COPPER SORPTION ON KAOLINITE

By

PETER VILKS, BSC., MSC.

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AUTHOR:　Peter Vilks, B.Sc.　(Dalhousie University)

　　　　　　　　　　　　M.Sc.　(McMaster University)

SUPERVISOR:　Professor J.R. Kramer

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ABSTRACT

In order to improve our ability to predict sorption reactions, the rates of copper sorption on kaolinite were measured to determine the number and type of mechanisms' responsible for trace metal sorption on clay minerals. From a theoretical consideration of Cu^{+2} chemistry and kaolinite surface properties, it is probable that copper sorption is controlled by several mechanisms, with different sorption rates. These mechanisms include nonspecific coulombic attraction, coordination to one or two surface sites, induced surface precipitation, structural penetration, and sorption induced by kaolinite agglomeration. Cu^{+2} sorption on kaolinite, in a 0.05 M KNO_3 medium at pH 6.2, was followed with a specific ion electrode for up to 2.5 weeks. The kinetic data revealed an instantaneous sorption, occurring within the first 1 to 5 seconds, followed by four concurrent first-order reactions. The mean rate constants of the first-order reactions are 0.7 ± 0.7, $(8 \pm 4) * 10^{-3}$, $(14 \pm 6) * 10^{-4}$, and $(9 \pm 6) * 10^{-5}$ (min.$^{-1}$).

In order to characterize and identify the apparent mechanisms resolved by kinetics, experiments were designed to test the properties of Cu sorbed on kaolinite. These tests included (1)varying the salt concentration (2)changing the pH, (3)measuring the H^{+}/Cu^{+2} exchange ratio, and (4)desorbing Cu^{+2} with water, Sr^{+2}, $^{64}Cu^{+2}$, nitric acid and cyanide. The results of these tests indicate that the instantaneous sorption is caused by complexation to surface sites, with a small amount of nonspecific sorption. The first-order reactions are

attributed to surface induced precipitation, coordination to two surface

sites, and Cu fixation in the kaolinite structure. Copper sorption

induced by centrifuging suggests that when clays are agglomerated, as in

a clay floc, metal sorption may be enhanced. Sorption mechanisms

observed on kaolinite may be applied to other clays, if differences in

surface properties are taken into consideration.

ACKNOWLEDGEMENTS

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CHAPTER I

INTRODUCTION

GENERAL BACKGROUND

The subject of this thesis considers the transfer of metal ions from an aqueous phase to a solid. Several terms have been coined to describe this phenomenon. Adsorption is defined to be the attachment of a dissolved species to the surface of a solid. If the dissolved component enters the interior of the solid through a defect or a network of capillaries then absorption takes place. In many cases both adsorption and absorption occur simultaneously, or it is not clear whether the dissolved species stays on the surface or enters the solid. The term sorption is very useful in this situation because it does not specify the location of the sorbed species.

The maximum concentrations of dissolved ions in natural waters are determined either by dissolution/precipitation equilibria or by sorption reactions. Sorption and precipitation are often difficult to distinguish because operationally they give similar results, particularly if the precipitating phase is not readily visible. The concentrations of many ions are in equilibrium with identified minerals. However, concentrations of some ions, such as the heavy metals, are apparently undersaturated in sea water with respect to natural minerals which contain them. This undersaturation can be explained by sorption reactions in sediments and in the water column (Parks, 1975). Even when

precipitation is the dominant mechanism surface reactions may affect this process by adsorbing other ions which enhance or inhibit the formation of new mineral at the solid surface. Sorption reactions may promote precipitation of some metals from waters which are undersaturated in these metals. For example, consider the migration of dissolved gold complexes through a hydrothermal vein. If these gold complexes are locally concentrated by adsorption onto a positively charged surface of a chlorite they might become supersaturated with respect to native gold. When the gold is observed in the resulting quartz vein there is no clue to a sorption reaction.

Sorption reactions have a profound influence on the chemistry of natural waters because they are one of the principal mechanisms of controlling ion concentrations. In many cases they may also influence another principle mechanism, namely precipitation. Therefore, when we study the natural environment we should not forget the possible effects of sorption reactions. The level of toxic metals and organic compounds which are available to plants and animals is reduced by sorption processes. The disposal of radionuclides requires a repository which is surrounded by a buffer material with a high sorption capacity for escaping radionuclides (Dayal et. al., 1979; Wilson, 1980; Bird, 1979). The purification of our water supplies depends upon absorption in beds of activated carbon. The understanding of sorption mechanisms is important to agriculture because sorption reactions can determine whether the amounts of nutrients and metals available to crops are at a level which is either deficient, just right, or high enough to be toxic. The availability of metals and nutrients to crops will eventually have

an effect on the health of the animals or humans which consume these crops (Jackson and Lim, 1982). Other fields of study which are affected by surface reactions include geochemical prospecting, ore deposition, weathering and diagenetic reactions. Even in the laboratory one must be careful of adsorption onto container walls, especially when working at trace concentrations.

Since so many fields of study are affected by sorption directly or indirectly it is important to understand and quantify as many of the common adsorption reactions as possible. Ideally researchers who must cope with sorption should have access to a data bank of distribution coefficients which can be applied to a wide range of conditions with confidence. Unfortunately with our present knowledge it is not possible to compile from the literature a reliable bank of distribution coefficients which can be applied to general cases because we simply do not understand enough about adsorption mechanisms. Usually sorption isotherms measured under one set of concentrations and solution conditions do not work for a different set of conditions. Mathematical models have been constructed to describe adsorption as a function of concentration and pH, but they are usually not successful for a universal set of conditions. The only way to successfully predict sorption for a new set of conditions is to have a thorough understanding of the mechanisms involved. The ability to predict sorption behavior is particularly important if we are dealing with a dynamic environment, such as an estuary, in which we must model adsorption as a function of changing conditions.

Interest in transition metals stems from the fact that they have an importance in the mining industry, and they can be toxic to living things if available in excess, while at the same time a minimum amount must be present for proper nutrition. Since transition metals are of considerable interest in environmental studies their sorption properties should be properly characterized.

In the early work on soil sorption reactions it became apparent that ion exchange reactions were controlled by fine particles in the clay size fraction (Way, 1852). Clay sized particles have a very large surface area available for sorption which leads one to think of clay minerals are an important sink for metals in various sediments and soils. Clay minerals by themselves may not have as high exchange capacities as some of the oxides and hydroxides of Si, Al, Fe and Mn, but because of their large volume clays still provide a large storage capacity for metals. Also clay minerals may act as a substrate for coatings of oxides, hydroxides and various organics which may give clays an apparent high sorption capacity (Jenne, 1977). Therefore, if one wants to model the sorption properties of a sediment or soil one must start with a knowledge of the sorption characteristics of clay mineral surfaces.

Since one of the chief approaches to investigating sorption mechanisms in this study was kinetics, it was necessary to use an analytical tool which could measure metal sorption quickly and without disturbing the clay suspension. The best analytical tool to meet these criteria is the specific ion electrode which can measure the activities of certain ions in their uncomplexed form. At present, copper and

silver are the only transition metals which can be measured at low levels with specific ion electrodes, and of these two copper was chosen as the model transition element. In the first transition series copper forms the strongest bonds with oxygen and therefore would be the most likely to test any binding mechanisms which involve the formation of oxygen bonds at the clay surface. Since the dominant copper species in solution will be the Cu(II) ion this metal will also be able to test nonspecific binding mechanisms controlled by electrostatic attraction.

Kaolinite is chosen as the model clay for this study because compared to other clay types it can be obtained in a form which is usually well crystallized and free of impurities. The kaolinite structure and chemistry have been well characterized. Kaolinite's structure does not swell because the interlayer regions of this clay are not hydrated with water molecules. Therefore, the sorption process will not be complicated by a large percentage of cations slowly diffusing into the interlayer regions. Kaolinite is a 1:1 clay whose structure consists of layers made up of one Si sheet in tetrahedral coordination and one Al sheet with a gibbsite structure. Other clays such as illite and montmorillonite have a 2:1 type structure with two tetrahedral sheets sandwiching one gibbsite sheet. The ideal composition of kaolinite is $Al_4Si_4O_{10}(OH)_8$. Kaolinite compositions do not vary greatly from the ideal and since there is not very much isomorphous substitution the kaolinite structure has a low negative charge imbalance compared to the other clays. Therefore, kaolinites have a low cation exchange capacity (typically 1 meq/100 g) with respect to other clays such as montmorillonite which may have exchange capacities over 100

meq/100 g. Although kaolinite has a lower exchange capacity and a 1:1 type structure it does share common surface types with the other clays. These surface types include the unreactive basal oxygens of the tetrahedral layer (kaolinite faces), the broken bonds of the tetrahedral sheet (edges), and the broken bonds of the octahedral layer (edges). The other clays display these surface types in different proportions compared to kaolinite. If the proportions of these surface types exposed on the other clays are known and if the sorption properties of these surface types are characterized on kaolinite then the sorption properties of the other clays could also be predicted. Therefore, the strategy of this study will be to examine the sorption mechanisms of a well characterized clay with the aim of using these results to predict sorption behavior on other clays.

GENERAL SORPTION PROPERTIES

The purpose of this section is to outline some general properties of metal sorption and some factors which should be considered in experimental design. Any sorption theory must be consistent with all the observed sorption properties. The sorption of metals is very pH dependent with sharp increases in adsorption between pH 5 and 8 (O'Connor and Kester, 1975; Payne and Pickering, 1976; and Farrah and Pickering, 1977). This sharp increase in sorption over a narrow pH range has been called the sorption edge. At very high pH sorption may decrease again because of the formation of soluble hydroxyl species. The effect of pH appears to be greatest for kaolinite and illite, and less for montmorillonite. The pH may affect sorption by (1) the effect

of H^+ as a counter ion in nonspecific adsorption, (2) the dependence

of some surface charges on pH, (3)the dissolution of Al at low pH, and

the effect of H^+ on the complexing capability of surface sites and the

precipitation of hydroxides. The presence of complexing ligands will

complicate sorption reactions, particularly their relationship to pH

(Farrah and Pickering, 1977). Ligands can reduce sorption by keeping a

metal in solution or they may enhance adsorption if the ligand has an

affinity for the surface.

The sorption of trace metals is reduced in the presence of salt

solutions, but it is not eliminated (O'Connor and Kester, 1975 and

Garcia-Miragaya and Page, 1976). As the salt concentration is increased

trace metals held by nonspecific electrostatic forces will be displaced

by the major salt cations. The amount of divalent metal ion held by

nonspecific sorption in the presence of a salt solution can be predicted

(Babcock, 1963). If the quantity of sorbed metal exceeds this predicted

value, as in the case of trace metals in sea water, then specific

chemical sorption must be significant. Sea water can also reduce the

sorption of a metal if the metal is complexed by the chloride ion such

as in the case of Cd.

Sorption is also a function of sorbate concentration as

illustrated in figure I-1. In some cases if the metal concentration is

very low or if the concentration range of interest is not large, the

amount of sorbed metal may increase linearly with metal concentration in

solution. In this simple situation the sorption isotherm can be

described by a distribution coefficient given by the ratio of sorbed

metal to metal still in solution. Distribution coefficients have been

used to describe metal sorption in marine sediments (Aston, 1973) and on

clays when the metal concentration is low (McLaren, 1981, and Inskeep

and Baham, 1983).
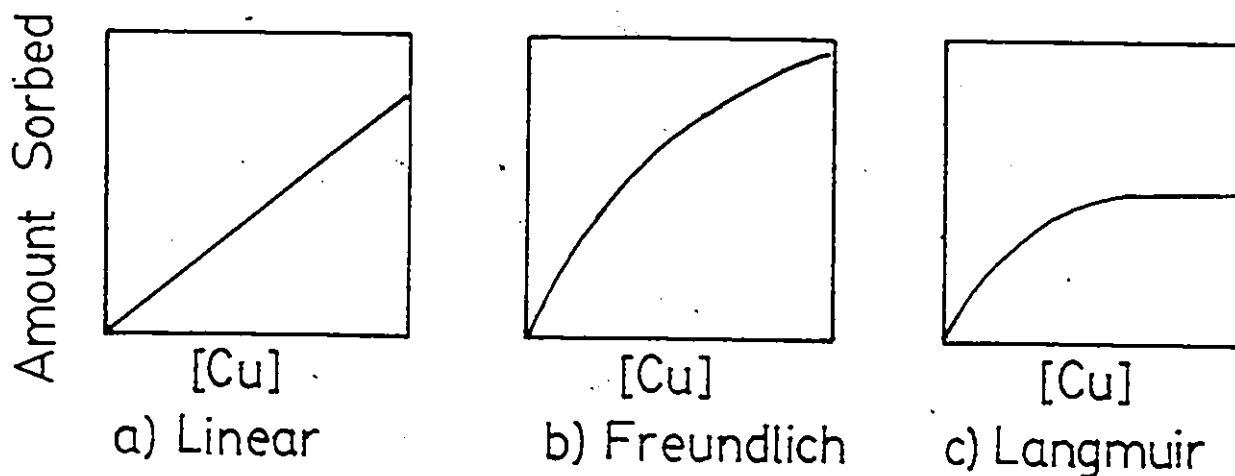
Figure I-1. Adsorption isotherms. a) linear distribution coefficient.
b) Freundlich. c) Langmuir.

When sorption on clays is measured over a wider range of metal

concentrations it is often found that the amount of sorbed metal is no

longer linear with metal concentration in solution (figure I-1b).

Sorption isotherms which are curved and do not reach a sorption maximum

can be described by the empirical Freundlich equation. Some

applications of Freundlich isotherms describing metal sorption on clays

are given by Inskeep and Baham (1983), Heydemann (1959), and

Garcia-Miragaya (1976). Sometimes when the metal concentration in

experiments is high an adsorption maximum is reached, after which higher

concentrations of metal in solution do not lead to more sorption (figure

I-1c). These isotherms often can be described by the Langmuir equation

which includes a term for the sorption capacity and a constant which

represents the energy of sorption. Applications of Langmuir equations
are given by McLaren et al. (1973), Guy et al. (1974), Du Plessis et al.
(1971), Ferrell et al. (1978), Payne and Pickering (1975), and Harter
(1979). The Langmuir equation can be expanded to include several sites
with different sorption capacities and binding constants, and it can
account for competition between different ions (Steger, 1973). Appendix
I is a summary of various mathematical models used to describe sorption
isotherms.

There are other factors which should be considered when designing
and interpreting sorption experiments. Surface area is very important
to sorption because the amount of area at the interface ultimately
determines the quantity of sites available for adsorption. Surface area
is determined by a mineral's crystallinity, surface morphology and grain
size. Therefore one has to make sure that experiments refer to similar
surface areas before differences in measured sorption are attributed to
other surface properties. It has been observed that the concentration
of sorbed metals decreases as the concentration of solid particles is
increased, particularly in suspensions with low solid/liquid ratios.
Our choice of experimental solid/liquid ratio is limited by the need to
have enough solid to produce a measurable change in solution metal
concentration. In salt solution clay particles coagulate into flocs
which may affect the sorption process by either blocking sorption sites
or by enhancing sorption by raising metal concentrations in the
interstitial water of the clay floc. Another problem encountered by
sorption studies on clay minerals is the purity of the clay sample. It
is possible that sorption is masked by the presence of surface oxides of

Fe, Mn or Al and/or surface complexing ligands (Jenne, 1977 and Lim et al., 1980). Procedures have been developed for removing some impurities (Ostram, 1961; Fordham, 1969 and Anderson and Jenne,1970), but in some cases severe treatments can alter the clay surface and create new sorption sites.

TABLE I-1

FACTORS IMPORTANT TO SORPTION REACTIONS

	Parameter	Comment
1)	pH	Strong increase in metal sorption in the mid pH range.
2)	sorbate concentration	Depending on the concentration the increase in sorption can be linear or nonlinear with concentration.
3)	surface area	Determines the amount of available surface sites.
4)	salt concentration	Reduces nonspecific sorption.
5)	complexing ligands	Can reduce or enhance sorption.
6)	clay purity	Surface impurities can mask sorption.
7)	clay pretreatment	Can standardize a surface, but can also produce artifacts. Sorption results can be affected by the amount of time the clay is conditioned in the experimental ionic medium.
8)	flocculation	effects uncertain
9)	solid/liquid ratio	Can affect sorption at low solid concentration

Table I-1 summarizes some of the parameters which must be considered in experimental design and which must be consistent with any sorption theories.

It has become apparent that sorption is not a simple process, and there are differing views as to which mechanisms control sorption properties. For example, McBride (1976) demonstrates that in his experiments Cu sorbed on kaolinite is mobile and is held by electrostatic attractions, while Farrah and Pickering (1976) suggest that in their experiments Cu may be taken up by kaolinite by a surface induced precipitation. This is probably a good example of how experiments carried out under different conditions can emphasize different sorption mechanisms and lead investigators to come to differing conclusions regarding the sorption of a given metal on a certain mineral.

Ideas on the sorption mechanisms of metal ions fall into several general categories. Most solid surfaces carry some sort of charge resulting from either ionic substitutions in the structure or through surface reactions. Therefore, the coulombic attraction of ions by charged surfaces has received a great deal of attention and has resulted in considerable use of the Gouy-Chapman theory of the diffuse double layer and the Stern theory of a sorbed surface monolayer. Coulombic attraction is considered to be an important mechanism in cation exchange reactions. There had been great hope that sorption models based on coulombic attraction would have had great predictive power. However, in many cases it became obvious that coulombic attraction cannot be the driving force since trace metals can be sorbed in the presence of

concentrated salt solutions and positively charged metals can sorb onto positively charged goethite. These observations are evidence for the existence of chemical sorption reactions which are specific to certain metals. These specific chemical interactions with the surface may involve complexation to surface sites or may result from surface induced precipitation reactions. It has been observed that some metals can become fixed by soils or clay minerals. To explain this phenomenon it is necessary to call upon some irreversible surface reaction or to a penetration of the mineral structure, making the metal inaccessible to mild acid treatment or complexation with strong ligands in solution. Other sorption processes which involve combinations of the above mechanisms include sorption in the interstitial waters of clay flocs and diffusion into capillaries of porous solids.

METHODS OF STUDYING SORPTION MECHANISMS

Many approaches have been used in order to define sorption mechanisms. One approach is to come up with theoretical models which can rationalize sorption responses to changes in pH, salt level and sorbate concentration. Some studies have compared the relative affinity of some ions for given surfaces and proposed models which can explain this affinity in terms of chemical differences between the competing ions. Another approach assumes that the type of sorption isotherm, or the changes in the slope of the isotherm will tell us something about the mechanism or mechanisms involved. This has led to the development of mathematical models which try to recreate sorption isotherms on the basis of one or more surface sites. Sometimes these models indicate the

existence of several surface sites, but unfortunately these mathematical models do not prove the existence of given mechanisms because the same sorption isotherms can be reproduced by more than one model (Morel et al., 1981). However, a more rigorous evaluation of sorption mechanism is obtained when sorption isotherms are considered together with the effects of varying physical parameters such as pH and salt concentration.

There are other approaches for looking at mechanisms which do not measure the amount of sorbed metal, but instead look at changes in the metal's bonding environment or the effect of sorption on the clay's structure. X-ray diffraction (XRD) has often been used to study the effect of cation exchange on the interlayer spacing of montmorillonites and vermiculites (Grim, 1968). Infrared spectroscopy (IR) has been used to study the changes in the orientation of clay hydroxyls as the octahedral layers are penetrated by sorbing cations (McBride et al., 1974). Electron spin resonance spectroscopy (ESR) has been used to study the bonding environment of adsorbed copper. McBride (1976), used ESR to show that Cu loaded onto kaolinite existed as square planar complexes which could move freely on the surface. On the other hand Cu sorbed onto Al hydroxides was shown to be either bonded to surface oxygens or was precipitated at nucleation centers (McBride, 1982, McBride et al. 1984). Although XRD, IR, and ESR can tell us something about the bonding environment of a sorbed metal they may not be applicable to trace element systems because these techniques require a heavy metal loading on the clay surface to create measurable changes in the mineral's structure and to have enough copper present for ESR work.

To perform any measurements the clay must be separated from the suspension and partially dried. The bonding conditions for a trace metal in a clay suspension may be totally different from those in a partially dried clay plug that has been saturated with metal.

Kinetic studies are another approach to the study of sorption mechanisms. Most studies have ignored kinetics except for some consideration of equilibrium time. Some researchers have looked into the kinetics of sorption processes in order (1) to determine equilibrium times, (2) to measure sorption rates to be used in dynamic environments where equilibrium cannot be reached, and (3) to investigate sorption mechanisms. (Kurbatov,1949; Ahrland et al., 1960; Fordham, 1970; Fruh and Lee, 1967; Malcom and Kennedy, 1969; McKenzie, 1972; McBride, 1982; Inskeep and Baham,1983, and Harter and Lehman, 1983). From these studies it appears that sorption rates can be very fast (seconds) if they involve simple ion exchange, or they can be very slow (months) if surface precipitation is involved. The more detailed kinetic studies indicate that sorption may result from a combination of several fast and slow reactions.

WHY USE KINETICS IN SORPTION STUDIES?

A reason for studying sorption and desorption kinetics is that detailed kinetic studies of metal sorption on clays are lacking. However, the best reason for using kinetics is that a kinetic approach may give us valuable insight into sorption processes which classical methods of studying sorption do not. Most approaches to sorption studies are essentially equilibrium studies which can be handled by

thermodynamics. Thermodynamics compare the energetics of the products
and reactants without considering any of the steps between the
transformation of product to reactant.

.Measured rate constants and activation energies can act as
fingerprints for certain reaction types. Nonspecific sorption and
simple cation exchange are limited only by diffusion so that they have
very fast reaction times ranging from instantaneous to several seconds.·
Surface precipitation reactions may last from hours to days, while
penetration of the mineral structure or some surface fixation reactions
may last from days to months. Activation energies for diffusion in water
will be less than 21 KJ/mole, while more difficult reactions controlled
by solid state diffusion may have activation energies as high as 502
KJ/mole. When a reaction results from a combination of steps or
elementary reactions then the arrangement of these steps will determine
the kinetics. For example, if the elementary reactions are consecutive
then the overall rate will be determined by the slowest step. If the
reactions are parallel then the fastest steps will control the overall
rate.

If kinetics are considered in light of the effects of physical
parameters such as pH, metal concentration and salt level, and if the
structure and chemistry of the system is rigorously defined then
considerable insight might be gained into the mechanisms of metal
sorption on clay minerals.

STATEMENT OF PURPOSE:

The purpose of this study is to improve our power to predict
sorption reactions by resolving sorption mechanisms with a kinetic
approach and relating the observed mechanisms to kaolinite
crystal-chemical properties.

OBJECTIVES:

The following are the principle objectives of this thesis.

1) Identify the number of mechanisms responsible for Cu^{+2}
sorption. Sorption kinetics and a close examination of an ideal
kaolinite grain indicates the existence of several potential
sorption mechanisms. The existence of several sorption processes
may change our concepts of equilibrium and of modeling sorption
reactions.

2) Relate the observed sorption kinetics to the crystal-chemical
properties of kaolinite. The sorption reactions resolved by
kinetics must be linked to kaolinite structure and chemistry. This
is fundamental to understanding sorption mechanisms. Once these
links are established we can predict metal sorption on kaolinite
minerals under a variety of conditions, and since other clays have
similar structures we can relate our sorption concepts to them.

3) A very important and practical distinction to make is whether
nonspecific coulombic mechanisms contribute significantly to
sorption or whether only specific chemical type reactions are
important. These two classes of sorption mechanisms have distinctly
different properties.

4)   Establish the identity of specific chemical sorption reactions. Specific chemical reactions may include surface coordination, surface induced precipitation, and structural penetration. The type of sorption mechanism will determine the rate of the sorption reaction, the sorption capacity and the desorption characteristics.

5)   Study the _reversibility_ of Cu sorption. Reversibility is an extremely important aspect of sorption, and it is often overlooked in the measurement of sorption reactions and in the application of measured adsorption isotherms. Reversibility is a key factor in crop nutrition, as well as the disposal of toxic wastes. Aside from these practical considerations, reversibility is a useful tool for studying sorption mechanisms because desorption studies indicate the strength of the bonds which most be broken to remove Cu from the surface.

6)   Rationalize the effect of experimental factors such as _coagulation_, _solid/liquid ratio_, and _centrifuging_ on sorption reactions. It has been noted that sorption decreases with increasing solid/liquid ratios, and no reasonable theoretical explanation has been presented to account for this phenomenon. In salt solutions clays tend to coagulate and form clay flocs. Although this process may alter sorption the effect of floculated clay has been ignored in sorption studies.

APPROACH:

(1)   Chemical kinetics are used to resolve sorption reactions with the assumption that different mechanisms have different reaction rates. Cu sorption is monitored as a function of time and the data are plotted as the logarithm of sorbed copper versus time in order to identify pseudo-first-order reactions and their rate constants. In order to reduce reaction rates to pseudo-first-order, parameters such as Cu^{+2}, pH, temperature and ionic strength are kept constant.

(2)   The apparent sorption mechanisms resolved by sorption kinetics must be evaluated in light of potential reactions which can be predicted from fundamental chemical and physical properties of the kaolinite suspension. In order to do this it is necessary to look at kaolinite structure. The type and bonding properties of atoms found at a kaolinite surface are determined by the crystal structure and the manner in which the exposed surface cuts the structure. Sorption mechanisms can be postulated by considering the properties of Cu^{+2} ions in solution and their ability to interact with the various surface types of an ideal kaolinite grain. The interactions between kaolinite grains in suspension may also be considered when predicting sorption mechanisms.

(3)   To evaluate the relative importance of specific sorption one must look at the effects of experimental parameters on Cu sorption. The theoretical amount of Cu^{+2} which can sorb by nonspecific coulombic attraction can be calculated for the experimental Cu^{+2} and salt concentration, and the kaolinite's cation exchange capacity. Observed Cu sorption which is in excess of the predicted Cu sorption must represent specific adsorption. A relatively high sorption dependence on pH

distinguishes specific sorption from coulombic sorption which should be independent of pH on minerals dominated by a constant charge. Finally the results of the desorption studies indicate whether strong bonds must be broken to achieve desorption or whether the limiting factor is only diffusion as in the case of nonspecific sorption.

(4)   The various specific sorption mechanisms can be identified with the help of sorption kinetics, desorption, and with carefully chosen experimental conditions. Structural penetration can be distinguished by its resistance to desorption and its slow sorption kinetics, lasting for a month or more. Surface complexation may be faster (seconds) than surface precipitation (minutes to hours) and it may be less prone to desorption at constant pH. The ratio of H^+ desorbed per Cu adsorbed can be used to distinguish between surface complexation and induced precipitation.

(5)   The amount of Cu which is desorbed depends upon the method used to reverse the sorption process. If the Cu is completely reversible as predicted for nonspecific adsorption then a dilution of the solution Cu reduces the sorption to a level where the clay shows no signs of having been exposed to higher concentrations of Cu. Cu sorbed by nonspecific sorption is very sensitive to desorption induced by increasing the salt level. Operationally, copper which has formed strong bonds with the surface can be be removed by a strong Cu complexing ligand or by acidifying the system to pH 2 or 3. Cu which has penetrated the clay structure is not available to desorption and is therefore fixed. The kinetics of the desorption process can give some indication of the number of desorption mechanisms.

(6)   The achievement of objective 6 will require an understanding of
some of the basic sorption mechanisms identified through objectives 2
and 5. The effects of centrifuging, coagulation and changing
solid/liquid ratio may be related in that they involve changes in
solid-solid interaction and increases in local clay concentration
(formation of a clay floc). The induced sorption due to centrifuging is
characterized and then an analogy is made between a clay floc and a
centrifuged clay plug covered with the supernatant solution. Theories
which try to explain the effect of solid/liquid ratio on sorption are
evluated in light of (1) observations made during centrifuge
experiments, (2) sorption kinetics and (3) the crystallinity of the
solid.

CHAPTER II

KAOLINITE STRUCTURE AND POTENTIAL SORPTION MECHANISMS

INTRODUCTION:

Ideally we should have the capability of predicting sorption on
any mineral from its surface properties. Unfortunately the true surface
interactions with the liquid are difficult to look at directly and must
be inferred from the overall effects on solution composition. Since we
cannot directly see the atoms exposed at the solid interface we must
predict the character of the interface from something else such as the
crystal structure. Surface properties must be directly related to
mineral structure because the solid interface is merely an interruption
of this structure. As pointed out by Devore (1963), the way in which a
surface cuts the crystal structure will determine the composition and
properties of the solid/liquid interface. This is true for the sheet
silicates whose composition along the 001 plane can be drastically
different from the composition at any edge face, cutting the main
structural sheets at right angles. Once we have derived surface
properties from the crystal structure we should be in a position to
predict potential sorption mechanisms onto the mineral's surfaces. The
next task is to test the predicted mechanisms and to establish whether
or not our concept of the surface is valid. Once we have linked sorption
properties to crystal structure for one clay mineral we can export these
concepts to other clay systems and predict sorption properties.

The purpose of this chapter will be to first review the crystal structure and chemistry of kaolinite and to look at their influence on the surface properties of various kaolinite faces. The next part of this chapter will discuss potential sorption mechanisms which can be predicted from surface properties. The principle sorption mechanisms which can be predicted include nonspecific coulombic adsorption, specific chemical sorption in the form of surface complexation and induced surface precipitation, and penetration of the kaolinite structure. Another form of Cu sorption which may involve some of the above mechanisms is excess sorption due to the formation of kaolinite flocs. The properties of these sorption mechanisms are outlined in the final summary section at the end of this chapter. The reader may refer to this section to avoid reading this chapter or to get an overview before starting to read this chapter.

STRUCTURE AND CHEMISTRY OF KAOLINITE:

The main structural sheets of clay minerals are made up of layers of octahedrally coordinated aluminum or magnesium which are attached to sheets of tetrahedraly coordinated silica and aluminum. Since these octahedral and tetrahedral sheets are the basic building blocks of clays they will be first described individually.

The basic octahedral sheet is usually made up of Al or Mg (with minor Fe) which are in octahedral coordination with six hydroxyls (figure II-1a). If aluminum is the main component the octahedral sheet has a gibbsite structure with a composition of $Al_2(OH)_6$. Gibbsite is monoclinic with a 2/m symmetry. It is dioctahedral because only two

of every three octahedral sites are occupied by aluminum. Magnesium

octahedral sheets have a brucite structure with a composition of

$Mg_6(OH)_6$. Brucite is trigonal with a $\bar{3}$ 2/m symmetry. Since all

three octahedral sites are filled brucite is trioctahedral. The average

distance between hydroxyls in each octahedron is 2.94 angstroms. The

maximum radius of the cation which can fit into the space between the

hydroxyls is about 0.61 angstroms. The Pauling radii of Al^{+3} and

Mg^{+2} are 0.50 and 0.65 angstroms respectively. In a gibbsite sheet

the alumina are arranged in hexagons (figures II-3c and II-3d).
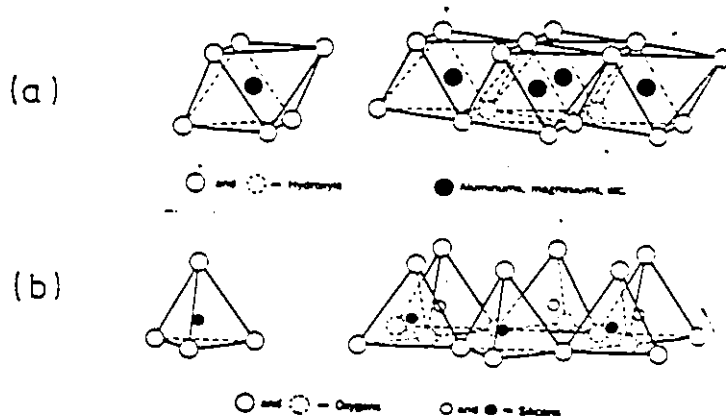
Figure II-1. The basic structural components of clay minerals. (a)A
single octahedral unit and the sheet structure of the octahedral units
(Grim, 1968). (b)A single silica tetrahedron and the sheet structure of
silica tetrahedrons arranged in a hexagonal network (Grim,1968).

The tetrahedral sheet is made up of Si, with some Al, in

tetrahedral coordination with four oxygens (or hydroxyls). A single Si

tetrahedron (figure II-1b) will probably be coordinated to four

hydroxyls in an aqueous medium, except at pH's above 9. When $Si(OH)_4$

tetrahedra attach to other tetrahedra the oxygens which they share lose

their H^+. Therefore, when the tetrahedra have formed into a hexagonal

sheet (figures II-1b and II-2), the bases of the tetrahedra will contain

oxygens while the apices may contain hydroxyls, unless they are

coordinated to another silicate structure through oxygen. The

composition of a tetrahedral sheet is $Si_4O_6(OH)_4$. In a

tetrahedron the average distance between oxygens is 2.55 angstroms,

which allows a cation with a maximum radius of 0.55 angstroms into

tetrahedral coordination.
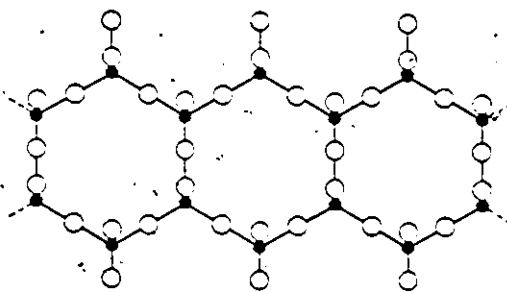
Figure II-2 Double chain of silica tetrahedrons projected on the plane
of the base of the tetrahedrons. (Grim, 1968)

When an octahedral sheet becomes attached to a tetrahedral sheet

two out of five octahedral hydroxyls are converted to oxygens which are

shared by the apex positions of the tetrahedral sheet (figure II-4). If

the hexagonal cell of the tetrahedral layer is considered as a

rectangular cell with a and b dimensions, the theoretical value for b

can be calculated as 9.05 angstroms. The observed b dimension for

kaolinite is 8.95 angstroms, while for micas and chlorite it ranges from

9.2 to 9.3 angstroms. The b parameter for the octahedral framework is

calculated to be 8.01. Therefore, in order to fit the octahedral and

tetrahedral frameworks together there must be severe departures from

ideal geometry. To fit the sheets together the following things could

happen (Radoslovich and Norrish, 1962): (1) The hexagonal rings are

distorted by rotating tetrahedron (figure II-3). (2) The otahedral
layer is expanded causing a reduction of its thickness and changing the
size of octahedral sites. Dioctahedral layers are more severely
distorted. The cell dimension of the octahedral layer corresponds to an
equilibrium between (1) cation-cation repulsion across shared octahedral
edges, (2) anion-anion repulsion along shared edges and (3) cation-anion
bonds within octahedra.
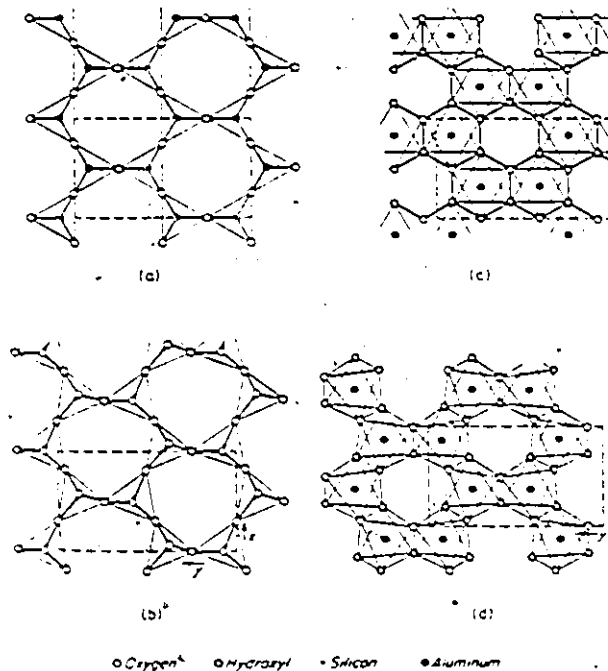
Figure II-3. Distortions in tetrahedral and octahedral layers produced
when these layers are joined in kaolinite minerals (Brindley, 1961).

The kaolinite minerals consist of layers made up of a single
tetrahedral and a single octahedral sheets joined by common oxygens
contained in a plane (figure II-4). The layers may be held together by
hydrogen bonding between the basal oxygens of the tetrahedral sheet in
one layer and the octahedral hydroxyls of the   t layer. The region
between kaolinite layers is not hydrated.
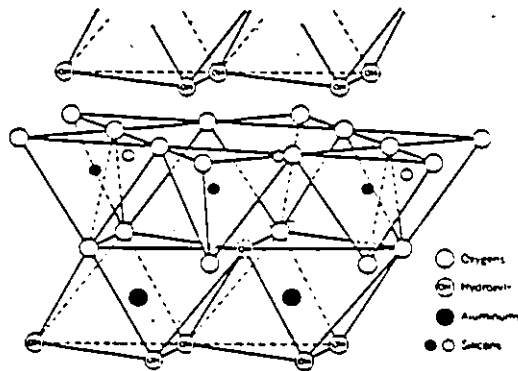
Figure II-4. Structure of a kaolinite layer. (Grim, 1968)

Since the octahedral cations are chiefly aluminum, kaolinites are

dioctahedral. Figure II-5 shows the arrangement of the three octahedral

sites with respect to a hexagonal ring of the tetrahedral sheet. In a

true kaolinite successive octahedral layers have a vacancy in the same

position C (or B). This leads to a triclinic structure. In poorly

crystalline kaolinite the location of the vacant site may vary. Dickite

differs structurally from kaolinite because the vacant site alternates

regularly between C and B in successive layers. This produces a two

layer monoclinic superstructure. Dickite could be viewed as a regular

alternation of right and left-handed kaolinite layers. In the natural

environment kaolinite may consist of a collection of variously deformed

individuals. Another kaolinite mineral is anauxite whose unit cell

consists of six kaolinite layers. It has a c spacing of 43 angstroms.

(Kaolinite's c dimension is 7.15 angstroms.)
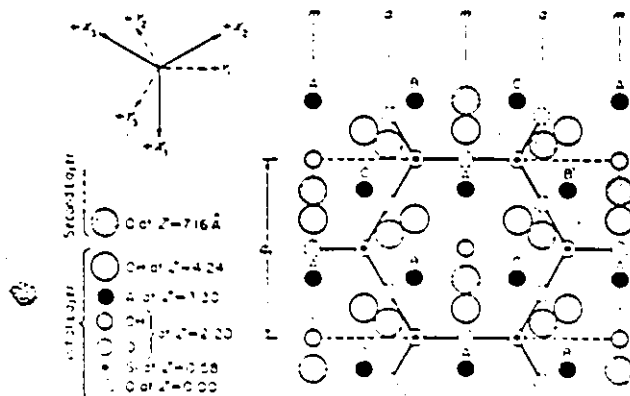
Figure II-5. Normal projection onto (001) of and undistorted 7 angstrom layer of space group Cm. The three possible octahedral sites are labeled A, B, and C. (Grim, 1968)

Anauxite has a very high silica to alumina ratio. It may consist of kaolinite layers sandwiching units of double silica tetrahedral sheets. The double tetrahedral layer is held together by sharing apex oxygens. These sheets fit well with the kaolinite sheets because of their similar size.

Kaolinite may acquire a permanent charge when Al^{+3} substitutes for Si^{+4} in the tetrahedral layer and when minor amounts of Mg^{+2} replace Al^{+3} in the octahedral sheet. Some researchers believe that it could also have a variable charge on some parts of its surface. The basal oxygens of the tetrahedral layer would not have a variable charge because their bonding is fully satisfied and they would have no tendency to acquire a hydrogen ion. However, when the octahedral and tetrahedral layers are interrupted at edges unsatisfied bonds are created. To satisfy these bonds H^+ will coordinate with exposed oxygens at edge sites creating a variable charge surface. The hydroxyls on the surface of an exposed octahedral sheet may also have a tendency to deprotonate

but their amphoteric behavior will not be the some as those hydroxyls exposed at edges.

The structural composition of kaolinite is $Al_4(Si_4O_{10})(OH)_8$, which gives an ideal composition with 46.54 % SiO_2, 39.5 % Al_2O_3, and 13.96 % H_2O. Kaolinites usually contain excess SiO_2 or Al_2O_3. Langston and Pask (1969) showed that excess SiO_2 was present as amorphous silica (readily soluble) bonding kaolinite flakes together. Amorphous silica was believed to range from 0.2 to 27.5 %. Excess Al may substitute in the tetrahedral sheet, but it may also be adsorbed on surfaces as a hydroxide. Kaolinites also contain small amounts of Fe_2O_3, TiO_2, MgO, CaO, K_2O, and Na_2O. Mineral impurities include quartz, anatase, rutile, pyrite, limonite, feldspar, mica, montmorillonite, and various iron and titanium oxides. Mineral impurities such as anatase can be flocculated or dispersed independently of kaolinite. Therefore, laboratory pretreatment will have an effect on the amount of mineral impurities remaining with the clay. Iron may be present in iron oxides, pyrite, iron titanium complexes, and in the kaolinite structure as suggested by leaching experiments. Magnesium may be present in biotite, Fe-Ti oxides, or it may be adsorbed. Other exchangeable surface cations include H^+, K^+, Na^+, and Ca^{+2}. It is possible that surface impurities such as montmorillonite and various oxides or hydroxides may significantly contribute to kaolinite's cation exchange capacity and surface charge.
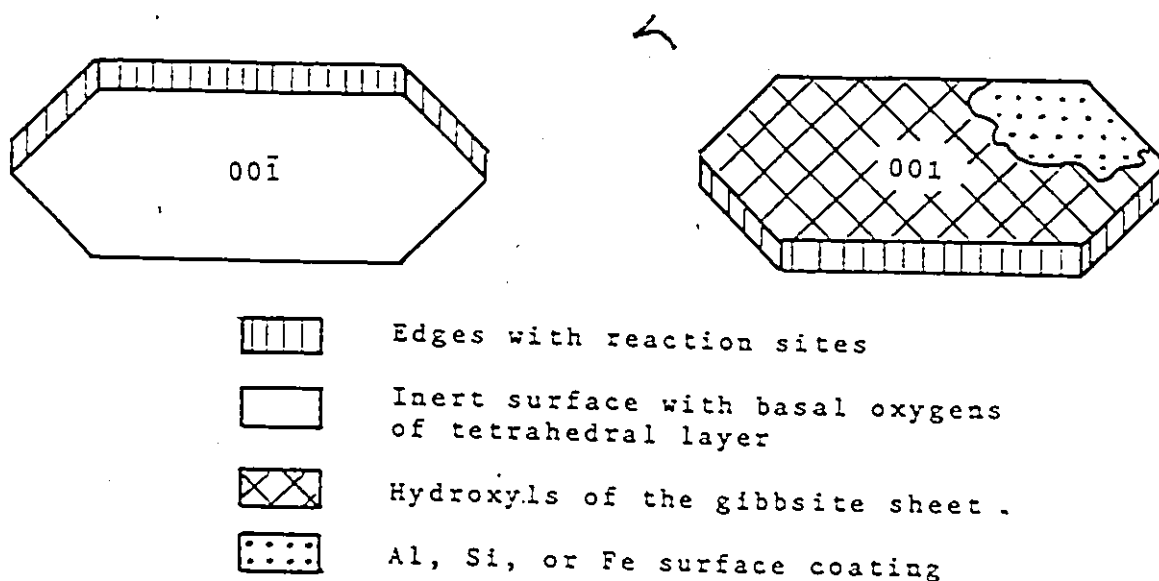
Figure II-6. Kaolinite morphology and surface types.

Often kaolinite can be found as well crystallized pseudohexagonal grains as shown in figure II-6. The main structural sheets run parallel to the upper and lower faces. Therefore, these surfaces are made up either of the inert basal oxygens of the silica layer or the relatively inert hydroxyls of the gibbsite layer. The edge faces interrupt the main structural sheets so that the edges become a chemically active surface with exposed oxygens or hydroxyls which are coordinated to Si or Al. Since the hydroxyls at the edges are coordinated to only one Al or Si they are more reactive than the hydroxyls on the upper or lower surfaces which are coordinated to two Al (McBride, 1982; Parfitt, 1978). On the edges hydroxyls joined to Si will have different properties than those attached to Al. The surfaces of kaolinite grains can be further complicated by the presence of adsorbed oxides and hydroxides of Fe, Al, and Si. Since the behavior of exposed Al and Si layers at the edges is similar to their respective hydroxides, the presence of adsorbed Al and

Si hydroxides will increase the apparent surface area of edge type sites. Sorbed Fe impurities can be more easily identified than Al of Si coatings and can be removed.

NONSPECIFIC COULOMBIC SORPTION:

Most mineral surfaces which are immersed in water, carry some sort of charge. If the charge is positive it will be compensated by anion adsorption at the surface, and if it is negative cations will be adsorbed. This simple type of coulombic attraction has been used to account for many reversible cation exchange reactions. It is also the underlying principle of more complicated models which describe ion accumulation as a function of distance from a charged surface. These models have been used to explain the floculation behavior of clay suspensions (Stumm and Morgan,1981), the effect of surface charge on surface coordination reactions (Schindler, 1972; Hohl, 1976), electrophoric mobilities, osmotic pressures, surface conductances and membrane potentials (Van Olphen, 1977).

Coulombic adsorption is probably very important for group IA and IIA elements which do not form very strong oxygen bonds in most aqueous environments. Even though coulombic attraction may not be very important for the transition elements its effects should not be overlooked. Therefore, the purpose of this discussion will be to evaluate the causes and properties of coulombic adsorption on kaolinite.

The kaolinite surface may acquire a charge either from a permanent charge imbalance in the structure or from potential determining reactions at surface sites. A negative charge imbalance in

the structure can result from the substitution of small quantities of Mg^{+2} for Al^{+3} in the octahedral layer or from the replacement of Si^{+4} by Al^{+3} in the tetrahedral layer. Kaolinite analysis show only small amounts of Mg (Deer et al., 1962) so that any negative charge resulting from isomorphous substitution in the octahedral layer will not be large. The amount of Al substituting for Si in the tetrahedral layer is difficult to determine because this Al cannot be distinguished analytically from Al in the octahedral layer. One could try to estimate the structural charge imbalance by doing a normative calculation which places all the Si in the tetrahedral layer and which makes up any deficiency with Al. Another way of estimating the charge on a clay from its composition is to add up all the cations (Na, K, Mg, Ca) which are likely to neutralize the surface charge and hope that the hydrogen ion did not make a significant contribution to charge neutralizing ions.

The charge on a clay surface will be determined by the charge in the structure if the atoms at the surface do not interact with the solution to produce a different charge. On kaolinite this condition is fulfilled at those upper or lower faces which consist of the inert basal oxygens of the tetrahedral layer. Hydroxyls from the gibbsite layer which are exposed at the upper or lower faces may also satisfy this condition. On the other hand, the edges of the kaolinite grains contain broken bonds resulting from the interruption of the gibbsite and silica sheets. Once exposed to water the reduced coordination of oxygen atoms at the surface will be quickly satisfied by coordinations with one or two hydrogen ions. Any exposed silica or alumina will coordinate with oxygen in water molecules. In either case we will end up with a surface

containing oxygens which can coordinate with one or two hydrogen ions.
If this surface is dominated by oxygens with two hydrogens then it will
be positively charged. If no hydrogens are found on the oxygens a
negative charge will result. If only one hydrogen is found on each
oxygen or if the positive and negative sites are equal then no charge
will result. (See figure II-7)
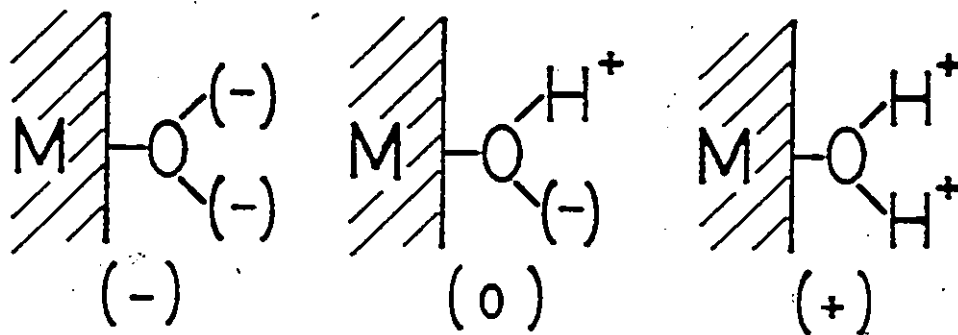
Figure II-7. Development of surface charge on a variable charge
surface by reactions with the hydrogen ion.

Since the kaolinite edges are made up of alternating silica and
aluminum layers one would expect that any variable charge developed
there could be predicted by mixing the charges of silica gel with that
of gibbsite, both of which have been determined independently. Above pH
2.5 silica is negatively charged, so that the edge surface of the silica
sheet should carry a negative charge under most natural pH conditions.
Only the edges of the silica sheet can have a variable charge since the
bonding of the basal oxygens is satisfied and in kaolinite the apex
oxygens are attached to the gibbsite layer. Gibbsite carries a net
positive charge below pH 9.7 to 10. The positive charge probably
originates at the edges of the gibbsite layers where the hydroxyls are
coordinated to only one Al. Above pH 10 the surface hydroxyls will begin

to lose their H^+ and gibbsite will acquire a negative charge. At such

high pH's it might be possible for the hydroxyls on the gibbsite

(kaolinite) 001 faces to lose their H^+ and give these surfaces an

increased negative charge.

Follet (1965) has attempted to locate positive and negative

charges on the surfaces of kaolinite grains. He used electron

micrographs to show that positively charged ferric hydroxide sols

adsorbed on the faces of kaolinite grains. Negatively charged gold sols

adsorbed only on the edges of kaolinite grains. Therefore, the faces

appear to be dominated by a negative charge as predicted by the

structure. The sorption of gold sols on the edges suggests that they

are dominated by a positive charge from the gibbsite layer. The

predicted negative charge contribution from the silica layer appears to

be ineffective, at least in repulsing negative gold sols. The charge

distribution on a kaolinite grain is summarized in figure II-8.
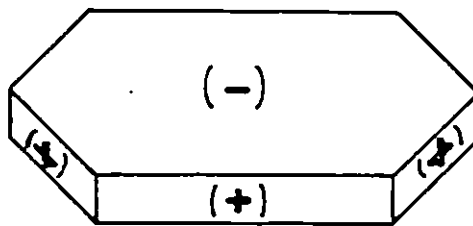
Figure II-8. Charge distribution on a kaolinite grain.

Positive and negative charges on mineral surfaces can also be

estimated by measuring the adsorption of index anions and cations. It

is essential that the chosen index anions and cations participate in

only coulombic adsorption. If the negative charge is constant and

independent of solution composition then the observed negative charge,

as determined by the index cation, will not vary with pH. Flegmann et
al. (1969) used Na^+ and Cl^- to measure surface charge on Cornish
kaolinite from pH 4 to 10. They concluded that the kaolinite possessed
2 meq/100 g of permanent charge, as well as a pH dependent charge. On
the other hand, Ferris and Jepson (1975) could not find a permanent
negative charge using ^{22}Na. Bolland et al. (1976) used Na, K and Cs
to measure negative charge on kaolinite, and used Cl^- and NO_3^- to
measure positive surface charge. They found that the adsorption of the
index cation was pH sensitive if the sorption of Al^{+3} was not taken
into account. At pH's less than 6.0 the amount of aluminum dissolving
from kaolinite becomes significant and the Al^{+3} ion starts to
interfere with the adsorption of index cations. To overcome the problem
of aluminum interference one can (1) measure the adsorbed Al and add its
contribution to the index cation, (2)use short adsorption time to reduce
Al dissolution, or (3) use high concentrations of divalent index cations
to swamp the Al effect. Once Al interference was accounted for, Bolland
et al. (1976) found that the measured negative charge on kaolinite was
independent of pH, and ranged from 1.4 to 3.6 meq/100 g on various
kaolinites. The positive charge measured with NO_3^- started around
pH 8 and increased to about 1 meq/100 g at pH 3.5.

According to figure II-9, the Cu^{+2} ion will be attracted by the
negative charge on the upper and lower faces of kaolinite grains. The
distribution of cations around a negatively charged surface can be
described by the Gouy-Chapman theory of the diffuse-double layer, in
some combination with the Stern theory of an adsorbed monolayer at the
surface. (Bolt, 1955, 1955b; Overbeek, 1952; Stern, 1924; Van Raij and

Peech, 1972; Stumm and Morgan, 1981 and Dixon and Weed, 1977). The
diffuse layer and the Stern layer are two distinct regions surrounding a
charged particle (figure II-9). Although cations in both of these
regions may be held by electrostatic forces it is worth while to make
the distinction between these zones because the properties of an ion in
the diffuse layer may be slightly different from an equivalent ion in
the Stern layer. The concept of a diffuse layer in combination with a
surface monolayer is important for surface science because these
theories attempt to describe the transition from a solution to the space
immediately adjacent to the solid interface.
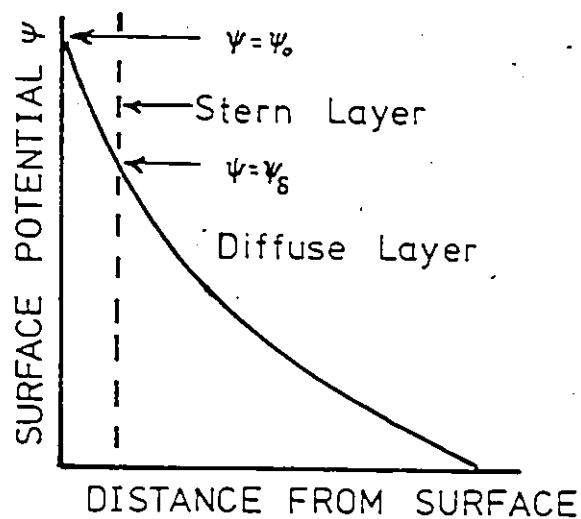
Figure II-9 The diffuse layer and the Stern layer.

The forces acting on cations near a negatively charged surface
include the electrostatic pull of the surface and the kinetic energy of
the cations which tries to pull them away from the surface. As a
consequence of these two opposing forces the ions adjacent to the
surface form a diffuse layer which is known as the electric double

layer. Ions which have the opposite sign as the surface and which balance the surface charge are known as counter ions, while ions which have the same charge as the surface are known as co-ions. The counter ion concentration is maximum immediately adjacent to the surface and decreases away from the surface as described by the Boltzman function (Parks, 1967). Good summaries of equations used to calculate charge distribution in the double layer are given by Stumm and Morgan, 1981 and Dixon and Weed (1977).

The influence of the diffuse layer can extend more than 100 Angstroms away from the solid surface. As the electrolyte concentration is increased or if the salt is changed from a 1:1 to a 2:2 salt then the thickness of the diffuse layer will decrease (20 Angstroms). Once the diffuse layer thickness is decreased clay particles can flocculate more easily because the cations in the diffuse layers of colliding particles are then less effective in repelling the collision. Once clay particles have joined together in flocs their sorption properties can be altered through the action of a Donnan potential. A Donnan potential is created when ions are able to migrate between two regions which have a charge difference. In this case the clay floc has an excess charge compared to the free solution. Therefore, the properties of the diffuse layer not only influence the sorption of ions directly, but they also affect the interaction of fine particles which may indirectly enhance or hinder sorption.

The Gouy-Chapman theory of the diffuse layer does not work for surfaces with very large potentials because the theory does not account for the volume taken up by cations in solution. At high potential

surfaces Gouy-Chapman theory predicts unreasonably high cation concentrations. To overcome this problem Stern (1924) proposed the existence of a surface monolayer in which the total amount of adsorbed ions is restricted by their size and the available surface area. Therefore, Stern theory includes a term for maximum sorption capacity. The Stern layer neutralizes some of the charge on the surface so that the diffuse layer outside the Stern layer must neutralize a smaller charge than is found at the immediate surface. The Stern layer may also contain ions that are bonded to the surface by specific chemical interactions and so Stern theory includes a factor which accounts for specific chemical interactions. This specific chemical term is a convenient fudge factor which can account for any sorption which cannot be explained by a purely electrostatic model.

In the diffuse layer ions are able to move freely as in the free solution, so that there is a minimal entropy decrease with sorption. Therefore, adsorption in the diffuse layer should not be affected by temperature. In the Stern layer ion movement is more restricted, causing an entropy loss during sorption. Consequently less should be adsorbed at higher temperature. In the Stern layer cations must compete for space so that ions with smaller hydrated radii will be preferred. Also, since ions with smaller hydrated radii can approach the surface more closely Coulomb's law predicts that they will be sorbed more strongly. Gouy Chapman theory of the diffuse double layer does not distinguish between ions by any property other than charge. Nonspecific coulombic sorption should be completely reversible because no bonds have to be broken to remove a sorbed ion. Since diffusion is the only rate

limiting step sorption and exchange rates should be very fast. As salt levels are increased any trace cations will be displaced from the surface by the mass action affect of the salt.

Double-layer theory does predict that ions with a higher charge will be preferred over cations of a lesser charge. This property is relevant to the experimental system in this study because Cu^{+2} will have to be sorbed in the presence of a much greater concentration of K^+ ions which make up the background electrolyte. To calculate the amount of Cu^{+2} which can be sorbed by nonspecific coulombic attraction we must be able to determine the relative ability of Cu^{+2} to compete with K^+. Babcock (1963) derives from double layer theory an equation which calculates the fraction of the surface charge neutralized by monovalent ions in a mixture of monovalent and divalent salts.

1) $$\frac{C_1}{C} = \frac{r}{C(B)^{-1/2}} \sinh^{-1}\left(\frac{C(B)^{-1/2}}{r + 4v_d(m_2)^{-1/2}}\right)$$

C_1 = charge neutralized by monovalent cations

C = total surface charge density

$r = m_1/(m_2)^{-1/2}$

m_1 = monovalent salt concentration in bulk solution

m_2 = divalent salt concentration in bulk solution

$B = 8000\pi F^2/DRT$ (when T is 25^0C B = $1.08 * 10^{15}$ cm mole/meq^2)

$F = 2.982 * 10^{-11}$ esu/meq

v_d = cosh y at the midplane between clay particles (assumed to be 1)

Gast, 1977, gives an example calculation with equation 1. Upton Wyoming montmorillonite with a surface charge density of $5.17 * 10^4$ esu/cm^2 is placed in a solution containing 0.004M Ca^{+2} and 0.01216M

Na^+. Even though there is about three times as much Na as Ca, the Na neutralizes only 11 percent of the surface charge.

In summary, coulombic sorption, which is probably located on the upper and lower faces of kaolinite grains, has very rapid sorption and desorption kinetics and is very reversible. It is an important sorption mechanism for group IA and IIA cations which do not form as strong bonds with oxygen as transition metals do. Higher valent cations are preferred, but cations of the same valence have only a slight relative selectivity determined by their hydrated radii. The temperature dependence of nonspecific sorption should be small. In practice it will probably not be feasible to distinguish between nonspecific sorption in the diffuse layer and in the stern layer. Nonspecific coulombic sorption cannot explain the sorption of trace metals in salt solutions.

SPECIFIC CHEMICAL SORPTION:

There are several sorption phenomenon which are not compatible with nonspecific coulombic attraction. For example, positively charged metal ions have been known to sorb onto positively charged goethite at pH's below 7. Since nonspecific coulombic attractions interact with ions as if the ions were point charges without other significant chemical properties, the cations of a salt solution should displace trace cations from surfaces by mass action. Selectivity produced by differences in hydrated radii and by the divalent charge on metals will not be great enough to allow significant nonspecific trace metal sorption in the presence of salt solution. Yet, in this study Cu^{+2} was able to sorb onto kaolinite even in the presence of a 1 molar KNO_3

solution. O'Connor and Kester (1975) were able to measure significant amounts of Cu and Co sorption onto illite in the presence of sea water. Due to this ability of metals to be sorbed in sea water, Jenne (1977) operationally defined specific chemical sorption as "that quantity adsorbed from microconcentrations of the trace element in the presence of macroconcentrations of alkaline earth or alkali cations, and which is largely desorbable by chemically similar elements".

Another feature which is difficult to explain by nonspecific coulombic interaction is the sharp increase in sorption with pH produced in the mid pH ranges. This phenomenon has been described for transition metal sorption on oxides of Si, Al, Fe and Mn by Kurbatov et al. (1951), Dugger et al. (1964), Grimme (1968), James and Healy (1972), Schindler et al. (1975), and Hohl and Stumm (1976). A similar sorption relationship with pH has also been described for clays by Hodgson (1960), O'Connor and Kester (1975), Payne and Pickering (1975), and Farrah and Pickering (1976a, 1976b, 1979). The sharp increase in metal sorption cannot result from a nonspecific competition from H^+ ions because in some experiments metal concentrations (10^{-4} M) greatly exceed hydrogen ion concentration (pH 5 to 7). The sorption jump for different metals occurs at different pH's, which would not be the case if the sorption jump was caused by a change in the surface charge. The cations with the strongest hydrolysis constants have their adsorption jumps at lower pH's, suggesting the formation of metal oxygen bonds. These adsorption jumps cannot be explained away as simple hydroxide precipitation since metal solubility was not exceeded in the bulk solution. At lower pH, Al^{+3} could dissolve from the clay and

interfere with nonspecific sorption, but again this would have the same effect on all divalent cations.

Further evidence for the existence of specific chemical adsorption comes from the observed irreversibility of metal sorption reactions as noted by Hodgson (1960) and Farrah and Pickering (1978). As pH is raised adsorption may exceed a clay's cation exchange capacity, which is attributed to the permanent negative charge of the clay structure. Kaolinites have low cation exchange capacities which may fall in the range of 2 to 15 meq/100 g. Farrah and Pickering measured 30 mmoles Cu /100 g (60 meq/100 g) on a kaolinite exposed to 1.6 * 10^{-4} molar Cu at pH 6.5.

Theories which have been put forward to explain increased adsorption fall into three categories which are (1) complexation with surface oxygens, (2) adsorption of anions on positively charged surfaces followed by induced metal precipitation, and (3) enhanced sorption because of the formation of $M(OH)_n^{(2-n)}$ species.

Surface complexation has been widely proposed to explain metal adsorption on oxides (Dugger et al., 1964, Schindler et al., 1975, Hohl and Stumm, 1976, and Davis et al., 1978). Oxide surfaces and the edges of clay minerals have broken bonds where unsatisfied oxygen atoms are exposed. These oxygen atoms quickly bond H^+ from the surrounding water. The ability of metal ions to sorb and displace H^+ from these surface oxygens depends upon the pH and the composition of the solution. Therefore, the sorption of a metal can be treated as a coordination reaction with a surface ligand. (See figure II-10 and reactions 1 to 5.) Using this approach Schindler et al.(1975) were able to model Fe, Cu, Cd

and Pb adsorption on silica, and Hohl and Stumm (1976) were able to model Pb on gamma Al_2O_3.

The surface precipitation mechanism is conceptually distinct from the surface complexation mechanism, but unfortunately the effects are very similar, particularly when the precipitating species are hydroxides. Surface precipitation of metals by OH^- has been proposed by Farrah and Pickering (1976a, 1976b, 1979), Payne and Pickering (1975), and Bingham et al. (1964). Surface precipitation by silicic acid has been described by Tiller (1967).

Surface induced precipitation occurs when the solubility product of a potential precipitate is exceeded at the surface, but not in the free solution. The solubility product of a copper precipitate will be exceeded if the Cu concentration and/or the complexing anion concentration are raised. Copper concentrations higher than the free solution are found at the upper and lower faces of kaolinite grains because of the negative charge on these faces. The edges of kaolinite grains are positively charged so that concentrations of anions such as OH^- are concentrated at the edge surfaces (Farrah and Pickering, 1979). The higher pH's found near the edges of kaolinite grains may promote the precipitation of metal hydroxides, particularly if there is a collision between a kaolinite face with high metal concentration and an edge with a higher pH. Although OH^- is probably the most common anion to produce precipitation Farrah and Pickering (1976a, 1976b) have shown that phosphate will produce Cu and Pb precipitation, and sulphate will precipitate Pb. Bingham et al. (1964) measured increased Cu and Zn precipitation in the presence of acetate.

Although surface precipitation by some anions such as phosphate and SO_4 can be demonstrated, the more general case of precipitation with OH^- is very difficult to distinguish from complexation reactions with surface oxygens. Both models involve the formation of metal oxygen bonds and so are very similar. Under some circumstances it might be possible to distinguish between surface precipitation and complexation by the ratio of H^+ released to Cu^{+2} sorbed. Figure II-10 gives potential precipitation and complexation reactions with their appropriate H^+/Cu^{+2} stoicheiometries.

In this study more than 90 percent of the copper in solution is Cu^{+2} and the experiments are conducted in a 0.05 M KNO_3 solution. Under these conditions a measured H^+/Cu^{+2} ratio of 0 would indicate that either the sorption was coulombic in nature or that it was dominated by reactions 1 and 2 in figure II-10. If the H^+/Cu^{+2} ratio was 1 then the sorption would be by reaction 3. If the ratio was 2 then either the surface complexation reaction 4 was operating or the copper was being precipitated by reaction 7. An observed H^+/Cu^{+2} ratio between 1 and 2 would indicate that sorption was dominated by a combination of reaction 3 with either reaction 4 or 7. A further complication in the interpretation of measured H^+/Cu^{+2} arises from the ability of the clay suspension to buffer pH by adsorbing hydrogen ion at other sites or by using it up in dissolution reactions.

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Complexation H^+/Cu^{++}

(1) Cu^{++} + ▨–O⁻ ⇌ ▨–O–Cu⁺   0

(2) Cu^{++} + ▨$\langle$–O⁻ / –O⁻ ⇌ ▨$\langle$–O / –O $\rangle$Cu   0

(3) Cu^{++} + ▨–O–H ⇌ ▨–O–Cu⁺ + H⁺   1

(4) Cu^{++} + ▨$\langle$–O–H / –O–H ⇌ ▨$\langle$–O / –O $\rangle$Cu + 2H⁺   2

(5) $CuOH^+$ + ▨–O–H ⇌ ▨–O–CuOH + H⁺   1

Precipitation

(6) $CuOH^+$ + H_2O ⇌ $Cu(OH)_2(s)$ + H⁺   1

(7) Cu^{++} + H_2O ⇌ $Cu(OH)_2(s)$ + 2H⁺   2
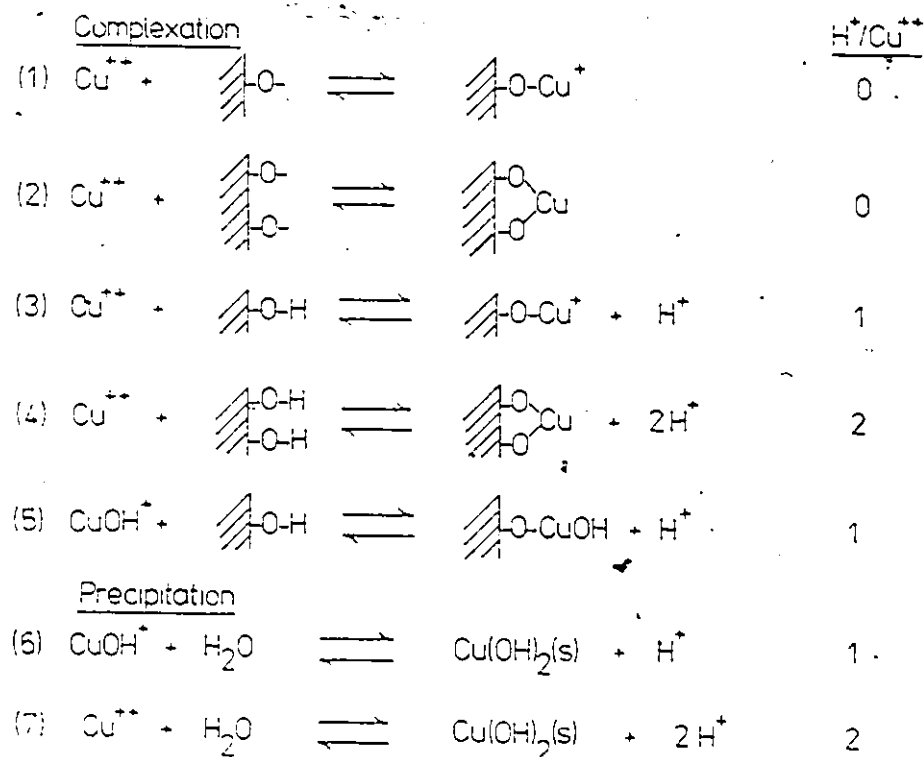
Figure II-10. Surface complexation and induced precipitation reactions and their respective hydrogen/copper exchange ratios. Charge balance is maintained by exchange with the dominant K⁺ ion.

Table II-1 lists some H^+/Cu^{+2} ratios reported in the literature. Most of these ratios were probably obtained by plotting the logarithm of the metal's distribution coefficient versus pH (Kurbatov plot). Assuming that the metal exchanges with hydrogen ion on a surface site it can be shown that:

2) $\log D = \log[K(HX)^n] + npH$

   D = distribution coefficient K = equilibrium constant

   (HX) = concentration of H^+ on surface sites

   n = H^+/Cu^{+2} ratio

TABLE II-1

H^+/METAL EXCHANGE RATIOS REPORTED IN THE LITERATURE

Reference	Surface	Metal	H^+/M^{+2}	Comment
Farrah and Pickering (1976)	kaolinite	Cu	0.4	up to pH 6.5
Farrah et al. (1980)	kaolinite	Pb	1.0	around pH 5
"	kaolinite	Cd	1.0	"
"	"	Zn	1.0	"
"	"	Mg	1.0	"
"	"	Cu	0.5	"
"	"	Ca	0.5	"
"	"	Pb	1.2 to 1.5	Kurbatov plot
"	"	Cd	1.2 to 1.5	including
"	"	Zn	1.2 to 1.5	sorbed H^+
"	"	Mg	1.2 to 1.5	"
"	"	Cu	1.0	"
"	"	Ca	1.0	"
James et al. (1975)	FeOOH	Cd	1.0	
"	TiO_2	Cd	0.6	
Gadde and Laitinen (1974)	Fe oxide	M^{+2}	1.0 to 2.0	
Grimme (1968)	goethite	M^{+2}	1.0	
Forbes et al. (1976)	"	M^{+2}	2.0	
Kinniburgh (1983)	ferrihydrite	Ca	0.9	back
"	"	Zn	1.7	titration

M^{+2} represents several metals.

If log $[K(HX)^n]$ is constant during the experiment then a plot of log D versus pH will give a straight line with a slope of n, which gives the stoicheiometry of the metal exchange with hydrogen ion. A better method of measuring the H^+ ratio is to observe the drop in pH during sorption and then back titrate with base. This helps to account for hydrogen ion lost to adsorption on other parts of the clay.

From table II-1 it appears that the ratio of released protons to sorbed copper can be as low as 0.4. However, when the adsorption of hydrogen ions is accounted for this ratio becomes unity. Since the work of Farrah et al. (1980) was conducted at a pH where Cu^{+2} is the dominant Cu species a hydrogen/copper ratio of unity would suggest that the surface complexation reaction 3 was controlling sorption. However, these experiments were not conducted in the presence of a background electrolyte so that a portion of the copper was probably sorbed by nonspecific coulombic attraction. Therefore, unless the experimental conditions are chosen well the observed hydrogen/copper ratio could be difficult to interpret.

It has been observed that cations with the stronger first hydrolysis constants are also more strongly adsorbed by silica (Dugger et al., 1964), and transition metals with with stronger hydrolysis constants have their adsorption jump at lower pH's. Unfortunately this observation supports the precipitation mechanism as well as surface complexation. The first hydrolysis constants give a measure of the relative ability of metals to bind with oxygen bonds. Farrah and Pickering (1979) found that metal sorption on cellulose was similar to that on clays whose surface oxygens are expected to be different from

those on cellulose. Precipitation reactions which are less dependent on the type of surface sites could be used to explain similar sorption properties of clays and cellulose. Further evidence for precipitation comes from the work of O'Connor and Kester (1975), who found similar sorption relationships to pH for Cu on illite and polyethylene, and for Co on illite and sand.

McBride (1982) used ESR to distinguish a surface complexation reaction and a precipitation reaction controlling Cu sorption of Al hydroxides. Cu which was believed to coordinate to surface sites sorbed more rapidly, and according to the ESR spectra it was spaced evenly on the mineral surface. Precipitated Cu sorbed more slowly (hours) and the ESR spectra indicated that the Cu ions were bunched together at nucleation sites. When the Al hydroxides were subjected to NH_3 vapor it was found that the precipitated Cu was easily desorbed while the Cu bound to surface sites resisted desorption.

McBride also found a correlation between mineralogy and the type of sorption mechanism. Poorly crystalline Al and boehmite have a large surface area where the exposed oxygens are bound to only one Al, while the better crystallized gibbsite has fewer edge sites with oxygens bonded to only one Al. The minerals with more oxygens bonded to one Al had higher sorption capacities and were dominated by surface coordination, whereas sorption on gibbsite was dominated by surface precipitation. Therefore it seems that oxygens bonded to only one Al are prime candidates for active surface sites (Parfitt et al., 1977).

The work on Al hydroxides should be applicable to kaolinites because these clays contain interrupted gibbsite layers at the edges and some of the upper or lower faces may be made up of gibbsite hydroxyls. However, the use of ESR to look at chemical sorption on kaolinite is not practical because in order put enough Cu on the surface to measure an ESR spectrum one must have a lot more Cu in solution than was necessary for the Al hydroxides. To prevent copper from precipitating, the pH must be kept at low levels which are not favorable to chemical sorption. McBride (1976) looked at Cu sorption on kaolinite and found that most of the Cu on the surface was in the form of the uncomplexed Cu^{+2} ion.

In summary, specific chemical sorption accounts for the sorption of trace metals in sea water and it can explain the sorption of metal cations on a positively charged surface. Specific sorption is very sensitive to pH and is most important for cations which form strong bonds with oxygen. It is more sensitive to temperature and is less reversible than nonspecific sorption. Surface complexation is faster, but less reversible than induced surface precipitation. Surface complexation is also restricted to surfaces with reactive sites (oxygens bonded to only one Al) and therefore, is limited by the number of available sites. Surface precipitation does not need an active surface and is not restricted by the number of sites.

STRUCTURAL PENETRATION:

Copper and other metals do not form solid solutions in kaolinite octahedral and tetrahedral layers so that it would seem unlikely for these metals to be attracted into the structural sheets. Nevertheless, the penetration of clay structure by metals has been proposed by some researchers as one possible mechanism to explain metal fixation on clays. Zinc fixation in soil minerals can be an important problem in agriculture and therefore has been seriously looked at (Elgabaly, 1950, Nelson and Melsted, 1955, Tiller and Hodgson, 1960, and Reddy and Perkins, 1974). Nelson and Melsted (1955) defined nonexchangeable zinc on kaolinite and bentonite as that fraction which could not be extracted with 1 M NH_4Ac, but could be extracted with 2.5 % HAc. Initially fixation was rapid in the first 3 days, but then slowed to a steady rate for the next 12 weeks. Elgabaly (1950) also defined fixed Zn as that which could not be extracted with NH_4. He believed that some of the fixed zinc remained on the surface while the rest of it penetrated the clay's octahedral layer where it reduced the cation exchange capacity if it entered vacant sites in dioctahedral layers. Using the same definition of fixed zinc Reddy and Perkins (1974) observed that the amount of fixed zinc increased with long sorption times. This may represent structural penetration of clay, although the authors favored precipitation of $Zn(OH)_2$ or strong adsorption at edge sites.

Hodgson (1960) looked at Co sorption on montmorillonite in the presence of 0.1 M $CaCl_2$, which is expected to reduce or eliminate electrostatic adsorption of cobalt. Evidence was found for two types of

chemically bound Co. (1) Initially Co is sorbed by a fast reaction over several hours, after which Co uptake continues at a slower rate for at least 10 days. The initial sorption depends on pH and sample pretreatment while the second reaction maintains a constant rate regardless of pH and sample pretreatment. (2) Part of the sorbed Co cannot be displaced by EDTA or 2.5 % acetic acid. (3) This so called exchangeable Co reaches saturation in about three days, while the nonexchangeable Co shows a slight rate change in the beginning, but then maintains a constant rate for the next 30 days. Hodgson believed that the faster, reversible reaction represented chemisorption in a surface monolayer, while the slow irreversible sorption represents Co entering the montmorillonite structure.

The fixation of a metal by a clay does not prove that it has entered the crystal structure unless it can be shown that the desorption method releases all forms of metal fixed on the surface. Farrah and Pickering (1978) carried out a series of desorption studies of Pb, Cu, Cd and Zn adsorbed on kaolinite, illite, and montmorillonite. The metals were sorbed at pH 5 and 7 over a 24 hour period so that most of the sorbed metal was probably still on the surface. Ammonium acetate, ammonium oxalate, and acetic acid did not remove all the sorbed metals. EDTA was completely successful at pH 5, but did not get all the metals sorbed at pH 7, although the authors felt that a stronger dose of EDTA would have removed all the metals. Studies of metal fixation provide evidence for structural penetration, but they do not prove it because it is likely that a portion of the fixed metal is still on the surface.

The next question which must be answered is whether or not heavy metals can fit into clay structure. Calvet and Prost (1971) heated Li saturated montmorillonite until the interlayer Li had dehydrated. Using infrared spectroscopy they showed that octahedral hydroxyls were reorientated as Li entered octahedral sites. They modeled Li entry into vacant octahedral sites and proposed that cations larger than around .70 angstroms would not be able to enter the clay structure. McBride and Mortland (1974) looked at Cu fixation in montmorillonite by heating a Cu saturated clay to various temperatures up to 270^0C. Loss of cation exchange capacity after heating was attributed to penetration of the clay sheets by Li or Cu, which neutralized part of the clay's permanent negative charge. Li was more effective than Cu in reducing the cation exchange capacity.

Calvet and Prost (1971) and McBride and Mortland (1974) suggest that as cations are dehydrated they enter the hexagonal holes of the tetrahedral layer and if they are small enough they may pass to vacant octahedral sites. If these cations remain in the hexagonal hole they may be rehydrated, while if they are in the octahedral layer they remain fixed when water is added to the clay. When Li or Cu sit in the hexagonal site they are directly above an octahedral hydroxyl, whose dipole moment and deformation vibration are perturbed. This perturbation is picked up by infrared spectroscopy. Movement of Cu into the octahedral layer produces another shift in the octahedral hydroxyls which is picked up by infrared spectroscopy.

Table II-2 lists some cations in order of increasing ionic radius
(Ahrens, 1952). McBride and Mortland (1971) have shown that cations as
large as Cu could enter the octahedral layer. Calvet and Prost (1971)
have shown that K, Ca and probably Na are too large to enter the
octahedral layers. Therefore, from table II-2 it appears that Cd is too
large to enter the structure, while Zn may or may not be too large.
However, when making these conclusions one must remember that there is
uncertainty in the values of ionic radii. Table II-2 also gives values
for radii determined by Goldschmidt and Pauling. If Goldschmidt radii
are used then Co may be too large to enter the structure, while Zn would
definitely be small enough.

The previous discussion on the maximum cation size permitted to
enter the structure has assumed that cations migrate into the structure
through the hexagonal holes in the tetrahedral layer. However, should
cations enter into fractures, cleavages or other defects then these size
restrictions may no longer hold.

Cations must dehydrate before they can get into a clay structure.
Due to the large enthalpies of hydration (table II-2), McBride and
Mortland (1974) believe that under most conditions at the earth's
surface, cations will not dehydrate and therefore will only enter clay
structures under diagenetic conditions, where higher temperatures may
favor dehydration. In some situations Cu dehydration might be achieved
if the hydration of some other cation partially overcomes copper's
enthalpy of hydration (as in a cation exchange reaction). Dehydration
may also be favored by the formation of hydroxy complexes or bonds with
surface oxygens. If this were the case, then structural penetration

would be favored by higher pH, making this process difficult to distinguish from a slow surface precipitation reaction. However, the slow sorption reaction of Co on montmorillonite does not seem to be affected by pH, (Hodgson, 1960).

In summary, structural penetration is a very slow process limited by dehydration and solid state diffusion. Any cations which have penetrated the structure will be irreversible. Structural penetration will be limited to cations with a radius not greater than around 0.74 angstroms if the cations must pass through the tetrahedral layer. Penetration of the clay structure may be favored by higher pH and by higher temperatures.

TABLE II-2

IONIC RADII (ANGSTROMS) AND ENTHALPY OF HYDRATION

Element	Ahrens	Goldschmidt	Pauling	Enthalpy of hydration (kJ/mole)
Be^{+2}	0.35	0.34	0.31	-2494
Mg^{+2}	0.66	0.78	0.65	-1921
Li^+	0.68	0.78	0.60	- 519
Ni^{+2}	0.69	0.68	0.69	-2105
Cu^{+2}	0.72	0.72		-2100
Co^{+2}	0.72	0.82	0.69	-1996
Zn^{+2}	0.74	0.69	0.74	-2046
Cd^{+2}	0.97	1.03	0.97	-1808
Na^+	0.97	0.98	0:97	- 406
Ca^{+2}	0.99	1.06	0.99	-1577
K^+	1.33	1.33	1.33	- 322

CONCENTRATION OF IONS IN COLLOIDAL AGGREGATES

In any weak salt solution clay particles will become coagulated, forming clusters with trapped interstitial water. Does this interstitial water have the same composition as the free solution or is the composition of this interstitial water altered by the high clay/water ratio in the clay floc? To test for increased sorption, produced by Cu accumulation in the interstitial water of kaolinite flocs, a sorption experiment could be conducted in which the clay flocs are broken up with a sonic probe to see whether sorption is different in the absence of coagulated kaolinite. Unfortunately there is a possibility that the sonic probe may also destroy the Cu electrode. Another approach for studying the effects of flocculation on sorption is to draw an analogy between a clay floc and a centrifuged clay plug which is covered by the clear supernatant. Both the clay floc and the clay plug represent a situation where a small volume with a high clay/water ratio is in contact with a relatively clay free solution.

The following discussion will deal with the partitioning of ions from free solutions to regions with high solid/liquid ratios, and with the effects of colloidal suspensions on electrode measurements. These two phenomenon are difficult to separate because the measurement of ion distribution between regions of high and low solid/liquid ratio may involve the interpretation of electrode measurements which are probably not independent of changing solid/liquid ratio.

In the beginning of the twentieth century it was observed that colloidal suspensions had a significant effect on potentiometric measurements of pH. Christensen and Jensen (1923) measured the pH of

clay suspensions and their filtrates with a H^+ electrode-saturated calomel electrode combination. In contrast to the filtrates, the pH of the suspensions varied with colloid concentration. Hydrogen soil suspensions were more acidic and alkaline soils were more basic than their respective filtrates. Pallman (1930) and Wiegner (1931) measured the pH of many different suspensions and their filtrates. Their results also showed a lower pH in the suspension, and the term suspension effect was introduced. Not all clays under acidic conditions showed a lower pH in suspension since clays saturated with divalent Ca showed a higher pH in suspension. Experiments in this study have shown that Cu measured with a Cu electrode is higher in suspension than in the centrifuged supernatant. To back up the electrode results the kaolinite suspension was sampled before centrifuging and the solution was separated by filtration. Atomic absorption analysis of the solution before and after centrifuging also showed that the Cu was lost to the kaolinite during centrifuging.

The phenomenon of an apparent higher Cu content in the kaolinite suspension compared to the supernatant requires attention for a couple of reasons. Not only can it be used to interpret sorption into a clay floc, but it also may have a significant effect on the interpretation of Cu measurements in clay suspensions. Many adsorption experiments involve separating the equilibrium liquid by centrifuging. If the process of centrifuging concentrates extra metal on the solid phase then the observed sorption would be significantly higher than if the solid was separated by filtration, which doesn't seem to induce extra sorption.

Before looking further into explanations for the suspension

effect one should consider why filtered solutions are less depleted in

Cu than centrifuged solutions. Both filtration and centrifuging are

processes which involve the separation of a solid from a liquid and one

would not expect any differences in ion distribution. However, there

are two factors which might help to explain why there is an apparent

loss of metal to sorption during centrifuging. In many cases the clay

accumulated on the filter paper does not remain in contact with the

solution for as long as the centrifuged clay remains in contact with the

supernatant. This extra contact time may allow the centrifuged clay to

equilibrate with the supernatant in a way which the filtered clay

cannot. A better explanation for the difference between centrifuging

and filtering is that the filtered clay is flushed by most of the water

in the suspension, while the flushing action in the centrifuged clay is

very poor. The flushing action in the filtered clay may prevent metal

accumulation in the clay's interstitial water and it may even remove

cations from the double layer. Bolt (1961) evaluated the effects of

pressure filtration on colloidal suspensions using both Donnan and Gouy

models. He concluded that if the volume of water was not too low, the

filtrate would be very close to the composition of the initial

interstitial solution of the suspension.

Explanations for the suspension effect fall into three main

categories. (1) Measurements with electrodes could be affected by a

change in liquid junction potential produced by the interaction of the

colloid with the reference electrode. (2) The electrode may respond to

cations which are loosely adsorbed to the surface. Ions in the diffuse

double layer will probably be registered by the electrode if the clay surface is almost in contact with the electrode surface. When the clay is separated by centrifuging the ions in the double layer remain with the clay and are not measured in the supernatant. (3) The concentration of ions in the interstitial water is real. This concentration may result from the net negative charge of the colloid, or the clay/water ratio of the clay aggregate may be high enough to induce some specific chemical reactions.

The remaining discussion will examine the above explanations for the suspension effect. First we will assume that the cation accumulation in centrifuged clay is real and we will look at possible explanations for this effect. Then the discussion will look at the viewpoint that the suspension effect is produced by the junction potential of reference electrodes. Finally we will look at the possibility that the suspension effect is produced by the close proximity of adsorbed cations.

Most of the literature which has looked at ion concentration in charged colloids has focussed on an electrostatic model in the form of Donnan equilibrium. Donnan equilibrium controls the distribution of ions between a colloidal mass and an equilibrium solution which are separated by gravity or a semi-impermeable membrane and between which there is an electrostatic potential difference. This system is illustrated by Figure II-11.

Colloid   Membrane   Solution

$$M-clay,$$
$$M_c^{+n}, A_c^{-m}$$

$$M_s^{+n}, A_s^{-m}$$
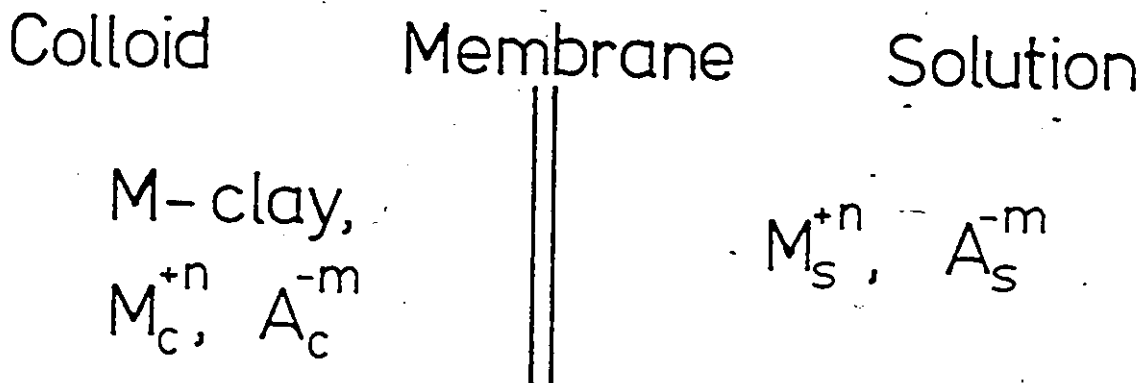
Figure II-11. Donnan system.

In the treatment of Donnan systems the following assumptions are usually made. (1) The dissociation of the colloid is complete (no chemical adsorption). (2) The ion distribution throughout the colloid is uniform. (3) The volume of water in the colloid is constant. The first two assumptions do not really hold in a clay system, but on the other hand they may not be essential. Chemical sorption takes place with transition metals, but it could be accounted for by the use of activity coefficients. The major problem with chemical sorption is that it will produce a degree of irreversibility. The distribution of charge is actually not uniform in a clay suspension. Each solid surface is surrounded by a diffuse layer in which there is a decrease in counter ion concentration away from the surface. Also, clay suspensions contain a mixture of negatively and positively charged surfaces. However, the Donnan treatment deals with an average distribution of ions and potential in the clay suspension.

In an equilibrium system the electrochemical potential of an ion must be the same everywhere. Assume that the colloid has an average electrostatic potential P_c, and that the solution has an electrostatic potential, P_s. If the salt MA is present in the system then the

following relationship can be derived from the expressions for electrochemical potentials of the cation and anion in solution and in the colloid.

3) $\qquad RT\ln[(M)_c/(M)_s] \doteq RT\ln[(A)_s/(A)_c]$

$\qquad = zF(P_c - P_s)$

$\qquad z = $ valance of salt $\qquad F = $ Faraday

$\qquad (\ )$ denotes activity

Therefore, the activity ratio of a cation between colloid and solution depends on the potential difference between the colloid and solution (Donnan potential). Actually the activity of an ion in the colloid is a geometric space average of all the activities of this ion in various parts of the colloid. These activities cannot be added as simply as activities in a true solution, but instead are given by:

4) $\qquad (A)_{average} = (A_1)^{n1}(A_2)^{n2}(A_3)^{n3} \cdots$

When dealing with anions and cations in a Donnan system often a distinction is made between those ions originating in the solution and those which dissociate from the clay. With this type of treatment, X is usually denoted as the salt concentration in the equilibrium solution. Y is the salt concentration in the interstitial water of the colloid and Z is the concentration of the counter ion dissociated from the colloid. For a general electrolyte of type M_nA_m the following relationship is apparent from equation 3.

5) $\qquad [(M)_c/(M)_s]^{1/m} = [(A)_s/(A)_c]^{1/n}$

Equation 5 can be rewritten in terms of X, Y and Z.

6) $\qquad [(Z_M + Y_M)/X_M]^{1/m} = [X_A/Y_A]^{1/n}$

If a system has more than one electrolyte, equations 5 and 6 are valid for each type of electrolyte. When the values of X and Y are determined with specific ion electrodes the activity of the cation adsorbed on the surface, Z, can be calculated with equation 6. If we really want to distinguish between the adsorbed cation and the cation associated with the interstitial salt then an anion electrode would be useful for determining $Y_A = Y_M$. A specific cation electrode could be used to measure Y_M, but there may be a danger that the specific cation electrode may respond to a portion or the sorbed cation. If the the amount of adsorbed cation calculated by equation 6 is less than the amount of cation which is known to be adsorbed then some specific chemical sorption must also be taking place.

As shown by equation 3, the distribution of cations between a colloid and a solution is related to the potential difference between the colloid and solution. When a calomel electrode placed in a colloid is connected to another calomel which is in a solution that is in equilibrium with the colloid a potential difference will be recorded. The same potential difference will be given by the difference in pH readings between the colloid and the equilibrium solution (providing that the calomel electrode is used as the reference for the pH readings). Some researchers (Marshal, 1964) have argued that the potential difference measured by the calomel electrode represents the Donnan potential and can be used in equation 3. Others have argued that potential differences between the colloid and the suspension are partially or totally the result of liquid junction potentials produced by the calomel electrode (Jenny et al., 1950, and Overbeek, 1953).

Those who believe in Donnan potentials argue that the agreement between measured Donnan potentials and measured ion distributions is not bad and that any differences are caused by geometric space averaging problems.

According to Donnan theory divalent cations are preferred over monovalent cations. The selectivity for divalent cations increases as the volume of water inside the colloid goes down (Marshal, 1964). Also, as in double layer theory, the colloid's preference for divalent cations increases as the free solution becomes more dilute.

The effects of specific chemical adsorption on the suspension effect are not commonly discussed in the literature. When it was known that the adsorbed concentration of a particular ion was higher than predicted from Donnan theory then activity coefficients were introduced, which would take care of specific chemical interactions. In this study, preliminary examination of centrifuge effects on the kaolinite copper system suggest the existence of some specific chemical sorption during centrifuging. Table II-3 shows pH and copper concentration before and after centrifuging. Donnan theory predicts that the pH of the supernatant should be higher than in the suspension. The lower pH shown for the supernatant could result from hydrogen ions being produced by chemical sorption of copper. When the centrifuged clay is resuspended the copper concentration of the suspension doesn't immediately return to its original level. The slow desorption of Cu sorbed during centrifuging suggests that relatively strong bonds have to be broken to produce the desorption.

TABLE II-3

CHANGES IN pH AND pCu DURING CENTRIFUGING AND AFTER RESUSPENSION

	suspension	supernatant	15 minutes after resuspension
pH	6.19	6.12	6.14
pCu	5.46	5.58	5.51

What properties of a centrifuged clay might induce chemical sorption? Donnan potential may raise the copper content of the interstitial water. Since this higher Cu concentration is sheltered from the diluting effects of the free solution, the rate of sorption by surface coordination or precipitation is greatly speeded up. The high solid/liquid ratio in the centrifuged clay may lead to more edge to face collisions. This would induce Cu precipitation because the kaolinite faces have higher Cu concentrations, while the edges have higher local pH's. The high concentration of surface area in the clay floc may lead to higher sorption rates.

An argument against improved adsorption during agglomeration has been the possibility of blocking adsorption sites. This may be true for large ions and molecules. However, hydrated Cu, even with its 4.4 angstrom radius, should be able to squeeze between the contact of two clay particles. A centrifuged clay still contains over 90 percent water, allowing a high degree of mobility in the kaolinite mass. Syvitski and Murray (1980) have photographed clay flocs after filtering. Flocs with clay larger than 2 micrometers have a very open structure, and flocs with particles of less than 2 micrometers still have a moderately open structure. Figure A-1 in Appendix A-7 also shows that there is a lot of open space in a filtered kaolinite mass.

A question which cannot be avoided when studying Donnan equilibria or when making any electrode measurements in a suspension, is what is the significance of junction potentials. Junction potentials are produced at reference electrodes as a result of ions diffusing from the electrode to the solution under study. Jenny et al. (1950) proposed a theory which showed the importance of liquid junction potential in the measurement of potentials in colloidal suspensions. A liquid junction potential is produced at the salt bridge when there is a difference in the mobilities of K^+ and Cl^-. Jenny et al. (1950) derived an equation for liquid junction potential between two solutions of different KCl activity, separated by a colloid which was assumed not to affect the KCl activity.

7) $E_L = (T_+ - T_-)(RT/F)\ln(a_2 - a_1)$

T_+ = fraction of current carried by K^+

T_- = fraction of current carried by Cl^-

a_1 and a_2 are the mean KCl activities in solutions 1 and 2

The transference number for Cl^- (T_-) decreases with increasing cation exchange capacity of the colloid. This effect is more pronounced at lower solution concentrations of KCl. Jenny et al. (1950) found reasonable agreement between measured potential and liquid junction potential calculated from transference numbers. Therefore, they felt that liquid junction potential could not be dismissed in potentiometric measurements.

Peech et al. (1953) used potential difference measurements across a membrane to calculate the osmotic pressure across that membrane. The calculated osmotic pressure did not agree well with the measured osmotic

pressure, so the authors concluded that their potential measurements were affected by errors due to junction potentials. Marshal (1953, 1964) criticized these interpretations and suggested that liquid junction potential was overrated.

Overbeek (1953) derived an expression for Donnan potential which did not relate the Donnan potential to net charge, but instead related the potential to ion conductances in the double layer and the relative mobility of ions and particles. Overbeek believes that liquid junction potential may explain why some measured Donnan potentials are lower than predicted. This contrasts with the interpretation of others, who believe that these differences between measured and predicted potentials can be explained by incomplete dissociation of ions from the surface (ie. chemisorption).

In the previous discussion it has been pointed out that liquid junction potentials may affect the measurement of potentials in suspensions. However, it has not been proved that the junction potential, alone, can account for the observed Donnan potential. Therefore, although the junction potential probably does not cause the suspension effect, its influence cannot be ignored when making emf measurements. The junction potential seems to have a minimum effect on copper measurements since concentrations measured with the electrode closely match the results from atomic absorption.

The third explanation for the difference in apparent Cu concentration between the suspension and the supernatant might be that in the suspension the Cu electrode actually sees some of the Cu which is in the diffuse layer of the clay particles. The agreement between

electrode measurements and the analysis of filtered samples may be explained if the filtration is able to remove copper from the diffuse layer of clay particles. If this is true then the formation of a clay floc or the centrifuging process does not produce extra sorption. Also the reactivity of sorbed metal to a plant root or other organism will depend upon the closeness of that root or organism.

To test this third theory one might try to raise the salt level which would tend to compress the diffuse layer, making it harder for the Cu electrode to detect Cu in the diffuse layer. Unfortunately Donnan theory also predicts that increasing salt levels will reduce the selectivity for divalent cations. If electrodes do respond to cations in the double layer then the pH of the suspension should be lower than in the supernatant. As was mentioned earlier the pH of the supernatant was lower indicating that H^+ was released while Cu was actually sorbed during the centrifuging. A final indication that the third theory cannot account for the apparent sorption during centrifuging is that when the clay is resuspended the measured Cu does not immediately return to its original value.

In summary, the formation of a clay floc may induce extra Cu sorption as indicated by the apparent sorption of Cu during centrifuging. The sorption during centrifuging is probably real because it is not fully reversible and it is supported by atomic absorption measurements. The lower pH in the supernatant indicates that some of the sorption during centrifuging is specific chemical in nature, and it disproves the junction potential theory which predicts that the change in the emf of the Cu and hydrogen electrodes would be the same since

they were both connected to the same reference electrode.

SUMMARY OF SORPTION MECHANISMS:

Several sorption mechanisms can be predicted from kaolinite's structure and chemistry .(See figure II-12.) The upper and lower faces of a kaolinite grain are nonreactive and probably experience the constant negative charge due to isomorphous substitutions in the structure. Therefore, these faces can be expected to adsorb copper by nonspecific coulombic attraction if the salt level is low. The kaolinite edges contain broken bonds which make these surfaces reactive to metals and hydrogen ion. Nonspecific Cu sorption on the edges is unlikely because they appear to be positively charged. The edges do contain surface sites where copper can complex to reactive oxygens by specific chemical sorption. Another form of specific chemical sorption may be induced surface precipitation which does not need reactive surface sites. Surface precipitation may start at the edges where the positive surface charge causes an increase in the local pH of the diffuse layer. Precipitation may also be induced by Cu accumulations at the upper and lower faces. With increasing sorption time metals appear to become fixed on clays. One explanation for this fixation is that metals are able to enter the clay structure through defects or through the pseudohexagonal holes in the tetrahedral layer. A further complication to Cu sorption on kaolinite is the effect of kaolinite flocs. If a centrifuged kaolinite is an accurate analogy to a kaolinite floc then the formation of clay flocs may induce extra Cu sorption.

It is probable that all the mechanisms predicted by the kaolinite
structure contribute to Cu sorption. The relative contribution of each
mechanism will depend upon pH ,salt concentration, and time. Because of
this it is possible to design experiments which may identify these
mechanisms. A summary of the characteristics of these mechanisms is
given in the following tables. Some of these characteristics will be
useful in identify the sorption mechanisms.
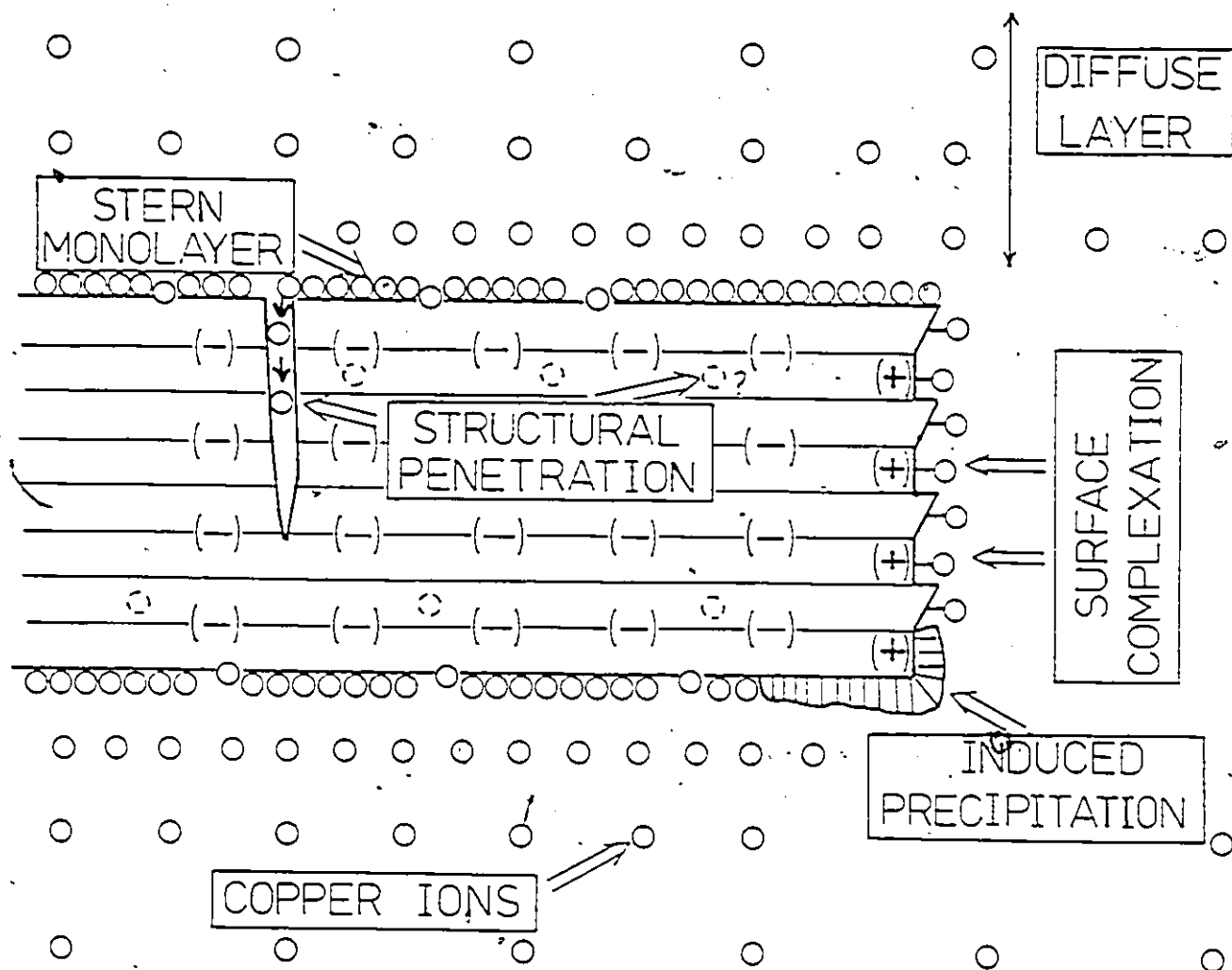
Figure II-12. Sorption mechanisms on kaolinite.

TABLE II-4

PROPERTIES OF NONSPECIFIC COULOMBIC ATTRACTION

Diffuse layer	Stern monolayer at surface
1) No preference between ions of of the same charge.	Slight preference for ions with smaller hydrated radii.
2) Independent of temperature.	Slight decrease with temperature.
3) Important for group IA and IIA cations which form weak bonds with oxygen. (Have low first hydrolysis constants compared to metals.)	
4) Reversible.	
5) Rapid adsorption and exchange properties.	
6) Adsorption of trace cations decreases with increasing salt level.	
7) Higher valent cations are preferred, particularly at low salt levels.	

TABLE II-5

PROPERTIES OF STRUCTURAL PENETRATION

1) Very slow sorption kinetics. .

2) Irreversible. (Structural penetration would be proven by irreversibility to a desorption technique which is known to remove all copper adsorbed on the surface.)

3) May be restricted to cations with an ionic radius smaller than .74 A.

4) Cation dehydration is a major obstacle.

5) May be favored by higher pH where dehydration is easier.

6) May be favored by higher temperatures which make solid state diffusion and dehydration easier.

TABLE II-6

PROPERTIES OF SPECIFIC CHEMICAL SORPTION

Surface complexation	Induced surface precipitation
1) More resistant to complexation by ligands in solution.	Subject to ligand complexation followed by desorption.
2) Faster sorption (minutes).	Slower sorption (hours to weeks).
3) Smaller sorption capacity limited by the amount of specific sites.	Larger capacity not limited by sites.
4) Cu well spread out on surface.	Cu bunched together.
6) Associated with surfaces with oxygens bonded to one Al.	Associated with surfaces with nonreactive oxygens.

7) Sharp increase in sorption over a narrow pH range. The pH of this

sorption jump depends on the element's hydrolysis constants.

8) Sorption decreases with temperature due to entropy loss during

sorption.

9) Important only for elements which form strong bonds with oxygen.

10) Less reversible than nonspecific coulombic sorption.

a

TABLE II-7

SORPTION IN CLAY FLOCS AND INDUCED BY CENTRIFUGING

1) A centrifuged clay can be considered an analogy to a clay floc.

2) The apparent sorption during centrifuging is real.

3) The sorption during centrifuging has a specific chemical component.

4) This sorption is not fully reversible.

CHAPTER III

CHEMICAL KINETICS

INTRODUCTION:

Studies of chemical reactions which do not measure the effects of time are essentially equilibrium type studies which may be described with the aid of thermodynamics. Thermodynamics describe reactions by comparing the energy levels of the reactants with the products without being concerned with the energetics of the pathways leading from products to reactants. Thermodynamics can adequately predict reactions if the pathways are simple and have no energy barriers which prevent the attainment of equilibrium. However, many reactions are sufficiently complex and/or slow so that the reaction steps cannot be ignored. A very useful method of studying these reaction paths is to monitor reactions as a function of time, which brings us into the realm of kinetics. Kinetic studies may be able to separate fast and slow steps in a given reaction, and when measured reaction rates are considered in light of variable chemical environments a great deal of insight may be gained into important reaction mechanisms.

Since this study will make significant use of kinetics in the investigation of sorption mechanisms on clay minerals it is necessary to provide some background into kinetic theory. This chapter will initially outline the basic principles of kinetic theory. Then it will describe some kinetic applications in the study of sorption on clay

sized materials, and will discuss their relevance to Cu sorption on kaolinite.

PRINCIPLES:

Kinetic theory has been described in considerable detail by Benson (1960), Laidler (1965), Edwards (1965), Sykes (1966), and Pennetier and Souchay (1967). Condensed reviews of kinetic theory can be found in Lasaga and Kirkpatrick (1981) and Stumm and Morgan (1981). This section is a brief review of some of the principles found in these references.

Most reactions are made up of a combination of elementary reactions, which each represent a single step in the overall reaction. Unlike the chemical process under study each elementary step is path independent. The mechanism or mechanisms which control the overall reaction are made up of some combination of elementary steps. The overall reaction rate is given if all the elementary reaction rates are known. If an overall reaction is described by equation (1) and if the stoicheiometry is correct then the rate law given by (2) is correct.

1) $aA + bB \ldots \longrightarrow pP + qQ$

2) $\text{rate} = \frac{1}{a}\frac{d[A]}{dt} = \frac{1}{b}\frac{d[B]}{dt} = \ldots = \frac{-1}{p}\frac{d[P]}{dt} = \frac{-1}{q}\frac{d[Q]}{dt}$

The concentration terms in rate laws, $[X]$ can be in moles per liter if the reaction is homogeneous. Heterogeneous processes, which involve reactions across phase boundaries, should be described by rate laws in which the concentration terms include the specific area between the phases (ie moles/cm^2/liter or moles liter/cm^2). Often rate laws

can also be expressed as follows.

3) $\quad\quad\quad$ rate = $k[A]^{nA}[B]^{nB} \dots [P]^{nP}[Q]^{nQ}$

In equation 3, k is the rate constant which must be determined by experiment. The exponents, nX, can be positive or negative integers or fractions, and must also be determined by experiment. The order of a rate expression is given by the sum of these exponents. If the sum of exponents is zero then the rate is zero order, and if it is n the overall reaction is considered to follow nth order kinetics.

Rate expressions for elementary reactions of different orders have different forms and it is worthwhile reviewing them. The unimolecular reaction given by equation 4 follows a first order rate law given by equation 4.

4) $\quad\quad\quad$ A $\xrightarrow{\ k\ }$ B

5) $\quad\quad\quad$ $\dfrac{-d[A]}{dt}$ = $k[A]$

The first order rate constant, k, has units of time^{-1}, and it relates the disappearance of A to the remaining concentration of A. First order rate laws are commonly used to describe many reactions in solution, and they have widespread use in the description of radioactive decay. Reactions which involve the interaction of two reactant molecules, equations 6 and 8, can be described by second order rate laws, equations 7 and 9.

6) $\quad\quad\quad$ A + B $\xrightarrow{\ k\ }$ C

7) $\quad\quad\quad$ $\dfrac{-d[A]}{dt}$ = $k[A][B]$

8) $\qquad$ A + A $\xrightarrow{k}$ C
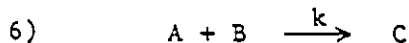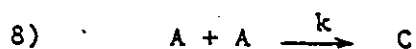
9) $\qquad$ $\dfrac{-d[A]}{dt} = k[A]^2$

In equation 7 the overall rate law is second order with a rate constant, k, which may have units of concentration^{-1} time^{-1}. However, with respect to the individual species A and B the disappearance of A is still first order. Since equation 8 involves two molecules of A the rate law given in (9) is second order with respect to A. Some reactions appear to have a constant rate which is independent of concentration. If reaction 10 is controlled by such zero order kinetics it can be described by the rate law in equation 11. The zero order rate constant will have units of concentration per unit time.

10) $\qquad$ A $\xrightarrow{k}$ P

11) $\qquad$ $\dfrac{-d[A]}{dt} = k$

In order to work with rate expressions and to determine rate constants it is necessary to integrate rate laws. Some complex rate expressions can be very tedious to integrate. The following are some simple examples of integrations for the previously mentioned rate laws. The zero order rate law shown in (11) is easily integrated to (12).

12) $\qquad$ $[A] = [A]_0 - kt$

The half life for this reaction is given by:

13) $\qquad$ $t_{1/2} = \dfrac{[A]_0}{2k}$

The original concentration of A is given by $[A]_0$. The first order rate law (5) is integrated to:

14) $\ln[A] = \ln[A]_0 - kt$

The half life for a first order reaction is given by:

15) $t_{1/2} = \dfrac{\ln 2}{k}$

The integrated form of higher order reactions, where n is the order, is given by:

16) $\dfrac{1}{[A]^{n-1}} - \dfrac{1}{[A]_0^{n-1}} = (n-1)kt$

When reactions of first order and higher begin to approach equilibrium or a steady state, reverse reactions may start to influence the rate. If the reaction is so fast that it cannot be monitored far enough away from equilibrium for the forward reaction to dominate then one must account for the reverse reaction in the rate expression. When the forward and reverse rates have equal magnitude the first order kinetics must be written as:

17) $\dfrac{d[A]}{dt} = k([A]_{equil} - [A])$

18) $\ln \dfrac{[A]_{equil} - [A]}{[A]_{equil} - [A]_0} = -kt$

$[A]_{equil}$ = equilibrium concentration of A

$[A]_0$ = initial concentration of A

In order to understand the reaction mechanism one tries to analyze the overall reaction rate by determining the contribution of each species to the rate law. Unfortunately many reactions are so

complex that it is difficult to obtain a meaningful rate constant, not to mention worrying about the order of participating species. Two experimental strategies have been developed to simplify the rate laws so that the kinetics can be evaluated. One of these is the <u>initial rate</u> method which can be used if the overall reaction is slow or if the concentrations of some species are buffered. The basic strategy is to measure the initial rate after the reaction has been started. At this point the concentrations of the reactants have not changed much and significant amounts of products have not been built up to initiate reverse reactions. In order to determine the contribution of a given reactant to the rate law, experiments are started with different initial amounts of that reactant while the concentrations of other reactants remain constant. The relation between the initial rate and the initial concentration of A will tell us what contribution A will make to the overall rate law. If the rate law is:

$$19) \qquad \frac{d[P]}{dt} \quad = \quad [A]_0^{nA} [B]_0^{nB} [C]_0^{nC}$$

Holding the initial concentrations ($[B]_0$, $[C]_0$) constant the rate becomes:

$$20) \qquad rate \quad = \quad \frac{d[P]}{dt} \quad = \quad k'[A]_0^{nA}$$

$$21) \text{ or: } \quad \log rate \quad = \quad \log k' + nA \log[A]_0$$

In equation 20 the rate law assumes a first order form with respect to the initial concentration of A. The rate constant, k' is conditional to fixed concentrations of B and C. Plotting log rate against log $[A]_0$ gives nA as the slope. This procedure can be

repeated with the other reactants to get nB and nC.

Many natural reactions are too complex for the initial rate
method. Plots of concentration versus time are curved and there is no
way of unambiguously defining the initial rate. For this situation one
can employ the method of isolation. The object is to try to find a
condition where one or more of the components will remain constant. This
can be accomplished by having some of the reactants in excess, by having
them buffered, or by adding more reactant as it is being consumed. For
example, if the reaction is:

22) $A + B = C + D$
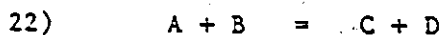
23) $\dfrac{-d[A]}{dt} = k[A][B]$

If $[B]_0 \gg [A]_0$

24) Then: $\dfrac{-d[A]}{dt} = k[B]_0[A] = k'[A]$

By simplifying equation 23 we have reduced the order of the
reaction, making it easier to determine the rate constant. The rate
constant is determined from the integrated form of equation 24 (see
equation 14) by plotting Ln [A] versus time. The slope of this line
will give the rate constant, k'. Life would be made even easier if the
rate law could be reduced to a zero order form as in equations 11 and
12. Then a plot of [A] versus time would give a straight line with a
slope of -k'. To determine the effect of A on the rate law one can do
several experiments with different initial concentrations of A. Then
the initial rate method can be used to determine nA.

TABLE III-1

SOME EXAMPLES OF HOW ELEMENTARY REACTIONS COMBINE TO FORM A RATE LAW

Opposing reactions:

reaction

$$A \xrightleftharpoons[k_{-1}]{k_1} B$$

rate law

$$\frac{-d[A]}{dt} = k_1[A] - k_{-1}[B]$$
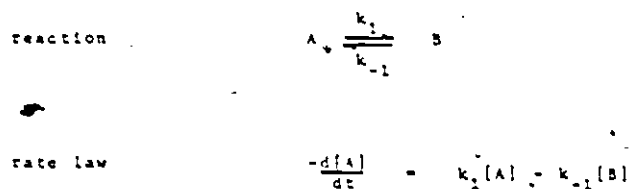
consecutive irreversible reactions

reaction

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

rate laws

$$\frac{d[A]}{dt} = -k_1[A]$$

$$\frac{d[B]}{dt} = k_1[A] - k_2[B]$$
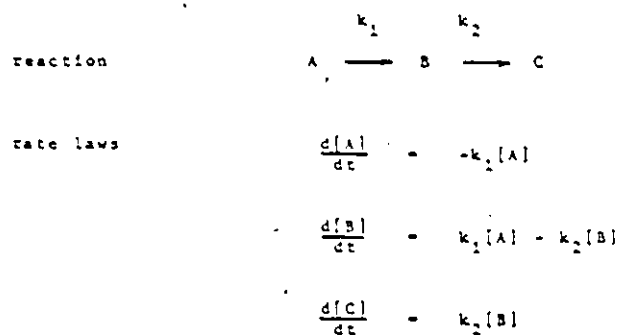
$$\frac{d[C]}{dt} = k_2[B]$$

If the intermediate product is at a steady state then its concentration can be replaced by [A] and the equilibrium constant between A and B.

$$\frac{d[C]}{dt} = k_2 K[A]$$

Concurrent or parallel reactions forming the same product

reactions

$$A \xrightarrow{k_1} C$$

$$B \xrightarrow{k_2} C$$

$$A + B \xrightarrow{k_3} C$$

rate law

$$\frac{d[C]}{dt} = k_1[A] + k_2[B] + k_3[A][B]$$
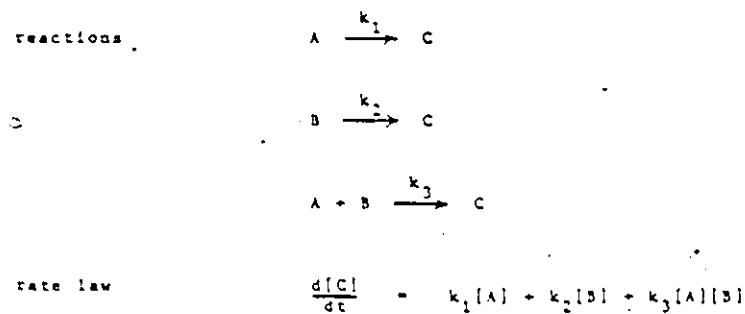
There are various possible combinations of elementary reactions which can make up a rate law. Each combination can give the rate law a different form. Table III-1 illustrates several examples of how elementary reactions can combine to make up a rate law.

Kinetics are related to thermodynamics by the principle of detailed balancing (or microscopic reversibility) which states that at equilibrium the rates of forward and reverse microscopic processes are equal for every elementary reaction. If this is not true we only have a steady state and not true equilibrium. The equilibrium constant is given by the overall forward and reverse rate constants. The equilibrium constant for the reaction in equation 25 is given by equation 26.

25)
$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B$$

26)
$$\frac{[B]}{[A]} = \frac{k_1}{k_{-1}} = K$$

Reaction rates can be determined either by transport processes such as diffusion or by chemical reactions which might involve breaking or forming bonds, and/or changes in various entropy contributions. In solution fast reactions are usually only limited by transport mechanisms, while slow reactions are controlled by chemical processes.

If the rate of a reaction is only limited by the collision frequency of reacting molecules then a calculation of this collision rate will give us the speed of the reaction. The Smoluchowski

expression for encounters through diffusion will give us the collision rate for two uncharged molecules in solution.

27) $$\text{collision rate} = k = \frac{4\pi N}{1000}(D_A + D_B)r_{AB}$$

The separation distance upon a collision between A and B is r_{AB}. N is Avogadro's number. The diffusion coefficients, D_A and D_B, can be calculated with the Stokes-Einstein equation for spherical particles.

28) $$D = \frac{RT}{6\pi n r N}$$

The radius of the spherical particle is r and the viscosity is given by n. Collision rates calculated from equation 45 fall into the range of 10^{10} (moles/liter)$^{-1}$sec^{-1}, which is in the range of many observed hydrolysis reactions (see table III-3). If the interacting particles have like charges then the collision rate will be reduced, while if they have opposite charges the reaction rate will increase.

Reactions with rate constants as low as 10^{-11} (moles/liter)$^{-1}$ sec^{-1} are much too slow to be controlled by transport processes in solution and must be limited by chemical interactions. The two theories which have been devised to evaluate these chemical processes are collision theory and transition state theory.

According to collision theory a reaction will only take place when the reactants come together in the proper orientation and configuration, and with enough energy to become an activated complex. The rate constant for two molecules to interact is given by:

29) $$k = pZe^{-E/RT}$$

In equation 29 p is an empirical, dimensionless steric factor which accounts for the fraction of collisions having the right orientation and configuration to permit the reaction to take place. Z is the specific collision rate with units of $(moles/liter)^{-1}$ $time^{-1}$. The energy associated with the fraction of collisions having enough energy to enter the activated state is given by E, which is approximately equal to the activation energy.

In transition state theory a reaction doesn't happen until the reactants form an activated complex which then readily transforms itself into products. The difference from collision theory comes from the fact that transition state theory assumes that the reactants are in equilibrium with the activated complex. If the energy required to form the activated complex is very large, so that its formation constant is very low, the reaction will be sluggish.

The change in the rate constant with temperature is related to the activation energy. Arrhenius used the Van't Hoff equation as an analogy to develop the following expression to relate the temperature dependence of the rate constant to the activation energy.

30) $$\frac{d\ln k}{dt} = \frac{Ea}{RT^2}$$

If the activation energy is temperature independent then equation 30 can be integrated to equation 31.

31) $$k = A \exp(-E_a/RT)$$

In equation 31, A is known as the probability factor and may be a function of temperature (T). E_a is the activation energy which can be expressed as:

32) $$E_a = \frac{-R\ d\ln k}{d(1/T)}$$

The activation energy will be given by the slope of a plot of $\ln k$ versus temperature. If the plot is curved then E_a is a function of temperature. The activation energy of the overall reaction is made up of the sum of activation energies from the elementary reactions. Not only do activation energies give the temperature dependence of the reaction rate but they also give an indication of the reaction mechanism. Fast reactions tend to have large probability factors and/or small activation energies. Slow reactions have small probability factors and large activation energies. Some sample activation energies are given in the following table.

TABLE III-2

EXAMPLES OF ACTIVATION ENERGIES EXPECTED FOR DIFFERENT REACTION TYPES

Reaction type	activation energy (kcal/mole)
diffusion in water	< 5
surface controlled reactions	10 to 20
diffusion in minerals	20 to 120

Sorption reactions will have similarities to ion interactions in solution. In both cases metals will experience electrostatic interactions with other ions, and they may undergo coordination changes by forming or breaking metal oxygen bonds. The main difference is that reactions in solution are homogeneous while sorption reactions are heterogeneous, involving two phases. The kinetics of sorption reactions should be similar to ion interaction in solution except that sorption

processes will be slowed down by (1)the availability of surface area, (2)the transport of ions to and from the surface, and (3)a significant change in entropy produced by sorption. Factors 1 and 2 will reduce the collision probability between a metal and a surface sites. With these reservations, it is still useful to compare sorption kinetics to the kinetics of ion interactions in solution. Table III-3 gives the rate constants of some selected reactions in solution in order illustrate the range of rate constants expected for some common reaction types.

Table III-3 illustrates that acid - base reactions, and the formation of ligand complexes can be very fast. Therefore, reactive edge sites on clays, which are easily accessible, may be expected to rapidly coordinate metal ions and to quickly respond to changes in hydrogen ion activity. On the other hand, reactions which require a ligand exchange with a previously existing complex can be very slow. Metals bound to some surface sites may be slow to react with ligands added to the clay system because the metal clay bonds are hard to break.

TABLE III-3

SELECTED RATE CONSTANTS

reaction	rate constants		
acid - base reactions	$k_1 (M\ sec)^{-1}$	$k_{-1}\ sec^{-1}$	
$H^+ + OH^- = H_2O$	$\geq 1.3 * 10^{11}$	$2.3 * 10^{-5}$	(1)
$H^+ + SO_4^{-2} = HSO_4^-$	$1 * 10^{11}$	$1 * 10^9$	(1)
$H^+ + HCO_3^- = H_2CO_3$	$4.7 * 10^{10}$	$8 * 10^6$	(1)
$H^+ + NH_3^- = NH_4$	$4 * 10^{10}$	24	(1)
electron transfer	$k (M\ sec)^{-1}$		
$Cu^{+2} + e^- = Cu^+$	$2.9 * 10^{10}$		(1)
$CO_2 + e^- = CO_2^- + H^+$ COOH	$7.7 * 10^9$		(1)
exchange for inner sphere water	$k\ sec^-$		
$Cu(H_2O)^{+2} + H_2O$	$8.3 * 10^9$		(1)
$Mn(H_2O)^{+2} + H_2O$	$3.1 * 10^7$		(1)
$Fe(H_2O)^{+2} + H_2O$	$3.2 * 10^6$		(1)
$Ni(H_2O)^{+2} + H_2O$	$2.7 * 10^4$		(1)
reactions with ligand complexes	$k_1\ sec^-$	$k_{-1}\ sec^-$	
$Ni(en)_3^{+2} = Ni^{+2} + 3en$	86.6		(1)
$Cu^{+2} + SO_4^{-2} = CuSO_4$	10^7	$1 * 10^6$	(2)
$Mg^{+2} + SO_4^{-2} = MgSO_4$	$1 * 10^5$	$8 * 10^5$	(2)
$Be^{+2} + SO_4^{-2} = BeSO_4$	$1 * 10^3$	$1.3 * 10^3$	(2)
$Co^{III}(NH_3)_5X^{+2} + H_2O$ $Co^{III}(NH_3)_5H_2O^{+3} + X^-$			
$X = HCO_3$	$1.6 * 10^{-3}$		(1)
$X = NO_3$	$2.6 * 10^{-5}$		(1)
$x = Cl$	$1.67 * 10^{-6}$		(1)

1) Sykes (1966)   2) Edwards (1965)

CHEMICAL KINETICS IN SORPTION STUDIES:

The purpose of this section is to review some applications of kinetics to the study of sorption reactions. Most of the example studies deal with metals being sorbed onto soil materials. The last part of this review will mention some mathematical models which have been used to study phosphate and pesticide sorption in soils.

Chen et al. (1973) found that phosphate sorption on kaolinite and Al oxide was controlled by a fast reaction, lasting from 12 to 24 hours, and a slow mechanism which continued for 60 days. The slow reaction increased with a larger surface area and a lower pH. The activation energy for this reaction was 10 kJ/mole and at pH 5 the first order rate constant was $2 * 10^{-4}$ day^{-1}. Nucleation and growth were believed to be the rate limiting factors. Griffin and Jurinak (1974) also found two sorption reactions in the uptake of phosphate by calcite. The fast mechanism had a second order rate constant of $.26 * 10^{-1}$ M^{-1} sec^{-1} and was believed to represent the adsorption of phosphate on the calcite surface. The slower reaction had a first order rate constant of $.15 * 10^{-4}$ sec^{-1} and was probably controlled by the surface arrangement of phosphate clusters into Ca phosphate heteronuclei.

Rophael and Malati (1972) measured Ca sorption on Mn dioxide with an electrode and observed that there were two first order sorption mechanisms. The fast reaction lasted up to six minutes and had an activation energy of 18.1 KJ/mole. The slower reaction was measured from 6 to 18 minutes and had an activation energy of 32.9 KJ/mole. Ahrland et al. (1960) measured the sorption of Na^+, Ca^{+2}, Ba^{+2}, UO_2^{+2}, Gd^{+3}, Zr(IV), Nb, U(IV), Pu(IV) on silica gel. The

sorption of nonhydrolyzed ions was rapid (5 min.), while the uptake of hydrolyzed ions was slow (2 to 50 hours). From the diagrams of sorption versus time it appears that there is an initial fast sorption followed by a curve which might change to a line with increasing time. Kinniburgh (1983) looked at the H/Zn and H/Ca exchange stoicheiometries on ferrihydrite. Upon addition of Zn or Ca to a suspension of ferrihydrite there was an instantaneous drop in pH. As base was added the pH stopped dropping after one minute. The ratio of H^+ released to Zn^{+2} sorbed remained constant with time. The H/Ca ratio was constant for 900 minutes and then slowly increased with time. After six minutes the amount of Zn or Ca sorbed increased with time (about 2 days).

Bunzl et al. (1976) measured the sorption of Pb, Cu, Cd, Zn and Ca from deionized water by peat. Sorption kinetics were monitored by conductivity and showed that equilibrium was reached after about 2 minutes. Sorption rates increased with higher metal concentration. Absolute sorption rates decreased with different metals according to the order Pb>Cu>Cd>Zn>Ca. The authors believe that film diffusion was probably the rate limiting step.

Singhal and Gupta (1978) measured Zn sorption on dickite using a centrifuge separation, and observed two reaction rates. The faster mechanism lasted for an hour and had a first order rate constant of (2 to 7) $* 10^{-3}$ min^{-1}. The mechanism was believed to result from ion exchange and was limited by film or particle diffusion. The slower reaction which lasted from one hour to at least six hours was attributed to structural penetration or to a surface fixation. With higher Zn loadings the sorption kinetics increased and the sorption became more

sensitive to pH. Inskeep and Baham (1983) looked at Cu and Cd sorption
on Na montmorillonite at pH's of 4, 5, and 6. Cu sorption was followed
with an electrode and it was found that the millivolt readings did not
significantly change after two minutes. A slight pH dependence for
sorption was observed, but it was smaller than for oxides and it was
completely reversible. Malcolm and Kennedy (1969) investigated Ba, Ca
and Mg exchange for.K and Na on kaolinite, illite and montmorillonite
with the help of electrodes. Ba/K exchange on kaolinite and illite was
75 percent complete in three seconds. Ca/K, Mg/K, Ca/Na, and Mg/Na
exchange on the above clays was also very rapid. Vermiculite, however,
showed a fast and slow exchange. The slow exchange probably resulted
from diffusion in the interlayer spaces as indicated by a linear plot of
exchange versus the square root of time.

Shainberg (1973) used conductivity measurements to monitor the
hydrolysis of montmorillonite when it was dialyzed. When a clay is
exposed to a large supply of deionized water surface cations are
replaced by hydrogen ions. A fast and slow reaction were observed. The
fast reaction was postulated to be the initial exchange of hydrogen ion
for surface cations. The slower reaction probably resulted from a
penetration of the structure by hydrogen ion, followed by the release of
octahedral Al or Mg. The activation energies for the second reaction
ranged from 96 to 119 kJ/mole.

Griffin and Burau (1974) found that boron desorption from Western
California desert soil followed three rates. The fastest desorption
reaction was complete in less than one hour and had a pseudo-first-order
rate constant of .5 to .9 hours^{-1}. The second pseudo-first-order

reaction was complete in 20 hours and had a rate constant of .04 to .11 hours^{-1}. Both of these reactions were believed to represent exchange on different surface sites, and desorption measured within their time frame followed a two site Langmuir model. From 20 to at least 72 hours a slow boron desorption was observed which may have represented diffusion from interior clay sites.

Harter and Lehmann (1983) observed that within the first 20 minutes the exchange of Cu, Ni, Ca, Mg and hydrogen ion on soil showed three separate adsorption regions. First there was an instantaneous reaction which was attributed to cation exchange. This was followed by an exponential region for the next six minutes, after which time there was a slow sorption drift. The authors wanted to look at only ion exchange reactions so they used sorption kinetics to extrapolate the sorption back to the time of the instantaneous reaction attributed to ion exchange.

The results of kinetic studies of sorption processes are summarized in table III-4. Most of the studies on metal sorption on soil materials revealed that two or more sorption rates were controlling the metal uptake, which suggests that more than one mechanism is responsible for sorption. Some studies, which have used fast measuring techniques, have reported instantaneous sorption reactions. These very fast sorptions may have similar rates to acid - base or complex formation reactions in solution (table III-3). They have been also attributed to ion exchange and are probably limited by film or particle diffusion. Some of the slow reactions are believed to result from surface precipitation, fixation reactions or even structural penetration.

TABLE III-4

SUMMARY OF SELECTED KINETIC SORPTION STUDIES REPORTED IN THE LITERATURE

Many kinetic sorption studies have revealed the existence of more than one sorption rate. In some cases there is an instantaneous sorption followed by one or more (first or second order reaction rates. This table indicates how many sorption rates were observed. The time span of each rate is indicated, and rate constants are given if they have been measured.

Reference	Sorbate	Sorbent	Instantaneous	Sorption Rates	
				1	2
Chen et al. (1973)	phosphate	kaolinite		12 to 24 hr. 2.6×10^{-7} sec.$^-$	steady drift for at least 60 days
Griffin and Jurinak (1974)	phosphate	calcite		< 10 min. .026 sec.$^-$	up to 2 hr. 1.5×10^{-5} sec.$^-$
Raphael and Malati (1972)	Ca	Mn dioxide		6 min. first order	at least 18 min. first order
Kinniburgh (1983)	Zn, Ca	ferrihydrite		< 6 min.	at least 6 days
Bunzl et al. (1976)	Pb, Cu, Cd, Zn, Ca	peat		2 min.	
Singhal and Gupta (1978)	Zn	dickite		1 hr. 8×10^{-5} sec.$^-$	6 hr. $(.03$ to $2) \times 10^{-5}$ sec.$^-$
Inskeep and Baham (1983)	Cu, Cd	montmorillonite		< 2 min.	
Malcolm and Kennedy (1969)	Ba, Ca, Mg	kaolinite illite montmorillonite vermiculite	yes yes yes yes	100 sec. 100 sec. 100 sec. 1000 sec.	
Shainberg (1973)	H	montmorillonite	yes	at least 170 hr. first order	
Griffin and Burau (1974)	B desorption	desert soil from Western California		1 hr. 2×10^{-4} sec.$^-$	20 hr. $(1$ to $3) \times 10^{-5}$ sec.$^-$
Harter and Lehmann (1983)	Cu, Ni, Ca, Mg, H	soil (Paxton A, Christiana B)	yes	6 min. (curved)	slow drift for at least 20 min.

The best way to deal with kinetic sorption data may be to plot the logarithm of the sorbed ions versus time. Regions which plot as linear segments could be interpreted as being controlled by pseudo-first order reactions. Regions which cannot be linearized this way could be treated by reversible first-order-kinetic expressions, or by some other model. Before kinetic data can be divided into mechanisms it must be shown statistically that the rate for each mechanism is significantly different from the other rates.

The half lives for various sorption mechanisms reported in the literature vary from instantaneous to many days. The reported rates will of course be a function of the sorbate and sorbent used in the study. However, experimental conditions will also influence the observed sorption kinetics because factors such as ionic medium and pH can determine which mechanism(s) will control the overall sorption rate. The method of measuring sorption will also influence the observed kinetics. If samples have to be separated by filtering or centrifuging the very fast mechanisms cannot be followed. Also, errors introduced by the separation process may mask subtle changes produced by very slow reactions. The use of specific ion electrodes or conductivity measurements is essential to follow very fast kinetics.

Soil scientists recognized that many reactions in soil are slow and therefore they have found the need to develop mathematical models to account for sorption kinetics. Some of these models are based on opposing sorption and desorption reactions, while others are just empirical expressions. Travis and Etnier (1981) give an excellent review of various kinetic expressions used in the soil science

literature. The following is a summary of these models.

First-order kinetic sorption models include reversible linear (equation 33) and reversible nonlinear (equation 34) expressions.

33)
$$\frac{dS}{dt} = k_1(v/d)C - k_{-1}S$$

S = sorbed sorbate   v = soil water content

C = dissolved sorbate   d = soil bulk density

k_1 = forward rate k_{-1} = reverse rate

34)
$$\frac{dS}{dt} = k_1(v/d)C^n - k_{-1}S$$

n = constant: When n = 1 equation 34 equals equation 33

Both the reversible linear and nonlinear models have found use in modeling sorption reactions of organics, herbicides, pesticides and phosphate. Enfield (1974) devised a kinetic product model (equation 35) to describe phosphate sorption in soil. This model is empirical with no theoretic basis and it has no way of accounting for sorption capacity. However, for phosphate it seemed to reproduce the sorption better than the first-order-kinetic models.

35)
$$\frac{dS}{dt} = aC^b S^d$$

a, b, and c = empirical constants

The bilinear adsorption model (equation 36) is a kinetic version of the the Langmuir isotherm.

36)
$$\frac{dS}{dt} = k_1 C(b - S) - k_{-1}S$$

b = sorption capacity

The bilinear adsorption model has the same foundations as the Langmuir equation. However, it has not been popular in ground water studies because with this equation there is not an analytical solution to the convective-dispersive transport equation. Vermeulen and Heister (1973) developed a mass transfer model (equation 37) which was used to describe phosphate transport across a boundary layer surrounding solid surfaces.

37) $$\frac{dS}{dt} = k(C - C^*)$$

k = sorption rate parameter accounting for the diffusive transport of a solute through a boundary layer surrounding each solid

C = concentration in liquid

C^* = concentration in liquid at the immediate solid phase

The Elovich model developed by Roginsky and Zeldovich (1934) has been used to describe the sorption of gases on solids, and the uptake of phosphate by soil. It takes the form of:

38) $$\frac{dq}{dt} = A_1 \exp(-B_2 q)$$

q = fraction of surface sites occupied by solute

A_1 and B_2 = parameters

The Fava and Eyring (1956) model is based on first-order-kinetics and was designed to describe the sorption of detergent by fabric and has been used for pesticide sorption in soil.

39) $$\frac{dO}{dt} = 2kO \sinh bO$$

k and b = constants

O = difference from equilibrium divided by the initial difference from equilibrium

$$O(t) = \frac{S(t) - S(eq)}{S(0) - S(eq)}$$

S(0) = initial amount sorbed

S(eq) = amount sorbed at equilibrium

Two-site kinetic models have been developed by Selim et al. (1976) and Cameron and Klute (1977). These models assume the existence of fast (1) and slow (2) sorption sites. The total sorption rate is given by the sum of the sorption rates on the two sites. The sorption on the fast site can be described by either a Freundlich or a linear isotherm since equilibrium is attained quickly. On the slow site sorption is controlled by a linear first-order model. Under fast flow conditions in soil, sorption is dominated by site (1), while if the flow is slow site (2) will have an influence on the total sorption.

In summary, soil scientists have developed a number of mathematical models which can account for the kinetics of sorption processes. These models are convenient for reproducing observed sorption in soil systems. However, the purpose of this study is to use kinetics to separate sorption mechanisms without being restricted to one of these preconceived models.

CHAPTER IV

MEASURED SORPTION KINETICS

INTRODUCTION:

PURPOSE: The crystal structure and chemical properties of kaolinite suggest that metal sorption can occur by several mechanisms. These potential mechanisms may be separated on the basis of their sorption rates. For example:

(1)Nonspecific coulombic attraction and surface complexation are predicted to occur within seconds or minutes.

(2)Surface induced precipitation is likely to be slower, lasting from hours to days.

(3)Structural penetration is likely to be extremely slow, with a half life of weeks to months.

The purpose of this chapter is to present and evaluate the data on copper sorption kinetics with the aim of determining whether one or more sorption mechanisms are required to explain the uptake of copper by kaolinite. Once apparent sorption mechanisms are resolved by kinetics then hypothetical reactions can be assigned to these apparent mechanisms on the basis of similar rate constants. (Nonspecific sorption and surface complexation would be assigned to the fastest apparent mechanism.)

Sorption rates by themselves cannot positively identify sorption mechanisms. Copper sorbed by the various apparent mechanisms must be tested by other experimental factors such as pH, salt concentration, copper concentration, and reversibility. This chapter will also look at the effects of copper concentration on sorption rates, which may tell us something about the mechanism involved. In chapter V the apparent sorption mechanisms will be tested by different pH and salt levels in order to separate nonspecific from specific sorption. H/Cu exchange ratios will be measured in order to distinguish surface complexation from precipitation. Chapter VI will test the apparent sorption mechanisms with various desorption techniques in order to test the strength of the bonds between copper and clay.

APPROACHES TO TREATING AND INTERPRETING SORPTION KINETICS: It is necessary to examine possible approaches to the treatment of kinetic sorption data before a description is given of experimental procedure and results. In this study the reacting species are the free copper ion, several different types of surface sites and the hydroxyl ion. The product(s) are various forms of copper attached to the kaolinite surface. Therefore, copper sorption in the experimental kaolinite suspension can be described by the following general equation.

1) $Cu^{+2} + nX^- = Cu(X)_n^{(2-n)}$
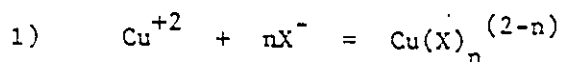
The term $Cu(X)_n^{(2-n)}$ represents any form of sorbed copper. Since copper may be sorbed by several different mechanisms the term X^- is a variable whose meaning is determined by the type of sorption mechanism. If the mechanism is nonspecific coulombic attraction then

X^- may represent the portion of surface charge neutralized by copper. If copper is complexed to kaolinite edges then X^- may be a reactive surface site. In the case of induced surface precipitation X^- would be a hydroxyl ion or some other anion which can form a precipitate with copper. The kinetics of CuX formation from X^- and copper may be written as:

(2) $$\frac{d[CuX]}{dt} = \frac{-d[Cu^{+2}]}{dt} = \frac{-d[X^-]}{dt} = K\ [Cu^{+2}]\ [X^-]$$

Equation 2 suggests that the kinetics of Cu sorption may be second order if both $[Cu^{+2}]$ and $[X^-]$ contribute to the sorption reaction. However, in many instances the concentration of either Cu or X may remain relatively constant during the sorption reaction. In soils X is likely to remain relatively constant because the solid/liquid ratio is extremely high. The sorption experiments in this study were conducted with kaolinite suspensions where the solid/liquid ratio is very low compared to soils. Therefore, X is much more likely to limit the sorption reaction because there is a large reservoir of copper in solution. Furthermore, if the concentration of copper is maintained at a constant level the sorption kinetics reduce to:

(3) $$\frac{d[CuX]}{dt} = \frac{-d[X^-]}{dt} = K'\ [X^-]$$

Equation 3 is a pseudo-first-order reaction whose rate constant K' is specific for a given copper concentration. The rate constant K'(and K) may also be specific to a given pH since the concentration of X may be pH dependent and the speciation of dissolved copper is pH dependent. If X represents hydroxyl ion, as in the case of surface

precipitation, and if the solution pH is maintained at a constant level then there is the possibility that the supply of X at the kaolinite surface is constant. If the concentration of copper is also maintained at a constant level then the kinetics of copper sorption may reduce to pseudo-zero-order kinetics.

(4) $\quad \dfrac{d[CuX]}{dt} = K''$

Equations 2 to 3 may describe the elementary reactions of individual sorption mechanisms. If there is only one sorption mechanism and if the sorption rate of this reaction is not limited by some other process (ie diffusion, changes in surface charge, and coagulation) then equations 2 to 3 may describe the overall sorption reaction. However, it is more likely that the overall sorption rate is determined by several reactions and that it may be affected by other processes such as diffusion. Possible combinations of elementary sorption reactions are given in figure V-1.

If sorption is controlled by one pseudo-zero-order reaction then the rate of copper uptake will be constant with time. Zero-order kinetics can only be expected if precipitation takes place at constant pH and copper concentration. Also, if the sorption rate is very slow then the kinetics may appear to be zero-order. Most sorption curves for metals and organics do not show a constant slope with time for the entire reaction period, so that one zero-order reaction cannot explain the observed sorption kinetics. The amount of copper sorbed by zero order kinetics is given by:

(5) $\quad [CuX] = k\,t$

POSSIBLE RATE LAWS

A) ONE FORWARD ELEMENTARY REACTION:

FIRST ORDER

Amount Sorbed

Time

ZERO ORDER

Amount Sorbed

Time
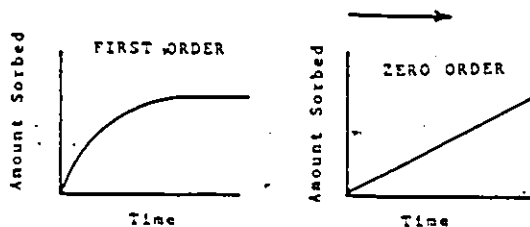
B) OPPOSING REACTIONS:

Amount Sorbed

Time
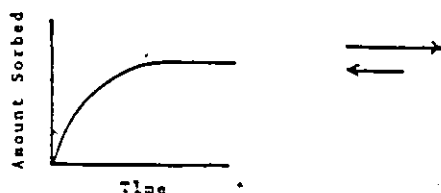
C) CONCURRENT, INDEPENDENT REACTIONS WITH DIFFERENT RATES:

Amount Sorbed
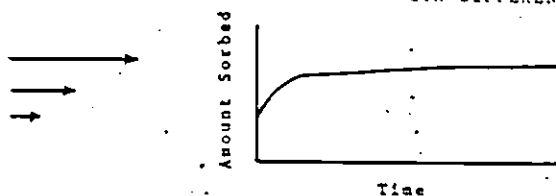
Time

D) CONCURRENT, INDEPENDENT REACTIONS AS WELL AS SOME
SOME REVERSE REACTIONS:

Amount Sorbed
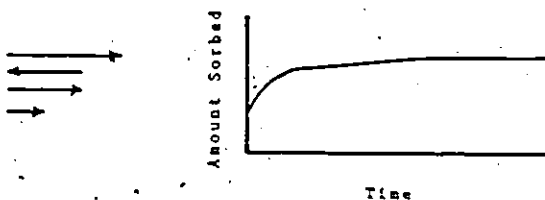
Time

E) SEQUENTIAL AND CONCURRENT REACTIONS:

Amount Sorbed
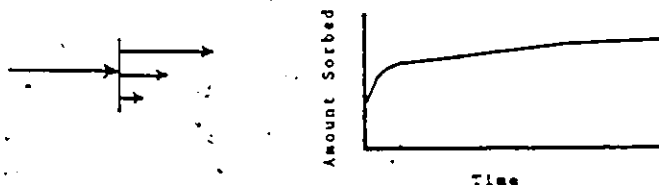
Time

Figure IV-1. Possible rate laws which might be encountered in sorption reactions. The variation of sorbed Cu with time shows that several rate laws can explain the same sorption pattern. However, a single zero-order reaction is distinct. A single first-order reaction is difficult to distinguish from two opposing first-order reactions. A rate law with several reactions (C, D, E) is distinct from a single first-order or zero-order reaction.

Copper sorbed by <u>one pseudo-first-order reaction</u> increases with time until a plateau is reached where one of the reactants is used up. Evidence for first-order kinetics would be given by a linear plot of the logarithm of sorbed copper versus time. Many sorption reactions do not reach a sorption plateau if the reaction is monitored for extended periods of time. In these cases a single first-order reaction does not adequately explain the sorption kinetics. The amount of copper sorbed by a single first-order reaction under conditions of constant copper concentration is given as a function of the initial X concentration, $[X^-]_0$, and the first order rate constant.

(6) $\quad [CuX] = [X^-]_0 (1 - e^{-kt})$

There is a possibility that sorption kinetics may result from <u>competing forward and reverse reactions.</u> Competing first-order reactions may resemble a single first-order reaction. However, a plot of the logarithm of sorbed copper versus time would underestimate the rate constant for the forward reaction. In situations where equilibrium or a steady state is reached rapidly so that the forward rate cannot be distinguished from the reverse rate, it is necessary to study the reaction by measuring its approach to equilibrium. The first-order rate constant which describes this approach to equilibrium is given by a plot of $\ln[([CuX]_s - [CuX])/([CuX]_s - [CuX]_0)]$ versus time. The steady state concentration of copper is $[CuX]_s$ and the initial amount of copper before the reaction is $[CuX]_0$. As with the single first-order reaction the entire sorption kinetics cannot be explained by two competing first-order reactions unless a steady state sorption is observed. The amount of copper sorbed by the opposing reactions can be

calculated once the rate constant, k, is known.

(7) $[CuX] = [CuX]_s - ([CuX]_s - [CuX]_0)e^{-Kt}$

If the forward rate constant can be measured without interference

and if the reverse rate can be measured or determined by the principle

of detailed balancing then the effect of competing reactions can also be

treated with the rate expression shown in equation 8. Equation 8 has an

advantage over the approach to equilibrium method in that it gives a

more detailed picture of the mechanisms involved. If the reverse rate

constant is sensitive to certain surface properties such as local charge

then the approach used in equation 8 may explain sudden changes in the

sorption rate caused by an alteration of some surface property. The

disadvantage of equation 8 is that the reverse rate constant must be

known. Desorption rates may be important for sorption mechanisms which

are reversible such as nonspecific ion exchange. Their significance

probably decreases with less reversible reactions such as surface

complexation or structural penetration.

(8) $\dfrac{d[CuX]}{dt} = K [Cu^{+2}] [X^-] - K_- [CuX]$

It is possible that the sorption rate law is made up of several

concurrent reactions which proceed independently of each other. Since

kaolinite has different types of surfaces it is possible that several

sorption mechanisms operate independently of each other. If the

concurrent reactions are first-order and if they have different sorption

rates then a plot of the logarithm of sorbed copper versus time would

yield a curve which can divided into linear segments. Initially the

fastest mechanism dominates the sorption kinetics, producing a steep

slope. As this mechanism reaches equilibrium or a steady state the next fastest mechanism takes over and the plot of log[CuX] versus time acquires a new slope. The parallel reactions do not all have to be first order. Many sorption studies display an instantaneous initial sorption which is too fast to consider with first-order kinetics. With very long sorption times the slowest reaction may appear to be zero order.

All the sorption mechanisms may not be entirely independent of each other. For example, the increased concentration of copper at the kaolinite faces which is produced by nonspecific sorption , may promote surface precipitation or structural penetration. On the other hand, nonspecific sorption is very rapid compared to precipitation or structural penetration. Therefore, after a few seconds the kinetics of copper sorbed by the slower mechanisms are no longer affected by nonspecific sorption which remains constant.

Copper sorbed by a number of independent mechanisms can be calculated by a summation of the contributions from each mechanism. The following equation is an example of copper sorbed by several different types of mechanisms. This example contains an instantaneous sorption given by $[CuX]_1$, two first-order reactions with rate constants $K(2)$ and $K(3)$, and a very slow pseudo-zero-order reaction with a rate constant $K(4)$. The terms $[X]_2$ and $[X]_3$ represent the sorption capacities available to mechanisms 2 and 3. These sorption capacities will vary with pH and copper concentration in solution.

9) $$[CuX]_{total} = [CuX]_1 + [X]_2(1-e^{-K(2)t}) + [X]_3(1-e^{-K(3)t})$$
$$+ K(4)t$$

Up to this point we have not considered higher order reactions as shown by equation 2. By designing sorption experiments so that copper concentration remains constant or nearly constant it is hoped that sorption kinetics will be reduced to pseudo-first order or pseudo-zero order. Higher order kinetics will only be invoked in the event that the observed sorption cannot be successfully treated by first-order kinetics. Higher order kinetics are obeyed if a plot of $1/[CuX]^{(n-1)}$ versus time yields a straight line. The value of n which gives the straight plot is the order of the reaction.

The contributions of elementary reactions to the overall sorption rate may be partially masked by other factors. The initial sorption kinetics also be affected by the time it takes to properly disperse kaolinite once it has been added to the copper solution. Kaolinite doesn't have an expandable interlayer region into which cations have to diffuse in order to participate in cation exchange reactions. However, kaolinite does flocculate in the presence of a salt solution and copper may have to diffuse through the pore water of the flocs in order to reach sorption sites.

Sorption kinetics on gravel sized micas and vermiculites have been interpreted as diffusion controlled by Barshad (1954), Walker (1963) and Keay and Wild (1961). If it is assumed that diffusion proceeds along a front of constant length then there, should be a linear relationship between sorption and the square root of time. As the reaction front proceeds toward the center of a clay particle or clay floc the length of the reaction front will change. This will invalidate the basic assumption of this diffusion test and the plot of sorption

versus the square root of time will begin to deviate from linearity as reaction proceeds (Malcolm and Kennedy, 1969).

MATERIALS AMD METHODS:

The kaolinite used in this study was kaolinite #4 described in the API Project 49. Kaolinite #4 was sampled at the O'Neal Pit in Macon, Georgia. The surface area of this well crystallized kaolinite was found to be 18.3 m^2/gm by the B.E.T. method. The cation exchange capacity determined by Mg adsorption was found to be 11.1 ± 1.8 milliequivalents per 100 grams. See the appendix for a further description of kaolinite #4. The kaolinite was gently broken up in the wet form to minimize damage to the clay surface. The less than two micron fraction was recovered by suspending the kaolinite in deionized water and allowing the larger than two micron particles to settle out. After sizing, the kaolinite was washed three times in 0.05 M KNO_3, which is the background electrolyte used in all the sorption experiments. Prior to use in sorption experiments the kaolinite was allowed to age in the KNO_3 solution for at least a month. These pretreatment procedures are believed to produce a kaolinite sample whose surface will be stable for the duration of the sorption experiments, and whose surface charge will be neutralized mainly by the K^+ ion.

Sorption experiments were conducted in glass beakers which were also used for the copper calibrations. The effect of sorption on the walls of the beaker was believed to be insignificant for the experimental copper concentrations, and if this sorption did take place it was compensated by the calibration curves. To maintain a constant

25° C temperature the reaction beakers were placed into water jackets which were connected to a circulating supply of constant temperature water. Copper solutions or acid and base solutions were added to the reaction vessel with Gilmont microburettes. To prevent reactions with the glass walls of the burettes the copper, acid and base solutions were contained in teflon tubes attached to the burettes, which themselves were filled with decane. Decane is immiscible in water so that it can be used to push aqueous solutions from the teflon tubes out into the reaction vessel. During some experiments the microburette with copper solution was attached to a stepping motor which was connected to an Apple computer. This arrangement was useful for maintaining a constant Cu^{+2} concentration. As $[Cu^{+2}]$ dropped because of sorption the computer caused the burette to add more copper to maintain a constant $[Cu^{+2}]$. The concentration of the free Cu^{+2} ion in solution was measured by a copper specific ion electrode distributed by Graphic Controls. The pH was measured with a Ross electrode. The reference electrode for both the copper and pH electrodes was a glass, sleeve type, double junction Ag/AgCl electrode. The lower compartment of the double junction electrode was filled with .05 M KNO_3. The purpose of this lower compartment was to prevent Cl^- from leaking into the reaction vessel where Cl^- would complex Cu^{+2} and introduce an error in the copper measurements. An Orion 701 A pH meter was used to measure the emf produced by the copper electrode. The water used in this study was purified by the Milli-Q water purification system manufactured by Millipore. The KNO_3 solutions were made from AnalaR KNO_3 manufactured by BDH chemicals. Stock copper solutions were prepared by

dissolving copper wire in nitric acid.

The copper electrode was calibrated by titrating a 0.05 M KNO_3 solution with copper. A plot of millivolts versus pCu gave a straight line down to copper levels of pCu 6.5 (In this discussion pCu refers to $-\log [Cu^{+2}]$). At higher copper concentrations than pCu 6.5, five to seven calibration points generally produce a straight line with an r^2 value of 1.000 and errors for the slope and intercept which are less than 1 percent. Since the copper calibration may change with time, the calibration is checked periodically during the run of the experiment. The copper measured by the electrode agreed within five percent of that copper measured in filtrates by atomic absorption. Further details of copper electrode properties are given in appendix 10. The pH electrode was calibrated with commercial buffers with pH's of 4.00 and 7.00.

Most copper sorption kinetics were measured at a pH of 6.2 which is in the pH range of minimum kaolinite solubility. Suspensions of kaolinite #4 in 0.05 M KNO_3 tend to naturally maintain a pH around 6.2. At pH 6.2 most of the dissolved copper is still present as the Cu^{+2} ion which is necessary for the use of the copper electrode. To obtain and to maintain a pH of 6.2 throughout the experiment, HNO_3 or KOH was added to the reaction vessel. Copper concentrations were kept below pCu 4.7 to make sure that copper solubility with respect to tenorite was not exceeded in the free solution. Generally the experimental copper concentrations were not below pCu 6.0 to insure a relatively fast and trouble free response from the copper electrode. A 0.05 M KNO_3 background electrolyte was used for proper copper electrode operation and to make sure that the copper activity

coefficient remained constant with changing copper concentration.

Prior to the sorption experiment the copper electrode was allowed to equilibrate in the reaction vessel with 100 ml of copper solution. To initiate the sorption reaction, 10 ml of kaolinite stock solution were added to give a clay concentration of about 0.3 g/100 ml. Initially copper concentrations were recorded at 5 to 10 second intervals. If the Cu^{+2} was to be maintained at a constant level manually then more copper was added after 45 seconds. If the Cu^{+2} was maintained by the computer then Cu additions commenced after the first 5 seconds. During the first minute KOH was added volumetrically to neutralize the H^{+} ions liberated by the Cu sorption. After one or two minutes the pH of the kaolinite suspension stabilized without further base additions. Once the sorption reaction was terminated the kaolinite was separated from the solution by centrifuging and after drying the kaolinite was weighed.

The amount of sorbed copper was obtained by a mass balance calculation using the measured $[Cu^{+2}]$, the total amount of added copper, the solution volume and the dry weight of clay. The sorbed copper was reported in units of moles/kg/liter or moles liter/kg. To reduce the effect of different solid/liquid ratios in kinetic experiments, sorption reactions should be reported as moles per specific surface area which is given by area per volume of solution. This gives units of moles liter/cm^2. Operationally the surface area of a clay is determined by weight so that the square centimeters are replaced by kilograms. For easier comparison to other studies in the literature the sorption data in this study can be converted to moles/kg by dividing by 0.11 liters, which was the experimental volume used in these

experiments.

Errors in the measured Cu sorption can come from (1)the calibration curve, (2)drift in the electrode calibration (3)errors in the volume of added copper and (4) error in the measured weight of kaolinite. Other factors which may affect the sorption process and alter our interpretation of the observed kinetics, include small changes in pH, and excessively rapid additions of Cu to adjust $[Cu^{+2}]$. These latter factors are not considered in error calculations, but must be avoided or taken into account when observed. The error in the measured weight of kaolinite will affect the comparison of data taken from different experiments, but it will not affect the measured sorption rates from a single experiment where the amount of clay remains constant. The greatest error in kaolinite weight comes from small losses caused by clay sticking to the electrodes and from losses during the recovery of clay by centrifuging or filtration. These losses are probably less than ten percent, as shown by the reproducibility of sorption curves shown in figure IV-5. The error in the volume of added copper will not affect the kinetics of an experiment where the total copper remains constant, but it can be a factor in an experiment where additional Cu is added to maintain a constant $[Cu^{+2}]$. Periodic calibration checks are made to eliminate error due to changes in the calibration curve. The best estimate for the success of calibration corrections comes from the reproducibility of sorption curves. Errors in the in the original calibration curve result mainly from variations in electrode measurements. Errors for the calibration slope and constant can be obtained from the confidence limits of the regression line going

through the calibration points. These errors in the slope and intercept can be used to calculate an estimate for potential error in the sorbed copper. It is believed that the error calculated for the calibration line may adequately estimate the confidence limits of sorbed copper within a given experiment.

RESULTS:

ELECTRODE RESPONSE AND OBSERVED SORPTION RATES: The measured rate of copper sorption on kaolinite is ultimately limited by the response time of the copper electrode. Figure IV-2 shows the response of the copper electrode to a simple dilution of copper in solution. This response is compared to the electrode's response to copper sorption on kaolinite. The copper electrode's response to dilution is not instantaneous, but it is slightly faster than the sorption process. Therefore, rates for sorption reactions which last from 10 to 20 seconds can be measured, but any reactions faster than that are operationally defined as instantaneous. Actually it is not surprising that the kinetics of the electrode's response are of the same magnitude as a fast sorption because the copper electrode can only detect copper once it has been sorbed on the electrode's surface.

Typical copper sorption curves for different copper concentrations are given in figure IV-3. In all cases there is a rapid initial sorption which appears to be instantaneous. This is followed by a period of rapid sorption lasting for about one to three minutes. Sorption continues for the next one and a half hours at a significantly reduced rate. It appears from the lower two curves that equilibrium or

a steady state in Cu sorption may eventually be achieved. However, when

the time scale is expanded to one or two weeks it is evident that

sorption continues at a very slow rate (figure IV-6). This sorption

rate is so slow that if one had to measure copper by atomic absorption

the errors introduced by filtration or centrifuging may mask the slow

increase in sorption and one would be inclined to conclude that

equilibrium had been achieved.
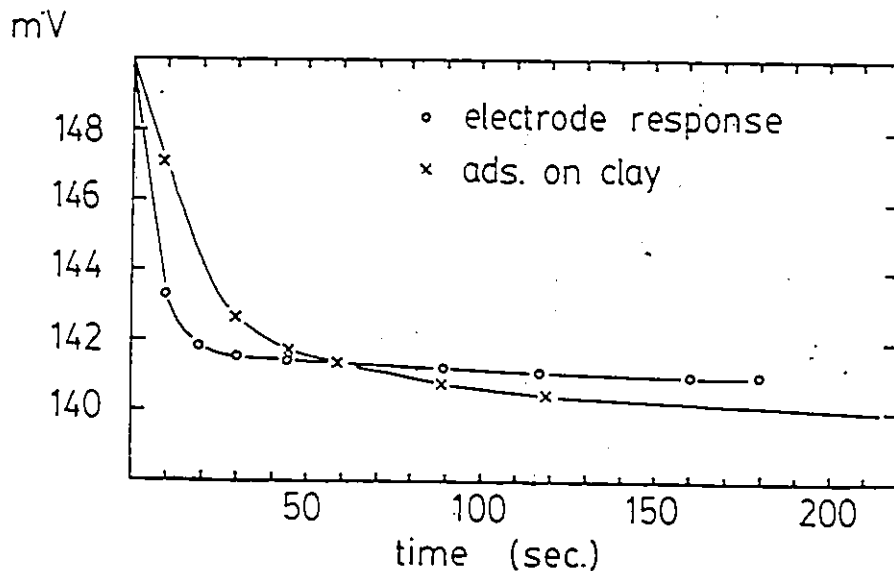
Figure IV-2. Cu electrode response compared to the initial sorption
kinetics.
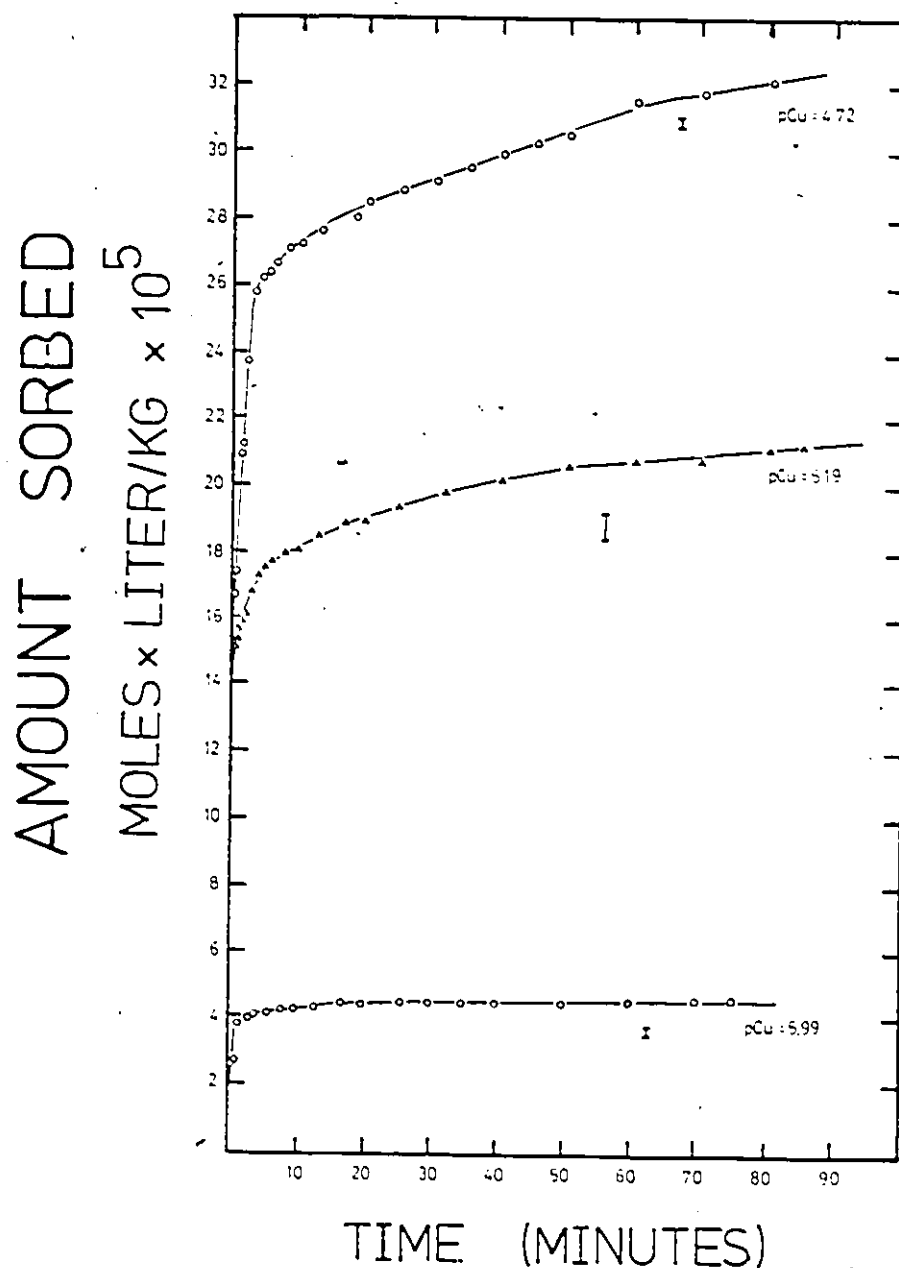
Figure IV-3. Copper sorption versus time for three different constant Cu concentrations. Precision bars for each experiment are determined from the 99 percent confidence intervals on the calibration constants of the Cu electrode. (appendices A-8 and A-10)

TREATMENT OF KINETIC DATA: In order to identify sorption mechanisms and to study the effect of copper concentration on rate constants one must establish what type (order) of kinetics are responsible for the observed sorption rates. Upon examination of figure IV-3 it is apparent that the instantaneous sorption is too rapid to analyze kineticaly and it will have to be operationally defined as instantaneous. The remaining portion of the sorption curve may consist of one or more pseudo-first order reactions. They cannot be zero-order reactions because experiments over a two week period indicate that sorption continues at a reduced rate. Second order reactions will be called upon only if first order kinetics fail to describe the observed sorption rate.

One way of interpreting the sorption rate of a reaction shown in figure IV-3 is with a pair of opposing first-order reactions. The data for the middle curve in figure IV-3 are plotted in figures IV-4 a and b as $\ln[([CuX]_s - [CuX])/([CuX]_s - [CuX]_0)]$ versus time for steady state sorption concentrations of 180 and 205 micromoles*liter/kg. The 180 micromoles*liter/kg steady state value assumes that the fast sorption reaction lasting for 8 minutes has ended and that a slower mechanism has taken over the sorption kinetics. Figure IV-4c compares the observed data with the sorption curves which can be calculated from the rate constants obtained from the slopes of figures IV-4 a and b. It is obvious that if the steady state sorption is taken to be 205 micromoles*liter/kg or higher then a single pair of opposing reactions do not explain the observed sorption rate. However, if the fast sorption lasting for about 8 minutes is considered separately then it can

adequately be described by a pair of opposing first-order reactions.
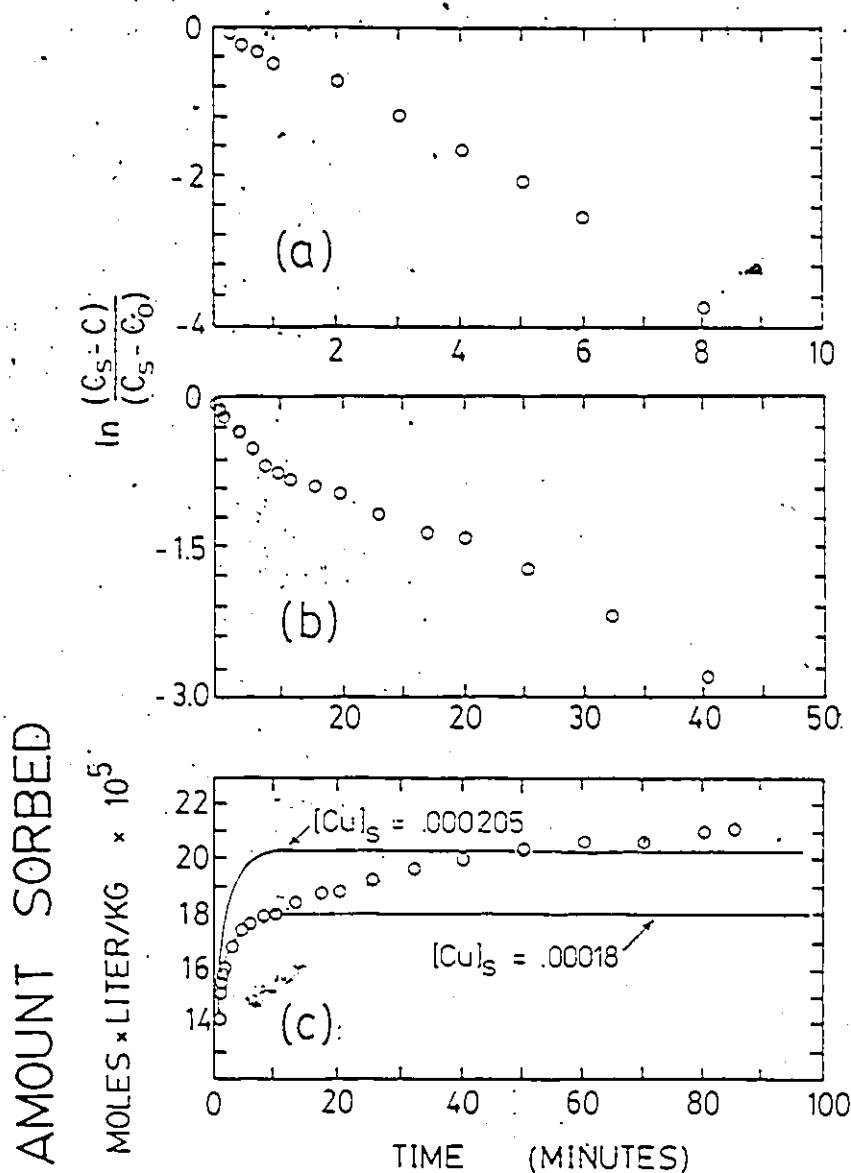
Figure IV-4. Modelling soprtion kinetics with an approach to equilibrium model. Figure 4a assumes that a fast reaction reaches an equilibrium concentration of .00018 moles *liter/kg in about 10 minutes. Figure 4b tries to measure the rate constant assuming equilibrium is reached at .000205 moles*liter/kg. Figure 4c attempts to reproduce the sorption data with the rate constants measured from 4a and 4b.

Another method of interpreting the sorption data is to assume that the overall kinetics are controlled by independent concurrent reactions which are not significantly affected by reverse reactions. If these reactions are pseudo-first-order and if they have different rate constants then a plot of the logarithm of sorbed copper versus time will yield a curve which can be divided into linear segments. The advantage of this treatment is that it can easily deal with several concurrent first-order reactions without initially worrying about equilibrium or steady state sorption levels. Furthermore, if the forward sorption rates are not affected by reverse reaction we may get a better picture of separate sorption mechanisms. Figure IV-5 shows the data of figure IV-3 replotted as the logarithm of sorbed copper versus time. Figure IV-5 also illustrates an instantaneous copper sorption followed by a rapid sorption which appears to be linear with time. A curved region separates this rapid sorption from the next linear portion of the graph. Linear portions of figure IV-5 can be interpreted as representing regions of pseudo-first-order kinetics, while the curved region can be interpreted as a transition period between two regions with different kinetics. The rate constants for the regions which obey first-order kinetics are given by 2.303 times the slope of the linear segment. As reverse reactions become stronger the faster sorption reactions approach equilibrium or a steady state and the sorption kinetics are taken over by the next fastest reaction.
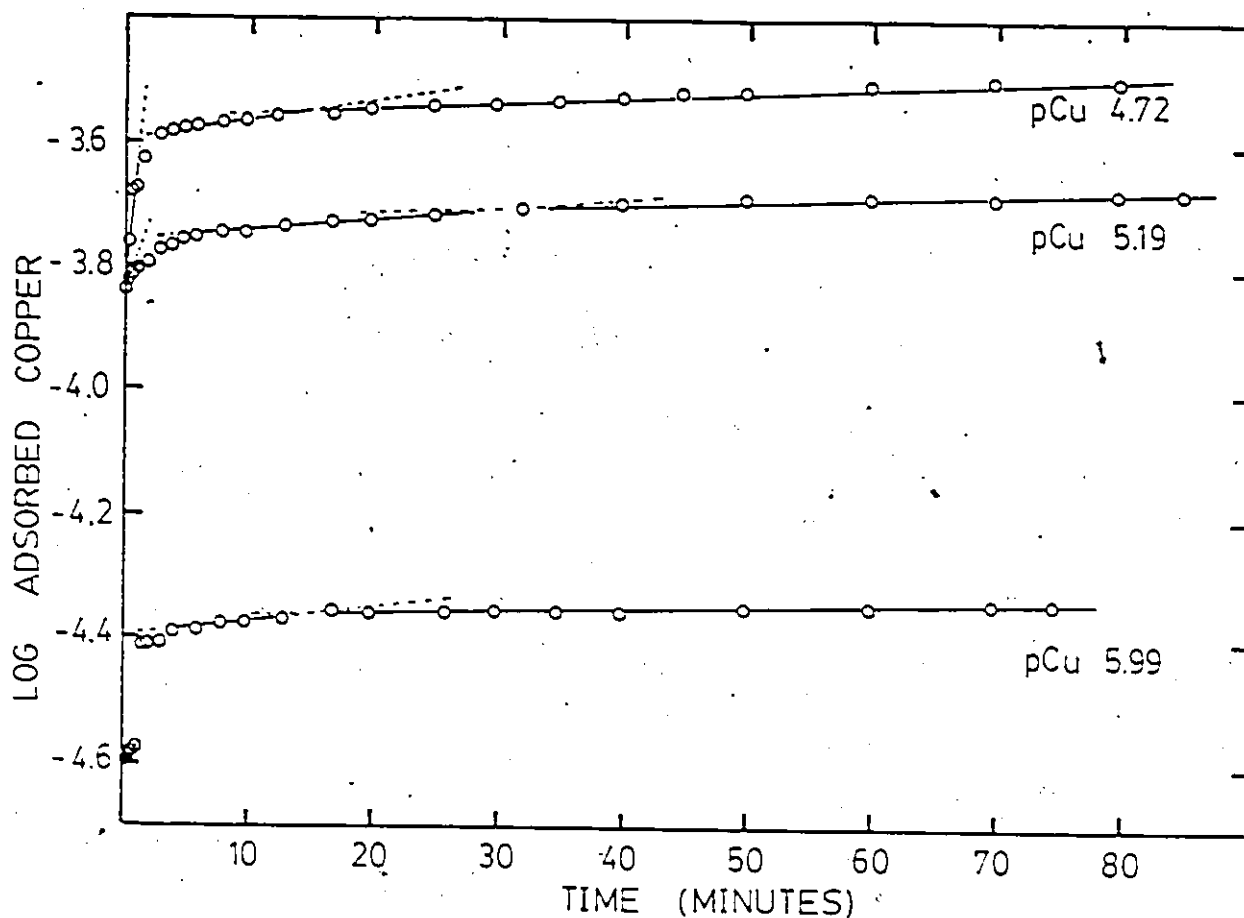
Figure IV-5. Data of figure IV-3 plotted in logarithm form. The separation of linear segments is discussed in the next section. Linear regression is used to determine which points belong to a given segment.

The assumption of independent concurrent reactions must be checked by recalculating the sorption curve using the rate constants measured from figure IV-5. The amount of sorbed copper at any time during the reaction is calculated by summing the contributions from the different apparent sorption mechanisms. This summation can take on a form similar to equation 9. Figure IV-6 illustrates this type of calculation for a data set from figure IV-3. An instantaneous sorption of 142 micromoles*liter/kg is used as the starting sorption

concentration. From equation 9 it is apparent that we need to have a sorption capacity for each first-order mechanism. These capacities can be estimated for a given mechanism by looking for a capacity which gives the best fit to the data. The effect of changing sorption capacities is illustrated in figure IV-6. Figure IV-6a shows that one first-order mechanism combined with an instantaneous reaction is not enough to explain all the sorption kinetics. However, when the second first-order reaction is added in figure IV-6b then the observed sorption kinetics can be reproduced. Figure IV-6a illustrates a problem which is sometimes encountered when the sorption rate of the initial first-order reaction (segment II) is measured. In some cases, when there are fewer data points within the first 30 seconds of reaction, the measured forward rate constant appears too low to properly fit the observed sorption curve. The rate constant measured for segment II was 0.097 min⁻ and the predicted sorption curves which were calculated from this rate constant are shown by dashed lines. When the rate constant was increased to 0.28 (similar to results in other experiments) there was a much better fit between observed and predicted results. In other experiments, where there were more measurements within the first 30 seconds of reaction, it was not necessary to increase the measured rate constant of segment II (figure 4c). This illustrates the fact that if the forward rate of segment II is not measured early enough a reverse reaction may interfere with the measurement of the rate constant.

Figure IV-6. Modelling sorption data with several concurrent
first-order reactions. Figure 4a models the data with only segments I
and II. The solid lines represent two sorption capacities for segment
I, using a rate constant of .28. The dashed lines represent the same
sorption capacities, but with a lesser rate constant (.10). Sorption
capacities used in this calculation are summarized below. (in the
notation of eq. 9)

$[CuX]_1$ = .00014

$[X]_2$ = .00004 and .00005

Figure 4b models the same data with the addition of segment
III. Sorption rates and capacities for this calculation are
summarized below.

$[CuX]_1$ = .00014

$[X]_2$ = .00004
$[X]_3$ = .00008, .00010, and .00012

$K(2)$ = .28
$K(3)$ = .0042

Figure 4c models another sorption experiment with segments I
to IV. The sorption capacities and rates are summarized below.

$[CuX]_1$ = .000036

$[X]_2$ = .00004

$[X]_3$ = .00004

$[X]_4$ = .00004

$K(2)$ = .81
$K(3)$ = .013
$K(4)$ = .0023

For this exercise the best model fit to the data was
obtained by a visual comparison. The purpose of this excercise
was to demonstrate that several mechanisms are required to
explain the sorption data. The intention was not to obtain
accurate estimates of sorption capacities.
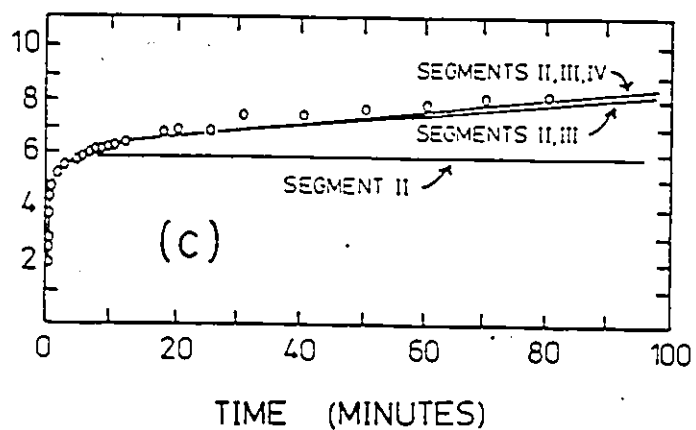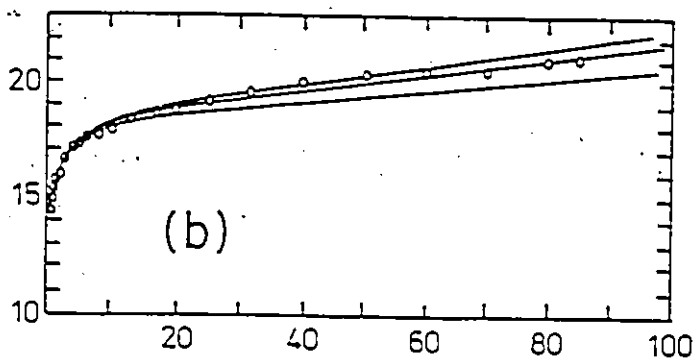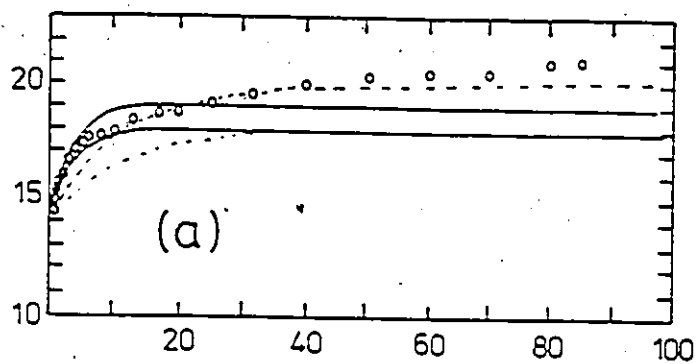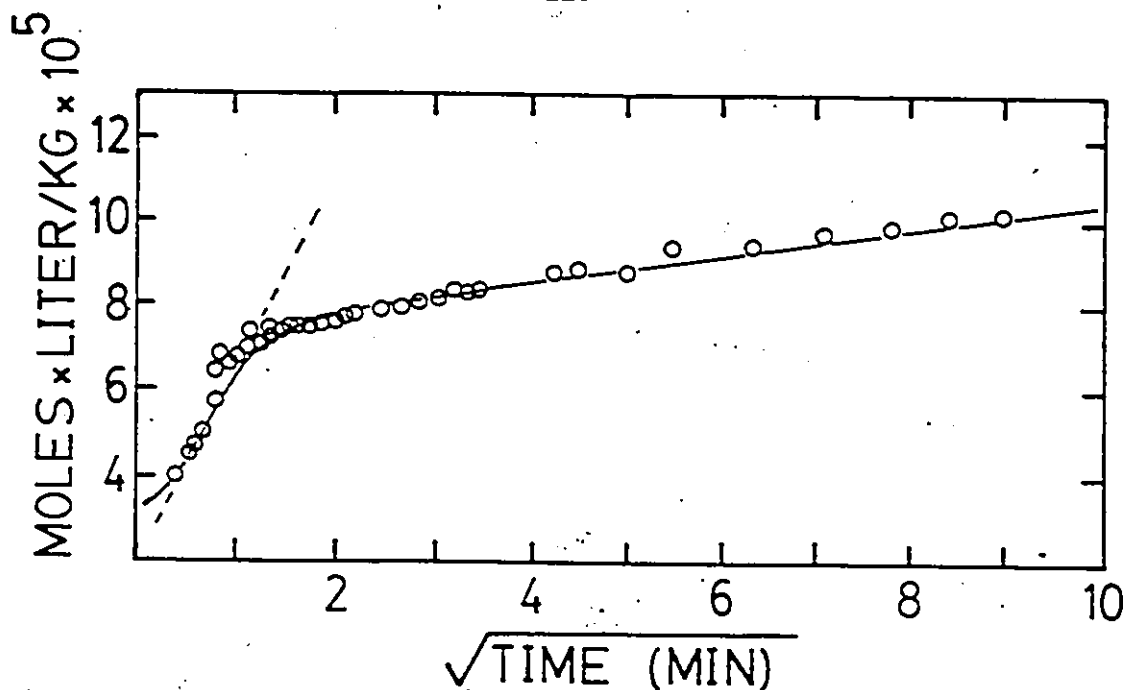
Figure IV-7. Copper sorption versus the square root of time.

In order to evaluate the effects of diffusion in kaolinite flocs, the data of April 6/84 have been plotted as sorption versus the square root of time in figure IV-7. The data within the first one minute of reaction could be fit to a straight line, suggesting that sorption during this period could be diffusion controlled. However, when the copper sorption predicted by a combination of concurrent first-order reactions is plotted in figure IV-7 (solid line) then the sorption curve within the first minute also appears linear. Therefore, this diffusion test does not conclusively show that sorption within the first minute is diffusion controlled. We can only speculate on the possibility that diffusion in the clay floc may act to slow sorption within the first minute of reaction.

It appears that a first-order treatment of the sorption data is a useful method of resolving sorption mechanisms. Except for some problems encountered with the measurement of the rate constant for segment II, the observed rate constants can reproduce the experimental data. An approach to equilibrium treatment of segment II would guarantee a better fit to the experimental data. However, to be consistent, segment II will be treated in the same manner as the remaining sorption data, keeping in mind that the measured rate constant for this segment may be low in some cases. It is not necessary to invoke higher order kinetics because the data can be fitted to a first order model. This is not surprising because in many experiments copper was maintained at a constant level so that sorption kinetics would be reduced to first-order.

SEPARATION OF SORPTION SEGMENTS: From figure IV-5 it appears that differences in the slopes of the slower reactions are not very great and a question arises as to whether the data should be treated as one reaction or should the data be divided into several linear portions. If the data are to be separated into linear segments then the division between segments must be made in some unbiased way which separates areas that are significantly different. The best way to achieve this is to fit the data points to a linear regression model which will indicate how well the data points fit a linear model and what the confidence limits are for the slope. From figures IV-3 and IV-5 one can estimate which regions might fit into linear segments and the data in these segments are regressed to linear models. The coefficient of determination (r^2)

indicates what fraction of the data fits a linear equation. To optimize r^2, data at the beginning or end of a segment can be added or deleted to get the best boundary for each linear segment. Once the boundaries are established for linear segments, the slopes of neighboring segments are compared to see if their differences are greater than their errors (predicted from the regression model). Two linear segments are considered significantly different only if their difference cannot be explained by the errors on their slopes. If the errors of two slopes are close to overlapping then a student's t test can be used to test the significance of the difference between the two slopes.

The data in figures IV-3 and IV-5, as well as data from longer experiments (such as in figure IV-14), suggest the existence of five sorption segments which are summarized in table IV-1. The segments in table IV-1 are distinguished according to (1) their order of appearance, (2) their length of duration, and (3) their rate constant. Segment I represents the instantaneous sorption whose rate is too fast to measure. To estimate the magnitude of this reaction one can extrapolate the sorption curve within the first minute to time zero. This extrapolation is given by the intercept of the linear regression model given by segment II. This approach was used by Harter and Lehmann (1983) to separate instantaneous cation exchange reactions in soils.

TABLE IV-1

KINETIC SORPTION SEGMENTS

	SEGMENT I MOLES*L/KG * 10^5	SEGMENT II TIME (MIN)	SLOPE	SEGMENT III TIME (MIN)	SLOPE * 10^3	SEGMENT IV TIME (MIN)	SLOPE * 10^4	SEGMENT V TIME (MIN)	SLOPE * 10^5
1	14.2 ± 1.0	.33 to 1.0	.10 ± .10	8 to 32	4.17 ± 1.1	32 to 85	13 ± 4.6		
2	2.5 ± .1	.33 to 1.0	.07 ± .04	4 to 17	5.94 ± 1.9	17 to 75	8.1 ± 2.5		
3	14.5 ± 9.0	.33 to 1.0	.41 ± .69	3 to 13	6.4 ± 2.8	17 to 80	22 ± 3.5		
4	9.6 ± 2.2	.17 to 1.0	.16 ± .15	3 to 40	6.91 ± 1.1				
5	3.1 ± 0.4	.33 to 1.0	.09 ± .18	1 to 162	7.4 ± 2.8				
6	12.0 ± 70	.17 to .8	.2 ± 3.5	1 to 60	5.32 ± 1.2				
7	3.5 ± .7	.10 to .3	3.2 ± .99	2 to 6	10 ± 3.0				
	8.5 ± 1.0	.40 to 1.5	.30 ± .12						
8	1.0 ± 2.5	.17 to .4	1.6 ± 2.5	7 to 80	9.9 ± 5.1				
	2.1 ± .1	.07 to 2.0	.19 ± .04						
9	1.3 ± 1.0	.17 to .5	1.9 ± 1.6	5 to 22	7.4 ± 2.3				
	2.5 ± .4	.25 to 2.0	.41 ± .12						
10	10.9 ± .5	.15 to 3.0	.28 ± .05	3.5 to 55	6.17 ± .48	60 to 97	12 ± 3.0		
11	3.6 ± .4	.17 to .83	.81 ± .21	1.4 to 12	13.0 ± 2.2	20 to 80	23 ± 8.5	190 to 1150	14.1 ± 1.4
12	1.6 ± .1	.16 to .75	.55 ± .09	3.5 to 9	11 ± 3.5	15 to 90	16 ± 5.1	120 to 1320	12.6 ± 1.7
13	3.3 ± .3	.10 to .86	1.1 ± .2	2.5 to 40	2.71 ± .48	40 to 100	15.3 ± 1.6	305 to 1300	9.3 ± 1.3
						100 to 210	6.8 ± 1.1		
14	7.7 ± .8	.35 to 2.3	.28 ± .09	3.0 to 19	20 ± 3.0	60 to 253	5.7 ± .90	450 to 998	14.2 ± 2.0
15	4.5 ± 3.5	.17 to 1.0	1.0 ± .58	3.0 to 19	7.1 ± 4.1	26 to 96	12.9 ± 2.2		
16	4.4 ± 7.4	.16 to .75	.74 ± 2.0						
17								4380 to 24000	1.39 ± .15
								210 to 24000	3.06 ± .67
18	2.4 ± 1.1	.17 to 1.0	.39 ± .59	6.0 to 50	5.41 ± .55	60 to 120	15.4 ± 6.7		
19	6.1 ± 2.7	.17 to .75	.46 ± .75	10 to 60	3.72 ± .33				
20	.7 ± .6	.33 to 1.0	.49 ± .84						

	Date	Constant?	pCu or pCut	pH	gm/100 ml		Date	Constant?	pCu or pCut	pH	gm/100 ml
1	26/07/83	pCu	5.19	6.20	.24	11	06/04/84	pCut	5.26	6.20	.30
2	02/08/83	pCu	5.99	6.20	.36	12	13/04/84	pCut	5.25	6.20	.81
3	05/08/83	pCu	4.72	6.20	.54	13*	15/04/84	pCu	5.2	6.20	.99
4	10/12/83	pCu	5.20	6.20	.70	14*	19/04/84	pCu	5.2	6.20	.33
5	12/11/83	pCu	5.11	5.36	.58	15&	31/05/84	pCu	5.24	6.20	.29
6	11/01/84	pCu	5.24	6.20	.30	16	06/84	pCut	5.26	6.20	.36
7*	16/02/84	pCu	5.22	6.20	.24	17	06/84	pCu	5.2	6.20	.28
8*	15/03/84	pCut	4.74	6.20	1.01	18	06/12/82	pCu	5.60	6.20	.38
9	29/03/84	pCut	5.27	6.20	.31	19	29/12/82	pCu	5.46	6.18	.20
10*	02/04/84	pCu	5.25	6.20	.23	20	10/01/83	pCu	6.14	6.20	.39

Table IV-1 lists the rate constants measured in the various experiments
of this study. The last segment for each experiment represents the
sorption rate which was measured before the experiment was terminated
because of time constraints. The date, copper concentration, pH and
solid/liquid ratio are listed for each experiment. The column with the
heading, Constant?, indicates whether the copper activity was maintained
at a constant level (pCu), or whether the total copper in the experiment
remained constant (pCut).

Segments II to V have been distinguished by linear regression as described above. Segment II was the only one which required a close scrutiny of r^2 to establish its boundary. This was particularly true in experiments where the initial sorption measurements were taken at five second intervals instead of every ten seconds. In experiment 6 segment II could be divided into two regions which gave different slopes and intercepts. Therefore, the errors associated with segment II can be large and are sensitive to where the boundaries are drawn. The boundaries of regions III to V are much more clear and can be easily identified from a plot of copper sorption versus time.

The reproducibility of sorption measurements is illustrated in figure IV-8, where sorption curves are given for similar copper concentrations. Each experiment shows a similar sorption trend with a fast initial sorption followed by various slower sorptions. The spread in sorption curves at 80 minutes is about $4 * 10^{-5}$ moles*L/kg, which is 20 percent of the sorption level at that point. This spread results from errors in kaolinite weight as well as drift in the electrode, which affects the amount of copper added to maintain a constant pCu. Although the concentration of free copper was the same in these experiments after two minutes, two experiments had different initial Cu concentrations before the start of sorption. This produced a higher initial sorption in segment I. Once the solution Cu concentrations became similar, the rate constants no longer reflected any difference in the initial Cu concentration (Table IV-2). In the May experiment the kaolinite had been treated with citrate buffer to remove any surface iron. This treatment has not significantly alter the kaolinite's sorption

characteristics. There is some variation in the measured sorption rates
between the five experiments. These sorption rates are summarized in
table IV-2.
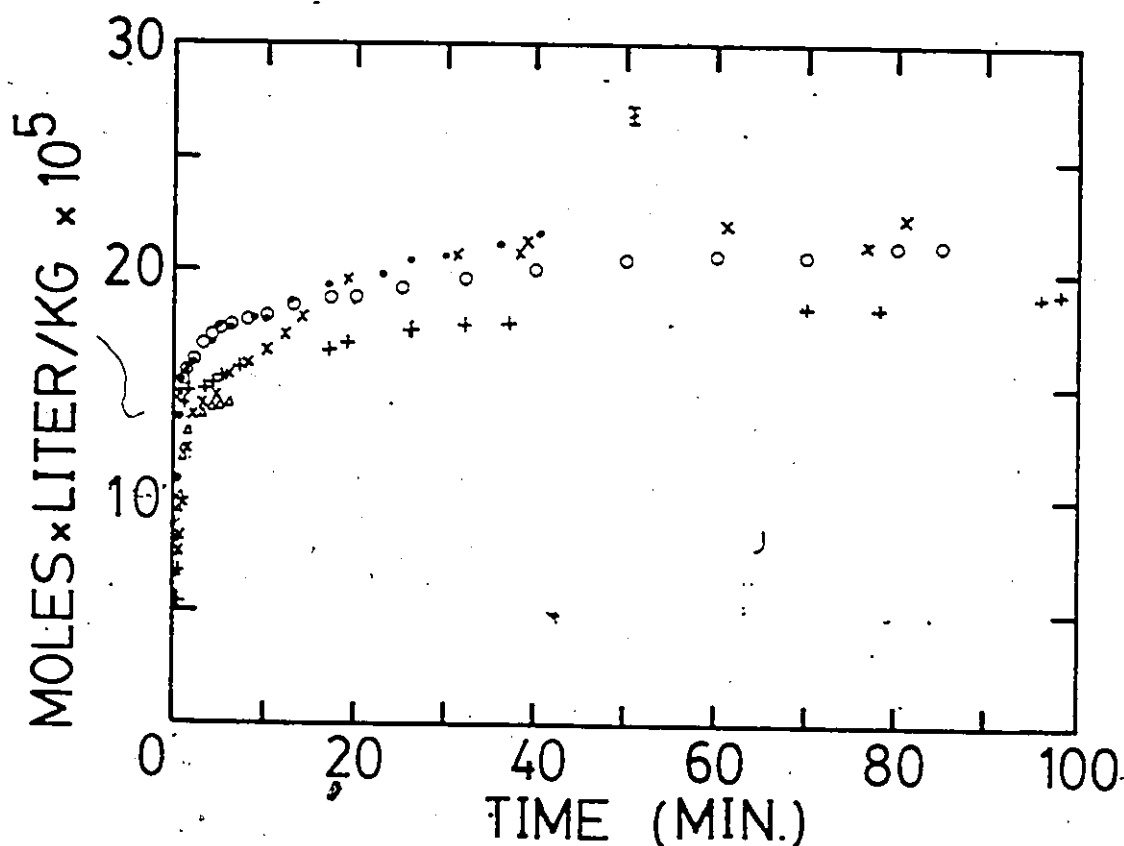
Figure IV-8. Comparison of five sorption curves measured in the
presence of the same copper concentration. (pCu 5.2). (o) July
26/83, (•) Nov. 10/83, (△) Feb. 16/84, (×) April 19/84, (+) May 31/84.
Error bar shows precision for an individual experiment.

Table IV-2 shows that the variations in the sorption rates of
segments II to IV between different experiments is greater than the
errors predicted for these rate constants. Therefore, due to
experimental factors which are difficult to compare and control between

different studies (pCu, clay preparation, clay purity) the variation in

measured sorption rates between different experiments and studies may be

much larger than the statistical errors determined for one individual

experiment. Even though there is a variation in sorption rates between

experiments, the different sorption segments can still be distinguished

and the rate constants of a segment such as III do not overlap with the

constants of another segment.

TABLE IV-2

RATE CONSTANTS MEASURED AT pCu 5.2 TO ILLUSTRATE REPRODUCABILITY

EXPERIMENT	INITIAL pCu	COMMENT	SEGMENT I	SEGMENT II	SEGMENT III $\star 10^3$	SEGMENT IV $\star 10^4$
July 26/83	4.98		14.2 ± 1.0	0.1 ± .1	4 ± 1	13 ± 5
Nov. 10/83	4.92		9.6 ± 2.2	0.2 ± .2	7 ± 1	
Feb. 16/84	5.22		3.5 ± .7	3.2 ± 1.0	10 ± 3	
			8.5 ± 1.0	0.3 ± .12		
April 19/84	5.22		7.7 ± .8	0.3 ± .1	20 ± 3	6 ± 1
May 31/84	5.22	citrate treated	4.5 ± 3.5	1.0 ± .6	7 ± 4	13 ± 2
mean			8.0	0.8	10	11
standard dev.			3.8	1.2	6	4

Although it is possible to separate sorption segments with a

linear regression analysis, a question which comes to mind is whether

the data itself covers a wide enough time span to adequately restrain

all the observed rate constants. In other words, are all the observed

sorption segments necessary to explain the observed data? One way of addressing the question of time scale is to consider the half life of the reaction under consideration. The half life for a first order reaction is given by ln2/K, where K is the rate constant. Table IV-3 illustrates the range of half lives calculated for the sorption segments.

TABLE IV-3

SEGMENT	HALF LIFE (MINUTES)
II	0.7 to 7
III	33 to 150
IV	300 to 1000
V	5000 to 50000
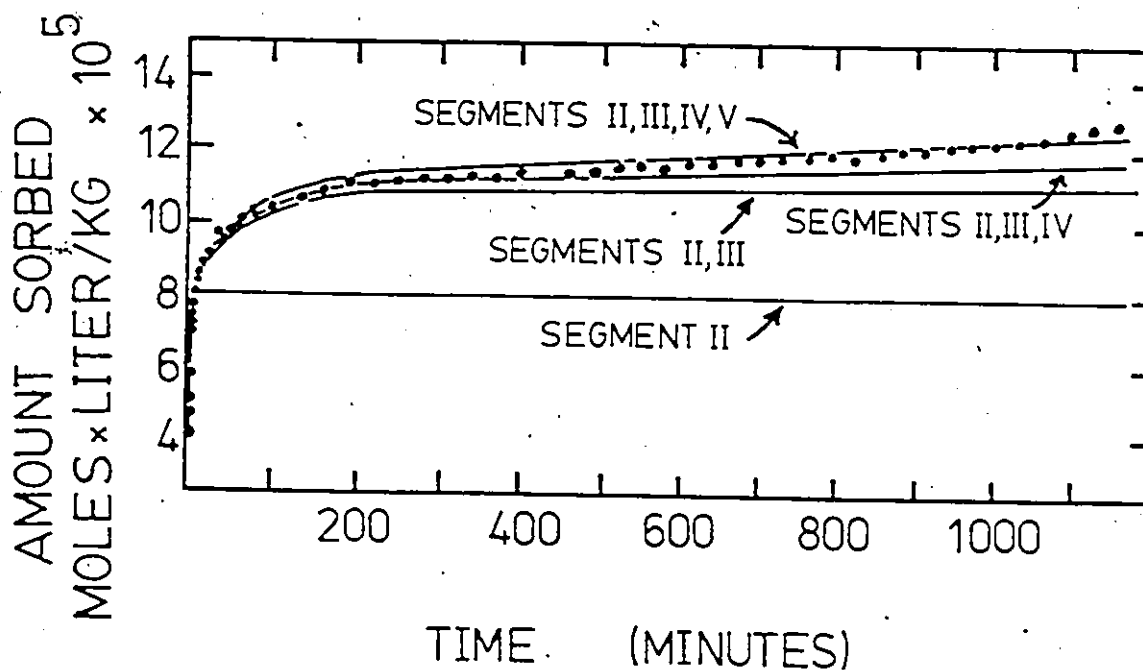
Figure IV-9. Contributions of sorption segments to a 1400 minute reaction.
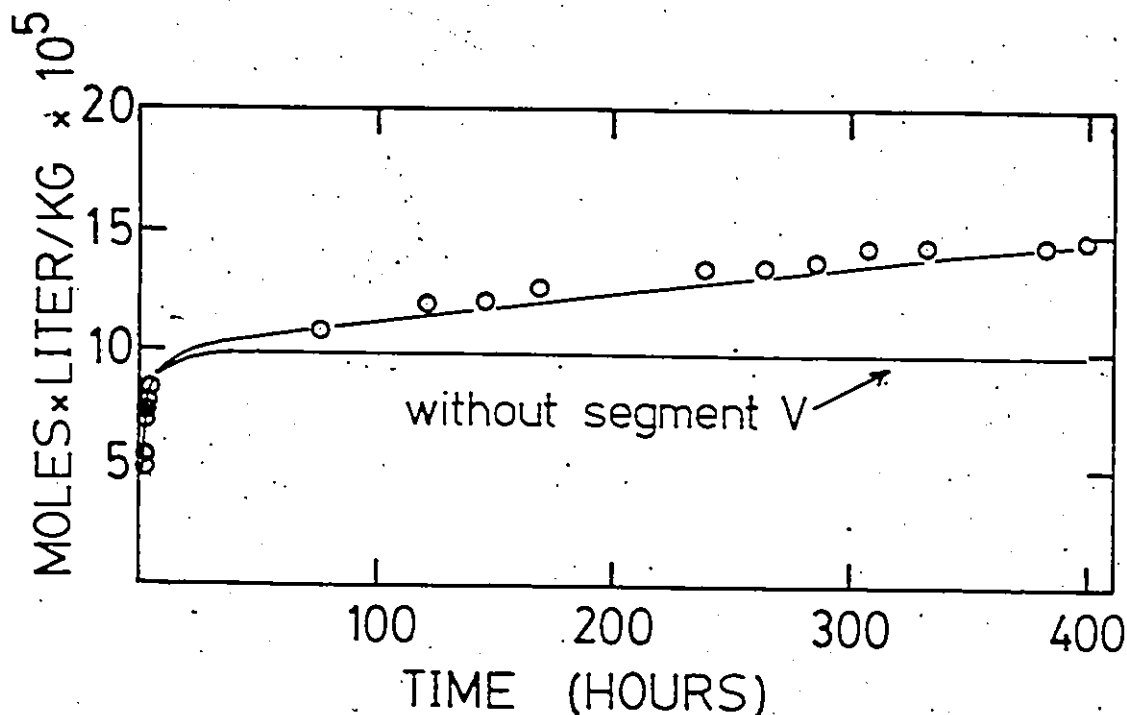
Figure IV-10. Contribution of copper sorbed in segment V (rate = .000014) to a 2.5 week sorption.

In order to adequately define a slow first order reaction the experimental time should be somewhere near the half life of the reaction. Figure IV-9 illustrates the modeling of sorption data from an experiment which lasted 1200 minutes. Figure IV-6c shows that segments II and III are required to explain the sorption kinetics monitored for 100 minutes. The addition of segment IV, with a half life of 300 minutes, does not significantly influence the calculated sorption within the the first 100 minutes. However, when sorption is monitored for 1200 minutes segment IV is required to explain the sorption data. Segment V (half life = 4900 minutes) cannot be adequately justified over the 1200 minute time span. Figure IV-10 shows the results of an experiment which lasted 400 hours. Segment V (half life = 523 hours) was required to

explain the sorption kinetics measured over 400 hours.

Therefore, when the kinetics of copper sorption are considered over a two and a half week period the existence of five sorption segments is justified. However, with the exception of the 2.5 week experiments the last sorption segment in most experiments is not well constrained by the duration of the reaction.

THE EFFECT OF COPPER CONCENTRATION ON SORPTION RATES: From figure IV-3 it is evident that the amount of sorbed copper and the initial sorption rate increase with higher copper concentration. The slower sorption rates also appear to increase with copper concentration. This suggests that if the copper concentration in solution decreases during sorption then the kinetics may be affected. Figure IV-11 illustrates the sorption kinetics of two experiments started at similar initial copper concentrations. The pCu of one experiment is maintained by copper additions while the total copper concentration of the other experiment remains constant and pCu is allowed to vary. If pCu is kept constant the amount of Cu sorption is higher than if the Cu^{+2} concentration is allowed to drop. The greatest difference in sorption rates appears to be in the initial minutes of reaction (segment II). The greatest drop in solution copper concentration occurs within the first minute. After 20 minutes the sorption rate appears to be much less sensitive to copper concentration.
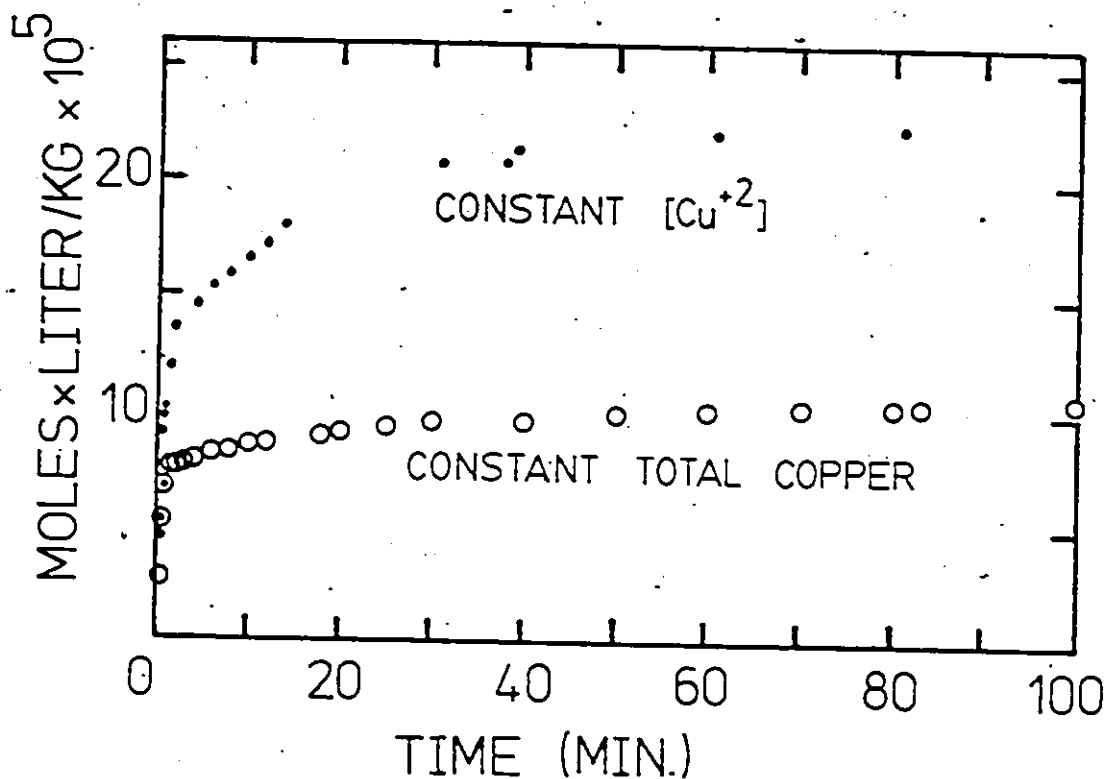
Figure IV-11. Comparison of sorption from a solution of constant copper concentration to an experiment where the total Cu remains constant.

Actually it is impossible to control precisely the copper concentration within the first one minute even if a copper stat is used to automatically control the copper concentration. Figure IV-12 illustrates copper sorption and the variation of solution copper throughout the first seven minutes of an experiment where a computer controlled copper stat is used to maintain pCu. At the 0.5 minute mark the copper concentration has dropped 32 per cent below the desired level. It is impossible to precisely maintain a constant copper concentration within the first minute because the copper stat is limited by the copper electrode's response time to changes in copper concentration. The kaolinite sorbs copper faster than the copper stat

can add it.
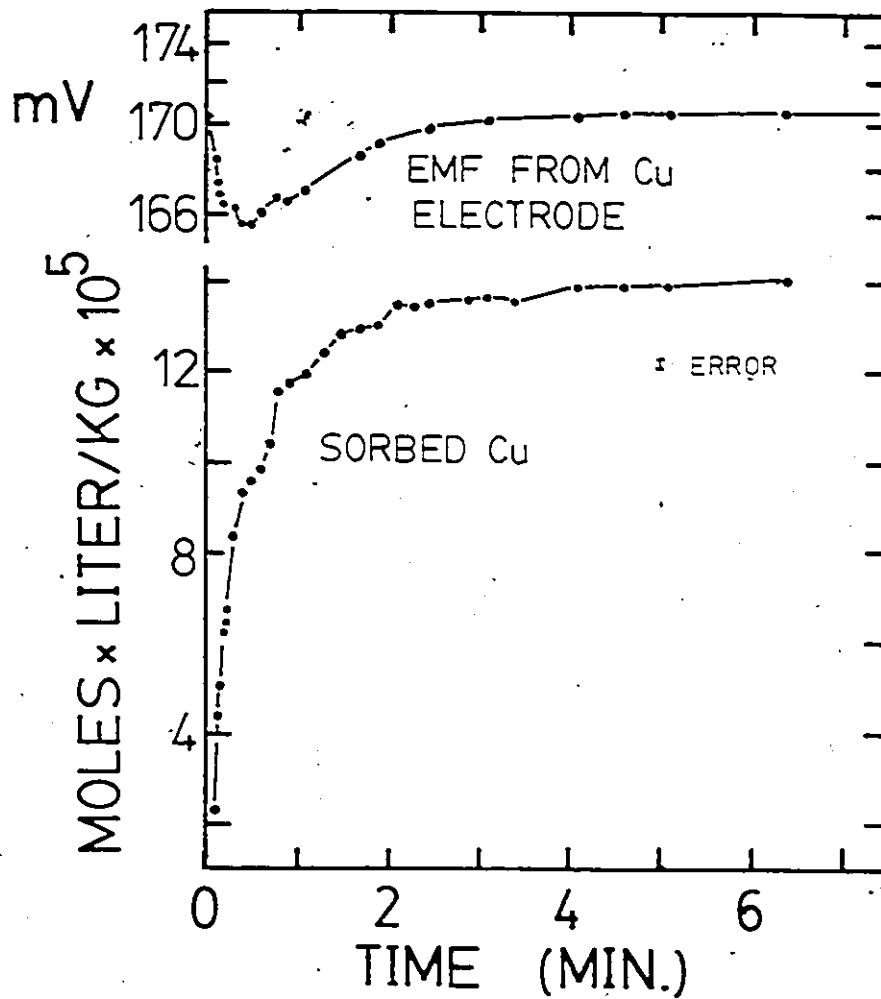
Figure IV-12. Variation of copper sorption and solution concentration within the first seven minutes of a Cu stat controlled experiment.

The only way to insure a constant copper concentration is to have a very low solid/liquid ratio so that the supply of copper in solution is not affected by sorption. Unfortunately, under these circumstances the copper electrode cannot be used to measure rapid changes in sorption.

An attempt was made to compare copper sorption at constant total copper measured over a two week period (figure IV-13) with an experiment where the copper stat was used to maintain pCu (figure IV-14). Unfortunately the experiment with the copper stat was not entirely successful because of occasional drifts in the copper electrode which caused excess additions of copper. These copper additions produced sharp rises in copper sorption at points A, B, and C, while a pH adjustment produced the increase at D. The rate constants for these sorption jumps are presented in table IV-4.

TABLE IV-4

SORPTION KINETICS INDUCED BY Cu ADDITION OR pH ADJUSTMENT

Sorption Jump	Rate Constant $* 10^4$
A	53 (two point estimate)
B	11 ± 5
C	5 ± 7
D	6 ± 3

The points A, B, C, and D refer to the periods of increased sorption rate in figure IV-14. These sorption jumps were caused by Cu additions or pH adjustments.
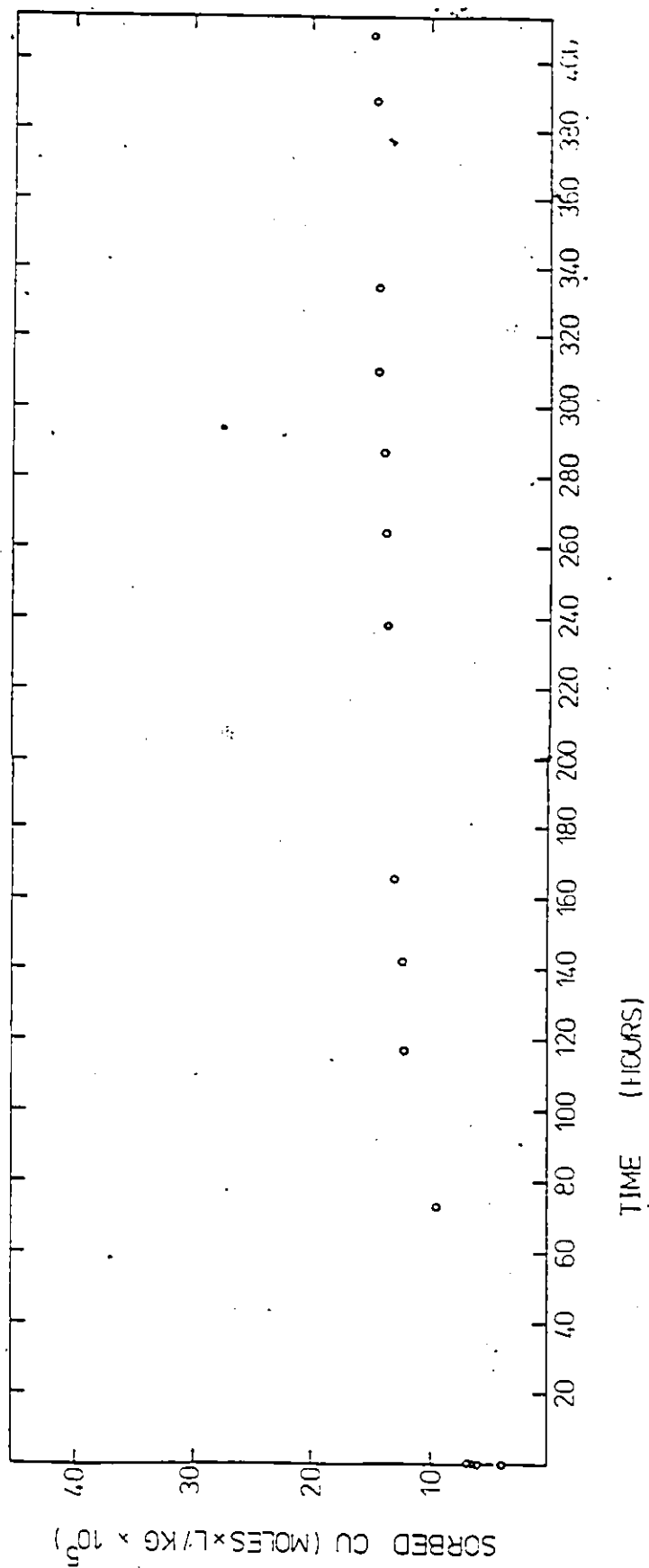
Figure IV-13. Sorption over a 2.5 week period without maintaining a constant copper concentration.
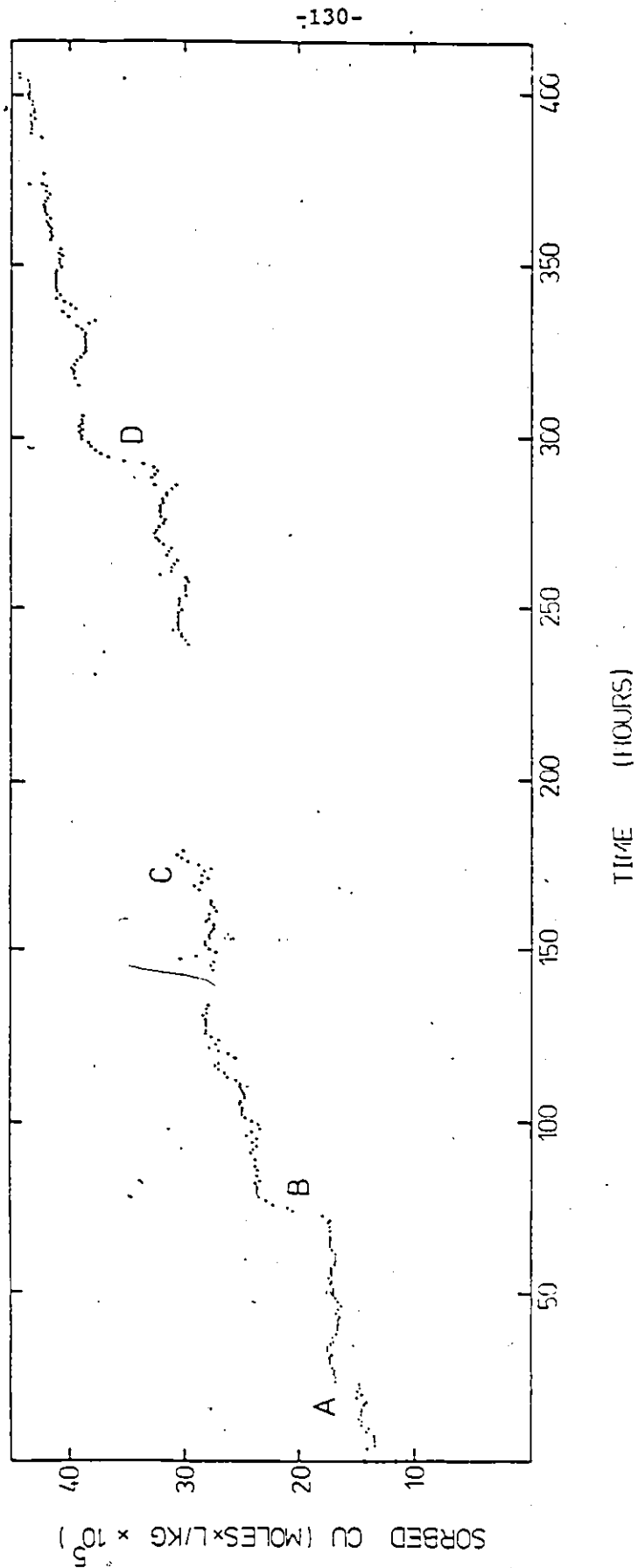
Figure IV-14. Sorption over a 2.5 week period while the copper concentration in solution is maintained with a copper stat.
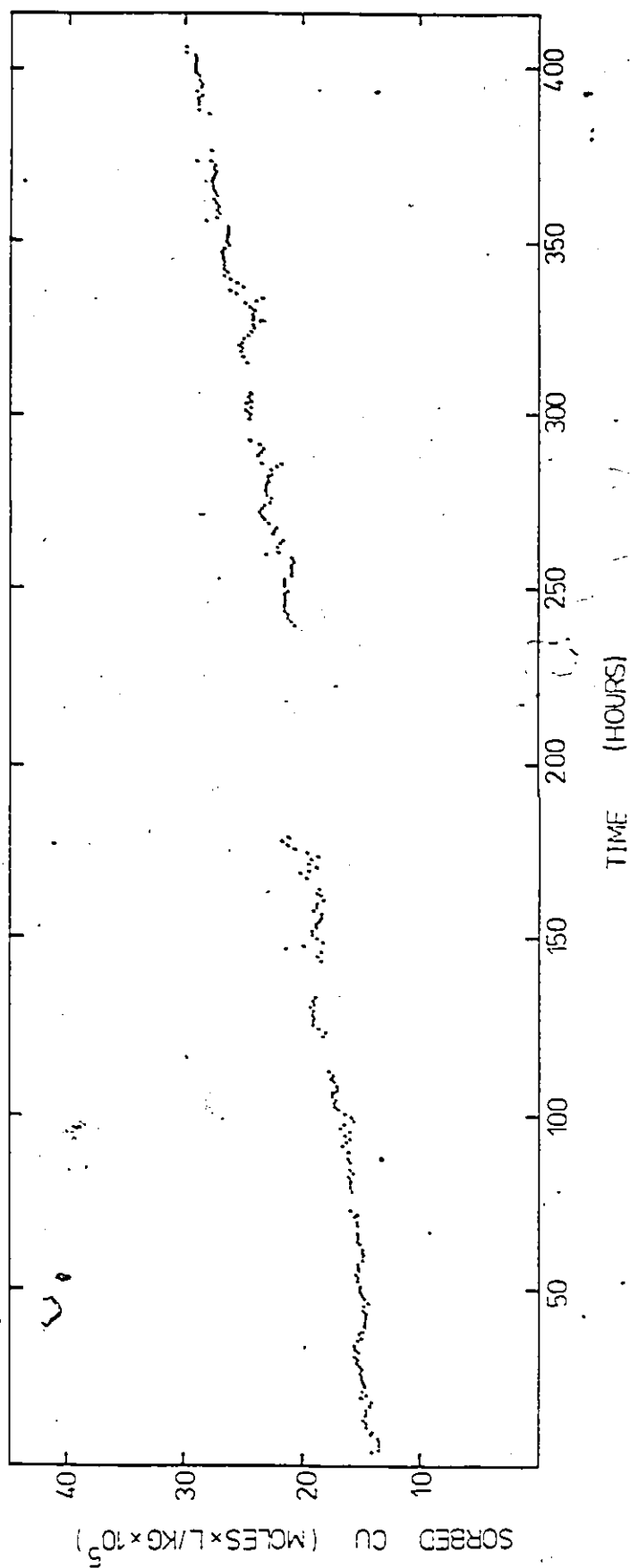
Figure IV-15. The data of figure 14 have been replotted without the sudden sorption jumps which were caused by excessive copper additions.

Generally the rate constants of the sorption jumps in figure IV-14 appear to fall in the range of segment IV rate constants. The segments between these sorption jumps appear to share a similar sorption rate. Therefore, an attempt was made to remove the effects of these sorption jumps and to combine the remaining data in order to estimate what the sorption rate would have been had these copper additions not been made (figure IV-15). The rate constant given by the data in figure IV-15 is $3.1 \pm .7 * 10^{-5}$, while the rate constant given by the experiment at constant total copper (figure IV-13) is $1.4 \pm .2 * 10^{-5}$. The removal of the sorption jumps to produce figure IV-15b is probably valid because the linear segments between the jumps gave rate constants which were similar to the overall rate but were subject to much more error because of their relatively short time intervals. Once the sorption jumps are removed from the constant pCu experiment the rate constant for a two week period is only slightly higher than in the experiment with constant total copper.

The contribution of the solution Cu to the observed adsorption rate is given by:

10) $\text{rate} = K [Cu^{+2}]^n$

11) $\log (\text{rate}) = \log (K) + n \log [Cu^{+2}]$

If the logarithm of the sorption rate, measured at a given copper concentration, is plotted against pCu then the slope will give n, which is a measure of the rate's dependence on copper concentration. Figure IV-16 shows a plot of the initial sorption given by segment I versus pCu. This figure illustrates that the magnitude of the instantaneous sorption is very sensitive to copper concentration. The estimated value

for n is 1. The rates for segments II, III and IV are plotted versus pCu in figure IV-17. It is evident that these sorption rates are much less sensitive to copper concentration than the initial sorption was. There is too much variation in segment II to make any conclusions regarding the effect of copper concentration. This variation may result from the inability to properly control copper concentration within the first two minute period. Segment III shows no contribution of copper concentration to the sorption rate. Segment IV shows a slight increase in sorption rate with copper concentration with an estimated n value of .3 ± .5. Therefore, as noted from the previous sorption curves the rates of copper sorption after the first minute are not very sensitive to copper in the concentration range of these experiments.
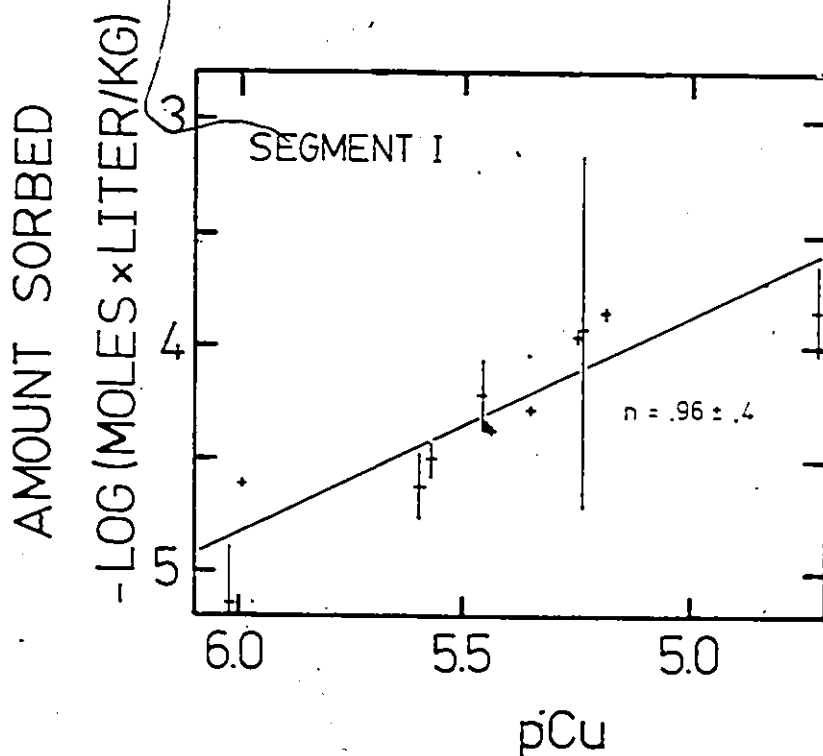
Figure IV-16. The variation of segment I with the negative log of [Cu]. Error bars are determined from the confidence interval of the intercept of segment II with time zero.
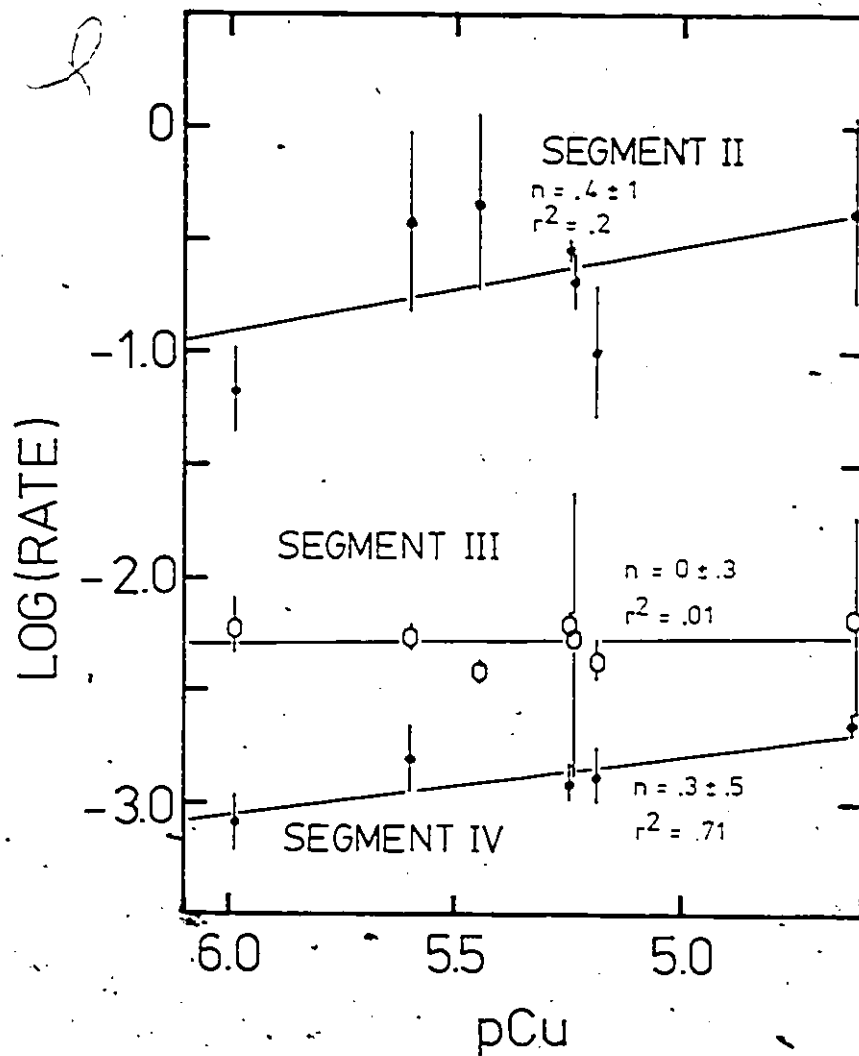
Figure IV-17. Variation of the sorption rates of segments II, III, and IV with copper concentration. The error bars were determined from the 99 percent confidence interval of the measured rate constant.

DISCUSSION:

The approach used to treat the kinetic data on copper sorption has been to assume that the sorption process is controlled by concurrent pseudo-first-order reactions which can be identified by linear segments of a plot of the logarithm of sorbed copper versus time. In some experiments the measured rate constant for segment II appears too low to account for the observed sorption kinetics. This may be caused by a reverse reaction which interferes with the measurement of the forward rate constant, as suggested by the curvature between segments II and III. Another possibility is that the sorption kinetics for segment II are perturbed by the rapid additions of Cu which were required within the first minute to maintain a constant Cu concentration in solution. Another approach which may be useful for analyzing the kinetics of segment II is the approach to equilibrium method which guarantees a good fit to the data of segment II. However, the equilibrium sorption value for segment II is not entirely clear and it was felt that it would be better to look at the initial linear part of region II which hopefully is away from the influence of any reverse reactions. Also this is more consistent with the treatment of the remaining kinetic data and it eliminates the need for having a mixed rate constant containing both forward and reverse reactions. Actually the choice of method does not really matter to this study because both the first-order treatment and the approach to equilibrium method distinguish segment II as a separate mechanism.

On the basis of a plot of the logarithm of sorbed copper versus time five sorption regions can be resolved. For any given sorption curve the sorption rates in neighboring segments are significantly different. Therefore these segments probably do mark time intervals where the sorption follows different rates which are caused by different mechanisms. The order of appearance of these segments is the same for every experiment. However, the time span of each segment and the rate constant may vary between experiments. Table IV-5 outlines the time spans and the range of rate constants found for the various sorption segments.

TABLE IV-5

KINETIC SORPTION SEGMENTS AND EXAMPLES OF SORPTION RATE CONSTANTS FROM THE LITERATURE

	Time Range		Rates	Literature rate constants (min) with references ( )
I	instantaneous		1 to $14 * 10^{-5}$ moles L/kg	(4), (5), (6)
II	10 sec.	to 1 - 3 min.	$.1$ to 3 min^{-1}	(2) 1.56,
III	1 - 10 min.	to 9 - 160 min.	1 to $9 * 10^{-3} min^{-1}$	(3) $5 * 10^{-3}$
IV	15 - 100 min.	to 75 - 253 min.	6 to $23 * 10^{-4} min^{-1}$	(2) $9 * 10^{-4}$, (6) $6 * 10^{-4}$
V	2 - 7 hrs.	to 7 - 400 hrs.	1 to $14 * 10^{-5} min^{-1}$	(1) $2 * 10^{-5}$, (3) $2 * 10^{-5}$

Reference	Sorbate	Sorbent
1) Chen et al. (1973)	phosphate	kaolinite
2) Griffin and Jurinak (1974)	phosphate	calcite
3) Singhal and Gupta (1978)	Zn	dickite
4) Malcolm and Kennedy (1969)	Ba, Ca,	kaolinite
5) Shainberg (1973)	H	montmorillonite
6) Griffin and Burau (1974)	B desorption	desert soil

Examples of more than one rate constant have been reported in the literature. Some examples are given in table III-4. Values similar to the sorption rate constants measured in this study have also been reported in the literature. Table IV-5 gives some examples of sorption rate constants which are similar to the sorption segments of this study. If the segments in table IV-5 do correspond to different sorption mechanisms then the next task must be to identify the mechanisms which are responsible for the observed sorption segments. Table IV-6 lists various potential sorption mechanisms which can be assigned to each sorption segment on the basis of matching rate constants.

Nonspecific coulombic attraction is a logical choice for the instantaneous reaction in segment I because cation exchange reactions controlled by coulombic attraction are known to be extremely rapid. Malcolm and Kennedy (1969) found that alkali exchange reactions on clay were 75 percent complete in three seconds. The instantaneous reaction in segment I could also result from a coordination reaction to surface oxygens. Coordination to surface oxygens may be similar to a hydrolysis reactions which can be extremely rapid. However, sorption is a heterogeneous reaction which requires copper to diffuse towards the surface. This diffusion, as well as the necessity for the copper ion to collide with an active surface site may slow the surface complexation reaction so that it still occurs in segment II. Diffusion into the interstitial waters of clay flocs may also limit the sorption rate in segment II. Morgan and Stumm (1964) found that Mn uptake by MnO_2 slowed down when the MnO_2 suspension was flocculated by salt solutions, and Kurbatov and Wood (1951) found that flocculation also

slowed the kinetics of Co coprecipitation with Fe gel. Kaolinite is added to the reaction vessel in the form of a concentrated suspension which may take five to twenty seconds to disperse properly. The mixing of the kaolinite suspension may contribute to the kinetics of segment II, and may even be responsible for some of the variability of segment II rate constants.

TABLE IV-6

POTENTIAL SORPTION MECHANISMS

Segment	Possible Mechanisms
I	-nonspecific coulombic attraction
	-specific surface coordination to one site
II	-specific surface coordination to one site limited by diffusion
	-nonspecific coulombic attraction limited by diffusion
	-induced surface precipitation
	-specific surface coordination to two sites
	-(May be influenced by dispersion of kaolinite after clay addition.)
III	-induced surface precipitation
	-specific surface coordination to two sites
IV	-induced surface precipitation
	-specific surface coordination to two sites
V	-induced surface precipitation
	-specific surface coordination to two sites
	-structural penetration

A surface coordination reaction to two surface sites will probably be slower than coordination to one site because copper must position itself in a location where the two sites are close enough to interact with the copper ion. Induced surface precipitation may be limited by nucleation reactions and by the necessity of bringing higher copper concentrations together with surface regions of higher pH to induce precipitation. Therefore, surface precipitation reactions are slower than surface coordination. McBride (1982) found that after an hour Cu sorption on aluminum hydroxides was taken over from surface coordination by precipitation reactions which continued for several weeks. The rate constant for this sorption, which was measured around pH 5, is about $1 * 10^{-4}$ min^{-}. At pH 6.2 the rate of precipitation may be higher, and surface precipitation may start to make a contribution in segment II. and continue into segments IV and V. There is a possibility that structural penetration may also contribute to the very slow reaction in segment V. Structural penetration is expected to be very slow because it would require copper dehydration and solid state diffusion into the structure.

It has been shown that instantaneous sorption in segment I is very sensitive to copper concentration in solution. This would agree with a nonspecific coulombic attraction or with a surface complexation mechanism. On the other hand, segments II to V are much less sensitive to copper concentration. The lack of a clear relationship between the sorption rate of segment II with copper concentration may result from the poor control over copper concentration during the first minute of sorption. The control over copper concentration in segment III is much

better, yet the sorption rates of this segment appear to be independent of the copper concentrations used in these experiments. This may suggest that the rate limiting step for segment III is some sort of diffusion or surface reorganization process which is not affected by changes in the copper content of the solution. The rate constants of segment IV show a small dependence on solution copper, and the rates in segment V may also be slightly sensitive to copper as indicated by the difference in the two week sorption rates measured at constant pCu and constant total copper. This may be consistent with a surface coordination reaction to two sites which depends upon copper concentration as well as the ability of a copper ion to find a favorable surface location where it can bind with two sites.

Now that various theoretical mechanisms have been assigned to the observed sorption segments (table IV-6) it is necessary to test the copper sorbed in these segments in order to confirm or eliminate the theoretical mechanisms which have been assigned to the segments. This will be done in chapters V and VI where pH, salt concentration and desorption properties will be used to distinguish nonspecific sorption, surface coordination, surface precipitation and perhaps structural penetration.

CHAPTER V

THE EFFECTS OF HYDROGEN ION AND SALT CONCENTRATION

INTRODUCTION.

In chapter IV it was shown that copper sorption kinetics could be divided into five segments which had different sorption rate constants and which lasted for different time periods after the initiation of the sorption process. These segments can be produced by as many as five different sorption mechanisms which may include (1) nonspecific coulombic attraction, (2) complexation with surface oxygens, (3) induced surface precipitation, (4) structural penetration, and (5) copper concentration in the interstitial waters of clay flocs. Sorption segments can also be produced by other factors such the dispersion time of the clay suspension once it has been added to the copper solution. The next objective is to characterize the response of these sorption segments to changes in experimental parameters such as pH and salt concentration. Once this is accomplished it may be possible to identify some of the mechanisms responsible for the sorption segments.

Nonspecific coulombic sorption does not preferentially sorb copper over any other divalent cation. If a clay is placed in a solution where an indifferent electrolyte, such as KNO_3, exceeds the copper concentration by several orders of magnitude then any copper sorbed by nonspecific coulombic attraction will be displaced by mass action. On the other hand, copper sorbed by specific chemical sorption

will not be affected by the concentration of indifferent electrolyte. Therefore, copper sorption, which persists as the salt concentration is raised to 1 M, must be explained by specific chemical attraction. In the presence of an indifferent salt, coulombic sorption on kaolinite should be independent of.pH, while specific chemical sorption should be very sensitive to changes in pH. The response time of copper sorption to changes in pH may tell us which sorption segments are most affected by pH and what type of specific chemical mechanism is involved. The ratio of hydrogen ion desorbed per copper ion sorbed can help us identify the dominant reaction mechanism. If this ratio is 0 in our experiments then nonspecific coulombic sorption is involved. If the ratio is 1 then surface complexation dominates. If the ratio is 2 then either copper is sorbed by surface precipitation or each copper ion coordinates to two surface sites.

This chapter will first look at the effects of different salt concentration on copper sorption to see whether there is a significant amount of nonspecific coulombic attraction involved. Then attention will be focused on the sensitivity of copper sorption to pH and on the kinetics of copper response to changes in pH. Finally the ratio of desorbed hydrogen ion to sorbed copper ion will be investigated in order to distinguish between surface complexation and surface precipitation.

MATERIALS AND METHODS.

With a few exceptions, the materials and methods used to measure the response of copper sorption to different pH and salt levels are the same as described in chapter IV. The copper electrode was not used to measure copper sorption in deionized water because the electrode requires a background electrolyte to work properly. Instead, radioactive ^{64}Cu was used as a tracer in the sorption experiment. After separating the solution from the suspension the copper concentration was determined by counting the activity of ^{64}Cu. In this experiment the amounts of kaolinite and solution were the same as in the previous experiments. Sorption at a given time was determined by taking a ten milliliter sample of the kaolinite suspension and immediately separating out the clay by filtration (one half minute). Further details of using radioactive ^{64}Cu as a tracer are given in appendix 11. The kaolinite used to measure copper sorption from deionized water was prepared by taking a portion of the stock kaolinite suspension (stored in .05 M KNO_3) and washing it three times with deionized water. Kaolinite was not stored in deionized water for long periods to prevent hydrogen ion from replacing adsorbed K^+ and causing damage to the kaolinite surface. The kaolinite used in the experiment with 1 M KNO_3 was washed with 1 M KNO_3 prior to use.

The HNO_3 used to adjust pH was calibrated by titrating a known amount of $CaCO_3$. This acid was then used to calibrate the KOH which was used to determine the amount of hydrogen ion liberated during copper sorption. The hydrogen ion desorbed by copper sorption was determined by titrating the kaolinite suspension back to the initial pH before the

addition of clay. If additional copper was added to maintain a constant $[Cu^{+2}]$ then the acidity of this copper solution was taken into account in the calculation of of hydrogen ion liberated by copper sorption.

RESULTS.

Copper sorption was measured in the presence of a 1 M KNO_3 background electrolyte and in the presence of deionized water. Both experiments had the same total copper concentration of pCu_t 5.24 ($-log[Cu]_T$). The results of these experiments are presented in figure V-1, which also shows copper sorption measured in a .05 M KNO_3 solution. As would be expected, copper sorption in the absence of a background electrolyte is much higher than in the presence of a salt solution. Sorption from the dilute solution would have been much higher if the copper concentration in the solution phase had not dropped to pCu 7.6. The concentration of copper in the 1 M KNO_3 solution only dropped to pCu 5.4 because the kaolinite did not sorb as much copper. It is interesting to note that copper sorption in a 1 M KNO_3 solution is very similar to sorption from .05 M KNO_3 solutions.

In figure V-1 copper sorption from the dilute solution as well as from the 1 M KNO_3 solution has been measured using radioactive ^{64}Cu, while the other sorption curves were determined with the copper electrode. The sorption curves measured with the electrode appear to be smoother and more error free, probably because they are not subject to errors introduced by sampling and filtration. The increase of sorption with time in the .05 M solutions is subtle and probably would not be detected if a copper electrode had not been used.
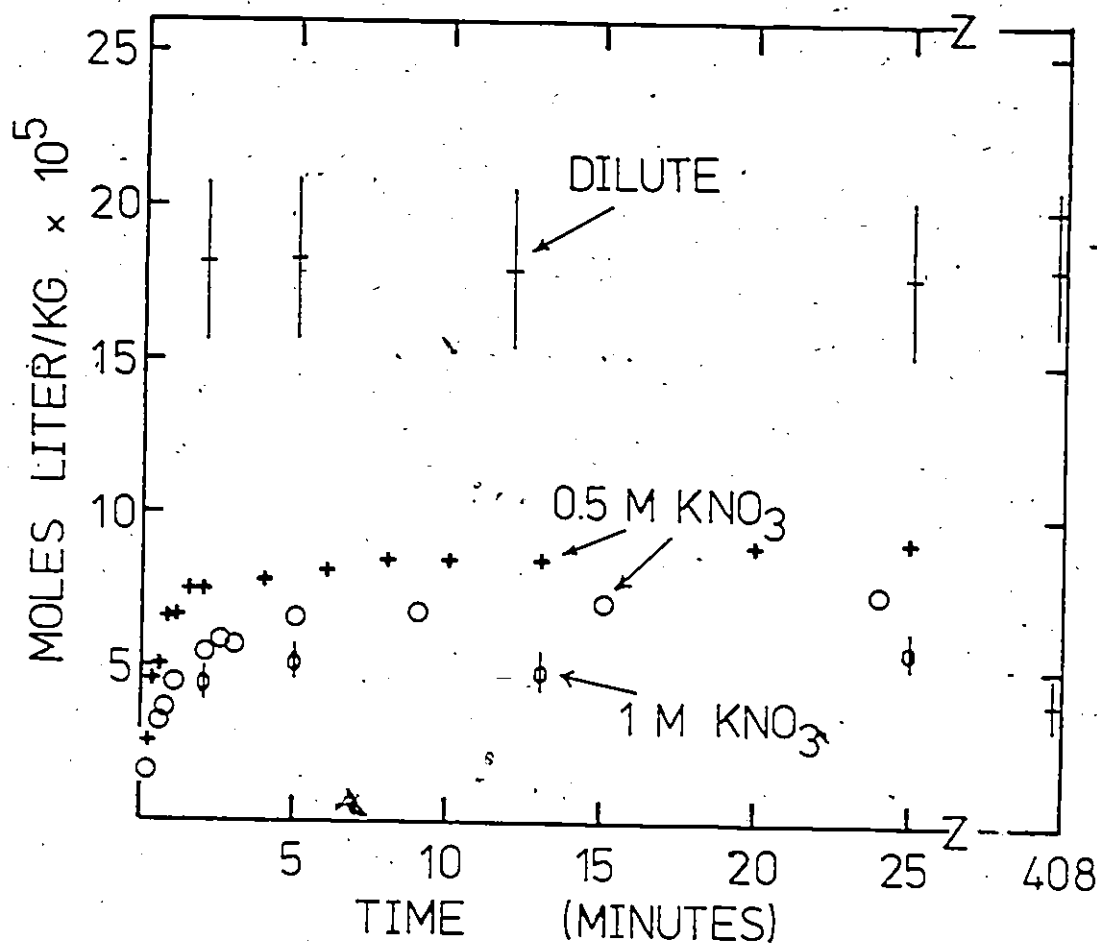
Figure V-1. Copper sorption at different salt levels. The solution Cu concentration was not maintained at a constant level.

The variation of copper sorption with changes in pH is illustrated in figures V-2 and V-3. In figure V-2 sorption was started at pH 6.2 and the copper concentration was maintained at pCu 5.2 for the first 42 minutes. After 42 minutes further copper additions were stopped and KOH was added to the kaolinite suspension to raise the pH to 6.7. This produced an extremely rapid jump in copper sorption. During the first minute after the addition of base the apparent sorption produced a peak which appeared to level off during the next 8 minutes. When acid

was added to drop the pH there was a very rapid desorption. When the pH had returned to 6.2 the amount of copper sorbed appeared to be similar to the level expected for pH 6.2.
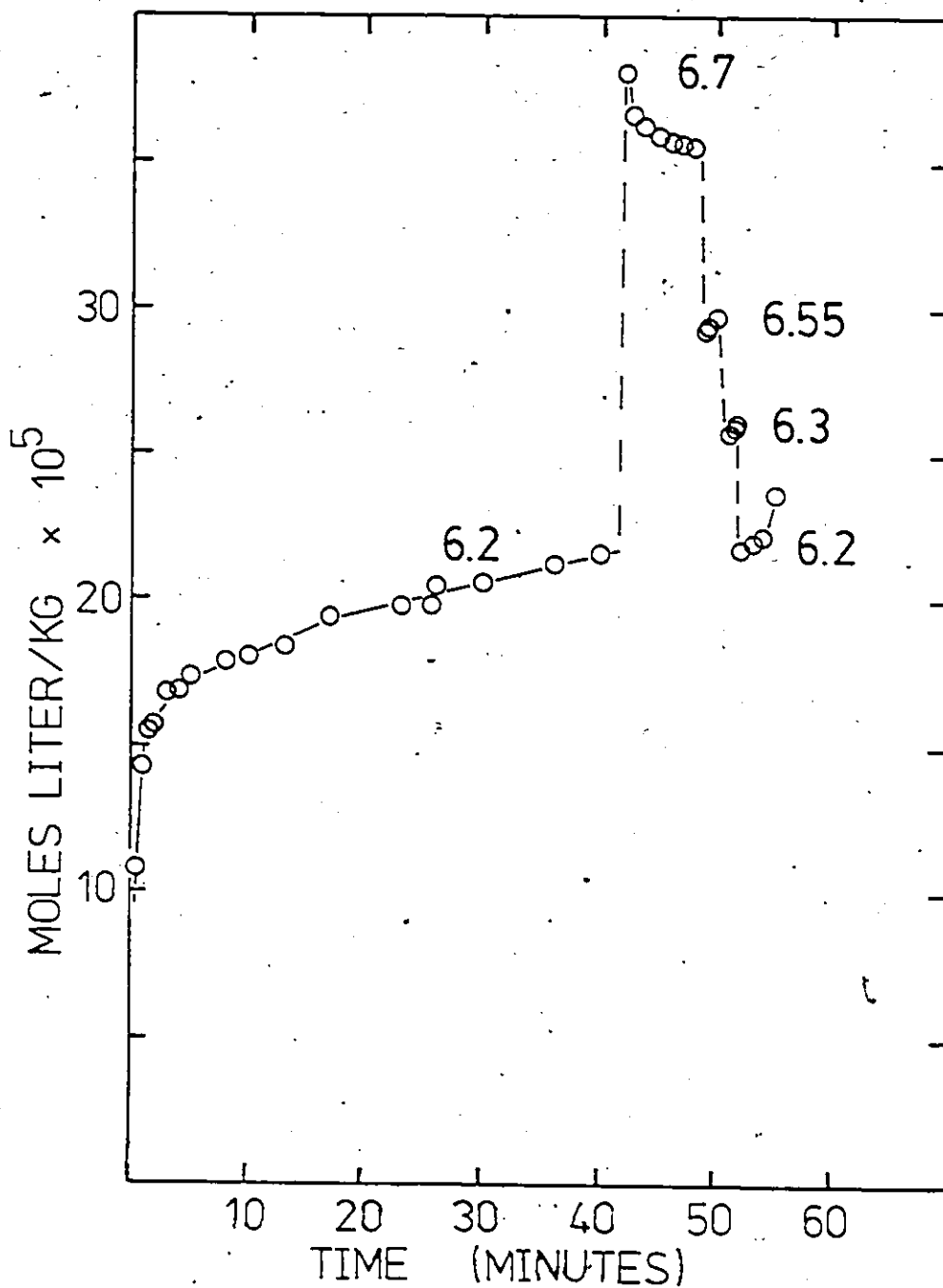
Figure V-2. Response of Cu sorption to changes in pH.

Figure V-3 illustrates copper sorption started at pH 5.36 with a
constant copper concentration of pCu 5.1. The level of copper sorption
expected for this copper concentration at pH 6.2 is much higher than was
observed at pH 5.36. After 162 minutes further copper additions were
stopped and base was added to raise the pH to 6.2. Again there was a
very rapid sorption which produced an apparent sorption peak that droped
to a lower value within 1.5 minutes. The copper sorption at pH 6.2 is
similar to other experiments conducted at pH 6.2 (Jan 9, pCu$_t$ 5.05,
figure IV-7). The rate constants measured for copper sorption at pH
5.36 and when the pH was raised to 6.2 are given in the following table.

TABLE V-1

COMPARISON OF RATE CONSTANTS MEASURED AT pH'S 5.36 AND 6.2 (FIGURE V-3)

pH	segment I * 10^5 (moles liter/kg)	segment II (min)	segment III * 10^3 (min)
5.36	3.1 ± .4	.04 ± .08	3.2 ± 1.2
6.2			8.2 ± 1.6

The initial sorption in segment I for pH 5.36 is low compared to
the amount expected for a solution at pH 6.2 and, with a copper
concentration of pCu 5.1. From figure IV-11 the predicted sorption for
segment I at pH 6.2 and in a copper solution of pCu 5.1 is 11.7 * 10^{-5}
moles liter/kg.

In figure V-3 the pH is dropped to 5.32 at 290 minutes. The rate
of acid addition was not as rapid as in figure V-2 and no excess
desorption peak was observed. Instead there was a rapid initial
desorption followed by a gradual desorption process lasting for 18 hours
at which time the sorption was at a level expected for pH 5.3.
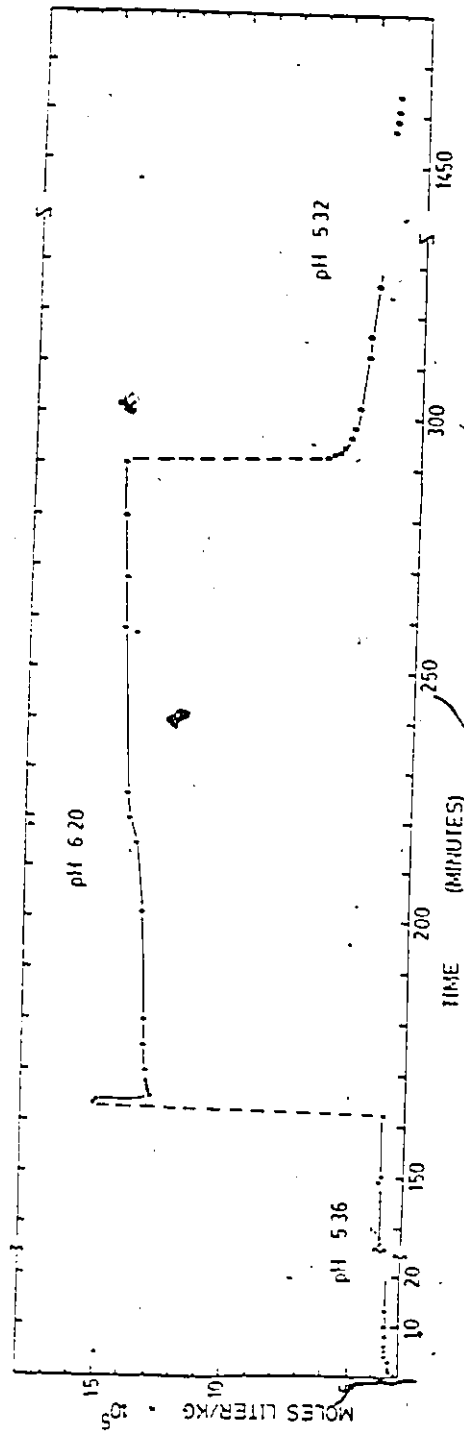
Figure V-3. Response of copper sorption to changes in pH.

When copper sorption is initiated by adding 10 ml of stock
kaolinite suspension to 100 ml of copper solution, which has the same pH
as the kaolinite suspension, a drop in pH is observed. The change in pH
upon sorption is illustrated in figure V-4. The drop in pH is rapid and
is almost complete within the first minute. In general the pH
stabilizes after several minutes and may remain constant throughout the
duration of the experiment. If copper is added to maintain a constant
pCu then a slow drop in pH may be observed for as long as 40 minutes.
This drop in pH during the initial sorption period may result from
desorbed hydrogen ion as well as contributions from the acidity of
copper solution added to maintain a constant copper concentration.
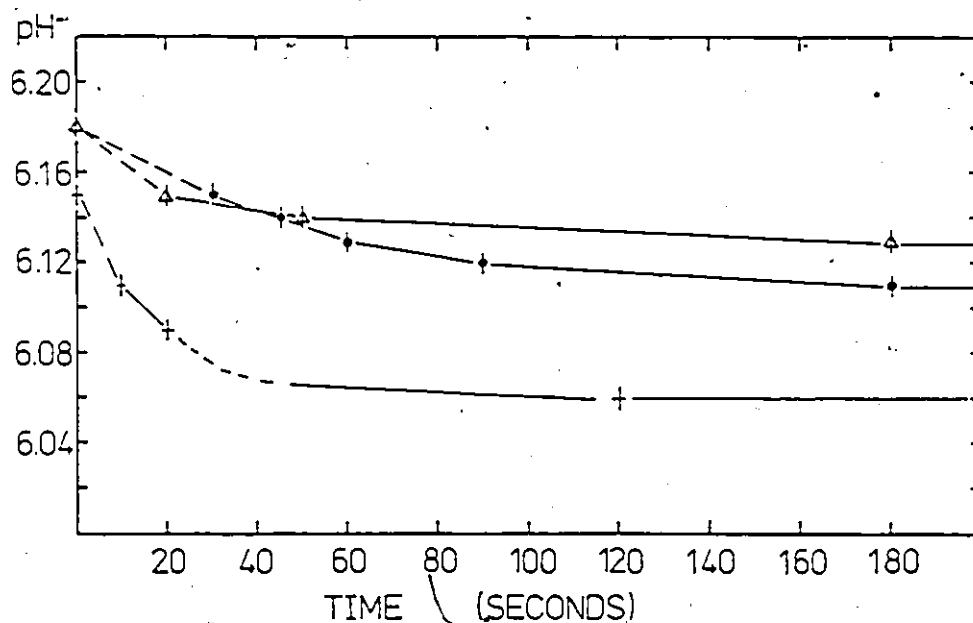
Figure V-4. Change in pH produced by copper sorption.

The best way to measure the ratio of desorbed H^+ to sorbed Cu^{+2} is to titrate the kaolinite suspension back to the pH of the solution before sorption was started. At pH 6.2 the kaolinite suspension is able to buffer the pH. It was found that if an aliquot of acid or base is added 90 percent of it is consumed by the kaolinite. The only way to accurately account for the H^+ which is liberated by Cu sorption and which is then consumed by the clay is by a back titration. The measured hydrogen ion release must be corrected for the acidity introduced by the addition of copper solution which generally had a pH between 3 and 4. Table V-2 summarizes H^+/Cu^{+2} ratios measured in various experiments. In this table the reported times correspond to the instant where the liberated hydrogen ion is first successfully titrated and to the times where measurable changes in pH initiate a back titration.

Table V-2 shows that in general the ratio of liberated hydrogen ion to sorbed copper is between 1 and 2 for experiments conducted in a salt medium. There is some variation in the H/Cu ratio with time, which is illustrated for selected examples in figure V-5. After 2 minutes there appears to be a slight increase in the H/Cu ratio with time until the pH stabilizes. It was difficult to measure the H/Cu ratio for a reaction time of less than one minute, which is unfortunate because it would be useful to obtain the H/Cu ratio for the initial sorption in segment I. In order to estimate the H/Cu ratio for segment I the amount of desorbed hydrogen ion was extrapolated back to time zero for the data from April 2 and 19 (figure V-6). The liberated hydrogen ion at time zero was divided by the amount of copper sorbed in segment I to give

ratios of 1.00 ± .04 and 1.08 ± .1 respectively.

TABLE V-2

MEASURED H/Cu RATIOS

Date	Time (min)	pCu	H/Cu	Precision	gm clay/100 ml
(Copper added to maintain a constant $[Cu^{+2}]$)					
16/02/84	0.8	5.36	1.31	0.04	0.24
	2.5	5.24	1.21	0.04	
	3.0	5.23	1.34	0.04	
	5.0	5.22	1.42	0.04	
02/04/84	1.5	5.26	1.27	0.04	0.23
	2.5	5.26	1.57	0.05	
	3.0	5.25	1.63	0.05	
	4.0	5.25	1.69	0.05	
	6.0	5.26	1.69	0.05	
	8.0	5.25	1.69	0.05	
15/04/84	0.5	5.26	1.98	0.07	0.99
	1.5	5.27	1.64	0.06	
	3.0	5.18	1.68	0.06	
19/04/84	1.5	5.23	1.58	0.07	0.33
	2.0	5.21	1.65	0.07	
	5.0	5.22	1.61	0.07	
	10.0	5.21	1.63	0.07	
	14.0	5.22	1.65	0.07	
	19.0	5.21	1.76	0.08	
	39.0	5.20	1.69	0.07	
31/05/84	3.0	5.24	1.28	0.05	0.29
	5.0	5.24	1.25	0.05	
	19.0	5.24	1.31	0.05	
	32.0	5.24	1.41	0.06	
(Constant total copper)					
29/03/84	1.0	5.37	1.55	0.06	0.31
	2.0	5.40	1.54	0.06	
06/04/84	0.8	5.41	1.72	0.07	0.30
	1.5	5.44	1.94	0.08	
13/04/84	1.5	5.62	2.24	0.09	0.81
	3.0	5.65	2.20	0.09	
25/04/84	1.5		2.14	0.17	0.28
03/05/84	1.5	5.41	1.63	0.06	0.30
10/05/84	1.5	5.39	1.57	0.20	0.44 1 M KNO_3
10/05/84	1.5	7.60	0.52	0.07	0.38 no background salt

The salt concentration is 0.05 M, except where stated otherwise.
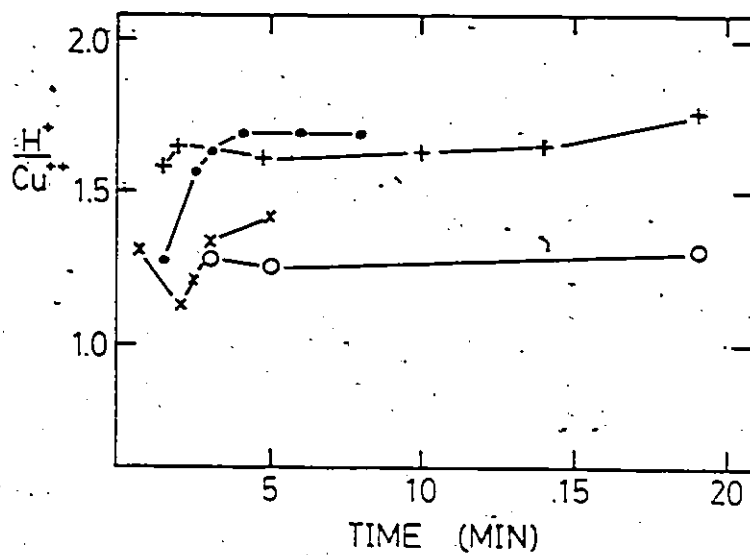
Figure V-5. Variations of H/Cu ratios with time.
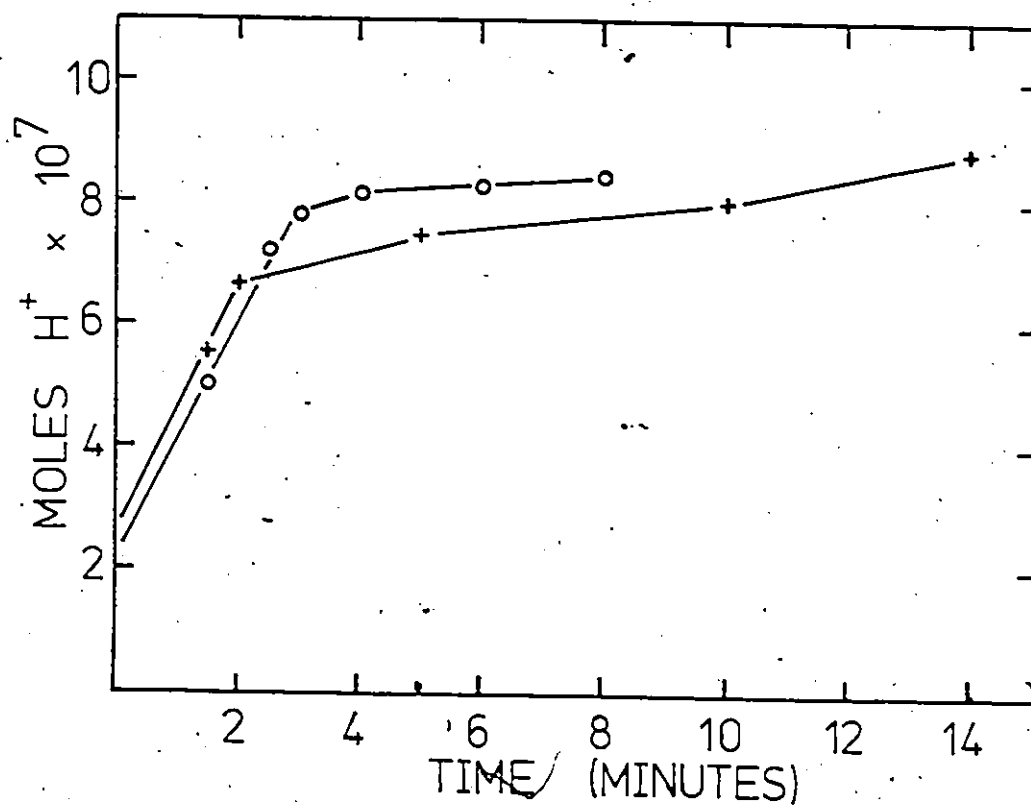
Figure V-6. Liberated hydrogen ion as a function of time.

From table V-2 it appears that in experiments with a constant total copper concentration measurable changes in pH stop after 3 minutes, whereas in experiments which are maintained at constant pCu, H^+ desorption can be measured for as long as 40 minutes. The average H/Cu ratio in experiments with constant total copper (1.84 ± .29) is slightly higher than the average ratio in experiments with a constant pCu (1.54 ± .20).

In the absence of salt solution the amount of hydrogen ion liberated by Cu sorption is small relative to the total amount of copper adsorbed. The experiment of May 10 (table V-2) illustrates the effect of salt on the measured H/Cu ratio for copper sorptions started with the same initial copper concentration.

DISCUSSION

Nonspecific sorption and the effect of salt concentration: It has been shown that in the absence of a background electrolyte copper sorption is much higher compared to sorption in the presence of 0.05 M KNO_3. This increased sorption must be caused by nonspecific coulombic attraction which is not inhibited by the presence of an overwhelming concentration of K^+ ions. Most of the nonspecific sorption is probably already eliminated at a salt concentration of 0.05 M because there is not much difference in copper sorption between a 0.05 M solution and a 1 M KNO_3 solution. This is reasonable because in a 0.05 M salt solution the copper represents only 0.01 percent of total cations in solution. Further changes in the salt concentrations probably would not make a very significant difference. In most natural waters copper sorption on

kaolinite by nonspecific coulombic attraction is inhibited by salt

concentrations. Although in streams the salt concentration may be 100

times less than that used in this study, natural copper concentrations

are also 100 times less than that used in this study.

It is interesting to compare the observed copper sorption

in the presence of salt solution to the amount of divalent cation

sorption predicted by electric double layer theory. Babcock (1963)

reviews various cation exchange theories including double layer theory,

mass action theory, and statistical thermodynamics. Mass action theory

is a formal way of describing a cation exchange which has already been

measured and it has no power to predict unmeasured exchange reactions.

Statistical thermodynamics assumes that cations are localized at

discrete surface sites, which may be partially true in a kaolinite

suspension where cations tend to concentrate on certain kaolinite faces.

The cation exchange constant depends upon the geometric arrangement of

the surface sites. Possible arrangements include (1) a multilinear

array of widely spaced rows, (2) an open-packed array of sites, and (3)

a close-packed array of sites. The predictive power of statistical

thermodynamics is limited because the cation exchange constant can be

changed by selecting a different geometric arrangement of sites. Double

layer theory assumes a uniform distribution of cations in the exchanging

phase, which is not strictly true but may be a reasonable approximation

for a kaolinite suspension. Double layer theory makes no assumptions on

the arrangement of surface sites and it only discriminates between

cations on the basis of their charge. Therefore, double layer theory

can be used to predict cation exchange between a divalent and a

monovalent cation.

Erickson (1952) has used double layer theory to develop an equation which predicts cation exchange reactions in the presence of a mixture of symmetrical electrolytes. This equation was introduced in chapter II and is presented here as equation 1. Experimental evidence to support Erickson's equation has been presented by Bolt (1955), Bower (1959) and Pratt and Blair (1962). This equation has been tested for Ca concentrations as low as 0.004 M but it does not appear to have been tried for situations where the divalent cation is found at low concentrations in the range of 10^{-5} to 10^{-6} molar.

$$1) \qquad \frac{C_1}{C} = \frac{r}{C(B)^{-1/2}} \, \sinh^{-1}\left(\frac{C(B)^{-1/2}}{r + 4v_d(m_2)^{-1/2}}\right)$$

C_1 = charge neutralized by monovalent cations

C = total surface charge density

$r = m_1/(m_2)^{-1/2}$

m_1 = monovalent salt concentration in bulk solution

m_2 = divalent salt concentration in bulk solution

$B = 8000\pi F^2/DRT$ (when T is 25^0C B = 1.08 * 10^{15} cm mole/meq^2)

$F = 2.982 * 10^{-11}$ esu/meq $R = 8.314 * 10^7$ ergs/deg mole

$D = 80$ esu^2/erg cm

v_d = cosh y at the midplane between clay particles (assumed to be 1)

TABLE V-3

COPPER SORPTION PREDICTED BY DOUBLE LAYER THEORY

moles/liter KNO$_3$	pCu	CEC meq/100 gm	charge density $* 10^7$	fraction of K$^+$ on surface	maximum sorbed Cu (moles/kg) $* 10^4$
.05	5.2	11	6.01	.884	63.8
.05	5.2	7.7	4.21	.934	25.4
.05	5.2	.44	.24	.9992	.035
1.0	5.2	11	6.01	.99957	.237
1.0	5.2	7.7	4.21	.99978	.085
1.0	5.2	.44	.24	.99991	.002
.05	5.4	11	6.01	.9188	44.7
1.0	5.4	11	6.01	.9997	.184

TABLE V-4

OBSERVED COPPER SORPTION AT TEN MINUTES

moles/liter KNO3	pCu	sorbed copper (moles/kg)
.05	5.2	(17.6 to 19.8) $* 10^{-4}$
.05	5.4	(7.7 to 9.0) $* 10^{-4}$
1.0	5.4	4.1 $* 10^{-4}$

In order to use equation 1 we must know the kaolinite's surface charge, which can be estimated from the kaolinite composition or from a cation exchange measurement. To estimate the charge imbalance in the kaolinite structure the clay's measured composition is recalculated to give a normative composition which will match an ideal kaolinite structure. To make this normative calculation assumptions are made as

to the location of Al and Si. There is no way of confirming these assumptions analytically because it is not possible to accurately determine how much aluminum goes into the tetrahedra layer, the octahedral layer, or is sorbed onto the surface. The cation exchange capacity which can be obtained from a normative calculation using the published composition of kaolinite #4 (given in the appendix) is .44 milliequivalents per 100 grams. The surface charge can be estimated from a measured cation exchange capacity if it is assumed that the exchangeable cation is held at the surface by mainly coulombic attraction. The cation exchange capacity of kaolinite #4 determined in this study by Mg sorption is 11 meq/100 gm. McBride (1976) found an exchange capacity of 11 meq/100 gm using Mg and an exchange capacity of 7.7 meq/100 gm using sodium. The cation exchange capacities determined for kaolinite #4 by Mg and Na are rather high compared to other kaolinites and may result from minor montmorillonite impurities. However, they probably represent a better estimate of the charge imbalance in the kaolinite sample than is given by the normative calculation. All the above cation exchange capacities were used to calculate potential copper sorption using equation 1.

When the copper sorption calculated by equation 1 (table V-3) is compared with the observed copper sorption in .05 M KNO_3 (table V-4) it is apparent that equation 1 overestimates the amount of copper uptake if the cation exchange capacities measured with Mg and Na are used. However, in 1 M KNO_3 equation 1 significantly underestimates copper sorption. If equation 1 can predict nonspecific sorption of trace amounts of copper from a 1 M KNO_3 solution then the observed copper

sorption which is higher than the predicted value must result from specific chemical sorption. Chemical sorption should not be affected by the concentration of an inert background electrolyte and therefore should be the same in the 0.05 M KNO_3 solution. The copper sorption in the 0.05 M solution is very similar to sorption in the 1 M solution. From this one may conclude that specific chemical sorption is significant in a 0.05 M solution and that the increase in nonspecific sorption is small when the electrolyte changes from a 1 M to a 0.05 M solution. However, the ability of equation 1 to accurately predict nonspecific sorption of trace metals in a salt solution is suspect because equation 1 overestimated copper sorption in the 0.05 M solution. Double layer theory does not take into account the contribution of ion size to selectivity and it is well known that K^+ is preferentially sorbed over Na^+ because K^+ has a smaller hydrated radius. Therefore K^+ may be able to compete more effectively with Cu for surface sites than is predicted by equation 1. Although equation 1 suggests the presence of specific chemical sorption in a 1 M KNO_3 solution further proof is needed to confirm this.

Specific sorption and the effect of pH: If copper sorbs by nonspecific coulombic attraction on a kaolinite which has been equilibrated with a KNO_3 solution then it must compete mainly with K^+ and not with H^+. Also, since kaolinite is presumed to carry a constant, pH independent charge, copper sorbed by nonspecific sorption will be independent of pH. In the present study it has been shown that copper sorption is very pH sensitive over the pH range 5.3 to 6.7. This pH range corresponds to the sorption edge for copper reported in the

literature. The sensitivity to pH in this study cannot be produced by Al^{+3} liberated from the structure at lower pH because the response of copper sorption to pH was rapid and reversible. The sorption edge is not likely to be produced by a local charge reversal at kaolinite surfaces because sorption edges for different metals are found at different pH's, depending upon the hydrolysis constant of the metal. Therefore, in this study the observed sensitivity of copper sorption to pH cannot result from nonspecific coulombic attraction.

The response to changes in pH is very rapid and is sensitive to the rate at which acid or base is added. If acid or base are added too rapidly then excess desorption or sorption peaks are produced which last for about a minute. These excess desorption or sorption peaks might be produced if the newly added acid or base has not had a chance to mix properly and temporary local conditions of extreme pH are created.

In figure V-3 the rapid response to pH adjustment from pH 5.36 to 6.20 produced a sorption change of $9 * 10^{-5}$ moles L/kg. This difference is similar to the difference in the initial sorption at pH 5.36 and the initial sorption at pH 6.2 (difference = $8 * 10^{-5}$). When the pH was returned to 5.3 there was an initial rapid desorption which was also similar to the difference in segment I between pH 5.36 and 6.2. Therefore, the rapid sorption drops created by moderate pH changes can probably be attributed to the same mechanisms responsible for segment I.

If acid addition is not too rapid then the desorption kinetics can resolve more than one mechanism, as shown during the pH drop from 6.2 to 5.3 in figure V-3. After the initial fast desorption there was a slower desorption process which lasted for about 1000 minutes. During

this time copper desorption was $1.5 * 10^{-5}$ moles L/kg, which is the same amount of copper sorbed during the slow sorption from 165 minutes to 290 minutes at pH 6.2. Therefore, the copper sorbed by the slow mechanisms in segments III and IV also appears to desorb more slowly when the pH is lowered. This observation might be consistent with a precipitation mechanism for segments III and IV. Precipitated copper ions are likely to be grouped together in a separate phase so that hydrogen ions cannot immediately attack every copper atom at once. The dissolution must proceed along a reaction front at the interface between the precipitate and the solution. If copper is coordinated to surface sites then it is evenly spread out along the kaolinite edges in a form that is easily accessible to hydrogen ions. If the mechanism responsible for segment I is surface complexation then this might explain the faster response of segment I to changes in pH. Another explanation for the slower desorption of copper is that segments III and IV represent the formation of a more stable configuration of adsorbed copper such as the bonding of copper to two surface oxygens, or the penetration of the kaolinite structure.

H^+/Cu^+ ratio: The ratio of desorbed hydrogen ion to sorbed copper was found to vary between 1 and 2 in the presence of a salt solution. Farrah et al. (1980) found that the H/Cu ratio for copper sorption on kaolinite was 1 when hydrogen ion sorption was accounted for (table II-2). Direct comparisons between the H/Cu ratios measured in this study and those ratios observed in other studies should not be made unless differences in experimental design are accounted for. For example, Farrah et al. (1980) measured metal sorption on kaolinite in

the absence of a background electrolyte and the initial copper concentration was higher (pCu = 3.77). The absence of a background electrolyte helps to promote nonspecific sorption, while the high copper concentration may initiate surface precipitation.

A combination of sorption mechanisms with H/Cu ratios of 1 and 2 may produce the observed overall H/Cu ratio. Potential sorption mechanisms with H/Cu ratios of 1 and 2 have been presented in chapter II (figure II-10). Since the dominant species in this study is Cu^{+2}, the only likely reaction to produce a H/Cu ratio of 1 is a surface complexation to one site. If the measured H/Cu ratio is 2 then copper could be precipitating on the surface or it could be coordinating to two surface oxygens.

When the H/Cu ratio is determined at any point during the sorption reaction this ratio must contain contributions from all the sorption processes which have occurred up to that point in time. Since the fastest determination of the H/Cu ratio was after 75 seconds it was impossible to directly measure the H/Cu stoicheiometry for the instantaneous reaction in segment I. However, this stoicheiometry was estimated by extrapolating the the measured H^+ release to time zero and by dividing this value by the moles copper in segment I. The estimated H/Cu ratio for segment I was around 1 suggesting that the instantaneous sorption of copper results from surface complexation. Since the measured H/Cu at 2 minutes is between 1.2 and 1.6, and since there appears to be a gradual increase in H/Cu with time it seems that after the initial sorption in segment I a mechanism with a H/Cu ratio of 2 takes over.

Eventually the pH of the kaolinite suspension stabilizes and no more H^+ desorption can be measured. This could mean that a sorption mechanism takes over which does not liberate hydrogen ions, such as structural penetration. On the other hand the rate of copper sorption and H^+ desorption may have decreased so much that any desorbed hydrogen ion is buffered by the clay and cannot be measured. While the latter possibility exists there is no point in trying to measure and interpret H/Cu ratios when the rate of copper sorption is very low.

It was observed that in experiments which were not maintained at constant pCu, hydrogen ion desorption stopped after only 2 minutes. Also the H/Cu ratio was higher than in the experiments which were maintained at constant pCu. This may be explained by the fact that when pCu was not maintained at a constant level the initial drop in copper concentration quickly stopped surface complexation and the remaining sorption process was dominated by a mechanism with a H/Cu ratio of 2. When copper was added to maintain a constant pCu some of this copper participated in surface complexation and the overall H/Cu ratio remained lower. The higher copper levels produced more sorption over a longer period of time and therefore hydrogen desorption could be measured for longer periods.

When copper sorption was measured in the absence of a background electrolyte (figure V-1) the H/Cu ratio was only 0.52, which represents a combination of a mechanism with a H/Cu ratio of 0 with one or more mechanisms having ratios of 1 or 2. Nonspecific coulombic attraction in this study should have a H/Cu ratio of 0 because the dominant counter ion is K^+. Although the kaolinite was washed with deionized water

before the sorption experiment K$^+$ remained as the dominant counter ion
because the deionized water did not contain enough H$^+$ to displace it.
In another experiment carried out under the same conditions, except for
the presence of 1 M KNO$_3$, the H/Cu ratio was 1.57. However, the
amount of hydrogen ion desorbed in both experiments was identical. This
suggests that the specific chemical sorption which dominated the
sorption process in the salt medium also contributed to copper sorption
in the absence of salt and may have raised the H/Cu ratio from 0 to
0.52. Therefore the amount of chemisorption which took place in the
dilute medium is given by the sorption curve for the 1 M KNO$_3$ medium
and represents 29 percent of the total copper uptake in the absence of
salt.

SUMMARY

In this study nonspecific coulombic attraction is practically
eliminated by the presence of 0.05 M KNO$_3$. Copper sorption is very
sensitive to, and rapidly responds to, changes in pH. Experiments
carried out over several hours appear to be reversible to pH changes.
Copper sorption released measurable amounts of hydrogen ion which can be
used to calculate H/Cu exchange stoicheiometry. The instantaneous
sorption in segment I is probably surface complexation as indicated by
the estimated value of H/Cu at time zero. Copper sorbed in segment I is
desorbed in less than one half minute when the pH is lowered. This may
be consistent with surface complexation where copper is found in a
configuration which is easily accessible to hydrogen ions in solution.
Sorption in segments II to III appears to have a contribution from
mechanism(s) with a H/Cu ratio of 2. These mechanisms could result from

surface precipitation or perhaps complexation to two surface sites.
Copper sorbed in segments II to III appears to desorb more slowly when
pH is lowered which may be consistent with surface precipitation.

CHAPTER VI

DESORPTION STUDIES

INTRODUCTION

In chapter IV copper sorption kinetics indicated that as many as five sorption mechanisms may be responsible for metal uptake by kaolinite. In chapter V the effects of salt concentration and pH on sorption were looked at. It was shown that in the presence of 0.05 M KNO_3 the amount of copper sorbed by nonspecific coulombic attraction is relatively small compared to metal uptake by specific chemical sorption. The observed H^+/Cu exchange stoicheiometry suggests that copper sorption starts with an instantaneous surface complexation reaction followed by surface precipitation or complexation to two surface sites. The H^+/Cu ratio is not useful for studying the slower sorption mechanisms (segments IV and V) because the rate of Cu sorption is so slow that the desorbed H^+ may be buffered by the kaolinite suspension. It was also shown that copper sorption is very sensitive to pH. The copper sorbed by segment I responded very quickly to changes in pH, while the response of copper sorbed by segment III was much slower. This may indicate that copper sorbed by segment III is less accessible to H^+ ions in solution or the copper is held more strongly by the surface (i.e. bonded to two surface sites). After having looked at the effects of pH, salt concentration, and copper concentration on sorption and its kinetics another method of identifying sorption mechanisms was

required.

A very useful technique for identifying sorption mechanisms is by desorption. The response of sorbed copper to pH drops illustrates this point by showing the presence of copper which quickly responds to pH changes, and the existence of copper whose response is more sluggish. The use of different desorption techniques can test the strength(s) of the bonds holding the copper to the surface, which in turn gives an indication of the mechanism(s) involved. From the response of sorbed copper to changes in pH we know that the hydrogen ion is very effective in displacing copper from its sorption sites. The reversibility of metal sorption is also of practical interest when predicting the effects of exposing contaminated sediments to natural waters. Reversibility also tests the validity of using so called equilibrium distribution coefficients in modeling metal migration through a sediment.

The purpose of this chapter is to look at the desorption properties of copper on kaolinite in order to gain a further understanding of the forces holding transition metals to clay surfaces. The response of sorbed copper to a drop in solution metal concentration is extremely important because this is probably the most common type of desorption reaction encountered in nature, aside from small fluctuations in pH. If copper sorption is 100 percent reversible then the bonds holding the metal to the surface are not very strong and might result from nonspecific coulombic attraction. The presence of nonspecific sorption can also be tested by adding a divalent alkali metal such as Sr which is likely to sorb mainly by coulombic attraction. Exposure to 0.001 M Sr will displace any copper sorbed by nonspecific attraction.

Not only is Sr 100 times more concentrated than Cu, but it is also divalent, and has a smaller hydrated radius compared to the other Group IIa metals. The isotopic exchange of ^{64}Cu for nonradioactive copper is also of interest because it indicates the degree with which copper on the surface exchanges with copper in solution. The ultimate test of the strength of the copper-kaolinite bonds may be shown by desorption with concentrated HNO_3 or with a strongly complexing ligand such as cyanide. It has been postulated that clays have an ability to fix metals through some irreversible surface reaction or by incorporating them into their structure. If fixed copper is defined as that which cannot be displaced by cyanide then an increase in fixed copper with long sorption times may be evidence for copper entering the kaolinite structure.

MATERIALS AND METHODS

Adsorptions were carried out using the same materials and methods described in chapter IV. Radioactive ^{64}Cu was also used in some experiments where the copper electrode was not useful. If ^{64}Cu is used then adsorbed copper can be measured directly by counting the activity of ^{64}Cu on solid kaolinite samples. Standards for this type of analysis were made by spiking solid samples of kaolinite with known amounts of ^{64}Cu solution, which was allowed to evaporate to dryness. Solid kaolinite samples were obtained by filtering 10 ml of clay suspension and rinsing the sample with deionized water to get rid of copper contained in trapped liquid.

To desorb copper by dilution it was necessary to separate a large portion of the copper solution from the kaolinite suspension and to replace it with an equal amount of Cu free KNO_3 solution which had the same pH. To accomplish this the clay suspension was centrifuged and about 80 percent of the supernatant was decanted. The copper concentration of the supernatant was measured in order to determine the total amount of copper removed from the system. The dissolved copper concentration of the suspension prior to centrifuging cannot be used for this calculation because the supernatant has a lower concentration after centrifuging. If the copper concentration of the supernatant is not used then the amount of copper removed from the system will be over estimated and the error in the mass balance calculations will be so high that kaolinite will appear to desorb more copper than was adsorbed in the first place. In order to monitor copper desorption the copper electrode was placed in the kaolinite slurry (about 30 ml) before the addition of copper free solution. Once initiated, desorption was monitored until the concentration of copper in solution stabilized.

Desorption with Sr was measured by adding one ml of 0.1 M $Sr(NO_3)_2$ to the kaolinite suspension to give a concentration of 0.001 M. The pH of the suspension was not changed significantly by the addition of Sr. The response of the adsorbed copper to Sr was monitored with the copper electrode for 50 minutes.

To study the isotopic exchange of adsorbed copper with copper in solution, ^{64}Cu was allowed to adsorb onto kaolinite using the usual procedures. After the sorption was monitored for four hours the clay suspension was centrifuged. All the supernatant was removed and the

remaining clay was rinsed with a minimum of deionized water. The
kaolinite was resuspended in a solution containing nonradioactive
copper. Copper sorption was monitored with an electrode while the
suspension was sampled in order to determine the amount of ^{64}Cu
released to the solution.

Desorption by HNO_3 was started by adding enough concentrated
nitric acid to the kaolinite suspension to give an acid concentration of
1.3 N. To start desorption with cyanide, enough 0.01 M KCN was added to
raise the CN^- concentration to between 0.04 and 1 millimolar. If the
CN^- concentration is 0.04 M then there are at least 6 CN^- ions for
every copper ion. The amount of copper desorbed by nitric acid or by
cyanide was determined by atomic absorption or with the help of ^{64}Cu.

RESULTS

The results of desorbing copper by diluting its concentration in
solution are shown in figures VI-1 and VI-2. Figure VI-1 shows the
results of two experiments where copper is sorbed from solutions of
similar copper concentration. After sorption both experiments were
centrifuged and desorption was initiated by adding copper free KNO_3
solution. Desorption for the upper curve started 90 minutes after the
start of sorption, while the desorption of the lower curve started 54
minutes after the start of the experiment. The dashed lines on the
right hand side of the figure show the expected levels of copper
sorption if equilibrium had been achieved during desorption. (These
values were estimated by comparing the results of copper sorbed for 60
minutes under different solution compositions from pCu 6.0 to 5.35.) In

.both experiments copper desorption stopped before the equilibrium concentrations were reached. A dramatic illustration of irreversibility is given in chapter VIII, where the distributions coefficients for these experiments are compared before and after desorption (figure VIII-4).
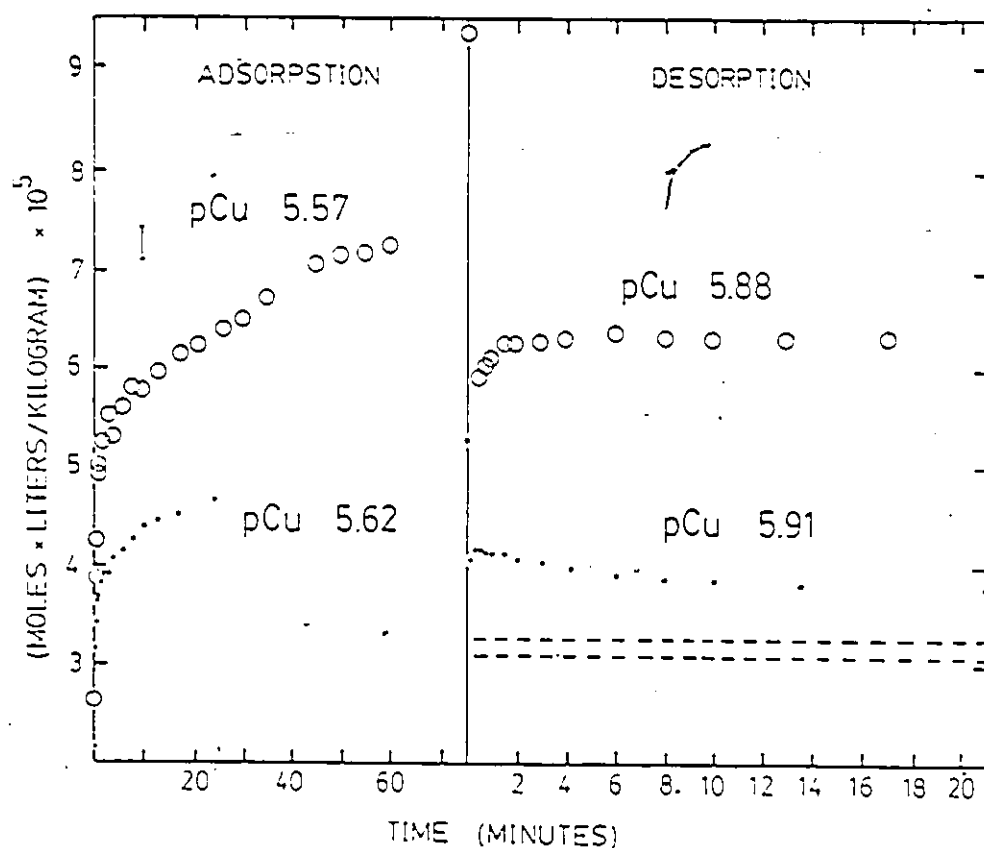
Figure VI-1. Copper sorption followed by desorption, which was induced by by diluting the concentration of copper in solution. The dashed lines indicate expected desorption levels for pCu 5.88 and 5.91. These desorption levels were estimated by comparing the results of copper sorbed for 60 minutes under different solution compositions.
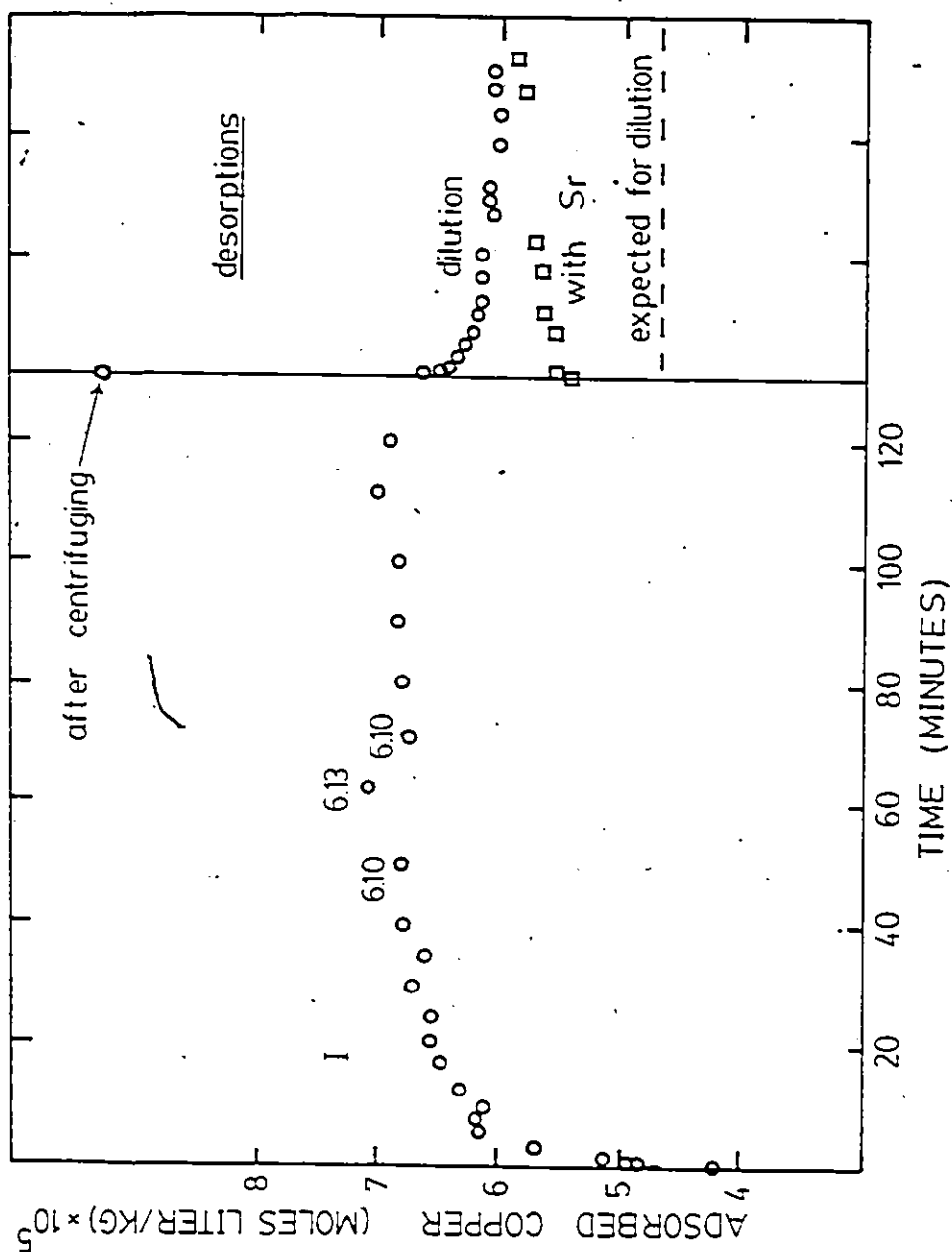
Figure VI-2. Sorption followed by desorption by diluting copper in solution. After desorption by dilution had been monitored for 30 minutes Sr was added to displace Cu held by nonspecific adsorption. ([Sr] in solution was 0.001 moles/liter).

Upon dilution there appears to be a very rapid desorption whose rate cannot be accurately measured because the copper electrode has to adjust from a relatively concentrated clay slurry to a more dilute suspension. After the initial desorption the upper curve stabilizes to a constant sorption concentration over the next 20 minutes. After the initial desorption in the lower curve there was a slow Cu leaching lasting for 14 minutes, after which the sorption level stabilized with time. The rate of this slow desorption was $-7.1 \pm 1.9 \times 10^{-3}$ (min.$^{-}$), which has a similar magnitude to the sorption rates in segment III. Figure VI-2 illustrates a two hour sorption followed by a dilution experiment. Note that the loss of copper from the supernatant during centrifuging has produced an apparent sorption which is significant. When the copper in solution is diluted there is an initial rapid drop in sorption followed by slower desorption for the next 40 minutes. The slow desorption can be broken down into a segment lasting from 1.5 minutes to 6 minutes, and a segment lasting from 11 minutes to 40 minutes. The desorption rate for the first segment is $-6.6 \pm 2.6 \times 10^{-3}$ (min.$^{-}$), which is not significantly different from the slow desorption observed in figure VI-1. The second segment has a desorption rate of $-9.8 \pm 5.3 \times 10^{-4}$ (min.$^{-}$), which is significantly different from the other two measured desorption rates. The desorption rate in the second segment is similar to the sorption rates in segment IV.

Figure VI-2 also illustrates the effect of adding Sr to the clay system. After desorption produced by dilution had been monitored for 50 minutes enough $Sr(NO_3)_2$ was added to raise the Sr concentration to one millimolar. The addition of Sr produced a small instantaneous

desorption ($.5 * 10^{-5}$), after which the amount of sorbed copper

remained constant for 8 minutes. However, with increased reaction time

copper sorption was observed with a rate of $9.6 \pm 1.5 * 10^{-4}$ (min⁻).

This rate is consistent with sorption rates observed for segment IV.
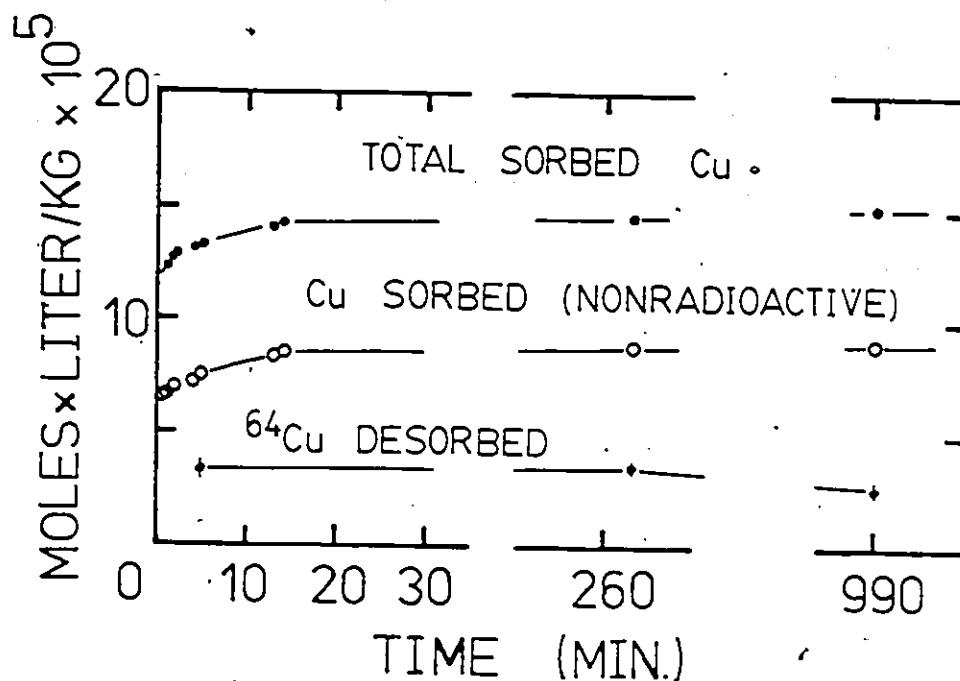
Figure VI-3. Desorption of ^{64}Cu when kaolinite was placed in a nonradioactive Cu solution. Sorption of nonradioactive Cu is included as well as the total sorption of both copper forms.

Figure VI-3 summarizes the experiment where adsorbed ^{64}Cu was

allowed to isotopicly exchange with nonradioactive Cu in solution.

Prior to the isotopic exchange, ^{64}Cu had been allowed to sorb onto

kaolinite for four hours, and had reached a concentration of $8.8 *$

10^{-5} moles liter/kg. At this time the concentration of ^{64}Cu in

solution was pCu 5.77. Figure VI-3 shows the amount of nonradioactive

copper sorption which was initiated when the kaolinite with ^{64}Cu was placed in a 100 ml solution with a copper concentration of pCu 5.39. The amount of copper sorbed is consistent with sorption from a solution with a pCu of 5.55. (Copper concentration dropped to pCu 5.55 because of sorption.) Figure VI-3 also shows that during the sorption of nonradioactive copper about $3 * 10^{-5}$ moles liter/kg of ^{64}Cu was desorbed within the first five minutes. This value did not significantly increase with time and may eventually have decreased as ^{64}Cu began to resorb. Therefore it appears that a portion of the sorbed copper is rapidly exchangeable, while the remainder remains fixed on the surface. The total amount of copper sorbed during the uptake of radioactive and nonradioactive copper is also shown in figure VI-3. The total adsorbed copper is about double the expected sorption from a copper solution of pCu 5.55. It appears that a portion of the previously sorbed ^{64}Cu did not take part in the second sorption and the uptake of nonradioactive copper was not affected by its presence.

In order to measure the amount of copper desorbed by cyanide or nitric acid it was necessary to use either atomic absorption or ^{64}Cu. Radioactive copper has the advantage of permitting the direct analysis of copper on solid kaolinite samples. However, because ^{64}Cu has only a half life of 12.7 hours it cannot be used in experiments which last for more than a few days. For the longer experiments it becomes necessary to measure copper by atomic absorption and to calculate the amount of sorbed copper by mass balance. Adsorbed copper determined by counting activity in solid samples was only 50 to 30 percent of the sorption obtained by mass balance. The difference may result from

copper losses incurred during the phase separation by filtration or it may result from geometric problems encountered during the measurement of copper activity on the solid samples. It seems probable that copper losses in the presence of nitric acid or cyanide solutions should be minimal.
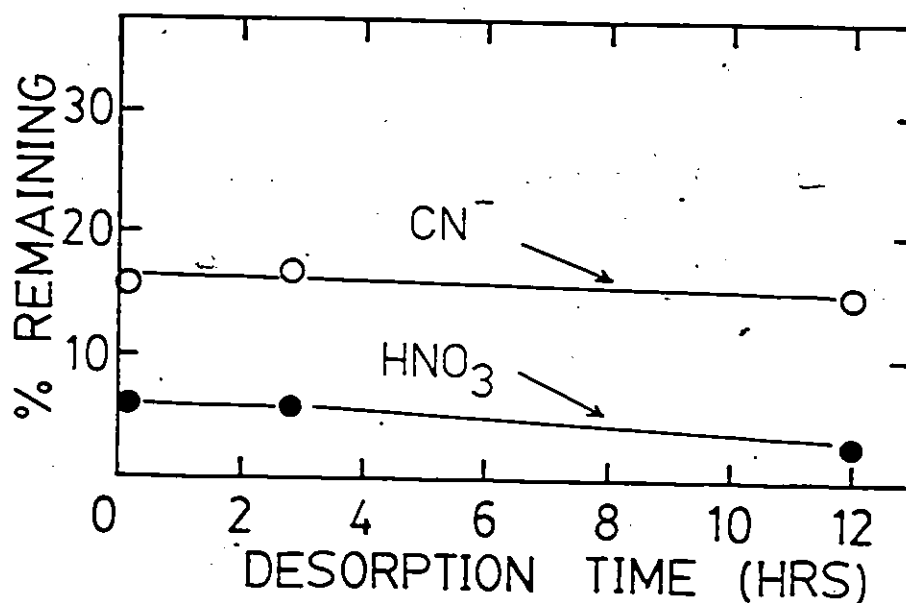
Figure VI-4. Relative abilities of CN^- and nitric acid to desorb Cu.

The results of desorption experiments with cyanide and nitric acid are summarized in tables VI-1 and VI-2. The relative abilities of nitric acid and cyanide to desorb copper are compared in figure VI-4. The 1.3 N nitric acid was able to desorb more copper than the 10^{-3} CN solution. After an initial rapid desorption the nitric acid appears to leach copper at a slow rate ($1.1 * 10^{-3}$ min$^-$). Figure VI-5 illustrates desorption with nitric acid over a 48 hour period. Again after an initial rapid desorption there is a gradual leaching of copper from kaolinite. From 9 minutes to 48 hours the desorption rate was -9.8

$\star$ 10^{-4} min^{-}. The copper which remained on the clay surface is probably not an experimental artifact because it was measured by counting ^{64}Cu activity on a solid kaolinite which had been filtered and rinsed with copper free nitric acid.

TABLE VI-1

DESORPTION WITH CYANIDE

Date	[CN]	Desorption Time	Sorption Time	Percent Cu Left	Log Total Cu Before Sorption
5/04/83	10^{-4}	1 hour	4 hours	43	-5.2
12/04/83	10^{-4}	3 hours	10 min	33	-5.3
"	"	"	20 hours	35	"
25/04/84	10^{-3}	1 hour	9 hours	17	-5.4
"	"	12 hours	"	15	"
19/06/84	10^{-3}	17 hours	2 hours	19	-5.3
"	"	24 hours	"	20	"
"	"	17 hours	1.5 weeks	30	"
"	"	24 hours	"	45	"
"	"	17 hours	2.5 weeks	53	"
"	"	24 hours	"	49	"
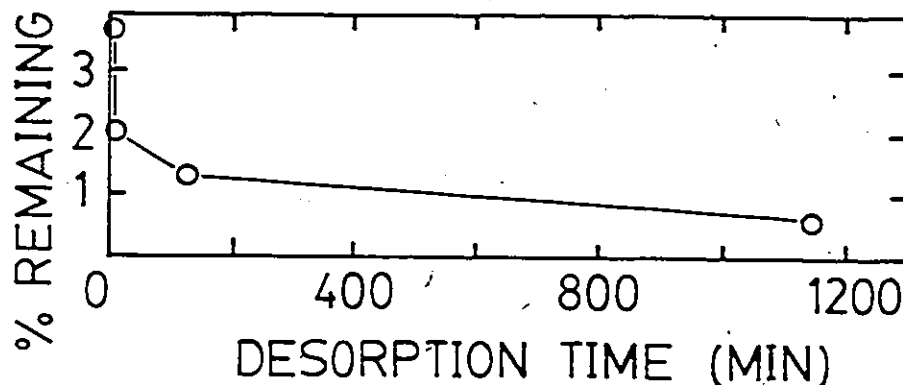
Figure VI-5. Desorption with 1.6 N HNO$_3$ for 48 hours.

The relative power of cyanide to desorb copper compared to dilution is illustrated by the experiment shown in figure VI-2. After desorption with dilution and Sr the amount of sorbed copper had dropped to just below $6 \div 10^{-5}$ moles liter/kg. After desorbing with 10^{-4} M CN for one hour the amount of sorbed copper had dropped to $2.9 * 10^{-5}$, which was 43 percent of the sorption level before any desorption experiments had been started. Figure VI-4 indicates that after an initial fast desorption with CN there is not a significant change in the amount of desorbed copper over the next 12 hours. Figure VI-6 shows desorption over a 24 hour period from kaolinites which had been exposed to copper for 2 hours, 1.5 weeks, and 2.5 weeks. Again desorption time does not significantly affect the amount of copper desorbed by cyanide.

TABLE VI-2

DESORPTION WITH NITRIC ACID

Date	$[HNO_3]$	Desorption Time	Sorption Time	Percent Cu Left	Log total Cu Before Sorption
25/04/84	1.3 N	10 min	9 hours	6	-5.4
		3 hours	"	6	"
		12 hours	"	3	"
3/05/85	1.6 N	5 min	2 hours	3.5	-5.3
		9 min	"	2.1	"
		2 hours	"	1.3	"
		48 hours	"	.6	"

(VI-6) DESORPTION TIME (HOURS)

(VI-7) SORPTION TIME (WEEKS)
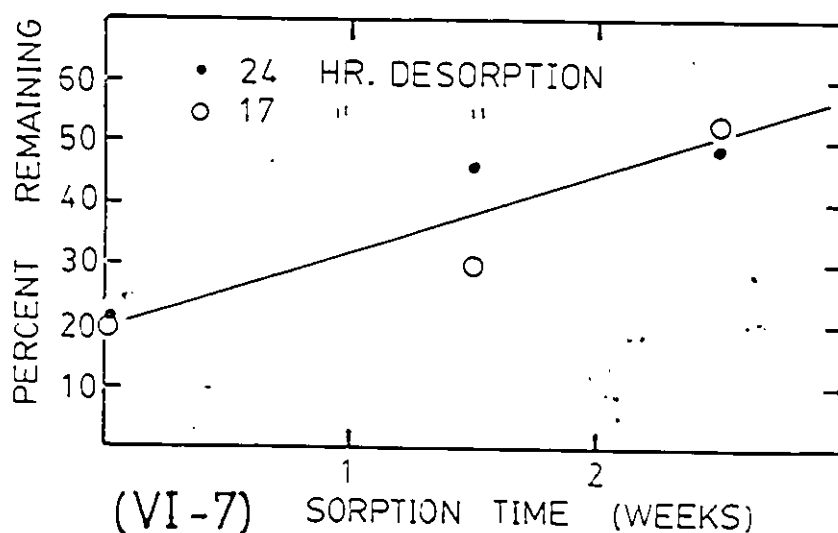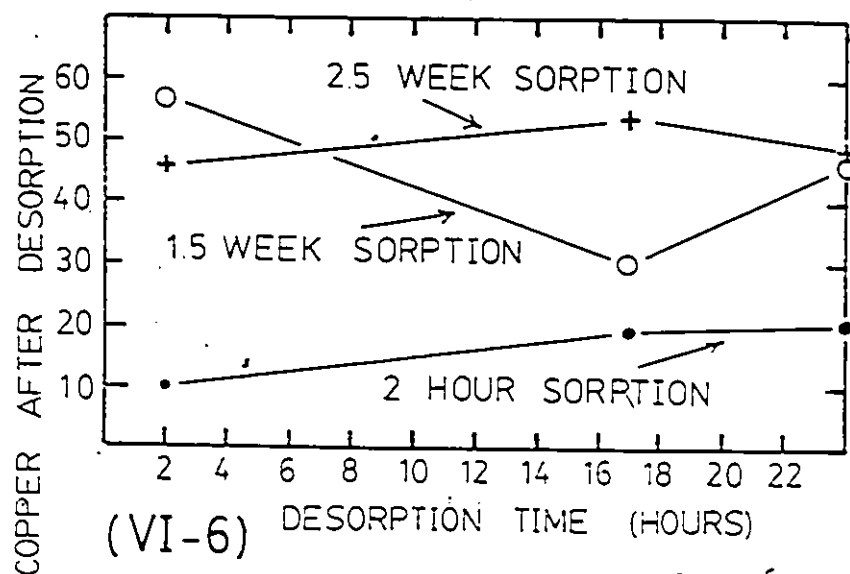
Figures VI-6 and 7. Figure 6 shows the effect of desorption time on Cu sorbed from 2 hours to 2.5 weeks. Figure 7 shows the effect of sorption time on Cu fixation. Each point is the average of two determinations which agreed within 5 percent.

We can define fixed copper as that which cannot be desorbed by cyanide because it is improbable that a stronger desorbing agent will be found in nature. It would be interesting to see if long sorption times

can produce more copper fixation since this would have implications for understanding sorption mechanisms and for modeling metal behavior in the environment. The data of April 12/83 indicate that over a 20 hour period there is not a significant difference in the amount of fixed copper (table VI-1). However, when the sorption time is extended over two weeks there appears to be an increase in the amount of fixed metal. Figure VI-7 shows a plot of fixed copper which had a sorption time ranging from 2 hours to 2.5 weeks. The amount of fixed copper increases from 20 percent at 2 hours to about 50 percent after 2.5 weeks. This increase is similar to the amount of Cu sorbed by segment V over a 2.5 week period. In figure IV-14, which illustrates sorption at constant total copper concentration, the amount of sorption by segment V after 2.5 weeks represents 25 percent of the total sorbed copper.

DISCUSSION:

The desorption experiments in this study have shown that copper sorption on kaolinite is not reversible and that different desorption techniques can extract differing amounts of copper. This is an indication that copper is bound to the kaolinite surface by several different mechanisms which have varying resistances to desorption.

DESORPTION BY DILUTION: When copper concentration in solution is diluted some copper desorbs, but not as much as might be expected if equilibrium was achieved. It would be interesting to know which sorption segments release copper when the solution is diluted. One approach to solving this problem is to compare the amount of desorbed

...+copper to the expected responses of segments I, II, and III to dilution. Before this is done we must note that there is an apparent additional sorption produced by the centrifuge process (figures VI-1 and VI-2). Sorption due to centrifuging will be discussed in greater detail in the next chapter. In figures VI-1 and VI-2 the excess sorption caused by centrifuging seems to disappear when the kaolinite is resuspended in a dilute copper solution. However, these figures do not prove that the all the copper adsorbed during centrifuging is desorbed upon resuspension. Figures VII-4 to VII-6 show the behavior of copper sorption when a centrifuged kaolinite is resuspended in the presence of the centrifuged supernatant. Upon resuspension the sorption does not immediately return to the level before centrifuging, but instead desorbs with a rate between $-3.5 * 10^{-3}$ and $-9 * 10^{-3}$ (min⁻). If the kaolinite had been resuspended in a copper free solution then the copper sorbed during centrifuging may have desorbed at a much faster rate. Therefore, the behavior of copper sorbed during centrifuging remains uncertain during the dilution experiments.

If there are assumed to be no effects due to resuspension , then one can compare the level of desorbed copper with the amount sorbed before centrifuging. Figure VI-8 summarizes the desorption curves in figures VI-1 and VI-2, and it shows the the amount of copper desorbed (moles liter/kg $* 10^5$) for various points along the desorption curve. The second and third desorption experiments shown in figure VI-8 show slow desorption steps after the initial rapid desorption, and therefore the amount of copper desorbed by these steps is also indicated.
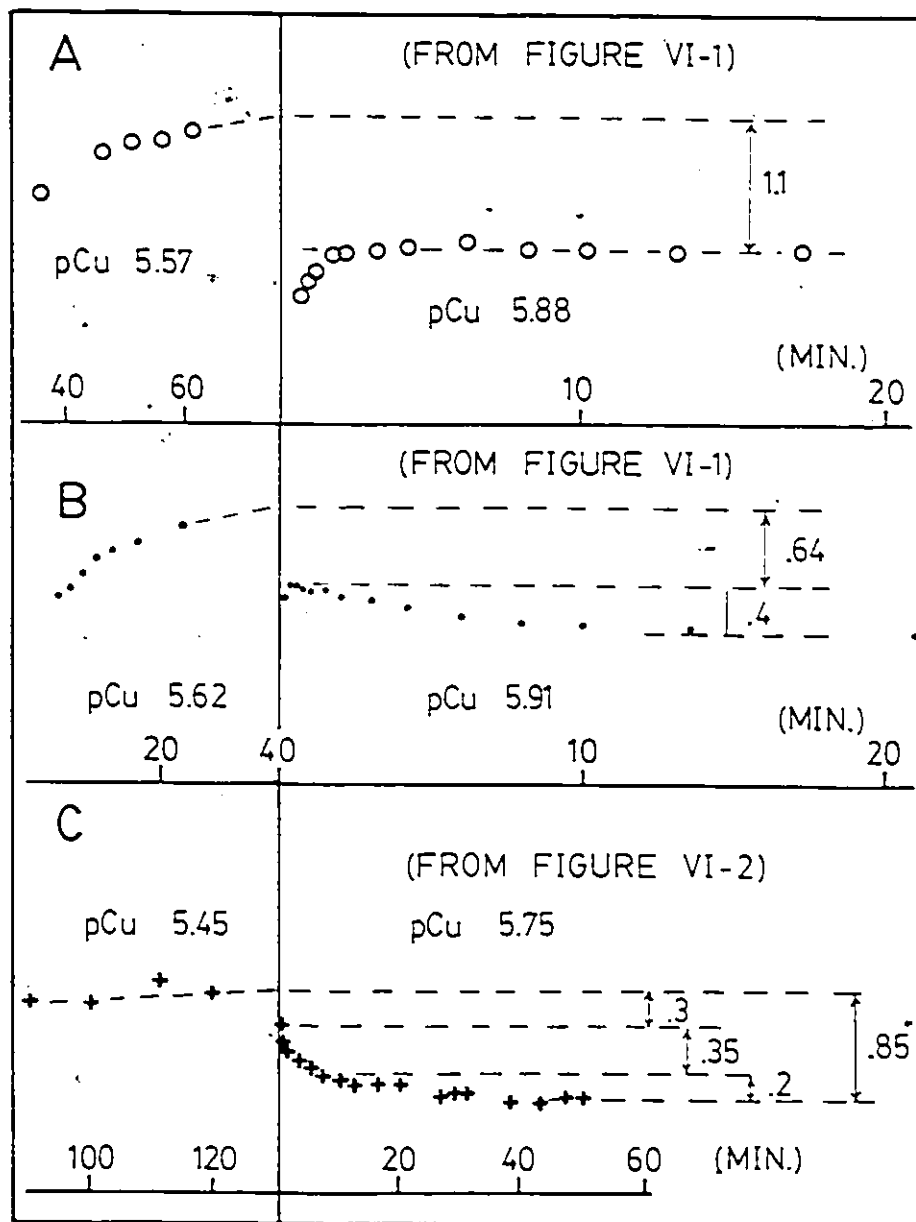
Figure VI-8. Summary of desorption experiments from figures VI-1 and VI-2. The y axis represents sorbed copper (moles*liter/kg * 10^{-5}).

The copper desorption shown in figure VI-8 cannot be interpreted in terms of the sorption segments I to III unless the amount of copper held by these segments is known as a function of copper concentration. The variation of these sorption segments with copper concentration can be estimated by combining data from experiments with different constant copper concentrations. Figure VI-9 shows the variation of segments I, II and III as a function of pCu. The copper content of segment I represents instantaneous sorption and is obtained by extrapolating copper sorption to time zero. The copper sorbed by the mechanism responsible for segment II can be calculated by taking the total amount of copper sorbed at the end of segment II and subtracting the amount of copper sorbed by segment I. The copper sorbed by the slower mechanisms (III, IV, and V) will be negligible by comparison because of their much slower sorption rates. Copper sorption by segment III starts at time zero and continues until segment III reaches a steady state at which point the mechanism of segment IV takes over the sorption process. The lower limit of sorption by segment III is given by the time zero intercept of the line which defines segment III. The upper limit of segment III sorption is given by the point where segment IV begins to dominate the sorption process.

If sorption was completely reversible, then upon dilution the copper sorbed by segments I to III should follow the trends illustrated in figure VI-9. Table VI-3 illustrates the changes expected for segments I to III if the copper concentration is diluted by the amounts shown in figure VI-8.
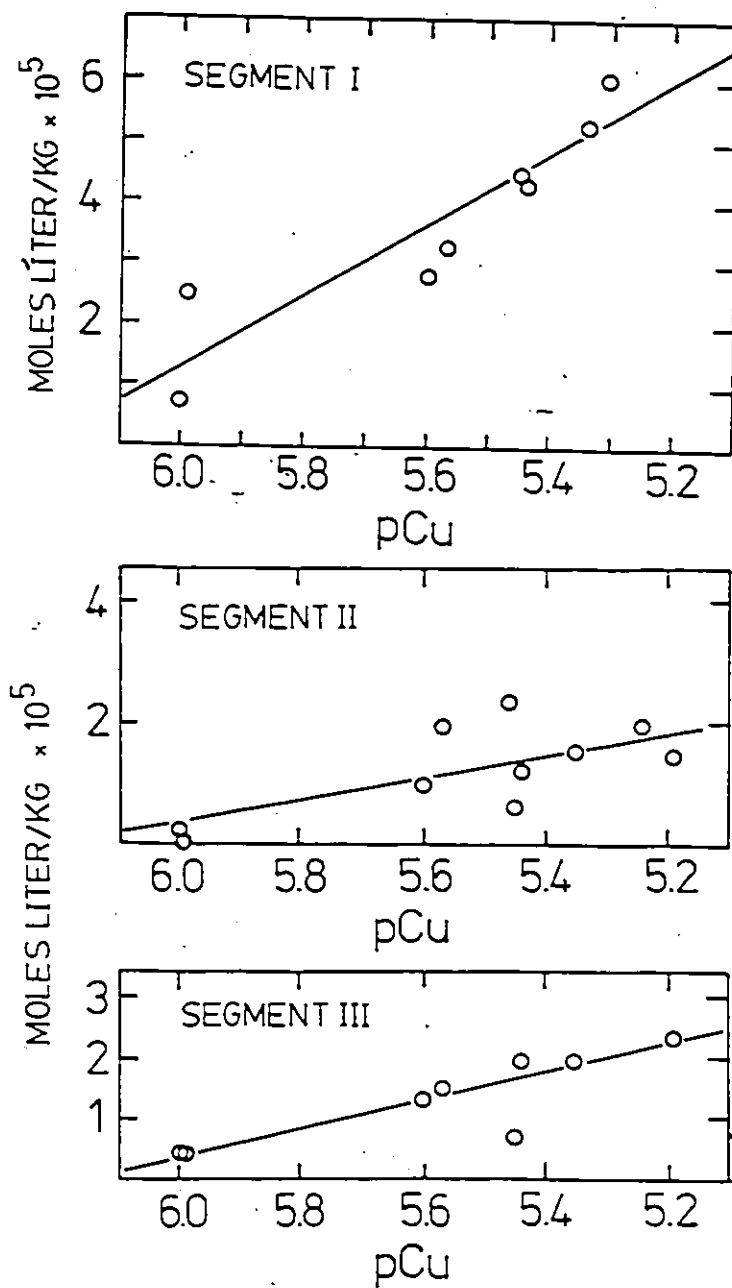
Figure VI-9. The effect of solution copper concentration on the amount of copper sorbed by segments I to III.

TABLE VI-3

PREDICTED CHANGE IN SORPTION UPON DILUTION   (MOLES LITER/KG $* 10^5$)

	High Cu (pCU)	Diluted Cu (pCu)	Change upon Dilution		
			Segment I	Segment II	Segment III
A	5.57	5.88	1.8	0.5	0.7
B	5.62	5.91	1.7	0.5	0.7
C	5.45	5.75	1.8	0.5	0.7

Figure VI-8 shows that the difference in the level of copper sorption before centrifuging and after desorption is around $1 * 10^{-5}$ moles liter/kg. This is about one half the expected amount of desorption for segment I. On the other hand the total expected desorption for segments II and III is close to $1 * 10^{-5}$ moles liter/kg. One could speculate that the copper desorption produced by dilution came from segments II and III, which could represent surface precipitation. This would be consistent with the work of McBride (1982), which indicated that copper sorbed by surface precipitation is easily desorbed, while copper complexed to surface sites (segment I) is difficult to remove. The slow desorption rate in B is similar to sorption rates in segment III, and the two slow desorption rates observed in C are similar to sorption rates in segments III and IV. This might be considered as evidence for the desorption of copper from segment III. However it must be remembered that when a centrifuged kaolinite is resuspended in the original supernatant solution, the desorption rate is also similar to the sorption rates of segment III. Therefore, the slow desorption rates observed in B and C could also be resuspension effects.

Desorption with Sr: When Sr was added to the experiment in figure VI-2, $0.5 * 10^{-5}$ moles liter/kg of copper was desorbed almost instantaneously. This must represent copper adsorbed by nonspecific coulombic attraction, which Sr^{+2} was able to desorb because it is more effective than K^+ in displacing copper held by electrostatic interactions. The amount of copper displaced initially by Sr is 8 percent of the total copper sorbed before Sr addition. Copper held by electrostatic attractions is likely to be contained in segment I, which is confirmed by the fact that desorption by Sr was instantaneous. The amount of nonspecificly sorbed copper, determined by Sr desorption, represents 18 percent of the copper sorption in segment I predicted for pCu 5.75.

Isotopic exchange of ^{64}Cu: The isotopic exchange of ^{64}Cu is a possible method of showing whether copper ions on the kaolinite surface can exchange with copper ions in solution. When a kaolinite with sorbed ^{64}Cu was placed in a nonradioactive copper solution, $3 * 10^{-5}$ moles liter/kg of ^{64}Cu were desorbed. This represented 34 percent of the total ^{64}Cu which had been previously sorbed. The desorption of ^{64}Cu is probably complete before 5 minutes of reaction time is up, which means that the reservoir of isotopicly exchangeable copper is quickly used up. Possible origins of isotopicly exchangeable copper are suggested in table VI-4.

TABLE VI-4

CAUSES OF ISOTOPICLY EXCHANGEABLE COPPER

Source	Reason
1) nonspecific sorption: (predicted capacity $.9 * 10^{-5}$)	Strong bonds do not have to be broken to exchange Cu.
2) surface complexation in segment I (predicted capacity $5 * 10^{-5}$)	Displacement of ^{64}Cu is very rapid which is consistent with reactions in segment I.
3) excess sorption due to centrifuging	The resuspension of kaolinite may have liberated some of the copper which had sorbed because the clay had become compacted during centrifuging.

If the ^{64}Cu was initially displaced from the population of electrostaticly sorbed copper then the lack of further ^{64}Cu desorption might be explained. However, the predicted amount of nonspecificly adsorbed copper appears to be too low to account for ^{64}Cu desorption. It is also possible that when nonradioactive copper was sorbing in segment I it displaced ^{64}Cu from edge sites. However, this does not mean that copper sorbed by surface complexation in segment I readily exchanges with copper in solution because there is no more ^{64}Cu desorption after 5 minutes. Since the total amount of ^{64}Cu in segment I has not been used up one would expect further isotopic exchange if copper, complexed to surface sites, was readily exchanging with copper in solution. To displace ^{64}Cu from segment I it may be necessary to have a strong pulse of copper sorption, which occurred when the kaolinite was placed in a fresh copper solution. Another explanation for the desorbed ^{64}Cu is that it originates from copper which had been

sorbed during centrifuging. However, it was shown that when centrifuged kaolinites were resuspended in solutions, which had similar copper concentrations to the clay suspension before centrifuging, copper desorption was slow.

Another curious feature with this experiment is that the sorption of nonradioactive copper did not appear to be inhibited by the presence the previously sorbed ^{64}Cu. Copper sorbed by surface complexation in segment I may displace some ^{64}Cu from surface sites, but it also finds new sites to complex with. Copper sorbed by surface precipitation would not be affected by previously sorbed copper, so that sorption in segments II, III and IV is not expected to be inhibited by ^{64}Cu.

Desorption with nitric acid and cyanide: In contrast to desorption by dilution, a solution of 10 percent nitric acid is a very powerful desorbing agent. Within a few minutes of contact with nitric acid only 3 to 6 percent of the sorbed copper remains on the kaolinite surface. With prolonged contact to nitric acid the remaining copper is slowly desorbed as the acid attacks the kaolinite structure. The copper which resists desorption by nitric acid must be either held by very strong bonds or has managed to penetrate the kaolinite structure through some faults or cleavages. It does not seem likely that this copper has penetrated the structure through dehydration reactions and solid state diffusion because the maximum sorption time was only 9 hours. Farrah and Pickering (1978) recovered 90 to 95 percent of the copper sorbed on kaolinite (at pH 7) by leaching it with 0.1 M nitric acid for 24 hours.

Since copper forms stronger bonds with CN than it does with oxygen, CN should be able to complex and remove copper which is precipitated or complexed to surface sites. In this study it was observed that when copper is added to a kaolinite suspension which contains cyanide, no sorption is observed. However, if copper is added to the kaolinite suspension before cyanide is introduced some copper remains on the surface. This suggests that some copper is either bonded very strongly to the surface or that it has moved away from the surface by penetrating cleavages or faults. Unlike nitric acid, CN does not attack the kaolinite surface, unless the surface is coated with iron. This may be confirmed by the fact the amount of copper desorbed by cyanide does not increased with long exposure times.

Cyanide was considered an ideal desorbing agent to define fixed copper because it strongly complexes the metal, but does not attack the clay surface. Metal fixation in soils has been investigated by soil scientists, but it is still not clear whether fixation is produced by the penetration of mineral structures or whether a fraction of the sorbed metals forms very strong bonds with mineral surfaces. Evidence for structural penetration would come from a measured increase in fixation over long reaction times of weeks or months. In this study an increase in copper fixation was observed over a two week period, which may be considered as evidence for structural penetration. However, fixation was also observed for a short reaction time of only 10 minutes which, is too fast for structural penetration. The only way of getting into the structure in ten minutes may be by diffusion into a cleavage or fault. Therefore, the presence of copper fixed at the solid/liquid

interface cannot be ruled out. It is possible that fixed copper may

consist of a combination of an irreversible surface reaction and a

structural penetration, which is shown by the gradual increase in

fixation over a two week period. Arguments for structural penetration

and surface fixation are given in table VI-5.

TABLE VI-5

Structural penetration	Surface fixation
1) Gradual increase in fixation over a two week period.	1) Fixation can occur during very short sorption times.
2) After several hours CN does not remove significantly more Cu.	2) Some surface fixation might also increase slowly with time.
3) Nitric acid continues to remove fixed copper as the acid attacks the clay structure.	
4) Diffusion into faults or cleavages might explain rapid fixation.	

SUMMARY:

It has been shown that copper sorption is not reversible relative to dilution and that it has a varied response to different desorption techniques. In this study the agents used to desorb copper from kaolinite were:

(1) Water was used to determine the amount of sorbed copper which is completely reversible to dilution.

(2) Strontium is able to remove copper held by nonspecific coulombic sorption, but it does not affect metals held by specific chemical bonds.

(3) Radioactive copper was employed to evaluate how much of the sorbed copper ions were were exchanging with copper in solution.

(4) Nitric acid is the most effective desorbing agent since it can desorb most of the sorbed copper. With increasing reaction time it attacks the kaolinite surface and releases any copper trapped in the clay structure.

(5) Cyanide desorbs copper by forming a very strong complex with the metal. Cyanide can remove any copper which has not penetrated the clay structure and which has not formed irreversible bonds with the kaolinite surface.

The amount of Copper desorbed during the dilution experiments may be consistent with the predicted response of segments II and III to dilution. These segments may represent surface precipitation, which McBride (1982) has shown to be more prone to desorption than copper complexed to surface sites. A large portion of copper sorbed by segment I, which may be complexed to surface sites, appears to be resistant to

desorption by dilution. Unfortunately the results of the dilution experiments are complicated by extra sorption produced during centrifuging. The addition of Sr to the kaolinite suspension has shown that about 20 percent of segment I may consist of nonspecific sorption. Isotopic exchange with ^{64}Cu has indicated that when kaolinite is introduced to a new copper solution some of the previously sorbed copper is displaced. However, after the initial contact with nonradioactive copper the isotopic exchange of ^{64}Cu either stops or can no longer be measured because of slow exchange kinetics. This suggests that, with the exception of nonspecific sorption, copper on the kaolinite surface does not readily exchange with copper in solution unless it is displaced by a vigorous Cu sorption (segment I). The presence of previously sorbed copper does not seem to significantly inhibit further copper sorption. Some copper resists desorption by 10 percent nitric acid and by 1 millimolar CN. It is not clear whether this copper has been fixed at the surface or whether it has penetrated the structure.

CHAPTER VII

SORPTION INDUCED BY KAOLINITE AGGLOMERATION

INTRODUCTION

Up to this point the discussion has dealt mainly with the sorption reactions produced by surface characteristics of kaolinite grains. Sorption has been envisaged as a transfer of copper ions from a uniform, free solution to the various surfaces of a kaolinite grain. The effect of neighboring kaolinite particles has not been considered. In nature clay particles usually do not occur as discrete grains because in the presence of a background electrolyte they tend to coagulate into flocs. In sediments clay particles are also found in close contact with neighboring mineral grains. In order to fully understand sorption reactions one must consider what effect particle interactions may have on sorption processes. It is believed that some sorption reactions are partially inhibited because contact between neighboring grains may block sorption sites. The water trapped between clay particles is likely to have a different composition (pH, Cu) than the free solution which is in contact with the sediment or clay floc. If the copper concentration in the interstitial water of a clay floc is higher than in the free solution then the sorption reaction which is observed is actually driven by a higher copper activity than is measured in the free solution. In this situation sorption may be higher than expected.

The effect of clay flocs on sorption is difficult to identify because flocculation cannot be prevented in a salt solution unless a dispersive agent is added. Dispersive agents are undesirable because they will change the properties of clay surfaces and they might interact with copper ions in solution. Clay flocculation can be controlled by changing the concentration of background electrolyte. Unfortunately the change in electrolyte will have a greater effect on sorption than the difference in clay floculation. A sonic probe might be used to disperse the kaolinite flocs, but unfortunately it would probably also disperse the copper electrode. The best way to look at the effects of clay flocs on copper sorption may be to draw an analogy between a clay floc and a centrifuged clay plug which is covered with the supernatant solution. In both situations there is a free solution which is in contact with a clay mass that contains interstitial water with a different composition than the free solution.

The interactions between kaolinite particles which are produced when kaolinite is concentrated during centrifuging may provide a practical example of the effects of particle interactions on sorption measurements. The effect of centrifuging on sorption is directly relevant to many sorption studies which use centrifuging as a method of phase separation. Centrifuge effects on sorption were first noticed in this study when an attempt was made to desorb copper by diluting the equilibrium solution. The kaolinite suspension was centrifuged and part of the supernatant was replaced with copper free solution. In order to calculate the amount of copper remaining on the surface it was necessary to determine how much copper had been removed from the system. When it

was assumed that the supernatant, which had been removed, had the same copper concentration as before centrifuging, the amount of removed copper was overestimated by so much that the kaolinite appeared to have a negative copper concentration. When the copper concentration of the supernatant was measured and compared to the copper concentration before centrifuging a significant decrease in copper was noted.

Explanations for the apparent drop in the supernatant copper concentration during centrifuging have been discussed in chapter II. These explanations can be divided into three principal types which are (1) that sorption takes place during centrifuging, (2) junction potential produces an apparent difference in copper concentration between the suspension and the supernatant, and (3) that while immersed in the suspension the copper electrode responds to some of the copper associated with kaolinite surfaces.

The purpose of this chapter is to present data which supports the conclusion that the apparent copper sorption during centrifuging is real and that the effect of liquid junction potential is not significant. Then an attempt is made to characterize sorption caused by centrifuging in order to get some insight into the mechanisms behind this phenomenon. The relationship between sorption and the concentration of copper in solution is looked at. The effects of previously sorbed copper, pH, salt concentration and solid/solid liquid ratio are noted. The interstitial water of a centrifuged clay is analyzed in order to determine whether the copper lost during centrifuging is concentrated in the pore water or whether it is attached to the clay surface. The reversibility of copper sorbed during centrifuging is investigated by

resuspending the centrifuged kaolinite.

MATERIALS AND METHODS

Copper sorption produced by centrifuging was measured as a routine procedure in numerous experiments. Therefore, the principal materials and methods used to acquire the data for this chapter have been described in previous chapters. The chief analytical tool was the copper electrode, although atomic absorption and ^{64}Cu were also employed to back up the electrode results and to analyze pore water extracted from a centrifuged kaolinite.

In a given sorption experiment the pH and copper concentration were measured immediately before the kaolinite suspension was centrifuged. The reaction vessel was then placed in the centrifuge and the clay suspension was centrifuged for 15 minutes at 500 rpm. After centrifuging the supernatant was decanted into another container. The copper concentration and pH were measured after 5 to 10 minutes. In order to reverse the effects of centrifuging the supernatant was returned to the reaction vessel and the kaolinite was resuspended.

RESULTS

The results of measuring copper sorption attributed to centrifuging are summarized in table VII-1. In most instances the measurement of copper sorption during centrifuging was a routine procedure to finish a sorption experiment. Therefore, the experimental pH's, solid/liquid ratios, sorption times and copper concentrations shown in table VII-1 were not chosen for the specific purpose of

studying sorption during centrifuging, but instead reflect the

objectives of the sorption experiment before centrifuging.

TABLE VII-1

SUMMARY OF COPPER SORBED DURING CENTRIFUGING

	date	gm per 100 ml	sorption time	moles l/kg before cent. $\times 10^5$	pCu before cent.	moles l/kg sorbed by cent. $\times 10^5$	D l/kg	pH	pH after
1	21/12/82	.36	21 min	4.65	5.62	0.61	23	6.12	6.12
2	22/12/82	.27	60 min	7.21	5.57	2.12	72	6.13	6.09
3	29/12/82	.20	60 min	12.26	5.46	5.20	136	6.19	6.12
4	10/01/83	.39	180 min	3.17	6.06	0.46	48	6.21	6.17
5	18/01/83	.44	52 min	12.17	5.66	1.75	73	6.18	6.16
6	18/01/83	.37	26 min	5.41	5.91	1.14	84	6.2	
7	07/02/83	.25	72 min	0.61	5.44	1.93	48	6.01	6.12
8	10/02/83	.29	160 min	12.25	5.43	1.93	47	6.11	6.08
9	15/02/83	.23	129 min	11.41	5.45	2.77	71	6.26	6.26
10	05/04/83	.24	120 min	6.89	5.43	2.61	64	6.11	6.10
11	12/07/83	.35	120 min	39.83	5.01	9.12	85	6.21	6.18
12	22/07/83	.39	90 min	19.82	5.06	13.78	144	6.39	6.33
13	26/07/83	.24	56 min	21.28	5.19	3.38	48	6.24	6.21
14	02/08/83	.36	75 min	4.63	6.00	0.48	44	6.24	6.23
15	04/08/83	.40	67 min	24.55	4.69	7.42	33	6.20	6.18
16	13/04/84	.51	22 hr	4.23	6.12	0.05	6	6.22	6.14
17	25/04/84	.28	37 min	11.11	5.60	3.65	132	6.21	6.10
18	03/05/84	.30	150 min	21.70	5.57	2.38	80	6.11	
19	22/06/84	.36	410 hr	14.74	5.93	0.99	77	6.21	6.13
20	22/06/84	.28	410 hr	44.29	5.11	6.33	74	6.18	6.11

1 M KNO$_3$

D = copper sorbed during centrifuging / concentration of Cu^{+2}

Before the data of Table VII-1 can be interpreted in terms of

copper sorption induced by centrifuging it must be shown that the

apparent copper sorption during centrifuging is real and not an artifact

of liquid junction potential or surface reactions on the copper

electrode. Table VII-2 compares atomic absorption and electrode

measurements of dissolved copper before and after centrifuging. In

order to measure the dissolved copper in the clay suspension by atomic

absorption, a sample of the suspension was filtered and the filtrate was

preserved by acidifying with nitric acid. The centrifuged supernatant was also preserved for atomic absorption analysis by adding a minimum amount of nitric acid. The atomic absorption measurements give similar results to the electrode measurements. Copper sorption during centrifuging is also shown by the atomic absorption measurements, although the amount of copper lost from solution appears to be less than that indicated by electrode measurements.

TABLE VII-2

COMPARISON OF ELECTRODE MEASUREMENTS WITH ATOMIC ABSORPTION

Date		AAS (mg/l)	electrode (mg/l)
29/12/82	before centrifuging	.215 ± .005	.220 ± .002
	after centrifuging	.185 ± .005	.180 ± .001
	Cu loss	.030	.040
22/07/83	before centrifuging	.573 ± .017	.551 ± .020
	after centrifuging	.438 ± .013	.398 ± .020
	Cu loss	.135	.153
26/07/83	before centrifuging	.395 ± .012	.414 ± .020
	after centrifuging	.369 ± .011	.372 ± .020
	Cu loss	.026	.042

Usually the pH of the centrifuged supernatant is lower than that of the kaolinite suspension. Measured pH's of clay suspensions and their respective centrifuged supernatants are given in table VII-3. Donnan theory and the effect of liquid junction potentials predict that the supernatant should have a higher pH than the clay suspension. Therefore, hydrogen ions must be liberated to the supernatant during the centrifuging process. Since these hydrogen ions are produced by copper

sorption it would have useful to determine the total amount of hydrogen ions liberated. Unfortunately a back titration with base is not very feasible because the supernatant would have to be returned to the reaction vessel where the kaolinite would be resuspended. This might reverse the effects of centrifuging and the amount of hydrogen ion desorption determined by the back titration would be inaccurate. The difference in the pH of the supernatant and the clay suspension also does not give the amount of desorbed hydrogen ion because the kaolinite readsorbs a significant portion of the H^+ which has been liberated by Cu sorption. Therefore, the data of table VII-3 can only be used as evidence for the release of hydrogen ions during centrifuging and they cannot be used to quantify the stoicheiometry of H^+/Cu^{+2} exchange.

TABLE VII-3

CHANGES IN pH PRODUCED BY CENTRIFUGING

date	pH before	pH after
21/12/82	6.12	6.12
22/12/82	6.13	6.09
29/12/82	6.19	6.12
10/01/83	6.21	6.17
18/01/83	6.18	6.16
10/02/83	6.11	6.08
15/02/83	6.26	6.26
05/04/83	6.11	6.10
12/07/83	6.21	6.18
22/07/83	6.39	6.33
26/07/83	6.24	6.21
02/08/83	6.24	6.23
04/08/83	6.20	6.18
13/04/84	6.22	6.14
25/04/84	6.21	6.10
22/06/84	6.21	6.13
22/06/84	6.18	6.11

TABLE VII-4

PORE WATER ANALYSIS OF CENTRIFUGED KAOLINITE

25/04/84 $[Cu]$ in original suspension $= 2.52 * 10^{-6}$ M

         $[Cu]$ in supernatant $= 1.74 * 10^{-6}$ M

         $[Cu]$ in pore water $= 3.44 * 10^{-6}$ M   (1.25 ml)

$[Cu]$ in pore water / $[Cu]$ in supernatant $= 1.98$

extra moles Cu in pore water $= (3.44 - 2.52) * 10^{-6} * 1.25 * 10^{-3}$

$$= 1.16 * 10^{-9}$$

moles Cu lost from solution $= (2.52 - 1.74) * 10^{-6} * 0.1$

$$= 7.76 * 10^{-7}$$

03/05/84 $[Cu]$ in original suspension $= 2.69 * 10^{-6}$ M

         $[Cu]$ in supernatant $= 2.39 * 10^{-6}$ M

         $[Cu]$ in pore water $= 5.21 * 10^{-6}$ M   (1.95 ml)

$[Cu]$ in pore water / $[Cu]$ in supernatant $= 2.18$ extra moles Cu in

pore water $= (5.21 - 1.97) * 10^{-6} * 1.95 * 10^{-3}$

$$= 6.33 * 10^{-9}$$

moles Cu lost from solution $= (2.69 - 1.97) * 10^{-6} * .05$

$$= 3.59 * 10^{-8}$$

An interesting question to address is whether the copper sorbed during centrifuging resides in the interstitial water of the clay floc or whether it has been sorbed on clay surfaces. The copper concentration of the interstitial water of a centrifuged clay can be estimated by placing the centrifuged kaolinite on a Nucleopore filter and recovering the pore water by vacuum filtration. The copper concentration of the pore water can be determined by counting the

activity of ^{64}Cu. Table VII-4 gives pore water concentrations from two

experiments, as well as the respective suspension and supernatant copper

concentrations. In both cases the pore water has a higher copper

concentration than the original kaolinite suspension. The excess copper

in the pore water compared to the suspension is given by the "extra

moles Cu in pore water" in table VII-4. When this value is compared to

total moles Cu lost from solution during centrifuging it is apparent

that the pore water does not account for all the copper lost from

solution. Therefore some of the copper lost from solution must have

sorbed to kaolinite surfaces and cannot be removed by vacuum filtration.

The experiments shown in table VII-1 cover a wide range of copper

concentrations which makes it feasible to look at the influence of

dissolved copper concentration on sorption during centrifuging. The

amount of copper sorbed during centrifuging is plotted versus pCu

(before centrifuging) in figure VII-1. All the data of table VII-1 are

included except for experiment 12, whose pH was 6.39. Although the

experiments in table VII-1 were not carried out at exactly the same pH

or solid/liquid ratio, figure VII-1 shows that the amount of copper

sorbed during centrifuging increases with the amount of Cu^{+2} in

solution. Seventy-four percent of the data in figure VII-1 fit a linear

relationship between sorbed copper and pCu. The slope of this line is

$(-5.8 \pm 2.1) * 10^{-5}$ and the intercept at pCu·0 is $(35 \pm 12) * 10^{-5}$

moles liter/kg. The dashed line in figure VII-1 gives the 99 percent

confidence interval for the mean response of sorbed copper to pCu.
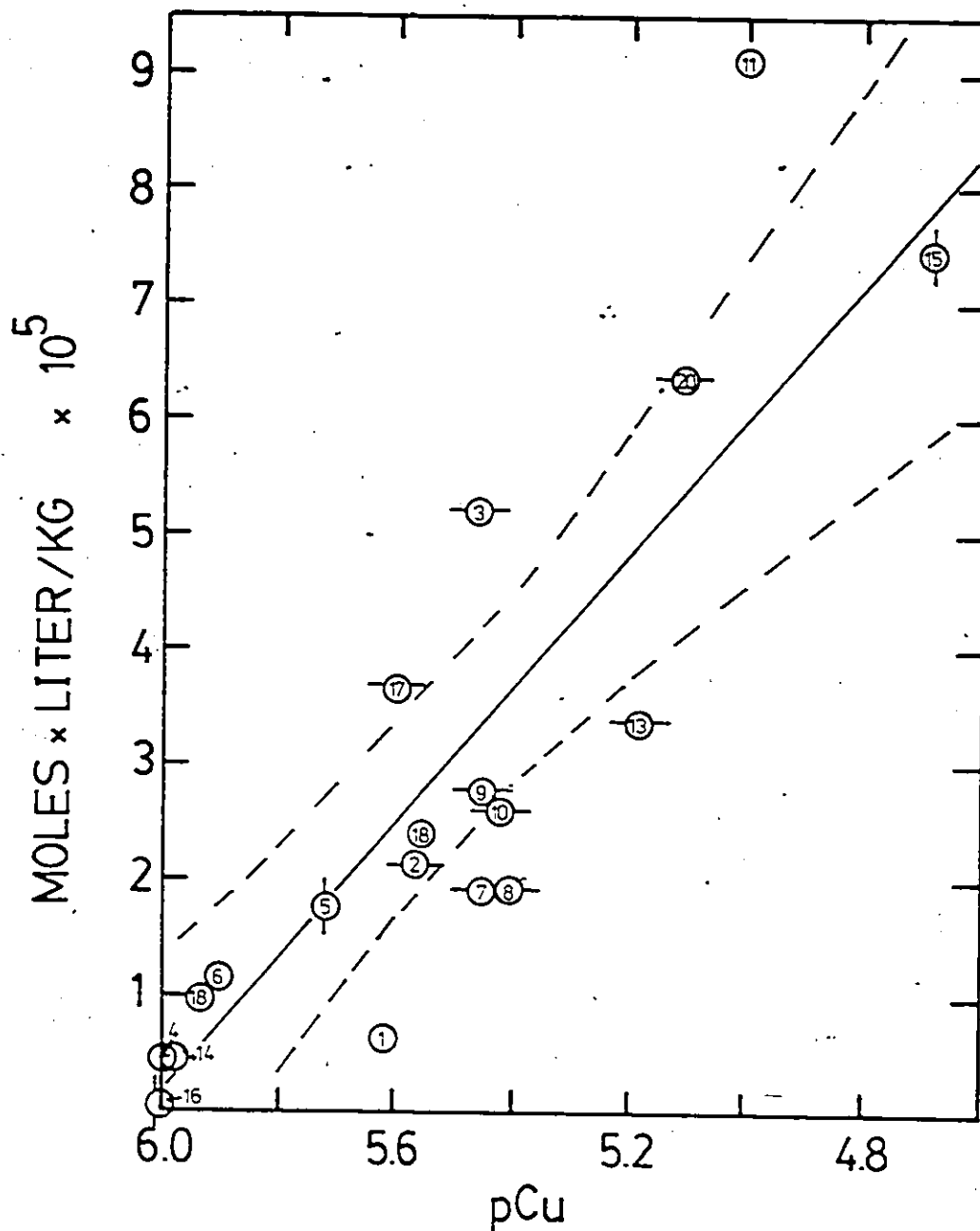
Figure VII-1. Copper sorbed during centrifuging plotted against copper Dconcentration before centrifuging. Points fall within the following solid/liquid ratios (gm/100 ml): ⊖ < 0.3, O 0.3 to 0.4, φ > 0.4.

The experiments in figure VII-1 have solid/liquid ratios varying

from 0.20 to 0.81 grams/100 ml. In order to see what effect these

solid/liquid ratios may have on copper sorbed during centrifuging, the

data in figure VII-1 are split into three arbitrary groups based on the
solid/liquid ratio. Those points with less than 0.3 grams/100 ml are
marked with a horizontal line, while those points with more than .4
grams/100 are marked with a vertical line. From figure VII-1 it seems
that in the range of 0.20 to 0.81 grams/100 ml the solid liquid ratio
does not have a significant effect upon the amount of copper sorption
during centrifuging.
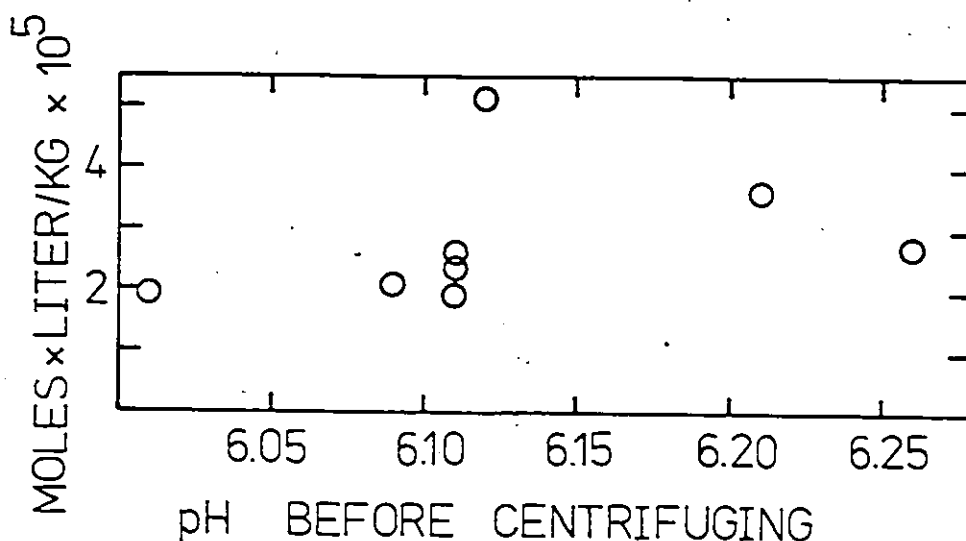
Figure VII-2. Copper sorbed during centrifuging plotted versus pH.

The pH may have an effect on copper sorbed during centrifuging,
particularly if the sorption is produced by surface complexation or
induced precipitation. Unfortunately the pH range of these experiments
is not very great with most of them falling between 6.01 and 6.24.
Nevertheless, an attempt was made in figure VII-2 to correlate sorption
during centrifuging with pH before centrifuging. In order to reduce the
effect of copper concentration, the experiments shown in figure VII-2
have a pCu range of 5.6 to 5.7. From figure VII-2 it apparent that the

relationship between pH and sorption during centrifuging is not very
significant over this pH range. Only 12 percent of the data fit a line
whose slope of $(5 \pm 18) \times 10^{-5}$ is not significantly different from
zero. Experiment 12 was carried out at pH 6.39 and its sorption value
of 7.57×10^{-5} is higher than the confidence interval of the mean
response for pCu 5.06 (figure VII-1). Unfortunately from one data point
we cannot make a statistically significant conclusion that sorption
during centrifuging increases with pH.

The only experiment in which sorption during centrifuging was
measured in the presence of a different electrolyte level (1 M KNO_3)
was experiment 7 in figure VII-1. The amount of Cu sorbed during
centrifuging in the presence of a 1 molar salt solution does not appear
to be significantly lower than sorption in the presence of a 0.05 molar
solution. This is consistent with the observation in chapter V that the
difference in Cu sorption between 0.05 and 1 molar KNO_3 solutions is
not very great.
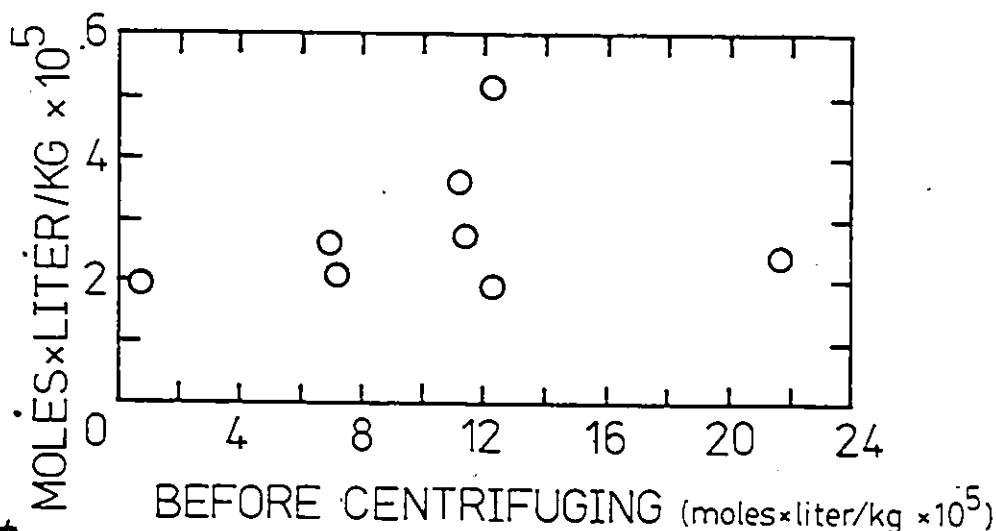
Figure VII-3. Cu sorbed during centrifuging versus Cu sorbed before
centrifuging.

An interesting question to answer is whether or not sorption induced by centrifuging is affected by the amount of previously sorbed copper. If copper sorbed during centrifuging is attached to surface sites then the presence of previously sorbed copper may inhibit further sorption. On the other hand, if centrifuging initiates copper precipitation then the presence of previously sorbed copper should have no effect. Figure VII-3 shows a plot of sorption during centrifuging versus previously sorbed copper for experiments which had dissolved copper concentrations between pCu 5.4 to 5.6. From this plot it is apparent that previously sorbed copper does not significantly affect sorption during centrifuging.

The reversibility of copper sorbed during centrifuging may be a valuable clue to the type of sorption mechanism which is initiated by centrifuging. Figures VII-4 to VII-6 illustrate the effect of centrifuging on the amount of sorbed copper. These figures also illustrate what happens to the sorbed copper when the supernatant is returned to the reaction vessel and the kaolinite is resuspended. When kaolinite is resuspended the sorption induced by centrifuging reverses at a slow rate. Desorption rates for these experiments are summarized in the table VII-5. The magnitude of these desorption rates appears to be similar to the sorption rates of segment III. In figure VII-6 the resuspended kaolinite was centrifuged for a second time, which caused the sorption to return to almost the same level it had been before the clay was resuspended.
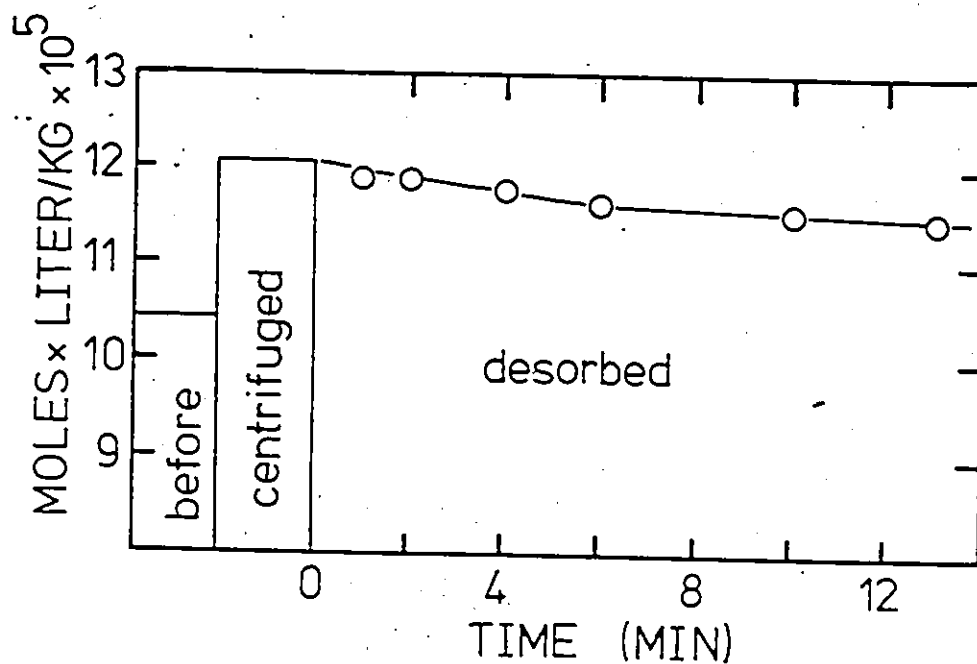
Figure VII-4. The effect of resuspending a centrifuged kaolinite. Cu sorption is shown before and after centrifuging, and after resuspension.
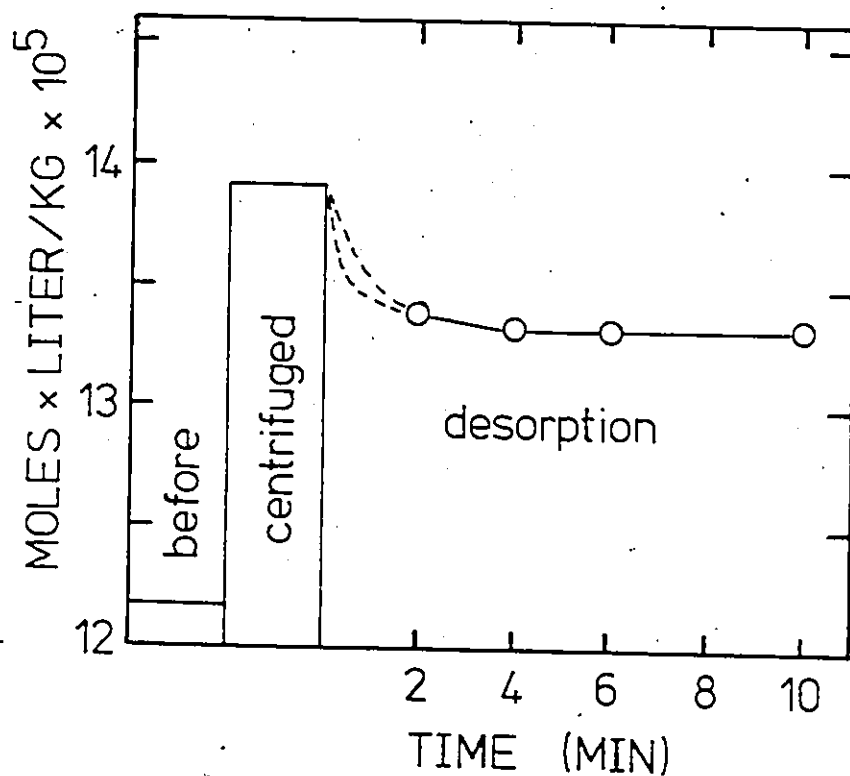
Figure VII-5. The effect of resuspending a centrifuged kaolinite.
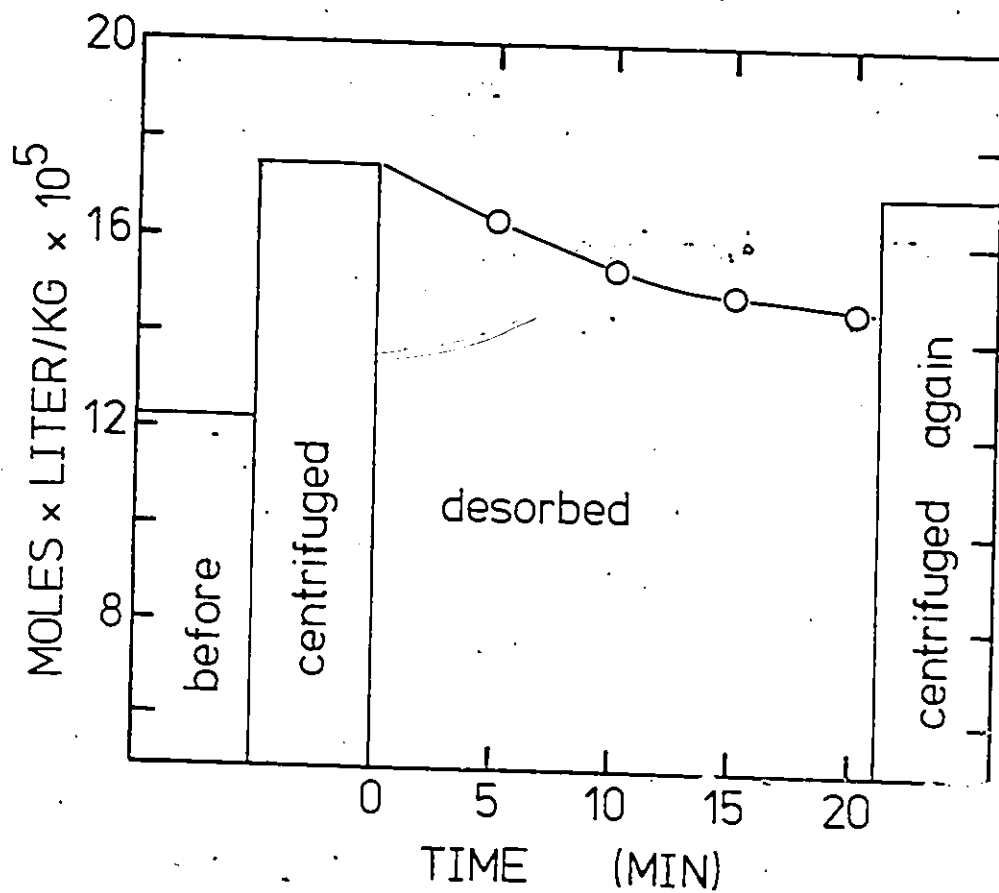
Figure VII-6. The effect of resuspending a centrifuged kaolinite, and then centrifuging again.

TABLE VII-5

Figure	Desorption rate during resuspension (min⁻.)
VII-4	$(-3.5 \pm 1.2) * 10^{-3}$
VII-5	$(-3.4 \pm 9\ ) * 10^{-3}$
VII-6	$(-4.0 \pm 2\ ) * 10^{-3}$

DISCUSSION

The copper sorption induced by centrifuging is also shown with atomic absorption. This indicates that apparent sorption measured with the copper electrode is not merely an experimental artifact produced by the copper electrode. However, the centrifuge induced sorption which is measured by atomic absorption is less than that measured with the copper electrode. This difference might be produced by (1) a liquid junction potential or (2) the possibility that the centrifuged supernatant may have contained a very fine (< 0.45 micron) particulate phase which contained sorbed copper. This copper could have been measured by atomic absorption. (3)There is also a possibility that during filtration the clay retains some excess copper, although this amount is less than that retained during centrifuging. The problem with comparing electrode measurements with atomic absorption is that the latter method requires a phase separation by filtration. One may wonder why should filtration be any different from centrifuging because both methods are a form of phase separation. When a clay is filtered the entire solution passes through the interstitial spaces of the clay plug on the filter paper. This tends to flush the clay and prevent copper from accumulating in the pore water of the clay. On the other hand, during centrifuging the clay plug is not flushed by the supernatant and the pore water of the clay plug remains undisturbed

During centrifuging copper sorption appears to release hydrogen ions as is shown by the drop in pH of the supernatant solution. This suggests that specific chemical sorption must be a significant component of the sorption induced by centrifuging. Unfortunately, it was not

possible to back titrate the hydrogen ion liberated by copper sorption and therefore it is not possible to distinguish between surface complexation and precipitation on the basis of H/Cu ratios. In this study the copper electrode and the pH electrode were connected to the same reference electrode. If there is a significant difference in liquid junction potential when the electrodes are immersed in the kaolinite suspension and when they are in the clear supernatant then this difference would have been the same for both the copper and hydrogen electrodes. Since in the centrifuged supernatant the emf of the copper electrode was lower relative to the suspension and the emf of the hydrogen electrode was higher, these differences in emf's were not produced by a liquid junction potential.

Further evidence for sorption induced by centrifuging comes from the observation that the interstitial water of the centrifuged clay is enriched in copper relative to the clay suspension. This enrichment in copper cannot account for all the copper lost from the supernatant during centrifuging. Therefore, some of the copper lost during centrifuging must have been sorbed by the kaolinite. The higher concentration of copper in the pore water may have been partially initiated by donnan potential. Donnan theory can be used to predict the ratio of a divalent cation between a centrifuged clay plug and the supernatant above it. We need the cation exchange capacity (0.11 meq/gm), the amount of clay (0.3 gm), the volume of the centrifuged clay (about 2 ml), and the salt concentration of the supernatant (0.05 M). Once the ratio of K^+ in the clay compared to the supernatant is calculated a similar ratio can calculated for a divalent cation

distribution. In a mixed electrolyte Donnan theory predicts that the ratios of all cations between the clay and supernatant are related by:

1) $([K^+]_{col}/[K^+]_{sol}) = ([Cu^{+2}]_{col}/[Cu]^{+2}_{sol})^2$

Appendix 13 summarizes the equations necessary to estimate the ratios in equation 1. Donnan theory predicts that the ratio of Cu^{+2} between centrifuged clay and supernatant is around 1.39. The observed copper ratios between the pore water of the centrifuged clay and the supernatant were 1.98 and 2.18 (table VII-4). Donnan theory does not account for hydrolysis of Cu^{+2} in the interstitial water of a clay plug unless activity coefficients are introduced (chapter II). It is possible that some of the copper measured (^{64}Cu) in the pore water recovered from the centrifuged clay included $Cu(OH)_n$ species. If these species are present Donnan theory will underestimate the concentration of copper in the pore water. Regardless of the actual cause of the increased copper concentration in the pore water this concentration effect may then promote more surface complexation or it may help to saturate the kaolinite surfaces with respect to $Cu(OH)_2$ and cause precipitation. Therefore, the elevated copper concentration in the pore water may be the driving mechanism of centrifuge induced sorption.

In this study the concentration of Cu^{+2} appears to be the key factor which determines the amount of centrifuge induced precipitation. This is reasonable because in chapter IV it was shown that the amount and rate of copper sorption is sensitive to copper concentration. The relationship between sorption and copper concentration shown in figure VII-1 is only valid between pCu 6 and 4.6. It would be interesting to

know whether centrifuging will induce sorption at copper concentrations which are much below pCu 6. If centrifuge induced sorption stops below pCu 6 then the results of this chapter are not applicable to most natural studies. Centrifuging or the formation of clay flocs will probably always enrich the interstitial water relative to the free solution. If the dominant sorption mechanism is surface complexation then the higher metal concentration in the interstitial water will produce more sorption. If precipitation is the important mechanism then it is likely that at very low copper concentrations the pore water will not be able to concentrate enough copper to induce precipitation.

The solid/liquid ratio in this study did not appear to have a significant effect on the amount of copper sorbed during centrifuging probably because the range of solid/liquid ratios was not great enough. This may also suggest that in this study the availability of surface sites was not a limiting factor, which might be consistent with a precipitation mechanism.

The pH did not appear to be a key factor in the pH range 6 to 6.2, although there appeared to be more centrifuged induced sorption at pH 6.39. Theoretically pH should be a key factor in copper sorption, particularly if surface complexation or precipitation are involved. It could be that in the narrow pH range of 6 to 6.2 the pH of the interstitial water was buffered well enough that the pH of the kaolinite suspension before centrifuging did not have a significant effect on copper sorption.

There was not much difference in sorption in the presence of a 1 M KNO_3 solution and a 0.05 M solution because nonspecific sorption is already significantly reduced by the 0.05 M solution.

The amount of copper sorbed during centrifuging does not appear to be affected by the concentration of previously sorbed copper. This suggests that copper sorption is not limited by the availability of free sorption sites which is consistent with precipitation. This does not rule out surface complexation, however, because the availability of free sites may actually have been the same and the differences in the amount of previously sorbed copper were accounted for by copper sorbed by other mechanisms such a precipitation.

When a centrifuged kaolinite is resuspended in the supernatant the copper sorbed during centrifuging is not immediately desorbed. Instead it desorbs slowly with an apparent first-order rate constant of around 4×10^{-3} min^{-}. The fact that resuspension does not immediately reverse the effects of centrifuging is further evidence that sorption induced by centrifuging is not an electrode artifact produced by a junction potential or by an ability of the electrode to register copper in the kaolinite's double layer. The slow reversibility also indicates that copper sorbed during centrifuging is held by stronger forces than just Donnan equilibria, which is essentially just nonspecific coulombic attraction. Given enough time (about 3 hours) the effects of centrifuging will probably be reversed. This is consistent with a precipitation reaction which is more reversible than surface complexation. If the kaolinite had been resuspended in copper free water then the desorption rate of the copper sorbed during centrifuging

may have been much greater. However, in the presence of copper free water some of the copper sorbed before centrifuging would also desorb. It would be very difficult to distinguish between this copper and that which had sorbed during centrifuging.

SUMMARY

Copper sorption induced by centrifuging appears to be real. Evidence for this is given by:

1) The analysis of filtrates and supernatant solutions supports the electrode measurements.

2) Hydrogen ion is liberated during centrifuging suggesting that it is liberated by copper sorption.

3) Upon resuspension the effects of centrifuging are not immediately reversed.

4) The pore water of centrifuged clay appears to be enriched in copper.

The main controlling factor for centrifuge induced sorption in this study appears to be the concentration of copper ion in solution before centrifuging. The driving force behind sorption during centrifuging may be the increased copper concentration in the pore water of the centrifuged clay. The kaolinite's negative charge may have initiated the increased pore water concentration. Hydrolysis reactions may have raised the pore water copper concentrations above those predicted by Donnan equilibria. The increase in pore water copper concentration would promote specific chemical sorption which is indicated by the release of hydrogen ion during centrifuging. The dominant form of copper sorption during centrifuging may be induced

precipitation. Evidence (but not proof) for this is given by :

1) The solid/liquid ratio did not affect the amount of copper sorbed, suggesting that the availability of surface sites was not a limiting factor.

2) The amount of previously sorbed copper did not affect sorption induced by centrifuging, also suggesting that surface sites were not a limiting factor.

3) The sorption induced by centrifuging seems to be reversible at a moderately slow rate. Copper complexed to surface sites appears to be irreversible (chapter VI).

Since the interstitial water of a centrifuged clay plug is enriched in copper compared to the supernatant it is reasonable to assume that the interstitial water of a clay floc will also be enriched relative to the free solution. Therefore, the formation of clay flocs may also induce some copper sorption which would not occur if floculation could be prevented. Due to the universal formation of clay flocs in the presence of minor salt concentrations the actual surface copper sorption reactions take place at a higher copper concentration than is measured in the clay suspension. The observations made in this study on centrifuge induced sorption might also be applied to sorption in clay flocs.

CHAPTER VIII

SUMMARY AND DISCUSSION

INTRODUCTION

The previous chapters of this thesis have discussed copper sorption kinetics on kaolinite, and on the basis of rate constants have proposed various mechanisms which might account for the observed kinetics. Several chapters attempted to characterize the sorption reactions responsible for the observed kinetics by looking at the effects of salt concentration, pH and various desorption procedures. Having characterized the sorption reactions we are in a much better position to judge which mechanisms are responsible for the observed kinetics. The purpose of this chapter is to evaluate copper sorption kinetics in light of the sorption mechanisms which can be predicted from the kaolinite structure and its influence on the clay's surface properties. This will be accomplished by first assigning potential mechanisms to the various sorption segments on the basis of similar rate constants. Then the results of the experiments described in chapters V to VII will be used to determine which of the mechanisms assigned to a given sorption segment is likely to control the sorption rate of that segment.

Once we have established a picture of the sorption mechanisms responsible for copper uptake by kaolinite we will be in a position to discuss other phenomenon observed with sorption reactions, such as the

effect of changing the solid/liquid ratio. Distribution coefficients have been used extensively to describe metal sorption in the environment. What implication does this study have on the use and interpretation of trace metal distribution coefficients? This chapter will also predict the sorption properties of other clay minerals on the basis of mechanisms inferred from the copper-kaolinite system. A comment will also be made on the implications of this study to the modeling of metal sorption reactions in the environment.

SORPTION KINETICS

The kinetics of copper sorption on kaolinite are similar to the sorption reactions of organic molecules and other metals in that there is an instantaneous initial sorption followed by a sorption rate which decreases with time. Since the sorption rate of copper decreases with time the order of the reaction must be at least as high as first order. Theoretically the sorption rate should be a function of the copper concentration in solution, and X, which can be the concentration of surface sites or the concentration of a ligand such as OH^-. In many experiments the concentration of dissolved copper was maintained at a constant level and in the remaining experiments there were only minor changes in concentration during large portions of the experiment. Since copper concentration remained constant or nearly constant the sorption kinetics were reduced to a pseudo-first-order rate law which was a function of X. The assumption of first-order kinetics was supported by a plot of the logarithm of copper concentration versus time, which yielded a curve with linear segments. These linear segments can be interpreted

as a set of concurrent first-order reactions which are independent of each other and which have different rate constants (and therefore different half lives). Initially the overall sorption rate is dominated by the fastest reaction. As this reaction reaches a steady state the next fastest reaction begins to dominate the sorption kinetics. The application of higher order kinetics did not give a better fit to the copper sorption data and therefore higher orders were not considered.

In other studies sorption kinetics have been interpreted as a set of opposing reactions which have equal rates at equilibrium. With this assumption sorption kinetics are modeled as an approach to equilibrium. The problem with this approach is that one must have an equilibrium or steady which can be used in the model. Copper sorption did not reach a steady state or an equilibrium after 2.5 weeks. The initial one to three minutes of reaction can be modeled as an approach to equilibrium, but this method cannot explain all the sorption kinetics without calling upon other first-order reactions. To avoid the need of picking several arbitrary equilibrium concentrations throughout the sorption curve it was decided that the best approach to treating the sorption data was with a first-order plot of the logarithm of sorbed copper versus time.

Apparent sorption mechanisms with different rates were resolved by identifying linear segments on a plot of the logarithm of sorbed copper versus time. The data were fitted to lines using linear regression. Neighboring linear segments were considered significantly different only if the difference in their slopes could not be explained by the 99 percent confidence intervals on these slopes. Using this approach five apparent sorption reactions or segments were distinguished

for a 2.5 week period. These sorption segments are summarized in table VIII-1. Segment I is an instantaneous reaction and therefore it is represented by the initial sorption which has been extrapolated to time zero using the data points from the first minute (segment II). The remaining segments represent first order reactions whose rate constants are almost an order of magnitude different from neighboring constants. Table VIII-1 represents experiments with different copper concentrations , solid/liquid ratios, and even pH (See table IV-1). This may explain the range in rate constants for each sorption segment.

TABLE VIII-1

OBSERVED SORPTION SEGMENTS

Segment	Range of rate constants (usually min$^-$)	Range of measuring time	$t_{\frac{1}{2}}$ (min) (from mean rate constant)
I	instantaneous (14 to .7) * 10^{-5} moles*l/kg mean = (5.5 ± 4) * 10^{-5}	extrapolated to time zero using segment II data	-
II	.07 to 3.2 mean = .7 ± .7	.17 to 3	1
III	(2.7 to 20) * 10^{-3} mean = (8 ± 4) * 10^{-3}	1 to 162	89
IV	(6 to 23) * 10^{-4} mean = (14 ± 6) * 10^{-4}	15 to 250	506
V	(1.4 to 14) * 10^{-5} mean = (9 ± 6) * 10^{-5}	120 to 24000	7615

To check the validity of this approach to treating sorption data, the measured rate constants of the sorption segments were used to recalculate the sorption kinetics. These calculations showed that the measured rate constants could reproduce the sorption kinetics and they

indicated that several mechanisms are required. It was also apparent that the slower mechanisms did not have a significant influence on the faster sorption kinetics. A sorption mechanism only begins to contribute significantly to the overall rate when the reaction time approaches the half life ($t\frac{1}{2}$) of the mechanism.

THEORETICAL SORPTION MECHANISMS

The apparent sorption reactions which are resolved by kinetics must be related to mechanisms which can be predicted from the structure and surface properties of kaolinite. Chapter II discusses kaolinite structure and the potential sorption mechanisms which might be produced by the expression of this structure on the surfaces of kaolinite grains. The properties of these mechanisms are summarize by tables II-4 to II-7.J Our immediate concern is to assign these potential mechanisms to the observed sorption segments on the basis probable similarities in rate constants. The following paragraphs summarize the potential sorption mechanisms developed in chapter II, as well as their probable reaction rates.

1) <u>Coulombic attraction</u>: Nonspecific cation exchange reactions are very rapid and have been shown to occur within a few seconds. They are only limited by diffusion in free solution or pore water.

2) <u>Surface complexation</u>: Complexation to surface sites is probably very rapid as was shown by the work of McBride (1982). Complexation to <u>single</u> surface oxygens is similar to hydrolysis reactions which can be extremely rapid. These reactions are probably diffusion controlled. Copper complexation to <u>two</u> sites is probably more

difficult and slower because the copper ion must position itself in a location where it can reach two bonding sites. This increased ordering could put up an entropy barrier which slows the reaction.

3) Surface induced precipitation: Precipitation at the kaolinite surface is probably slower and may last from minutes to weeks. McBride (1982) has shown that Cu precipitates on aluminum hydroxides for as long as 2.5 weeks. Precipitation rates are limited by (1) nucleation and crystal growth, (2) the need to bring regions of high pH (edges) in contact with regions of high copper concentrations (faces), and by the fact that $Cu(OH)_2$ is undersaturated in the free solution.

4) Structural penetration: The penetration of the clay structure is probably a very slow process because copper must dehydrate to get into the structural sheets. Once inside, it can only move away from the solid/liquid interface by solid state diffusion. On the other hand, if copper enters the kaolinite grain through a fault or cleavage plane then the penetration of the solid may be much more rapid.

There are other factors which may influence the overall sorption kinetics. Due to the presence of a background electrolyte the kaolinite in these experiments is flocculated. Copper must diffuse through the interstitial water of these flocs to reach surfaces inside the flocs. This diffusion may slow some of the faster sorption reactions. A plot of copper sorption versus the square root of time suggests that diffusion might occur within the first minute, but it does not prove it. Diffusion in the free solution is not a factor because the kaolinite

suspension is constantly stirred. The interstitial waters of the kaolinite flocs are probably enriched in copper with respect to the free solution. This means that on some kaolinite surfaces sorption is occurring under the influence of a higher copper concentration than is found in free solution.

Another factor which might influence the initial sorption kinetics is the dispersion of the kaolinite clay once it is added to the copper solution. Ten to twenty seconds may elapse before the clay is properly dispersed so that the initial sorption kinetics might be slightly affected. In order to maintain a constant copper concentration there must be a rapid addition of copper within the first minute. Differences in the addition rate of this copper can introduce some variation in the initial sorption kinetics.

Having summarized the expected rates for the potential sorption mechanisms, these mechanisms are assigned to the observed sorption segments in table VIII-2. Some mechanisms such as precipitation or coordination to two surface sites are assigned to several sorption segments because the exact rates of these mechanisms are unclear. In order to make a more exact determination of the mechanisms responsible for a given sorption segment it is necessary to compare the observed properties of these sorption segments with the predicted properties of the theoretical mechanisms.

TABLE VIII-2

POTENTIAL SORPTION MECHANISMS

Segment	Possible Mechanisms
I	-nonspecific coulombic attraction -specific surface coordination to one site
II	-specific surface coordination to one site limited by diffusion -nonspecific coulombic attraction limited by diffusion -induced surface precipitation -specific surface coordination to two sites -(May be influenced by dispersion of kaolinite after clay addition.)
III	-induced surface precipitation -specific surface coordination to two sites
IV	-induced surface precipitation -specific surface coordination to two sites
V	-induced surface precipitation -specific surface coordination to two sites -structural penetration

EVALUATION OF THEORETICAL SORPTION MECHANISMS

The tests used to evaluate the existence of certain sorption mechanisms have been presented mainly in chapters V and VI. With the help of figures VIII-1 to VIII-5, speculations are made on the validity of the mechanisms assigned to each sorption segment. In some cases the identity of the sorption mechanism is relatively clear, but for the slower segments the choice of sorption mechanism becomes increasingly difficult. It is harder to perform a conclusive test on a slower mechanism because the total amount of sorbed copper contains significant contributions from the faster mechanisms. In these cases the choice of mechanism is speculative. It is hoped that with the help of figures

VIII-1 to VIII-5 the reader will have a better overview of the
properties of each sorption segment and he may come to his own
conclusions regarding sorption mechanisms.

The choice of mechanisms for the instantaneous sorption in
segment I can probably be limited to nonspecific coulombic attraction
and specific coordination to one surface site. In these experiments the
presence of a 0.05 M KNO_3 background electrolyte is believed to
significantly reduce the amount of copper held by coulombic forces.
However, because there is slightly more sorption in the 0.05 M solution
compared to a 1 M solution, and because the addition of Sr is able to
desorb some copper it is probable that a small portion (about 18%) of
copper sorbed in segment I is held by nonspecific coulombic attraction.
Evidence that the remaining portion of segment I consists of
specifically sorbed copper comes from the sensitivity of copper sorption
to changes in pH. In the presence of a large amount of K^+ ions,
nonspecific sorption of copper on a constant charge surface should be
independent of pH. In this case one cannot explain the variation of
nonspecific sorption with pH by interference with Al^{+3} ions liberated
at lower pH because the response of copper in segment I to changes in pH
is reversible and very rapid. Copper sorbed in segment I resists
desorption by dilution suggesting that it is held by strong
copper-oxygen bonds. The coordination of copper to one surface site is
distinguished from other mechanisms, such as precipitation, by the fact
that the ratio of hydrogen ion desorbed per copper ion sorbed is 1.0.
Therefore, segment I consists of coordination to one surface site and
nonspecific coulombic attraction, whose magnitude depends upon the salt

concentration.

SEGMENT I

Amount sorbed is directly proportional to $[Cu^{+2}]$.

Sorption in .05 M potassium nitrate is much
lower than in the a salt free solution.

There is slightly more sorption in the .05 M
potassium nitrate solution than in the 1 M
solution.

The addition of Sr removes a small amount of
adsorbed copper.

Sorption is very pH sensitive.

Responds rapidly to minor pH changes.

Resists desorption by dilution.

H/Cu ratio is 1

Nonspecific sorption

Coordination to
one surface site

Other

Figure VIII-1. Properties of sorption segment I.
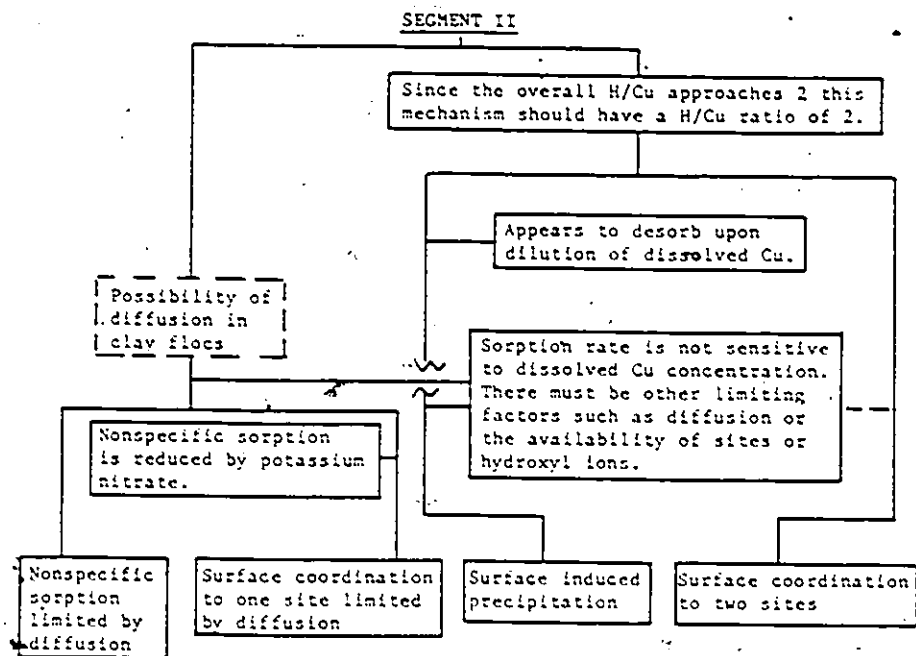
Figure VIII-2. Properties of sorption segment II.

A number of mechanisms may fit the sorption kinetics of segment
II. Nonspecific sorption and coordination to one surface site may still
be operating if they are limited by Cu diffusion through the
interstitial waters of clay flocs. Surface induced precipitation or
coordination to two surface sites may also be responsible for the
kinetics of segment II. Diffusion in the clay flocs is a possibility,
but it cannot be proven. The strongest factor which may eliminate
nonspecific sorption and coordination to one surface site is that the
mechanism in segment II appears to have a H^+/Cu^{+2} exchange ratio of
2. This leaves us with the need to choose between precipitation and
coordination to two sites. It appears that the copper sorbed by segment
II desorbs upon dilution. This suggests a precipitation reaction since
coordination to one site is irreversible and coordination to two sites

should be even less reversible. The sorption rate is independent of copper concentration suggesting that the rate depends on other factors such as diffusion, the availability of sites or hydroxyl ions, collisions between kaolinite grains, or the establishment of high surface pH. The coordination reaction in segment I is very sensitive to copper concentration, so that coordination to two sites might also be sensitive to concentration. Although precipitation should also be sensitive to copper concentration it is possible that the precipitation rate is determined by other factors such as the establishment of high surface pH or collisions between edges and faces. Therefore, on the basis of reversibility and the independence of sorption rate on copper concentration it is probable that surface induced precipitation is responsible for segment II:

SEGMENT III

H/Cu ratio is probably 2

Sorption rate is independent of copper concentration. Rate is limited by other factors such crystal growth, collisions between kaolinite faces and edges, or the the establishment of high surface pH.

Slowly responds to minor pH drops.

May desorb upon dilution.

Surface induced precipitation

Surface coordination to two sites
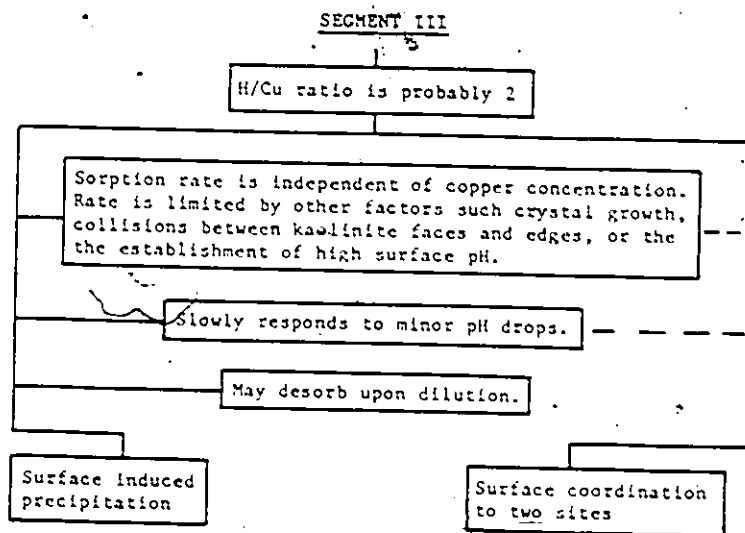
Figure VIII-3. Properties of sorption segment III.

Surface induced precipitation and complexation to two sites are the likely candidates for the mechanism responsible for segment III. The rate of this reaction is probably too slow to be limited by diffusion, and the H^+/Cu^{+2} exchange ratio appears to be around 2. As with segment II, the sorption rate is independent of copper concentration and the copper appears to desorb upon dilution. These factors may favor a precipitation reaction. The response time of segment III to minor drops in pH appears to be much longer than the quick response of segment I. This observation might be consistent with both precipitation and complexation to two surface sites. The quick response of segment I to pH changes indicates that copper coordinated to surface sites is very reversible to pH changes (but not Cu dilution). If copper is bonded to two sites it may be less prone to desorption. Copper which is precipitated may form a separate phase and may not be as accessible to fast dissolution by hydrogen ions. Dissolution would have to proceed at the solid/liquid interface of this new phase. This contrasts with copper ions coordinated to surface sites which are evenly spread out and accessible to hydrogen ions. The probable mechanism responsible for segment III is precipitation because the sorption rate is independent of copper concentration and the copper appears to desorb upon dilution. The precipitation rate in segment III may be slower than segment II because the kaolinite particles are stabilizing in their flocs and there are fewer collisions between high pH edges and Cu rich faces.

The choices for segment IV are again surface precipitation and coordination to two sites. However, the number of tests which can be applied to this segment are limited. The sorption rate is too slow to

determine the H^+/Cu^{+2} exchange ratio. The response of this segment

to a drop in pH may be slow. However, it is difficult to make this

interpretation because the effects of segment II cannot be eliminated.

Segment IV can be distinguished from segments II and III by the

observation that the sorption rate is influenced by copper

concentration. This would be more consistent with a surface

complexation reaction because the segments dominated by precipitation

showed no relation to copper concentration. Also, the complexation

reaction in segment I is highly dependent upon concentration.

SEGMENT IV

| H/Cu ratio? |

Sorption rate increases with copper concentration.

May respond slowly to minor drops in pH.

Surface induced precipitation

Surface coordination to two sites
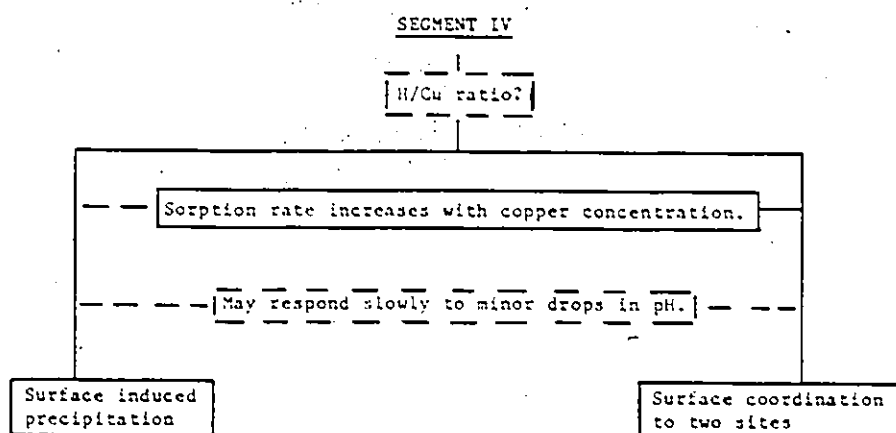
Figure VIII-4. Properties of sorption segment IV.

Structural penetration is included with precipitation and

surface complexation as possible mechanisms to explain segment V. One

can speculate that the sorption rate of segment V increases with copper

concentration with the observation that the sorption rate appears to be

higher when copper concentration is maintained at a constant level.

When copper is maintained at a constant concentration the sorption rate

appears to be constant suggesting pseudo-zero-order kinetics. This

would imply that the availability of surface sites was not a limiting

factor and would favor precipitation or structural penetration. The

strongest property of segment V seems to be its apparent ability to fix

copper. This should eliminate a precipitation mechanism. Structural

penetration is the most likely mechanism to resist desorption by

cyanide. Although copper bonded to two surface oxygens may be in a very

stable configuration, copper forms much stronger bonds with cyanide than

with oxygen. Therefore, structural penetration may be the most likely

mechanism for segment V, although coordination to two surface sites

cannot be conclusively eliminated.

SEGMENT V

| H/Cu ratio? |

Sorption rate may increase with Cu concentration.

At constant Cu concentration the kinetics might be pseudo-zero-order. This would imply that the availability of sites is not a limiting factor.

Cu fixation increases over a two week period and the the increase in fixation corresponds to the amount sorbed by segment V.

Surface induced precipitation

Structural penetration

Surface coordination to two sites

Figure VIII-5. Properties of sorption segment V.

SORPTION MODEL

In the previous discussion we have gained a picture of copper

sorption on kaolinite which includes several different sorption

mechanisms. As illustrated by the cartoon in figure VIII-6, the

importance of a given sorption mechanism depends upon the duration of

the reaction. The existence of nonspecific sorption and coordination to one surface site in segment I is relatively certain. It is very likely that segment II represents a precipitation reaction. The interpretation of segments III to V is less certain. Whether or not segment V is actually a penetration of the structure may not be as important as the fact that it represents a form of metal fixation.
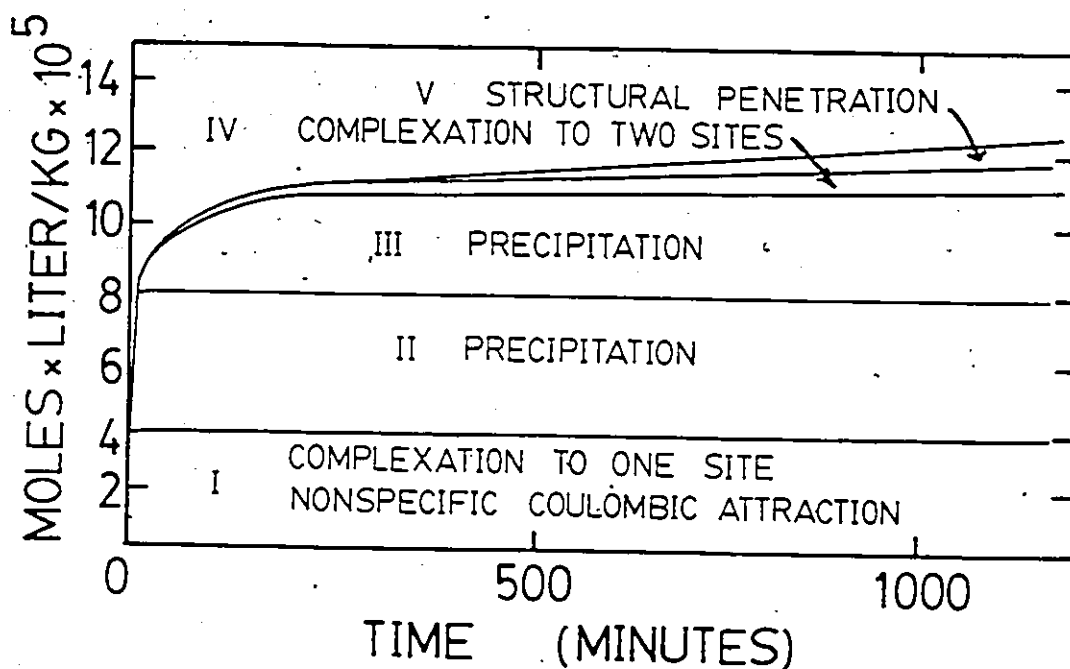
Figure VIII-6. Contributions of sorption mechanisms as a function of time.

With the present concept of copper sorption mechanisms we are in a position to predict sorption not only as a function of time and copper activity, but also pH and salt concentration. The amount of copper sorbed by nonspecific attraction on a constant charge kaolinite surface will only be a function of the surface charge, copper activity, and the salt concentration. The copper sorbed by specific surface complexation and by surface induced precipitation will depend upon pH and copper

activity. Indirectly the salt concentration may affect specific sorption reactions through the effects of nonspecific sorption. In the absence of salt, the higher build up of nonspecifically sorbed copper on the faces may promote more precipitation and surface complexation when an edge collides with a face. Table VIII-3 summarizes some of the factors which must be considered for predicting the total copper sorption on a kaolinite as a function of pH and salt concentration.

TABLE VIII-3

THINGS TO CONSIDER FOR ESTIMATING SORPTION ON KAOLINITE

1) Cation exchange capacity: 2 meq/100 g (10 millimoles Cu per kg)

2) Surface area : 18 m^2/g

3) The effect of pH on specific sorption: This may be estimated by establishing a relationship between the kaolinite/solution distribution coefficient and pH. This relationship was estimated to be :

$$\log k_D = -3.522 + pH$$

4) Copper concentration, speciation, and solubility

Figure VIII-7 summarizes the predicted effects of pH and salt concentration on sorption from a solution with a constant copper activity of pCu 5.2. This figure illustrates the extreme cases where a 1 M salt solution eliminates nonspecific sorption, and where the absence of a salt allows copper and hydrogen ion to neutralize the clay's surface charge. In the absence of a salt the competition between Cu^{+2} and hydrogen ion is predicted by equation 1 in chapter V. This accounts for the pH variation of copper sorption up to pH 4, in the absence of a competing salt. This calculation is extended down to pH 2 merely to illustrate the competing effect of a monovalent ion. If the pH were

dropped to 2 then the sorption pattern illustrated. in figure VIII-7 would be very temporary because the hydrogen ion would begin to destroy the kaolinite surface. In the real world waters will contain salts and clays will have other counter ions on their surfaces, so that the middle sorption curve is more realistic.
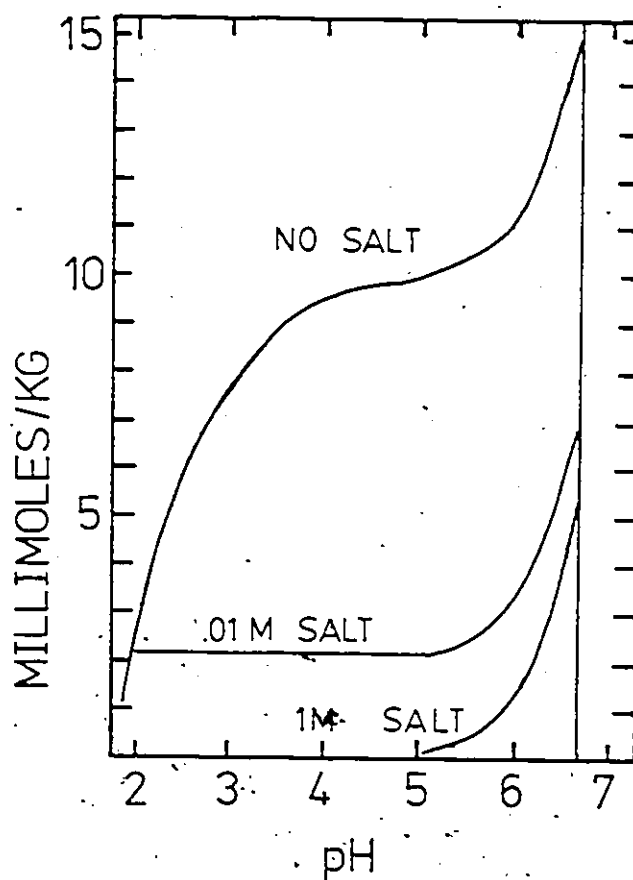
Figure VIII-7a. Predicted sorption on kaolinite as a function of pH and salt concentration. The copper concentration in solution is maintained at pCu 5.2. The sorption curves are terminated on the high pH side by the beginning of precipitation.
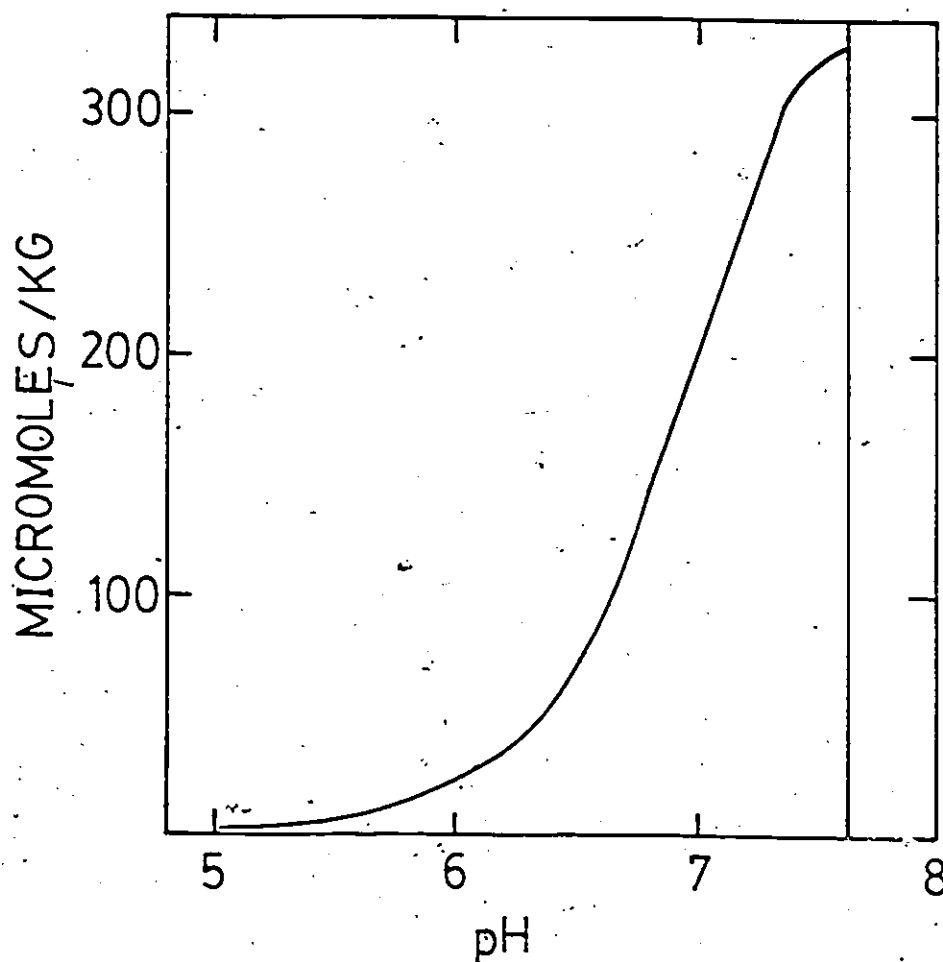
Figure VIII-7b. Predicted sorption on kaolinite from a pCu 7 solution with a 1 M salt.

The lowest curve in figure 7a illustrates sorption dominated by specific chemical sorption in the presence of a concentrated salt solution. The highest pH is determined by the solubility limit of the pCu 5.2 solution. Natural waters contain smaller amounts of dissolved copper, so that the importance of sorption·reactions will extend to higher pH. Figure VIII-7b illustrates specific sorption from a pCu 7.0 solution. This was constructed assuming that the same distribution coefficient variation with pH is valid at the lower copper

concentration. As the pH of the solubility limit is approached the sorption curve begins to level off due to the formation of $CuOH$, $Cu(OH)_2$, and $CuCO_3$ complexes. The patterns in figure VIII-7 should be similar for the other transition metals, except that the actual shapes will be modified by the strength of the other metals' hydrolysis constants. At pH's below 5 the amount of sorption will depend upon the salt concentration and the clay surface charge. As the pH increases to the sorption edge, specific sorption begins to dominate with an increase in overall metal uptake. At the higher pH's the effects of salt concentration become diminished.

A very important component of any sorption model is reversibility. Our definition of reversibility should be related to the problem we want to solve. If it is necessary to establish the degree of true thermodynamic equilibrium, or if we want to model the dumping of contaminated sediments in unpolluted water then we need to measure desorption by simple dilution. If one must model soil leaching with natural organic complexing ligands then a much stronger desorption test is required. The combination of sorption mechanisms shown in figure VIII-6 predicts that reversibility will be a function of sorption time, salt concentration and pH. Since the reversibility of these mechanisms is approximately known we can estimate the desorption properties of copper sorbed on kaolinite by predicting the dominant sorption mechanisms. Figure VIII-8 summarizes the predicted effects of sorption time and salt concentration on irreversibility of metal sorption at pH 6.2. The relative amount of irreversibility will increase with higher salt concentrations and longer sorption times. Higher pH will also

favor irreversibility. With very long sorption times the amount of

fixed copper could become significant. Metal fixation would be speeded

up by heating and drying the clay.
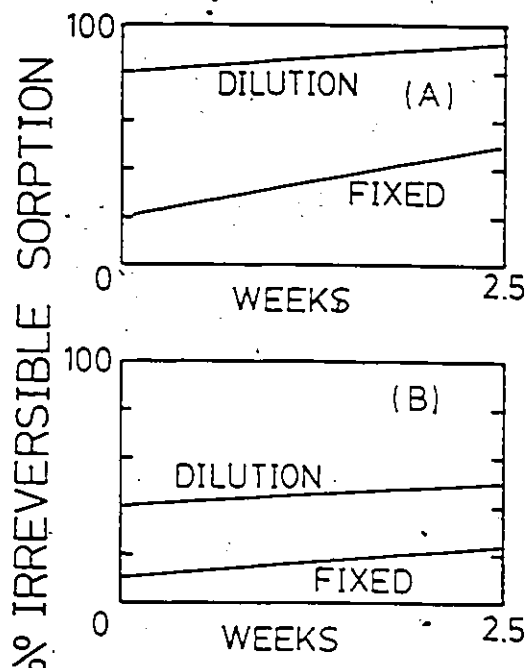
Figure VIII-8. Predicted irreversible sorption on kaolinite at pH 6.2
in the presence of a 1 M salt (A) and in the absence of salt (B).

PREDICTED SORPTION ON OTHER CLAYS

All clay minerals have a sheet silicate structure which produces

surface types commonly shared by all the clays. These surface types

include the inert basal oxygens of the tetrahedral layer which are

exposed on clay faces, and the reactive oxygens or hydroxyls of the

broken silica and alumina layers exposed at the edges. The kaolinite

type minerals also have a gibbsite layer exposed on one face, and

chlorites have a positively charged brucite layer exposed on a face.

Differences in the sorption properties of clays are explained by different proportions of the basic surface types and by differences in the composition of main structural layers. Since the basic structure and chemistry of the common clays are known we can use the sorption mechanisms observed on kaolinite to explain metal uptake on other clay minerals.

Table VIII-5 summarizes the information needed to predict metal sorption on a clay mineral. The sorption mechanisms observed on kaolinite will be applied to predicting the sorption characteristics of copper on montmorillonite and illite, which are two commonly discussed clays.. The necessary properties of these clays are summarized in table VIII-4.

TABLE VIII-4

PROPERTIES OF MONTMORILLONITE AND ILLITE

	Montmorillonite	illite	
cation exchange capacity (meq/100 g)	80 - 150	10 - 40	(2)
surface area m^2/g	38 - 109 (2)	56	(1)
expandable?	yes	no	
two or three layer structure	three	three	
anion exchange capacity (meq/100 g)	31	13	(1)

(1) Grim (1968)

(2) Dixon and Weed (1977)

TABLE VIII-5

REQUIREMENTS FOR PREDICTING METAL SORPTION ON OTHER CLAY MINERALS

SOLUTION CHEMISTRY

1) Valence of cation: Determines selectivity of coulombic attraction.

2) First hydrolysis constant: Estimates the relative strength of metal oxygen bonds which determines the magnitude of specific sorption.

3) Metal's ionic radius: Gives an indication of the cation's ability to penetrate the clay structure.

4) Salt and metal concentration: Determines the importance of nonspecific sorption.

5) pH: Determines the magnitude of specific chemical sorption.

CLAY PROPERTIES

1) Surface area: This is a fundamental sorbent property which defines the availability of binding sites and helps to determine charge density.

2) Crystallinity: Decides the relative portion of reactive edge sites compared to a charged, but inert face area.

3) Negative structural charge imbalance: The constant negative charge, originating in clay structures, is the driving force of nonspecific sorption on these minerals.

4) Expandable or nonexpandable structures: If a clay has an expanding interlayer then the interlayer cations which neutralize the structural charge can participate in nonspecific ion exchange reactions with cations in solution. If the interlayer does not expand then the interlayer cations do not exchange with cations in solution and the clay has a low cation exchange capacity.

5) Two layer or three layer structure: A two layer structure has sheets consisting of one silica tetrahedral layer and one octahedral layer. Three layer structures have two tetrahedral layers sandwiching one octahedral layer. In a two layer structure cations do not have to pass through the tetrahedral layer to get into the octahedral layer. These structural types may also have a difference in edge charges. Two layer structures such as kaolinite may have positive edge charges up to pH 7.3 (Rand and Melton, 1975), which results from the exposed alumina layer. With the extra silica layer (whose zero point of charge is around pH 2), three layer structures may have a lesser positive charge on the edges. Consequently three layer clays may have a smaller increase in pH at the edges, which would be less favorable to surface induced precipitation.

6) Surface impurities: Surface coatings of oxides or complexing organics may drastically alter a clay's sorption properties. However surface impurities will not be considered in the present discussion.

The main differences between kaolinite and the other two clays is that kaolinite has a smaller structural charge (cation exchange capacity) and surface area, and it has a two layer structure. The amount of nonspecific metal sorption can be estimated from the clay's cation exchange capacity and surface area and from the salt and metal concentration of the equilibrium solution. The amount of specific chemical sorption will depend on the surface area of reactive edge sites. Electron micrographs of kaolinites usually show well defined crystals with distinct edges. Montmorillonites can appear as broad undulating sheets which can be easily broken up into very fine particles. This indicates that the edge area of montmorillonites is very sensitive to sample pretreatment. Micrographs of illite appear similar to montmorillonite except that illite is larger and has better defined edges. Since it is difficult to estimate edge areas from micrographs, the anion exchange capacity has been used as a measure of edge area. The average edge area of various kaolinite samples measured by chloride exchange capacity is 1.6 m^2/g (Quoted by Dixon and Weed, 1977), which represents 9 percent of the total surface area of kaolinite #4. For the purpose of this calculation it will be assumed that specific sorption is directly proportional to edge area, and that a measure of the edge area is given by the anion exchange capacity.

Illite has a similar anion exchange capacity to kaolinite so for this calculation it is assumed that the specific sorption on illite is the same as on kaolinite. The anion exchange capacity reported for montmorillonite is higher than kaolinite so that the specific sorption is increased by a factor of 31/13 for montmorillonite. Figures VIII-9

and VIII-10 illustrate predicted copper sorption on an illite (CEC = 30; surface area = 56 m^2/g) and a montmorillonite (CEC = 100; surface area = 100 m^2/g). In both examples the copper concentration is pCu 5.2.
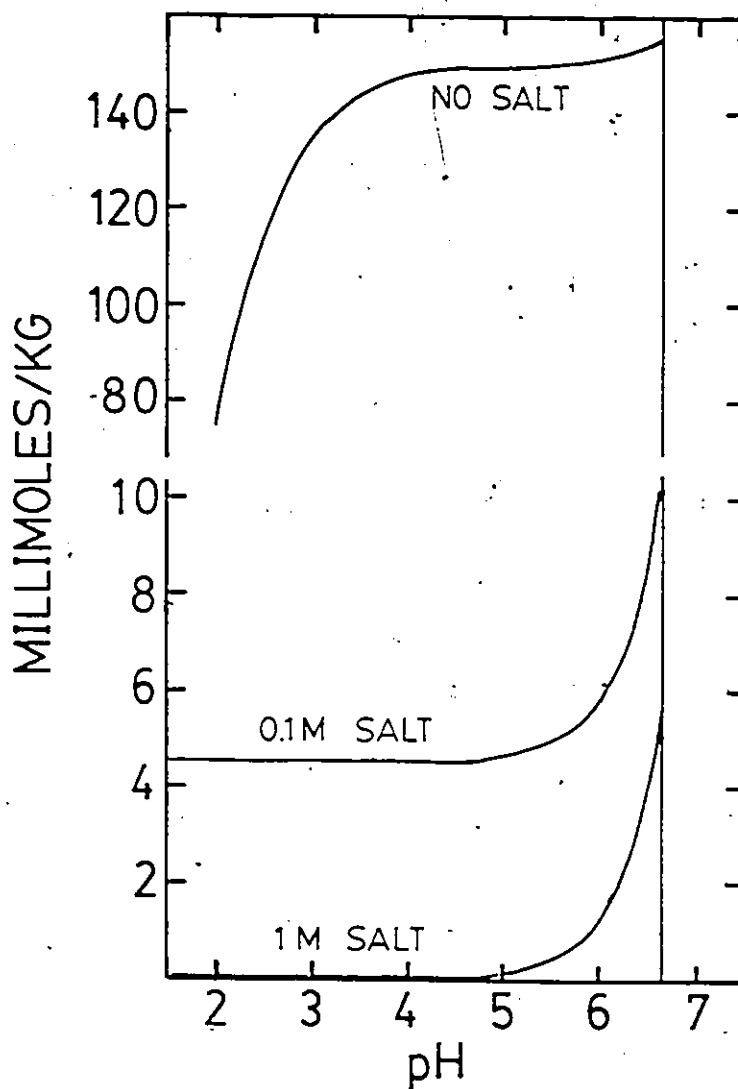
Figure VIII-9.   Predicted Cu sorption on illite from a pCu 5.2 solution. The specific sorption in the presence of a 1 M salt is assumed to be the same as on kaolinite.
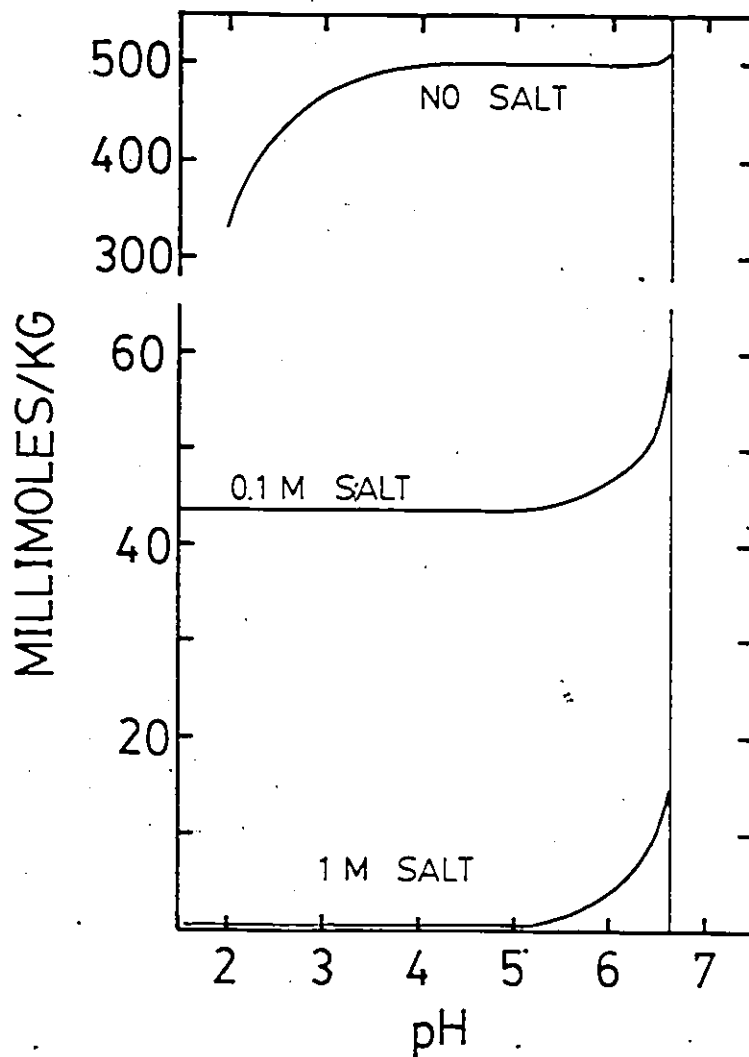
Figure VIII-10. Predicted Cu sorption on montmorillonite from a pCu 5.2
solution. Nonspecific sorption is assumed to be higher than on
kaolinite by a factor of 31/13.

As with kaolinite, the presence of a 1 M indifferent salt

solution eliminates virtually all nonspecific sorption. If the salt

contains an anion such as chloride, which complexes copper, then the

amount of metal complexation must be accounted for. As the salt

concentration is reduced it becomes apparent that the clays with the

high cation exchange capacities will become dominated by nonspecific

sorption. In the presence of moderate amounts of salt solution the

relative change in sorption with pH on montmorillonite is much less than

on illite or kaolinite.
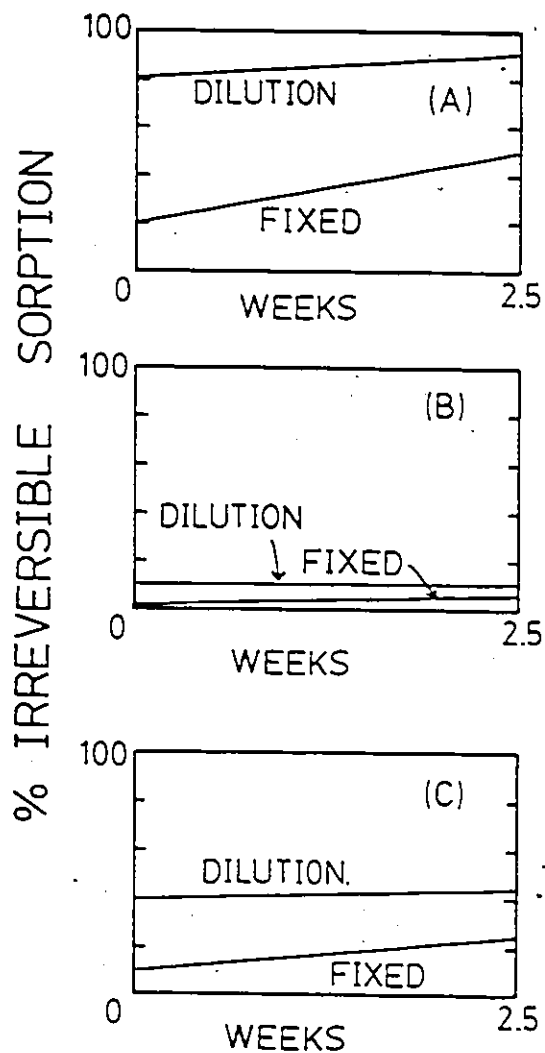
Figure VIII-11. Percent irreversible sorption on illite and
montmorillonite at pH 6.2. (A)Predicted irreversible sorption for
both clays in the presence of a 1 M salt. Irreversible sorption from
a 0.1 M salt is given for (B) montmorillonite and for (C) illite.

The difference in these clays is also apparent in the irreversibility of metal sorption (figure VIII-11). In the presence of a 1 M salt only specific sorption dominates and the reversibility is about the same for all three clays. However, as the salt concentration decreases, the clay with the high cation exchange capacity has a much higher percentage of reversible metal sorption. Since specific chemical sorption determines irreversibility, salt concentration and pH must be considered when evaluating the results of desorption experiments.

EFFECT OF SOLID/LIQUID RATIO ON SORPTION REACTIONS

It has been noted in the literature that sorption may decrease with increasing solid/liquid ratio, particularly at low sediment concentration. Aston and Duursma (1973) noted that sediment/water distribution coefficients for Cs, Ru, Zn, and Co decreased with increasing concentrations of sediment. Sanchez et al. (1982) found that the distribution coefficients of Sr, Ru, Am, and Cm decreased with increasing concentrations of Hudson River Sediments. Li et al. (1984) observed that the distribution coefficients of Sb, In, Au, Cs, Ce, and Sn between red clays and sea water decreased with sediment concentration. However, the distribution coefficients of Co and Mn increased with solid/liquid ratio. Inskeep and Baham (1983) found that Cd sorption decreased with higher concentrations of Na montmorillonite. O'Connor and Connolly (1980) summarize the effects of solid/liquid ratio on the distribution coefficients of DDT, heptachlor, lindane, and kepone. Not all studies found an inverse relationship between sorption and solid/liquid ratio. Balistrieri and Murray (1984) did not find a

change in distribution coefficients for sediment concentrations between 1 and 100 mg/liter. The metals investigated by these authors were Pb, Fe, Sn, Co, Mn, Cu, Be, Sc, Ni, Zn, Cd, Ba, and Cs.

The inverse relationship between solid concentration and sorption has been reported often enough that it requires an explanation. Up to this point there has not emerged a common consensus on the cause of this phenomenon. The object of this discussion is to evaluate the explanations for the effect of solid/liquid ratio in light of some of the observations made in this study. Since the effect of solid concentration has been observed for a large variety of sorbates it is probable that one explanation may not be valid for all cases and probably the mechanism for metals is different than for organics.

One explanation for the apparent increase in distribution coefficient with decreasing solid concentration is the formation of colloids (Aston and Duursma, 1973). Colloid formation is operationally defined as that metal retained by a 0.45 micron membrane which cannot be accounted for by sorption (measured by a second membrane). If a fraction of sorbing metal always forms a colloid which is retained by the membrane then a decrease in the sediment concentration will lead to an apparent increase in in the amount sorbed per kilogram solid. The measured colloid formation can represent several possibilities. The metal may actually form a true colloid in solution, which is most likely for metals with strong hydrolysis constants. However, colloid formation has been measured in solutions which are undersaturated with respect to the solubility of the metal under study. Another explanation for the apparent colloid formation may be sorption or nucleation onto fine dust

particles which are retained by the 0.45 micron membrane. A third explanation for the apparent colloid formation is that the filter paper has sorbed a fraction of the metal in solution. To avoid the sorption problem a blank membrane is placed directly behind the first membrane which collects the colloid. It is assumed that this blank membrane will estimate the amount of sorption on the membrane so that the metal retained on the first membrane can be corrected for this sorption. If this assumption is not correct then the observed colloid formation may include a sorption term. Regardless of the true significance of the apparent colloid formation it does provide an explanation for the inverse relationship between sorption and sediment concentration. If colloid formation is the proper explanation then the inverse relationship between sorption and sediment concentration is actually an experimental artifact.

A decrease in distribution coefficient with solid concentration will occur if some sorption reactions only require a minimum surface area to get started . If the sorption mechanism is a precipitation or coagulation then after a minimum surface has been provided for nucleation an increased amount of solid may not be required for the reaction to proceed. Evidence for a precipitation or coagulation, which is independent of increasing surface area, would be given by pseudo-zero-order kinetics in the presence of constant sorbate concentration. In this study copper did not sorb at a constant rate which implies that metal sorption is limited by a surface capacity (at least in the initial stages of reaction).

Another explanation for the decrease in distribution coefficients with solid concentration is that with increasing solid concentration there are more collisions between solid particles. These collisions lead to coagulation and the blockage of surface sites. This may be an important factor for fine grained, poorly crystalline metal oxides with high surface areas. When these particles coagulate there may be a tendency to recrystallize with the subsequent loss of surface area. When any solid particles become closely packed it becomes more difficult for large organic molecules to access all the surfaces. On the other hand, crystalline clays and sediments, which have floculated in suspension are probably not that closely packed to be inaccessible to metal ions. Furthermore, in this study it has been shown that metal sorption can increase when clay is concentrated during centrifuging or in a floc. Therefore, it does not seem likely that the blockage of surface sites is a good explanation for a decrease in metal sorption with sediment concentration. (An exception might be made for poorly crystalline oxides.)

The results of this are most consistent with the "colloid" formation theory as an explanation for the inverse relationship between metal distribution coefficients and the solid/liquid ratio. Copper sorption kinetics were not dominated by zero-order reactions indicating that sorption was not independent of the available surface area. The blockage of surface sites does not seem likely because the formation of flocs probably enhances sorption. This interpretation might not apply to other sorbates such as large organic molecules.

DISTRIBUTION COEFFICIENTS

Distribution coefficients (K_D) are generally defined as the concentration of sorbate on the solid divided by the dissolved sorbate concentration. Distribution coefficients are used as a simple method to account for the effect of sorbate concentration on sorption reactions. K_D's can be relatively easy to measure and are not difficult to use in mathematical models. Since distribution coefficients account for variations in sorbate concentration they may also compensate for the effect of variable solid-liquid ratios.
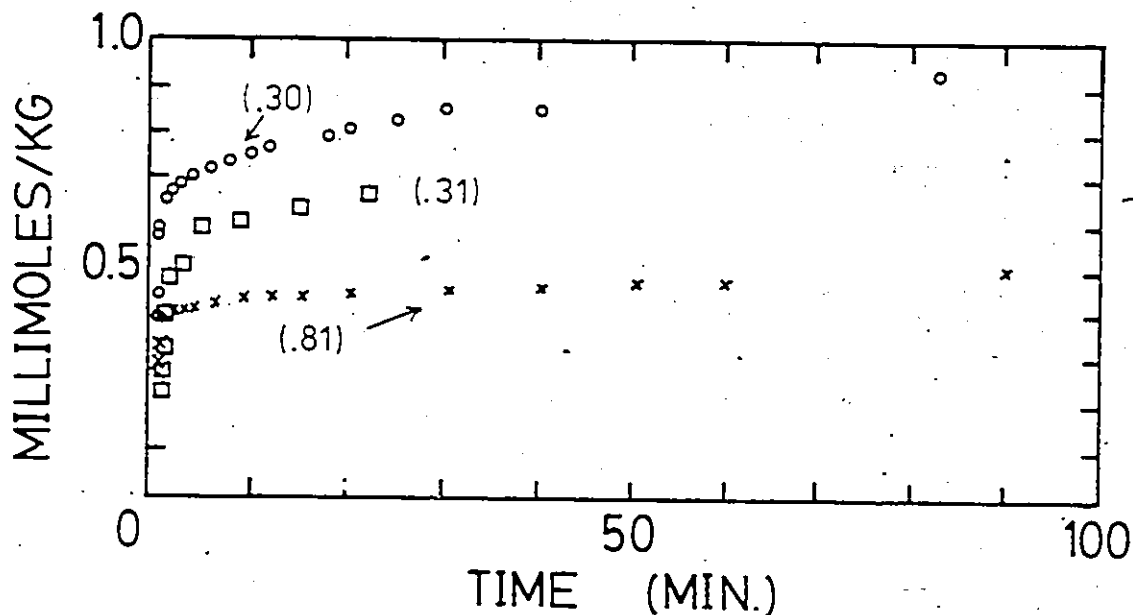
Figure VIII-12. Copper sorbed in kaolinite suspensions with different solid/liquid ratios. Copper concentration was not controlled. The numbers in brackets indicate grams clay/100 ml.

In this study it was observed that when experiments were started at the same copper concentration and the copper was not maintained at a constant level, the experiments with higher solid/liquid ratios sorbed less Cu per kg of clay (figure VIII-12). With more clay present there

was a greater drop in dissolved copper and the initial sorption rate was reduced. However, when copper sorption was expressed with a distribution coefficient (figure VIII-13) the effect of solid/liquid ratio became negligible.
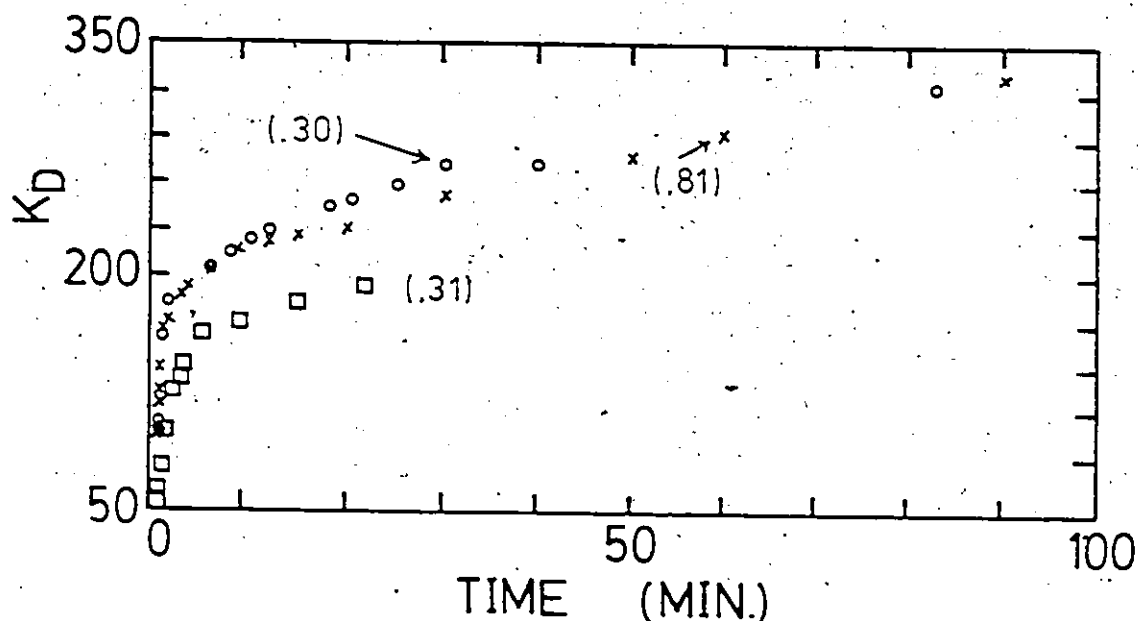
Figure VIII-13. The data in figure 13 are replotted as distribution coefficients versus time.

Although distribution coefficients are a very convenient method of reporting sorption data, we should be careful as to how we use them. As long as we are modeling a unidirectional sorption reaction, distribution coefficients work quite well within certain sorbate and solid concentration limits. However, some applications, such as the modeling of metal migration through a sediment, require a reversible distribution coefficient. A distribution coefficient may be reversible if it represents a single sorption mechanism in which the sorbate is not attached with strong bonds. This criteria may be met by the alkali metals, which do not have strong hydrolysis constants and which

participate mainly in nonspecific cation exchange reactions. On the other hand, transition metals with strong hydrolysis constants are much less likely to have reversible distribution coefficients. This study showed that copper sorption was not reversible to simple dilution. Figure VIII-14 shows that when copper in solution is diluted there is a strong, irreversible increase in the distribution coefficient. When this is considered in light of the fact that copper becomes fixed with long sorption times it is obvious that copper distribution coefficients are not reversible.
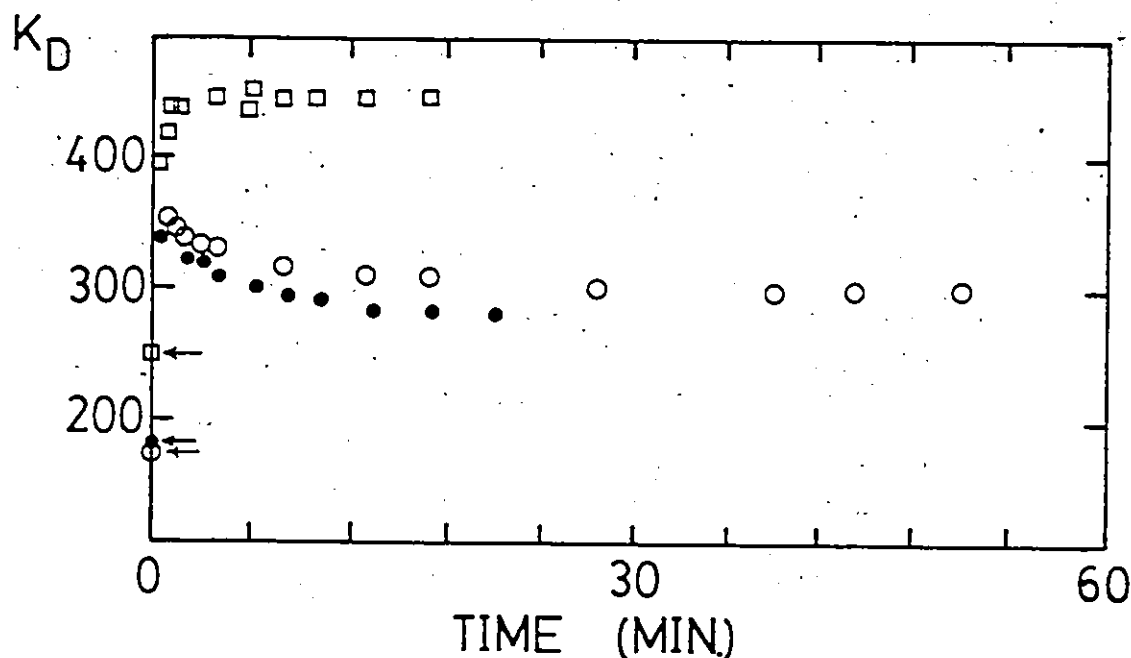
Figure VIII-14. The effect of desorption by dilution on Cu distribution coefficients. The arrows mark the K_D's before desorption. The data were taken from figure VI-1 ($\square$, $\bullet$) and figure VI-2 ($\circ$).

Copper sorption may appear to be reversible under certain experimental conditions. If desorption is carried out with a high solid/liquid ratio then there is a possibility that the dissolved copper

concentration will rise too fast to truly test the reversibility of the sorbed metal. Sorption carried out on negatively charged surfaces in the absence of a background electrolyte will contain a large portion of metal attached by nonspecific attraction. The distribution coefficients measured under these conditions will be reversible. However, most pore waters probably do contain dissolved salts so that reversible, nonspecific sorption of trace quantities of transition metals should not be counted on. A different set of distribution coefficients will be required to model desorption reactions. To complicate matters, this set of desorption K_D's may also be a function of the metal's residence time on mineral surfaces.

ENVIRONMENTAL IMPLICATIONS

The ultimate purpose of measuring sorption reactions is to apply the results to modeling trace metal behavior in the environment. A complete model must be able to account for the effects of pH or salt concentration which may change during diagenesis or during sediment transport. In order to model sorption reactions in a dynamic environment we must first understand sorption mechanisms. Once we have identified the mechanisms we can calibrate each mechanism as a function of pH, salt concentration, and availability of reaction sites in the sediment. Sorption is then determined as a summation of all these mechanisms. This is better than empirically calibrating the overall sorption as a function of pH and salt concentration.

This study has shown that one mineral such as kaolinite can sorb copper by several mechanisms, which can be predicted from the structures of mineral surfaces. From this it follows that if sorption in a sediment is considered as an interaction with only one type of site then the reaction will not be properly defined. If sorption occurs on each mineral by several mechanisms then it is conceivable that a sorption model for a sediment would have to include a very large number of different reactions. However, as was pointed out by Devore (1963), although each mineral has surfaces with different compositions and structures, minerals also share similar surface types. For example, the exposed edges of dioctahedral Al layers sorb metals by the same mechanism(s) regardless of the clay mineral. This was the approach used to predict sorption on montmorillonite and illite in a previous part of this chapter. Therefore, when modeling the sorption properties of a sediment we should pay attention to the quantities of different surface types instead of the different types of minerals present. For example, specific sorption of copper is probably the same on the exposed Al oxides at clay edges as on separate Al oxide phases. Therefore, we need to obtain the total surface area of all Al oxides in the sediment and consider copper sorption on these surfaces to be the same.

Once we have obtained a measure of all the surface types in a sediment (clay faces, oxides of Si, Al, Fe, Mn, and Mg, and organic coatings) we will be in a position to model sorption reactions by summing the contributions from all the identified surface types. This may be practical for simple or hypothetical systems, but unfortunately most common sediments are complex mixtures. It is probably not feasible

to identify all the surface types in sediments as a routine analysis. It is necessary to define some operational properties to best describe the sediment's sorption characteristics. The quantities which could best characterize a sediment's sorption properties are the cation exchange capacity, specific sorption, and reversibility. The following discussion outlines some approaches which could be used to characterize a natural sediment.

The cation exchange capacity can be measured with a divalent cation such as Mg which does not hydrolyze readily and is unlikely to participate in specific sorption. Clay minerals have a pH independent constant charge so that one cation exchange capacity determination is enough. However, natural sediments may contain significant quantities of Fe, Al, and Mn oxides which have a pH dependent charge. Therefore, the cation exchange capacity should be measured at two or more pH's in order to estimate its variation with pH.

Specific sorption can be evaluated by measuring the distribution coefficient of a reference metal, such as copper, in the presence of a 1 M salt solution to eliminate nonspecific sorption. These measurements should be made at several pH's in order to obtain a variation with pH. Sorption times of at least 24 hours should be used. Longer times might be preferable, but are not essential because reaction times are very slow after the initial few hours. An untreated sediment will give specific sorption attributed to a number of surface types, including organic coatings. If time permits, it may be useful to remove organics and/or various oxides from the sediment in order to evaluate their contributions to the total specific sorption.

Once the relative amounts of nonspecific and specific sorption are estimated, one can make a qualitative prediction of the system's reversibility as a function of pH and salt concentration? However, a better estimate of the reversibility can be made by desorbing the specifically sorbed metal by a dilution procedure or by adding a complexing ligand. In order to insure that the reversibility of all the sorbed metal is properly tested during a desorption experiment, the amount of liquid phase must be large enough to prevent a quick build up of dissolved metal. Another interesting experiment would be to look at the response time of the sorbed metal to minor changes in pH.

A knowledge of sorption mechanisms is also very useful for making a decision on what type of clay to use as a barrier to the migration of toxic wastes. For example, the decision on the proper clay to use as filler in a nuclear waste repository may involve the following factors:

1) sorption capacity

2) predictability of the sorption reactions

3) reversibility of the sorption process

4) stability of the clay structure and surface (including oxide coatings) during diagenesis

5) swelling/shrinking properties associated with changes in water content

From the point of view of maximum sorption capacity and predictability, montmorillonite may be a good choice for a buffer material. However, it must be remembered that montmorillonite's high sorption capacity results from nonspecific sorption which is easily reversible. Further more, in the presence of a concentrated brine the

nonspecific sorption of trace metals or radionuclides on montmorillonite is drastically reduced. Under these conditions montmorillonite may have little advantage over kaolinite or illite. Since montmorillonite is a swelling clay it will probably shrink when it is heated and dehydrated. This would produce cracks through which any radionuclides could quickly by pass the clay barrier. Illite and kaolinite may not have this problem because they are nonexpanding clays.

The purpose of the proceeding paragraph has been to illustrate the need of having a good understanding of sorption mechanisms. While on face value the high cation exchange capacity of montmorillonite makes this clay appear to be a logical choice for a barrier, a closer examination of the sorption mechanisms and the solution conditions in a deep repositories may place illite or kaolinite in a more favorable light.

The results of this study are most directly applicable to sediments with high concentrations of kaolinite. High concentrations of kaolinite are typically found in the humid tropics, where intense weathering rates promote the formation of kaolinite. Rivers, such as the Amazon and the Congo, recieve large quantities of weathered, kaolinite rich soil material. The oceanic sediments, which have been fed by these rivers, may have kaolinite as the dominant mineral.

APPENDICES

APPENDIX 1

HISTORY OF KAOLINITE #4

Kaolinite #4 is part of a collection of reference clay minerals described in the American Petroleum Institute (API) research project NO. 49, 1951. Kaolinite #4 was sampled near Macon, Georgia, from the O'Neal pit, which belonged to the Georgia Coating Clay Company. Sample #4 was taken from the Upper Cretaceous Middendorf formation, which is made up of cross-bedded white micaceous and kaolinitic sands. Lenses of kaolinite reach a thickness of 35 feet. The sediments of the Middendorf formation are believed to originate from the erosion of the Piedmont Plateau and were deposited in alluvial fans. The primary igneous rocks of the Piedmont Plateau are highly feldspathic and were probably highly weathered before being eroded. Before the Piedmont uplift the climate was believed to be mild and very wet so that the rocks were extensively leached, with ground waters rich in organic acids. Consequently the Piedmont sediments lost much of their iron and have been enriched in aluminum.

APPENDIX 2

PURITY AND COMPOSITION

The kaolinite from the O'Neal pit has been described as a hard, white clay which contains no grit. Mica is believed to be the main impurity. Kerr et al. (1950) have used a microscopic investigation to look at mineral impurities in API reference clay samples. The results of this study are summarized in the following table, where the estimated amounts other minerals are given as volume percents.

TABLE A-1

KAOLINITE IMPURITIES

KAOLINITE	1a	1b	3	4	10	6	8	9a	9b	17	MEAN
QUARTZ	1.5	2	2	2.5	2	2	1.5	0.75	1.5	0	1.58
ORTHOCLASE	1.5	2	0.01	1.5	0	0.01	1.5	0.01	0.5	1	0.8
SERICITE	0.01	1	0	2.5	0.01	3	1	1.25	1.25	0	1
TITANITE	1.5	0.3	0	2.5	0	0	0	1.25	0	0	0.56
LEUCOXENE	0	0	0.01	0	2	1	1	0	0	0	0.4
ALBITE	0.25	1.5	0	1.5	0	0	0	0	0	0	0.33
LIMONITE	0.01	0.01	0.01	0.5	0.01	0.01	1.25	0.5	0	4	0.63
CARBONACEOUS MATTER	0	2	2	0	2	0.01	0	0	1.5	6	1.35
PYRITE	0	0	0	0.01	0	0	0	0	0	0	0
Fe-Mg MINERALS	0.75	0.01	0	0.35	0	0.01	0	0	0	0	0.11
MUSCOVITE	0	0	0	0	0	0.01	0	0	0	0	0
PLAGIOCLASE	0	0	0	0	0	0	0	0.01	0.01	1	0.1
ZIRCON	0	0	0	0	0	0	0	0.01	0	0	0
LEUCITE	0	0	0	0	0	0	0	0	0	2	0.2
ALUNITE	0	0	0	0	0	0	0	0	0	0.01	0
CORUNDUM	0	0	0	0	0	0	0	0	0	0.01	0

TRACE = .01

MURFREESBORO, PIKE COUNTY, ARKANSAS	1a, 1b
MACON, GEORGIA	3, 4, 10
BATH, SOUTH CAROLINA	6, 8
MESA ALTA, MEW MEXICO	9a, 9b
LEWISTOWN, MONTANA	17

In the Preliminary Report No. 7 of the API Project 49, Kerr et al. (1950) report a chemical analysis of various reference clays. Table A-2 summarizes the results of these analysis for kaolinites. An XRF analysis of the kaolinite #4 used in this study is given in Table A-3 in the form of weight percents.

TABLE A-2

KAOLINITE ANALYSIS   (API PROJECT)

	4	1a	3	5	6	7	9b
SiO2	44.82	45.48	45.2	45.58	45	45.4	45.98
Al2O3	37.2	38.84	37.02	37.62	38.78	35.74	37.61
Fe2O3	0.41	0.19	0.27	1	0.41	1.7	0.63
FeO	0.07	0	0.06	0.13	0.13	0.19	0.13
MgO	0.25	0.17	0.47	0.03	0.16	0.01	0.01
CaO	0.58	0.24	0.52	0.32	0.27	0.3	0.354
Na2O3	0.4	0.24	0.36	0.42	0.36	0.4	0.32
K2O	0.43	0.42	0.49	0.49	0.47	0.57	0.44
H2O+	12.92	13.66	13.27	13.42	13.41	13.11	13.46
H2O-	1.76	0.71	1.55	0.63	0.57	0.83	0.46
TiO2	1.26	0.86	1.26	1.42	1.3	1.48	0.5
MnO	0	0	0	0	0	0	0
SO3	0	0	0	0	0	0	0.01
C	0	0	0	0	0	0	0
IMPURITIES	7.52	2.81	6.7	4.82	4.89	9.29	4.7
ADSORBED WATER	1.76	0.7	1.5				
SiO2/Al2O3	204:100	198:100	207:100	205:100	197:100	216:100	208:100

Murfreesboro, Arkansas   1a

Macon, Georgia   3, 4

Bath, South Carolina   Commercial 5, Crude 6, Commercial 7

Mesa Alta, New Mexico   9b

TABLE A-3

XRF ANALYSIS OF SELECTED AIP REFERENCE KAOLINITES   (WEIGHT PERCENT)

(analyst: Otta Mudroch)

	#3	#4	#5	#9	Precision sdev/mean	Limit of detection
SiO_2	45.71	44.60	44.89	46.22	.3 %	.25
Al_2O_3	37.08	38.10	38.50	37.75	.6 %	.10
Fe_2O_3	0.31	0.67	.58	.81	1 %	.20
MgO	0.30	0.19	0.05	0.25		.05
CaO	0.50	0.30	0.12	0.40		.05
Na_2O_3	0.22	0.34	0.04	0.07	8 %	.20
K_2O	0.09	0.15	0.12	0.06	31 %	.05
TiO_2	1.66	1.60	1.49	0.53	2 %	<.01
MnO	0.06	<0.01	0.06	0.05	3 %	<.01
P_2O_5	0.03	0.04	0.07	0.00	10 %	.01
loss on ign.	14.07	14.00	14.31	13.86		
Total	100.00	100.00	100.00	100.00		
SiO_2/Al_2O_3	209/100	200/100	212/100	208/100		

XRF ANALYSIS OF TRACE METALS (PPM)

Cr	152	282	134	19	.5 %		10
Co	-	1	-	-	-		3
Cu	48	37	45	38	7	%	3
Zn	20	18	24	18	3	%	3
As	0	0	0	16	100	%	16
V	222	212	235	41	1	%	3
Ni	96	96	81	31	2	%	3
Rb	25	23	25	24	7	%	
Sr	15	14	64	12	9	%	
Y	57	48	50	80	8	%	3
Zr	309	289	183	650	4	%	5
Nb	40	45	34	59	8	%	3

Tessier et al. (1979) proposed a sequential extraction technique for determining the location of trace metals held by a sediment. Five extraction steps are applied to a sediment in order of increasing strength. These are operational steps designed to estimate the fractions

of trace metals which are (1)exchangeable, (2)bound to carbonates, (3)bound to Fe-Mn oxides, (4)bound to organics, and (5)found in the residual silicate matrix. These extraction steps are not 100 percent specific to the form of metal they are supposed to extract, but they do give a very good measure of the strength of the bonds holding the metal in the sediment. The extraction steps for a 1 g sample are summarized very briefly below. The results of a Tessier extraction on kaolinite #4 are presented in table A-4.

(1) Exchangeable: Extracted for one hour with 8 ml of either 1 M $MgCl_2$ (pH 7) or 1 M NaOAc (pH 8.2).

(2) Bound to carbonates: Leached with 8ml of 1 M NaOAc (pH 5) for 5 hours.

(3) Bound to Fe-Mn oxides: The residue form (2) is extracted with 20 ml of either (0.3 M $Na_2S_2O_4$ + 0.175 M Na-citrate + 0.025 M H-citrate) or (0.04 M $NH_2OH \cdot HCl$ in 25% (v/v) HOAc). The extraction is carried out at 96°C for 6 hours.

(4) Bound to organic matter: Three ml of 0.02 M HNO_3 and 5 ml of 30% H_2O (adjusted to pH 2 with HNO_3) are added to the sample which is heated to 85° C for 2 hours. A second 3 ml portion of 30% hydrogen peroxide is added and the sample is heated for 3 more hours. After cooling, 5 ml of 3.2 M NH_4OAc in 20% HNO_3 are added to prevent sorption of dissolved metals.

(5) Residual: Residual material is dissolved with a mixture of HF and $HClO_4$, or aqua regia.

TABLE A-4

TESSIER SEQUENTIAL EXTRACTION OF KAOLINITE #4. (analyst: Jill Gleed)

Metal	Exchangeable (mg/kg)	Bound to carbonates (mg/kg)	Bound to Fe-Mn oxides (mg/kg)	Bound to organics (mg/kg)	Residual (mg/kg)
Cd	0.84	0.89	0.17	0.15	0.74
Pb	10.50	8.88	0.74	1.62	6.35
Cu	0.15	0.93	0.10	0.10	1.36
Zn	1.34	3.44	1.27	1.51	2.27
Co	2.83	3.06	0.73	0.58	1.06
Ni	5.87	5.96	0.63	0.66	2.64
Mn	2.72	0.91	0.80	0.33	1.29
Fe	3.19	4.65	273	10.7	1270

APPENDIX 3

CATION EXCHANGE CAPACITY

The cation exchange capacity (CEC) is a measure of the maximum exchangeable cations which can be adsorbed by a solid. If the CEC is measured with an alkali cation, such as Mg, which does not participate in specific chemical interactions with the surface, then the CEC can give an estimate of the negative charge on the solid surface. Cation exchange capacities are commonly measured by saturating the solid with an index cation. After the solid is separated from the saturating solution the index cation is displaced from the solid by another cation such as K^+, Sr^{+2}, or H^+. In CEC measurements the separation of the clay from the saturating index cation solution is always a problem because the saturating salt is left in the pore water of the clay mass. To overcome this problem one can either wash the clay and risk loosing sorbed cations or one can try to estimate the amount of trapped solution and make the appropriate corrections. In this study both approaches

were used.

In this study the CEC was measured by first saturating the kaolinite with 0.01 M $MG(NO_3)_2$, at pH 7. The kaolinite was separated from the saturating solution by filtration. Some kaolinites were rinsed with deionized water to remove excess Mg salts. In other cases the amount of excess Mg salts trapped in the kaolinite were estimated by the amount of water retained during filtration. The weight percent water retained during filtration was determined with other filtered kaolinite samples, not used in the CEC measurements. Magnesium was displaced from the kaolinite with 0.1 M $Sr(NO_3)_2$ at pH 7. Five CEC determinations gave a mean of 11.1 meq/100g with a standard deviation of 1.8.

McBride (1976) measured CEC on kaolinite #4 using Cu, Mn, Mg and Na chlorides as index cations. Kaolinite saturated with an index cation was washed with deionized water until no more chloride was liberated. The index cations were displaced with 0.5 N HCl. The results of these CEC measurements are presented in the following table. The CEC determined in this study agrees with McBride's CEC measured with Mg. The measured Cu and Mn CEC's probably include contributions from specific sorption since this study has shown that specific sorption can be reversed by the hydrogen ion. If Sr had been used to displace Cu and Mn then the measured CEC would probably have been lower.

TABLE A-5

CATION EXCHANGE CAPACITY OF KAOLINITE #4 (MCBRIDE, 1976)

Metal used to determine CEC	CEC (meq/100g)
Cu	13.0
Mn	13.1
Mg	11.1
Na	7.7

APPENDIX 4

SURFACE AREA DETERMINATION

The surface area of kaolinite #4 was determined with the BET method using nitrogen sorption to estimate surface area. The surface area was estimated to be 18.3 meters^2 per gram kaolinite. This falls within the range of surface area measurements on Georgia clays, quoted by Wayman (1967) (10 to 25 meters^2/gram).

APPENDIX 5

POWDER X-RAY DIFFRACTION ANALYSIS OF KAOLINITE #4

X-ray diffraction was used to test the purity of the kaolinite #4 sample, and to determine whether the sizing and long term storage of kaolinite in .05 M KNO_3 has significantly affected the clay. kaolinite in 0.05 M KNO_3 has significantly affected the clay. Kaolinite samples were X-rayed with copper radiation which has a ＞wn in table A-6 include an untreated sample, a kaolinite which has been sized to < 2 microns and which has been stored in KNO_3 for a year, and a sample of the sized kaolinite which has been heated at 500°C for two hours.

The powder X-ray patterns of the untreated and the sized kaolinite samples are similar except that the basal spacings (001, 002, 003 and 004) in the sized sample are much more pronounced. The kaolinite was sized by suspending the clay in a one liter cylinder and allowing the greater than 2 micron size fraction to settle out. This procedure may have also preferentially collected flat kaolinite grains. These grains tend to become oriented parallel to the glass slide and

give stronger basal reflections during XRD analysis.

TABLE A-6

POWDER XRD RESULTS FOR KAOLINITE #4

Unsized Angstroms	I	Sized Angstroms	I	Heated Angstroms	I	Kaolinite hkl
15.29	5	11.95	4	12.57	4	
7.173	100	7.11	100	7.138	100	001
4.453	10	4.433	1	4.446	1	020
4.366	9	4.343	1	4.348	1	110
4.170	6	4.171	1	4.171	1	$11\bar{1}$
3.579	65	3.566	93	3.570	96	002
2.565	7	2.557	1	2.557	5	$20\bar{1}$
2.530	5	2.524	1	2.531	5	$13\bar{1}$
2.498	8	2.495	1	2.497	5	200
2.386	6	2.382	12	2.382	12	003
2.343	11	2.338	2	2.335	1	$20\bar{2}$
2.298	6	2.293	1	2.288	.4	$11\bar{3}$
1.996	2	1.988	1	1.994	.4	$20\bar{3}$
1.898	2	1.892	1	1.895	1	042
1.789	3	1.789	6	1.789	5	004

All the d spacings observed in the kaolinite samples could be attributed to kaolinite except for a small broad peak around 12 to 15 angstroms. This may represent an impurity such as vermiculite or montmorillonite. However, when the kaolinite was heated for two hours at 500 °C there were no significant changes in X-ray diffraction pattern. The diffraction pattern was characteristic of a well crystallized kaolinite. The amount of impurities were too small to make a significant contribution to the diffraction pattern.

APPENDIX 6

KAOLINITE PREPARATION

In any sorption study it is important that the surface of the adsorbent be in equilibrium or in a steady state with respect to the liquid phase. Therefore it is necessary to condition the kaolinite with 0.05 M KNO_3, so that when the experiment is started the kaolinite surface no longer reacts with the KNO_3 solution. Another consideration is the particle size distribution of the kaolinite grains, which influences the surface area per mass of clay. It is important to have a control over the kaolinite surface area if comparisons are to be made between different experiments. Another consideration is the purity of the adsorbent surface. Kaolinite #4 is believed to be relatively free of impurities. Therefore, except for one experiment, no attempt was made to remove impurities from the kaolinite sample because of the possibility that such treatments may actually damage the surface. The preparation of kaolinite for sorption experiments consisted only of sizing the clay and conditioning it to the KNO_3 matrix solution.

Kaolinite was sized by exploiting Stockes law which states that larger particles with more mass will settle out from solution faster than smaller particles. The kaolinite #4 sample was gently ground in a wet form to reduce damage from grinding. The ground kaolinite was then suspended with deionized water in 1 liter settling tubes. After settling for 14 hours the upper 20 cm of suspension was recovered. Potassium nitrate was added to the recovered clay, which was later concentrated by centrifuging. The sized clay was washed three times with 0.05 M KNO_3. The sized clay was allowed to age for at least a

month before being used in sorption experiments. An indifferent salt such as KNO_3 is ideal for storing a clay because the potassium ions insure that hydrogen ions do not become a significant counter ion. Should significant amounts of hydrogen ion accumulate at the surface they may damage the clay through dissolution reactions. The storage of kaolinite in KNO_3 also helps to insure that K^+ will displace other metals from counter ion positions.

APPENDIX 7

SCANNING ELECTRON MICROGRAPHS

Kaolinite #4, which had been aged in 0.05 M KNO_3 for over a year, was investigated with the scanning electron microscope in order to establish its general morphology and to see whether the aging process had affected the sample. One of the micrographs is reproduced in figure A-1 as a summary of the overall results. About 5 to 10 percent of the sample consisted of large kaolinite stacks with a mean diameter of about 2.3 micrometers. The size of the remaining sample ranged from 1.6 to 0.07 micrometers, with a mean of about 0.9.

Most of the kaolinite appears as well crystallized, pseudo-hexagonal grains. The grains have sharp corners and do not seem to display any etch pits. Therefore, it appears that the kaolinite has not been altered by the KNO_3 solution and is stable in that medium, at least for the duration of this study.

Figure A-1.   SEM micrograph of kaolinite #4 sample.   The scale is shown as a 0.478 micrometer bar.

It would be useful to have a good view of the kaolinite edges so that it would be possible to estimate the ratio between edge area and total surface area. Unfortunately, most of the grains are lying flat so that their edges are not visible. There are a few exceptions such as the one in the lower left hand corner of figure A-1. The ratio of edge area to total surface area can be estimated if kaolinite is assumed to be hexagonal. A measure of the height of the edge face, and the distance across the top of the grain can be used to calculate edge and face areas. In the micrograph the grain, whose edge is visible, appears to have 20 percent edge area. Other estimates give as much as 30 percent edge area. These estimates may not represent the edge area of the kaolinite sample because most grains do not display their edges and it is more likely that thin grains with small edge areas are lying flat. Many grains appear as if they are able to split into thinner sheets, which would significantly reduce the relative the amount of edge area. A better estimate of edge area is probably given by a measure of anion adsorption.

The the kaolinite faces appear to be very even and free of cracks at this magnification. This suggests that there is a lack of defects through which copper could rapidly penetrate the structure. However, some of the larger grains, which have some visible edges, appear to have partings, along 001 cleavage planes, exposed at the edges. It is possible that copper may penetrate some of these cleavage planes. Cyanide may not be able to extract copper from these cleavage planes since their negative charge may restrict penetration by CN^-.

The micrograph represents a densely packed kaolinite on a filter paper. Even though the kaolinite grains are packed closely together there are still numerous open spaces which are readily accessible by copper ions. Since the clay is already well crystallized it is unlikely that the grains will recrystallize when they contact their neighbors. Therefore, a loss of reactive surface area to copper ions probably does not occur when kaolinite grains are brought together.

APPENDIX 8

CONFIDENCE LIMITS ON LINEAR REGRESSION ANALYSIS

Linear regression analysis has been applied in several areas of this study, including the definition of a calibration curve for the copper electrode and the measurement of first-order rate constants. In these applications it is necessary to have confidence limits for the estimated linear coefficients representing the slope and intercept.

Theoretically, a linear model should fit the calibration curve for the copper electrode because the Nernst equation predicts a linear response of measured emf to changes in the negative logarithm of copper activity (pCu). If first-order kinetics are obeyed then a plot of the logarithm of sorbed copper versus time should also produce a straight line. The application of a regression analysis to the calibration curve and the first-order plot of the sorption data is simplified by the fact that in both cases we have an independent variable with minimum error (concentration of Cu standards and time). In both cases the majority of error is associated with the dependent variable which is measured by the electrode.

If there is a linear relationship it should be possible to regress the dependent variable (Y) on the independent variable (x) to obtain straight lines. The mean value of Y should be related to the independent variable x by a linear equation:

(1) $$Y_i = \alpha + \beta x_i + E_i$$

In equation 1 the true values of the slope and intercept are represented by β and α. E_i represents the difference between a single value of Y and the mean response of Y predicted by the linear model. It is assumed that E_i is a random variable with a mean of zero. This is a reasonable assumption in the present applications because nonrandom drifts in the electrode measurements can be detected and accounted for. In a simple linear regression analysis we obtain estimates for α and β given by a and b. Each pair of observations satisfies the equation:

(2) $$y_i = a + bx_i + e_i$$

In equation 2, e_i represents the difference between a measured y_i and the line with coefficients a and b which is an estimate of the true line given by equation 1. Generally e_i is called the residual. The strategy in linear regression analysis is to find a set of values for a and b which minimize the sum of squares of the residuals.

(3) $$SSE = \sum_{i=1}^{n} e_i^2 = \sum_{i=1}^{n}(y_i - a - bx_i)^2$$

The process of minimizing the sum of squares of the residuals is known as the method of least squares. SSE is differentiated with respect to a and b. The partial derivatives of SSE with respect to a and b are set to zero. After rearranging the terms we end up with

equations for a and b.

(4)
$$b = \frac{n \sum\limits_{i=1}^{n} x_i y_i - (\sum\limits_{i=1}^{n} x_i)(\sum\limits_{i=1}^{n} y_i)}{n \sum\limits_{i=1}^{n} x_i^2 - (\sum\limits_{i=1}^{n} x_i)^2}$$

(5)
$$a = \overline{y} - b\overline{x}$$

The confidence limits of our estimates for the linear coefficients are obtained with the following assumptions. (1)The mean of E_i is zero with a variance σ^2. (2)E_i is normally distributed and is independent from measurement to measurement. Then a and b are considered as random variables, A and B, whose means are equal to the true constants α and β of the linear equation. The variances of both A and B are related to the variance of E_i, σ^2. An unbiased estimator of this variance, with n-2 degrees of freedom, is given by:

(6)
$$s^2 = \frac{SSE}{n-2}$$

The value of s^2 reflects the variation about the regression line. It can be shown that the $(1 - \alpha)100\%$ confidence interval for the true slope of the line, β , is given by:

(7)
$$\beta = b \pm \frac{t_{\alpha/2} s}{\sqrt{S_{xx}}}$$

The $(1 - \alpha)100\%$ confidence interval for the intercept is given by:

(8)
$$\alpha = a \pm \frac{t_{\alpha/2} s \sqrt{\sum\limits_{i=1}^{n} x_i^2}}{\sqrt{n S_{xx}}}$$

where: $t_{\alpha/2}$ is a value of the t distribution with n - 2 degrees of freedom. The number of data pairs are given by n.

$$(9) \quad S_{xx} = \sum_{i=1}^{n}(x_i - \bar{x})^2 = \sum_{i=1}^{n}x_i^2 - \frac{\left(\sum_{i=1}^{n}x_i\right)^2}{n}$$

$$(10) \quad S_{yy} = \sum_{i=1}^{n}(y_i - \bar{y})^2 = \sum_{i=1}^{n}y_i^2 - \frac{\left(\sum_{i=1}^{n}y_i\right)^2}{n}$$

$$(11) \quad S_{xy} = \sum_{i=1}^{n}(x_i - \bar{x})(y_i - \bar{y}) = \sum_{i=1}^{n}x_i y_i - \frac{\left(\sum_{i=1}^{n}x_i\right)\left(\sum_{i=1}^{n}y_i\right)}{n}$$

The value of SSE can be quickly calculated with:

$$(12) \quad SSE = S_{yy} - b S_{xx}$$

The confidence interval for the mean response of y can also be calculated.

$$(13) \quad \bar{y} \pm t_{\alpha/2}\, s\, \sqrt{\frac{1}{n} + \frac{(x_o - \bar{x})^2}{S_{xx}}}$$

$$(14) \quad \text{The coefficient of determination} = r^2 = \frac{(S_{xy})^2}{S_{xx}\, S_{yy}}$$

APPENDIX 9

COPPER SPECIATION

The speciation of copper must be known as a function of pH and total copper concentration before any meaningful sorption experiments can be designed. The type of copper species in solution will influence sorption mechanisms and may ultimately determine the amount of metal uptake. Since the copper electrode responds mainly to the free Cu^{+2} ion it is essential to know how the concentration or activity of this ion will change with pH. Copper solubility must be known as a function

of pH to avoid sorption experiments with solutions which are saturated with respect to copper. Since copper speciation is essential to a proper interpretation of sorption reactions a speciation model has been calculated to fit the experimental conditions of this study.

In this study the only ligands in solution which can form complexes with copper are OH^- and CO_3^{-2}. Therefore, the total dissolved copper concentration may be given by the following equation.

(1) $[Cu]_T = [Cu^{+2}] + [CuOH^+] + [Cu(OH)_2] + [Cu(OH)_3^-] + [Cu(OH)_4^{-2}]$
$$+ 2[Cu_2(OH)_2^{+2}] + [CuCO_3] + [Cu(CO_3)_2^{-2}]$$

The concentrations of the various copper complexes can be given in terms of conditional stability constants, free ligand concentrations, and pH.

(2) $[Cu]_T = [Cu^{+2}] \left(1 + \dfrac{B_1^{OH}}{[H^+]} + \dfrac{B_2^{OH}}{[H^+]^2} + \dfrac{B_3^{OH}}{[H^+]^3} + \dfrac{B_4^{OH}}{[H^+]^4} \right.$

$$\left. + 2[Cu^{+2}] \dfrac{B_{22}^{OH}}{[H^+]^2} + \dfrac{B_1 K_1 K_2 K_H P_{CO2}}{[H^+]^2} + \left(\dfrac{B_2 K_1 K_2 K_H P_{CO2}}{[H^+]^2} \right)^2 \right)$$

The stability constants are defined as follows:

$$B_{nm}^{L} = \frac{[Cu_m L_n][H^+]_n}{[Cu^{+2}]_m [HL]_n}$$

The carbonate ion has been related to the partial pressure of CO_2 by the following relationships:

$$[CO_3^{-2}] = \frac{K_1 K_2 K_H P_{CO2}}{[H^+]_2}$$

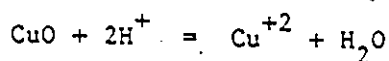K_H = Henry's law constant = $[CO_2]/P_{CO2}$

$$K_1 = \frac{[HCO_3^-][H^+]}{[H_2CO_3]}$$

$$K_2 = \frac{[CO_3^{-2}][H^+]}{[HCO_3^-]}$$

Equation 2 can be rearranged to give the ratio of free copper to total copper.

$$(3)\quad A_0 = \frac{[Cu^{+2}]}{[Cu]_T} = [Cu^{+2}]\left(1 + \frac{B_1^{OH}}{[H^+]} + \frac{B_2^{OH}}{[H^+]^2} + \frac{B_3^{OH}}{[H^+]^3} + \frac{B_4^{OH}}{[H^+]^4}\right.$$
$$\left. + 2[Cu^{+2}]\frac{B_{22}^{OH}}{[H^+]^2} + \frac{B_1 K_1 K_2 K_H P_{CO2}}{[H^+]^2} + \left(\frac{B_2 K_1 K_2 K_H P_{CO2}}{[H^+]^2}\right)^2\right)$$

Once A_0 is determined for a given pH and copper concentration, $[Cu^{+2}]$ is easily determined from the total copper concentration. Then the concentration of any copper species can be calculated. Since equation 3 contains $[Cu^{+2}]$ on both sides, the equation must be rearranged into a quadratic form, which can easily be solved.

After $[Cu^+]$ has been calculated it is necessary to check whether or not the solubility concentration of $[Cu^{+2}]$ has been exceeded. The solubilities of potential copper minerals are checked and the mineral with the least solubility ultimately determines the maximum copper concentration in solution. In a KNO_3 solution exposed to atmospheric CO_2 the copper minerals which should be considered are tenorite, malachite and azurite. Their solubilities can be expressed by the following equations.

$$CuO + 2H^+ = Cu^{+2} + H_2O$$

tenorite

$$Cu_2(OH)_2CO_3 + 4H^+ = 2Cu^{+2} + 3H_2O + CO_2$$

malachite

$$Cu_3(OH)_2(CO_3)_2 + 6H^+ = 3Cu^{+2} + 4H_2O + 2CO_2$$
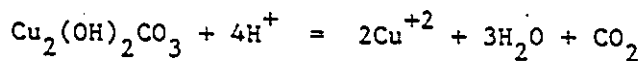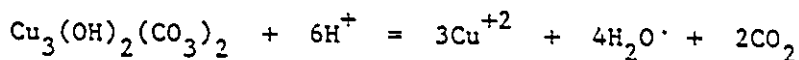
azurite

TABLE A-7

CONDITIONAL STABILITY CONSTANTS

Constant	-log	Ionic strength	Reference
B_1^{OH}	8.125	0.05	Paulson and Kester (1980)
B_2^{OH}	16.41	"	"
B_3^{OH}	26.87	1	Smith and Martell (1976)
B_4^{OH}	39.56	1	"
B_{22}^{OH}	10.86	0.035	Perrin (1960)
B_1^{CO2}	-6.1	0.1	Bilinski et al. (1976)
B_2^{CO2}	-9.7	"	"
K_H	1.51	1	Nilsson (1958)
K_1	6.20	0.05 *	Smith and Martell (1976)
K_2	10.06	"	"
$K_s^{tenorite}$	-7.65	"	Schindler (1967)
$K_s^{malachite}$	-14.54	"	"
$K_s^{azurite}$	-21.80	"	"

Conditional constant adjusted to 0.05 ionic strength.

The stability constants used in this model calculation are presented in table A-7 . Where possible the constants are taken from measurements in a medium with an ionic strength of 0.05. If activity coefficients were available then the constants were adjusted to an ionic

.strength of 0.05. This model assumes that the solution is exposed to atmospheric CO_2 which has a partial pressure $10^{-3.5}$ atmospheres. Figure A-2 shows the speciation of a solution with a total copper concentration of pCu 4. Up to a pH of 6 the free copper ion is the dominant species. At pH 6 the solubility of tenorite is exceeded and copper begins to precipitate. As the pH is increased tenorite determines the maximum total copper concentration. Although hydroxide and carbonate species begin to increase, at pH 7 seventy-five percent of the total dissolved copper is still a free ion. However, by pH 8 the free copper ion is reduced to 18 percent.
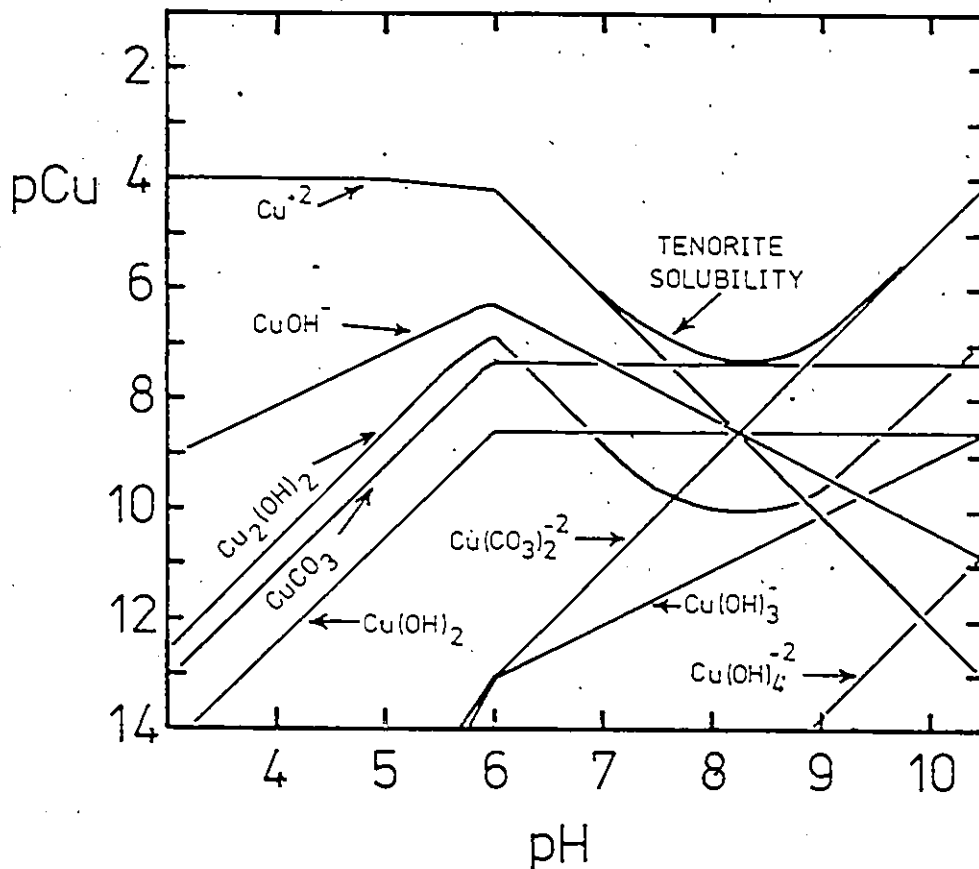

Figure A-2. Speciation of a pCu 4 solution. Once solubility is exceeded tenorite determines the total copper concentration.

APPENDIX 10

SPECIFIC ION ELECTRODES

Basic principles: Most solid-state membrane electrodes contain
one or two crystalline compounds. If only one solid compound is used
the electrode could take the form of a single crystal of that compound.
Two-compound electrodes and some single-compound electrodes are made
from many small crystals which are compressed or sintered into a disc.
In two-compound electrodes the two different crystals are intimately
mixed and only one crystal has to be ionically conducting. The two
different crystal types have a common ion and they both must be in
equilibrium with the solution. Materials used in commercial electrodes
are given in table A-8 (from Midgley and Torrance, 1978).

One type of solid-state electrode is made by attaching the
crystal to one end of a hollow plastic tube. The plastic tube contains
a Ag/AgCl reference electrode and a reference solution with a constant
concentration of the ion which the electrode is designed to measure.
The-standard potential of this type of solid-state electrode depends on
the standard potential of the internal Ag/AgCl electrode and on the
reference solution activities of Cl^- and of the ion to be measured.
If the solid-state electrode contains a silver salt crystal then the
internal reference electrode and filling solution are not required. The
standard potential of this type of electrode is characteristic of the
membrane material. The plastic tube of this electrode only contains a
metallic conductor connecting the membrane to the millivoltmeter.

TABLE A-8

COMPOSITIONS OF COMMERCIAL MEMBRANE SPECIFIC ION ELECTRODES

Ion	Membrane material	
fluoride	LaF_3	
chloride	AgCl	or $AgCl + Ag_2S$
bromide	AgBr	or $AgBr + Ag_2S$
iodide	AgI	or $AgI + Ag_2S$
thiocyanate	$AgSCN + Ag_2S$	
sulfide	Ag_2S	
silver	Ag_2S	
copper	$Cu_{1.8}Se$	or $CuS + Ag_2S$
lead	$PbS + Ag_2S$	
cadmium	$CdS + Ag_2S$	

All solid-state electrodes have one charge carrying species to which the electrode exclusively responds. The electrode experiences a primary response if changes in its emf are produced only by changes in the activity of the charge carrying species (Ag, F, and some Cu electrodes). However, if the electrode also responds to the counter ion of this charge carrying species through a solubility product reaction, a secondary response is produced. For the case of a crystal, MA, the solubility is given by:

$$K_s = [M][A]$$

The emf of the electrode is given by:

$$E = E° + RT/nF \ln(10) \log[M]$$

F = Faraday   n = valance of M

In a solution containing M the emf is determined by the activity of M. However, if the solution contains only the counter ion A then the emf is determined indirectly by A:

$$E = E^\circ + RT/nF \ln(10) (\log K_s - \log[A])$$

Therefore, this M selective electrode might also be used to measure the activity of A in a solution containing no M. The solubility reactions at the surface can also explain interferences to electrode measurements. If the metal forms an insoluble salt with another anion, R, then the surface of the electrode may change from MA to MR if $[R]/[A] > K_s^{MR}/K_s^{MA}$. As the surface is converted to MR the activity of M is then controlled by the solubility product of MR. As the change from MA to MR is usually gradual the change in the electrode's response to M may go undetected and may be impossible to calibrate.

A tertiary electrode response can occur in membranes which contain more than one crystal (Pb, Cd and some Cu electrodes). If a copper electrode of composition $CuS + Ag_2S$ is placed in a copper solution the aqueous copper ion controls the activity of sulfide at the surface through K_s^{CuS}. The sulfide activity then determines the silver activity through K_s^{Ag2S}. The emf of the electrode is given by:

$$E = E^\circ + RT/2F \ln(10) (\log K_s^{Ag2S} - \log K_s^{CuS} + \log[Cu])$$

The silver ion can also influence the activity of S, so that the presence of Ag or any other metal which reacts with sulfide will interfere with copper measurements.

Reference electrode: Since it is only possible to measure the

difference in emf between two electrodes, a reference electrode must be

used in conjunction with a specific ion electrode. A very popular

electrode is the Ag/AgCl electrode because it is reversible, compact, and

can quickly recover from temperature changes. This electrode is made by

electroplating AgCl on a silver wire or a silver-plated platinum wire.

This wire is suspended in a Ag saturated KCl solution. The half cell of

this electrode is constant at constant temperature because the silver

activity in the filling solution remains constant.

The Ag/AgCl electrode is connected to the sample solution by a

liquid junction. A good liquid junction must have the following

properties: (1)There should be a minimal effect from stirring or from

streaming of the sample solution. (2)The junction should not clog and

it should be easy to clean. (3)The junction should not carry over

sample solution from one sample to the next. There must be a small but

steady flow of AgCl solution from the reference electrode to the sample.

If this flow rate is altered there will be a change in the liquid

junction potential which will affect the measured emf. A problem with

using the Ag/AgCl reference in conjunction with a copper electrode is

that both the silver and chloride given off by the reference will

interfere with and even damage the copper electrode. To avoid

contaminating the sample with AgCl, a double junction reference

electrode is used. The Ag/AgCl reference electrode is connected through

a porous frit to another compartment which contains a KNO$_3$ solution.

This other compartment is connected to the sample through a porous frit

or a sleeve type junction. The KNO$_3$ solution in the second

compartment dilutes the AgCl escaping from the reference electrode and significantly reduces sample contamination. Nevertheless, manufacturers of Ag_2S based specific ion electrodes recommend that these electrodes not be stored in the same solution with double-junction electrodes for extended periods of time.

The emf of the combined copper electrode and Ag/AgCl reference can be expressed by the following equation.

$$E + E° + RT/2F \ln(10) \log[Cu^{+2}]$$

The standard potential of this cell contains the standard potential of the copper electrode, the half cell potential of the Ag/AgCl electrode and the liquid junction potential between the solution and the reference electrode.

$$E° = E_{Cu}° + E_{Ag/AgCl} + E_{liquid\ junction}$$

Copper electrode used in this study: The copper electrode used in this study was distributed by Graphic Controls (PHI 96200). There are a number of manufacturers who produce copper electrodes, but the most common electrode mentioned in the literature is the Orion 94-29A (Saar et al.,1980; Ohzeki et al., 1980; Nakagawa, 1975; and Midgley and Torrance, 1978). The linear (Nernstian) response of the Orion electrode has been reported to extend to concentrations as low as pCu 6. The Graphic Controls electrode used in this study appears to have a linear response down to pCu 6.5. Below this concentration the calibration line becomes curved and although measurements can be made, calibration becomes difficult and the electrode response time becomes slow.

Theoretically the lowest measurable copper activity is determined by the solubility of CuS. However, in practice the detection limit is much higher than CuS solubility (Nakagawa et al., 1975). This could be produced by the presence of another aqueous species which increases the solubility of sulfur. However, Nakagawa et al. (1975) suggest that at low copper levels the sorption of Cu at the electrode surface prevents the electrode from seeing the true Cu activity in the free solution. If measurements are carried out in a Cu buffered solution which contains a ligand that strongly complexes Cu and Ag then the detection limit of Cu activity can be extended to very low levels. The ligand is believed to reduce Cu sorption so that the electrode can respond to copper in the free solution. If the ligand does not complex Ag as well as Cu (EDTA) then the Ag is adsorbed and interferes with Cu measurements.

The copper electrode is affected by pH, particularly below pH 4 and above pH 6. The effect is most noticeable for low copper concentrations. Between pH 4 and 6 there is very little effect on Cu solutions down to pCu 5. At increasing pH's above 6 the amount of free copper ion is reduced by hydrolysis reactions, while at low pH, measurements of low copper concentrations may be affected by increased solubility of CuS and Ag_2S, followed by Cu adsorption on the electrode.

Graphic controls claim that the reproducibility of their electrode is ± 1 mV or about 8 percent for copper concentrations from pCu 6 to 5. They define reproducibility as the mean deviation of the measured potential when the electrode is transferred from a pCu 4 to a pCu 3 solution.

The response time is defined as the time it takes an electrode to reach a steady reading after it has been rinsed and placed into a solution which is 10 times more or less concentrated than the solution in which the electrode had equilibrated previous to the rinsing. Midgley and Torrance (1978) report a response time of less than two minutes for the Orion electrode for copper concentrations greater than pCu 4 and 5 minutes for lesser concentrations. Graphic controls claim a response time of 20 seconds for concentrations greater than pCu 4, and 2 minutes for lesser concentrations.

In this study it was found that when the range of copper concentration was less than one order of magnitude the electrode could reproduce copper standards by ± 0.1 to 0.2 millivolts. However, over time periods of an hour or more there may be a drift in the standard potential, E°, of around 1 mV. These drifts must be accounted for by periodic calibrations. In the sorption studies the change in copper concentration was kept to a minimum to greatly improve the electrode's response time. This was accomplished by equilibrating the electrode in the copper solution and then adding the clay to this solution. The response of the electrode to minor changes in copper concentration is described in chapter IV.

The electrode response is related to copper concentration by:

$$E = E° + RT/2F \; \ln(10) \; \log(Cu^{+2})$$

$$E° = E_{standard\,Cu} + E_{reference} + E_{junction} + RT/2F \; \ln f_{Cu}$$

$$f_{Cu} = \text{activity coefficient}$$

At constant ionic strength f_{Cu} is constant and the electrode responds to changes in the activity of Cu^{+2}. The electrode can be calibrated by titrating a constant ionic medium with copper. By plotting E (emf) against $-\log(Cu^{+2})$, (pCu), one obtains a line with a slope of $-RT/2F \ln(10)$ and an intercept at pCu 0 of E°. The slope should remain fairly constant for different calibrations at the same temperature. However, E° can change if activities are used instead of concentrations, if the liquid junction potential changes because of different flow rates in the reference electrode, and if the surface of the copper electrode is altered.

At 25°C the ideal slope of emf versus pCu is -29.6 mV/pCu unit. Therefore, a 1 mV change in emf corresponds to 0.034 pCu units (8 %). If the reproducibility is 0.1 to 0.2 mV (as suggested by repeat measurements of copper standards) then reproducibility in pCu units is 0.003 to 0.007 (1 to 2 %). The reproducibility of the copper electrode can be estimated from the calibration curve by calculating the confidence intervals of the slope and intercept. This procedure is described in appendix 8. From the confidence intervals of the slope and E° we can estimate the error of the emf measurement. Usually this error falls between 0.003 and 0.010 pCu units. Unfortunately E° does not always remain stable with time. Therefore it is necessary to check the calibration at least once an hour. If the temperature remains constant it is reasonable to assume that the slope remains constant and that electrode drifts are produced by a shift in E°. Unless it is obvious at which point in time E° began to change, the change in E° must be evenly distributed over the time period between calibrations. With this

procedure it is hoped that electrode drifts are eliminated and that errors associated with copper measurements are given by the calibration curve.

APPENDIX 11

CU RADIOTRACER ANALYSIS

The application of a radiotracer in copper analysis is based upon the fact that a fraction of the copper introduced into the experiment is the unstable ^{64}Cu isotope. As ^{64}Cu decays it gives off gamma rays which can be measured. The measured disintegration rate in a sample is proportional to the amount of ^{64}Cu present, which is proportional to the total amount of copper in the sample. The ^{64}Cu is produced by placing nonradioactive copper in a neutron flux. The amount of ^{64}Cu is determined by the total amount of irradiated Cu, the neutron flux, the irradiation time, and the time elapsed after irradiation. The use of ^{64}Cu is advantageous because small amounts of copper can be easily measured without chemical interference and contamination problems. However, because the half life of ^{64}Cu is only 12.71 hours experimental times are limited to only two or three days.

In this study ^{64}Cu was produced by irradiating an accurately weighed copper wire (3 to 6 mg) in a neutron flux of $1 * 10^{13}$ neutrons/cm^2/sec. After irradiating for two hours the copper wire was not handled for another seven hours to allow its activity to drop to a safe level. The copper wire was dissolved in a minimum amount of nitric acid and diluted to 100 ml with deionized water. This copper solution was used to spike the sorption experiments and it was also used to make

standards which could relate measured activity to copper concentration.

In this study a sodium iodide detector was used to measure gamma
.rays emmitted from copper with an energy of 511 keV. There were no
interferences because copper was the only active element in the samples.
After counting for one minute an integrated area was obtained for the
copper 511 peak and for the background activity, which was estimated
from the shoulders of the copper peak. The activity of ^{64}Cu in the
sample is given by the area under the copper peak minus the background
activity. The energy levels of the gamma rays emitted by Cu are
believed to follow a Poisson distribution so that the statistical error
associated with counting copper activity can be estimated by the square
root of the total area under the copper peak. Therefore, the percent
error associated with counting copper activity is given by:

% error = [(area under peak + background)$^{\frac{1}{2}}$/area under peak] * 100 %

In this study both solid and liquid samples were measured for
copper radioactivity. When measuring activity it is important to have a
constant sample geometry for both the copper standards and the unknowns.
Therefore, to analyze liquid samples, 10 ml of liquid were always
counted in the same type of plastic test tube. The geometry of the
solid samples was more difficult to control. Solid samples consisted of
5 to 15 mg of kaolinite which had been separated from filter papers (to
exclude counting the activity of copper sorbed to filter paper).
Standards for the solid samples were made by spiking 10 mg of powdered
kaolinite with know amounts of active copper solution. Solid samples
were also placed in plastic test tubes and were counted in the dry
state. In this study the counting of samples was generally started

about 30 hours after the copper had been irradiated (over 2 half lives).
Although the change in copper activity with time was no longer very
great, a note was made of the time each sample was counted. The
measured activities of the samples and standards were normalized to a
standard time.

The errors associated with counting were generally small. If the
amount of copper in the sample was between 100 and 1 nanomoles then the
counting error was less than 1 %. The samples with the lowest amount of
copper (.1 nanomole) had counting errors as high as 4%. The greatest
errors associated with this technique probably are not statistical
counting errors. Errors associated with geometry may be significant for
solid samples, and liquid samples may be affected by copper loss during
filtration. The difference between copper concentration measured with
an electrode (in the suspension) and determined with the radiotracer are
less than 30 %. Usually the radiotracer analysis of copper solutions
gives a lower concentration, suggesting losses produced by filtration.
Adsorbed copper determined by counting solid samples directly was only
50 to 30 percent of sorbed copper calculated by mass balance. This can
also be explained by copper loss during filtration. However, in several
cases this difference was observed when cyanide or acid had been added
to the clay suspension before filtration. The presence of cyanide or
acid should have eliminated copper losses during filtration. This
suggests that a geometric factor may have influenced the counting
efficiency of solid kaolinite samples.

APPENDIX 12

MATHEMATICAL MODELS USED TO DESCRIBE SORPTION ISOTHERMS

In any adsorption study one usually needs to describe the sorption process with some mathematical expression which relates the amount of sorbed adsorbate with that remaining in solution. The following section describes some of the more common equations used to describe sorption under assumed equilibrium conditions. Travis and Etnier (1981) should be consulted for a more complete description and set of references describing sorption equations. Babcock (1963) gives a good review of cation exchange equations. Each of the following expressions is an attempt to present sorption data in a meaningful way. Some expressions give more insight to the sorption process than others, but they all have their uses, depending upon the object of the study.

Ion exchange is a popular way to describe sorption reactions because it is recognized that soils can exchange one cation for another, and the concept of ion exchange does not allow for the creation of a charge imbalance at the surface or in solution. Ion exchange is most useful when a surface's total cation exchange capacity is filled by two exchanging cations in roughly similar proportions. An ion exchange reaction as shown in (1) can be described by a Nernst-Berthelot distribution coefficient (2).

(1) $\quad bC_A^{+a} + aS_B^{+b} = bS_A^{+a} + aC_B^{+b}$
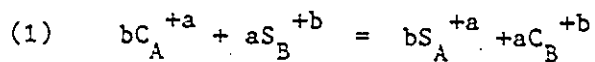
$\quad\quad$ C = cations in solution $\quad\quad$ S = sorbed cation

(2) $\quad K_{A/B} = (S_A^{\ b} * C_B^{\ a}) / (S_B^{\ a} * C_A^{\ b})$

The Nernst-Berthelot distribution coefficient usually changes with the composition of exchanging ions and it is the starting point for all thermodynamic treatments of cation exchange (Gaines and Thomas, 1953; Eberl, 1980). El-Sayed (1974) looked at the thermodynamics of Cu/Ca exchange on bentonite. Maes and Cremers (1975) measured Co and Zn exchange on montmorillonite and Egozy (1980) looked at Cd/Co reactions on clays. Aluminum and calcium exchange on smectite was investigated by McBride (1977). In situations where one cation occurs at trace levels and only covers a small fraction of the surface exchange capacity the use of an ion exchange technique is no longer justified. Cation exchange is also impractical if it is not clear which ions, if any, the adsorbate replaces. If the trace element concentration is low enough then sorption can be linear with concentration and a simple distribution coefficient can describe the adsorption.

(3) $K_D = S/C$

  S = sorbate on surface C = sorbate in solution

The distribution coefficient is a convenient and simple way of calculating metal adsorption. However, it is empirical and by itself tells us very little about the reaction mechanism. It may change with pH, solid/liquid ratio and ionic strength, and if Henry's law is not obeyed at high metal concentrations it becomes a function of concentration. To account for the problem of changing sorption as the surface becomes loaded with sorbate, soil scientists have adopted the use of the Langmuir isotherm. The Langmuir isotherm was originally developed to describe monolayer adsorption of gases onto solids. When it was adapted for adsorption from a liquid to a solid, it retained two

useful parameters which were the maximum adsorption capacity, S_{max}, and a constant, b, related to the binding energy. The following are Langmuir equations for the adsorption of a single ion, more than one ion, and several ions on two different sites.

(4) $S = (S_{max}\ b\ C) / (1 + b\ C)$

        S = adsorbate on surface   C = adsorbate in solution

(5) $S = (S_{max}\ b_1\ C_1) / (1 + b_1\ C_1 + b_2\ C_2)$

(6) $S = (S_{max1}\ b_{11}\ C_1) / (1 + b_{11}\ C_1 + b_{12}\ C_2)$

                                        (site 1)

        $+ (S_{max2}\ b_{21}\ C_1) / (1 + b_{21}\ C_1 + b_{22}\ C_2)$

                                        (site 2)

        b_{ij} = binding constant for sorbate j on site i

        C_j = concentration of sorbate j in solution

        S_i = sorption capacity for site i

The Langmuir equation has the advantage of giving a maximum sorption capacity which is present on most surfaces, and it gives a constant which represents the adsorption energy. Also the equation can be expanded to account for competition from other ions (5). The adsorption model can also include several adsorption sites with different capacities and binding constants (6).

The Freundlich isotherm (7) is an empirical expression which is useful for describing adsorption on multi-site surfaces. If it is assumed that the heat of adsorption decreases exponentially with increased surface coverage then the Freundlich isotherm can be derived from a multi-site Langmuir equation (Kinniburgh and Jackson, 1981). The Freundlich equation has been useful for describing sorption on clays and

some oxides. Unfortunately this isotherm does not have a parameter to express maximum adsorption and at low metal concentrations it does not become linear as predicted by Henry's law. Also, like the distribution coefficient, the Freundlich isotherm is only valid at a given ionic strength and pH.

(7) $S = K \, C^{1/n}$

   K = constant

   n = constant $(n < 1)$

Another method of treating sorption is with a stability constant approach in which solid surfaces are considered to have sites which can complex metal ions. Using this approach these sites can be treated as complexing ligands. If the total weight of surface area of solid is known, for a given volume of solution then the concentration of surface sites can be converted from moles/kg or moles/area to moles/liter. Adsorption can then be described as in the form of conditional stability constants as used in solution chemistry.

(8) $B_i = ([MC_i^{(z-1)}]) \, / \, ([M^{z+}] \, [C^-]^i)$

      or:

(9) $^*B_i = ([MC_i^{(z-1)}] \, [H^+]^i) \, / \, ([M^{z+}] \, [HC]^i)$

   $[C^-]$ = concentration of deprotonated surface sites

   $[HC]$ = concentration of protonated surface sites

   $[MC_i^{(z-1)}]$ = concentration of sorbed metal

The presence of a MC complex implies that the metal only binds to one surface site while in a MC_2 complex the surface metal coverage is low enough and the the surface sites are close enough that each metal can complex two sites. This adsorption formulation is easy to use in

speciation calculations which may want to take into account the presence of suspended particulate matter in a body of water. The constant B_i can be evaluated using similar techniques which are employed in the determination of stability constants with dissolved constituents. Competition for surface sites by hydrogen and other metal ions can also be accounted for. This mathematical expression has similar modeling capabilities to the multi-site Langmuir isotherm.

Most often sorption isotherms of metals on soils and clays are reported as either distribution coefficients, Langmuir equations, or Freundlich expressions. Distribution coefficients have been used to describe the sorption of Cs, Zn, Co, and Ru by marine sediments (Aston, 1973) and the adsorption of Cu on clays from Cu solutions of less than 4 $* 10^{-4}$ moles/liter (McLaren, 1981). Inskeep and Baham (1983) found that Cd and Cu sorption on montmorillonite could be described by either a distribution coefficient or a Freundlich isotherm. O'Connor and Connolly (1980) discuss the effect of experimental solid/liquid ratios on the distribution coefficients of various metals and organics. The Freundlich isotherm has been used to describe Cu sorption on clays (Hedemann, 1959) and Cd adsorption on montmorillonite (Garcia-Miragaya, 1976). McLaren found that when clays were exposed to relatively high levels of Cu (up to $1.6 * 10^{-4}$ moles/liter) sorption followed a Langmuir isotherm. Guy et al. (1974) found that the sorption of Cu, Cd and Zn on bentonite was described by a freundlich isotherm, but that their adsorption on MnO_2 fitted a Langmuir equation. Other examples of Langmuir isotherms are given by Du Plessis (1971) (Cu adsorption on montmorillonite and kaolinite); Ferrel (1978) (Cd on clays); Payne and

Pickering (1975) (Cu and various ligands on clays); Farrah et al. (1980)
(Cu, Cd, Pb, Zn on kaolinite, illite and montmorillonite); Harter (1979)
(Cu on soils); and John (1972) (Cd on soil). Steger (1973) used a
double site, multicomponent Langmuir model to describe Cu adsorption on
bentonite as a function of pH.

The stability constant approach to sorption has found use in
adsorption studies on oxide minerals. Some studies have used this
approach in conjunction with double layer theory to describe cation
sorption on oxide surfaces and the effect of this sorption on surface
charge (Schindler, 1972 and Hohl, 1976). Other models have employed the
Stern layer in which the charge of the potential determining ions has
been reduced by the adsorption of inert electrolyte (Yates et al., 1974;
and Davis, 1977).

APPENDIX 13

DONNAN CALCULATION OF ION DISTRIBUTION BETWEEN A COLLOID AND A SOLUTION

In order to use Donnan theory to calculate ion distribution
between a clay and a free solution one needs to know (1) the cation
exchange capacity of the clay, (2) the clay weight, (3) the water
content of the clay mass, and (4) the salt concentration of the free
solution. To perform this calculation one assumes that all ions are
just point charges, with no volume, hydration energy or any other
specific chemical properties. Therefore, there is no selectivity between
ions of like charge, and in our present experimental system the
following relation is true.

1) $\dfrac{[H^+]_c}{[H^+]_s} = \dfrac{[K^+]_c}{[K^+]_s} = \dfrac{[Cu^{+2}]_c^{\frac{1}{2}}}{[Cu^{+2}]_s^{\frac{1}{2}}} = \dfrac{[NO_3^-]_s}{[NO_3^-]_c}$

The value of these equations can be determined with the help of equation 2, applied to KNO_3.

2) $\dfrac{Z_K + Y_K}{X_K} = \dfrac{X_{NO_3}}{Y_{NO_3}}$

where: Y = salt concentration in interstitial water of the colloid (meq/l)
$\quad\quad$ X = salt concentration of equilibrium solution (meq/l)
$\quad\quad$ Z = concentration of adsorbed potassium ion = m * CEC/v

$\quad$ CEC = cation exchange capacity (meq/g)
$\quad\quad$ m = grams clay
$\quad\quad$ v = volume of interstitial water (l)

Rearranging equation 2 and remembering that X_K equals X_{NO_3}, and that Y_K equals Y_{NO_3}, we have the following equation:

3) $Z_K Y + Y^2 = X^2$

Equation 3 is a quadratic equation in which the constants are:

$\quad$ a = 1
$\quad$ b = Z_K
$\quad$ c = $-X^2$

4) $Y = \dfrac{-b + (b^2 - 4ac)^{\frac{1}{2}}}{2a}$

Once we have the value for Y we can calculate a number for the ratios in equation 1.

5) $\dfrac{[K^+]_c}{[K^+]_s} = \dfrac{(Z_K + Y)}{X} = \dfrac{[Cu^{+2}]_c^{\frac{1}{2}}}{[Cu^{+2}]_s^{\frac{1}{2}}}$

REFERENCES

Ahrland, S.; I. Grentle, and B. Noren (1960),. The ion exchange properties of silica gel. I The sorption of Na^+, Ca^{+2}, Ba^{+2}, VO_2^{+2}, Gd^{+3}, Zr(IV)+, Nb, V(IV) and Pu(IV). Acta Chem. Scand., 14, 1059-1076.

Anderson, B.J. and E.A. Jenne (1970),. Free-iron and manganese oxide content of reference clays. Soil Science, 100, 163-169.

Aston, S.R. and E.K. Duursma (1973),. Concentration effects on Cs, Zn, Co, and Ru sorption by marine sediments with geochemical implications. Netherlands Journal of Sea Research, 6, 225-240.

Babcock, K.L. (1963),. Theory of the chemical properties of soil colloidal systems at equilibrium. Hilgardia, 34, 417-452.

Balistrieri, L.S. and J.W. Murray (1984),. Marine scavenging: Trace metal adsorption by interfacial sediment from MANOP site H. Geochimica et Cosmochimica Acta, 48, 921-930.

Barshad, I. (1954),. Cation exchange in micaceous minerals: II Replaceability of ammonium and potassium from vermiculite, biotite, and montmorillonite. Soil Science, 78, 57-76.

Benson, S.W. (1960),. The Foundations of Chemical Kinetics. McGraw-Hill.

Bilinski, H.; R. Huston and W. Stumm (1976),. Determination of the stability constants of some hydroxo and carbonato complexes of Pb(II), Cu(II), Cd(II) and Zn(II) in dilute solutions by anodic stripping voltammetry and differential pulse polarography. Anal. Chim. Acta, 84, 157-164.

Bingham, F.T.; A.L. Page and J.R. Sims (1964),. Retention of Cu and Zn by H-montmorillonite. Soil Science Society of America Proc., 28, 351-354.

Bird, G.W. (1979),. Geochemistry of radioactive waste disposal. Geoscience Canada, 6, 199-204.

Bolland, M.D.; A.M. Posner and J.P. Quirk (1976),. Surface charge onkaolinites in aqueous suspension. Australian Journal of Soil Research, 14, 197-216.

Bolt, G.H. (1955a),. Ion adsorption by clays. Soil Science. 79, 267-276.

Bolt, G.H. (1955b),. Analysis of the validity of the Gouy-Chapman theory of the electric double layer. Journal of Colloid Science, 10, 206-218.

Bolt, G.H. (1961),. The pressure filtrate of colloid suspensions. I-Theoretical considerations. II-Experimental data on homoionic clays. Kolloid-Z., 175, 33-39, 144-150.

Bower, C.A. (1959),. Cation-exchange equilibria in soils affected by sodium salts. Soil Science, 88, 25-35. .

Brindley, G.W. (1961),. X-ray Identification and Crystal Structures of Clay Minerals. 2nd ed.,. Mineralogical Society, Clay Minerals Group, London.

Bunzl, K.; W. Schmidt and B. Sansoni (1976),. Kinetics of ion exchange in soil matter. IV Adsorption and desorption of Pb(II), Cu(II), Cd(II), Zn(II), Ca(II) by peat. Journal of Soil Science, 27, 32-41. .

Calvet, R. and R. Prost (1971). Cation migration into empty octahedral sites and surface properties of clays. Clays and Clay Minerals, 19, 175-186. .

Cameron, D.R. and A. Klute (1977),. Convective-dispersive solute transport with a combined equilibrium and kinetic adsorption model. Water Resour. Res., 13, 183-188. .

Christensen, H.R. and S. Touborg-Jensen (1923),. Untersuchengen bezuglich elektametrischen methoden. Intern. Mitteilungen fur Bodenkunde, 13, 12 .

Davis, J.A. (1977),. Adsorption of trace metals and complexing ligands at the oxide/water interface. Ph.D. Thesis, Stanford University.

Davis, J.A.; R.O. James and J.O. Leckie (1978),. Surface ionization and complexation of the oxide/water interface I: Computation of electrical double layer properties in simple electrolytes. Journal of Colloid and Interface Science, 63, 480-499.

Dayal, R. and R.J. Wilke (1981),. Role of clay minerals as backfill in radioactive waste disposal. In International Clay Conference, 1981, (eds. H. Van Olphen and F. Veniale), Elsevier Scientific Publishing Co..

Deer, W.A.; R.A. Howie and J. Zussmann (1962),. Rock Forming Minerals. 3,. Longmans, London.

4

Devore, G.W. (1963),. Compositions of silicate surfaces and surface phenomena. Contributions to Geology, 2,21-37.

Dixon, J.B. and S.B. Weed (1977),. Minerals in Soil Environments. Soil Science Society of America.

Dugger, D.L.; J.H. Stanton; B.N. Irby; B.L. McConnell; W.W. Cummings and R.W. Mautman (1964),. The exchange of twenty metal ions with the weakly acidic silanol group of silica gel. Journal of Physical Chemistry, 68, 757-760.

Duplessis, S.F. and R.D.T. Burger (1971),. Die Spesifiekts adsorpsie van koper deur kleiminerale en grandfraksies. Agrochemophysica,. 3, 1-10.

Eberl, D.D. (1980),. Alkali cation selectivity and fixation by clay minerals. Clays and Clay Minerals, 28, 161-172.

Edwards, J.O. (1965),. Inorganic Reaction Mechanisms: An Introduction.. W.A. Benjamin.

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

El-Sayed, M.H.; R.G. Burau and K.B. Babcock (1970). Thermodynamics of copper(II)-calcium exchange on bentonite clay. Soil Science Society of America Proc., 34, 397-400.

Elgabaly, M.M. (1950),. Mechanism of zinc fixation by colloidal clays and related minerals. Soil Science, 69, 167-174.

Enfield, C.G. (1974),. Rate of phosphorus sorption by five Oklahoma soils. Soil Science Science Society of America Proc., 38, 404-407.

Erikson, E. (1952),. Cation-exchange equilibria on clay minerals. Soil Science, 74, 103-113.

Farrah, H. and W.F. Pickering (1976a),. Sorption of copper species by clays. I Kaolinite. Australian Journal of Chemistry, 29, 1167-1176.

Farrah, H. and W.F. Pickering (1976b),. The sorption of copper species by clays. II Illite and montmorillonite. Australian Journal of Chemistry, 29, 1167-1176.

Farrah, H. and W. F. Pickering (1977a),. Influence of clay-solute interactions on aqueous heavy metal ion levels. Water, Air and Soil Pollution, 8, 189-197.

Farrah, H. and ·W.F. Pickering (1977b),. Sorption of lead and cadmium species by clay minerals. Australian Journal of Chemistry, 30, 1417-1422.

Farrah, H. and W.F. Pickering (1978),. Extraction of heavy metal ions sorbed on clays. Water, Air, and Soil Pollution, 9, 491-498.

Farrah, H. and W.F. Pickering (1979),. pH effects in the adsorption of heavy metal ions by clays. Chemical Geology,. 25, 317-326

Farrah, H; D. Halton, and W.F. Pickering (1980),. The affinity of metal ions for clay surfaces. Chemical Geology, 28, 55-68.

Fava, A. and E. Eyring (1956),. Equilibrium and kinetics of detergent adsorption. A generalized equilibration theory. Journal of Physical Chemistry, 60, 890-898.

Ferrell, R.E. Jr. and C.A. Price (1978),. An experimental study of Cd ion exchangeability. Clays and Clay Minerals, 26, 41-44.

Ferris, A.P. and W.B. Jepson (1975),. The exchange capacities of
kaolinite and the preparation of homoionic clays. Journal of
Colloid and Interface Science, 51, 245-259.

Flegmann, A.W. ;J.W. Goodwin and R.H. Ottewill (1969);. Rheological
studies on kaolinite suspensions. Proc. of the British Ceramic
Society, 13, 31-45...

Follett, E.A.C. (1965),. The retention of amorphous, colloidal ferric
hydroxide by kaolinites. Journal of Soil Science, 16, 334-341.

Forbes, E.A.; A..M. Posner and J.P. Quirk (1976),. The specific
adsorption of divalent Cd, Co, Cu, Pb and Zn on goethite.
Journal of Soil Science, 27, 154-163.

Fordham, A.W. (1969),. Sorption and precipitation of iron on kaolinite.
I Factors involved in sorption equilibria. Australian Journal of
Soil Science, 7, 185-189.

Fordham, A.W. (1970),. Sorption and precipitation of iron oxides on
kaolinite. III The solubility of iron(III) hydroxides
precipitated in the presence of kaolinite. Australian Journal
Soil Research, 8, 107-122.

Fruh, E.G. and G.F. Lee (1967),. Sorption of cesium on stratified mica.
In Principles and Applications of Water Chemistry. (eds. S.D.
Faust and J.V. Hunter), John Wiley and Sons Inc.

Frydman, M.; Nilsson, G.; T. Rengemo and L.G. Sillen (1958),. III The
acidity constants of H_2CO_3 and H_2SO_3, and $CaCo_{34}$ +
$CaSO_3$. Equilibria in $NaClO_4$ medium at 25°C. Acta Chemica
Scandinavica, 12, 878

Gadde, R.R. and H.A. Laitinen (1974),. Studies of heavy metal adsorption by hydrous iron and manganese oxides. Analytical Chemistry, 46, 2022-2026.

Gaines and Thomas (1953),. Adsorption studies on clay material: II A formulation of the thermodynamics of exchange adsorption. Journal of Physical Chemistry, 23, 2322-2326.

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 Science Society of America Journal, 40, 658-663.

Gast, R.G. (1977),. Surface and colloid chemistry. In Minerals in Soil Environments (eds. J.B. Dixon and S.B. Weed), Soil Science Society of America.

Griffin, R.A. and R.G. Burau (1974),. Kinetic and equilibrium studies of boron desorption from soil. Journal Soil Science Society of America (Proc.), 38, 892-897.

Grim, R.E. (1968),. Clay Mineralogy. (2nd ed.),. McGraw-Hill.

Grimme, H. (1968),. Absorption of manganese, cobalt, copper, and zinc-dilute solutions by goethite. Z. Planzenernahr Bodente, 121, 58-65.

Guy, R.D., C.L. Chakrabarti, and L.L. Schramm (1974),. The application of a simple chemical model of natural waters to metal fixation in particulate matter. Canadian Journal of Chemistry, 53, 661-669.

Harter, R.d. and R.G. Lehman (1983),. Use of Kinetics for the study of exchange reactions in soils. Soil Science Society of America Journal, 47, 666-669.

Harter, R. (1979),. Adsorption of copper and lead by A and B horizons of several Northeastern United States Soils. Soil Science Society of America Journal, 43, 679-683.

Heydemann, (1959),. Adsorption aus sehr verdunnlen kupferlosungen an reinen tonmineralen. Geochimica et Cosmochimica Acta, 15, 305-329.

Hodgson, J.F. (1960),. Cobalt reactions with montmorillonite. Soil Science Society Proc., 29, 165-168.

Hohl, H. and W. Stumm (1976),. Interaction of Pb(II) with hydrous Al_2O_3. Journal of Colloid and Interface Science, 55, 281-288.

Inskeep, W.P. and J. Baham (1983),. Adsorption of Cd(II) and Cu(II) by Na-montmorillonite at low surface coverage. Soil Science Society of America Journal, 47, 660-665.

Jackson, M.L. and C.H. Lim (1982),. The role of clay minerals in environmental Science. In International Clay Conference, 1981, (eds H. Van Olphen and F. Veniale), Elsevier Scientific Pub. Co.

James, R.O. and T.W. Healy (1972),. Adsorption of hydrolyzable metal ions ot the oxide-water interface. Journal of Colloid and Interface Science, 40, 65-81.

Jenne, E.A. (1977). Trace element adsorption by sediments and soils: sites and processes. In Molybdenum in the Environment, V2 (eds. W.R. Chappell and K.K. Peterson), Marcel Dekker Inc..

Jenny, H.; T.R. Nielsen; N.T. Coleman and D.E. Williams (1950),. Concerning the measurement of pH, ion activities and membrane potentials in colloid systems. Science, 112, 164-167.

John, M.K. (1972),. Cadmium adsorption maxima of soils as measured by the Langmuir isotherm. Canadian Journal of Soil Science, 52, 343-350.

Keay, J. and A. Wild (1961),. The kinetics of cation exchange in vermiculite. Soil Science, 92, 54-60.

Kerr, P.F.; P.K. Hamilton; R.J. Pill; G.V. Wheeler, D.R. Lewis; W. Burkhart; D. Reno; G.L. Taylor; R.C. Mietnz; M.E. King and N.C. Schictz (1950), Analytical data on reference clay materials. API Project 49, Report 7,. Columbia University.

Kinniburgh, D.D. (1983),. The H/M exchange stoichiometry of calcium and zinc adsorption by ferrihydrite. Journal of Soil Science, 34, 759-768.

Kurbatov, M.H. (1949),. Rate of adsorption of barium ions in extreme dilution, by ferric oxide. Journal of the American Chemical Society, 71, 858-863.

Kurbatov, M.H.; G.B.Wood and J.D. Kurbatov (1951),. Isothermal adsorption of cobalt from dilute solutions. Journal of Physical Chemistry, 55, 1170-1182.

Laidler, K.J. (1950). Chemical Kinetics.. McGraw-Hill.

Langston, R.B. and J.A. Pask (1969),. The nature of anauxite. Clays and Clay Minerals, 16, 425-436.

Li, Y.; L. Burkhardt; M. Buchholtz, P. O'Hara and P.H. Santschi (1984), Partition of radiotracers between suspended particles and sea water. Geochimica et Cosmochimica Acta, 48, 2011-2019.

Lim, C.H.; M.L. Jackson; R.D. Koons and P.A. Helmke (1980),. Kaolins: sources of differences in cation exchange capacities and cesium retention. Clays and Clay Minerals, 28, 223-229.

Maes, A. and A. Cremers (1975),. Cation exchange hysteresis in montmorillonite - a pH-dependent effect. Soil Science, 119, 198-202.

Malcolm, R.L. and V.C. Kennedy (1969),. Rate of cation exchange on clay minerals as determined by specific ion electrode techniques. Soil Science Society of America, Proceedings. 33, 247-253.

Marshall, C.E. (1953),. Free energy in cation interchange as illustrated by plant root-substrate relationships. Journal of Physical Chemistry, 57, 618-621.

Marshall, C.E. (1964),. The Physical Chemistry and Mineralogy of Soils. V1 Soil Minerals.. John Wiley and Sons Inc..

McBride, M.B. (1976a),. Exchange and hydration properties of Cu on mixed-ion Na-Cu smectites. Soil Science Society of America Journal, 40, 452-456.

McBride, M.B. (1976b),. Origin and position of exchange sites in kaolinite: an ESR study. Clays and Clay Minerals, 24, 88-92.

McBride, M.B. (1982),. Cu(II) adsorption characteristics of aluminum hydroxide and oxyhydroxides. Clays and Clay Minerals, 30, 21-28.

McBride, M.B. and M.M. Mortland (1974),. Copper II interactions with
montmorillonite: evidence from physical methods. Soil Science
Society of America Proc., 38, 408-415.

McBride, M.B. and P.R. Bloom (1977),. Adsorption of aluminum by a
smectite. II An Al(III)-Ca(II) exchange model. Soil Science
Society of America Journal, 41, 1073-1077.

McBride, M.B.; A.R. Fraser and W.J. McHardy (1984),. Cu(II) interaction
with microcrystalline gibbsite. Evidence for orientated
chemisorbed copper ions. Clays and Clay minerals, 32, 12-18.

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

McLaren, R.G. and D.V. Crawford (1973),. Studies on soil copper(II).
The specific adsorption of copper by soils. Journal of Soil
Science, 24, 443-452.

McLaren R.G.; R.S. Swift and J.G. Williams (1981),. The adsorption of
copper by soil materials at low equilibrium solution
concentrations. Jour. of Soil Science, 32, 247-256.

Morel, F.M.M.; J.G. Yeasted and J.C. Westall (1981),. Adsorption
models: A mathematical analysis in the framework of general
equilibrium calculations. In Adsorption of Inorganics at
Solid-Liquid Interfaces. (eds. M.C. Anderson and A.J. Rubin), Ann
Aarbor Science.

Morgan, J.J. and W. Stumm (1964),. Colloid chemical properties of
manganese dioxide. Jour. Colloid Science, 19, 347-359.

Nakagawa, G.; H. Wada and T. Hayakawa (1975),. Use of the
copper(II)-selective electrode for the determination of the
stability constants of copper II complexes. Bull. Chem. Soc.
Japan, 48, 424-427.

Nelson, J.L. and S.W. Melsted (1955),. The chemistry of zinc added to
soil and clays. Soil Science Society of America Proc., 19,
439-443.

O'Connor, T.P. and D.R. Kester (1975),. Adsorption of copper and cobalt
from fresh and marine systems. Geochimica et Cosmochimica Acta,
39, 1531-1543.

O'Connor, D.J. and J.P. Connolly (1980),. The effect of concentration
of adsorbing solids on the partition coefficient. Water
Research, 14, 1517-1523.

Ohzeki, K.; M. Saruhashi and T. Kambara (1980),. Use of copper(II)
ion-selective electrode for the determination of the stability
constant of binuclear copper(II) complex with
3,6-dioxaoctane-1,8-diamine-N,N,N, N'-tetraacetric acid. Bull.
Chem. Soc. Japan, 53, 2548-2551.

Ostrom, M. E. (1961),. Separation of clay minerals from carbonate rocks
by using acid. Jour. Sed. Petrol., 31, 123-129.

Overbeek, J.T.G. (1953),. Donnan-emf and suspension effect. Journal of
Colloid Science, 8, 593-605.

Pallmann, H. (1930). Die Wasserstaffaktivitat in dispersionen und.
kalloiddispersen systemen. Kolloid-chemische Beihefte, 30, 334

Pannetier, G. and P. Souchay (1967),. Chemical Kinetics.. Elsevier.

Parfitt, R.L. (1978),. Anion adsorption by soils and soil materials. Adv. Agron., 30, 1-50.

Parks, G.A. (1967),. Aqueous surface chemistry of oxides and complex oxide minerals. Isoelectric point and zero point of charge. In Adv. in Chem. Series 67, 121-160, (ed. R.F. Gould).

Parks, G.A. (1975),. Adsorption in the marine environment. In Chemical Oceanography (eds J.P. Riley and G.Skarrow),. 1, 2nd ed, Academic Press.

Paulson, A.J. and D.R. Kester (1980),. Copper(II) ion hydrolysis in aqueous solution. Journal Solution Chemistry, 9, 269-278.

Payne, K. and W.F. Pickering (1975),. Influence of clay-solute interactions on aqueous copper ion levels. Water, Air, and Soil Pollution, 5, 63-69.

Peech, M.; R.A. Olsen and G.H. Bolt (1953),. The significance of potentiometric measurements involving liquid junction in clay and soil suspensions. Soil Science Society of America Proc., 17, 214-222.

Perrin, D.D. (1960),. The hydrolysis of copper II ion. Journal of the Chemical Society, Part 3, 3189-3196.

Pratt, P.F. and F.L. Blair (1962),. Cation exchange properties of some acid soils of California. Hilgardia, 33, 689-706.

Radoslovich, E.W. and K. Norrish (1962),. The cell dimensions and symmetry of layer-lattice silicates. I Some structural considerations. American Mineralogist, 47, 599-616.

Reddy, M.R. and Perkins, H.F. (1974),. Fixation of zinc by clay minerals,. Soil Science Society of America Proc., 38, 229-231.

Roginsky, S.Z. and Z. Zeldovich (1934),. Die Katakytische oxidation von
kohlenmonoxyd auf mangandioxyd. Acta Physicochim. U.R.S.S., $\underline{1}$,
554-594.

Rophael, M.W. and M.A. Malati (1972),. Characterization of manganese
dioxides. I The rate and activation energy of adsorption of
calcium ions by B-manganese dioxide. Chemistry and Industry,
768-769.

Saar, R.A. and J.H. Weber (1980),. Comparison of spectrofluorometry and
ion-selective electrode potentiometry for determination of
complexes between fulvic acid and heavy-metal ions. Analytical
Chemistry, $\underline{52}$, 2095-2100.

Sanchez, A.L.; T.H. Sibley; E.A. Wurtz and W.R. Shell (1982),.
Distribution coefficients for radionuclides in aquatic
environments. NUREG/CR-1853, U.S. NRC, Washington, D.C..

Schindler, P. (1967);. Heterogeneous equilibria involving oxides,
hydroxides, carbonates and hydroxide carbonates. In Equilibrium
Concepts in Natural Water Systems. Advances in Chemistry Series,
No. 67. American Chemical Society, Washington , D.C..

Schindler, P.W. and H. Gamsjager (1972),. Acid-base-reactions of the
TiO_2(anatase)-water interface and the point of zero charge of
TiO_2 suspensions. Kolloid-Z. U.Z. Polymere, 250, 759-763.

Schindler, P.W.; B. Fuerst; P.V. Wolf and R. Dick (1976),. Ligand
properties of surface silanol groups. (1) Surface complex
formation with Fe(III), Cu(II), Cd(II) and Pb(II). Journal of
Colloid and Interface Science, $\underline{55}$, 469-475.

Selim, H.M.; J.M. Davidson and R.S. Mansell (1976),. Evaluation of a
2-site adsorption-desorption model for describing solute
transport in soils. In Proc. 1976 Summer Computer Simulation
Conf., Washington, D.C., 12-14, July 1976. Simulation Councils,
Inc., La Jolla,+Calif., p 444-448.

Shainberg, I. (1973),. Rate and mechanism of Na-montmorillonite
hydrolysis in suspensions. Soil Science Society of America
Proc., 37, 689-694.

Singhal, J.P. and G.K. Gupta (1978),. Reactions of zinc with acid and
base saturated dickites. Clays and Clay Minerals, 26, 365-371.

Smith, R.M. and A.E. Martell (1976),. Critical Stability Constants..
Plenum.

Steger, H.F. (1973),. On the mechanism of the adsorption of trace
copper by bentonite. Clays and Clay Minerals,. 21, 429-436.

Stern, O. (1924),. Zur theorie der elecktrolytischen doppelschict. Z.
Electrochem., 30, 508-516.

Stumm, W. and J.J. Morgan (1981),. Aquatic Chemistry. 2nd ed.,. John
Wiley and Sons.

Sykes, A.G. (1966),. Kinetics of Inorganic Reactions.. Pergamon.

Tiller, K.G. (1967),. Silicic acid and the reaction of zinc with clays.
Nature, 214, 852

Tiller, K.G. and J.F. Hodgson (1960),. The specific sorption of cobalt
and zinc by layer silicates. Clays and Clay Minerals, 9,
393-403.

Travis, C.C. and E.L. Etnier (1981),. A survey of sorption relationships for reactive solutes in soils. Jour. Environ. Qual., 10, 8-17.

van Olphen, H. (1977),. An Introduction to Clay Colloid Chemistry. 2nd ed.,. John Wiley and Sons.

van Raij, B. and M. Peech (1972),. Electrochemical properties of some oxisols and alfisols of the tropics. Soil Science, 36, 587-593.

Vermeulen, T. and N.K. Heister (1973),. Adsorption and ion exchange. In Chemical Engineers Handbook, 5th ed. (eds. R.H. Perry and C.H. Chilton), McGraw-Hill.

Walker, G.F. (1963),. The cation exchange reaction in vermiculite. International Clay Conference Proc., 177-181.

Way, J.T. (1852),. On the power of soils to adsorb manure. Jour Roy. Agr. Soc. Eng.,. 13, 123-143.

Wayman, H.C. (1967),. Adsorption on clays. In Principles and Applications of Water Chemistry. (eds. S.D. Faust and J.V. Hunter), John Wiley and Sons Inc.

Wiegner, G. (1931),. Some physico-chemical properties of clays. II Hydrogen clay. Jour. Soc. Chem. Ind., 103, T

Wilson, B.D. (1980),. Clay conversion reactions for immobilization of special radionuclides. Atomic Energy of Canada Limited technical record TR-105.