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DESORPTION OF COPPER FROM ILLITE CLAY USING A CHELATING RESIN ENCAPSULATED BETWEEN POROUS MEMBRANES

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University of New Hampshire   PH.D.   1980

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DESORPTION OF COPPER FROM ILLITE CLAY

USING A CHELATING RESIN

ENCAPSULATED BETWEEN POROUS MEMBRANES

By

JOHN L. PLUDE

B. S. (Chemistry), University of Connecticut, 1975

A DISSERTATION

Submitted to the University of New Hampshire

in Partial Fulfillment of

the Requirements for the Degree of

Doctor of Philosophy

Graduate School

Department of Chemistry

September 1980

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Date July 30, 1980

This thesis is dedicated to my wife, Patty, and to my parents.

Acknowledgements

I wish to express my gratitude to the members of my dissertation committee who have been a continual source of guidance, knowledge, and inspiration. Special thanks are extended to Dr. C. L. Grant whose professionalism in research and academic matters will always be a model to emulate.

I wish to thank the Center for Institutional and Industrial Development (CIID) for the use of equipment and lab space.

Finally, the author is indebted to his wife, Patty, whose inspiration, personal sacrifices, understanding and love, made it all possible.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

Abstract

DESORPTION OF COPPER FROM ILLITE CLAY

USING A CHELATING RESIN

ENCAPSULATED BETWEEN POROUS MEMBRANES

by

John L. Plude

University of New Hampshire, Sept. 1980

Toxicity studies have established the need for
information concerning species distribution of heavy metals
in the environment. In aquatic environments, the nature of
trace metals, whether free, adsorbed, or complexed controls
impact on biota. Often, major portions of the trace metals
present in an aquatic system are immobilized on suspended
particulates. Changes in environmental conditions such as
pH, soluble ligand concentration and type, and concentration
of suspended particulate material in the water column, can
affect speciation of a metal. Filter feeding organisms are
especially susceptable to these environmental changes. High
bioconcentrations of trace metal species which are available

to organisms can retard growth or cause mortality as well as posing a hazard to human ingestion.

In an attempt to investigate the bioavailability of particulate-bound metals under varying environmental conditions, we have developed a syringe drive system employing a membrane sandwiched chelating resin. The device consists of a cassette containing 100 mg of Chelex-100 sandwiched between two 0.40 um Polycarbonate membranes. While the device is similar to the one described by Kerfoot and Vaccaro (1975), it has been modified from a passive system dependent upon diffusional processes to an active mode in which a syringe draws solution through the cassette and then expels it to the bulk solution. Free metal ions, metal complexes in solution, and some particulates which are smaller than 0.40 um pass the membrane and are retained in the cassette. The construction allows a great deal of versatility in choice of membranes, their porosity, and the chelating resin used. The exchange rate with the primary solution may also be varied within a large range by appropriate selection of the step-function speed reducer connected to the drive motor. This versatility enables the experimenter to match the performance of the device to his needs.

Early experiments with pure copper nitrate solutions established the reproducibility and effectiveness of the method as a trace metal scavenging technique. Mathematical

simulation results were matched closely by experimental data obtained with atomic absorption spectrometry. To study the release characteristics of trace metals, illite clay was "contaminated" with known amounts of trace metals and suspended in aqueous solutions. Continuous agitation was provided. As the cassette removes metal from solution, the clay is driven by equilibrium considerations to desorb more metal ions to the system. In numerous trials, it has been possible to achieve mass balance for metal collected in the cassette compared to metal lost by the clay. The desorption curves generated at various pH levels show features which can be interpreted to yield speciation characteristics of the solutions. Ion selective electrode work in conjunction with atomic absorption spectrometry has aided in elucidating the ratio of free to total trace metal content of the solutions. Results from this research may be utilized in predicting the impact of the changes in environmental variables such as pH and the disposal of metal-rich wastes.

CHAPTER I

AN OVERVIEW OF TRACE ELEMENT
SPECIATION IN THE AQUATIC ENVIRONMENT

Trace metal imputs to aquatic systems, both natural and anthropogenic, are generally concentrated in the sediments. However, this does not mean that they are permanently immobilized. Inorganic and organic particulates in sediments and in the water column are ingested by a variety of aquatic organisms. The specific forms of soluble and particulate-bound elements influence metal bioavailability and distribution within the system. It is, therefore, important to identify the major trace element sinks in sediments, determine the quantity of trace elements in each sink, determine the speciation characteristics of the elements in the sinks, and develop chemical techniques for estimation of bioavailability. This thesis is primarily concerned with the latter two points.

Diagenetic processes may affect the availability of solid forms of trace elements. As minerals are altered,

binding characteristics change and, therefore, trace metal

availability changes. Equilibrium concentrations in

solution are related to the concentration of trace element

present in each sink, the quantity of each sink present,

particle size distribution, and the reactivity of the trace

element in the solute phase. Luoma and Jenne (1977) found

that equilibrium solution concentrations are strongly

influenced by the dominant trace-element sink.

The availability of trace elements to aquatic organisms
may be influenced by at least four factors:

1. The physiological characteristics of the organism,

2. The forms of dissolved trace elements,

3. The forms of trace elements associated with particulate
   solids, and

4. The chemical and physical characteristics of the water
   column.

Bioavailability (and toxicity) of dissolved trace

elements depends on the chemical forms of the elements.

Compared to organic and inorganic complexes in natural

waters, the free hydrated (aquo) forms are of highest

toxilogical significance. Inorganic

speciation significantly influences bioavailability of

solute [1] trace elements in natural waters. For example,

----

[1] Solute complexes is a term employed by many reseachers
in aquatic chemistry. It refers to molecular or colloidal
species which are able to pass a 0.45 um filter.

Stiff (1971) showed decreased trace element toxicity in fresh water as water hardness increased. The results of studies conducted by Pagenkopf, et al. (1974) suggested that the formation of inorganic solute complexes was the most important factor in reducing copper toxicity in hard waters. Physicochemical factors that influence the bioavailability of trace elements in such waters include (1) precipitation of insoluble hydroxides, carbonates and hydroxy carbonates, (2) the formation of inorganic solute complexes with carbonate, hydroxide, phosphate or sulfate and (3) competing effects of alkali and alkaline earth cations for particulate adsorption sites.

The extent to which organic complexation of trace elements occurs in natural waters and its effect on the bioavailability of trace elements is still inadequately understood. Organic complexation is usually associated with reduced availability of solute forms of trace elements. In one study the toxicity of copper to algae was investigated and increased in the order copper EDTA $>$ copper citrate $>$ Cu^{2+} (Lee 1973). Immobilization of organic complexes on particulates in the water column has been studied (van den Berg and Kramer 1979, Davis and Leckie 1978), and modeled (Bhatty et al. 1978). Organic complexation of solute trace elements may enhance their availability to biota (DeKock and Mitchell 1957, Lindberg and Harriss 1974). Increased trace-element uptake through organic complexation could result from:

1. A decrease in rate and extent of trace-element sorption
    by sediments due to competition,

2. Solubilization of solid forms of trace elements in soils
    and sediments, and

3. Formation of physiologically active complexes.

More work and basic data is needed in all of these areas.

Very few studies have attempted to determine the
influence of different physicochemical forms on the
bioavailability of solid species of trace elements to biota.
Desorption studies of trace elements from natural and
synthetic sediments have indicated that the process is
accelerated by reduced pH and chlorosity and possibly by an
increase in dissolved organic substances present in the
water (Wolfe and Coburn, Jr. 1970, Feick, et al. 1972).

An experimental assessment of trace-element
bioavailability from sediment and particulate-bound sources
is difficult because it is necessary to separate uptake from
dissolved forms. Since organisms are in contact with both
solution and particles simultaneously, this distinction is
not easily achieved. In general, dissolved species are more
efficiently assimilated by biota than are particulate-bound
species. However, the concentration of the bound species is
usually very large relative to the concentration of
dissolved species, and, therefore, of equal or greater
importance.

It is the purpose of this thesis to investigate and relate trace element release from particulate-bound sources to environmental parameters important in natural water systems. The approach has consisted of studies using model "contaminated" clay samples and a syringe drive system employing a membrane-sandwiched chelating resin. The device can be used under conditions similar to those found during dredge or waste disposal operations, or during storm events, i.e., high suspended particulate concentrations in the water.

CHAPTER II

LITERATURE REVIEW

Introduction

A comprehensive study of the fate of a trace metal in the aquatic environment requires a knowledge of the chemical forms which the element may assume and the degree of mobility these forms possess in the environment. The interrelationships of these trace metal properties can be useful in interpreting data from natural water studies. Knowledge of the behavior of a trace element in differing chemical environments may allow predictions of probable chemical speciation.

Trace metals in the aquatic environment are subdivided into two general categories; a "soluble" trace metal fraction and those sorbed upon or contained within particulates. "Soluble species" have been defined as those which are able to pass a 0.45 um membrane filter. The particulate fraction is retained upon the membrane. This

operational definition is of minimal use in determining the chemical form of the element in question because the filter operates by physical size separation. Sorption of chemical species by the filter membrane must also be considered (Truitt 1980). A complete description may be accomplished by a more careful study of inorganic and organic complexation, adsorption, desorption, and precipitation processes occurring in the aquatic environment.

The general equilibria which control trace element behavior in aquatic systems can be expressed as:

$$MeL \rightleftharpoons Me^{n+} + L^{n-} \qquad (1)$$
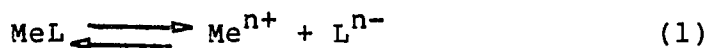
for metal ligand interactions in the solute phase, and:

$$Clay-Me \rightleftharpoons Clay^{n-} + Me^{+} \qquad (2)$$

for metal particulate interactions. The greatest difficulty in examining trace element behavior in aquatic systems is the dynamic character of these equilbria. Any experimental method which removes a soluble specie for analysis perturbs the soluble versus bound trace element distribution of the sample. Such shifts in equilibria greatly complicate experimental measurements. A variety of approaches have been taken in order to determine the extent and effect of these general equilibria on trace metal speciation.

Soluble Species

Elucidation of the chemical species present in the dissolved fraction can be grouped under three broad headings.

Theoretical methods. Sylva (1976) approached the problem of copper speciation in aquatic systems by employing theoretical considerations. Assumptions were made of a typical composition of fresh water and those equilibria of major importance in speciation. From these it was predicted that the processes of hydrolysis, precipitation, complexation, and adsorption would reduce the free copper(II) concentration to extremely low levels, even in the presence of relatively large concentrations of total copper. Other investigators have also employed this approach using different assumed water composition or values for equilibrium constants (Perrin and Sayce 1967, Zirino and Yamamoto 1972, Garrels and Thompson 1962).

A major deficiency in the treatment of trace metal speciation via theoretical calculations is the inability to account for the presence of organo-metallic complexes. Although general predictions of the effects of organic matter on speciation may be presented (Sylva 1976), the paucity of stability and ionization constants for organo-metallic complexes remains a major problem. The role of organic complexing agents in the aquatic environment is important (Siegel 1971, Giesy et al. 1977, Foster and Morris

1971, van den Berg and Kramer 1979, Steelink 1977).

The most widely used model for organic complexation is
the one by Morel and Morgan (1972). They have applied the
chemical equilibrium approach which solves a set of
nonlinear equations that result from mass law and mole
balance equations. Their work has been formatted in Fortran
and is applicable to systems containing thousands of
species. However, the method is limited by inability to
account for changes in ionic strength and
oxidation-reduction processes.

Direct measurements. Electrochemical techniques can be
utilized directly to distinguish certain chemical species in
natural waters. Ion selective electrodes have been used
extensively. The electrodes are selective for the elements
incorporated in the sensing membrane. Detection capability
is dependent upon the activity of ionic species present.
The copper ion selective electrode has been applied to
distinguish between free and bound cupric ion (Midgley 1976,
Hansen et al. 1972, Smith and Manahan 1973, Chau and
Lum-Shu-Chan 1974, Bresnahan, 1977). It has been used in a
wide variety of waters including marine (Hulaniki et
al. 1977), fresh water (Stella and Ganzerli-Valentini 1979),
and simulated fresh water (Javinski et al. 1974).
Unfortunately the analyses are not straight-forward. This
is in part due to their detection limit of approximately
10^{-7} M and their slow response time (Blaedel and Dinwiddie

1974). The detection limit can be extended to lower concentrations by the addition of complexing agents to samples (Stella and Ganzerli-Valentini 1979) to mask membrane interferences which arise as the solubility product of the electrode sensing element is approached. However, such additions are undesirable when studying natural water. Despite these drawbacks, ion selective electrodes presently represent one of the best methods to study complexation and to estimate formation constants in systems of defined composition.

Anodic stripping voltammetry (ASV) has received much attention because of its great sensitivity for several metals of environmental concern. ASV does not measure total metal concentrations, but detects some fraction of the soluble metal species. In a given environmental sample this may include the free (hydrated) ion, and part or all of the inorganic complexes, such as chloro, hydroxo, and carbonate species, and various organic complexes. The dependency of ASV on metal speciation has led to its application to studies of in situ metal-ligand interactions. One approach compares ASV measurements (i.e. peak current, i_p) on untreated samples versus ion content at a low pH where organic complexes are assumed to be dissociated. The difference in these values is attributed to non-reducible (organic) complexes. Chau and Lum-Shue-Chan (1974), and, Florence and Batley (1976) have used the less specific terms "labile" and "non-labile" complexes for similar

measurements.

Speciation studies using this technique are unable to account for the presence of colloidal species and surface active substances in the solution which can coat the mercury electrode, thereby decreasing metal deposition (Florence and Batley 1976, Brezonik et al. 1976, Ernst et al. 1975). Coating of the electrode may, in some cases, also be pH dependent, further confusing interpretation of ASV data (Brezonik et al. 1976). Finally, there exists the possibility of shifts in equilibria during the time frame for the plating step.

Batley and Florence (1976) proposed a scheme based on conventional labile:bound discrimination using ASV but combined with additional sample treatment. The scheme employs a discrimination of species in the labile and non-labile fractions using the chelating resin, Chelex-100 (Biorad). The resin contains iminodiacetic acid functional groups which strongly bind certain metals and metal species. Results indicated metal species in seawater predominately as metal adsorbed on organic colloids. The presence of 0.1-0.5 um organic matter in seawater passed through a 0.45 um membrane filter has been demonstrated (Ogura 1970). Earlier workers had assumed that most of the ASV labile metal in seawater was present in the form of inorganic complexes (Chau and Lum-Shue-Chan 1974). Although this approach appears to represent a significant advance in speciation

methodology, it suffers from the disadvantage that the ASV measurements are made using conditions which may cause shifts of the species distributions from those present in the original samples. Consequently, extrapolations of the laboratory results to field situations are suspect (Skogerboe et al. 1980).

Shifts in half-wave potentials with changes in pH have also been studied to determine metal-ligand stability constants in synthetic solutions and natural waters (Nurnberg 1978). It seems doubtful that this approach will find broad application to natural aquatic systems, however, due to low natural metal concentrations and problems with the presence of surface active agents.

Separation methods with and without chemical pretreatment. The separation methods discussed here include dialysis, solvent extraction, ultrafiltration, gel filtration, ion exchange, and centrifugation. These techniques have been applied to speciation studies in natural waters singly and in combination.

Dialysis consists of immersing a semi-permeable membrane containing pure water directly into a natural water system. Only those molecules and ions smaller than the diameter of the "pores" of the membrane can pass into the dialysis cell. The process is diffusion controlled and proceeds until the concentration of the ions within the cell equals that outside. This type of monitoring is stated to

measure the truly dissolved forms of trace elements in natural waters (Benes and Steinnes 1974). Truitt (1980) has shown that substantial low molecular weight organic matter also passes; this presumably is material in solution. Because the dialysis cell is both the sampler and storage device in analysis, Benes and Steinnes (1975) argue that species alterations are eliminated.

Dialysis membrane cells have been used as a means for evaluating the impact of pollutants on plankton (Powers et al. 1976). In this study the growth rates of a marine dinoflagellate in dialysis cells were compared when exposed to DDE, a pesticide, and uncontaminated water. Conflicting results were ascribed to adsorption of DDE to the membrane surface.

Benes (1980) has proposed the inclusion of a strong adsorbent for the element of interest in the dialysis bag. With a large excess of the adsorbent in the internal stirred solution of the dialysis cell, the diffusion of elemental species into the cell should become constant. Periodic measurement of metal concentration in the cell would allow monitoring of concentration variations of elemental species in natural systems. Experimental work to validate this proposal is in progress.

The use of dialysis is not without experimental difficulties, however. The diffusion process may be very slow, especially for negatively-charged complexes (Benes and

Steinnes 1974). The greatest difficulties with the method
continue to lie in metal contamination of the membranes
during manufacture and the adsorption of trace metals and
trace metal species on the membrane surface (Smith 1976).
Solubility of the membrane material can also be a problem
(Truitt 1980).

Dialysis and ultrafiltration both were used in
speciation studies undertaken by Rona et al. (1962). Their
objective was to measure speciation of zinc and manganese in
seawater. Results indicated a percentage of the elements
exist in seawater in the form of high molecular weight
complexes. Slowey and Hood (1971) used dialysis and solvent
extraction to study seawater. Up to 70 % of zinc present in
seawater was in dissolved forms. The remaining zinc was
thought to be associated with organic matter. Mayer (1976)
postulated organic matter association of trace elements in
order to interpret results of a similar nature.

Bender et al. (1970) used gel filtration chromatography
(Sephadex G-50) to study the forms of copper in sewage
effluents. No free copper was found in the samples, which
produced two distinct chromatographic peaks; the first
contained approximately 13 % of the copper in the sample and
was associated with molecular weights of 10^4 or greater,
while the remaining copper was in the second peak,
equivalent to molecular weights in the range 500-1000.
Templeton (1980) used gel filtration and high pressure

liquid chromatography to separate organic components of interstitial anoxic waters. These fractions were then evaluated for trace metal content. Each fraction had a distinct trace metal composition which changed when samples were exposed to oxygen.

The very characteristics which make gel filtration suitable as an analysis tool for interstitial waters, i.e., small sample volume requirements and high solvent/sample volume ratios, make it a difficult technique to use for determining metals in unpolluted natural waters. Preconcentration of the metals eluted with large volumes of solvent becomes necessary before a conventional analysis, such as flame atomic absorption spectrophotometry, may be employed. Another problem associated with gel filtration is the absorption of metal species onto the gels. For example, both Fe^{3+} and humic acid interact with sephadex gels (Posner 1963). The effect of gel filtration on the general reaction:

$$MeL \rightleftharpoons Me^{2+} + L^{2-} \qquad (3)$$
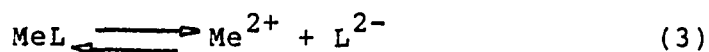
must also be considered (Guy and Chakrabarti 1976). As gel filtration separates complex ions from aquo ions, the equilibrium is shifted to the right, and the resulting chromatogram consists of broad peaks and shallow valleys (Mantoura and Riley 1975).

Early work with strong acid and chelating ion exchange resins for trace metal analyses of seawater promoted a belief that such resins would quantitatively preconcentrate metals without prior chemical treatment (Leyden and Underwood 1964, Riley and Taylor 1968a). In contrast, Abdullah et al. (1976) suggested that these resins did not alter composition of the metal species in the sample. Florence and Batley (1976) in their use of Chelex-100 resin, argued that the fraction of trace metal which was not removed from natural water samples by the resin was associated with inorganic and organic colloidal particles. They arrived at this conclusion by estimating the pore size of Chelex-100 was much smaller than colloidal particles. The weakness in this argument is the assumption that colloidal particles must enter resin pores to be retained. Owing to the ability of such resins to sorb organic compounds from natural waters, (Pakalas et al. 1978, Junk et al. 1974, Stepan et al. 1978), there may be immobilization of significant quantities of large metal-organic complexes in natural water samples by the resin matrix. This would lead to low estimates of total metal-organic associations.

Chelating materials have been put on other substrates as selective preconcentrating agents. Membranes with ion exchange functional groups sorbed (van Griekan et al. 1977, Campbell et al. 1966) or directly attached to the membrane surface have been prepared (Horvath et al. 1977). Leyden and Luttrell (1975, 1976a, 1976b) immobilized chelating

groups on controlled pore glass beads via silyation. Use of
this material allowed essentially quantitative recoveries of
spiked copper samples from fresh water at flow rates of 50
mL/min. However, the recovery of an ionic spike is not
necessarily an accurate estimate of the recovery of a metal
naturally present in the water (Florence and Batley 1975).

Various workers have used selective chemical reactions
combined with extractions to distinquish between chemical
forms of metals in natural waters. Florence and Batley
(1976) combined Chelex-100 separations with ASV
measurements. Ultraviolet irradiation of the separated
fractions was employed to distinguish metals bound as
organic complexes from "free" ionic form metals. Alexander
and Corcoran (1967) carried out a similar study on copper in
seawater using neocuproine extractions. Determinations of
copper content of the seawater were made before and after an
oxidation using perchloric acid. The difference in copper
concentration was equated to organically-bound copper.
Morris (1974) also studied the concentrations of ionic and
organically associated zinc, copper and nickel in water from
the Menai Straits. A portion of each sample was irradiated
with ultraviolet light before it was passed through a column
of Chelex-100 chelating resin. Determination of metals
content of the elutriate was accomplished using X-ray
fluorescence. The difference between the amount of metals
found in a UV irradiated and non-UV irradiated sample was
ascribed to organically-associated metal.

In an effort to eliminate the problems associated with chelation-extraction methods employed to determine speciation characteristics of metals, Slowey et al. (1967) developed a procedure in which 500 mL samples of filtered seawater were extracted with three 15 mL portions of chloroform. This extraction yielded data which suggested that 10-50 % of copper present in the dissolved state was associated with organic complexes. The study did not demonstrate that all copper adsorbed on organic colloids would be extracted by the method or take into account charged organo-copper complexes which would not be extracted. Both of these errors would tend to give low results for organic associated copper. On the other hand, inorganic copper complexes which would tend to accumulate at the phase interface might well be included in the measurement, giving a tendency toward high results. Duplicate measurements were not presented.

The major drawback with all these extraction techniques is the possibility that the estimate of organically bound metal is substantially lower than that actually present in natural waters. In theory, the large formation constants of the chelating agents employed for extraction would be expected to effect complete recovery of metals from natural water complexes whose affinity for the metal is less than that of the complexing agent added. However, the degree to which this process actually occurs is difficult to estimate due to the variability of the organic matter in water and

the paucity of suitable ionization and stability constants for organo-metallic complexes present in natural aquatic systems.

Particulate-Bound Species

Clay as a "binding-particulate". Two very simple units of structure are common to all the crystalline clay minerals. These are the silicon tetrahedron, modified somewhat as to size when the aluminum atom proxies for silicon, and the aluminum octahedron in which the central atom, usually aluminum, magnesium or iron, is surrounded by six oxygen atoms. All the crystalline clay minerals have in common a two-dimensional arrangement of silicon and oxygen, forming a hexagonal sheet of composition $[(Si_2O_3)^{2+}]$. The oxygens satisfying the fourth silicon valency normally form a second sheet of composition $[(O_2)^{4-}]_n$, less closely packed than the first.

The structures of clay may be regarded essentially as formed by the condensation of sheets of SiO_4 tetrahedra with sheets of alumina or magnesia octahedra. The major types are designated 1:1, 2:1 and 2:2 or 2:1:1 depending on the ratio of tetrahedral to octahedral sheets in one negative layer. Kaolin is a 1:1 type, montmorillonite, mica and illite are 2:1 types and the chlorites are an example of the 2:1:1 type. Illite has been defined as a member of the hydrous mica group of crystalline clay minerals. It is

relatively close to muscovite in chemical composition but contains less potassium and more water. An idealized structure for illite is presented in Figure 1. In the illite group the degree of hydration is not as great as that of other members of the hydrous micas such as vermiculite where double layers of water molecules can separate the structural units of the mineral. Water in the illite structure may arise from two sources. The first possibility is the exchange of hydrogen for potassium in the chemical structure. The hydronium ion $(H_3O)^{3+}$ might then occupy some of the potassium positions. The second possibility is that random interposed layers of water occur as in vermiculites.

The presence of exchangeable potassium atoms in the chemical structure of illite along with the possibility of random water layers allows for the possibility of cation exchange at the surface sheets, at crystalline edges, and within the body of the structure to an extent allowed by penetration of the water layers.

Cation exchange capacity. The clay minerals that constitute the main inorganic exchange materials include, illite, montmorillonite, kaolin and occasionally vermiculite or hydrobiotite. The cation-exchange capacity (C.E.C.), being different in magnitude among clay mineral types, has been used as a means of characterization of a given mineral or mineral group. Typical C.E.C. values for clays range
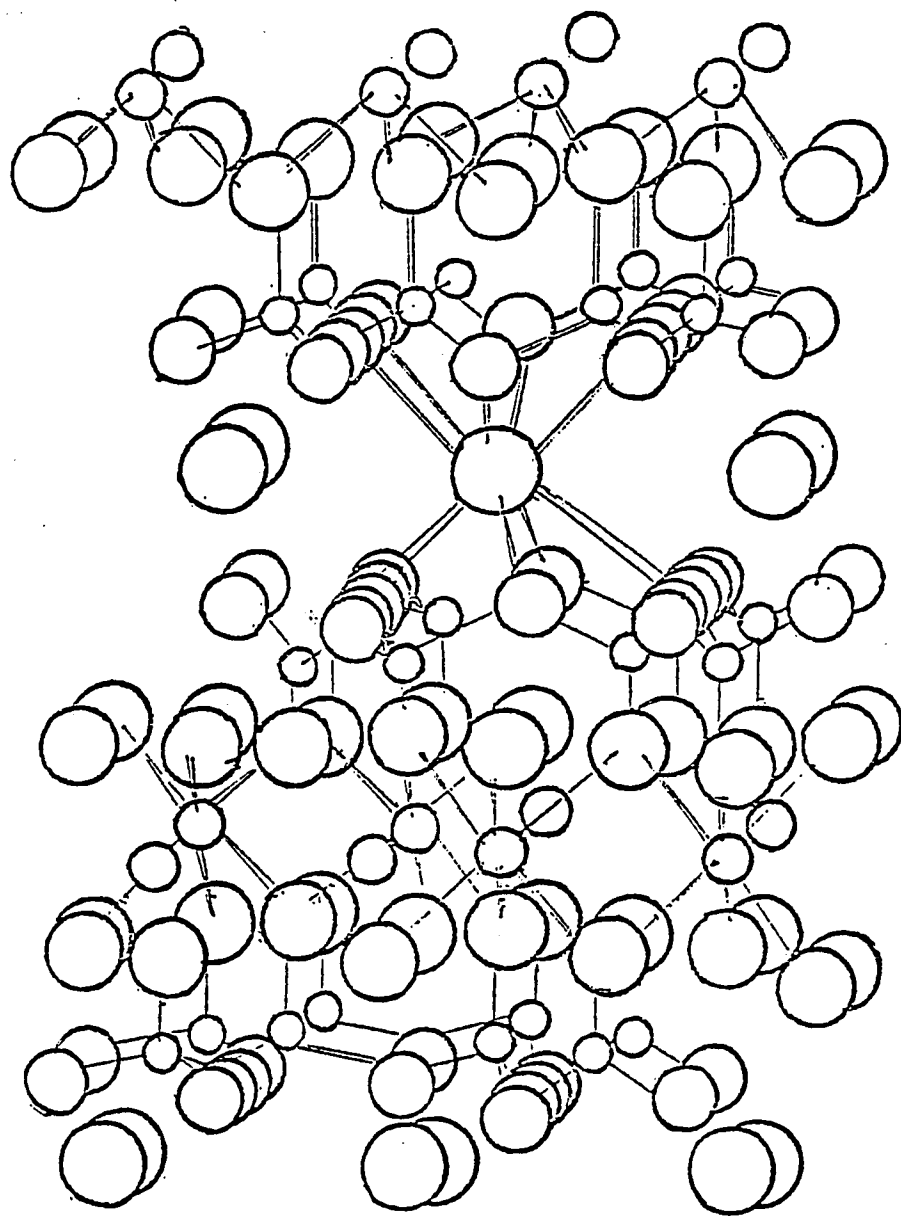
Figure 1.   Unit structure of illite clay.

from 1 meq/g for montmorillonite to less than 0.1 meq/g for some kaolins. The C.E.C. of clays is strongly influenced by components of the hydrous-oxide, organic matter (e.g. humates) skin, which normally coats particles found in the natural environment. The formation of this metal oxide and/or organic film is a dominant force in determining the surface properties of suspended particles (Hunter and Liss 1979). Electrical and surface properties affecting coagulation and flocculation rates are modified (Hunter and Liss 1979). Most of the biologically important cations are bound by exchange-active clay minerals and are correspondingly difficult to displace. The order of difficulty of displacement is approximately (Mitchell 1964): Cu>Pb>Ni>Co>Zn>Ba>Rb>Sr>Ca>Mg>Na>Li but the relative positions in such a series vary with concentration in solution and the nature of the exchange-active material.

The measured C.E.C. of a clay is greatest when determined for elements such as Zn^{2+}, Cu^{2+}, Fe^{3+} or Th^{4+}, elements which tend to form hydroxy salts (Bower and Truog 1940). Hydroxylated exchange ions, $CuOH^{+}$, are thought to be the species predominately present on clay surfaces at pH values above 7.0 (Davis and Leckie 1978, Farrah and Pickering 1976). Copper speciation diagrams prepared from equilibria and precipitation data support this view (Zirino and Yamamoto 1972). Additional evidence for the presence of hydroxylated species on clays has been obtained by infrared (DeMumbrum and Jackson 1956), and ESCA

studies (Koppelman and Dillard 1977). This behavior, if it occurs at the very low natural abundance concentrations of trace elements, might be of importance in assessing bioavailability of the elements.

In clay minerals, one set of properties may be ascribed to the diffuse double layer of ions surrounding the particles. These properties are generally common to negatively-charged colloidal systems . Superimposed on these properties is a second set whose origin lies in the chemical structure of the clay mineral. In addition, each clay particle displays unique surface properties as a function of degree of crystalline imperfection. This is particularly true in the micas and related clays due to the contrasts between exposed planar sheets and edges. In short, surface charge distributions of soil colloids vary greatly from one to another.

The simplest expression of an exchange reaction is shown by a schematic equation, such as:

$$Na \ Exchanger + KCl = K \ Exchanger + NaCl \qquad (4)$$

or

$$Na^+ \ Exchanger- + K^+ + Cl^- = K^+ \ Exchanger- + Na^+ +$$
$$Cl^- \qquad\qquad (5)$$
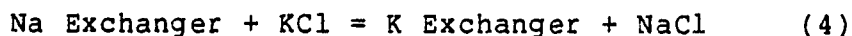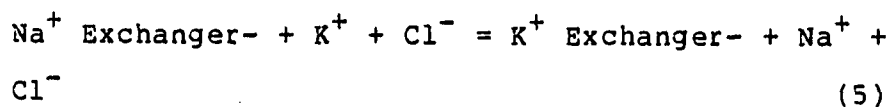
The second equation, written in terms of ions, implies that the chloride ion might be omitted as being purely a spectator ion. However, its association with the cationic species is certainly different in solution than in the clay:diffuse double layer matrix. A further implication of these equations is that all exchange sites are equivalent, which is not the case.

Cation or anion exchange is normally studied in two ways: as equilibrium systems or through the kinetics of approach to equilibrium. General exchange relationships for different cations on clay surfaces have been evaluated by the method of dilute exchange. The selectivity coefficient, a measure of the degree of affinity of the clay surface for one cation over a second, is plotted against percent saturation of the surface by exchangeable ions. In most cases the curves are complex indicating that the cations are held with a range of bonding energies (Marshall 1964). Upon exchange with a salt solution, the system can arrive at the condition of minimum free energy for more than one substrate composition. This implies a variation in the exchange capabilities of a clay due, in part, to prior environmental conditioning. Changes in the surface exchangeable ions of a clay by prior cation exchange leads to a wider range of available bonding energy sites. Consequently, it is extremely important that the same batch of clay with exactly the same methods of preparation be used throughout exchange studies to obtain consistent results. Clay samples from a

given deposit consisting of the same major mineral may vary due to isomorphous replacements in the lattice (Lim et al. 1980). Differences in method of preparation are manifested by varying proportions of H and Al in acidic clays and the presence of traces of residual electrolyte impurities.

Certain limitations have been accepted in most mathematical treatments of exchange reactions. The ion exchanger has been assumed to possess constant exchange capacity, although many cases are known in which the capacity varies with the nature of the exchangeable ion as well as the pH of the system. Simple stoichiometric equivalence between ions taken up and released is assumed. Finally, perfect reversibility is usually taken for granted. This latter point is particularly critical when predictions are to be made concerning trace metal desorption from land fill sites or dredging operations. Complete reversibility of adsorption behavior cannot be assumed in projecting desorption characteristics of a system.

Clay desorption theory. Different cations influence clays and colloidal systems in two ways: directly, and indirectly by their effects on the relationships of other cations and molecules adsorbed to the clay surface. Direct comparisons can be made through cationic, mean-free bonding energies (Marshall 1964). Bonding energy curves for various clays have been prepared by various workers. A general

trend in this work is the inverse relationship of ionization of surface-bound elements with free bonding energy. The ratio of ionized to bound ion in a two component system can be expressed as a selectivity coefficient for the ion. Thus it is possible to relate free bonding energy to an order of selectivity in a mixed system.

The 1:1 and 2:1 lattice clays, which includes illite, all show bonding energy curves with a maximum followed by a steep decline beginning somewhat before exchange capacity of the clay is reached. In all the 2:1 clays, the maximum appears as a plateau. In most cases the steep fall in the region of cation exchange saturation corresponds to the occupancy of weaker sites and a bonding energy dimunition compared to sites already occupied. The indirect influence of different cations on clays is summed up in Jarusov°s Rule. As a result of his experiments on cation exchange in soil systems, Jarusov (1937) concluded that the exchangeability of a given ion was not a constant, but was a function of its amount in relation to the amount and kind of other ions present. In terms of binding energy the consequence is that with two different cations present, the cation having the higher bonding energy pre-empts those positions on the surface or that part of the diffuse layer which corresponds to the greatest energy release, leaving for the cation of lesser bonding energy only those positions which afford smaller energy release. In this way one ion influences another through the free energy relationships of

the diffuse double layer and the ionizing surface. This
rule expresses the way in which a dissociating surface with
several cations adjusts itself to the thermodynamic
requirement that the total free energy be as small as
possible.

Clay desorption studies. Heavy metal ions are
exchanged from aqueous solution by clay suspensions. The
uptake of heavy metals varies with the nature of the clay
(Koppelman and Dillard 1977), solution pH (Farrah and
Pickering 1977a, 1977b, McBride and Blasiak 1979),
concentration of competing ions (Mattigod et al. 1979, Chu
and Johnson 1979) and the nature and concentration of
ligands present (Davis and Leckie 1978). Ligands influence
adsorption behavior by introducing protonated ions which
compete for sites and by promoting the formation of stable
complex species. The latter can have a reduced affinity for
the clay surface (particularly if anionic) and often inhibit
the formation of sparingly soluble hydroxy compounds. The
uptake/release characteristics of trace metals is determined
by the sum of these interactions.

Experimental determination of trace metal sorption is
accomplished by contacting a particulate sample with
solutions containing known concentrations of the trace
metal-of-interest. Sorption is followed by analysis of the
solution concentration after separation from particulates.

The Freundlich Equation can be expressed as:

$$X/m = Kp^{1/n}$$ (6)

where x/m is the concentration adsorbed on mass m of adsorbent, p the concentration of cation remaining in solution, and k and n are constants. This is the equation of a parabola. No adsorption maximum is indicated as the amount of replacing cation in the solution is increased. However, the exchange capacity of a clay is a finite quantity. Therefore, the Freundlich equation cannot accurately represent cation exchange over a wide range of concentration.

Langmuir proposed an equation of the form:

$$X/m = \frac{K \cdot S \cdot C}{1 + KC}$$ (7)

in order to avoid this dilemma. Here x/m is the amount adsorbed on mass m of adsorbent; c, the concentration of cation remaining in solution; s, the adsorption maximum and k is the equilibrium constant for the adsorption. The equation is that of a hyperbola. A plot of the quantities c/(x/m) versus c yields a straight line with a slope of 1/s and an intercept of 1/sk. The application of Freundlich or Langmuir isotherms as descriptive indices of trace metal

adsorption behavior in natural systems has limited use
(Farrah and Pickering 1976a, 1976b, van den Berg and Kramer
1979).

The usefulness of these equations to predict eventual
release of trace metals from particulates to the surrounding
water as environmental conditions change has not been
substantiated. The problem of desorption of trace metals
from highly contaminated wastes suggests a need for such
predictive capability. Mobilization of trace metals in the
environment is more than a matter of surface water
contamination (Pahren et al. 1979, Kirkham 1975).
Bioaccumulation of trace quantities of hazardous materials
may result in significant elevation of biotic trace metals
content (Laube et al. 1979, Kirkham 1975). This effect may
be transmitted through the food chain producing damage to
the entire environmental community.

Investigations concerning desorption profiles of trace
metals from particulates in the environment have centered on
three major fields of research. They are: (1) free ionic
element:particulate interactions, (2) trace element
inorganic complexation:particulate interactions, and (3)
trace element organic complexation:particulate interactions.
The variables of interest can broadly be outlined as:

1. Equilibration time between sediment and trace elements,
2. pH,

3. Sediment content of the water,

4. Trace element concentration of the water,

5. Speciation of the trace elements,

6. The composition and metal-binding properties of the sediment particulates,

7. Competing ion effects, and

8. Ligand effects.

Variation in any one, or a combination of the above variables can cause extreme changes in the desorption profiles of a trace element.

Methods involving Dialysis. Dialysis is the oldest technique employed by reseachers for investigating desorption of trace elements from sediments and soils. Root uptake of nutrients, which can be considered a dialysis phenomena, has been investigated using synthetic clay minerals and natural colloidal clays as cation-supplying materials (Wiklander 1957). Albrecht et al. (1938) stated that this use

> ...provides a means whereby more complete chemical analyses of the soil and seed at the outset, and soil and plant at the close are possible with an accuracy and interrelation of results never before possible in such high degree of approach to actual soil conditions.

Ratner et al. (1946) endeavored to determine the relative importance of contact exchange versus nutrient transfer by solution phase to root systems by separating roots and clay suspensions by means of collodion and parchment bags. Unfortunately, no definitive results were obtained. This

principle has been employed for years in the dialysis culturing of microorganisms. Algae in dialysis cultures have been used to study desorption properties of clay suspensions (Laube et al. 1979) and for monitoring the nutritional capacity of seawater (Jensen and Rystad 1973).

The role of particulate versus dissolved trace metal bioavailability was examined by Luoma and Jenne (1977). Filter feeders were placed in a clay suspension and in dialysis bags in contact with the clay suspension. From these two measurements, they distinguished assimilation of trace metals from solution versus uptake from particulates. Large differences in pH and dissolved oxygen content between the external slurry phase and the internal dialysis phase are often found in dialysis experiments of this type. This indicates that diffusion in the system, which depends on mechanical stirring as well as the diameter, thickness and porosity of the dialysis bag, is not efficient enough to keep both phases homogeneous (Dor 1975).

Methods involving radiochemical techniques. Processes by which heavy metal concentrations are regulated by adsorption/desorption phenomena in neutral waters have been investigated using radioisotope labeling and neutron activation techniques. These methods have been used to follow ion mobilization in environmental and laboratory settings at natural abundance levels. Samples spiked with radioisotopes have been used in speciation studies. In

theory, they should mimic naturally occurring elements.
Unfortunately the equilibration process is lengthy and
poorly understood. Samples analyzed under non-equilibrium
conditions will exhibit differing specie distributions.
(Luoma and Jenne 1977). In the natural environment, the
Columbia River, its estuary and coastal area have been
extensively studied. Radionuclide measurements have been
made in water, biota and the sediment (Nelson et al. 1966,
Gross et al. 1965). Accumulated data indicated that one
possible mechanism to account for trace-element
concentration variations, especially in coastal regions near
river outflows, is the uptake of radionuclides or stable
elements by fresh-water sediments. Partial release of these
particulate-bound elements occurred when they came into
contact with brackish or seawater (desorption). Murray and
Murray (1973) studied the adsorption/desorption equilibria
of some radionuclides under laboratory conditions simulating
sediment-fresh water and sediment-seawater systems.
Individual elements exhibited widely different
adsorption/desorption behavior. Thus, predictions of the
behavior of several cations under conditions where
adsorption or desorption may occur cannot be made from
observation of an individual element.

Trace element uptake by biota in running streams was
simulated by Knaus and Curry (1979). Mn-56 was injected
into an artificial stream where willow shoots were growing.
The trace element concentration in the water column was

monitored by liquid scintillation. In order to follow the process as the ambient concentration of Mn-56 in the water became very low, they performed a double activation analysis. This consisted of further irradiating the water and samples of the willow roots to produce more Mn-56 (from previously inactive Mn-55) and monitoring the concentrations with a Ge(Li) detector. Their results indicated a direct relation between soluble Mn-56 concentration and uptake by the root samples.

Methods involving biota. The development of water quality criteria to protect aquatic life is a complex issue. A principal concern is the ability of the biota to respond to stress imposed by variable concentrations of pollutants in the environment. The degree of exposure may vary due to a number of causes. Seasonal rainfall and runoff variations, river flow regulation, water-level control, and intermittant waste discharge all cause pollutant concentration variations (Seymour et al. 1978). The degree and extent of variation of such exposure becomes relevant when we consider the establishment of standards to safeguard our waterways. Biota in some polluted rivers survive only because occasional periods of cleaner flow allow some excretion of accumulated poisons (De L. G. Solbe et al. 1976).

Studies of heavy metal effects have used plants (Kallquist 1978) and animals (Pickering et al. 1977, Brungs et al. 1976, Wass 1967). Benthic invertebrates have been used as indicators of water quality (Occhiogrosso et al. 1979, Anderson 1977, D°Silva and Kureishy 1978). Benthic invertebrates can be classified as integrating monitors. Accumulation of copper and zinc in the green mussel was linear for five weeks (D°Silva and Kureishy 1978). However, the usefulness of filter feeding organisms as trace metal monitors in natural waters remains unclear. Terhaer et al. (1977) found fresh water mussels to be poor indicator species for metal contamination. Manley and Davenport (1979) reported that the common mussel Mytilus edulis (L.) is capable of detecting and avoiding potentially lethal concentrations of copper delivered intermittantly. This behavior would preclude the use of the organism as a true integrating sampler of the environment. Despite these shortcomings, the current lack of viable alternatives should guarantee the continuation and expansion of monitoring programs employing biota as detection devices.

Trace elements are a biological necessity. For example, copper is a necessary constituent in the heme pigment of mollusks (Greig 1979). However, elevated concentrations of heavy metals can adversely affect an environment. Undesirable or normally minority taxa can predominate due to reduced biological competition. Human populations can be affected by using the water as a drinking

source. Elevated levels of copper have been associated with
increased cardiovascular mortality (Calabrese and Tuthill
1978). The implications are clear that more information is
needed concerning the fate of trace elements in the
environment and our concern must include both deficiencies
and excesses.

CHAPTER III

ION EXCHANGE
DIFFUSION CONTROLLED AND FLOW THROUGH SYSTEMS

Ion Exchange Kinetics

Ion exchangers consist of three-dimensional polymeric
or crystalline networks carrying fixed ionic groups with
exchangeable counterions. Ordinary ion exchange is
essentially a redistribution of the exchanging counterions A
and B by diffusion. In an exchange of counterions A and B,
specie B must migrate from the well stirred solution to the
ion exchanger and specie A must migrate from the exchanger
into the solution. The rate controlling step was shown by
Boyd et al. (1947) to be diffusion either in the ion
exchanger particles or in an adherent stagnant liquid layer
surrounding the particles. In an intermediate range of
conditions both mechanisms affect the rate, but the slower
of the two becomes rate controlling.

The generally accepted Nernst-Plank model for particle diffusion as the rate controlling step in ion exchange kinetics has been studied in great detail (Helfferich 1962, 1958, Plesset et al. 1958). Their approach replaced Fick°s Law, which used a constant interdiffusion coefficient for the flux equation, with an expression which contained an additional term for electric transference. Further constraint in their description was that the interdiffusion coefficient (D) was not a constant but depended upon the relative concentration of A and B. Therefore, the expression predicts that as the concentration of either ion approaches zero, the interdiffusion coefficient approaches the diffusion coefficient of that ion, i.e., the interdiffusion rate is controlled predominately by the ion of lesser concentration. The corrective action of the electric field portion of the Nernst-Plank equation can be viewed as directed against the high concentration specie so that the interdiffusion rate is controlled by Fickian diffusion of the low concentration specie.

A reaction scheme of the form

$$C_s + C_c \xrightleftharpoons[k_d]{k_a} A \qquad (8)$$
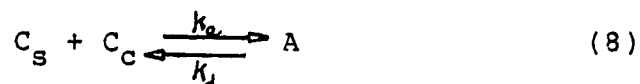
is suggested for steady state fixation kinetics (Overman and Chu 1977), where C_s represents the concentration of trace element in solution, C_c, the concentration of adsorptive sites on the resin, and A, the concentration of adsorbed

trace element per unit volume of solution. The kinetic equation for this reaction may be described by examining the rate of change in trace element concentration in solution, dC_s/dt:

$$dC_s/dt = -K_a C_s C_c + K_d A \qquad (9)$$

where $K_a C_s C_c$ represents second-order adsorption and $K_d A$ represents first order desorption. Examination of the kinetics equation indicates that the rate of adsorption of trace element in a batch system depends upon the solution concentration and the amount of adsorbent in the system. In batch adsorption systems the solution concentration declines with time.

Solution and adsorbent concentration effects on rate of adsorption in non-flow systems were examined in experiments conducted by Snoeyink and Weber (1968) and DiGiano and Weber (1973). Adsorbate was added to a non-flow system at a rate sufficient to maintain a constant concentration in the vessel. With solution concentration constant, the adsorption rate was constant. Bell and Molof (1975) found the rate of adsorption of dodecylbenzene sulfonate (DBS) on activated charcoal to be a linear process when corrected for the effect of concentration decline in their reactors. Therefore, in closed systems, non-linear adsorption rates are due to solution concentration decline.

Passive Transport Studies

Preparation of ion-exchanger. Chelex-100 resin
(100-200 mesh), supplied in the Na^+ form, was used in
trace metal collection studies. One gram of dry resin was
washed with three 25 mL portions of analytical grade
methanol to remove possible contaminating reagents from the
manufacturing process. Following a deionized water rinse,
the resin was allowed to swell in water for three hours.
Fines were removed by placing approximately 2 grams (wet) in
a 100 mL graduated cylinder with water and allowing the
resin to settle undisturbed for one minute. At the end of
this time the solution containing fines was discarded. A
portion was removed for conversion to the hydrogen form with
2 M HCl (Eastman). Conversion was accomplished in a column
by adding the 2 M HCl in 25 mL portions and eluting at a
rate of 0.5 mL/min. Elution of sodium was monitored using a
Nichrome wire loop to sample eluate which was heated to
observe the yellow flame indicating the presence of sodium.
A total of 100-150 mL of hydrochloric acid was normally
sufficient to effect complete conversion of the resin.
After rinsing the column with approximately 150 mL water,
the lower 2/3 of the resin column was kept and stored in a
polyethylene container. The upper third which tended to
concentrate trace element contaminants from the reagents was
discarded.

Conversion of Chelex-100 from the Na^+ to the NH_4^+ form for use in trace metal accumulation studies was accomplished in a similar manner. The NH_4^+ solution used in the conversion process was 1 M and had been previously passed through a 3 cm column of Chelex-100 Na^+ form to remove trace metal contamination. This cleaned NH_4^+ solution was used to convert a column of Chelex-100 Na^+ form, and the lower 2/3 of the converted resin stored wet in a polyethylene container.

Diffusion controlled exchange experiments. The utility of integrating passive devices has been demonstrated by Brainard and Kerfoot (1975) in monitoring natural water systems over extended time periods. Their ersatz oyster consisted of an activated charcoal matrix, alone or with adsorbed complexing ligands, sandwiched between two membranes. The accumulation of trace metals by the device was controlled solely by diffusion processes. Lack of adsorbent selectivity for the species of interest and the long contact periods necessary for sufficient metal accumulation, continue to limit the usefulness of these devices.

In order to further explore this means of monitoring trace metals as well as to gain experience in sample manipulation and treatment, similar devices were constructed. As illustrated in Figure 2, the "resin cassette" device measured 3 cm in diameter and was

RESIN

POLYPROPYLENE HOLDER

&MEMBRANES

3 CM

0.4 CM
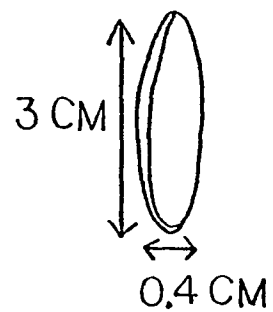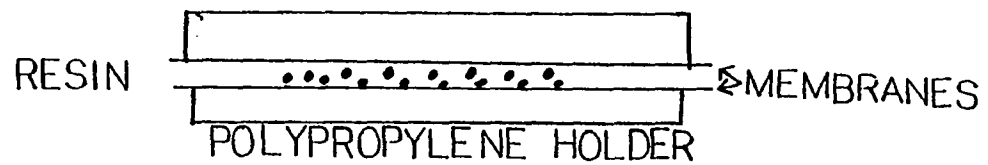
Figure 2. Schematic of diffusion controlled "passive"
cassette construction. The polypropylene device is
made from interlocking bands and Nucleopore (polycar-
bonate) membranes.

constructed of polycarbonate Nucleopore membranes and a
polypropylene body. Hydrogen form Chelex-100 (100-200 mesh)
was sandwiched between the membranes. Chelex-100 offers the
advantage of selective cation exchange in fresh and salt
water matrices. From preliminary experiments it was
established that a satisfactory wet weight of resin to place
in the cassette was 100 mg.

The rate of trace metal uptake by the resin in direct
contact with stirred Cu^{2+} solutions was examined in batch
experiments. A similar series of experiments was conducted
using Cd^{2+} as the trace metal of interest. When the resin
was extracted with 2 N HCl, less metal was found than had
been lost from solution. A literature search revealed this
to be a general problem when the resin is in the hydrogen
form but there is a lack of concensus on the exact cause
(Figura and McDuffie 1977, Abdullah et al. 1976). The resin
was changed to the ammonium form which was superior in
storage and binding characteristics (Riley and Taylor 1968b,
Abdullah et al. 1976). Batch resin trace metal collection
experiments were repeated and mass balance achieved.

Trace element accumulation characteristics of the
cassettes were investigated. Several Nalgene containers
were rinsed with deionized water and filled with 4 liters of
0.10 ppm Cu^{2+} solution. A cassette was placed in each
container and rotated at 2 rev/sec. After appropriate time
periods, cassettes were removed and extracted for trace

metal accumulation determinations. A portion of solution was analyzed for trace metal content at the start and end of each experiment for mass balance analysis.

The drawback to the use of a resin cassette as a trace metal collection device continued to be the long solution contact times necessary for significant trace metal accumulation.

Flow Through Systems

Introduction We wanted a means of removing trace elements from solution in which the rate of removal could be varied and controlled by the experimenter. Such a system is defined as "active" because methods are employed to bring fresh solution continually in contact with the trace metal collecting device. In contrast to a passive collection system, diffusion should not be rate controlling.

Conventional active systems employ a unidirectional flow of solution driven either by a peristaltic pump, gravity flow, or positive or negative pressure differentials. One problem associated with all of these methods is reduction in flow rate as detritus and sediment materials accumulate on the front surface of the collector. Insertion of varying size prefilters helps but does not solve this problem.

The use of adsorbent materials for collection and preconcentration of trace metals in water has taken a novel twist recently with the introduction of reagent impregnated polyurethane foams (Braun and Farag 1975). The use of polyurethane foam in a pulsed mode was demonstrated by Braun and Farag (1973). A foam impregnated with chloranil was packed into a glass syringe. The syringe was hand-operated causing external solution to enter or leave the syringe at a flow-rate of 60-100 mL per minute. A motorized version of this procedure was developed by Srikameswaran and Gesser (1978), in which the flexible support used was a polyester foam impregnated with PAN (1 -(2 - pyridylazo - 2) - naphthol). The foam plugs were squeezed mechanically in a metal cage and used to extract and concentrate copper, zinc and mercury from large volumes of water. The amounts of copper and zinc extracted had a linear relationship with the number of squeezes of the foam.

Most recently Braun and Palagyi (1979) have investigated the use of a pulsating column (a foam cylinder packed within a conventional medical syringe) to investigate separation efficiency in open and closed systems. An open system was defined as one in which, after equilibration in the syringe, each fraction of the sample was discarded and a fresh one drawn from the sample resevoir. A closed arrangement allowed each fraction to be dispensed back into the sample resevoir, effectively reducing the concentration of the remaining solute. For sufficiently high distribution

ratios (K_d) between the foam filling and the aqueous phase, essentially 100% separation efficiency was obtained in either arrangement. The authors noted that flexible foams were susceptable to leaching of reagent and sorbed analyte during the collection period. The possibility of contamination or metal loss to the glass syringe was not explored. Without a suitable prefilter the foam would quickly become clogged with particulates in natural water systems.

Active cassette variables. I first developed a hand driven collector which consisted of a cassette fastened to the end of a 50 mL syringe. With this device collection of a fresh solution sample took place in cycles. A cycle consisted of (1) inflow of fresh solution through the cassette resin package where trace metals were extracted as the plunger of the syringe was retracted and (2) outflow of solution through the cassette resin package where any residual trace metal remaining in solution was extracted. This outflow served to expel particulate matter which might have adhered to the cassette membrane on the inflow half of the cycle, thereby avoiding pressure buildup and flow reduction. The double contact of the solution with the resin package during the course of a cycle should help to achieve complete metal extraction.

To be useful for trace metal desorption studies from particulates, it was necessary to have control of several variables. These can be expressed as follows:

1. Variable sampling volume,

2. Variable inflow, outflow rate,

3. Variable membrane pore size,

4. Inertness, and

5. Cation, anion selectivity.

The first characteristic was controlled in two ways. Variation in the length of stroke of the syringe plunger varies the amount of solution drawn into the cassette. Changing the size of the syringe also satisfies this requirement. Flow rate is controlled by the use of a variable speed motor connected to a gear reduction device. This arrangement allows the choice of an inflow, outflow rate which, for a given cycling rate, depends on syringe size. Variable particulate size rejection is achieved by choice of suitable membrane porosity. Cation or anion selectivity is possible to a degree through appropriate choice of adsorbent material. Chelex-100 was chosen as the adsorbing material for these studies. Chelex-100 has been tested by Davey and Soper (1975) for the concentration of trace metals from seawater and is recommended by the Environmental Protection Agency for the extraction of lead, copper, nickel, zinc, iron and manganese from seawater.

The requirement of inertness was satisfied by using polypropylene to construct all parts of the device which contact the solution. Blank studies showed no significant uptake or contamination of Cu^{2+} by the cassette or membranes.

Cassette design and testing. This original design of the cassette was satisfactory for experiments conducted in particulate free solutions. However, the introduction of clay to the solutions created a problem due to accumulation of clay particles at the cassette/membrane interface. This problem was eliminated by building a cassette in which the membrane holder was formed from a band of polypropylene which fit snugly around the cassette body.

Flow patterns in and out of the cassette membrane were checked. This was accomplished by placing methylene blue in the cassette and observing its outflow pattern in a beaker of water. The dye was ejected from the cassette through the membrane only. Determination that the inflow to the cassette was through the membrane only was performed in two separate ways. The first involved the injection of a small quantity of dye beneath the cassette as it began its inflow cycle. The dye flowed smoothly into the cassette through the membrane, as far as could be discerned visually. Therefore, in order to further establish that inflow into the cassette was via the membrane surface only, use was made of the immiscibility of chloroform and water. A beaker was

positioned beneath a cassette and filled so that the
chloroform level was to the halfway point of the membrane
holder band. Water was gently poured into the beaker so as
not to disturb the interface formed, until the cassette was
submerged. A halfcycle inflow stroke was made with the
syringe plunger. The cassette was removed from the beaker
and the contents ejected into a test tube. Upon examination
only one layer, chloroform, was present. The presence of
two layers would have indicated the influx of water between
the cassette and the upper portion of the membrane holding
band.

It was known that desorption studies would require
sampling during the course of an experiment, thereby leading
to lowering of the solution level. A connecting tube was
inserted between the syringe and cassette to permit
positioning of the cassette below the solution surface at
the outset of an experiment. Thus, repositioning of the
cassette in order to maintain solution contact during the
course of an experiment was eliminated. Volume
reproducibility was reexamined due to greater air volume in
the device. Within experimental error, reproducibility was
not affected by air compression. When using clay slurries,
the positioning of the cassette deep in the solution caused
a flow pattern to develop with a "quiet" zone. A
significant amount of clay settled to the bottom of the
container in this zone over a period of 4-5 hours. The
problem was corrected by rotating the container 90 degrees

every 3 hours.

An entire schematic is presented in Figure 3. The apparatus was easily moved and needed relatively little maintainance other than occasional oiling. The most critical detail in assuring smooth operation over an extended time was the condition of the syringe. This should be properly cleaned with acetone before each new experiment and lubricated. "Stir-Lube" (Ace Glass Inc. N.J.) was a satisfactory lubricant.

Theoretical considerations. Assuming that equal fractions of solution were drawn into and discharged from the cassette as it operated, the process can be mathematically modeled. Several assumptions are necessary in the derivation of an expression. Attainment of equilibrium between solution entering the cassette and the resin phase was assumed to occur during the period of solution:resin contact of each cycle. For this to occur, it was necessary that the extraction efficiency of the resin remain constant, or at least very high during the course of an experiment. This requirement was met by using an amount of resin which provided substantially greater exchange capacity than was required by the metal present. It was also necessary to assume that the volume of solution entering the cassette is constant for each cycle. This was investigated over a number of cycles and after long periods of operation in sediment loaded samples and was found
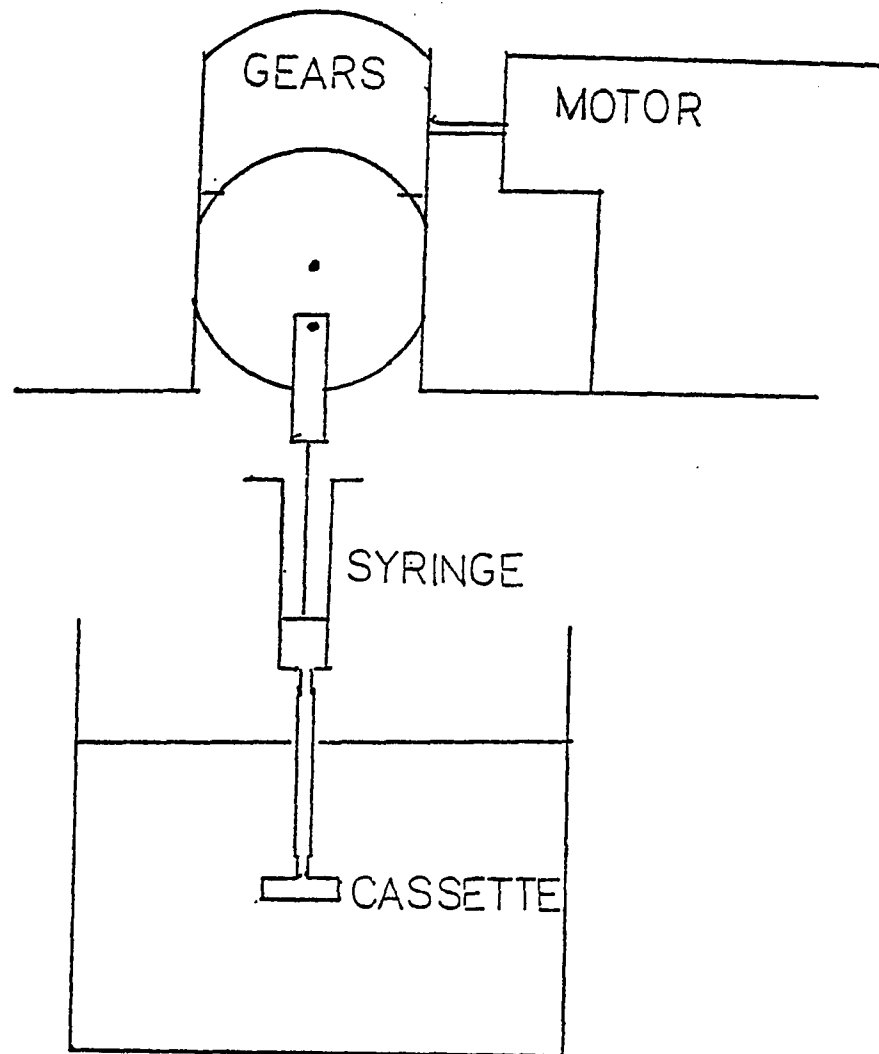
Figure 3.   Schematic of motorized syringe drive used
for active cassette evaluation and clay desorption
studies.

constant. (See supporting data presented in characterization studies). When these assumptions hold, the amount of solute removed by the cassette on each successive cycle should, in an ideal system (Figure 4), decline at an exponential rate. Studies conducted in pure copper nitrate solutions using the active cassette system over extended periods of time substantiated this behavior (Figure 5). As each data point in Figure 5 involved starting with a fresh cassette, no further experiments were performed to determine cassette uptake behavior at lower solution concentrations.

In its simplest form, the mass balance equation for a closed system can be presented as:

mass accumulated in cycle n by resin cassette
= mass removed from solution during cycle n.   (10)

Substitution of variables employed in experimental studies yields:

$$m_c, n = V_c [C_o - C_n - (m_c, n - 1)/V_c]$$ (11)

Thus, knowledge of the volume of the solution entering the cassette per cycle (V_c), the initial solution concentration (C_o), the current solution concentration (C_n), and the amount of solute collected by the resin cassette in the previous cycle ($m_c, n - 1$) allows prediction of the amount of solute to be collected by the
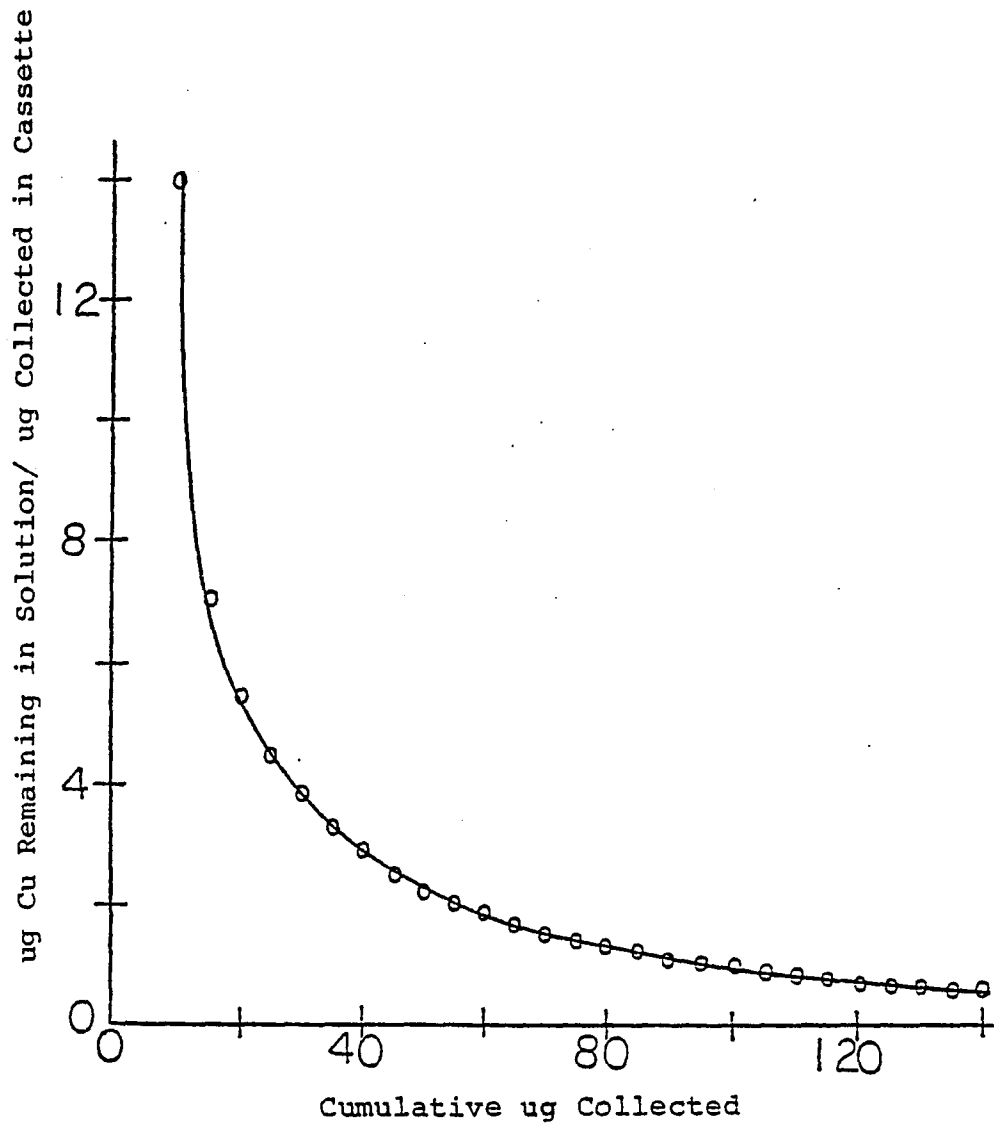
Figure 4. Theoretical model of copper
solution concentration decline in a closed
system. (150 ug Cu, 3% removal per cycle
assumed)
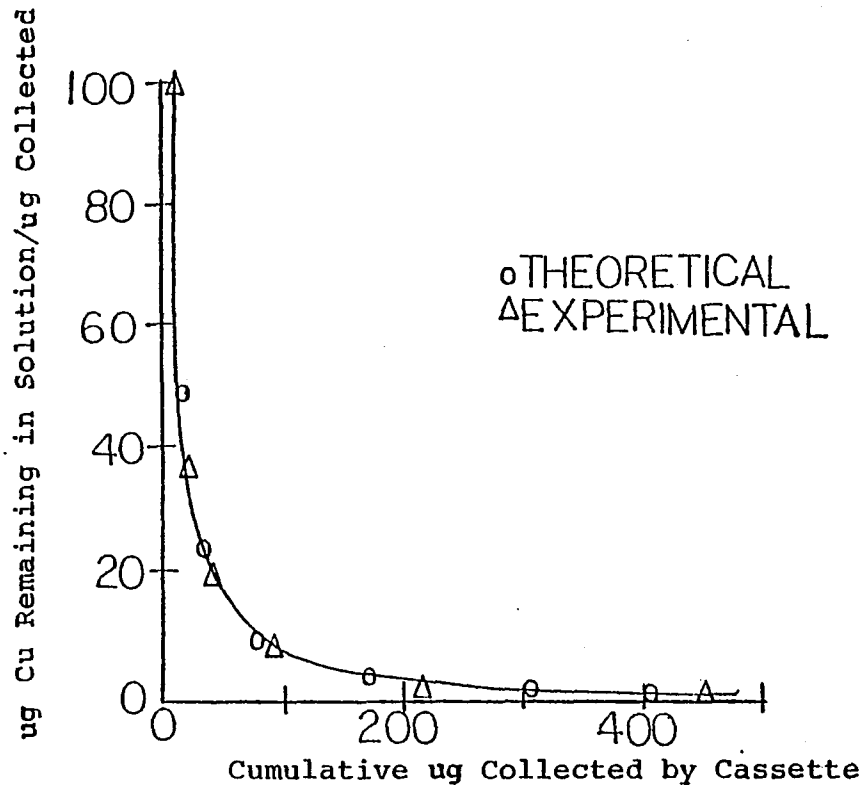
Figure 5. Experimental and theoretical copper
solution concentration decline in a closed system. (1%
remaining Cu removed every 60 cycles). During each
cycle the flow in and out of the cassette was 0.87 mL/min
and solution concentration was 0.20 ppm.

cassette in the present cycle (m_c, n). A feedback situation exists when applying this expression. Knowledge of the amount of solute collected in each cycle must be applied to the generation of a new solution concentration (Cn) at the start of the next cycle, before a prediction of the amount of solute collected in that cycle can be made. Prediction of the amount of solute collected after a number of cycles have been executed can then be obtained from:

$$\sum_{i=0}^{n} m_c, i \qquad (12)$$

where n is the number of cycles of the syringe drive system. In practice, the cycle time was set and constant. Time was equated to number of cycles of the cassette.

The exponential nature of solute collection by the resin cassette led to the following expressions for a model calculation:

Y = fractional part of ug Cu^{2+} remaining in solution after one cycle

$$(13)$$

Y^n = fractional part of ug Cu^{2+} remaining in solution after n cycles $\qquad (14)$

The fractional part of ug Cu^{2+} remaining in solution is evaluated from experimental data using:

$$Y = [m_o - (V_c \cdot C_n \cdot E)]/m_o \qquad (15)$$

where m_o is the initial mass of solute in the system, extraction efficiency (E) refers to the per cent of solute entering the resin cassette which is retained at the end of a cycle, and C_n is a steadily declining solution concentration as the cassette cycles. Then the expression:

$$mo - Y^n(mo) \qquad (16)$$

will yield the amount of solute collected by the cassette after n cycles. Although correct for predicting mass remaining in solution and cassette uptake of solute over a number of cycles, solution of the fractional equation as presented is wasteful of computer time. This arises from the necessity of redefining the value of C_n as the system cycles. In actual practice, use of a single value for C_n over a period of cycles was expedient and valid as a predictor of solute uptake by the cassette. The data presented in Table 1 bears out the validity of using a single value of C_n for several cycles. Theoretical and experimental values for five times (equated to number of cycles) are plotted in Figure 6. Solution concentration was 0.20 ppm Cu. After a suitable number of cycles, a new value
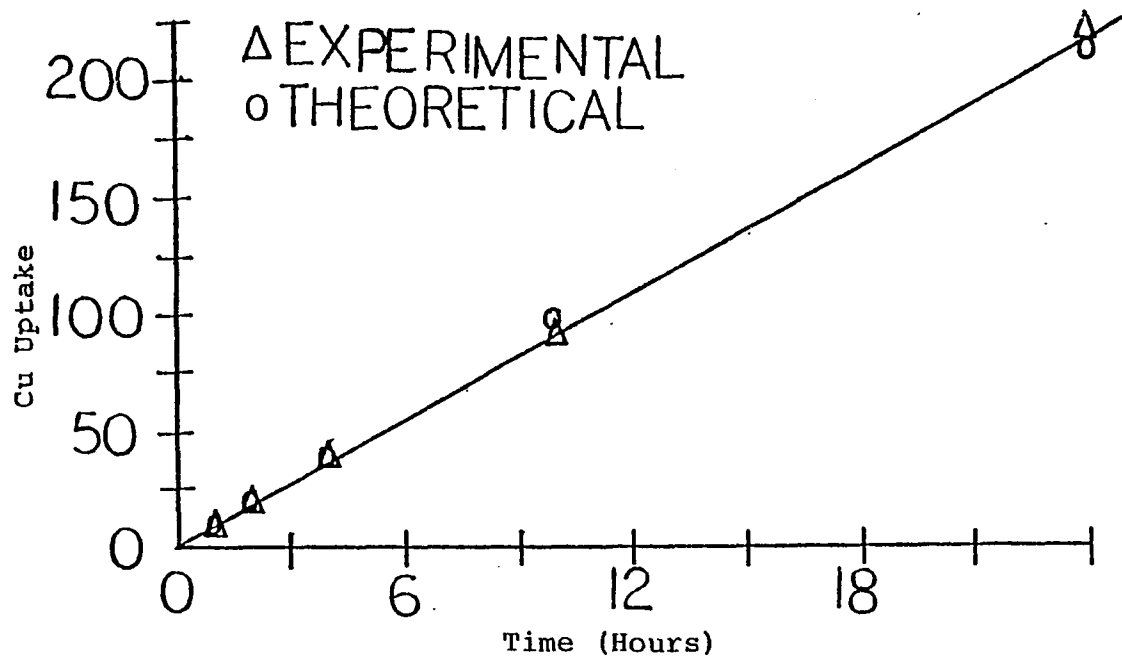
Figure 6. Theoretical and experimental values for
active cassette cumulative uptake of Cu over time.
Theoretical calculation assumes Cu concentration of
solution remains constant. Volume taken in and
discharged is 0.87 mL/min. Extraction efficiency of
the resin, 98%.

Table 1.   THEORETICAL AND EXPERIMENTAL
            UPTAKE OF COPPER
          BY ACTIVE CASSETTE

Time(hours)	Theoretical(ug)	Experimental(ug)
1	10.1	7.9
2	20.0	20.8
4	39.5	39.9
10	95.1	90.5
24	210	217

of C_n was inserted into the expression. Treating the model calculation in this manner was comparable to resetting the conditions used for prediction to the essentially linear first portion of the exponential curve. Modeling in the manner described above was particularly useful in predicting sampling times for determination of solution concentration in active cassette experiments on pure copper nitrate solutions. The usefulness of the expression was even more pronounced in metal desorption experiments . The release of metal to the solution from the clay as metal was removed from the solution by the cassette tended to maintain the solution concentration at fixed amounts over extended periods of time. Resubstituting C_n values after appropriate intervals of time was as good a predictive tool for sampling times as the use of the expression with a continually declining value for C_n.

Results and Conclusions

Batch experiments. When cassettes containing varying weights of resin in the hydrogen form were immersed in 500 mL solutions of distilled deionized water containing 50 ug of Cu and rotated at 120 rev/min, the Cu^{2+} recoveries presented in Table 2 were obtained. Amounts of Chelex-100 in excess of 100 mg did not improve the poor recoveries. This amount of resin has a capacity of 0.60 mmole Cu. Therefore, an excess capacity of approximately 80 fold was present in these experiments.

Table 2. COPPER COLLECTED FROM 0.10 PPM SOLUTIONS
AS A FUNCTION OF WEIGHT OF RESIN IN CASSETTE
PASSIVE MODE

ug Copper Collected/hr	% Copper Collected	Weight Wet Resin in Cassette
4.4	8.8	30 mg
6.5	13	50 mg
6.0	12	75 mg
7.4	15	100 mg
7.0	14	125 mg
3.1	6.2	300 mg
6.5	13	500 mg

Cu^{2+} loss to the container walls was a persistent problem. Aging of the containers at pH 7.0 with a 0.10 ppm Cu^{2+} solution was effective in satisfying presumably active sites on the container walls. Use of resin in the hydrogen form was discontinued due to discrepencies in solution content and resin uptake of metal.

Batch experiments were conducted using Chelex-100 resin in the ammonium form as the adsorbent in stirred solutions of varying Cu^{2+} concentration. Results of these studies presented in Appendix I and Figure 7 support the exponential adsorption model outlined previously. Maximum per cent recovery was 78 %.

Similar studies were conducted using resin packets as the adsorbing device. Results of these experiments are presented in Figure 8 and Appendix II. Where the batch experiments had shown maximum uptake after 50 hours, the resin packets had achieved only 68% of that uptake after 100 hours. The decreased rate of trace element uptake for the encapsulated resin versus "free-swimming" batch system was attributed to a film diffusion effect at the surface of the membrane sandwiches. Aging of the membranes utilized in forming the cassette had no effect on trace metal uptake by the cassette.
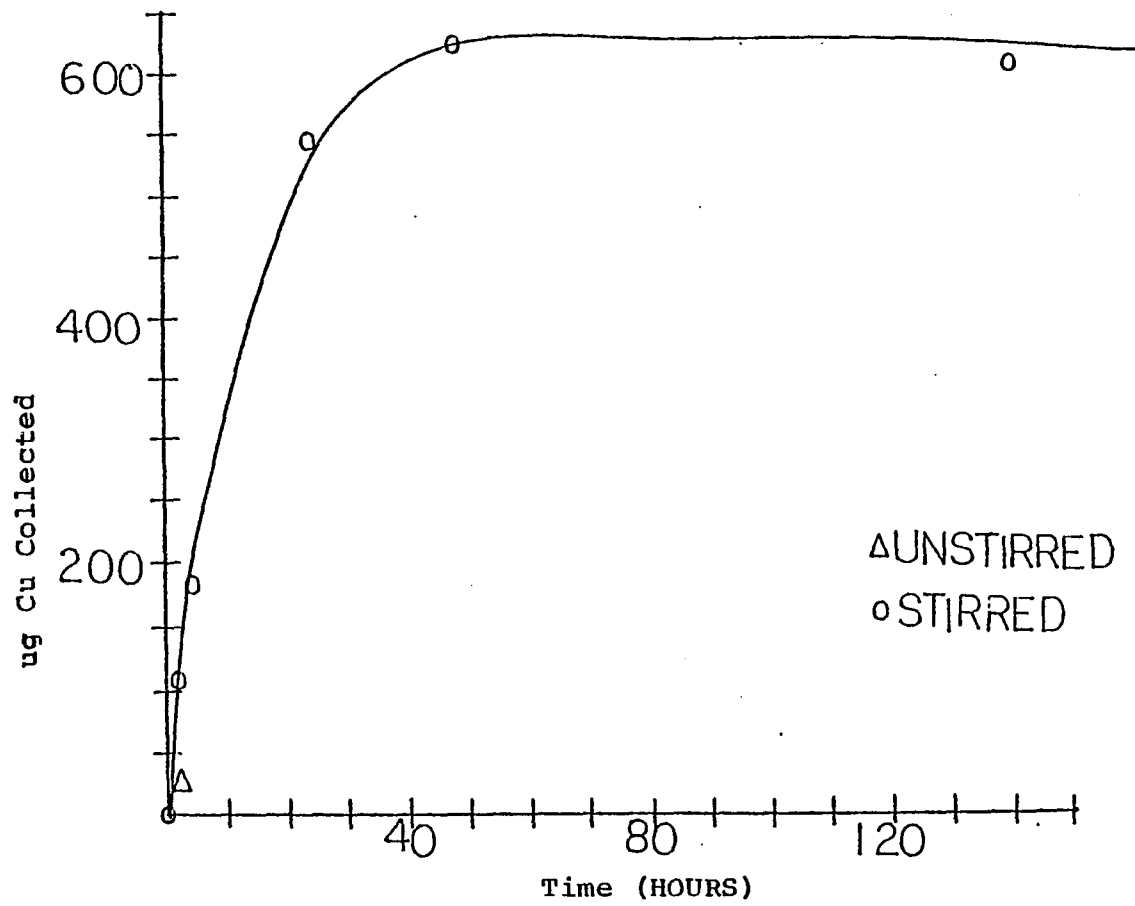
Figure 7.   Trace metal uptake using batch "free-swim" resin.
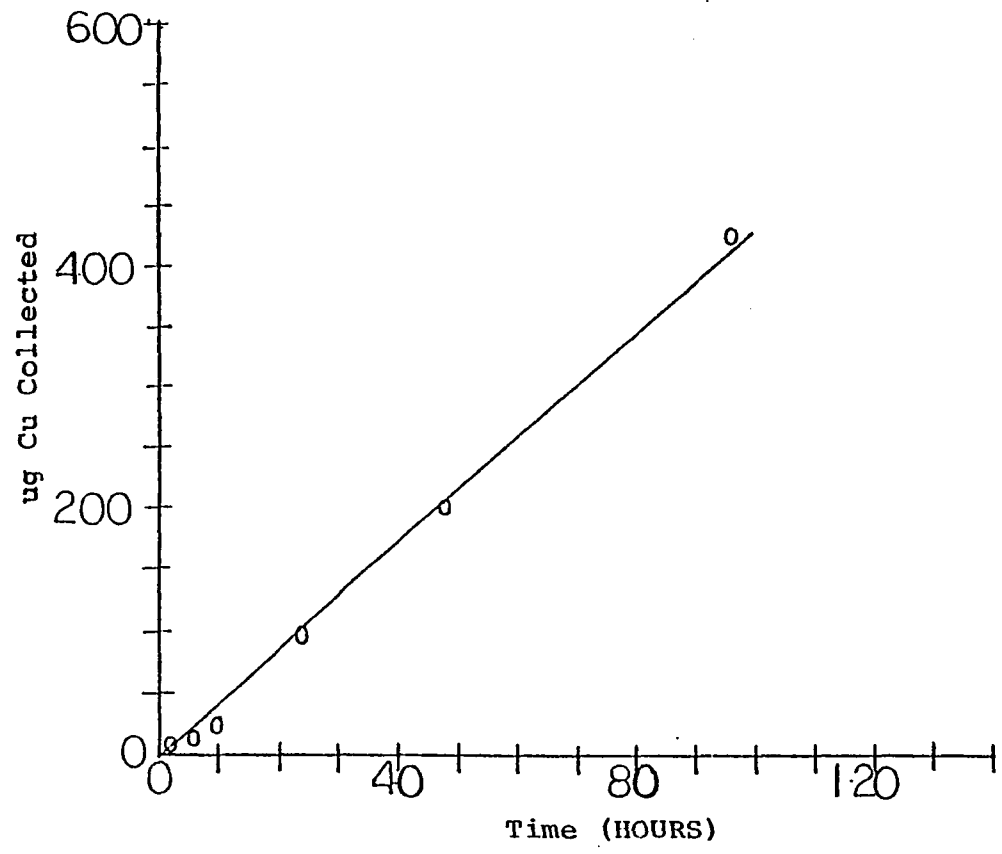
Figure 8. Trace metal uptake using a membrane encapsulated chelating resin (resin cassette). Accumulation is diffusion controlled.

<u>Characterization</u> <u>of</u> <u>active</u> <u>transport</u> <u>variables</u>.
Initial tests of the active cassette system were performed
using 4 liters of 0.20 ppm solution of Cu^{2+} in a Nalgene
container. The device was hand driven, withdrawing and
redispensing 25 mL of the solution every 15 seconds. After
60 cycles in which 1500 mL had been passed through the
device, the resin changed from its normal yellow to a blue
color indicating the successful chelating of the Cu^{2+} ion
by the resin.

Inflow, outflow volume reproducibility as the device
cycled was determined by first allowing the inflow portion
of a cycle to be completed in a beaker of water. The beaker
was then removed, the cassette membrane wiped dry with a
pass of tissue, and the contents of the cassette ejected
into a graduated glass centrifuge tube. This procedure was
repeated five times with findings of a mean volume ejection
of 1.74 mL and a standard deviation of 0.02 mL.

The 0.40 um Nucleopore membrane has been used in waters
containing up to 120 mg/liter of particulates with no
apparent flow decrease for up to 70 hours. However, the
0.20 um Nucleopore membrane clogged with accumulated
sediment in moderately-loaded waters.

Utilizing particulate free Cu^{2+} solutions, the effect
of membrane porosity on trace metal accumulation was
examined. As was anticipated the change of membrane
porosity from 3.0 um pore diameter to 0.4 um pore diameter

did not affect the solution volume exchange through the device. Determination of the Cu^{2+} content of the resin in cassettes with different membrane porosities cycled for two hours revealed cassette uptake with a range of 19.9 $\pm$ 4.00 ug at the 95% confidence level (Table 3-Conditions 4 and 5).

The effect of change in the rate of solution flow on trace metal uptake by the cassette was also determined. Cycle time of the cassette was varied using a step- function speed reducer (model 00140 Insco Corp.). This allowed the drive motor to be run at a high and constant rpm. The speed reducer converted the high rpm to a more useful range yet allowed retention of the torque developed by the drive motor run at the higher speed. Typical rpm reductions used were 1000:1; 500:1; and 200:1. Although use of lower motor speed reductions was possible, the tendency of the membrane package to rupture under the repeated stress of the greater inflow:outflow rates precluded their use. Copper uptake correlated with flow rate for this first portion of the accumulation curve (Table 3-Conditions 1-3). Appendix III lists values of Cu accumulation versus time for experiments of up to 70 hours in duration. Variables were as in Table 3-Condition 1.

Finally, the effect of solution concentration on trace metal accumulation by the cassette was examined. The results indicated that within the range of 0.10-0.20 ppm Cu^{2+} solution concentration, Cu^{2+} accumulation by the

Table 3.   COPPER UPTAKE BY THE ACTIVE CASSETTE
           FOR SEVERAL EXPERIMENTAL COMBINATIONS

Condition	Hours	ug Cu Collected	Membrane Pore Size	Soln Cu Conc	mL/min
1	1	7.9	3.0 um	0.20 ppm	0.87
2	1	16.1	3.0 um	0.20 ppm	1.74
3	1	40.1	3.0 um	0.20 ppm	4.35
4	2	20.8	3.0 um	0.20 ppm	0.87
5	2	18.9	0.4 um	0.20 ppm	0.87
6	2	10.5	3.0 um	0.10 ppm	0.87

cassette varied directly with solution concentration (Table 3-Conditions 4 and 6).

CHAPTER IV

STUDIES USING A MODEL

"CONTAMINATED" CLAY

Site Theory Of Cation Exchange

Selectivity coefficients (K_c) for ions on colloids vary with the ionic composition of the exchanger (Marshall 1964) as well as the ionic strength of the solution (McBride 1979). As a result, exchange equations have only semi-quantitative predictive value, although they are used to calculate selectivity coefficients for the exchanger. The relation between "activities" of adsorbed ions and the fraction of surface exchange sites occupied by the ions is reflected in the functional dependence of K_c on the ionic composition of the surface.

The selectivity coefficient, K_c, for the adsorption of K^+ on Cu^{2+} illite can be defined as:

$$K_c = [K^+]_s^2 / [Cu^{2+}]_s \cdot [Cu^{2+}]_{aq} / [K^+]_{aq}^2$$

(17)

67

where $[K^+]_s$ and $[Cu^{2+}]_s$ are fractions of the total

clay exchange sites occupied by K^+ and Cu^{2+}, and

$[K^+]_{aq}$ and $[Cu^{2+}]_{aq}$ are the respective solution

activities at equilibrium. A plot of K_c as a function of

$[Cu^{2+}]_{aq}$ demonstrates the nonconstant nature of the

selectivity.

The form of the ion-exchange equation used to obtain

K_c was based upon the hypothesis put forward by Vanselow

(1932) that "activities" of surfaced-adsorbed ions are

proportional to the fraction of sites occupied. This

required the assumption that surface-adsorbed ions form an

ideal binary "solution", with any departure from ideal

behavior being manifested by small variations in K_c with

changing surface composition. Drawing upon the work of

Adamson (1976) in statistical mechanics for the derivation

of the chemical potential of surface ions, McBride (1979)

suggested that variations in K_c arose from site localized

behavior of weakly hydrated ions.

Experimental

Clay preparation. Experimental studies with clay to

determine desorption characteristics were conducted using

illite #36 (Wards Scientific Co.). Twenty grams of the clay

as received was ground and sieved through a 325 mesh screen

to remove coarse particles. The clay was divided and washed

in 250 mL Nalgene centrifuge bottles. Initial cleanup

consisted of 3(50 mL) washes with 2 N HCl prepared from redistilled 6 N HCl. The portions were centrifuged at 10,000 rpm for 15 minutes between washes and the supernatant decanted. Acid washes were followed by 3(50 mL) deionized water rinses, 2(15 mL) anhydrous methanol rinses and 2(15 mL) acetone rinses.

The clay portions in the centrifuge bottles were dried under vacuum at 60 C for five hours. The collected dry portions of clay were placed in a Nalgene centrifuge bottle. 500 mL, of 1 M NaCl, previously cleaned by passage through a Chelex-100 resin column, was added. The mixture was stirred for 24 hours. At the end of the equilibration period the NaCl solution was decanted. The remaining slurry was divided evenly between four Nalgene centrifuge bottles and centrifuged at 10,000 rpm for 15 minutes. Supernatant was decanted and the clay was rinsed with 2(25 mL) portions of deionized water, centrifuging and decanting the supernatants between portions. A final rinse with 15 mL of anhydrous methanol was made and the clay was centrifuged, and dried under vacuum at 60 C for 24 hours.

Three grams of the Na form illite were placed in a Nalgene centrifuge bottle. A solution consisting of 10.00 mL of 1000 ppm Cu^{2+} solution and 200 mL of distilled, deionized water was added. The mixture was placed on a stirrer plate set at moderate speed and allowed to equilibrate 24 hours. Following equilibration, the slurry

was placed in 4 Nalgene centrifuge bottles, spun at 10,000 rpm for 15 minutes, and the supernatant decanted into a 250 mL volumetric flask. Two washes using 5 mL portions of anhydrous methanol were combined with the previous decantate. The Cu illite was dried in the bottles at 60 C for 6 hours under vacuum. All the clay portions were combined and stored in a dessicator containing silica gel.

Results and Conclusions

Clay analysis. Subsequent analysis of clay extracts (2 N HCl) and the combined decantates showed mass balance for Cu. The clay contained 1728 ug Cu per gram. Previously illite adsorbed 1530 ug per gram (Potash 1977).

Desorption experiments with the prepared Cu illite clay were hampered by an initial massive desorption of Cu to the solution. The most probable source of this Cu was some remaining interstial Cu plus some that was very weakly bound and, therefore, readily desorbed. pH affected the initial desorption of Cu. Essentially complete desorption occurred below pH 3, while above pH 6.5 the Cu was "fixed" to the clay either as aquo ions, or colloidal hydroxy, carbonate species. Similar behavior has been observed using illite and other clay minerals (Farrah and Pickering 1976a, 1976b, Guy and Chakrabarti 1976).

Model contaminated clays. The pH dependency of Cu

binding was used to prepare clays containing lesser amounts

of copper than the material described above. The general

scheme was to take an initial clay portion and place it in a

solution previously adjusted to pH 6.5 using 0.1 N NH_4OH.

The pH was slowly lowered by adding portions of 0.1 N HCl

and the copper concentration of the clay monitored by

analyzing samples. When desorption had reduced the copper

concentration on the clay to a desired concentration, the

clay slurry was decanted into centrifuge bottles and

centrifuged at 10,000 rpm for 15 minutes. The supernatant

was decanted, the clay washed with anhydrous methanol, and

dried under vacuum for 6 hours.

By this method, clays with copper concentrations of 750

and 1067 ppm were prepared. The Cu desorption

characteristics of these clays were investigated at various

pH levels in both deionized water and 3 x 10^{-3} M KNO_3.

For both model clays, copper desorption paralleled that seen

in the original copper spiked clay, except the initial

amount of copper released to solution was less. Presumably

the copper readily desorbed in preparing the model clays was

interstitial and weakly bound. The implication was that the

degree of desorption of copper from a clay subjected to an

environmental stress such as a change in ambient pH was

similar although the magnitude of actual elemental release

to the environment depended upon the initial amount present

in the clay.

The effect of competition for adsorption sites on the clay surface is seen by comparing Figures 9 and 10 where results obtained for both clays in 3 x 10^{-3} M potassium nitrate and deionized water are presented. Equilibrium concentrations were attained after four hours of shaking. This ionic strength was comparable to levels in natural water systems. The competition of potassium for sites on the clay surface resulted in a greater desorption of copper at natural water pH levels than observed in distilled water. The slopes for the curves in 3 x 10^{-3} M potassium nitrate (Figure 10) indicate much less copper remaining on the clay than for equivalent conditions in distilled water (Figure 9). Remaining bound copper occupied higher binding energy positions in a competing ion situation, therefore, at low pH, copper bound to clay in the absence of competing cations desorbed more readily. The different slopes in KNO_3 and H_2O were used to calculate percent copper desorption per pH unit. For the clays studied, percent desorption of copper did not depend upon the initial copper concentration on the clay. However, it was dependent upon solution composition.

Syringe Drive Cassette and Clay Desorption Experiments

Experimental design. Having studied desorption characteristics of the Cu-illite clay as a function of pH, the investigation of the desorption characteristics of the clay using the syringe drive cassette device was begun.
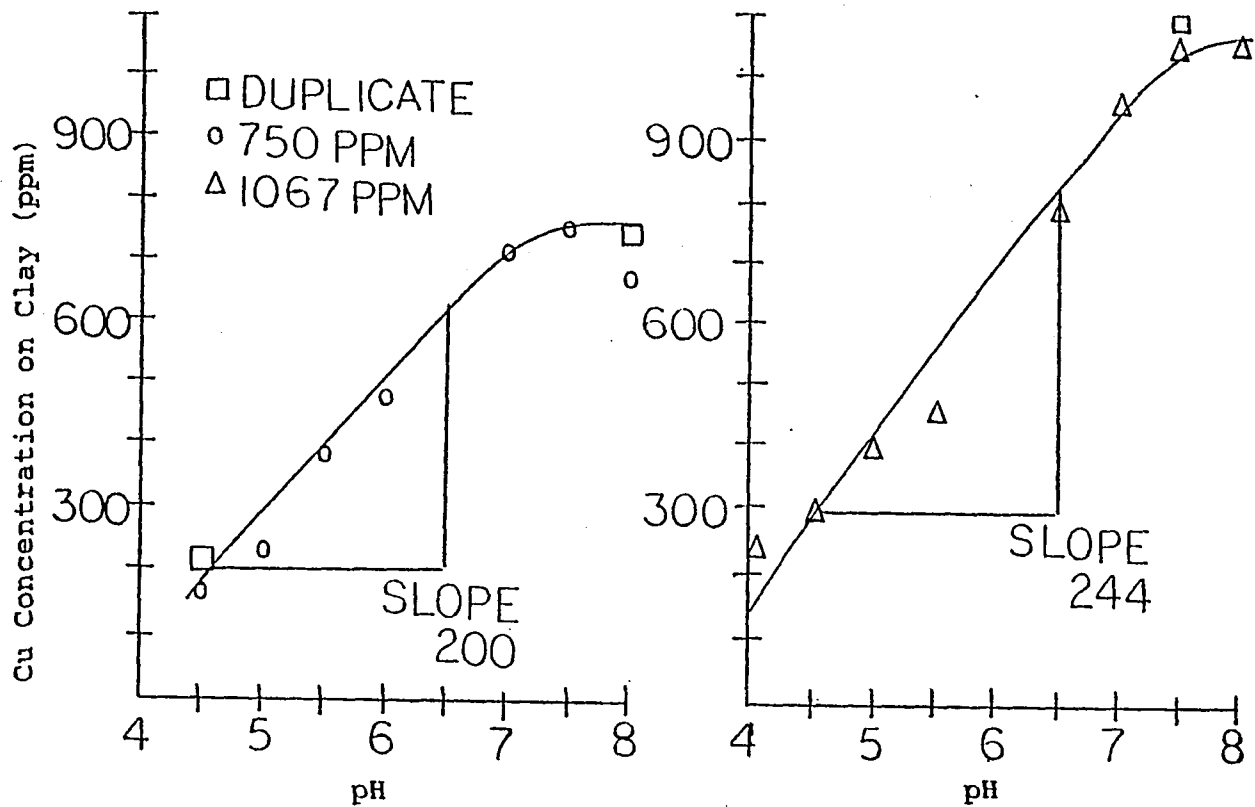
Figure 9. Copper desorption from 1067 and 750 ppm "contaminated" clay in distilled water as a function of pH.
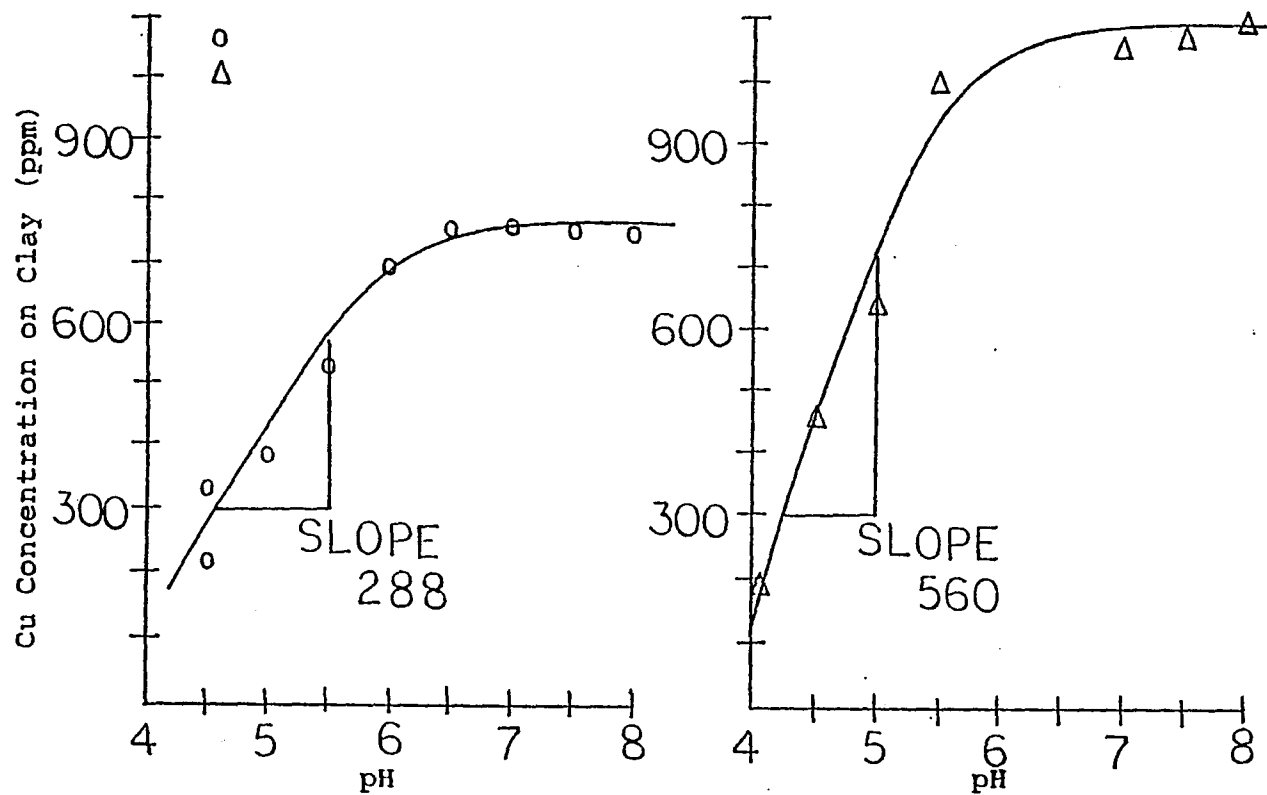
Figure 10. Copper desorption from 1067 and 750 ppm
"contaminated" clay in 3 x 10^{-3}M KNO_3 as a function
of pH.

Copper in solution was removed by the chelating resin and the spent solution returned to the main body of the solution on the next half cycle. Introduction of the spent solution to the main body of the solution lowered the solution concentration of copper. Clay particulates are then required by equilibrium conditions to release adsorbed copper to the solution. This process has been designated Equilibrium Drive. The process continued until the copper on the clay was all desorbed or was so firmly bound as to be irreversibly adsorbed. Due to analytical limitations, I was not able to determine if there was a very small concentration that was irreversibly bound.

The important point to note was the dependence upon reducing solution concentration in the system as the cause for release of trace element from the clay particulates.

Conditions. Standard conditions for the desorption experiments were established. Two liter solutions of 3 x 10^{-3} M KNO_3 were placed in Nalgene containers and the pH adjusted to the desired value by addition of either 0.1 N HCl or NH_4OH. A weighed portion of Cu-contaminated clay (0.240 g) was added and stirred with a floating stirrer bar for 24 hours. The syringe drive cassette device was placed in the solution. Volume exchange in the cassette was set to 4.00 mL/min. Samples were taken with a thief at appropriate intervals to monitor the progress of the desorption. Each sample of the clay slurry was filtered on a preweighed 0.20

um Nucleopore filter. The filtrate was acidified with 2 N HNO_3, reduced in volume on a hot plate, and made to 10.00 mL in a volumetric flask. The collected clay was dried at 60 C in a vacuum oven, weighed, and extracted with 2(4 mL) portions of 2 N HCl. The extract was collected in a Nalgene centrifuge tube, transferred to a 10.00 mL volumetric and analyzed using flame atomic absorption spectrometry. Due to the greater manipulation involved in the preparation of the clay sample extracts, the uncertainty in their analysis was greater than that of the filtrates. Duplicate samples taken during the course of an experiment bore this out. The pooled per cent relative standard deviations for clay and filtrate analyses were 6.5 and 5.3 %, respectively.

Results And Conclusions

Desorption experiments. The results of a typical Cu desorption experiment at pH 5.5 using the 750 ppm Cu "contaminated" illite clay are presented in Figure 11 . Duplicate points taken during the course of the analysis are included. Data presented in Appendix IV for this experiment illustrates the agreement between experimentally found values for copper uptake by the cassette, derived from clay and solution concentration data, and the mathematical prediction of copper uptake. Analysis of cassette contents, and the final clay and solution concentrations of copper, showed that mass balance had been achieved in the experiment.
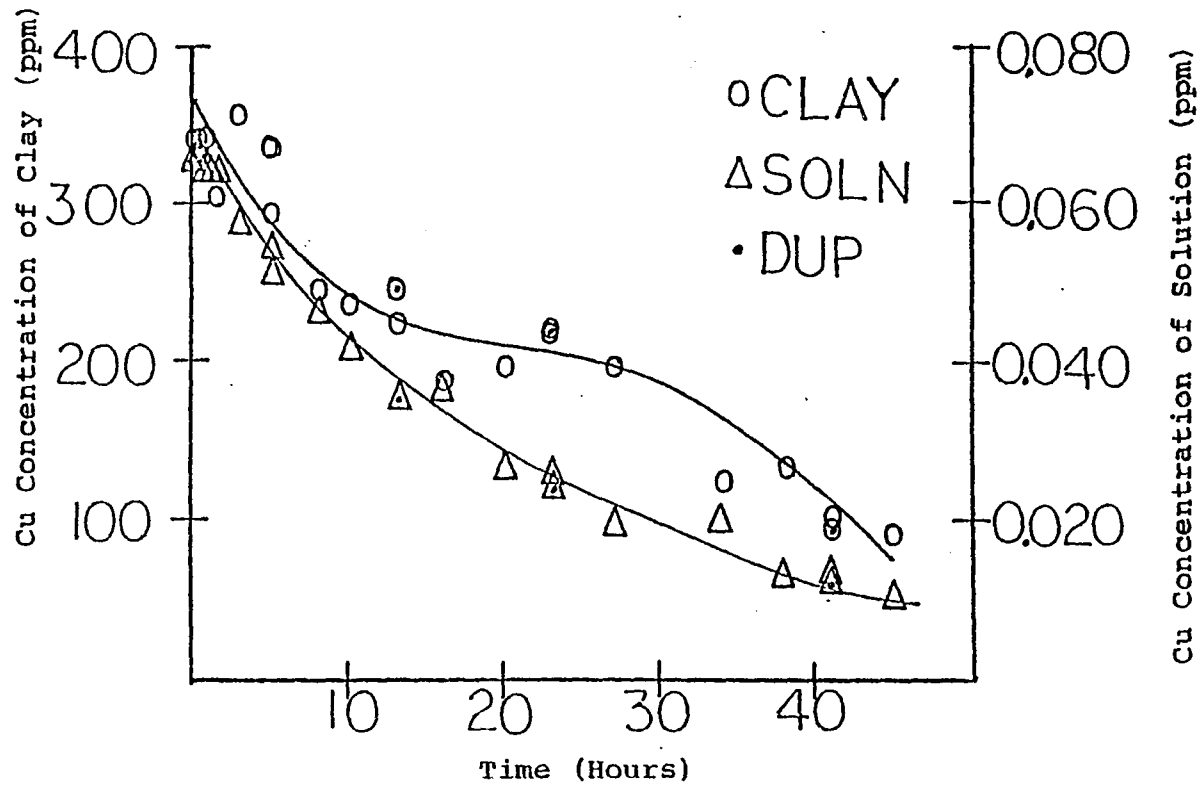
Figure 11. Copper desorption from 750 ppm Cu-illite in pH 5.5 KNO₃ solution. Decline of Cu concentration in solution and clay phases.

Similar studies were conducted at pH 6.5, 5.8 and 4.8. Figure 12 is a composite of the clay desorption curves for the various pH values. Comparable solution concentrations are presented in Figure 13. Mass balance was obtained within the limits of experimental error in all of these experiments.

In order to further examine the complex shapes of these desorption curves, I plotted per cent of original copper remaining on the clay versus mass of Cu collected. This related the desorption behavior of the clay to the amount of metal removed rather than to a time function (Figure 14). Copper desorption behavior plotted in either manner showed marked dependence upon pH. Desorption was greatest for highly contaminated clays placed in low pH environments. As seen in Figure 14, this effect was lessened as copper concentration levels on the clay approached naturally occurring levels. These findings were due to differences in copper speciation at the four pH levels examined. At pH 4.5 copper was primarily in the aquo (ionic) form whereas at pH 6.5 approximately 95 % was hydroxylated (Zirino and Yamamoto, 1972). Curvature in the desorption plots is ascribed to binding energy changes. Binding energy as previously discussed, will depend upon amount and form of adsorbed cation.
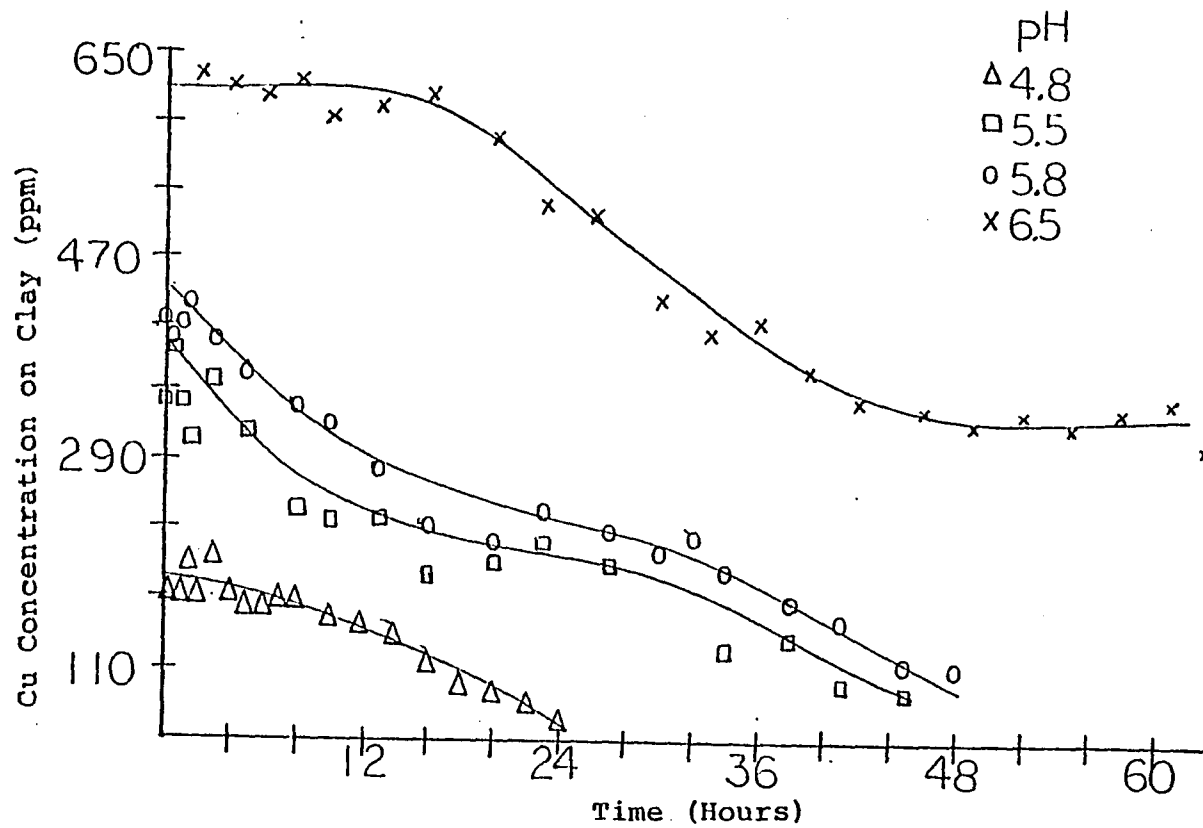
Figure 12.   Desorption of copper from 750 ppm
Cu-illite using the active cassette system.   The
four curves are for four different pHs.
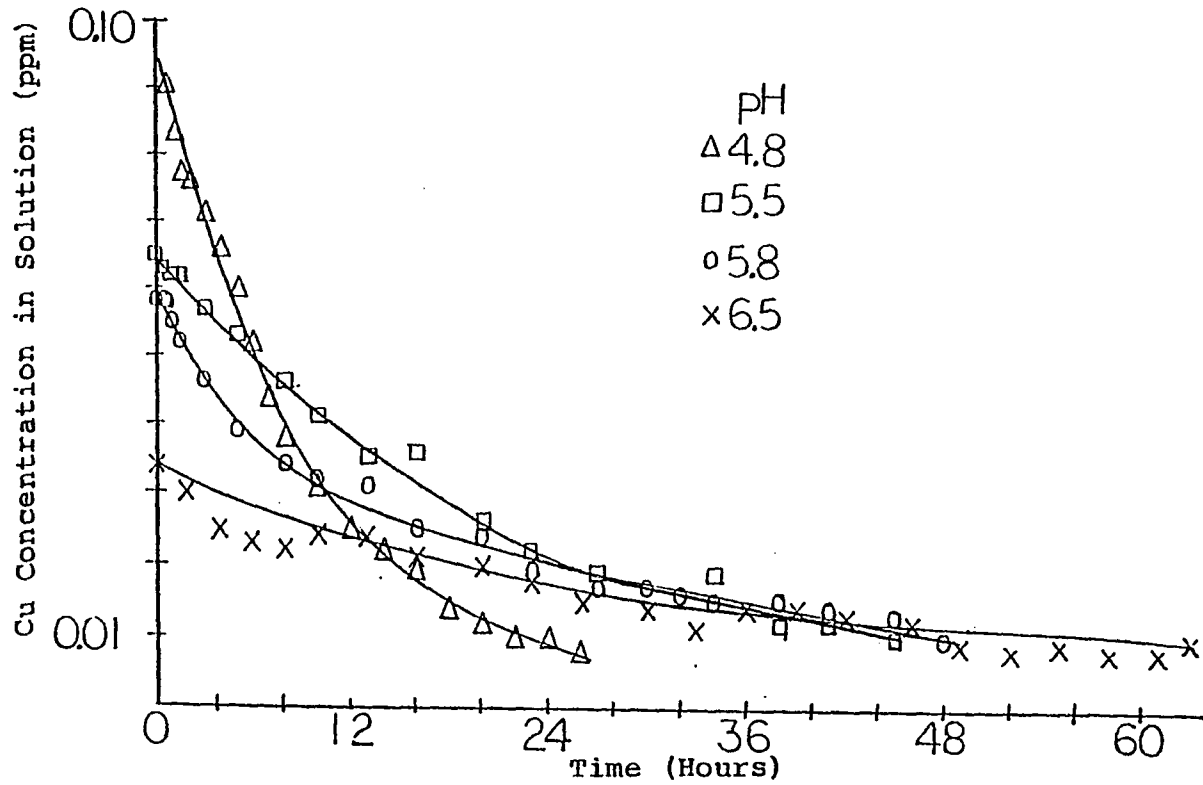
Figure 13. Decrease of copper concentration in
solution for the active cassette system with 750 ppm
Cu-illite at four different pHs.
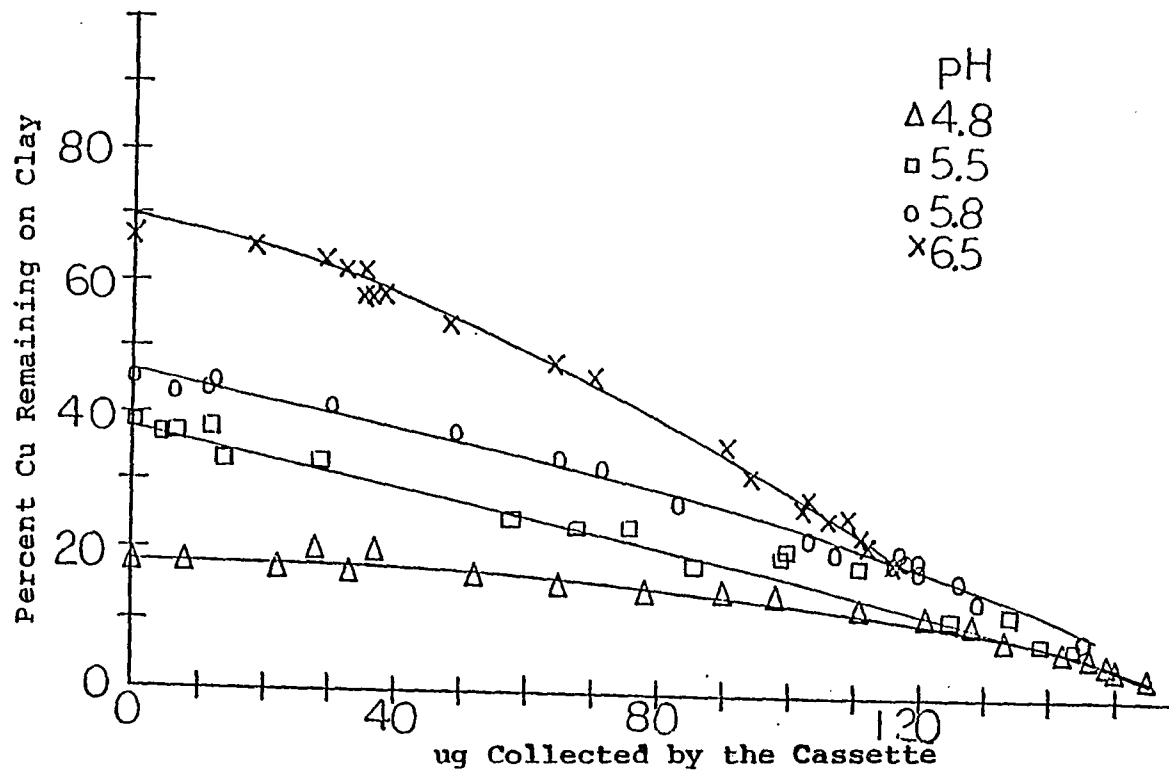
Figure 14. Desorption of copper from 750 ppm
Cu-illite using the active cassette system. The time
axis has been converted to mass copper removed from the
system. The four curves are for four different pHs.

In figure 15, I have plotted desorption as a function of copper remaining in both solution and particulate phases versus copper removed. Since the amounts of copper in clay and solution were measured in the concentration unit of ppm, the function expressed as 1/(1 + ug soln/ug clay) is a form of K_c for desorption of Cu^{2+} from illite where:

$$K_c = [Cu^{2+}]_{aq}/[Cu^{2+}]_s \qquad (18)$$

The slopes were similar at different pH°s, changing in the same manner as Cu concentration in solute and solution was reduced. The linear behavior seen at the pH levels examined indicates K_c was relatively constant at a single pH, but there is an apparent slight change as desorption progresses.

I am convinced that the complex shapes of the clay desorption versus time curves were an artifact of the time variable. Solution concentration, not time, was the primary variable in this case. A decrease in solution concentration results in a decrease in cassette uptake of metal. With the cassette removing less Cu from solution, the equilibrium drive characteristic of the device slowed. In short, the solution concentration directly affected the cassettte uptake characteristics and through equilibria requirements the clay desorption process. Biota presumably affect their environment in a similar manner.
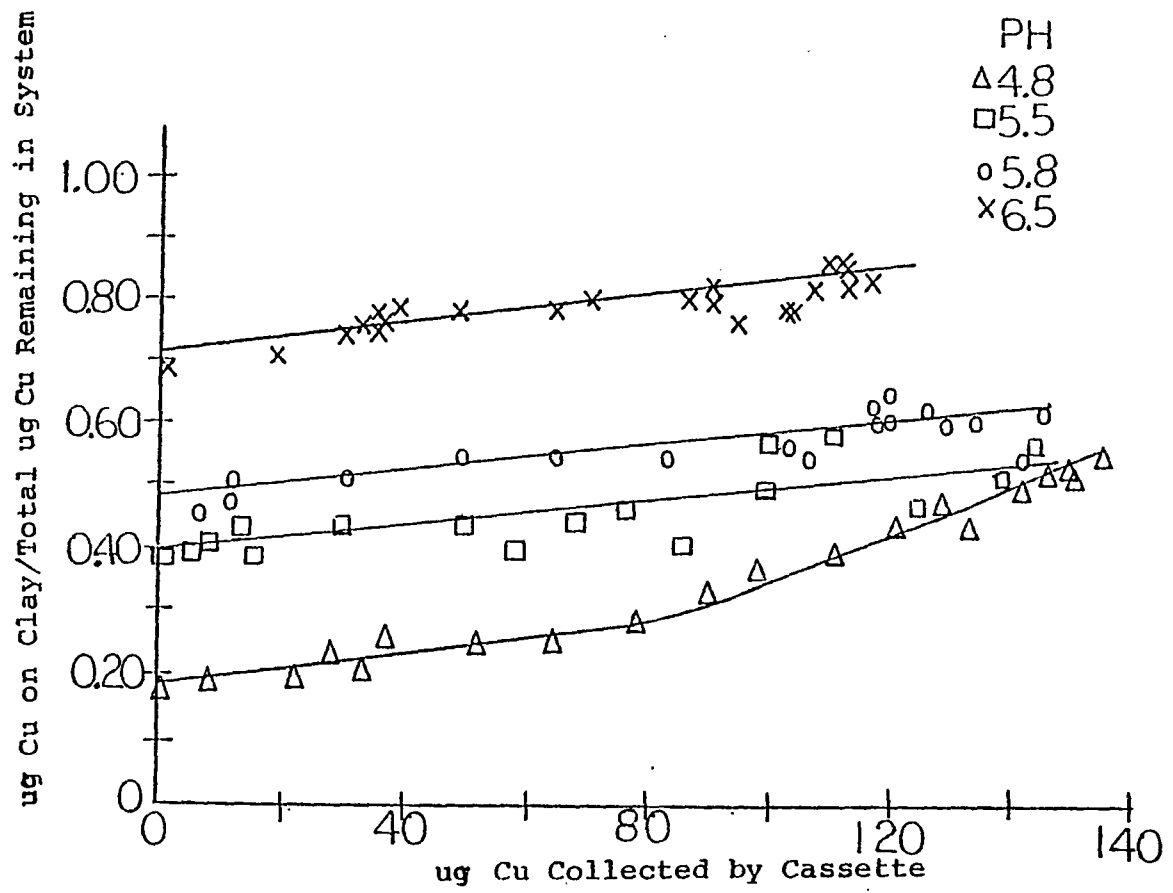
Figure 15. Desorption of copper as a type of K_c function at four different pHs.

Speciation experiments. Experiments were conducted to
obtain a better understanding of the transmission of various
copper species through the membranes. Clay portions were
allowed to equilibrate in potassium nitrate solutions of
ionic strength 3×10^{-3} for 24 hours. Portions (50 mL) of
this clay slurry were filtered through 0.40 um Nucleopore
filters. The filtrate was collected and split into two
equal samples. One of these samples was acidified with 2 N
HNO_3, concentrated by volume reduction, and analyzed by
atomic absorption spectrometry. This was the same procedure
used in the desorption studies for analyswas of the filtrate
and yields a result for the total copper content. The
second 25 mL sample was analyzed using Ion Selective
Electrode (ISE) potentiometry. The pH of the sample was
monitored using a miniature pH electrode (Corning). In
small increments, the pH of the solution was lowered to
approximately pH 4, and then raised to pH 7. The millivolt
output of the ISE was recorded at each increment and related
to "free" i.e. ionic copper concentration in the sample.
The experimental schematic for this procedure is presented
in Figure 16. Typical data obtained are presented in
Appendix V. The graph of this data and those for ISE
studies of filtrates obtained from clay slurries of
different pH levels are presented in Figures 17 and 18.

From AA studies conducted on Cu illite and ISE data
obtained at pH 4, it can be concluded that the copper in
solution at this pH is essentially free cupric ion.
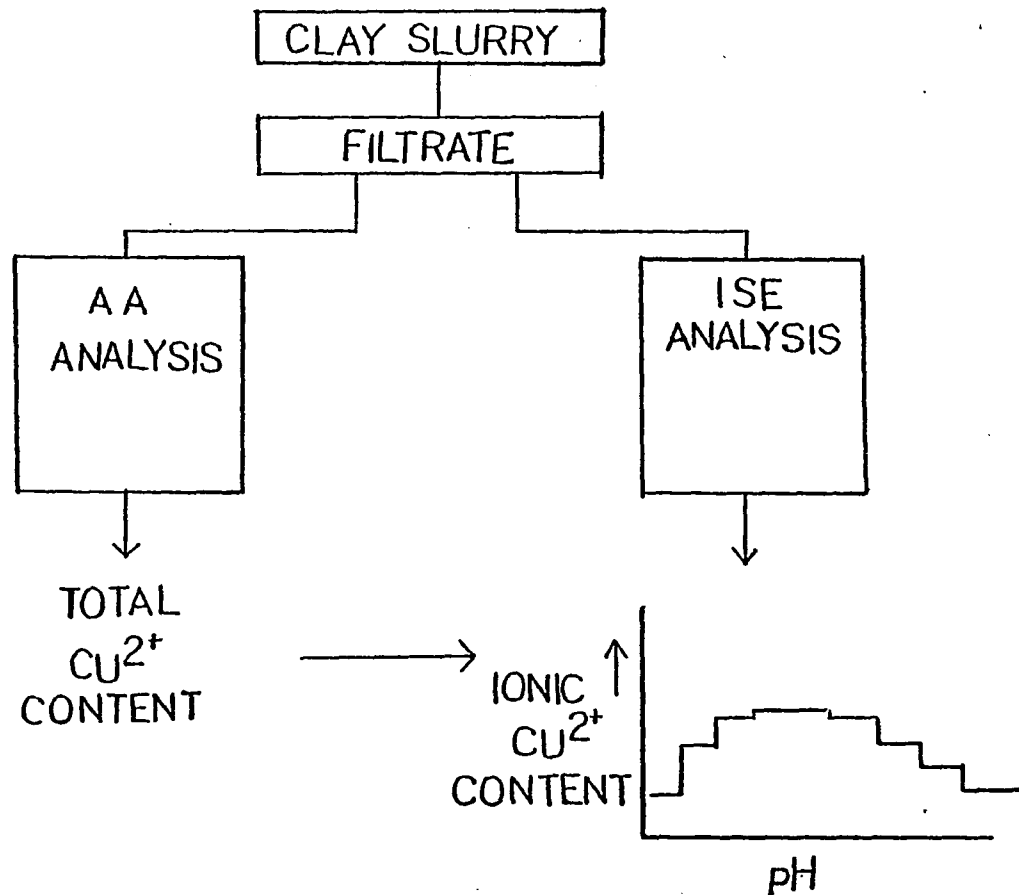
Figure 16. Schematic of ISE and AA split
sample analyses of clay slurry filtrates.
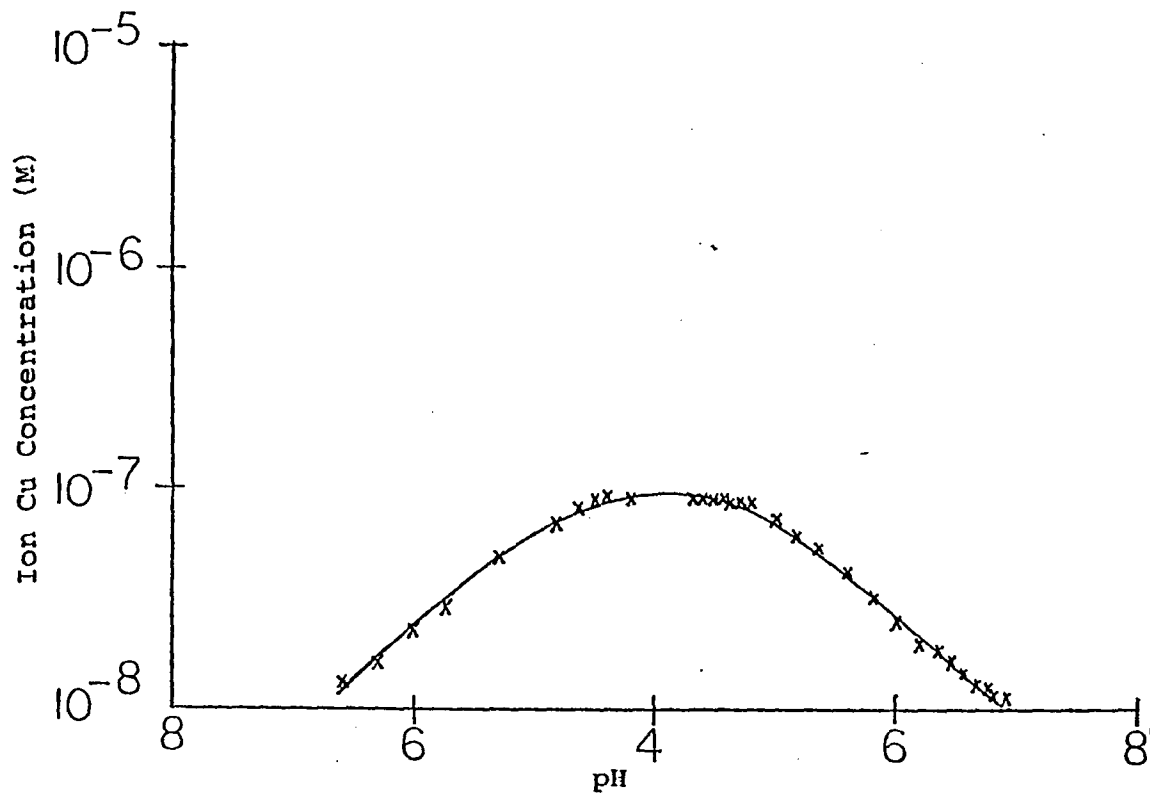
Figure 17. Effect of changing pH on ionic Cu
concentration using ISE measurements for initial
pH 6.6 clay slurry filtrate.
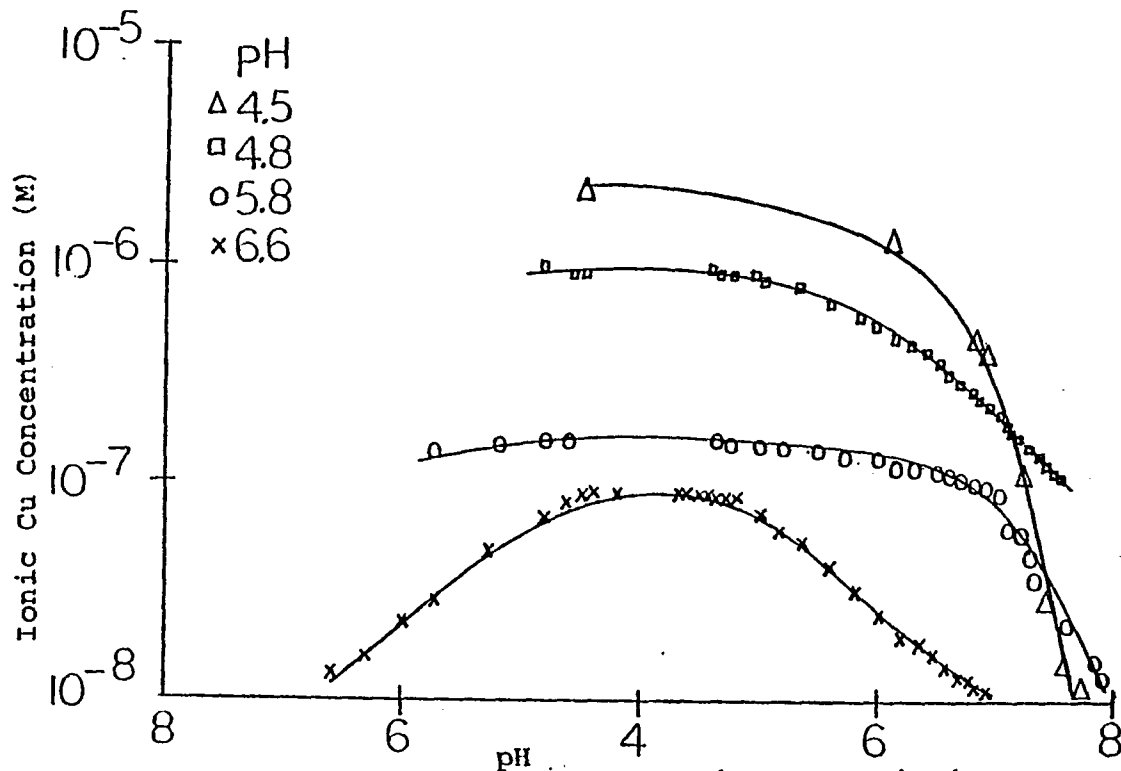
Figure 18. Effect of changing pH on ionic Cu concentration using ISE measurements of clay slurries and a 1 x 10^{-5}M Cu filtrate. The curves are for four initial pH levels.

Therefore, the total copper concentration of the filtrate sample analyzed by atomic absorption should equal the copper concentration found at the lowest pH value of the ISE experiments. The data in Appendix VI supports this conclusion. The atomic absorption data were used as an outside experimental check on the accuracy of the ISE measurements. Reversibility of the speciation characteristics of the systems studied was shown by raising the pH value back to its original value or higher.

I conclude that at pH values comparable to natural waters, up to 62 % of copper is in the form of particulate or colloidal species below 0.40 um. Due to the reversibility shown, these are probably inorganic soluble species. Emission spectrographic analysis of filtrates from pH 6.6 and 4.0 clay slurrys revealed Si,Al,Mg and Fe in the filtrates. This was regarded as evidence for clay particulate passage through the membrane. However, visual and microscopic examination of cassette contents after extended desorption experiments gave no indication of significant collection of clay. A quantitative measure of particulate quantity passing through the membrane was not obtained.

Analysis of solutions passed through Nucleopore membranes of 0.20 and 0.40 um size revealed no significant difference in Cu^{2+} content when measured using atomic absorption . Therefore, the size range of material passing

the filter in non-ionic form is below 0.20 um. Similar
findings are being debated in the literature. Emerson
(1976) presented evidence indicating that membrane porosity
has a negligible effect on filtrate concentration of trace
metals. On the other hand, work has been reported in which
elemental concentration in filtrates varied substantially
with changes in membrane porosity (Kennedy et al. 1974,
Durham and Haffty 1963). The individual element and its
chemical nature are extremely important in regard to the
magnitude of this effect. The evidence presented for the
negligible effect of porosity in my clay slurry filtrations
cannot be quantitatively extrapolated to other elements.

Concluding Remarks.

I have studied trace metal accumulation in batch and
flow-through collection systems using Chelex-100 resin
encapsulated between polycarbonate Nucleopore membranes.
Although the cassette system performed as expected in closed
systems, diffusion control of trace metal accumulation was
unsatisfactory for future clay desorption studies. A flow
through system was constructed using a syringe drive to
increase the rate of trace metal accumulation. This device
was applied to desorption studies of model copper
"contaminated" illite clay. Complex desorption curves
obtained were an artifact of the use of collection time as a
variable. Substituting cumulative copper collection as the

independent variable shows desorption was a function
dependent upon copper concentration of the clay, solution
concentration and pH. Speciation studies using both ISE and
AA analyses reveal copper in the form of inorganic solute
species at pH values of 6.0 or above. Membrane porosity
studies show that these species can pass into the resin
cassette where some fraction can be immobilized.

The method as described in this thesis is unique in its
use of equilibrium requirements between particulate and
solution phase to determine cation desorption
characteristics. It may be possible to relate this
desorption behavior to bioavailability through comparative
studies with biota.

APPENDIX I

Uptake Of Cu Over Time In A Closed System

By Batch "Free-Swim" Resin

BATCH RESIN EXPERIMENTS

Time(hrs)	Condition	ug Cu Collected	Initial Cu Conc. ppm
2	unstirred	27.5	0.20
2	stirred	109	0.20
4	stirred	182	0.20
24	stirred	545	0.20
48	stirred	623	0.20
140	stirred	608	0.20
163	stirred	367	0.10

APPENDIX II

Uptake Of Cu Over Time In A Closed System Using

A Membrane Encapsulated (Passive) Resin Cassette

PASSIVE CASSETTE COLLECTION DATA

Time (hours)	ug Copper Collected
3	1.6
6	15
10	24
24	98
48	201
96	426

APPENDIX III

Cumulative Uptake Of Cu By Active Cassette Over Time

ACTIVE CASSETTE COLLECTION DATA

Time (Hours)	ug Copper Collected
1	7.9
2	20.8
4	39.9
10	90.5
24	217
48	371
70	455

(a) All solutions originally 0.20 ppm Copper

APPENDIX IV

Data Set For pH 5.5 Active Cassette Clay Desorption

Study Using 750 ppm Cu "Contaminated" Illite Clay

PH 5.5

ACTIVE CASSETTE EXPERIMENTAL DATA

Time (hours)	mg clay sampled	ppm Cu on clay	ug Cu on clay	ppm Cu in soln	ug Cu in soln	Total Cu in system	Δ	Theor. Cu uptake
0	2.93	340	81	0.065	128	209		
0.5	2.31	333	78	0.062	120	198	9	9
0.5	2.36	343	79	0.065	124	203		
1	2.14	341	78	0.062	116	194	6	7
1.5	2.51	306	70	0.062	114	184	16	7
5	2.81	333	73	0.051	91	164		
5	2.36	292	64	0.054	95	159	22	26
8	2.34	243	52	0.046	79	131	31	34
10	2.32	235	50	0.041	69	119	12	18
13	2.18	224	47	0.035	58	105		
13	1.96	248	52	0.035	57	109	12	25
16	2.06	188	39	0.036	57	96	11	25
20	2.17	198	41	0.026	41	82	14	19
23	2.00	216	44	0.023	35	79		
23	2.15	218	44	0.022	33	77	4	17
27	2.27	198	39	0.019	28	67	11	19
34	4.59	124	24	0.019	27	51	16	31
38	4.22	133	25	0.012	16	41	10	11
41	4.78	92	17	0.012	16	33		
41	4.57	100	18	0.013	16	34	7	9
45	4.90	90	16	0.010	12	28	6	9

APPENDIX V

Data Set For ISE, pH Variation Study Using

Filtrate Of A pH 6.6 Clay Slurry

ISE ANALYSIS
pH 6.6 CLAY SLURRY FILTRATE

pH	Concentration (M)	pH	Concentration (M)
6.60	2.10×10^{-8}	4.70	1.05×10^{-7}
6.35	2.89×10^{-8}	4.82	1.01×10^{-7}
6.08	3.78×10^{-8}	4.96	9.26×10^{-8}
5.75	5.24×10^{-8}	5.14	8.55×10^{-8}
5.27	7.24×10^{-8}	5.35	7.72×10^{-8}
4.87	8.62×10^{-8}	5.59	6.59×10^{-8}
4.65	9.79×10^{-8}	5.83	5.58×10^{-8}
4.51	1.05×10^{-7}	6.02	4.76×10^{-8}
4.37	1.13×10^{-7}	6.18	4.13×10^{-8}
4.27	1.17×10^{-7}	6.32	3.52×10^{-8}
4.33	1.16×10^{-7}	6.45	3.03×10^{-8}
4.37	1.16×10^{-7}	6.55	2.63×10^{-8}
4.42	1.15×10^{-7}	6.65	2.31×10^{-8}
4.47	1.15×10^{-7}	6.74	2.06×10^{-8}
4.53	1.12×10^{-7}	6.84	1.80×10^{-8}
4.60	1.11×10^{-7}	6.92	1.60×10^{-8}

APPENDIX VI

ISE And AA Analyses Of Split Sample

Clay Slurry Filtrates

IONIC VERSUS TOTAL COPPER MEASUREMENTS USING AN
ION SELECTIVE ELECTRODE AND ATOMIC ABSORPTION SPECTROMETRY

Sample	pH	ug Cu by ISE	ug Cu by AA	ISE Sample Analyzed by AA (a)
1	4.8	---	1.60	---
1	4.8	1.56	---	1.56
2	5.8	---	0.35	---
2	5.8	0.45	---	0.45
3	6.6	---	0.22	---
3	6.6	0.18	---	0.18

(a) The split samples were analyzed by AA to evaluate sample homogeniety.

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