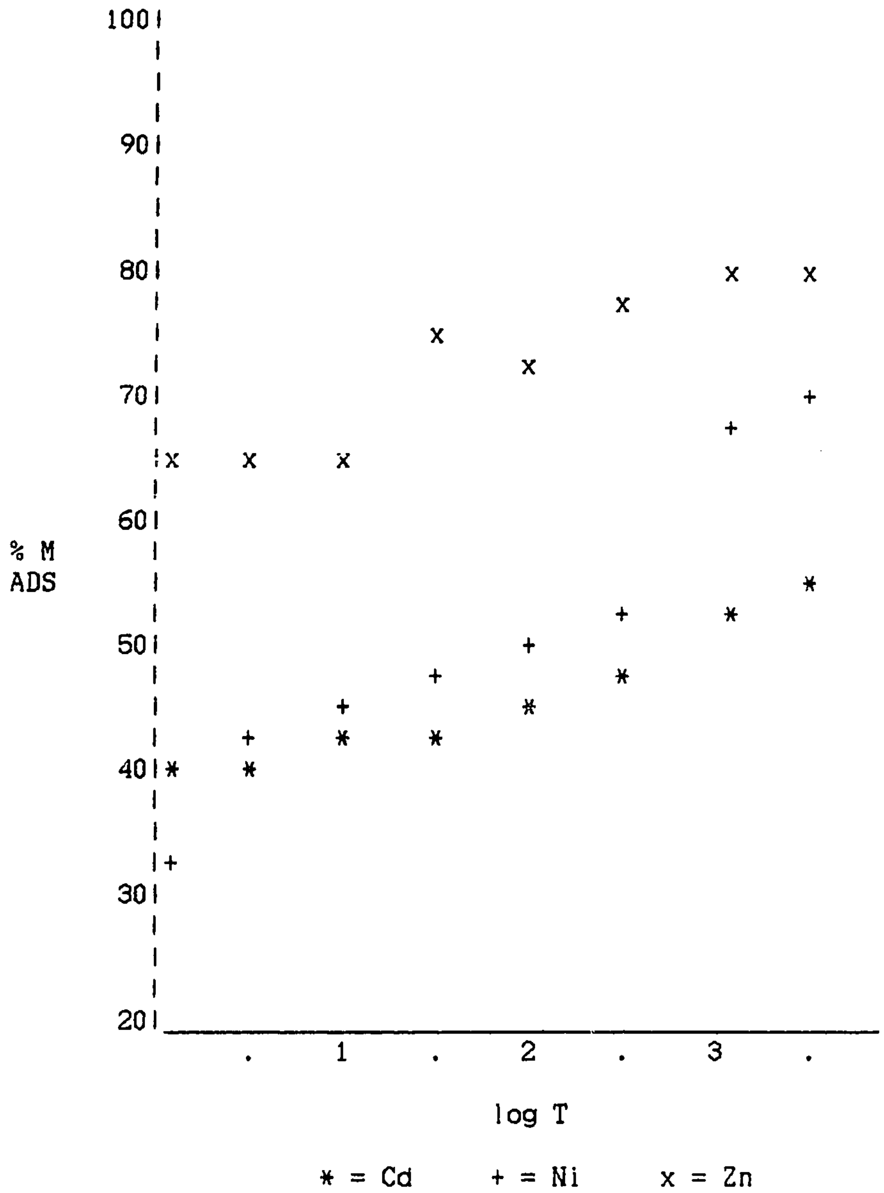

Figure C11.

Kinetics of Cd, Ni and Zn adsorption in chloride (pH 6.5) on montmorillonite.

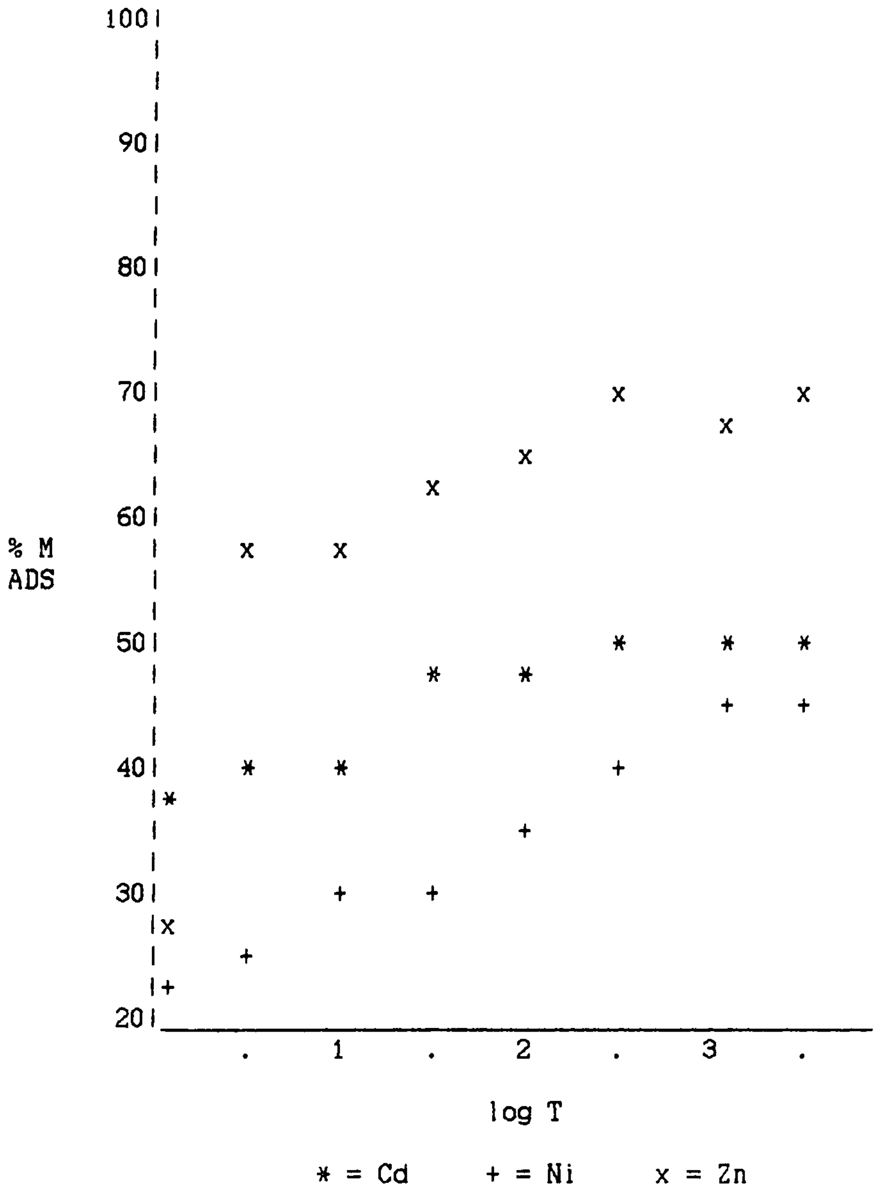

Figure C12.

Kinetics of Cd, Ni and Zn adsorption in chloride (pH 5.5) on montmorillonite.

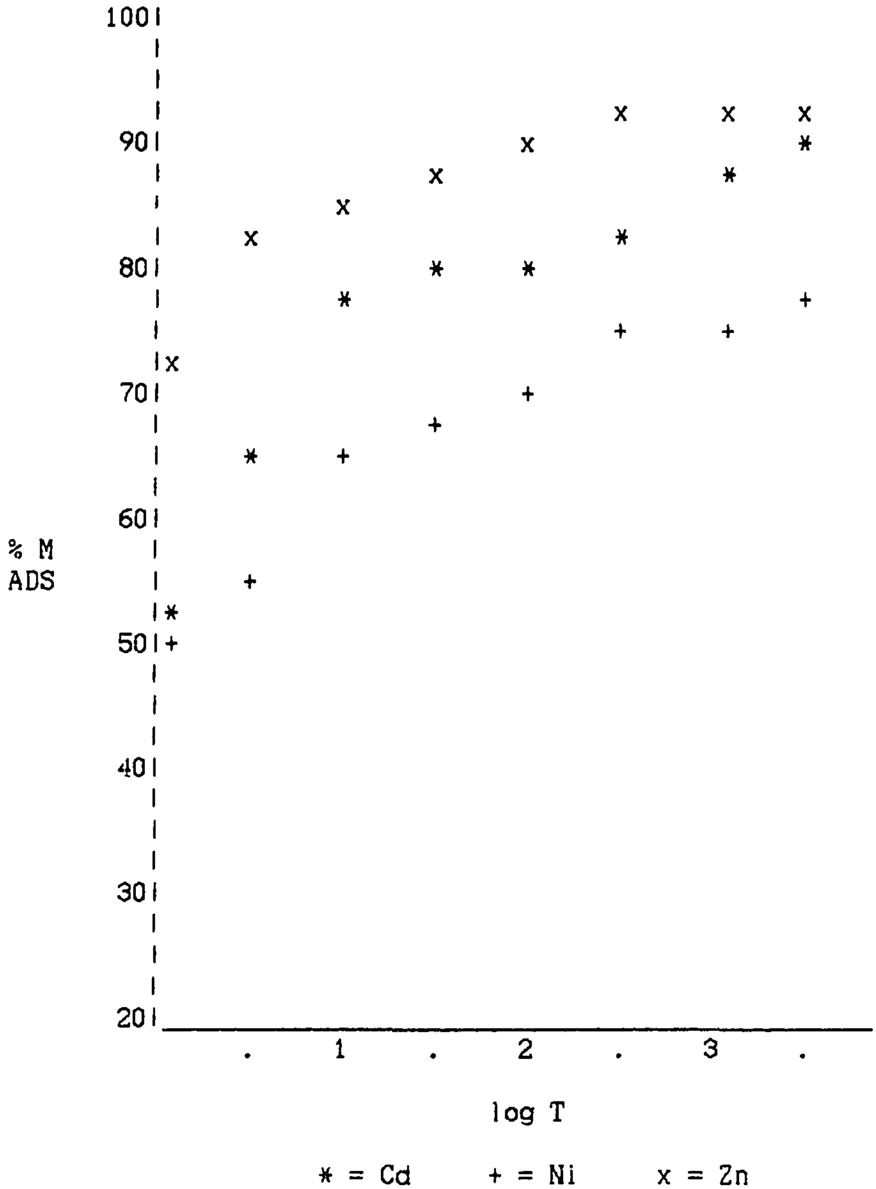

Figure C13.

Kinetics of Cd, Ni and Zn adsorption in sulphate (pH 7.5) on kaolinite.

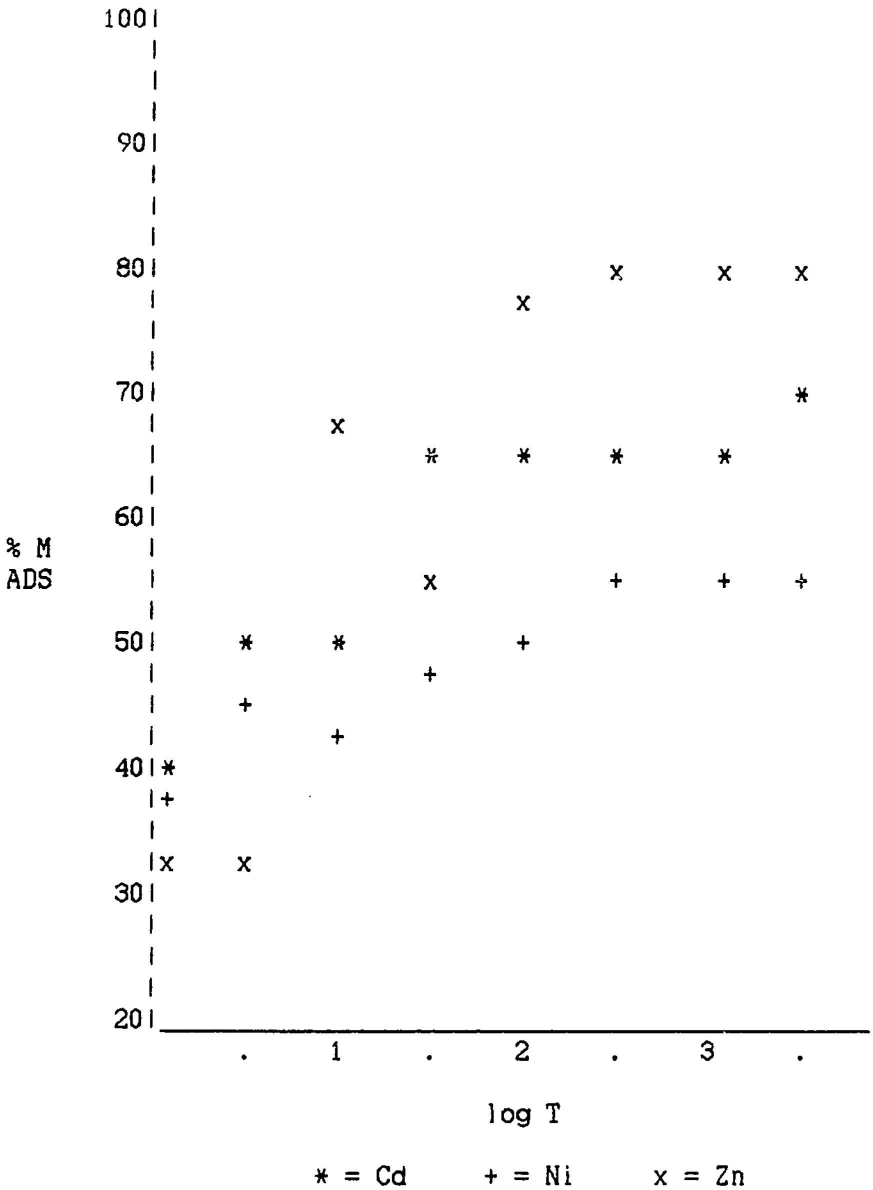

Figure C14.

Kinetics of Cd, Ni and Zn adsorption in sulphate (pH 6.5) on kaolinite.

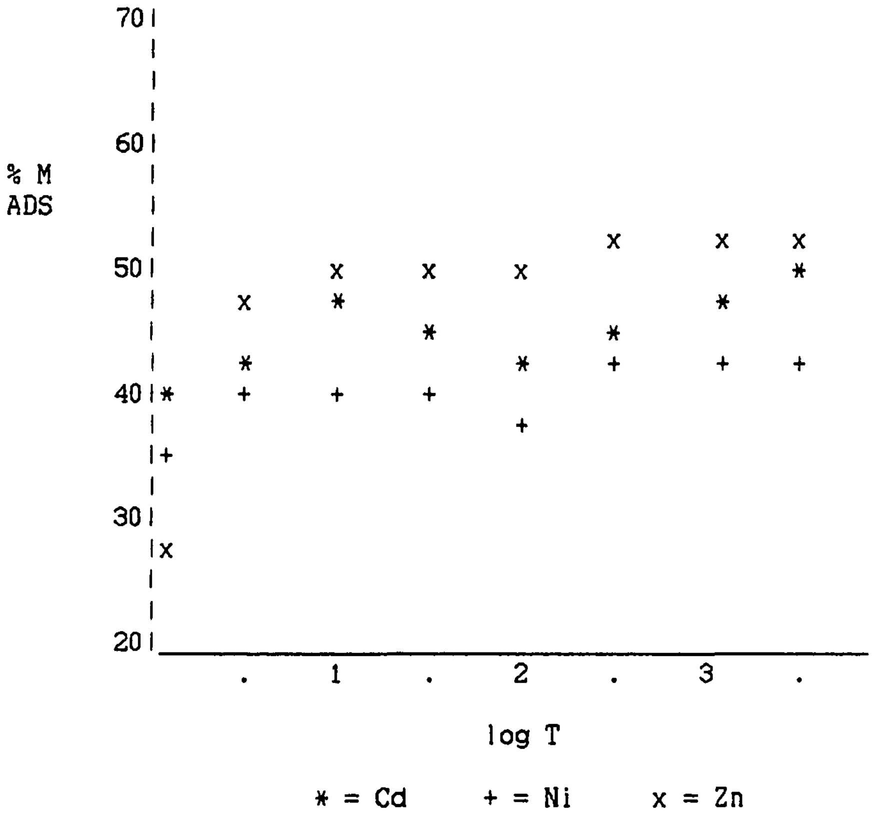

Figure C15.

Kinetics of Cd, Ni and Zn adsorption in sulphate (pH 5.5) on kaolinite.

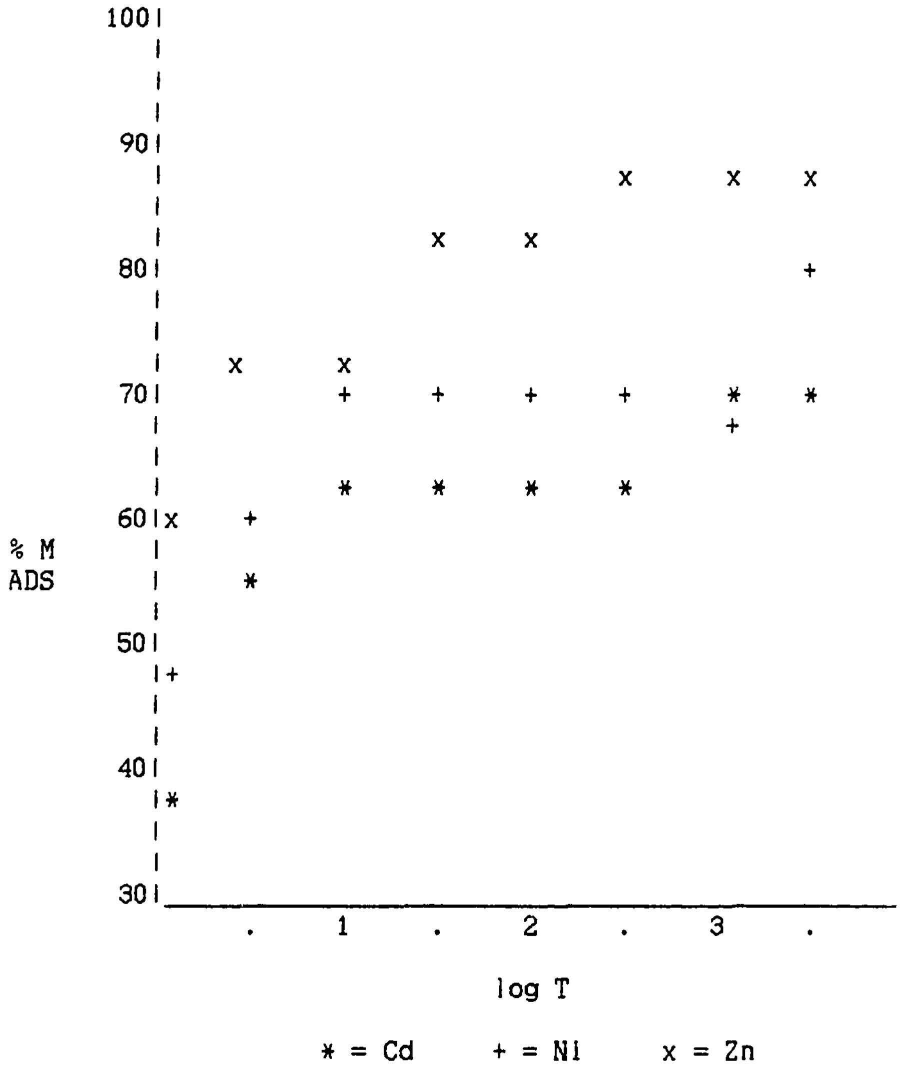

Figure C16.

Kinetics of Cd, Ni and Zn adsorption in sulphate (pH 7.5) on montmorillonite.

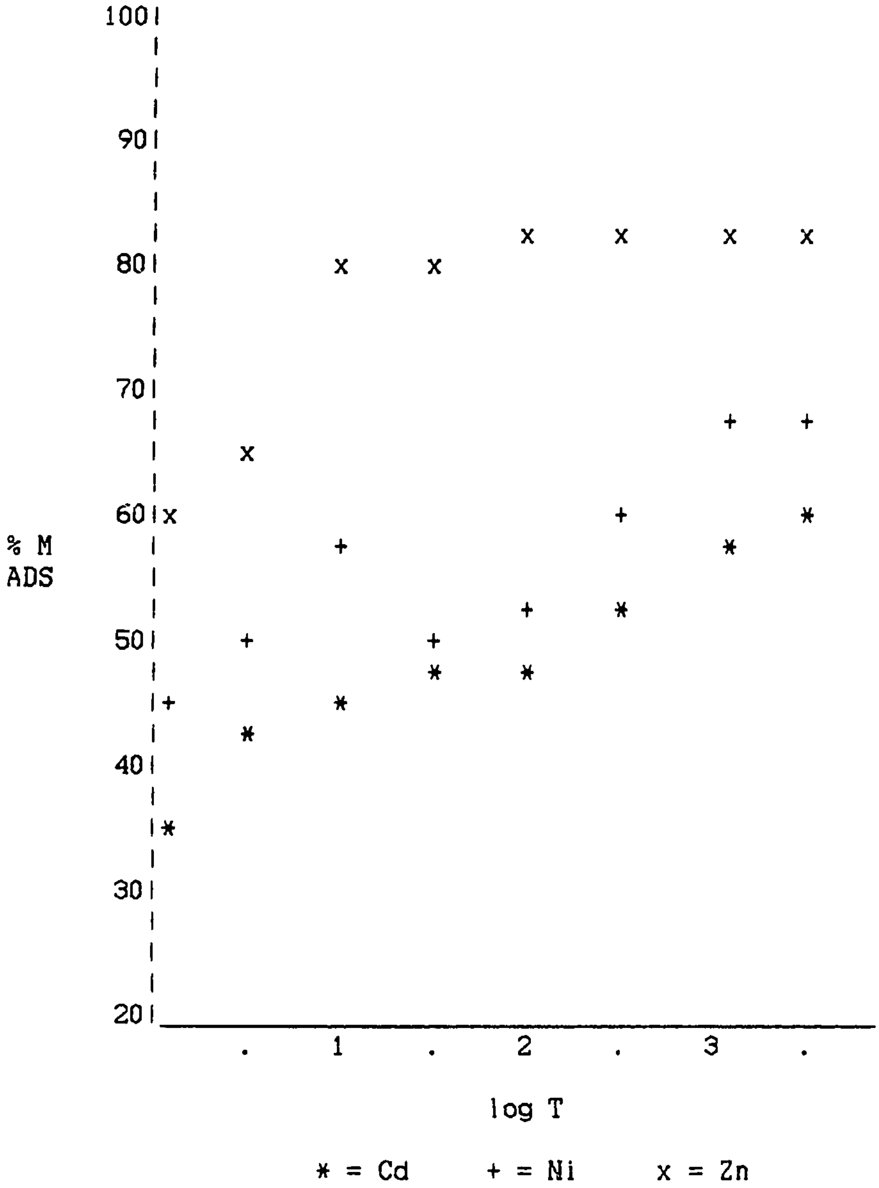

Figure C17.

Kinetics of Cd, Ni and Zn adsorption in sulphate (pH 6.5) on montmorillonite.

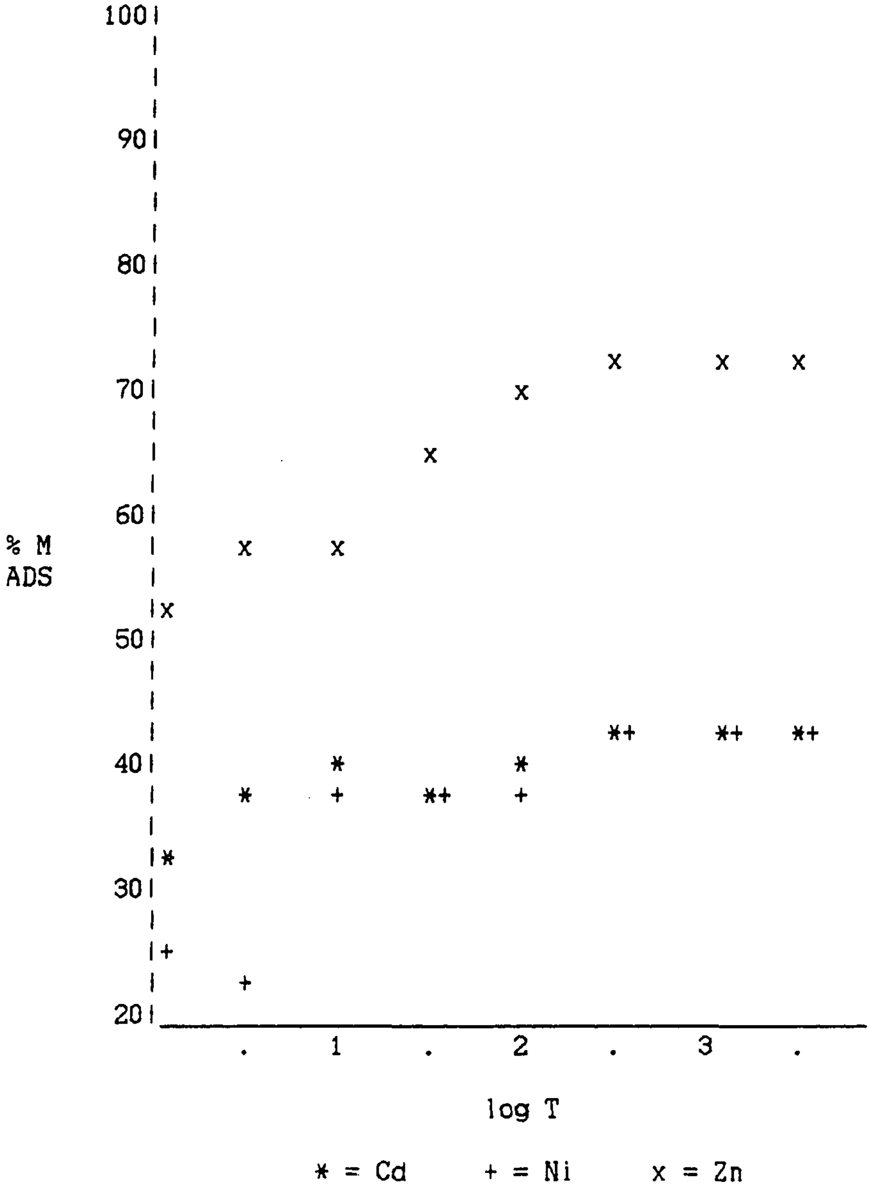

Figure C18.

Kinetics of Cd, Ni and Zn adsorption in sulphate (pH 5.5) on montmorillonite.

LIST OF REFERENCES

Abd-Elfattah, A., and K. Wada. 1981. Adsorption of lead, copper, zinc, cobalt, and cadmium by soils that differ in cation exchange materials. Soil Sci. 124:121-134.

Anderson, M.A., and A.J. Rubin. 1981. Adsorption of inorganics at solid-liquid interfaces. Ann Arbor Science Publ.

Aringhieri, R., P. Carrai, and G. Petruzzelli. 1985. Kinetics of copper and cadmium adsorption by an Italian soil. Soil Sci. 139:197-204.

Baes, C.F., and R.E. Messner. 1976. The Hydrolysis of Cations. John Wiley and Sons. N.Y.

Bansal, O.P., H. Singh, and R.N. Goyal. 1980. Reactions of nickel with acid and base saturated montmorillonites. J. Indian Chem. Soc. 57:1050-1053.

Barrow, N.J., J.W. Bowden, A.M. Posner, and J.P. Quirk. 1981. Describing the adsorption of copper, zinc and lead on a variable charge mineral surface. Aust. J. Soil Res. 19:309-321.

Benjamin, M.M. 1983. Adsorption and surface precipitation of metals on amorphous iron oxyhydroxide. Environ. Sci. Technol. 17:686-692.

Benjamin, M.M., and J.O. Leckie. 1982. Effects of complexation by Cl, SO_4, and S_2O_3 on adsorption behavior of Cd on oxide surfaces. Environ. Sci. Technol. 16:162-170.

Benjamin, M.M., and J.O. Leckie. 1981. Conceptual model for metal-ligand-surface interactions during adsorption. Environ. Sci. Technol. 9:1050-1056.

Benjamin, M.M., and J.O. Leckie. 1981. Multiple-site adsorption of Cd, Zn, and Pb on amorphous iron oxyhydroxide. J. Colloid Interface Sci. 79:209-221.

Biddappa, C.C., M. Chino, and K. Kumazawa. 1981. Adsorption, desorption, potential and selective distribution of heavy metals in selected soils of Japan. J. Environ. Sci. Health. B16(4):511-528.

Bittell, J.E., and R.J. Miller. 1974. Lead, cadmium, and calcium selectivity coefficients on a montmorillonite, illite, and kaolinite. J. Environ. Quality. 3:250-253.

Bohn, H.L., B.L. McNeal and G.A. O'Connor. 1979. Soil Chemistry. John Wiley & Sons.

Bolland, M.D.A. 1970. Zn phosphate interaction on goethite. B. Sci. Agric. (Hons.) Thesis, Univ. West. Aust.

Borggaard, O.K. 1982. The influence of iron oxides on the surface area of soil. J. of Soil Sci. 33:443-449.

Bowden, J.W., M.D.A. Bolland, A.M. Posner, and J.P. Quirk. 1973. Generalized model for anion and cation adsorption at oxide surfaces. Nature Physical Sci. 245:81-83.

Bowman, R.S., M.E. Essington, and G.A. O'Connor. 1981. Soil sorption of nickel: influence of solution composition. Soil Sci. Soc. Am. J. 45:860-865.

Brummer, G., K.G. Tiller, U. Herms, and P.M. Clayton. 1983. Adsorption-desorption and/or precipitation-dissolution processes of zinc in soils. Geoderma 31:337-354.

Bruninx, E. 1975. The coprecipitation of Zn, Cd and Hg with ferrric hydroxide. Phillips Res. Repts. 30:177-191.

Buhler, D.R. 1973. Environmental contamination by toxic metals. In F.J. Burgess (ed.). Heavy metals in the environment. Seminar conducted by the Water Res. Research Inst. Oregan State Univ.

Bunzl, K., W. Schmidt, and B. Sansoni. 1976. Kinetics of ion exchange in soil organic matter. IV. Adsorption and desorption of Pb^{2+}, Cu^{2+}, Cd^{2+}, Zn^{2+} and Ca^{2+} by peat. J. of Soil Sci. 27:32-41.

Cavallaro, N. and M.B. McBride. 1978. Copper and cadmium adsorption characteristics of selected acid and calcareous soils. Soil Sci. Soc. Am. J., 42:550-556.

Chubin, R.G., and J.J. Street. 1981. Adsorption of cadmium on soil constituents in the presence of complexing ligands. J. of Environ. Quality. 10

Davies. J.A., and J.O. Leckie. 1978. Effect of complexing ligands on trace metal uptake by hydrous oxides. Environ. Sci. Technol. 12

Davis, J.A., and J.O. Leckie. 1978. Surface ionization and complexation at the oxide/water interface. J. Colloid Interface Sci. 67:90-107.

Day, P.R. 1965. Particle fractionation and particle-size analysis. In Methods of soil analysis. ASA.

Doner, H.E. 1978. Chloride as a factor in mobilities of Ni(II), Cu(II), and Cd(II) in soil. Soil Sci. Soc. Am. J. 42:882-885.

Egozy, Y. 1980. Adsorption of Cadmium and cobalt on montmorillonite as a function of solution composition. Clays and Clay Minerals. 28:311-318.

Farrah, H., and W.F. Pickering. 1977. The sorption of lead and cadmium species by clay minerals. Aust. J. Chem. 30:1417-1422.

Forbes, E.A., A.M. Posner, and J.P. Quirk. 1976. The Specific adsorption of divalent Cd, Co, Cu, Pb, and Zn on goethite. J. of Soil Sci. 27:154-166.

Forbes, E.A., A.M. Posner, and J.P. Quirk. 1974. The specific adsorption of inorganic Hg(II) species and Co(II) complex ions on geothite. J. Coll. Interface Sci. 49(3).

Forbes, E.A. 1973. The specific adsorption of heavy metal cations on goethite. Ph.D. Thesis. Univ. of W. Aust.

Fuller, W.H. 1977. Movement of selected metals, asbestos and cyanide in soil. Application to waste disposal problems. EPA-600/2-77-020. Environmental Protection Tech. Serv.

Gadde, R.R. and H.A. Laitnen. 1974. Studies of heavy metal adsorption by hydrous iron and manganese oxides. Anal. Chem. 46:2022-2026.

Garcia-Miragaya, J., R. Cardenas and A.L. Page. 1985. Surface loading effect on Cd and Zn sorption by kaolinite and montmorillonite from low concentration solutions. Water, Air and Soil Pollution. 27:181-190.

Garcia-Miragaya, J., and A.L. Page. 1978. Sorption of trace quantities of cadmium by soils with different chemical and mineralogical composition. Water, Air and Soil Pollution. 9:289-299.

Garcia-Miragaya, J., and A.L. Page. 1976. Influence of ionic strength and inorganic complex formation on the sorption of trace amounts of Cd by montmorillonite. Soil Sci. Soc. Am. J. 40:658-663.

Guy, R.D., C.L. Chakrabarti, and L.L. Schramm. 1975. The application of a simple chemical model of natural waters to metal fixation in particulate matter. Can. J. Chem. 53:661-669.

Hahne, H.C.H., and W. Kroontje. 1973. Signifigance of pH and chloride concentration on behavior of heavy metal pollutants: mercury(II), cadmium(II), zinc(II), and lead(II). J. Environ. Quality. 2:444-451.

Harding, I.H., and T.W. Healy. 1979. Cadmium uptake on organic and inorganic constituents of soils. Prog. Wat. Tech. 11:265-273.

Heald, W.R., M.H. Frere and C.T. de Wit. 1964. Ion adsorption on charged surfaces. Soil Sci. Soc. Am. J. 28:622.

Hendrickson, L.L., and R.B. Corey. 1980. Effect of equilibrium metal concentrations on apparent selectivity coefficients of soil complexes. Soil Sci. Soc. Am. J. 46:163-170.

Huheey, J.E. 1978. Inorganic chemistry. Harper and Row Publ.

James, R.O., and M.G. McNaughton. 1977. The adsorption of aqueous heavy metals on inorganic minerals. Geochem. Cosmochim. Acta 41:1549-1555.

James, R.O. and T.W. Healy. 1972. Adsorption of hydrolyzable metal ions at the oxide-water interface. I. Co(II) adsorption on SiO_2 and TiO_2 as model systems. II. Charge reversal of SiO_2 and TiO_2 colloids by adsorbed Co(II), La(III), and Th(IV) as model systems. III. Thermodynamic model od adsorption. J. Colloid Interface Sci. 40:42-81.

Kalbasi, M., G.J. Racz, and L.A. Loewen-Rudgers. 1978. Mechanism of zinc adsorption by iron and aluminum oxides. Soil Sci. 125:146-150.

Loganathan P. and R.G. Burau. 1973. Sorption of heavy metal ions by a hydrous manganese oxide. Geochem. Cosmochim. Acta. 37:1277-1293.

Mattigod, S.V., A.S. Gibaldi, and A.L. Page. 1979. Effect of ionic strength and ion pair formation on the adsorption of nickel by kaolinite. Clays and Clay Minerals. 27:411-416.

McBride, M.B. 1980. Interpretation of the variability of selectivity coefficients for exchange between ions of unequal charge on smectites. Clays and Clay Minerals. 28(4).

McKenzie, R.M. 1980. The adsorption of lead and other heavy metals on oxides of manganese and iron. Aust. J. Soil Res. 18:61-73.

McKenzie, R.M. 1972. The sorption of some heavy metals by the lower oxides of manganese. Geoderma. 8:29-35.

McNaughton, M.G., and James, R.O. 1974. Adsorption of aqueous mercury complexes at the oxide/water interface. J. Coll. Interface Sci. 47

Pauling, L. 1960. The nature of the chemical bond. 3rd ed. Cornell Univ. Press.

Pearson, R.G. 1968. Hard and soft acids and bases, HSAB. I. Fundamental Principles. II. Underlying Theories. J. of Chem. Ed. 45:581-587, 643-649.

Phillips, C.S.G. and R.J.P. Williams. 1965. Inorganic chemistry. Oxford Press.

Reid, J.D., and B. McDuffie. 1981. Sorption of trace cadmium on clay minerals and river sediments: effects of pH and Cd(II) concentrations in a synthetic river water medium. Water, Air and Soil Pollution. 15:275-286.

Salim, R. and B.G. Cooksey. 1980. Kinetics of the adsorption of lead on river-mud. Plant and Soil 54:399-417.

Shainberg, I. and W.D. Kemper. 1967. Ion exchange equilibria on montmorillonite. Soil Sci. 103:4.

Singer, P.C. 1973. Trace Metals and Metal-organic Interactions in Natural Waters. Ann Arbor Sci. Publ.

Sposito, G. 1984. The Surface Chemistry of Soils. Oxford University Press.

Sposito, G. 1981. The Thermodynamics of Soil Solutions. Oxford University Press.

Sposito, G., K. Holtzclaw, L. Charlet, C. Jouany, and A.L. Page. 1983. Sodium-cadmium and sodium-magnesium exchange on Wyoming bentonite in perchlorate and chloride background ionic media. Soil Sci. Soc. J. 4:51-55.

Stuanes, A. 1976. Adsorption of Mn^{2+}, Zn^{2+}, Cd^{2+}, and Hg^{2+} from binary solutions by mineral material. Acta Agriculturae Scandinavica. 26:243-250.

Sullivan, P.J. 1977. The principle of hard and soft acids and bases as applied to exchangeable cation selectivity in soils. Soil Sci. 124:117-121.

Tiller, K.G., J. Gerth, and G. Brummer. 1984. The sorption of Cd, Zn and Ni by soil clay fractions: procedures for partition of bound forms and their interpretation. Geoderma. 34:1-16.

Tiller, K.G., J. Gerth, and G. Brummer. 1984. The relative affinities of Cd, Ni and Zn for different soil clay fractions and goethite. Geoderma. 34:17-35.

Van Olphen, H. and J>J> Fripiat. 1979. Data handbbook for clay materials and other non-metallic minerals. Pergamon Press.

Vuceta, J., and J.J. Morgan. 1978. Chemical modeling of trace metals in fresh waters: role of complexation and adsorption. Environ. Sci. Technol. 12:1302-1309.

Vydra, F. and J. Gabla. 1969. Sorption von metallkomplexen an sillicagel. V. sorption von hydrolysen produkten des Co^{2+}, Mn^{2+}, Ni^{2+} and Zn^{2+} an sillicagel. Coiln. Czech. Chem. Comm. 34:3471-3478.

Wada, K., and Y. Kakuto. 1980. Selective adsorption of zinc on halloysite. Clays and Clay Minerals. 28:321-327.

Weast, R.C. 1985. CRC Handbook of chemistry and physics. CRC Press.

Zasoski, R.J., and R. G. Burau. 1978. Technique for studying the kinetics of adsorption in suspensions. Soil Sci. Soc. Am. J. 42:372-374.