SYNTHESIS AND CHARACTERIZATION OF
MODEL AQUATIC PARTICULATES FOR
USE IN SORPTION STUDIES

FREDERICK WILLIAM PAGE
SYNTHESIS AND CHARACTERIZATION OF MODEL AQUATIC PARTICULATES FOR USE IN SORPTION STUDIES

Abstract
The synthesis and characterization of single- and multi-component model aquatic particulars is the object of this dissertation. Particulates were synthesized from illite, humic and fulvic acids, and iron, aluminum, and manganese hydrous oxides. Characterization included measurement of cation exchange capacity (CEC), and attempts to determine surface area and the pH of zero point of charge. Each of these methods was tested to determine their applicability to aquatic particulates, and attempts were made to improve the methodology.

CEC varied with composition and time of aging. Pure hydrous oxides exhibited decreases in CEC over time. Aging effects were also shown by aluminum hydrous oxide-clay mixtures. The CEC of iron hydrous oxide-clay particulates increased with iron content on the clay. Similar trends in CEC with composition were observed for organic matter-containing particulates. CEC data, in conjunction with compositional data, suggested that hydrous oxide-clay particulates had a limited adsorption capacity for organic matter.

Attempts to measure surface area through adsorption of cationic dyes were unsuccessful. Dye adsorption on illite varied with the square root of the ionic strength of the dye solution. This trend was interpreted in terms of a simple model of charge density at the solid-solution interface and Gouy-Chapman theory. For metal hydrous oxide-containing particulates, the apparent surface area also depended on pH. This was indicative of a greater proportion of pH-dependent charged surfaces than with illite. In addition, a fluorescence method for determining the solution concentration of dye is presented. This method eliminates errors due to colloidal scattering and absorption by dye bound to colloids. The presence of colloids in supernatant solutions in a common problem in absorbance measurements.

Zero point of charge measurements for pure metal hydrous oxides agreed with values reported in the literature. However, attempts to measure the zero point of charge using acid-base titration were unsuccessful for clay-containing particulates. This failure was attributed to the non-specific adsorption of hydronium ions and the presence of a permanent exchange capacity.

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BY

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B.A., Dartmouth College, 1973
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DISSERTATION

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ABSTRACT

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by

Frederick William Page

University of New Hampshire, September, 1982

The synthesis and characterization of single- and multi-component model aquatic particulates is the object of this dissertation. Particulates were synthesized from illite clay, humic and fulvic acids, and iron, aluminum, and manganese hydrous oxides. Characterization included measurement of cation exchange capacity (CEC), and attempts to determine surface area and the pH of zero point of charge. Each of these methods was tested to determine their applicability to aquatic particulates, and attempts were made to improve the methodology, where necessary. Variation in characteristics as a function of particulate composition and aging was also studied.

CEC varied with composition and time of aging. Pure hydrous oxides exhibited decreases in CEC over time. Aging effects were also shown by aluminum hydrous oxide-clay mixtures. The CEC of iron hydrous oxide-clay particulates increased with iron content on the clay. Similar trends in
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Attempts to measure surface area through adsorption of cationic dyes were unsuccessful. Dye adsorption on illite was shown to vary as a function of the square root of the ionic strength of the saturating dye solution. This trend was interpreted in terms of a simple model of charge density at the solid-solution interface and Gouy-Chapman theory. For metal hydrous oxide-containing particulates, the apparent surface area also depended on pH. This was indicative of a greater proportion of pH-dependent charged surfaces than with illite. In addition, a fluorescence method for determining the solution concentration of dye is presented. This method eliminates errors due to colloidal scattering and absorption by dye bound to colloids. The presence of colloids in supernatant solutions is a common problem in absorbance measurements.

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CHAPTER I

INTRODUCTION

The ultimate goal of all research is additional understanding of processes and events which can, under proper conditions, facilitate the improvement of human life (1). Research on toxic and potentially toxic chemicals in aquatic ecosystems is directed at preventing man's exposure to lethal or sublethal but harmful doses of these chemicals. There are many sublethal effects including disruption of normal behavior, interference with thermoregulation, abnormal biological processes, decrease in reproductive success, changes in growth rate, and mutagenicity and carcinogenicity (2). The number of toxic and potentially toxic chemicals is large, particularly when it is recognized that there may be synergistic effects between various chemicals (2) and that some compounds, although initially not very toxic, are converted into highly toxic metabolic intermediates, e.g., polynuclear aromatic hydrocarbons (3). Therefore, concern has centered on the pathways by which man is exposed to these chemicals and on the natural processes which control the amount of exposure. For aquatic systems, research has been directed primarily at the availability of toxic chemicals through
drinking water supplies and through food obtained from aquatic systems.

Many factors operate to control the biological accumulation of toxic chemicals in man and in his diet. These include:

1. Characteristics of the organism.
   a. Feeding habits and predator-prey relationships. These control the level of exposure to various toxic chemicals and the form or species of the toxic chemical to which the organism is exposed.
   b. Ability to ingest a toxic chemical. This is dependent on the particular organism (4), the form of the toxic chemical, and the digestive environment. For example, a substantial amount of data in the literature suggests that dissolved forms of toxic chemicals are more rapidly assimilated and are more toxic than those associated with ingested detritus or food (3, 5, 6). In addition, the presence of other chemical species in the digestive tract may either stimulate or competitively inhibit assimilation of another substance (5, 7).
   c. Ability to immobilize or excrete a toxic chemical, or to convert the toxic chemical into a non-toxic form or a form which can be excreted. This affects the toxicity of a chemical, the length of exposure to the chemical, and the
accumulation of the chemical in the organism. The ability to excrete a toxic chemical or to change that chemical into a form which can be excreted helps the organism to purge itself of that chemical and may prevent accumulation of toxic levels. Such a mechanism appears to apply to polynuclear aromatic hydrocarbons (PAH's) which are converted by most aquatic animals into polar metabolites which are readily excreted (3). Unfortunately, these metabolites are often highly carcinogenic. In addition, many animals appear to be able to immobilize, and, thereby, detoxify many metals such as copper, zinc, mercury, etc., with the protein metallothionein (8). When metals are bound to this protein, they are effectively partitioned away from enzymes, nucleic acids, and other sites of toxic action.

d. Ability to mobilize toxic chemicals from various substrates.

There are several references in the literature which suggest that certain bacteria (9) and algae (4) are able to mobilize various toxic chemicals from sediments, such as cadmium and lead.

The ability to ingest a chemical, coupled with the inability to excrete it or to change it into a form which can be excreted, results in biological
accumulation or biological concentration of that chemical in the organism. There are many examples of this in the literature (e.g., 3, 11). It is because of this biological concentration of toxic chemicals that concern has been expressed over the possible effects of long-term, low-level exposure to various "cumulative" chemicals. In addition, if the ability to ingest a toxic chemical and the inability to excrete it continues up the food chain, the concentration of the toxic substance at higher trophic levels is greatly increased and is known as biological magnification or "biomagnification" (3).

Because of biological accumulation and biomagnification, even trace, i.e., sub-part-per-million (2) levels of a toxic substance may represent a significant hazard. In addition, many toxic chemicals produce substantial sublethal effects at very low concentrations. PAH's, for example, are acutely toxic to aquatic organisms at concentrations from 0.2 to 10 parts-per-million (ppm) and produce deleterious sublethal effects at concentrations of 5 to 100 parts-per-billion (ppb) (3).

2. Speciation of the toxic chemical.

The speciation or form of a chemical is intimately related to its assimilation and accumulation in organisms, and its toxicity. Speciation is also the most important factor in determining the distribution
of that chemical in, and its mobility or transport through, an aquatic ecosystem. In addition, speciation of organic compounds is a major factor in determining persistence in the environment and whether or not compounds will undergo biological or non-biological degradation.

3. Level of exposure.

This depends on the speciation of the chemical, the presence of any degradative pathways, distributive processes such as currents and sediment transport, and on the source or sources of the chemical. The levels of many toxic and potentially toxic substances have been enhanced as a result of man's activities. These anthropogenic inputs include sewage effluents, sludge disposal operations, effluents from electroplating plants and mining operations, dredging operations, disposal of dredge materials, and release of petroleum in waterways (8, 12, 13). The inputs may be either routine or accidental and either continuous or episodic. The magnitude of such inputs can be enormous. For example, the discharge of sewage effluents from Los Angeles and the surrounding counties results in the release of more than 5 metric tons of potentially toxic metals each day (8). The impact of such an input is enhanced when it is realized that the majority of the metals are concentrated in the sediments close to the discharge.
4. Duration of exposure.

This depends on the source of the chemical, the presence of any degradative pathways, the form of the chemical, and the ability of the organism to ingest and excrete the substance.

The overall impact of a toxic substance depends heavily on its speciation in an aquatic system (5, 14). Speciation affects not only the toxicity of a chemical but also its distribution among various biological and geochemical "sinks" or "reservoirs" (15), and the ease with which biological organisms can assimilate the chemical from each of these reservoirs. Table 1 gives a summary of the chemical species which are encountered in aquatic systems. Generally, "particulate" species will be found in the sediments whereas complexed, ionic, and alkylated species will be found in both surface and interstitial waters. Colloidal and fine particulate species, including precipitates and coprecipitates, as well as organisms will make up the majority of the suspended fraction and will also occur in the deposited sediments.

The distinction between soluble and particulate forms is important and requires elaboration. In the everyday usage of environmental science, "particulate" forms are defined as that fraction of a sample which is retained by a 0.40 or 0.45 µm. filter whereas "soluble" forms are defined as that fraction which is able to pass through the filter. The distinction between particulate and soluble fractions
Table 1. Chemical species commonly found in aquatic systems.

<table>
<thead>
<tr>
<th>Chemical Species</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>-Ionic or hydrated</td>
<td>$\text{Pb}^{+2}_{\text{aq}}$</td>
</tr>
<tr>
<td>-Alkylated</td>
<td>methyl mercury</td>
</tr>
<tr>
<td>-Complexed by inorganic ligand</td>
<td>$\text{PbCO}_3^0$</td>
</tr>
<tr>
<td>-Complexed or chelated by organic ligand</td>
<td>Pb-fulvate, protein-humate</td>
</tr>
<tr>
<td>-Precipitate</td>
<td>CuS</td>
</tr>
<tr>
<td>-Co-precipitate</td>
<td>Al-iron hydrous oxide</td>
</tr>
<tr>
<td>-Adsorbed or occluded onto colloidal or particulate hydrous oxide</td>
<td>Pb$^{+2}$-iron hydrous oxide</td>
</tr>
<tr>
<td>-Adsorbed or occluded onto colloidal or particulate organic matter</td>
<td>Cu$^{+2}$-humic acid, PAH-humate</td>
</tr>
<tr>
<td>-Adsorbed onto colloidal or particulate minerals</td>
<td>Pb$^{+2}$-illite</td>
</tr>
<tr>
<td>-Crystalline forms</td>
<td>illite</td>
</tr>
<tr>
<td>-Adsorbed on or incorporated in organisms</td>
<td>cobalamine</td>
</tr>
</tbody>
</table>

$^1$Adapted from Elzerman (2), Jenne and Luoma (5), Forstner (15), Florence and Batley (16), Davis and Leckie (17), Steelink (18), and Khan and Schnitzer (19).
is based on the observation that particles smaller than about 0.5 \( \mu m \) in diameter tend to travel with the fluid phase in aquatic systems, i.e., they tend to remain in suspension for long periods of time. Larger particles tend to settle out of the water column and form the surface layer of sediment (20). The distinction is based, therefore, on the hydrodynamic behavior of particles. There are several problems with this definition.

While the distinction between particles which tend to remain in suspension and those which tend to settle out of the water column is important, particularly in predicting the distribution of particles in, and transport through, aquatic ecosystems, it is nevertheless difficult to operationally obtain "particulate" and "soluble" fractions. It is well known that retention by a filter increases as the amount of filtered particulate material builds up on the filter (21), i.e., the effective pore size decreases with an increase in loading on the filter. Particles which are designated as "particulate" are composed, therefore, of particles which are greater than 0.40 or 0.45 \( \mu m \) in diameter and an unknown fraction of particles whose nominal diameters are less than 0.40 or 0.45 \( \mu m \).

A second problem with the operational definition is that the soluble fraction is actually composed of several forms, i.e., ionic, complexed, alkylated, and colloidal species (Figure 1). Each of these species has significantly different implications in terms of biological availability.
<table>
<thead>
<tr>
<th>Fraction</th>
<th>Approximate Size (nm.)</th>
<th>Chemical Species</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>Soluble</td>
<td>0.1</td>
<td>Ionic or hydrated</td>
<td>Pb$^{+2}$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Inorganic complexes; Organic chelates</td>
<td>PbHCO$_3^+$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Organic complexes</td>
<td>Pb-EDTA</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>Species bound to high MW organic material</td>
<td>Pb-fulvate</td>
</tr>
<tr>
<td>Colloidal</td>
<td>10</td>
<td>Species bound to colloids</td>
<td>Pb-humate</td>
</tr>
<tr>
<td></td>
<td>100</td>
<td>Species incorporated with organic particles and remains of living organisms</td>
<td>Pb-iron hydrous oxide</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>Mineral solids; species adsorbed onto solids; precipitates and co-precipitates</td>
<td>Pb-clay, PbCO$_3$(s)</td>
</tr>
<tr>
<td>Particulate</td>
<td>1000</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>10,000</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 1. Approximate size of various chemical species in an aquatic ecosystem.

1 Definition of various fractions is based on Krauskopf (22), Hoffmann et al. (23), and Harrison and Laxen (14).
2 Adapted from Harrison and Laxen (14).
3 Definition from Harrison and Laxen (14).
4 Definition from Lal (20).
and toxicity. Therefore, an analysis of the total concentration of a toxic substance in the "soluble" fraction is relatively meaningless, particularly when it is recognized that the truly soluble or ionic species, and, hence, the most toxic and/or biologically available form, is often only a minor component of the "soluble" fraction.

Finally, the definition of "soluble" and "particulate" fractions is based on the hydrodynamic behavior of particles. Use of the same terms when discussing the sorption properties of particles, i.e., binding capacity and binding strength, is inappropriate since colloidal particles generally exhibit similar sorption behavior as particles designated as "particulate." To avoid confusion, the terms "filterable" and "non-filterable" will be used in place of the operational definition of "particulate" and "soluble." This follows the suggestion of Harrison and Laxen (14). "Soluble" will hereafter refer to ionic, hydrated, alkylated, and complexed species, i.e., those species which are not filterable nor colloidal. "Particulate" will refer to those species that are bound to or make up colloidal and filterable particles including precipitates and coprecipitates but excluding the soluble species mentioned above (Table 1).

There are many factors which control the distribution of a chemical among the species listed in Table 1. These include:

1. Properties of the toxic chemical.
This includes oxidation state, polarizability, electronegativity, polarity, molecular size and weight, acid-base characteristics, nature of the functional groups if the compound is organic, water solubility, volatility, hydrophobicity, and photosensitivity.

2. Concentration of the toxic chemical (17, 24).
This determines the distribution among inorganic species and whether or not precipitates form and complexation and/or adsorption capacity is exceeded.

3. Chemical environment, including:
   a. Ionic media.
      This controls the concentration of inorganic complexing ions, the formation of precipitates or coprecipitates, adsorption onto particulates (25), competitive reactions for binding sites (5), ionic strength, and the activities of ions. For example, the ionic media is responsible for the precipitation of humic substances when rivers enter the sea (18, 26, 27).
   b. pH.
      This affects the distribution of ions (5), the dissociation of pH-dependent charged sites on particulates, and the distribution among soluble and particulate organic matter (18).
   c. Oxidation-reduction potential.
      This controls the oxidation state of a chemical
and may, in turn, control solubility relationships.

d. Oxygen content.
   This affects biological activity (28).

4. Physical environment, including:
   a. Temperature.
   This controls equilibria, rates of reaction and biological activity.
   b. Agitation.
   This affects the resuspension of sediments and particle size of suspended particulates (13).
   c. Light.
   This controls the rate of degradation for photosensitive compounds.

5. Concentration of various geochemical phases, including:
   a. Concentration of soluble and particulate organic matter.
   This affects the extent of chelation or complexation (5) and the oxidation-reduction potential (29, 30). For example, fulvic and humic acids are known to be able to reduce Hg(II) to Hg(0), Fe(III) to Fe(II), V(V) to V(IV), Np(VI) to Np(V), and Pu(VI) to Pu(V) (29, 30).
   b. Concentration of inorganic particulates including clays minerals and hydrous oxides (5).
   This affects primarily the concentration of ionic
13

species. In addition, some inorganic particulates can act as reducing agents, e.g., smectite can reduce Np(VI) to Np(V) (30), or can adsorb exchangeable cations which can act as electron acceptors (31).

c. Concentration and species of organisms present (28).
This controls biological accumulation and biological degradation of chemicals.

6. Time.
This controls the approach to equilibrium, the aging of hydrous oxides, and other kinetic processes.

The role of adsorption on particulates in determining the distribution of a substance among chemical species cannot be overemphasized. Many chemicals are concentrated in the sediments or on suspended particulates (4, 14, 32) due to adsorption onto hydrous oxides, organic matter, and minerals, primarily clay. Often, the sorbed fraction represents the major sink of a chemical in an aquatic system (3, 7, 33, 34, 35). Suspended particulates play a major role in the elemental cycles of the ocean, are responsible for most of the elemental concentration gradients and are an important vehicle for the transport of pollutants in the ocean (13). Suspended particulates and the surface layer of sediment should play a similar role for freshwater and estuarine systems.

Adsorption of a toxic chemical onto a particulate can
lead to either degradation of that chemical, "permanent" removal of the chemical from solution, or a buffering of the solution concentration of the compound (36). In the latter case, buffering of the concentration in solution via adsorption-desorption equilibria may result in a detoxifying effect if the buffered concentration of the toxic chemical is below the threshold of toxicity, or in prolonged action of the toxic chemical if the concentration is above the threshold of toxicity. Even though adsorbed chemicals are generally less biologically available, their impact, especially on filter-feeding and sediment-ingesting organisms, can be substantial because their concentration is often much higher in sediments than in solution (5). However, the main influence of adsorption on bioavailability may be in controlling the partitioning of a chemical between soluble and particulate forms (5, 7). This partitioning often results in toxic chemical concentrations being at the part-per-million to sub-part-per-billion level in solution (7, 8).

Many approaches have been used to study biological availability, speciation, or adsorption. Each of these approaches is aimed at answering at least a part of the question of what controls biological availability. They include:

1. Measurement of either the total amount of a toxic substance in a sample or measurement of the amount of a toxic substance in both the filterable and
non-filterable fractions. This approach is practically meaningless (5) because of the many species included in each of the two fractions. Bioaccumulation and biomagnification even make this approach a poor indicator of the maximum potential hazard.

2. Studies of sorption using natural particulates, including sediments. These studies often involve one or more of the following: (a) study of the adsorption properties, i.e., binding capacity, binding strength, and/or binding kinetics, of a chemical onto a natural sample of particulates, (b) selective extraction of the chemical associated with various components of the sample, and (c) correlation between sorption properties or the concentration of the toxic chemical in various sites with various sediment properties, e.g., cation exchange capacity or organic matter content. This is the most extensively used approach for study of sorption phenomena but is also one of the most problematic. The above discussion on the factors affecting speciation should serve as a warning that correlation analysis is ill-equipped to establish unambiguous cause-effect relationships. Often, many important parameters are not controlled or are not measured, and synergistic or antagonistic effects are not considered. "Selective" extraction
schemes are not necessarily selective (5, 14, 32). For example, the use of hydrogen peroxide to release substances associated with organic matter also releases substances associated with sulfides and manganese hydrous oxides (5). In addition, extractions have been found to be dependent on (a) sample handling and pretreatment, (b) extraction time, (c) solid to solution ratio, (d) the degree of crystallinity of the sample, and (e) the degree of hydration (5). Extension of results from the selective extraction of a toxic chemical to its bioavailability is hampered by (a) the lack of correlation between various extracts and truly biologically available forms, (b) the variation in solute levels of a toxic substance both spatially and temporally, (c) the particle-size dependent distribution of the chemical, and (d) the particle-size dependent feeding by organisms. In general, the selective extraction-correlation approach suffers from a lack of specificity in extraction procedures and a lack of control over many important parameters of the system.

3. Speciation studies using operational schemes.
Operational schemes attempt to divide a toxic chemical into various operationally defined "species." The scheme of Batley and Florence (37) is an example where metals are divided according to
whether or not they are ASV- (anodic stripping voltammetry) labile, released by ultraviolet irradiation, filterable, or removed by Chelex-100 resin (14). While such schemes may eventually prove to be of some practical use, they nevertheless represent an artificial division of a chemical into various subdivisions whose correlation with biological availability has yet to be established. In addition, the scheme as proposed by Batley and Florence uses the operational definition of filterable and non-filterable fractions. The ambiguity and potential problems of this definition have already been discussed.

4. Computer equilibrium or kinetic modelling.

This approach is potentially useful in determining what major species are present under a given set of environmental conditions and how the distribution of these species will change as the environmental conditions change. However, the models require that accurate equilibrium constants be available, that all significant interactions have been accounted for, that the system is at equilibrium (for equilibrium models), and that complete information about a sample or system be available (5, 14, 38). Rarely are these requirements met. The most serious drawbacks to this approach are our lack of knowledge about complexation with naturally occurring organic matter, the
difficulty in quantifying various geochemical sinks, and a lack of knowledge about reaction kinetics for natural processes (5).

5. Chemical assays.
This approach involves the use of extractants to evaluate biological availability (5). The assumption is that the concentration of a chemical which is extracted is the portion which is available to organisms or plants. Many extractants have been used including 0.1 N hydrochloric acid, ammonium acetate, EDTA, and acetic acid. The problem with this approach is that many of these extractants have been proposed without evidence for their correlation with bioavailability (5).

6. Biological assays.
This approach is the most direct way of assessing the biological availability of different chemicals. The problems with this approach are the variability both within and between species and the fact that it is time-consuming.

7. Studies of sorption using model particulates.
These include laboratory studies on clays, synthetic metal hydrous oxides, and organic matter which has been extracted either from water or soil. Two potential problems exist. The first is that the model particulate may differ from that which exists in nature, in which case the results from the laboratory
studies will be difficult to apply to natural systems (14). Such may be the case for metal hydrous oxides which are known to "age" or change form with time (39). Similarly, organic matter which is extracted from soil or water may either be altered as a result of the extraction (40-46) or may represent only a portion of the organic matter as it exists in nature. In the latter case, the extracted organic matter may have significantly different characteristics from the portion which is not extracted. A second potential problem is that the component being studied may not be important in nature due to other more significant processes. For example, studies on metal hydrous oxides suggest that they are very important in terms of binding toxic metals (47). However, the adsorption sites of many natural particulates may be dominated by the functional groups of bound organic compounds rather than simple hydrous oxide surfaces (17). If this is the case, metal hydrous oxides may not be as important in nature as the laboratory studies would indicate.

Of the seven different approaches, only the last two offer some promise of developing a fundamental understanding of the processes which control speciation and, hence, bioavailability. The biological assay approach is the ultimate test of whether or not a particular chemical species is biologically available, although it
does not address the question of what processes control chemical speciation. The model particulate approach is attractive because it allows control over particulate composition and, thereby, circumvents many of the problems encountered in sorption studies with natural particulates. When used in conjunction with biological assay techniques, model particulates should also prove useful in delineating some of the factors which control biological availability.

Objectives

The objectives of this study were:

1. To synthesize both single- and multi-component model particulates from illite, iron, aluminum, and manganese hydrous oxides, and humic and fulvic acids.
2. To characterize the model particulates with respect to cation exchange capacity, surface area, and surface charge properties, and to investigate the changes in these properties as a function of composition.
3. To critically evaluate the methodology used to synthesize and characterize model particulates.
4. To investigate the effects of "aging" on particulate characteristics.

It was hoped that model particulates could be developed which would simulate the actions of those which occur in nature. These model particulates could then be used in sorption studies in which various sorption characteristics, e.g., binding capacity, binding strength,
and the kinetics of adsorption, could be correlated with either particulate composition or other particulate characteristics.
CHAPTER II

CHARACTERISTICS OF ADSORPTION

Introduction

The purpose of this chapter is to examine the phenomenon of adsorption in general. The discussion will be used as a basis for later discussions of cation exchange capacity (CEC), surface area, surface charge properties, and the synthesis of particulates.

Nature of the Solid-Solution Interface

Adsorption takes place in the interfacial region between a solid particle and the surrounding solution. The nature of the interface and the interaction between an adsorbate and the molecules or atoms in the interfacial region are probably the two most important factors in determining adsorption. While our knowledge of solid-solution interfaces is far from complete, several important properties are known.

Most of the earth's surficial geological material consists of metal oxides or hydroxides. The surfaces of these oxides often contain metal atoms whose coordination spheres are not complete (48). The unsatisfied valences of these atoms attract water molecules to the surface which, then, adsorb onto the surface such that the coordination
spheres of the metal atoms are completed. Water may be adsorbed in two ways (49). In physical adsorption, the water molecule remains intact and is identical to water which forms the hydration spheres of atoms in solution. Chemical adsorption results in hydrolysis of the adsorbed water molecule with the hydroxyl ion forming part of the metal atom's coordination sphere and the proton being released into the interfacial region or into solution. The latter is equivalent to the adsorption of a hydroxyl ion. Surficial oxygens may also adsorb water either through hydrogen bonding (50) or through hydrolysis. Hydrolysis, in this case, is equivalent to the adsorption of a proton.

The net result of these processes is that the surface of metal oxides is covered with a layer of hydroxyl ions and/or coordinated water molecules. This layer of adsorbed water forms the primary hydration sphere of metal atoms, i.e., the water or hydroxyl ions are directly coordinated to the metal atoms. Additional layers of water adsorb, each layer being hydrogen bonded to the next closest layer to the surface. These secondary or higher hydration spheres are only indirectly coordinated to the metal atoms and thus possess greater mobility (51).

The properties of the adsorbed water differ from those of pure water in two significant respects. First, because adsorbed water is either coordinated directly to metal atoms or is hydrogen bonded to the next closest hydration sphere, the freedom of the water molecules to become
oriented in response to changes in the electrostatic field strength is restricted (52) and is reflected in a lower dielectric constant than pure water. Whereas pure water has a dielectric constant of 78.54 at 25 C., the dielectric constant of water adsorbed at the solid-solution interface has been estimated as varying from 6 to 30 (52, 53). Therefore, the dielectric constant of water in the interfacial region is similar to that of organic molecules.

The second significant difference between pure water and water adsorbed to a surface is its acidity (31). Water coordinated to metal atoms through the oxygen is polarized to a greater extent than pure water due to the withdrawal of electron density from the oxygen atom by the metal. This increase in polarity is reflected in the greater ease with which a proton may leave the coordination sphere of the metal, i.e., in its acidity (31). The acidity of the water in the interfacial region has been estimated to be up to 2 pH units lower than that in the bulk solution (25) and is dependent on the polarizing power of the cation (31, 54). The latter depends on the size and valency of the cation (51). The acidity of the interfacial region also increases as the surface becomes progressively less hydrated (31, 54).

**Forces Contributing to Adsorption**

Adsorption takes place when the interactions between a chemical and an adsorbent are energetically similar to or greater than solution interactions, such as solute-solvent
interactions and complexation by inorganic and organic ligands. Adsorption may be due to either a strong adsorbate-adsorbent interaction or a weak solute-solvent interaction. Many forces may contribute to the adsorbate-adsorbent interaction. These include:

1. Coulombic or electrostatic forces.
2. Forces due to hydrogen bonding.

Hydrogen bonds may occur between an adsorbate and either an adsorbed hydroxyl group or an adsorbed water molecule coordinated to a metal atom at the surface.

$\text{MOH}^{+n-1} \cdot \cdot \cdot \text{O}=\text{C}^{<_{R'}}$  

Hydrogen bonding through an adsorbed hydroxyl group.

$\text{M}^+\cdot\cdot\cdot\text{O}=\text{C}^{<_{R'}}$  

Hydrogen bonding through an adsorbed water molecule.

The latter case is important when the cation has a high solvation energy and, therefore, retains its hydration sphere. Hydrogen bonding, in this case, is said to occur through a "water bridge" (31, 56).

Hydrogen bonds may also occur directly with the
anions of the solid. If the anions are hydroxyl groups, then hydrogen bonding can occur through the hydroxyl hydrogen, similar to the case described above. If the anions are not hydroxyl groups, then hydrogen bonding occurs only when the surficial anions are not fully coordinated by the cations of the solid (31, 49, 51, 54). For example, most of the surficial oxygens in illite are fully coordinated by silicon atoms in the tetrahedral layers (see Chapter III for a description of the structure of illite). The oxygens in these siloxane groups are weak electron donors and, therefore, form only weak hydrogen bonds (31, 51, 54).

3. London-van der Waals forces.

London-van der Waals forces are present in any adsorbate-adsorbent interaction. The magnitude of each bond is small but the total force is the sum of the individual bonds (31, 56). Therefore, for large molecules where the number of contact points with the surface is large, the size of the force can be substantial (51).

4. Forces due to entropy effects.

When an adsorbate adsorbs onto a surface, water molecules are released into solution (51). When the size of the adsorbate is large, the number of released water molecules is also large. The corresponding increase in entropy results in a
driving force for adsorption (57). This driving force is significant for organic molecules of molecular weight greater than 200 and may be the dominant force for molecules with molecular weights of 400 or more (31).

5. Forces due to ion-dipole, dipole-dipole, or ion-induced dipole interactions.
These interactions are due to the partial transfer of electron density from an electron donor to an electron acceptor (31). The electron donor can be coordinated either directly to the electron acceptor or through a water bridge (51). Common electron donors are organic molecules containing functional groups with free electron pairs, such as alcohols and amines (31, 51). Electron acceptors include exchangeable cations (51) or cations which form part of the solid.

6. Forces due to pi bonds.
Pi bonds may form between cations containing d orbitals and the pi bonding orbitals in unsaturated organic molecules (31). The force from this sort of bond is weak and is probably not important except in dehydrated environments.

7. Forces due to covalent bonds.
Covalent bonds, such as silicon-carbon bonds, probably do not occur in nature and are, therefore, not important (31).
These forces contribute to the overall force of the adsorbate-adsorbent interaction and, therefore, are important factors in determining whether or not adsorption occurs. The magnitude of each of these forces varies with the type of interaction. Electrostatic and covalent interactions are the most energetic, having energies which are generally greater than 10 kcal./mole (55, 58). Hydrogen bonding, van der Waals interactions and entropy effects have variable energies depending on the size of the adsorbate, the number of contact points with the surface, and the polarizing power of the cation (51). The energies of these interactions are usually on the order of 2-10 kcal./mole. Dipole-type interactions and pi bonding are generally weak with energies of less than 2 kcal./mole. The distance over which these forces are important is generally small with the exception of electrostatic interactions which may be effective over large distances.

The relative importance of each of these interactions to adsorption is dependent upon the energy of the interaction, the distance over which it occurs, and the probability that the interaction occurs in nature. For these reasons, electrostatic interactions are probably the most important factor affecting adsorption. Hydrogen bonds, van der Waals interactions and entropy effects are important in the adsorption of non-ionic adsorbates and exert important secondary effects in the adsorption of ionic adsorbates. Dipole-type interactions, pi bonding, and
covalent bonding are generally not important due to either the low energy of these interactions or the low probability of their occurrence.

**Adsorption Mechanisms**

Adsorption may occur via a variety of mechanisms or processes. The mechanisms can be divided, rather arbitrarily, into three groups: simple adsorption, exchange reactions, and complex adsorption. The evidence for these mechanisms is based primarily on observations of vibrational frequency changes using infrared spectrophotometry and on stoichiometric data (51, 54).

**Simple Adsorption**

Simple adsorption may be represented by the following reaction

\[ X + A \rightarrow X-A \]  

(2-1)

where \( X \) is the adsorbent and \( A \) is the adsorbate. For aquatic systems, it is doubtful that simple adsorption ever occurs. The adsorption of any adsorbate displaces, at the very minimum, water molecules which are indirectly coordinated to the surface, i.e.,

\[ X-H_2O + A \rightarrow X-A + H_2O(aq) \]  

(2-2)

"Pure" simple adsorption is likely to occur only in a system where the adsorbent is under a high vacuum and the adsorbate is then introduced into the system. For the
purposes of the present discussion, simple adsorption is meant to refer to the exchange reaction given above (2-2) in which the water coordinated to the surface is in the second or higher hydration spheres of the surficial or exchangeable cations or anions. This is to distinguish it from ligand exchange which will be discussed later on.

**Adsorption of ions.** The simple adsorption of ions can be written as follows

\[
X + M^{n+} \rightarrow X-M^{n+} \quad (2-3)
\]

\[
X + A^{n-} \rightarrow X-A^{n-} \quad (2-4)
\]

where the ions may be either inorganic or organic. Generally, organic cations result from the protonation of nitrogen-containing groups, primarily amines (59), whereas anions are most often the result of dissociation of carboxylic acids.

The adsorption of ions is divided into two classes or groups based on the forces which control adsorption. Non-specific adsorption refers to adsorption which is due to primarily coulombic interactions (49). Some selectivity exists among different ions, but this is due primarily to differences in the charge and hydrated radius of the adsorbate (49) and not due to other forces. Ions which adsorb non-specifically do not react with the surface (48)

Specific adsorption refers to adsorption in which
non-coulombic interactions are significant (60). Specific adsorption is also called chemisorption, referring to the fact that ions which are specifically adsorbed generally react with the solid surface. Simple adsorption is primarily restricted to specific adsorption since non-specific adsorption generally involves an exchange reaction.

**Adsorption of polar molecules.** The simple adsorption of polar molecules generally involves hydrogen bonds either with adsorbed or surficial hydroxyl groups or adsorbed water molecules (31). Adsorption is dependent on the strength of the hydrogen bonds and, hence, on the polarizing power of the surficial cation(s). Polar molecules compete with water molecules for the same adsorption sites (31, 54).

In some instances, the adsorbed molecule is protonated after adsorption due to the generally greater acidity of the interfacial region (31, 54). Sources of protons include exchangeable protons, protons associated with water in the primary hydration spheres of surficial cations, and protons from other adsorbed species (31). The latter involves a proton transfer from one adsorbate to another, i.e.,

$$\text{AH}^+ + B \rightleftharpoons A + BH^+ \quad (2-5)$$

and depends on the dissociation constants and the activities of the molecules involved. In rare cases, when
the concentration of polar molecules exceeds the supply of available protons, hemisalts may be formed as shown below (31).

\[ 2B + H^+ \rightleftharpoons B_2H^+ \]  \hspace{1cm} (2-6)

(hemisalt)

**Adsorption of non-polar molecules.** The adsorption of non-polar molecules, also known as hydrophobic adsorption, is due more to a weak solute-solvent interaction than to a strong adsorbate-adsorbent interaction (55). Adsorption takes place due to van der Waals forces between the non-polar molecule and "hydrophobic cavities" on the adsorbent and due to an increase in entropy (36, 55). Non-polar molecules repel water and thus cause the water molecules immediately around the non-polar molecule to become more ordered relative to pure water. The resulting decrease in entropy is proportional to the total surface area of the non-polar molecules in solution. When these molecules aggregate or adsorb onto a surface with a hydrophobic cavity, the total surface area decreases and the degree of disorder increases. This entropy effect favors adsorption of the non-polar molecules.

Hydrophobic adsorption can also be thought of as a partitioning of the molecule between the polar aqueous phase and the non-polar stationary phase (55). Factors which decrease the water solubility of the adsorbate favor
adsorption (31). Thus, adsorption increases as the molecular weight increases and as the polarity of the molecule decreases. Non-polar molecules are also subject to salting out effects (31).

Exchange Reactions

Exchange reactions can be written as

\[ X-A + B \rightleftharpoons X-B + A \]  

(2-7)

where one adsorbate is adsorbed onto the surface while the other adsorbate is desorbed into solution. Two types of exchange reactions are common: ion exchange and ligand exchange. The latter is distinguished from simple adsorption in that it involves the primary hydration sphere of surficial ions whereas simple adsorption involves secondary or higher hydration spheres.

Ion exchange. Ion exchange, or the exchange of two ions, is generally thought to occur between two non-specifically adsorbed ions, although exchange of two specifically adsorbed ions or one specifically adsorbed and one non-specifically adsorbed ion is also possible. For non-specifically adsorbed ions, the exchange reaction is dependent on the charge, hydration radius, and total concentration or activity of each of the ions (47). For organic molecules in which the charge of the ion is the result of either protonation or deprotonation of a
functional group, the exchange reaction is also pH dependent (31). Maximum adsorption of the organic molecule generally occurs near the point where the pH of the solution is approximately equal to the pKa of the functional group.

**Ligand exchange.** Ligand exchange involves the exchange of an adsorbate with either a hydroxyl group or an adsorbed water molecule in the primary hydration sphere of surficial and/or exchangeable ions, usually cations. The reactions may be written as follows:

\[
(M-OH)^{+n-1} + A^- \rightleftharpoons (M-A)^{+n-1} \text{OH}^- \quad (2-8)
\]

\[
M^{n+} \text{H}_2\text{O} + A \rightleftharpoons M^{n+} \text{A} + \text{H}_2\text{O} \quad (2-9)
\]

The exchange of a polar compound with water molecules coordinated directly to a metal cation is dependent on the polarizing power of the cation (51). Cations which are more polarizing, i.e., smaller in hydrated radius and more highly charged, tend to give up their adsorbed water molecules more difficultly than those which are less polarizing. Ligand exchange of an anion with a hydroxyl group can be thought of as a special form of ion exchange, i.e., exchange of two specifically adsorbed anions. This type of exchange reaction usually results in an increase in the pH of the solution (59, 61).
**Complex Adsorption**

Complex adsorption is any type of adsorption which is composed of several simple adsorptive steps, i.e., a combination or series of simple adsorptions and/or exchange reactions. Its most common form is sequential adsorption in which the adsorption of one adsorbate leads to adsorption of a second.

A particularly important example is the adsorption of an organic molecule onto clay via a "cation bridge" (56, 59). Clays, such as illite, and most naturally occurring organic matter are both negatively charged. Therefore, adsorption of organic matter onto clay is minimal due to the electrostatic repulsion between the two substances. Metal ions, such as iron and aluminum, however, readily adsorb onto clay and are also strongly complexed by natural organic matter via a ligand exchange of carboxylate groups with adsorbed hydroxyl groups. These metal ions, therefore, act as positively charged "bridges" between the clay and the organic matter.

Another example is the adsorption of a single chemical by two different mechanisms. Such is the case for the adsorption of organic cations onto clays (51). Initially, the organic cation is adsorbed via a cation exchange reaction which continues up to the CEC of the clay. Once the CEC has been reached, further adsorption occurs due to van der Waals interactions and entropy effects. Ultimately, the charge on the surface due to adsorption of the organic
cation reaches the point where the attraction of the organic cation to the surface is exactly counteracted by the electrostatic repulsion. At this point, no further adsorption occurs.

Factors Affecting Adsorption

Adsorption occurs in competition with all of the other processes which affect a chemical in a system. Therefore, any factor which affects one of the processes also indirectly affects adsorption. Because of this, the number of factors which affect adsorption, either directly or indirectly, is large. Some of these factors have been reviewed in the Chapter I. In addition, several other factors can also be important. For example, clays, such as illite, are negatively charged due to isomorphous substitution in the crystal lattice. These negatively charged sites are discrete, i.e., they exist as points of negative charge on the clay surface (31). Therefore, adsorption of an organic cation, for example, is determined partially by the orientation of the molecule and the geometrical fit of the charge distribution on the cation to the charge distribution on the clay (31). Orientation of an adsorbed organic molecule also affects the magnitude of van der Waals interactions (31), and the availability of active sites on the organic molecule to other potential adsorbates (17). Adsorption can also be dependent on the crystallinity of the adsorbent (5), the crystallographic faces (61), and the presence of other adsorbates. For example, adsorption
of large organic molecules may mask adsorption sites on the surface and, thereby, affect adsorption of other chemicals (61).

However, the most important factor affecting adsorption is the development of charge on the adsorbent. Electrostatic interactions occur over relatively large distances and are highly energetic. Therefore, they exert a major influence over the adsorption of charged or polar chemicals to a charged substrate. Because many potential adsorbates and most natural particulates are charged, the development and variation of charge on these surfaces is clearly important. The theory governing development of charge at interfaces will be discussed in more detail in a separate section.

**Catalysis and Degradation**

Adsorption of a chemical, particularly an organic compound, can result in a variety of catalytic reactions. These reactions are brought about through protonation of the adsorbate, hydrolysis of the organic compound, oxidation reactions with surficial cations acting as electron acceptors, and photosensitization (18, 25, 31). Catalysis may result in degradation of a toxic organic compound (36) or in polymerization, such as in the production of humic substances (51, 62).

Adsorption can also inhibit reactions by binding reactive intermediates and/or conversion of these intermediates into non-reactive compounds (31, 51), and
through the stabilization of photosensitive chemicals (36). Adsorption also reduces the solution concentration of a chemical and, thereby, decreases the possibility of microbial degradation (26, 28, 31).

**Numerical Methods for Expressing Adsorption Data**

Adsorption data is usually expressed in the form of a graph or "adsorption isotherm" in which the amount of the adsorbate per unit mass of adsorbent is plotted on the y axis and the equilibrium solution concentration is plotted on the x axis (25, 58). Adsorption isotherms have been classified into four types based on the relative affinity of the adsorbent for the adsorbate (Figure 2; 25). Type "S" isotherms are indicative of a strong affinity of the solid for the solvent and, therefore, a weak affinity for the solute. Type "L" isotherms, or Langmuir isotherms, are observed when the solid has a relatively high affinity for the solute. Type "C" isotherms indicate that the solute can penetrate the solid more readily than the solvent, and type "H" isotherms are observed when the solid has a very high affinity for the solute. In all cases, the amount adsorbed per unit mass of adsorbent levels off at high solution concentrations of adsorbate. This "plateau" region demonstrates that most, if not all, adsorbents have a finite number of adsorption sites and, therefore, a finite adsorption "capacity."

Various numerical expressions for adsorption isotherms have been developed and the constants obtained from these
Figure 2. Classification of adsorption isotherms.$^1$

$^1$After Khan (25).
expressions have been used in the interpretation of data. The most commonly used numerical expressions are given below.

**Langmuir Adsorption Isotherm**

The Langmuir adsorption isotherm was originally developed for the adsorption of gases onto dry solids. It is based on several assumptions (25, 36, 55, 63).

1. A solid surface has a finite number of adsorption sites.
2. Each site can adsorb only one molecule.
3. The energy of adsorption is the same for each site and is independent of the number of sites occupied.
4. There is no interaction between sorbed molecules.

The mathematical expression for the isotherm is given as

\[
x/m = \frac{(KbC)}{(1+KC)}
\]  
\[(2-10)\]

where \(x\) is the amount of adsorbate on the solid, \(m\) is the mass of the adsorbent, \(C\) is the equilibrium solution concentration, \(K\) is a constant related to the binding energy of the adsorbate to the adsorbent, and \(b\) is the adsorption capacity (25, 55). The equation may be manipulated into any one of three linear forms (55).

\[
\frac{C}{(x/m)} = \frac{1}{Kb} + \frac{C}{b}
\]  
\[(2-11)\]

\[
\frac{1}{(x/m)} = \frac{1}{b} + \frac{1}{(KbC)}
\]  
\[(2-12)\]

\[
x/m = b - \frac{(x/m)}{(KC)}
\]  
\[(2-13)\]
Constants are evaluated using adsorption data and statistical regression methods.

Because adsorption energy sometimes varies and is often dependent on the number of sites occupied, the Langmuir adsorption isotherm is frequently not applicable (63).

**Freundlich Adsorption Isotherm**

The Freundlich adsorption isotherm is an empirically derived expression (25) which accounts for energy decreases with an increase in the number of sites occupied (63). The numerical expression is

\[ \frac{x}{m} = KC^{1/n} \]  

(2-14)

where \( x, m, \) and \( C \) are the same as those defined above, \( K \) is a partition coefficient, and \( n \) is a constant related to the adsorption capacity of the solid (25, 64). When \( n \) is equal to 1, the equation reduces to a partition equation (55), i.e.,

\[ K = \frac{(x/m)}{C} \]  

(2-15)

The equation is transformed into a linear form as shown below and the constants are found using statistical methods.

\[ \log \left( \frac{x}{m} \right) = \log K + \frac{1}{n} \log C \]  

(2-16)
Rothmund-Kornfeld Equation

Neither the Langmuir nor Freundlich equations are applicable if adsorption is due to an ion exchange reaction (25). In this case, the Rothmund-Kornfeld equation is used. The ion exchange reaction may be expressed as

\[ A^{+a} + \frac{a}{b} B^{+b} \rightleftharpoons \frac{a}{b} B^{+b} + A^{+a} \]  \hspace{1cm} (2-17)

The Rothmund-Kornfeld equation is then given as

\[ \frac{[B^{+b}(s)]^{a/b}}{[A^{+a}(s)]} = K \frac{[B^{+b}(aq)]^{a/b}}{[A^{+a}(aq)]^{1/n}} \]  \hspace{1cm} (2-18)

where \( A \) and \( B \) are two cations with valences of \( a \) and \( b \), respectively, and \( K \) and \( n \) are constants. When \( n \) equals 1, the equation reduces to a mass action equation. The linear form of the equation is obtained in an analogous fashion to the Freundlich equation.

Octanol-Water Partition Equation

For the case of hydrophobic binding where adsorption is determined more by solute-solvent interactions than by adsorbate-adsorbent interactions, adsorption has been found to be related to organic carbon content of the adsorbent and the octanol-water partition coefficient (65).
The general equation is

\[ \log \left( \frac{K_p}{OC} \right) = \log (K_{ow}) - C \]  \hspace{1cm} (2-19)

where OC is the organic carbon content of the adsorbent, \( K_p \) is the partition coefficient, \( K_{ow} \) is the octanol-water partition coefficient, and C is a constant which may vary with the system. The partitioning coefficients are defined as

\[ K_p = \frac{C_a}{C_s} \]  \hspace{1cm} (2-20)
\[ \text{and } K_{ow} = \frac{C_o}{C_w} \]  \hspace{1cm} (2-21)

where \( C_a \) is the amount of the solute which is adsorbed onto the adsorbent in moles per gram, \( C_s \) is the concentration of the solute in aqueous solution in moles per liter, \( C_o \) is the concentration of the solute found in the octanol layer of an octanol-water system in moles per liter, and \( C_w \) is the concentration of the solute found in the water layer in moles per liter.

**Electric Double Layer Theory**

As noted previously, most natural particulates and many potential adsorbates are charged entities. Because electrostatic interactions are energetically large and occur over relatively large distances, the development of charge at the surface of a particulate and the interaction of this "electric double layer" with charged adsorbates is the most important factor determining adsorption. Electric
double layer theory is the conceptual model which has been
developed to explain the development of charge at a
solid-solution interface and the interactions of this
surface charge with charged adsorbates.

**Origin of Charged Surfaces**

In general, charge develops at a solid-solution
interface through the differential sorption of anions and
cations across the interfacial boundary. This differential
adsorption may be the result of one or more of the
following processes.

**Surface chemical reactions.** Many metal oxides have a
hydroxylated surface. Surficial hydroxyl groups are
amphoteric and may undergo two types of surface reactions
(48, 49, 50, 58, 66).

\[
M\text{-OH} + H^+ \rightleftharpoons M\text{-OH}_2^+ \quad (2-22)
\]

\[
M\text{-OH} \rightleftharpoons M\text{-O}^- + H^+. \quad (2-23)
\]

The first reaction can be thought of as the adsorption of a
hydronium ion from solution whereas the second reaction
leads to desorption of a proton. The charge on the surface
of the oxide is determined by the relative balance between
these two reactions and is controlled by the pH of the bulk
solution. Similar pH-dependent surfaces are found in
organic particulates where amine groups are hydronium ion
acceptors and carboxylic acid groups are proton donors.
**Differential specific adsorption.** The surface chemical reactions discussed above are a special case of the more general phenomenon of differential specific adsorption. Differential adsorption occurs whenever the adsorptive forces of either the cation or anion of an otherwise neutral salt solution are greater than those of its counterion (50, 53, 58). This specific adsorption results in charge separation in which the charge of the specifically adsorbed ions at the surface is balanced by the charge of the counterions in solution (48).

**Non-stoichiometric dissolution of the solid phase.** When a solid is placed in water, part of it dissolves, the amount being determined by its solubility product. If the solid is ionic and if there is a differential preference for the aqueous phase between the cation and anion, differential dissolution will occur and will result in charge separation (53). Such is the case for silver iodide, in which the slightly polarizable silver ions prefer the aqueous phase more than the more polarizable iodide ions (53).

**Diffusion of counterions from solids containing lattice imperfections or isomorphous substitutions.** Many solids, particularly clays, contain lattice imperfections, such as site vacancies, or exhibit isomorphous substitution in which an atom of a given valence is substituted in the lattice structure for another atom of a different valence (49, 58, 66). In clays, common substitutions are magnesium
and ferrous iron for aluminum in octahedral sites, and aluminum for silicon in tetrahedral sites. The presence of lattice imperfections and/or isomorphous substitutions results in a net charge on the lattice which is balanced by counterions. When the solid is immersed in water, these counterions tend to diffuse into solution due to the low concentration of these ions in solution (48, 49). This process results in a charge separation and the development of a potential across the interface. Eventually, the tendency for the counterions to diffuse into solution is opposed by the electrostatic attraction of the counterions for the surface and further charge separation does not occur.

All of these processes result in what is known as the "electric double layer." The electric double layer consists of a charged solid surface and an oppositely charged region in solution known as the "diffuse layer" (60, 66).

**Types of Charged Surfaces**

Electric double layers can be divided into two types depending on the origin of the surface charge. "Constant charge" surfaces are those which result from isomorphous substitution or imperfections in the crystal lattice (48, 58). The charge on these surfaces is fixed by the amount of substitution and is, therefore, not dependent on the solution concentration of ions, provided that these ions are not specifically adsorbed. "Constant potential" surfaces result from the differential specific adsorption
or differential dissolution of ions across the interface. In this case, the potential of the surface is dependent on the concentration of all specifically adsorbed ions. This is analogous to an ion selective electrode in which the measured potential is proportional to the solution concentrations of the ions which make up the electrode. Because of this analogy, ions which are part of the solid or which are part of the solvent, e.g., hydronium and hydroxyl ions in the case of aqueous solutions, are said to be "potential determining ions" (58).

**Mathematical Descriptions of Constant Potential Surfaces**

A variety of numerical models have been developed to describe constant potential surfaces and their surficial reactions. While a comprehensive review of these models is not possible due to space limitations nor is it warranted given the purposes of the present discussion, a brief description of these models is presented. For a more detailed description including computational methods for fitting various model parameters to experimental data, the reader is referred to the references cited here and in Chapter VI.

**Equilibrium expressions for surface reactions.** Surface reactions can be written as equilibrium expressions in a manner analogous to that used to describe solution equilibria. There is, however, one significant difference between solution equilibria and surface equilibria involving charged adsorbates. To illustrate this, consider
the amphoteric dissociation of surficial hydroxyl groups.

Hydroxyl groups coordinated to surficial cations can undergo two dissociative reactions.

\[ \text{MOH}_2^+(s) \rightleftharpoons \text{MOH}^+(s) + H^+(s) \]  
\[ \text{MOH}^+(s) \rightleftharpoons \text{MO}^+(s) + H^+(s) \]

For these reactions, both hydronium and hydroxyl ions are specifically adsorbed and, therefore, are potential determining ions. The surface charge is pH dependent.

Equilibrium expressions for these reactions are

\[ K_a^1 = \frac{[\text{MOH}^+(s)][H^+(s)]}{[\text{MOH}^+(s)]} \]  
\[ K_a^2 = \frac{[\text{MO}^+(s)][H^+(s)]}{[\text{MOH}^+(s)]} \]

where \( [\text{MOH}] \) is the activity of surface hydroxyl groups, \( [H^+] \) is the hydronium ion activity, \( [\text{MO}^-] \) is the activity of deprotonated hydroxyl groups, and \( [\text{MOH}^+] \) is the activity of protonated hydroxyl groups (67). \( K_a^1 \) and \( K_a^2 \) are the first and second acid dissociation constants, respectively. The subscript \( (s) \) in the activity terms denotes the concentration in the interfacial region. The superscript \( s \) in the equilibrium constants denotes the equilibrium constant expressed in terms of interfacial activities. These equilibrium expressions are strictly correct, provided that the system is at equilibrium and the
reactions, as written, are representative of the reactions which take place at the interface.

Commonly, equilibrium reactions are written in terms of the solution activities of ions which are able to cross the interfacial boundary, e.g.,

\[
\text{MOH}_2^+(s) \rightleftharpoons \text{MOH}^-(s) + \text{H}^+(aq) \tag{2-28}
\]

\[
\text{MOH} \rightleftharpoons \text{MO}^- + \text{H}^+ \tag{2-29}
\]

To derive the appropriate equilibrium expressions for these reactions, consider the following reaction.

\[
\text{H}^+(s) \rightleftharpoons \text{H}^+(aq) \tag{2-30}
\]

Normally, this reaction could be expressed in terms of the chemical potential of the hydronium ion in the interfacial region and in solution. However, if the solid surface is charged, then the hydronium ion moves through a potential field and electrostatic interactions will then contribute to the energy of adsorption. For this system, the electrochemical potential must be used, i.e.,

\[
\bar{\mu}_{i,x} = \mu_i^0 + RT \ln(a_i) + z_i F \psi_x \tag{2-31}
\]

where \(\bar{\mu}_{i,x}\) is the electrochemical potential of the \(i\)th ion at a distance \(x\) from the solid-solution interface, \(\mu_i^0\) is the chemical potential in some defined standard state, \(a_i\) is the activity of the ion, \(R\) is the gas constant, and \(T\) is the
absolute temperature, $z_i$ is the charge on the ion, $F$ is the Faraday constant, and $\psi_x$ is the electrostatic potential at a distance $x$ from the surface. At equilibrium,

$$\bar{\mu}_{i,s} = \bar{\mu}_{i,aq} \quad (2-32)$$

where the subscripts $s$ and $aq$ have been substituted for $x=0$ and $x=\infty$, respectively. Therefore,

$$\mu^0_{i,s} + RT \ln(a_{i,s}) + z_i \psi_s F = \mu^0_{i,aq} + RT \ln(a_{i,aq}) + z_i F \psi_{aq} \quad (2-33)$$

Since

$$\sum v_i \mu^0_i = \Delta G^0_R = \mu^0_{i,aq} - \mu^0_{i,s} \quad (2-34)$$

where $v_i$ is the coefficient of the $i$th chemical species in the reaction equation (58), then, by successive rearrangement, the following expressions may be written.

$$-\Delta G^0_R + z_i F (\psi_s - \psi_{aq}) = RT \ln(a_{i,aq}/a_{i,s}) \quad (2-35)$$

$$-\Delta G^0_R/RT + (z_i F/RT)(\psi_s - \psi_{aq}) = \ln(a_{i,aq}/a_{i,s}) \quad (2-36)$$

$$a_{i,aq}/a_{i,s} = e^{-\Delta G^0_R/RT} e^{-z_i F(\psi_s - \psi_{aq})/RT} \quad (2-37)$$

The last equation is the general equilibrium expression for any simple adsorption reaction of an ion onto a charged surface. The equilibrium is governed by a chemical term and an electrostatic term. If $\psi_{aq}$ is defined as zero and the
chemical terms are incorporated into the equilibrium constants, then the dissociative reactions for surface hydroxyls may be expressed as

\[ K_{a1} = \frac{(\text{MOH}(s))(\text{H}^+(\text{aq}))}{(\text{MOH}^+(s))} e^{-\frac{z_i F \psi_s}{RT}} \quad (2-38) \]

\[ K_{a2} = \frac{(\text{MO}^-(s))(\text{H}^+(\text{aq}))}{(\text{MOH}(s))} e^{-\frac{z_i F \psi_s}{RT}} \quad (2-39) \]

where

\[ K_{a1} = K_{a1}^s e^{-\frac{\Delta G^o}{RT}} \quad (2-40) \]

\[ K_{a2} = K_{a2}^s e^{-\frac{\Delta G^o}{RT}} \quad (2-41) \]

In general, any reaction written in terms of interfacial activities can be converted into an expression in terms of the solution activities of adsorbable ions by making the following substitution.

\[ a_{i,s} = a_{i,aq} e^{\frac{\Delta G^o}{RT}} e^{-\frac{z_i F (\psi_s - \psi_{aq})}{RT}} \quad (2-42) \]

The above discussion has several important implications regarding adsorption. First, because adsorption is dependent on the surface potential which, in turn, is dependent on the amount of adsorbate bound on the surface, both the Langmuir and the Freundlich adsorption equations are strictly inappropriate for these systems.
since both assume that the surface is uncharged (53). Secondly, the energy of adsorption has commonly been divided into an electrostatic component, a chemical component, and an interaction or solvation term (52), i.e.,

$$\Delta G_{\text{adsorption}} = \Delta G_{\text{coulombic}} + \Delta G_{\text{chemical}} + \Delta G_{\text{solvation}}$$ (2-43)

The solvation term is derived probably from the chemical energy term in the simple adsorption case (Equation 2-37) and reflects changes in the free energy of water molecules in the hydration spheres of the adsorbate. The chemical energy term is derived from the equilibrium expression written in terms of interfacial activities (Equations 2-26 and 2-27). Using this conceptual division of adsorption energy, non-specific adsorption is represented by the case where

$$\Delta G_{\text{adsorption}} = \Delta G_{\text{coulombic}}$$ (2-44)

(53) and specific adsorption is represented as

$$\Delta G_{\text{adsorption}} > \Delta G_{\text{coulombic}}$$ (2-45)

Finally, the equilibrium constant, the potential at the surface, and the activities of the adsorbate in the interfacial region are all quantities which are difficult to evaluate, even for simple systems. Therefore, many scientists have opted to use selectivity coefficients and other simplifying assumptions in order to model adsorption. The limitations of these simplifications need to be
recognized when interpreting adsorption data.

Mathematical models of the electric double layer. There are at least five different models of the electric double layer in the literature (67). All of them are "surface complexation" models, i.e., they are based on the amphoteric behavior of surficial hydroxyl groups and the equilibrium expressions derived above. The models differ in the number of "mean planes of adsorption," the assignment of ions to each of these planes, and in the electrostatic equations used to relate surface potentials to surface charge (67, 68). The latter involves assumptions concerning the capacitance in each of the interfacial layers.

Westall and Hohl (67) examined each of the models using a computer equilibrium modelling program and tested their ability to fit mass balance (titration) data (see Chapter VI for a description of the method). They found that the parameters of the models were not independent, i.e., a wide range of parameter values were capable of producing optimal fit. In addition, parameters common to several different models did not have the same value from model to model and were, therefore, model specific. Since all models were able to fit the mass balance data equally well at a given ionic strength, they concluded that each of the models gave essentially the correct mathematical description of the interface but that the physical description of the interface was not necessarily accurate. They also concluded that the separation of adsorption
energy into electrostatic, chemical, and solvation components could not be done unambiguously. Consequently, only brief descriptions of the models will be given here.

Solid-solution interfaces are generally divided into three planes (Figure 3). The "o" plane is the actual surface of the solid. The "i" plane, also known as the Stern layer or Inner-Helmholtz plane, is located a small distance away from the solid surface. This distance reflects the finite size of adsorbed ions and corresponds to the distance of closest approach of these ions to the surface (48, 53). The "d" plane is located at a still greater distance from the surface and is also known as the diffuse layer, the Gouy layer or as the Outer-Helmholtz plane. The regions between each of these planes may or may not be assumed to have a finite capacitance (Figure 3). The presence and value of a capacitance between two planes determines the degree to which the electrostatic potential decreases in this region. In all models in which a capacitance is assigned to an interfacial layer, a linear decrease in potential with increasing distance from the surface is assumed, except in the diffuse layer.

Ions are assigned to each of these planes in two ways (Figure 3). Most models assign potential determining ions, i.e., those ions which constitute the solid plus the hydronium and hydroxyl ions, to the "o" plane. Other specifically adsorbed ions are assigned to the "i" plane whereas non-specifically adsorbed ions are excluded from
### Figure 3. Various "surface complexation" models of the electric double layer.

<table>
<thead>
<tr>
<th>Model</th>
<th>Assumed Structure for the interface</th>
<th>Assignment of ions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Constant Capacitance</td>
<td><img src="constant_capacitance.png" alt="Diagram" /></td>
<td>o-SAI, HI, LI i-CI</td>
</tr>
<tr>
<td>Diffuse Layer</td>
<td><img src="diffuse_layer.png" alt="Diagram" /></td>
<td>o-SAI, HI, LI</td>
</tr>
<tr>
<td>Basic Stern (AgI)</td>
<td><img src="basic_stern_agi.png" alt="Diagram" /></td>
<td>o-HI, LI i-SAI d-CI</td>
</tr>
<tr>
<td>Basic Stern (Hg)</td>
<td><img src="basic_stern_hg.png" alt="Diagram" /></td>
<td>o-SAI, HI</td>
</tr>
<tr>
<td>Triple Layer, Extended Basic Stern, or Graham-Blok</td>
<td><img src="triple_layer.png" alt="Diagram" /></td>
<td>o-HI, LI i-SAI d-CI</td>
</tr>
</tbody>
</table>

---

1. After Westall and Hohl (67).
2. Interfacial structures are illustrated by diagrams of electrostatic potential ($\psi$) versus distance from the solid surface. The subscripts "o," "i," and "d" refer to the solid surface, the Stern layer, and the diffuse layer, respectively. $C_1$ and $C_2$ refer to the capacitances between the solid surface and the Stern layer, and the Stern layer and the diffuse layer, respectively.
3. Assignment of ions is in reference to the mean planes of adsorption as described above. SAI=specifically adsorbed, non-potential determining ions; HI=hydronium and hydroxyl ions; LI=lattice ions; CI=counterions.
both the "o" and "i" planes and are assigned to the diffuse layer. This pattern for the assignment of ions to various mean planes of adsorption is known as the "silver iodide" model (67). In contrast to this, the "mercury model" does not consider the hydronium and hydroxyl ions to be potential determining ions and, therefore, excludes them from the "o" plane (67). All specifically adsorbed ions are assigned to the "i" plane in this model (60).

The equations used to relate the charge density in each of these planes to the electrostatic potential are complex. In all cases, several equations must be solved simultaneously, usually with the aid of a computer. Various constants or parameters are adjusted until the predicted values of surface charge versus pH are reasonably close to values calculated from experimental data. The adjustable parameters include interfacial capacitances, interfacial dielectric constants, equilibrium constants for adsorption reactions, and surface area. The details of these mathematical expressions will not be given here but can be found in Westall and Hohl (67) and the references cited therein.

**Generalized description of charge at the solid-solution interface.** The various models used to describe the electric double layer do not provide a completely satisfactory basis for later discussions of CEC, surface area, and surface charge properties. There is no evidence to support the use of one model over another and
the models do not apply to constant charge surfaces. In order to provide a common framework for later discussions, a general description of the solid-solution interface will be presented here. The approach is similar to that of Sposito (69) and does not depend on any detailed description of the electric double layer.

The solid-solution interface consists of a variety of surface charge densities which are the result of several processes. These charge densities may be defined as follows:

1. $\sigma_s$ is the net surface charge density in coulombs per square meter due to permanent structural charge, i.e., lattice imperfections and/or isomorphous substitutions.

2. $\sigma_H$ is the net proton charge density due to specific adsorption of hydronium and hydroxyl ions. It does not include charge density due to the non-specific adsorption of these ions.

3. $\sigma_p$ is the net charge density due to specific adsorption of ions which comprise the crystal lattice. These ions and specifically adsorbed hydronium and hydroxyl ions are defined as potential determining ions (PDI's).

4. $\sigma_i$ is the net charge density due to specific adsorption of non-potential determining ions.

5. $\sigma_d$ is the net charge density in the diffuse layer. Non-specifically adsorbed ions are included here.
The above division of charge density differs in several respects from that of Sposito (69) who does not include net charge densities due to specific adsorption of lattice and non-potential determining ions. Instead, he defines two other charge densities: the inner-sphere complex charge density and the outer-sphere complex charge density. Sposito equates these charge densities to specific structures at the surface. Inner-sphere complexes, by definition, do not include water bridges between the ion and the surface. Outer-sphere complexes include at least one water molecule between the ion and the surface. Sposito attributes inner-sphere complexes to chemisorption or specific adsorption. Outer-sphere complexes are presumed to be due to predominantly non-specific adsorption.

This division of charge density does not seem to be completely justified. Outer-sphere complex charge density is indistinguishable from the net charge density in the diffuse layer since both are due to non-specific adsorption. Also, the assignment of specific structures to certain charge densities presumes a relationship between structure and adsorption energy which may not be justified. For these reasons, the outer-sphere complex charge density has been included with the diffuse layer charge density and no reference to specific surface structures has been made in the division of charge density described above.

Two other relationships are needed to complete the description of the interface. Electroneutrality requires
that the sum of the charge densities equal zero, i.e.,

$$\sigma_s + \sigma_H + \sigma_p + \sigma_i + \sigma_d = 0$$

(2-46)

Secondly, the charge density in the diffuse layer can be described by the Gouy-Chapman Theory as

$$\sigma_d = -(8\varepsilon\varepsilon_o RTI)^{\frac{1}{2}} \sinh(F\psi_d/2RT)$$

(2-47)

where \(\varepsilon\) is the dielectric constant, \(\varepsilon_o\) is the permittivity of free space, \(I\) is the ionic strength, \(\psi_d\) is the potential at the inner-most plane of the diffuse layer (the "d" plane), \(F\) is the Faraday constant, \(R\) is the gas constant, and \(T\) is the temperature in degrees Kelvin (24). Derivation of this equation is given in Gast (49) and Stumm and Morgan (58).

This description of the charged interface is useful in several respects. In the absence of specific adsorption,

$$\sigma_s = -\sigma_d = -(8\varepsilon\varepsilon_o RTI)^{\frac{1}{2}} \sinh(F\psi_d/2RT)$$

(2-48)

For constant charge surfaces, e.g., when the surface charge density is constant due to isomorphous substitution, the net charge density in the diffuse layer is also constant. As the ionic strength \((I)\) increases, the potential at the inner-most boundary of the diffuse layer must decrease in order to maintain a constant net charge density (48). This is the reason why constant charge surfaces are also
referred to as "constant charge-variable potential" surfaces. Alternatively, if the net charge density due to isomorphous substitution is zero and in the absence of specific adsorption other than that due to PDI's, then

\[ \sigma_p + \sigma_H = -\sigma_d = (8\varepsilon \varepsilon_0 RTI)^{1/2} \sinh(F\psi_d/2RT) \quad (2-49) \]

For these constant potential surfaces in which the diffuse layer potential is constant, as the ionic strength increases then the charge density in the diffuse layer must also increase (48). These surfaces are, therefore, also known as "constant potential-variable charge" surfaces.

Other applications of this general description of the interfacial region will be given in later chapters.

Electrokinetic Phenomena

Many natural particulates move in response to an electric field. This "electrophoresis" is attributed to the existence of an electrostatic potential, called the zeta potential, located at the shear plane between water adhering to the surface of the particulate and the mobile water of the solution (48, 58, 60). The zeta potential is usually calculated from the electrophoretic mobility of a particulate using the following formula

\[ m_e = \zeta \varepsilon / 4\pi \eta \quad (2-50) \]

where \( m_e \) is the electrophoretic mobility, \( \zeta \) is the zeta potential, \( \varepsilon \) is the dielectric constant, and \( \eta \) is the
viscosity of the liquid (48, 58).

The usefulness of the zeta potential to study charged surfaces is questionable. Generally, several corrections are made to the calculation of the zeta potential which are difficult to quantify (48, 58). In addition, the position of the shear plane is not known and does not necessarily coincide with the position of the "d" plane used in electric double layer theory (48, 58, 60). This non-equivalence to the "d" plane is illustrated by the fact that the zeta potential is generally smaller than the potential at the "d" plane (58). Finally, adsorbed organics may cause the shear plane to be located some distance away from the actual particle surface due to extensions of the molecule into solution (70, 71). In these instances, the charge at the particle surface may have little to do with the particle's mobility in the electric field.

Coagulation and Flocculation of Natural Particulates

Coagulation and flocculation are important environmental processes which affect primarily the distribution and mode of transport of particulates in an aquatic system. Flocculation usually refers to the binding of several particles by a single large organic polymer, e.g., humic material (57). The polymer acts as a bridge between several particles and the resulting "floc" has a loose, porous structure. Flocculation can also occur in clays where the flat surface of a clay is a constant charge surface and the edges are constant potential surfaces which
are pH dependent (48, 58). If the pH is adjusted such that the edges are positively charged, then the edges of one clay particle can bridge between the negatively charged faces of two other clay particles in an edge to face orientation (48). The clays can be redispersed or "peptized" using various dispersants or peptizing reagents such as a dilute solution of sodium carbonate. Peptizing reagents work either by changing the pH of the solution or by being specifically adsorbed on the edges of clay (48). The edges become negatively charged and, therefore, are repelled by electrostatic interactions from the negatively charged faces.

Coagulation differs from flocculation in that it refers to the balance between van der Waals attraction and electrostatic repulsion of particles (48, 49). All particles are attracted to each other due to van der Waals interactions. This force is relatively constant with changes in ionic strength and, for two parallel plates, is inversely proportional to the cube of the distance between the particles (48). Electrostatic repulsion results from the interactions between the diffuse layers of two similarly charged particles. Because electrostatic interactions are inversely proportional to the square of the distance, they occur over larger distances than van der Waals interactions. In stable suspensions, the attractive force between two particles is successfully counteracted by the repulsive force in the diffuse layer (48, 49).
Coagulation occurs when either the charge on the particles is neutralized due to specific adsorption or the distance over which electrostatic interactions occur decreases to the point that van der Waals interactions are energetically greater than the electrostatic repulsion (48, 57, 60). This latter situation involves a "collapse" towards the surface of the particle of the diffuse portion of the electric double layer and is usually the result of an increase in ionic strength (48, 49). The double layer thickness (DLT) can be estimated from the ionic strength (I) (58, 72).

\[
\text{DLT} \approx \frac{(3.0 \times 10^{-8} \text{ cm.})}{I^{\frac{1}{2}}} \tag{2-51}
\]

The resulting "coagulum" is more dense than in the case of flocculation.

Coagulation has been used to distinguish between specific and non-specific adsorption (47, 60). If the minimum concentration of an ion needed to produce coagulation in a colloidal suspension (called the critical coagulation concentration) is plotted versus the concentration of colloids in the suspension, two types of results can occur. If the ion is specifically adsorbed, the critical coagulation concentration will be proportional to the concentration of the colloid in the system. If the ion is non-specifically adsorbed, the critical coagulation concentration will remain constant with respect to the
concentration of colloids. These results reflect the fact that coagulation in the case of specifically adsorbed ions is due to charge neutralization whereas in the case of non-specifically adsorbed ions, coagulation is due to collapse of the electric double layer. This collapse is dependent solely on the ionic strength of the solution. Coagulation occurs when a certain limiting value of ionic strength is reached, irrespective of the concentration of colloids in the system.

Adsorption is an extremely complex process which is dependent on a large number of factors. The most important interactions are those which occur between a charged surface and a charged adsorbate. As will be seen in the following chapters, these interactions affect the synthesis of model particulates and the determination of CEC, surface area, and the isoelectric point of the solid.
CHAPTER III

SYNTHESIS OF MODEL PARTICULATES

Introduction

Model particulates offer a number of advantages over natural particulates when studying adsorption of toxic chemicals. First, model particulates can be made in which the composition is known. This avoids the use of "selective" extraction techniques in order to quantify the various geochemical phases present. Secondly, by working with relatively simple systems, at least initially, the number of variables can be reduced to a manageable level. Therefore, studies with model particulates have a greater chance of unambiguously elucidating cause-effect relationships than in studies with natural particulates. Finally, interactive effects can be studied in a systematic manner and various hypotheses can be tested directly using model particulates.

Model particulates are subject to several potential problems. If the components used in constructing or synthesizing model particulates do not closely approximate those in nature or if an active component which occurs in nature is not used, then the extension of results from sorption studies to natural systems is questionable. This
also applies if the method of synthesis results in a model particulate whose structure is significantly different from natural particulates.

The purpose of this chapter is to review the sources and composition of natural abiotic aquatic particulates and to present the results of the synthesis of several model particulates. Subsequent chapters will describe the attempts to characterize these model particulates.

Natural Particulates

Natural particulates may be either autochthonous or allochthonous. In marine systems, particularly in areas away from the influence of continental runoff, the majority are autochthonous, being composed primarily of biological particles and inorganic precipitates. Closer to the continents, allochthonous sources of particulates such as suspended matter from continental runoff and airborne dust become increasingly important. In addition, particulates may be derived from cosmic material (13, 20).

In freshwater and estuarine systems, the majority of particulates are allochthonous, being derived from the physical erosion of adjacent land masses (26). In addition, two important autochthonous sources include the precipitation of humic material when rivers enter a more saline environment such as an estuary (18, 26), and the precipitation of iron and/or manganese hydrous oxides when anoxic waters are reoxygenated. The latter may occur in lakes and reservoirs during times of vertical mixing or
"turn over." Lakes and reservoirs often have hypolimnions which are anoxic as a result of biological respiration. These waters can contain substantial amounts of iron and manganese which have dissolved into the water column from the sediments. Precipitation of hydrous oxides also occurs in places where anoxic ground water flows into a more oxygenated environment.

Natural abiotic particulates are composed of mineral matter, organic matter, and/or metal hydrous oxides (13, 32, 55). These components may occur singly or as aggregates with the organic matter, metal hydrous oxides, and/or carbonates acting as a cementing material (13, 73). The mineral component can be any mineral which is stable or metastable under the conditions of an aqueous environment. However, the most common minerals in particulates include quartz, feldspar, micas, and clays (13). Clay minerals tend to dominate the mineral component of suspended particulates. Suspended particulates are generally less than 10 μm in diameter (20) and are the most active in terms of adsorption. The clay minerals are often illite (22, 74, 75) in both marine and aquatic systems. Smectite and kaolinite can also be important in freshwater environments.

The organic matter component consists largely of a heterogeneous mixture of brown or yellow acidic polymers known as humic material (26). Humics are the stable by-products of microbial transformation of a variety of
biochemical compounds derived from the dead cells and extracellular products of mainly land plants and aquatic algae. They are generally resistant to both chemical and biological degradation. Humics are usually divided into three groups of compounds based on their solubility in dilute acid and base. "Fulvic acid" is soluble in both acid and base whereas "humic acid" is soluble in base but not acid. "Humin" is insoluble in acid or base.

The chemical properties of humic and fulvic acids are shown in Table 2. Humic acid generally contains less oxygen, carboxylic acid and alcoholic groups, and more carbon than fulvic acid. Humic acid is the main component of organic matter in marine and estuarine sediments (26, 32) and can exist either as discrete particles or as coatings on clay and metal hydrous oxides (22, 55). Concentrations range from 0.04 % carbon in sediments from the mid-Pacific to 10.1 % in river sediments (4, 30, 32, 59, 64, 76, 77). Fulvic acid is more soluble than humic acid and generally makes up the dominant portion of the dissolved organic carbon in natural waters (17, 18, 78).

Metal hydrous oxides include both crystalline and amorphous compounds which, like organic matter, can exist both as coatings on other components and as discrete particles (13, 55, 56). The most common hydrous oxides in nature are those of iron, aluminum, silicon, and manganese (56, 79). Table 3 lists the various forms of these oxides. Not all of the listed compounds in Table 3 are common in
Table 2. Characteristics of humic and fulvic acids.

<table>
<thead>
<tr>
<th>Elemental Composition</th>
<th>Soil HA</th>
<th>Soil FA</th>
<th>Water FA</th>
<th>Soil HA used in this study</th>
<th>Soil FA used in this study</th>
</tr>
</thead>
<tbody>
<tr>
<td>% C</td>
<td>57.3</td>
<td>47.0</td>
<td>46.2</td>
<td>54.2</td>
<td>40.4</td>
</tr>
<tr>
<td>% H</td>
<td>5.1</td>
<td>4.4</td>
<td>5.9</td>
<td>4.67</td>
<td>3.02</td>
</tr>
<tr>
<td>% N</td>
<td>2.8</td>
<td>1.5</td>
<td>2.6</td>
<td>3.51</td>
<td>0.69</td>
</tr>
<tr>
<td>% S</td>
<td>0.6</td>
<td>0.7</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>% Fe</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.070</td>
<td>0.023</td>
</tr>
<tr>
<td>% Al</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.02</td>
<td>0.082</td>
</tr>
<tr>
<td>% Si</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.079</td>
<td>-</td>
</tr>
<tr>
<td>% Na</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.030</td>
<td>1.86</td>
</tr>
</tbody>
</table>

Functional Group Composition (meq./g.)

<table>
<thead>
<tr>
<th></th>
<th>3.7</th>
<th>8.9</th>
<th>-</th>
<th>3.85</th>
<th>7.73</th>
</tr>
</thead>
<tbody>
<tr>
<td>carboxyl</td>
<td>4.2</td>
<td>3.9</td>
<td>-</td>
<td>3.59</td>
<td>5.02</td>
</tr>
<tr>
<td>phenolic OH</td>
<td>2.3</td>
<td>4.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>alcoholic OH</td>
<td>3.1</td>
<td>2.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>carbonyl</td>
<td>0.3</td>
<td>0.4</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

1After Steelink (18).
2After Baur (86).
Table 3. Oxides and hydrous oxides of iron, aluminum, silicon, and manganese.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hematite</td>
<td>$\alpha Fe_2O_3$</td>
</tr>
<tr>
<td>Goethite</td>
<td>$\alpha FeOOH$</td>
</tr>
<tr>
<td>Lepidocrocite</td>
<td>$\gamma FeOOH$</td>
</tr>
<tr>
<td>Limonite</td>
<td>$FeOOH\cdot nH_2O$</td>
</tr>
<tr>
<td>Magnetite</td>
<td>$Fe_3O_4$</td>
</tr>
<tr>
<td>Boehmite</td>
<td>$\gamma AlOOH$</td>
</tr>
<tr>
<td>Diaspore</td>
<td>$\alpha AlOOH$</td>
</tr>
<tr>
<td>Gibbsite (or Hydrargillite)</td>
<td>$\gamma Al(OH)_3$</td>
</tr>
<tr>
<td>Bayerite</td>
<td>$\alpha Al(OH)_3$</td>
</tr>
<tr>
<td>Bauxite</td>
<td>$Al_2O_3\cdot nH_2O$</td>
</tr>
<tr>
<td>Allophane</td>
<td>$mAl_2O_3\cdot nSiO_2\cdot pH_2O$</td>
</tr>
<tr>
<td>Opaline Silica</td>
<td>$SiO_2\cdot nH_2O$</td>
</tr>
<tr>
<td>Pyroline Silica</td>
<td>$\beta MnO_2$</td>
</tr>
<tr>
<td>Cryptomelane</td>
<td>$KMn_8O_{16}$</td>
</tr>
<tr>
<td>Manganite</td>
<td>$MnOOH$</td>
</tr>
<tr>
<td>Psilomelane</td>
<td>$(Ba,Mn,R)<em>3Mn_8O</em>{16}(OH)_{6}$</td>
</tr>
</tbody>
</table>

1 Compiled from Krauskopf (22), Feitknecht and Schindler (39), Pettijohn (74), Degens (80), and Mackenzie (81).
nature. Pyrolusite, for example, is the most common form of manganese (22, 58, 79). Cryptomelane can be found occasionally but the other forms of manganese are rare (22, 80). Metal oxides of various valence states of manganese may also form, but these revert to pyrolusite on prolonged exposure to the atmosphere (22). Similarly, gibbsite or hydrargillite is the most stable form for aluminum (79). Bayerite is rare in nature and readily converts to gibbsite (80). Boehmite is metastable at all temperatures and pressures but conversion rates to other forms are slow (80).

For iron, goethite, lepidocrocite, and hematite are common (22, 79). Magnetite occurs in metamorphic and igneous rocks but does not form metal hydrous oxide coatings such as those on particulates. Limonite and amorphous "ferric hydroxide" are predominantly fine-grained, poorly crystalline goethite (22, 39, 82). This was shown using X-ray photoelectron spectroscopy in which hydroxyl ions, divalent oxygen, and adsorbed water could be differentiated on a dried metal hydrous oxide surface (82).

Both amorphous and crystalline forms of metal hydrous oxides occur in nature. Crystalline forms are generally less active in terms of adsorption than amorphous forms due to the lower surface area per unit mass (56). Non-crystalline forms are often unstable and revert to more crystalline forms. This "aging" of the metal hydrous oxides
can take from minutes to several years (56). There is some evidence that adsorption of organic matter onto amorphous hydrous oxides may prevent this aging effect (22).

Concentrations of the various hydrous oxides vary widely. Iron can range from 0 to 9.1 % in marine and estuarine sediments (30, 32, 64, 83). Aluminum can range from 0 to 3.4 % whereas silicon can range from 0.1 to 0.45 % in soils and sediments (64, 83). The concentration of manganese can range from 200 ppm to 1.3 % (30, 32).

Model Particulates

Model particulates were synthesized from illite, humic and fulvic acids, and iron, aluminum, and manganese hydrous oxides. Each of these components is described below.

Illite

The earth's crustal material can be viewed as a close-packed arrangement of oxygen atoms with smaller metal atoms occupying the interstitial regions between the oxygens. For clays, these metal atoms are coplanar and clay structure is generally viewed as consisting of layers or sheets of metal atoms with their associated oxygens. Two types of layers can be differentiated based on the coordination of the metal atoms. "Tetrahedral" layers contain silicon and aluminum whereas "octahedral" layers contain magnesium, iron, and/or aluminum. Octahedral layers can be further subdivided based on the number of metal atoms occupying metal atom sites. "Trioctahedral" layers have divalent metal atoms which occupy every available
site. "Dioctahedral" layers have trivalent metal atoms which occupy only two-thirds of all available sites. The classification of clays is based primarily on the number and arrangement of tetrahedral and octahedral layers, on the type of octahedral layer present, and on whether or not the clay expands upon addition of water. Detailed discussions of the classification of clay minerals are found in Grim (84), Theng (51), Mackenzie (81), and Weaver and Pollard (75).

Illite, or hydromica, is a non-expanding, three layer clay which consists of two tetrahedral layers surrounding a dioctahedral sheet (Figure 4; 51, 81). On the average, 0.6 aluminums substitute for silicon in the tetrahedral layer, and approximately 0.3 divalent cations substitute for trivalent cations in the octahedral layer (51, 75). These substitutions result in a net layer lattice charge of approximately -0.7 per unit cell (75, 85). This charge is balanced by counterions, predominantly potassium, located between the unit cells. The potassium ions are coordinated by hexagonally (48) or ditrigonally (51) arranged oxygen atoms in the tetrahedral layers from two adjacent unit cells. This 12-fold coordination and the relatively high charge density prevents illite from swelling (22, 48, 51, 75) and potassium ions from exchanging with other ions (48), except at the surface of the clay mineral.

**Humic and Fulvic Acids**

Samples of humic and fulvic acids were supplied by G.
Figure 4. Atom arrangement in the unit cell of illite.
August Baur (86). Both humic materials had been isolated using a base extraction technique from a podzolic soil sampled near Lee, New Hampshire, and were purified to remove iron and aluminum. Table 2 presents the compositional data for these two materials. The results are similar to those found by other authors (e.g., 18).

**Metal Hydrous Oxides**

Iron hydrous oxide was prepared by neutralization of an acidic ferric nitrate solution. The fresh precipitate is probably poorly crystalline goethite with excess adsorbed water rather than ferric hydroxide (39, 58, 82). It is unstable or "active" and ages to a variety of products including inactive amorphous material, more crystalline goethite and hematite (22, 39).

Aluminum hydrous oxide was prepared by the neutralization of acidic aluminum chloride solutions. The fresh precipitate is probably hydrous boehmite (50). Aging depends strongly on the temperature and pH of the suspension and probably involves a transition from boehmite to diaspore to bayerite and gibbsite (39, 50). At room temperature, the final product is probably a mixture of these compounds.

Manganese dioxide was prepared by a redox reaction

\[ 3 \text{Mn}^{+2} + 2 \text{MnO}_{4}^{-} + 2 \text{H}_{2}\text{O} \rightleftharpoons 5 \text{MnO}_{2} + 4 \text{H}^{+} \]  

(3-1)

This oxidation generally results in a mixed oxide of Mn(II) and Mn(IV) which may be represented by the formula $\text{MnO}_{x}$.
where \( x \) has been shown to vary from approximately 1.2 to 1.6 (22, 58, 87). This mixed oxide is due to the adsorption of Mn(II) onto freshly precipitated manganese dioxide (87). On aging, the oxide will oxidize more completely, presumably to manganese dioxide (22, 50).

**Adequacy of Model Components**

As mentioned earlier, one of the potential problems with model particulates is that the components chosen to synthesize model particulates may differ greatly in their sorptive properties from their counterparts in nature (32). This question needs to be examined in more detail.

Illite should be a good model for the mineral component of particulates. Clay is one of the principle types of adsorbents in marine and estuarine sediments (32) and illite is the most common clay mineral in these materials (22). In addition, more than half of all clay is illite (75). Therefore, illite should be a good model for many freshwater systems as well. Finally, small particulates, e.g., suspended particulates, are more likely to contain clay rather than other minerals due to the small size of clay minerals.

Humic and fulvic acids may not be good models of naturally occurring organic matter. Arguments against the use of humic and fulvic acids include:

1. The material used in this study was derived from soil and there is always the chance that it does not resemble organic matter in aquatic systems.
2. Humic and fulvic acids usually represent only a small portion of all organic matter in the soil. Use of these materials to represent all of the organic matter in particulates may be biasing experimental results.

3. There is some question as to whether both humic and fulvic acids are altered during the extraction procedure. If they are, the materials may not be representative of organic matter, including humic and fulvic acids, which occur in soils or in sediments.

Arguments for the use of humic and fulvic acids include:

1. Humic acid is believed to represent the main component of organic matter in marine and estuarine sediments (32).

2. Humic acid in freshwater and estuarine systems is most likely derived from soils, either due to physical erosion or to the leaching action of percolating waters (26). In estuarine systems, humic substances carried by freshwater rivers are precipitated when exposed to the saline estuarine environment.

3. Humic and fulvic acids are generally considered to be the most reactive fraction of organic matter and, therefore, would be the most important component of organic matter in terms of adsorption (5).

In general, humic and fulvic acids should be reasonably good models of naturally occurring organic
matter, especially in freshwater and estuarine systems where the majority of organic matter is derived from adjacent land masses. They are certainly the best models available at the time of this study.

The metal hydrous oxides used in this study may also be poor models of their counterparts in nature. The fresh precipitates are unstable and revert over time to more crystalline forms, usually with concurrent loss of water (17, 22, 32, 39, 56, 58, 82). This aging process is generally slow and may take from minutes to years to go to completion (22, 32, 50, 56). Most natural hydrous oxides would, therefore, be expected to be the more crystalline, aged products. These aged hydrous oxides have lower surface areas than the freshly precipitated material and, therefore, are likely to have lower adsorption capacities and slower kinetics of adsorption (5, 48, 56).

One potential solution to this problem is to increase the temperature of the suspension to accelerate the rate of aging. However, equilibrium conditions at these higher temperatures are different and equilibrium at the lower temperatures may be established slowly, even with slow cooling of the suspension (39).

There is some evidence that adsorption of other substances, notably organic matter, may prevent freshly precipitated hydrous oxides from aging (5, 56). For example, amorphous iron hydrous oxide was very stable in the presence of organic matter (56). Since freshly
precipitated iron and manganese hydrous oxides would be expected to occur in systems where anoxic waters containing substantial amounts of dissolved iron and manganese are reoxygenated (88). The use of freshly precipitated hydrous oxides as models for natural hydrous oxides may not be as bad as the aging data would indicate.

Another potential problem with freshly precipitated hydrous oxides is that the composition and properties are known to vary and to be dependent on temperature, rate of precipitation, concentration of solution(s), pH, and duration of aging (39, 66). Therefore, the properties and characteristics of these hydrous oxides may vary from batch to batch. In addition, several aging processes may take place at the same time and usually at different rates (39). Therefore, the hydrous oxides may undergo a continuous change in composition over a substantial period of time.

The model components used in this study probably represent the most active components of natural particulates. It is doubtful that a significant component has not been included, with the possible exceptions of biological organisms and smectite clay. Biological organisms were not included because of difficulty in quantifying their activity and because the original objective of the study was to examine the influence of abiotic particulates. Smectite was not included because of its low abundance in both marine and estuarine systems and in the coastal area of New Hampshire. In other areas, its
influence is substantially more important.

The relative importance of each of the model components in terms of adsorption may be different from what some authors would indicate. There is a growing opinion that organic matter is the most important component of particulates. Organic matter tends to coat or form a film on both metal hydrous oxides and clay (17, 25). The result is that little of the clay or metal hydrous oxide surface is accessible to the solution.

Finally, the properties of model particulates and, hence, their ability to mimic natural particulates could be dependent on the particular method of synthesis. Variations in particulate properties as a function of the methods used to synthesize these particulates were not investigated in this study. As will be shown later, deficiencies in the characterization methodology for particulates precludes such a study as present.

Methodology

Preparation of Illite

Samples of illite were prepared from two standard reference clays. The first was American Petroleum Institute Standard Reference Clay #36 from Morris, Illinois. The sample was available originally through Wards Scientific Establishment, Inc., Rochester, New York, but supplies have since been depleted and it is no longer available. The second illite was "Illite I-Mont-1" from Silver Hills, Montana, currently available from the Source Clay
Samples of illite were pulverized in a mortar and pestle and size fractionated by sedimentation to remove the very coarse material. The resulting suspension was treated to remove any cementing materials as follows:

1. Samples were tested for the presence of gypsum and soluble salts following the procedure of Kunze (89). Gypsum was not detected in either of the clays but soluble salts were.

2. Soluble salts were removed by dissolution in water following the procedure of Kunze (89) and van Olphen and Fripiat (90).

3. Carbonates were removed by dilute hydrochloric acid (90, 91). The suspension was warmed gently to hasten dissolution of any dolomite.

4. Organic matter was removed using the acidified hydrogen peroxide method (89, 90, 92, 93).

5. Amorphous iron hydrous oxides were removed using the sodium citrate-sodium bicarbonate-sodium dithionite (hydrosulfite) method (79, 89, 90, 93, 94).

Following removal of cementing materials, samples were dispersed in 0.01 M sodium carbonate (73, 79, 91, 92), stirred for several minutes and the less than 2 μm fraction was collected. Settling times were calculated from
where $t$ is the settling time in hours, $X$ is the particle diameter in μm., $g$ is gravitational acceleration in cm./s.$^2$, $\Delta p$ is the difference in density between illite and pure water in g./cm.$^3$, $n$ is the viscosity of water at a given temperature in centipoises, and $d$ is the distance through which the particle settles in cm. The equation is based on Stoke's Law (74, 92). Viscosity was calculated from the temperature using a formula from the Handbook of Chemistry and Physics (95). The gravitational constant was taken to be 981 cm./s.$^2$ and the density of illite was assumed to be 2.665 g./cm.$^3$ (84).

After the calculated settling time had elapsed, the suspension was slowly siphoned into another container. The fractionation was repeated until the suspension was reasonably clear. The clay fraction was concentrated and saturated with sodium through repeated additions of sodium chloride followed by centrifugation (93). The clay was washed with deionized water until the conductivity of the liquid was less than 1000 μmhos/cm. or until peptization occurred, and diluted to an appropriate working volume. The concentration of illite in the suspension was determined by pipetting a known mass of the suspension into a dry, preweighed plastic bottle, and drying the suspension at 60 C. under vacuum to constant mass.
Preparation of Metal Hydrous Oxides

Iron hydrous oxide was prepared by neutralization of an acidified 0.4 M ferric nitrate solution to pH 7.0 using carbonate-free 1 M sodium hydroxide (7, 17, 82, 96). The precipitate was washed with deionized water and centrifuged to separate the solid and solution phases. The pH and conductivity of each of the washes were measured and the washes were analyzed for iron. Concentration of the suspension was determined by dissolving a known quantity in dilute nitric acid and analyzing for iron by flame atomic absorption spectrophotometry.

Aluminum hydrous oxide was prepared by neutralization of an acidified 0.166 M aluminum chloride solution to pH 7.0 using carbonate-free 1 M sodium hydroxide (97). The precipitate was washed with deionized water and diluted to a suitable working volume. The washes were analyzed for pH, conductivity, and aluminum content, and the concentration of the suspension was determined.

Manganese hydrous oxides were prepared by adding a solution consisting of 0.4 M potassium permanganate and 0.8 M sodium hydroxide to a 0.6 M solution of manganous sulfate (7, 47). The precipitate was washed with deionized water and diluted to a suitable working volume. Washes were analyzed for pH, conductivity, and manganese content and the manganese content of the suspension was determined.

In all of the above preparations, pH was measured using a combination glass electrode and a Model 701A Orion
Research pH meter. Conductivity was measured using a Model 31 Yellow Springs Instrument Co. conductivity bridge. The cell constant was checked using standard potassium chloride solutions of known conductivity and was found to be 1.00 ± 0.01. All conductivity measurements were standardized to 25 C. Iron, aluminum, and manganese determinations were done using standard atomic absorption and atomic emission procedures on a Model 951 Instrumentation Laboratory Atomic Absorption/Emission Spectrophotometer. Standards were prepared by dissolving ferrous ammonium sulfate, aluminum wire, or manganous sulfate in dilute nitric acid.

**Preparation of Humic and Fulvic Acids**

Fulvic acid was prepared by dissolving a known quantity of dried fulvic acid in distilled-deionized water. The solution was centrifuged and decanted to remove any undissolved particles. Humic acid was prepared by dissolving dried humic acid in distilled-deionized water. Carbonate-free sodium hydroxide was added in small amounts to effect dissolution. The solution was centrifuged and decanted to remove undissolved particles. The concentrations of both solutions were determined by drying known volumes to constant mass at 50 C. and measuring the carbon, hydrogen, and nitrogen content of the dried material using a Model 240B Perkin-Elmer Elemental Analyzer.

**Preparation of Multicomponent Particulates**

Multicomponent particulates were prepared in a variety
of ways. Iron and aluminum hydrous oxide-clay mixtures were prepared by adding the acidified metal solution to a suspension of clay and then neutralizing the suspension with carbonate-free 1 M sodium hydroxide to pH 7.0. The suspension was washed with deionized water and diluted to an appropriate volume.

Manganese hydrous oxide-clay mixtures were prepared by adding a solution of manganous sulfate followed by a basic potassium permanganate solution to a clay suspension. The suspension was then washed and diluted to a suitable working volume.

Organic matter-metal hydrous oxide-clay mixtures were prepared by adding either an acidified iron or acidified aluminum solution to a clay suspension followed by a solution of either humic or fulvic acid. The suspension was then neutralized to pH 7.0 with sodium hydroxide and washed to remove excess salts.

**Composition and Concentration of the Particulates**

The concentrations of the particulate suspensions were determined by pipetting a known mass of each of the suspensions into preweighed plastic bottles and drying to constant mass in an oven at 50-60 °C. The composition of the metal hydrous oxide-clay particulates was checked by selectively extracting the metal hydrous oxide off the clay and analyzing the extract for iron, aluminum, or manganese, as appropriate. Extraction procedures included the sodium citrate-sodium bicarbonate-sodium dithionite method for
iron (79, 89, 90, 93, 94), the acidified ammonium oxalate method for aluminum (90, 94), and the acidified hydrogen peroxide method for manganese (79, 90). Organic carbon content of the organic matter-hydrous oxide-clay mixtures was determined using a Model 240B Perkin-Elmer Elemental Analyzer.

Reporting of Results

Because of the uncertainty in the form of the hydrous oxides, results for the metal hydrous oxide-clay mixtures and the pure metal hydrous oxide suspensions are reported as a percentage of metal per unit mass of pure clay or of suspension. Results are also presented in which the suspension concentration data has been used.

Results

Concentration Data

Table 4 lists the particulates, the components of each of the particulates, the nominal concentration of clay in the final suspension assuming there was no loss of clay during transfers from one container to another, the concentration of hydrous oxides corrected for losses due to washing, and the measured concentration of particulates. In general, the concentrations of the particulate suspensions as determined by drying to constant mass are approximately equal to the nominal concentrations calculated from the clay suspension assuming no loss during transfers. The determined concentrations range from 92 to 124 % of the nominal concentrations. While the higher values can be
Table 4. Composition and concentration of the model particulate suspensions.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Component(s)</th>
<th>Nominal Clay Concentration (ppm)</th>
<th>Nominal Hydrous Oxide Concentration</th>
<th>Measured Particulate Concentration (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>x</td>
<td>9400 ±302</td>
<td>1970 ppm</td>
<td>9170</td>
</tr>
<tr>
<td>F</td>
<td>x</td>
<td></td>
<td>3330</td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>x</td>
<td></td>
<td>4580</td>
<td></td>
</tr>
<tr>
<td>M</td>
<td>x</td>
<td></td>
<td>7380</td>
<td></td>
</tr>
<tr>
<td>FC1</td>
<td>x x</td>
<td>3360</td>
<td>1.32 %</td>
<td>3280</td>
</tr>
<tr>
<td>FC2</td>
<td>x x</td>
<td>3430</td>
<td>2.62 %</td>
<td>3310</td>
</tr>
<tr>
<td>FC3</td>
<td>x x</td>
<td>3570</td>
<td>3.94 %</td>
<td>3610</td>
</tr>
<tr>
<td>FC4</td>
<td>x x</td>
<td>3420</td>
<td>5.22 %</td>
<td>3620</td>
</tr>
<tr>
<td>AC1</td>
<td>x x</td>
<td>3430</td>
<td>1.31 %</td>
<td>3350</td>
</tr>
<tr>
<td>AC2</td>
<td>x x</td>
<td>3590</td>
<td>2.62 %</td>
<td>3640</td>
</tr>
<tr>
<td>AC3</td>
<td>x x</td>
<td>3520</td>
<td>3.78 %</td>
<td>3760</td>
</tr>
<tr>
<td>AC4</td>
<td>x x</td>
<td>3600</td>
<td>4.34 %</td>
<td>3900</td>
</tr>
<tr>
<td>MC1</td>
<td>x x</td>
<td>3450</td>
<td>301 ppm</td>
<td>3240</td>
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<tr>
<td>MC2</td>
<td>x x</td>
<td>3500</td>
<td>519 ppm</td>
<td>3230</td>
</tr>
<tr>
<td>MC3</td>
<td>x x</td>
<td>3590</td>
<td>772 ppm</td>
<td>3350</td>
</tr>
<tr>
<td>MC4</td>
<td>x x</td>
<td>3540</td>
<td>1030 ppm</td>
<td>3390</td>
</tr>
<tr>
<td>HFC1</td>
<td>x x x</td>
<td>3380</td>
<td>5.83 %</td>
<td>3620</td>
</tr>
<tr>
<td>HFC2</td>
<td>x x x</td>
<td>3540</td>
<td>5.74 %</td>
<td>3960</td>
</tr>
<tr>
<td>HFC3</td>
<td>x x x</td>
<td>3480</td>
<td>5.92 %</td>
<td>4000</td>
</tr>
<tr>
<td>HFC4</td>
<td>x x x</td>
<td>3480</td>
<td>5.77 %</td>
<td>3970</td>
</tr>
<tr>
<td>FaFC1</td>
<td>x x x</td>
<td>3490</td>
<td>5.88 %</td>
<td>3870</td>
</tr>
<tr>
<td>FaFC2</td>
<td>x x x</td>
<td>3510</td>
<td>5.80 %</td>
<td>3510</td>
</tr>
<tr>
<td>FaFC3</td>
<td>x x x</td>
<td>&quot;3500&quot; &quot;5 5.85%&quot; &quot;2820&quot;</td>
<td></td>
<td></td>
</tr>
<tr>
<td>FaFC4</td>
<td>x x x</td>
<td>3650</td>
<td>5.78 %</td>
<td>3580</td>
</tr>
<tr>
<td>Fage</td>
<td>x</td>
<td>3480 ppm</td>
<td>7900</td>
<td>6</td>
</tr>
<tr>
<td>Aage</td>
<td>x</td>
<td>3450 ppm</td>
<td>14300</td>
<td>6</td>
</tr>
<tr>
<td>FCage</td>
<td>x x</td>
<td>2520</td>
<td>5.09 %</td>
<td>2480</td>
</tr>
<tr>
<td>ACage</td>
<td>x x</td>
<td>2640</td>
<td>4.99 %</td>
<td>2870</td>
</tr>
<tr>
<td>HFCage</td>
<td>x x x</td>
<td>2620</td>
<td>5.08 %</td>
<td>2880</td>
</tr>
<tr>
<td>HACage</td>
<td>x x x</td>
<td>2730</td>
<td>5.00 %</td>
<td>3400</td>
</tr>
</tbody>
</table>

1 C=clay; F=iron hydrous oxide; A=aluminum hydrous oxide; M=manganese hydrous oxide; H=humic acid (HA); Fa=fulvic acid (FA); age=aging experiment sample.
2 Clay concentrations were calculated assuming no loss of particulates in transfer from bottle to bottle. Value for clay is mean of three determinations.
3 Concentrations for metal hydrous oxide-clay samples are expressed as the quantity of metal per mass of clay. Concentrations for pure metal hydrous oxides are expressed as parts-per-million (ppm) of metal in solution. The standard deviation for these values is ± 2%.
4 Standard deviation for these values is approximately ± 2.7%.
5 Part of the suspension was lost during synthesis due to spillage.
6 Concenulations are calculated assuming no loss.
7 These samples were not washed as thoroughly as previous samples.
attributed to the mass of the metal hydrous oxides and organic matter on the particulates, the lower values suggest that there was some loss of clay during transfers. An estimate of the losses can be obtained from the manganese hydrous oxide-clay mixtures since the total mass of the manganese hydrous oxides is only a small fraction (less than 0.2%) of the total mass of the particulates. The determined concentrations ranged from 92.3 to 95.7% of the nominal concentrations with an average recovery of 93.8%. Therefore, approximately 6% of the suspensions were lost, probably due to adhesion of clay to the plastic bottles.

The concentration data can also be used to estimate the composition of the pure metal hydrous oxides since both the concentration of metal in these oxides and the mass of the dried oxides are known. The major forms of iron, for example, can be written as mixtures of pure iron oxide and various amounts of adsorbed water, i.e.,

Hematite $\text{Fe}_2\text{O}_3$

Goethite, Lepidocrocite $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$

"Amorphous Ferric Hydroxide" $\text{Fe}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$

Using the concentration of iron in the suspension, the mass of the pure iron oxide can be determined. The remainder of the mass as determined from the concentration data is then assumed to be water which is either adsorbed or is part of the crystal structure. When this is done, a formula for the iron hydrous oxide of $\text{Fe}_2\text{O}_3 \cdot 1.6\text{H}_2\text{O}$ is obtained for the
dried material. The material in suspension is probably hydrated to a greater extent than the concentration data indicates.

In an analogous treatment, the major forms of aluminum are

**Diaspore, Boehmite** $\text{Al}_2\text{O}_3\cdot\text{H}_2\text{O}$

**Bayerite, Gibbsite** $\text{Al}_2\text{O}_3\cdot3\text{H}_2\text{O}$

When the concentration of the metal oxide is subtracted from the concentration data and the remainder of the mass is assumed to be water, a formula of $\text{Al}_2\text{O}_3\cdot1.7\text{H}_2\text{O}$ is indicated.

For manganese hydrous oxide, this treatment is not as direct because the various forms of manganese cannot be written as simple mixtures of manganese oxide or dioxide and water. In addition, manganese hydrous oxide is probably a mixture of various oxidation states, predominantly Mn(II) and Mn(IV), to which various amounts of water are adsorbed. If, however, it is assumed that the manganese is present solely as manganese dioxide, and that the rest of the mass is adsorbed water, then a formula of $\text{MnO}_2\cdot1.0\text{H}_2\text{O}$ is obtained. Alternatively, if the excess mass is assumed to be oxygen, then a formula of $\text{MnO}_3.1$ is indicated. This latter result is quite different from the formulas found by other authors (22, 58, 87) and implies that significant amounts of adsorbed water are present in the hydrous oxide.

**Extraction of Metal Hydrous Oxides**

Table 5 presents results of the extraction of metal
Table 5. Mass balance calculations and extraction efficiencies for metal hydrous oxide-clay particulates.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Metal Total in %</th>
<th>Metal on Clay</th>
<th>Nominal Conc.</th>
<th>Total Extracted 2</th>
<th>Extracted %</th>
<th>Measured Conc.</th>
</tr>
</thead>
<tbody>
<tr>
<td>FC1</td>
<td>12.5mg</td>
<td>0.06mg</td>
<td>0.46%</td>
<td>12.4mg</td>
<td>1.32%</td>
<td>14.1mg</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>114%</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>1.74%</td>
</tr>
<tr>
<td>FC2</td>
<td>24.8</td>
<td>0.11</td>
<td>0.43%</td>
<td>24.7</td>
<td>2.62%</td>
<td>25.3</td>
</tr>
<tr>
<td></td>
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<td></td>
<td></td>
<td>102</td>
</tr>
<tr>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>2.99%</td>
</tr>
<tr>
<td>FC3</td>
<td>37.1</td>
<td>0.04</td>
<td>0.11%</td>
<td>37.1</td>
<td>3.94%</td>
<td>36.0</td>
</tr>
<tr>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>97.0</td>
</tr>
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<td></td>
<td>3.98%</td>
</tr>
<tr>
<td>FC4</td>
<td>49.3</td>
<td>0.06</td>
<td>0.13%</td>
<td>49.2</td>
<td>5.22%</td>
<td>46.4</td>
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<td>4.85%</td>
</tr>
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<td>AC1</td>
<td>12.7</td>
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<td>3.17%</td>
<td>12.3</td>
<td>1.31%</td>
<td>13.6</td>
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<td></td>
<td></td>
<td></td>
<td>1.62%</td>
</tr>
<tr>
<td>AC2</td>
<td>25.2</td>
<td>0.49</td>
<td>1.95%</td>
<td>24.7</td>
<td>2.62%</td>
<td>23.1</td>
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<td>93.5</td>
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<td>2.57%</td>
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<td>AC3</td>
<td>38.0</td>
<td>2.44</td>
<td>6.43%</td>
<td>35.6</td>
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</tr>
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<td>3.04%</td>
</tr>
<tr>
<td>AC4</td>
<td>50.5</td>
<td>9.60</td>
<td>19.0%</td>
<td>40.9</td>
<td>4.34%</td>
<td>28.0</td>
</tr>
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<td></td>
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<td>2.88%</td>
</tr>
<tr>
<td>MC1</td>
<td>0.30</td>
<td>0.02</td>
<td>6.65%</td>
<td>0.28</td>
<td>301ppm</td>
<td>0.24</td>
</tr>
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<td>83.5</td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td>269ppm</td>
</tr>
<tr>
<td>MC2</td>
<td>0.53</td>
<td>0.04</td>
<td>7.61%</td>
<td>0.49</td>
<td>519ppm</td>
<td>0.41</td>
</tr>
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<td></td>
<td></td>
<td></td>
<td>476ppm</td>
</tr>
<tr>
<td>MC3</td>
<td>0.78</td>
<td>0.06</td>
<td>7.42%</td>
<td>0.73</td>
<td>772ppm</td>
<td>0.64</td>
</tr>
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<td></td>
<td></td>
<td></td>
<td>87.5</td>
</tr>
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<td></td>
<td></td>
<td></td>
<td>724ppm</td>
</tr>
<tr>
<td>MC4</td>
<td>1.05</td>
<td>0.08</td>
<td>7.13%</td>
<td>0.97</td>
<td>1030ppm</td>
<td>0.87</td>
</tr>
<tr>
<td></td>
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<td></td>
<td></td>
<td></td>
<td>89.4</td>
</tr>
<tr>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>964ppm</td>
</tr>
</tbody>
</table>

1c=clay; F=iron hydrous oxide; A=aluminum hydrous oxide; M=manganese hydrous oxide.

2Total extracted equals amount extracted from particulate minus amount extracted from a clay blank. Blank concentrations for iron, aluminum, and manganese were 0.20 %, 0.14 %, and 1.2 ppm, respectively.

3Measured concentration equals total extracted metal divided by the total measured mass of particulates.
hydrous oxides off the metal hydrous oxide-clay mixtures. The extractions were undertaken in order to compute mass balances since both the amount of starting material (metal) and the metal content of the washes were known. The wash data indicate that significant amounts of both aluminum and manganese were lost as a result of washing the suspensions. Losses of iron were negligible. The loss of aluminum, especially at higher concentrations, may indicate that the capacity of clay to adsorb the hydrous oxide was exceeded.

The wash data for manganese can be explained as being due to excess permanganate. The manganous sulfate used in the synthesis of manganese dioxide was the limiting reagent in the reaction. If all of the manganous sulfate added to the system is assumed to have reacted completely with potassium permanganate to form manganese dioxide, then the excess permanganate can be calculated (Table 6). When these excesses are expressed as a percentage of the total amount of manganese in the starting materials, the percentages are within 1.5 % of the percentage of manganese in the washes for three out of four samples. The excess permanganate would not be expected to adsorb onto either the clay or the manganese dioxide since both are negatively charged surfaces (see Chapter VI). Therefore, the manganese in the washes appears to be the result of excess permanganate in the system and not actual loss of manganese dioxide.

Mass balances for the iron hydrous oxide-clay mixtures range from 94.3 to 114 %, with a mean value of 102 %. These
Table 6. Comparison of the total amount of manganese in washes from manganese hydrous oxide-clay particulates to the total amount of manganese from excess permanganate.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Total Mn in Washes</th>
<th>% of Total</th>
<th>Total Mn in excess KMnO₄</th>
<th>% of Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>MC1</td>
<td>0.020 mg.</td>
<td>6.65%</td>
<td>0.040 mg.</td>
<td>13.1%</td>
</tr>
<tr>
<td>MC2</td>
<td>0.040</td>
<td>7.61%</td>
<td>0.040</td>
<td>7.55%</td>
</tr>
<tr>
<td>MC3</td>
<td>0.058</td>
<td>7.42%</td>
<td>0.046</td>
<td>5.92%</td>
</tr>
<tr>
<td>MC4</td>
<td>0.075</td>
<td>7.13%</td>
<td>0.063</td>
<td>6.05%</td>
</tr>
</tbody>
</table>
percentages appear to be reasonably good but, in fact, are probably less accurate than indicated if approximately 6% of the original sample was lost in transfers between containers. The data show a consistent decrease in recovery as the percentage of iron increases on the clay. This decrease could be due to a decrease in extraction efficiency as the concentration of iron in the extracts increases but is more likely caused by interferences in the flame atomic absorption determination of iron. Both citrate ion and nitric acid can cause interferences in the determination of iron (98). To test this, a solution of sodium citrate, sodium bicarbonate, and nitric acid in concentrations typically found in samples was added to a number of iron standards. The standards were then analyzed and the measured concentrations were compared to the original standards, with appropriate corrections made for dilution (Table 7). The percent relative deviation shows a pattern similar to that for the percent recovery. Therefore, the pattern in the percent recovery data is apparently caused by interferences in the determination of iron rather than a decrease in extraction efficiency.

Mass balances for aluminum hydrous oxide-clay mixtures show a similar trend of decreasing recovery as the percent aluminum increases. The percent extracted ranged from 68 to 111%. These poor recoveries could be due to interferences in determination of aluminum or due to poor extraction efficiencies.
Table 7. Relative deviations of measured iron concentrations caused by the addition of sodium citrate, sodium bicarbonate, and nitric acid.

<table>
<thead>
<tr>
<th>Standard Concentration</th>
<th>Measured Concentration</th>
<th>Percentage Relative Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.45 ppm</td>
<td>1.51 ppm</td>
<td>+4.36 %</td>
</tr>
<tr>
<td>2.79</td>
<td>2.66</td>
<td>-4.56</td>
</tr>
<tr>
<td>4.29</td>
<td>3.87</td>
<td>-9.75</td>
</tr>
<tr>
<td>5.06</td>
<td>4.47</td>
<td>-11.6</td>
</tr>
</tbody>
</table>

Percentage Relative Deviation =

\[
\frac{(\text{Measured Concentration} - \text{Standard Concentration}) \times 100}{\text{Standard Concentration}}
\]
The mass balance data for manganese hydrous oxide-clay mixtures are also low but, unlike iron and aluminum, increase slightly as the concentration of manganese increases. These low recoveries could be due to an incomplete extraction of manganese. To test this hypothesis, sequential extractions were done on the particulate with the highest manganese content. Each extract was analyzed for manganese (Table 8). The total amount of manganese extracted is similar to that listed in Table 5. In addition, the extraction was essentially complete after two extractions. Therefore, this explanation does not account for the low recoveries of manganese.

Other possible explanations include the loss of clay during transfers, interferences in the atomic absorption determination of manganese, and errors in the calculated concentrations of the starting materials. The first explanation could be expected to improve the results by an average of about 6%, but this still is not sufficient to explain the average recovery of about 86%. The second and third explanations are unlikely. The determination of manganese by flame atomic absorption is generally not subject to interferences and the concentrations of the starting materials were checked and were found to be correct. The most likely cause for the low recovery of manganese is cation exchange reactions with the clay. Manganese is a divalent ion in solution and would be expected to adsorb reasonably strongly onto the clay. In
Table 8. Total manganese extracted by each of four sequential extractions of a manganese hydrous oxide-clay particulate ("MC4").

<table>
<thead>
<tr>
<th>Extraction Number</th>
<th>Manganese Extracted</th>
<th>Percentage of Total Extracted</th>
<th>Cumulative Percentage of Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.0442mg.</td>
<td>95.5 %</td>
<td>95.5 %</td>
</tr>
<tr>
<td>2</td>
<td>0.0017</td>
<td>3.66</td>
<td>99.1</td>
</tr>
<tr>
<td>3</td>
<td>0.0002</td>
<td>0.45</td>
<td>99.6</td>
</tr>
<tr>
<td>4</td>
<td>0.0002</td>
<td>0.42</td>
<td>100.0</td>
</tr>
</tbody>
</table>

Total Manganese Extracted = 0.0463 mg.
Total Manganese on Clay = 0.0507 mg.
Percentage Extracted = 91.4 %
addition, only a small amount of manganese would have to be adsorbed for it to affect the results significantly since only a small amount of manganese was precipitated onto the clay. Finally, analysis of sodium acetate saturating solutions in connection with CEC measurements (see Chapter IV) showed that a significant quantity of manganese was present indicating that some of the manganese on the clay is in an exchangeable form.

**Organic Matter-Metal Hydrous Oxide-Clay Particulates**

Characteristics of the organic matter-metal hydrous oxide-clay particulates are listed in Tables 4 and 9. Initial attempts to coat organic matter onto illite failed, due to the electrostatic repulsion between the two negatively charged substances. Iron (and aluminum) hydrous oxides had to be introduced into the system in order to coat the clay with organic matter. These hydrous oxides most likely form cation bridges between the organic matter and the clay.

Observations made at the time of synthesis suggested that the clay-metal hydrous oxide system had a finite adsorptive capacity for organic matter. Attempts were made to place up to 15 % by weight of organic carbon onto the clay particles. The particulates with the lowest concentrations of organic matter had reasonably clear supernatant solutions after centrifugation, indicating that most of the organic matter was adsorbed by the particulates. Particulates with progressively higher
Table 9. Percent carbon, nitrogen, and hydrogen data for organic matter-containing particulates.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Component</th>
<th>% C</th>
<th>% N</th>
<th>% H</th>
<th>%C/%N</th>
<th>%C/%N</th>
</tr>
</thead>
<tbody>
<tr>
<td>HFC1</td>
<td>HA</td>
<td>2.14</td>
<td>0.27</td>
<td>0.73</td>
<td>7.8</td>
<td>2.9</td>
</tr>
<tr>
<td>HFC2</td>
<td>HA</td>
<td>3.81</td>
<td>0.34</td>
<td>0.81</td>
<td>11.2</td>
<td>4.7</td>
</tr>
<tr>
<td>HFC3</td>
<td>HA</td>
<td>4.98</td>
<td>0.54</td>
<td>0.88</td>
<td>9.2</td>
<td>5.7</td>
</tr>
<tr>
<td>HFC4</td>
<td>HA</td>
<td>5.40±.6</td>
<td>0.50</td>
<td>1.00</td>
<td>10.8</td>
<td>5.4</td>
</tr>
<tr>
<td>FaFC1</td>
<td>FA</td>
<td>2.22±.5</td>
<td>0.14</td>
<td>0.73</td>
<td>16.5</td>
<td>3.0</td>
</tr>
<tr>
<td>FaFC2</td>
<td>FA</td>
<td>1.40</td>
<td>0.10</td>
<td>0.65</td>
<td>14.1</td>
<td>2.2</td>
</tr>
<tr>
<td>FaFC3</td>
<td>FA</td>
<td>3.02</td>
<td>0.24</td>
<td>0.74</td>
<td>12.6</td>
<td>4.1</td>
</tr>
<tr>
<td>FaFC4</td>
<td>FA</td>
<td>1.51</td>
<td>0.14</td>
<td>0.64</td>
<td>10.9</td>
<td>2.4</td>
</tr>
<tr>
<td>HFCage</td>
<td>HA</td>
<td>3.03</td>
<td>0.25</td>
<td>0.83</td>
<td>12.1</td>
<td>3.6</td>
</tr>
<tr>
<td>HA2</td>
<td>HA</td>
<td>5.03</td>
<td>0.35</td>
<td>1.20</td>
<td>14.4</td>
<td>4.2</td>
</tr>
<tr>
<td>HA24</td>
<td>HA</td>
<td>42.4±.2</td>
<td>2.57</td>
<td>3.84</td>
<td>16.5</td>
<td>11.0</td>
</tr>
<tr>
<td>FA24</td>
<td>FA</td>
<td>39.5</td>
<td>0.71</td>
<td>3.34</td>
<td>55.6</td>
<td>11.8</td>
</tr>
<tr>
<td>HA25</td>
<td>HA</td>
<td>54.15</td>
<td>3.51</td>
<td>4.67</td>
<td>15.4</td>
<td>11.6</td>
</tr>
<tr>
<td>FA25</td>
<td>FA</td>
<td>40.41</td>
<td>0.69</td>
<td>3.02</td>
<td>58.6</td>
<td>13.4</td>
</tr>
<tr>
<td>HA25</td>
<td>FA</td>
<td>57.3</td>
<td>2.8</td>
<td>5.1</td>
<td>20.5</td>
<td>11.2</td>
</tr>
<tr>
<td>FA5</td>
<td>FA</td>
<td>47.0</td>
<td>1.5</td>
<td>4.4</td>
<td>31.3</td>
<td>10.7</td>
</tr>
</tbody>
</table>

1 C=clay; F=iron hydrous oxide; A=aluminum hydrous oxide; H=humic acid; Fa=fulvic acid; age=aging experiment.

2 HA=humic acid; FA=fulvic acid.

3 Standard deviations are ± 0.15% except where noted. Values represent the mean of two determinations.

4 Data from Baur (86).

5 Data from Steelink (18).
concentrations of organic matter also had supernatant solutions which were progressively darker in color, due to excess organic matter in solution. Both the concentration and percent carbon data in Tables 4 and 9 corroborate these observations. The last three samples of humic acid-iron hydrous oxide-clay particulates (HFC2-4, Table 4) all have approximately the same measured concentration of particulates in suspension. Since the nominal clay and metal hydrous oxide concentrations for these three samples were all approximately the same, the concentration data demonstrate that all three samples had approximately the same organic carbon content.

Similarly, the percent carbon data for humic acid-clay mixtures increases in a systematic manner from 2.1 to 5.4 % organic carbon (Table 9). The last three samples vary only from 3.8 to 5.4 %. However, based on the total amounts of humic acid used in the synthesis of these particulates, the percentages should have been 1.7, 4.9, 7.9, and 11.1 % organic carbon for the four samples, respectively. Again, saturation of the clay-metal hydrous oxide surface is indicated.

The data for fulvic acid suggest that even less organic matter was adsorbed onto the metal hydrous oxide-clay surface than in the case of humic acid. Predicted percentages for the four samples were 1.8, 6.0, "12.4," and 14.2 % organic carbon. The predicted percentage of organic carbon for the third sample is questionable.
since some of the sample was lost due to spillage immediately after addition of the organic matter solution. However, the conclusion that the clay-metal hydrous oxide particulate has a finite adsorptive capacity for organic matter is supported.

Table 9 presents the percent carbon, hydrogen, and nitrogen data as well as carbon to hydrogen and carbon to nitrogen ratios for the organic matter-metal hydrous oxide-clay particulates and the dried humic and fulvic acid samples. In general, the analyses for dried humic and fulvic acid solutions agree with those reported by Baur (86). Elemental analysis of the dried fulvic acid solution and the carbon to nitrogen and carbon to hydrogen ratios for the dried humic acid solution also agree with Baur. The absolute values of carbon, hydrogen, and nitrogen for humic acid are lower due to the addition of sodium hydroxide to the solution in order to dissolve the humic acid.

Carbon to nitrogen ratios for the organic matter-metal hydrous oxide-clay mixtures are all substantially lower than those for the original humic and fulvic acid samples. The ratios average 9.8 and 13.5 for the humic acid and fulvic acid mixtures, respectively, compared to 16.5 and 55.6 for the humic and fulvic acid solutions. There are two possible explanations for this. First, iron nitrate was used to make the iron hydrous oxide. Even though attempts were made to remove all excess salt (sodium nitrate) from the particulates, some nitrate undoubtedly remained with
the suspension. This would account for the proportionately higher nitrogen contents of the particulates and would result in lower carbon to nitrogen ratios. This explanation is supported by the organic matter-aluminum hydrous oxide-clay sample (HACage, Table 9). The metal hydrous oxide, in this case, was made from the chloride salt and, hence, would not be expected to contribute any nitrogen due to nitrate contamination. The carbon to nitrogen ratio of 14.4 for this sample is much closer to the value of 15.4 reported by Baur (86) than any of the humic acid samples containing iron hydrous oxide.

An alternative explanation for the observed data is that the organic matter is being fractionated. Nitrogen-containing functional groups are known to play an important role in adsorption (59). These groups are generally protonated and, therefore, are positively charged. The positively charged groups tend to adsorb onto the negatively charged clay. Therefore, organic matter which contains a higher proportion of nitrogen-containing functional groups would tend to be adsorbed to a greater extent than organic matter containing lower amounts of nitrogen.

The above explanation for the carbon to nitrogen ratio data could also be used to explain the relatively low adsorption of fulvic acid. Fulvic acid contains much less nitrogen than humic acid. Therefore, one would expect lower amounts of fulvic acid to adsorb onto the metal hydrous
oxide-clay particulates. Alternatively, the low adsorption of fulvic acid could be explained by its higher solubility, its higher proportion of carboxylic acid groups, or its lower molecular weight than humic acid. The higher proportion of carboxylic acid groups results in a more negatively charged organic molecule and, therefore, would result in a greater electrostatic repulsion between the fulvic acid molecules and the clay surface than in the case of humic acid. The lower molecular weight of fulvic acid means that the contribution to the adsorptive energy by van der Waals interactions and entropy effects is less than for humic acid.

In general, the data are consistent with the results of other investigators (59, 71). The carbon to nitrogen ratios are probably due to nitrate contamination of the particulate samples, although some fractionation of the organic matter could have occurred. In addition, fulvic acid does not adsorb in large amounts onto metal hydrous oxide-clay particulates and its significance as a component of natural particulates can be questioned. Finally, the percent hydrogen data and the carbon to hydrogen ratios for the organic matter-metal hydrous oxide-clay particulates are relatively meaningless in terms of the adsorption of organic matter since hydrogen can be contributed from all three components of the particulates. The low carbon to hydrogen ratios support this view.
Analysis of the Washes from the Synthesis of Pure Metal Hydrous Oxides

Figures 5, 6, and 7 present the results for washes collected during the synthesis of pure metal hydrous oxides. Similar data was obtained for the metal hydrous oxide-clay mixtures. In some cases, two sets of data appear for the same metal hydrous oxide; each applies to a separate subsample. Figure 5 presents the conductivity versus wash data. Generally, there was an exponential decrease in conductivity for all of the samples.

Figure 6 presents the pH versus wash data. For iron and managanese, the pH of wash solutions increased during the course of washing. Iron solutions increased from a pH of approximately 5.6 to 10.2 while manganese solutions rose from a pH of approximately 2.6 to 5. For iron, there was a sharp increase in pH between the second and third washes. This increase corresponded to a drop in conductivity below 5000 μmhos/cm. The pH of manganese wash solutions increased steadily as a function of the number of washes and did not show a sharp break in the pH versus wash curve. Aluminum solutions show a decrease in pH from about 7.2 to 5.9, with a sharp decrease occurring between the first and second washes. This also corresponded to a decrease in conductivity from 5000 to 1500 μmhos/cm.

Figure 7 presents the concentration of metal versus wash data. The concentration of both iron and manganese in the washes was generally low and total losses of metal in
Figure 5. Conductivity of each of the washes collected during the synthesis of pure metal hydrous oxides.
Figure 6. pH of each of the washes collected during the synthesis of pure metal hydrous oxides.
Figure 7. Metal concentration in each of the washes collected during the synthesis of pure metal hydrous oxides.
the washes were 3.0 % of the starting material in both cases. Aluminum washes, however, contained large quantities of aluminum, particularly in the second and third washes. These losses represented 80.3 % of the starting material. Similar behavior was noted for the aluminum hydrous oxide-clay system. In general, losses of metal increased as the conductivity of the suspensions decreased. These results suggest that stabilization of metal hydrous oxide colloids occurs as the conductivity of the suspension decreases and, consequently, as the thickness of the electric double layer increases.
CHAPTER IV

CATION EXCHANGE CAPACITY MEASUREMENTS

Introduction

Cation exchange is a form of ion-exchange. The reaction is usually between two non-specifically adsorbed cations (22) and may be written as

\[ X^-A + B \rightleftharpoons X^-B + A \] (4-1)

where \( X \) is the adsorbent and A and B are the exchangeable cations. The above reaction is for the exchange of two monovalent cations, but analogous reactions could be written for multivalent ions. Cation exchange reactions are generally diffusion controlled (i.e., kinetically fast), stoichiometric, and reversible (49, 99). Some selectivity between cations usually occurs which can be explained in terms of the properties of the exchanging ions.

Mathematically, cation exchange reactions can be modelled using the Rothmund-Kornfeld equation (Chapter I) or a selectivity coefficient, \( K_A^B \), defined as (100)

\[ \frac{[A^+][B^-X]}{[B^+][A^-X]} = K_A^B \] (4-2)

where \([A^+]\) and \([B^+]\) are the concentrations of A and B in
solution, and \([A^+ - X]\) and \([B^+ - X]\) are the concentrations of A and B on the adsorbent. Selectivity coefficients generally vary as a function of the concentrations of A and B on the surface.

Cation exchange capacity (CEC) is defined as the sum of the exchangeable cations on surfaces (99). It is essentially a measure of the total number of exchange sites. CEC is generally more important than anion exchange capacity in natural systems because most natural particulates are negatively charged (80).

The purpose of this chapter is to review the measurement of CEC and to present CEC data for the particulates described in Chapter III.

**Origin of CEC**

CEC originates whenever an electric double layer develops at a solid-solution interface such that the surface possesses at least some negative charge (80, 84, 90, 101). Isomorphous substitution, particularly in clays, and dissociation of acid groups in organic matter probably account for most of the CEC encountered in nature (80).

**Factors Affecting CEC**

CEC is dependent on a large number of factors including:

1. **pH** (80, 84, 90, 101)

   pH controls the dissociation of surface hydroxyl groups on oxide surfaces and functional groups on organic matter. Hydronium ions also compete with
other ions for cation exchange sites although the effect is negligible above pH 7 (100).

2. Particle size, surface area, and crystallinity (80, 84).
These control the number of broken bonds on the surface. In general, the more broken bonds there are, the higher the CEC.

3. Isomorphous substitution and/or imperfections in a crystal lattice and specific adsorption (22, 51, 80).
These determine, in part, the magnitude of the CEC.

4. Blocking of cation exchange sites by hydrous oxides and/or organic matter (25, 51, 84, 101).
Adsorption at one exchange site can result in other cation exchange sites being inaccessible to another absorbate. For example, adsorption of an organic cation will block cation exchange sites when the size of the organic cation exceeds the area per exchange site. In general, none of the clay in organic matter-clay particulates will be accessible to solution when the organic matter content exceeds approximately 6% (101).

5. Variability in the replaceability of ions.
This is primarily dependent on the charge, hydrated radius, and polarizability of the ions (8, 22, 25, 80, 84, 100). Generally, an ion has a higher affinity for the surface as charge and polarizability increase, and as the hydrated radius decreases.
6. Sample pretreatment, storage, and handling (84, 102).
These can affect the CEC by altering the surface of the material whose capacity is being measured. An example would be the aging of hydrous oxides (39).

7. Ionic strength or ionic media (80, 90).
Ionic strength affects the activities of ions as well as the competition for cation exchange sites by other ions.

8. Temperature (80, 84).
Temperature affects the equilibria governing competition between ions for cation exchange sites. As the temperature increases, the measured CEC decreases slightly.

9. Soil to solution ratio (102).
Because of variations in these factors, the determination of CEC is neither highly accurate nor precise (84). For example, CEC measurements of the same illite (90) using the same method varied from 22.8 to 31.4 meq./100g., with a mean value of 26.6 meq./100g. and a relative standard deviation of 14.3 %. Additional variation in measurements can be expected if several methods are used.

**Methods**

Five major types of methods have been used to measure CEC. They include:

1. Saturation of the sample with hydronium ions followed by titration of the sample with barium hydroxide to pH 7.0 or sodium hydroxide to pH 8.5 (99).
2. Displacement and summation of exchangeable cations (99).

3. Equilibration with Ca-45 and Ca-40 nitrate solutions (99).

4. Saturation of the sample with organic cations (90).

5. Displacement of exchangeable cations with cations from one salt solution followed by displacement of the cations from the first salt solution with cations from a second salt solution (80, 99, 103).

This last method is the most commonly used method of the five methods listed (99). Common saturating ions include alkalies such as 1 M sodium acetate at pH 7.0 or 8.2, ammonium ion such as 1 M ammonium acetate at pH 7.0, and alkaline earths such as 0.25 M barium chloride with 0.2 M triethanolamine solution at pH 8.2 (80, 99). Displacement solutions are usually one of the above, such as 1 M ammonium acetate at pH 7.0.

These methods generally give slightly divergent results due to variations in pH and composition of the saturating and displacing solutions (101). Composition of the solutions affects the relative ease with which ions are displaced and pH affects the contribution to CEC from pH-dependent charged surfaces. For these reasons, the method used to obtain CEC data should always be specified (99).

In addition, various errors may occur. For example, dissolution of calcium carbonate or calcium sulfate during
the displacement step will cause errors in the CEC if calcium is used as the saturating cation (99). Also, dissolution of these salts occurs when 1 M ammonium acetate at pH 7.0 is used as the saturating solution (99, 103). Because both calcium carbonate and calcium sulfate contribute to the overall CEC of calcareous materials, use of ammonium acetate is to be avoided. Sodium acetate (1 M; pH 8.2) is recommended as the saturating solution for these materials (99, 103).

Other sources of error include possible retention of excess salt in the interstitial spaces, alteration due to sample pretreatment such as drying (102), and loss of sample due to dispersion (49). In addition, organic matter may be lost when excess ammonium acetate is removed from the material with 95 % ethanol or 100 % methanol (99). Use of 99 % isopropanol is recommended in this case. Finally, determination of CEC via adsorption of organic cations is subject to interferences from the organic cation covering up more than one exchange site, and from adsorption beyond the CEC due to van der Waals interactions and entropy effects (51).

**CEC of Natural Materials**

CEC of natural materials such as soils and sediments can vary widely, ranging from less than 1 to more than 100 meq./100g. (64, 65, 99, 103). Generally, the CEC increases as the particle size decreases for the mineral component of soils and sediments. Therefore, the CEC of gravel, sand,
silt, and clay has been reported to be 0, 3.6, 32.8, and 80.5 meq./100g., respectively (52). Illite can have a range of CEC's, i.e., from 10 to 40 meq./100g., but most often it is between 15 and 25 meq./100g. (75, 80, 81, 90, 93, 100, 102). The CEC for illite is largely independent of ionic strength and pH.

Organic matter also has a high CEC due to the dissociation of carboxylic acid groups. In this case, the CEC is dependent on pH, ionic strength, and the saturating cation. For example, humic and fulvic acids have CEC's of 250-1190, 740-950, 1690-2580, and 1280-1520 meq./100g., when sodium, potassium, calcium, and magnesium were the saturating cations, respectively (27). At least two distinct exchange sites could be differentiated and others were discernible at lower ionic strengths. The CEC increased erratically for a given saturating cation as the ionic strength decreased.

**Methodology**

CEC was measured following the procedure given by Bower et al. (104) and cited in Chapman and Pratt (103) and Chapman (99). The method consists of saturating 50-100 mg. of sample with sodium using 1 M sodium acetate at pH 8.2, washing excess sodium from the material using 95 % ethanol, and, finally, displacing the sodium off the sample using 1 M ammonium acetate at pH 7.0. The ammonium acetate extracts plus an ammonium acetate blank were acidified with concentrated distilled nitric acid and were analyzed for
sodium by either flame atomic absorption or flame atomic emission on a Model 951 Instrumentation Laboratory Atomic Absorption Spectrophotometer. Standards for the sodium analyses were prepared from sodium chloride which had been dried overnight at 110 C. under vacuum.

Several attempts were made to validate the experimental methodology. These include:

1. Five sets of duplicate samples of the Montana illite were saturated four times with 10-ml. portions of 1 M sodium acetate solutions. The pH of the sodium acetate solution for each set was adjusted to values ranging from 3.93 to 8.20. The samples were washed with 95 % ethanol, extracted with 1 M ammonium acetate at pH 7.0 and analyzed for sodium. The purpose of this experiment was to check for any variation in CEC due to variations in pH of the saturating solution.

2. A sample of the Montana illite was saturated with sodium acetate at pH 8.2. The sample was then washed with 10-ml. portions of 95 % ethanol. Each wash was collected separately and analyzed for sodium. The sample was then extracted five times with 1 M ammonium acetate at pH 7.0. The extracts were collected and analyzed separately. The purpose of this experiment was to check for completeness of washing and completeness of extraction.

3. Samples of metal hydrous oxide-clay mixtures were
saturated four times with 10-ml. portions of 1 M sodium acetate at pH 8.2. The saturating solutions were combined and analyzed using atomic absorption spectrophotometry for iron, aluminum, or manganese, as appropriate. The purpose of this experiment was to verify that metal hydrous oxides were not being removed from the particulates by the saturating solution.

Finally, the CEC of several of the particulates varied over time, presumably due to aging of the metal hydrous oxides. To verify this, several samples of particulates were prepared using the methods described in Chapter III and were analyzed for CEC at frequent intervals. The particulates included pure samples, clay mixtures, and humic acid-clay mixtures of iron and aluminum hydrous oxides. The characteristics of these particulates are given in Tables 4 and 9. To differentiate them from the other particulates, these samples are denoted by the suffix "age."

**Results**

**Methodology Experiments**

Tables 10, 11, and 12 present the results from the experiments used to test the experimental methodology. Table 10 shows the variation in the CEC of illite as a function of the pH of the saturating sodium acetate solution. With the exception of the pH 3.93 samples, all of the values are within 1 meq./100g. of the mean for the pH
Table 10. Variation in the CEC of illite as a function of the pH of the sodium acetate saturating solution.

<table>
<thead>
<tr>
<th>pH</th>
<th>CEC</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.93</td>
<td>9.63 meq./100g.</td>
</tr>
<tr>
<td>4.96</td>
<td>16.5</td>
</tr>
<tr>
<td>5.85</td>
<td>17.8</td>
</tr>
<tr>
<td>6.92</td>
<td>16.2</td>
</tr>
<tr>
<td>8.20</td>
<td>17.2 ± 1.1</td>
</tr>
</tbody>
</table>

¹Values are the means of duplicate measurements. Variation between duplicates was less than 0.20 meq./100g.
Table 11. Sodium contents in the 95 % ethanol washes and the ammonium acetate extracts during the CEC measurement of illite.

<table>
<thead>
<tr>
<th>Wash Number</th>
<th>Sodium in Wash</th>
<th>Percentage of Total</th>
<th>Cumulative Percentage of Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>8.82mg.</td>
<td>95.5 %</td>
<td>95.5 %</td>
</tr>
<tr>
<td>2</td>
<td>0.371</td>
<td>4.02</td>
<td>99.5</td>
</tr>
<tr>
<td>3</td>
<td>0.023</td>
<td>0.25</td>
<td>99.7</td>
</tr>
<tr>
<td>4</td>
<td>0.013</td>
<td>0.14</td>
<td>99.9</td>
</tr>
<tr>
<td>5</td>
<td>0.011</td>
<td>0.12</td>
<td>100.0</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Extraction Number</th>
<th>Sodium in Extract</th>
<th>Percentage of Total</th>
<th>Cumulative Percentage of Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.342mg.</td>
<td>94.3 %</td>
<td>94.3 %</td>
</tr>
<tr>
<td>2</td>
<td>0.0182</td>
<td>5.03</td>
<td>99.4</td>
</tr>
<tr>
<td>3</td>
<td>0.0014</td>
<td>0.40</td>
<td>99.8</td>
</tr>
<tr>
<td>4</td>
<td>0.0005</td>
<td>0.14</td>
<td>99.9</td>
</tr>
<tr>
<td>5</td>
<td>0.0004</td>
<td>0.12</td>
<td>100.0</td>
</tr>
</tbody>
</table>
Table 12. Metal contents in the sodium acetate saturating solutions after saturation of pure metal hydrous oxides and metal hydrous oxide clay particulates.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Metal in Saturating Solution</th>
<th>Percentage of Total Metal in Sample</th>
</tr>
</thead>
<tbody>
<tr>
<td>FC1</td>
<td>0.0000mg.</td>
<td>0.00 %</td>
</tr>
<tr>
<td>FC2</td>
<td>0.0000</td>
<td>0.00</td>
</tr>
<tr>
<td>FC3</td>
<td>0.0000</td>
<td>0.00</td>
</tr>
<tr>
<td>FC4</td>
<td>0.0000</td>
<td>0.00</td>
</tr>
<tr>
<td>AC1</td>
<td>0.0000</td>
<td>0.00</td>
</tr>
<tr>
<td>AC2</td>
<td>0.0083</td>
<td>0.56</td>
</tr>
<tr>
<td>AC3</td>
<td>0.0082</td>
<td>0.41</td>
</tr>
<tr>
<td>AC4</td>
<td>0.0082</td>
<td>0.34</td>
</tr>
<tr>
<td>MC1</td>
<td>0.0058</td>
<td>37</td>
</tr>
<tr>
<td>MC2</td>
<td>0.0076</td>
<td>28</td>
</tr>
<tr>
<td>MC3</td>
<td>0.0053</td>
<td>13</td>
</tr>
<tr>
<td>MC4</td>
<td>0.0034</td>
<td>6.1</td>
</tr>
<tr>
<td>F</td>
<td>0.0173</td>
<td>0.12</td>
</tr>
<tr>
<td>A</td>
<td>0.0561</td>
<td>0.25</td>
</tr>
<tr>
<td>M</td>
<td>0.0110</td>
<td>0.06</td>
</tr>
</tbody>
</table>

1Values are corrected for the metal content in the sodium acetate solution and in a clay blank.
8.2 saturating solution. This variation is less than the estimated standard deviation of 1.1 meq./100g. for illite determined over a period of several months. The results indicate that the CEC for illite is relatively insensitive to variations in pH in the range from 5 to 8.5. A similar result for montmorillonite was reported by Theng (51).

The pH 3.93 samples produced CEC values that were substantially lower than the other samples. It was observed that the supernatant solutions for the first sodium acetate saturation of these samples were very cloudy, even after prolonged centrifugation. This indicates that significant amounts of the sample were lost due to dispersion.

Table 11 presents the results of the sequential washing and sequential extraction experiments. In both cases, better than 99% of the extractable sodium was removed by the second washing or extraction. These results agree with the findings of Houle (102).

Table 12 presents the results of the metal content experiment. Both iron and aluminum hydrous oxide particulates and their clay mixtures showed negligible extraction of metal as a result of saturation with sodium acetate. The same result was observed for pure manganese hydrous oxide. However, the saturating solutions for manganese hydrous oxide-clay particulates contained substantial amounts of manganese suggesting that part of the manganese in the sample was bound to cation exchange sites, presumably as Mn(II).
**CEC Measurements for Synthesized Particulates**

Table 13 presents the results of the CEC measurements. Results are reported on the basis of either the nominal concentration of clay ("Nominal" CEC) or the measured concentrations of particulates ("Measured" CEC; Table 4). The measurements represent an average of at least three determinations for each of the samples. Estimated standard deviations were 1.5 meq./100g. or less.

Illite had a CEC of approximately $17.2 \pm 1.1$ meq./100g. This is well within the range of values reported for other illites. The standard deviation of 1.1 meq./100g. includes samples taken at five different times throughout the period in which CEC measurements were made and is believed to be representative of the standard deviation of the method at this level. The relative standard deviation of 6.2 % is substantially lower than reported previously (90) and may reflect differences in methods and/or more consistent "operator error."

Iron hydrous oxides show an initial decrease in CEC over the first 5 days after synthesis followed by a gradual increase and, perhaps, a levelling off over a period of about 50 days (Figure 8). These results could reflect aging effects in which an intermediate substance of relatively low CEC is formed, or in which an initial precipitate ages to a more crystalline form, during approximately the first 5 days followed by a slower transformation to another material of higher CEC. The latter could also reflect
Table 13. CEC measurements of the model particulates.

<table>
<thead>
<tr>
<th>Particulate Sample</th>
<th>&quot;Nominal&quot; CEC</th>
<th>&quot;Measured&quot; CEC</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>-</td>
<td>17.2 ± 1.1 meq./100g.</td>
</tr>
<tr>
<td>F</td>
<td>a</td>
<td>a</td>
</tr>
<tr>
<td>A</td>
<td>a</td>
<td>a</td>
</tr>
<tr>
<td>M</td>
<td>a</td>
<td>a</td>
</tr>
<tr>
<td>FC1</td>
<td>15.8 meq./100g.</td>
<td>16.2</td>
</tr>
<tr>
<td>FC2</td>
<td>18.3</td>
<td>18.9</td>
</tr>
<tr>
<td>FC3</td>
<td>20.0</td>
<td>19.8</td>
</tr>
<tr>
<td>FC4</td>
<td>20.9</td>
<td>19.8</td>
</tr>
<tr>
<td>AC1</td>
<td>a</td>
<td>a</td>
</tr>
<tr>
<td>AC2</td>
<td>a</td>
<td>a</td>
</tr>
<tr>
<td>AC3</td>
<td>a</td>
<td>a</td>
</tr>
<tr>
<td>AC4</td>
<td>a</td>
<td>a</td>
</tr>
<tr>
<td>MC1</td>
<td>16.7</td>
<td>17.7</td>
</tr>
<tr>
<td>MC2</td>
<td>17.0</td>
<td>18.4</td>
</tr>
<tr>
<td>MC3</td>
<td>17.1</td>
<td>18.4</td>
</tr>
<tr>
<td>MC4</td>
<td>17.4</td>
<td>18.2</td>
</tr>
<tr>
<td>HFC1</td>
<td>29.9</td>
<td>27.9</td>
</tr>
<tr>
<td>HFC2</td>
<td>43.3</td>
<td>38.7</td>
</tr>
<tr>
<td>HFC3</td>
<td>41.7</td>
<td>36.2</td>
</tr>
<tr>
<td>HFC4</td>
<td>37.9</td>
<td>33.2</td>
</tr>
<tr>
<td>FaFC1</td>
<td>36.2</td>
<td>32.6</td>
</tr>
<tr>
<td>FaFC2</td>
<td>23.8</td>
<td>23.8</td>
</tr>
<tr>
<td>FaFC3</td>
<td>26.5</td>
<td>33.0</td>
</tr>
<tr>
<td>FaFC4</td>
<td>18.8</td>
<td>19.2</td>
</tr>
<tr>
<td>Fage</td>
<td>a</td>
<td>a</td>
</tr>
<tr>
<td>Aage</td>
<td>a</td>
<td>a</td>
</tr>
<tr>
<td>FCage</td>
<td>20.6</td>
<td>21.0</td>
</tr>
<tr>
<td>HFCage</td>
<td>34.8</td>
<td>31.6</td>
</tr>
<tr>
<td>HACage</td>
<td>49.3</td>
<td>39.6</td>
</tr>
</tbody>
</table>

1 C=clay; F=iron hydrous oxide; A=aluminum hydrous oxide; M=manganese hydrous oxide; H=humic acid; Fa=fulvic acid; age=aging experiment.

2 "Nominal" CEC's are calculated using the nominal concentration of clay (Table 4). "a"=sample CEC varied systematically over time.

3 "Measured" CEC's are calculated using the measured concentrations of the particulate samples (Table 4).
Figure 8. Variation in the CEC of pure iron hydrous oxide as a function of time after synthesis.
random variations in the CEC measurements (see below).

Aluminum and manganese hydrous oxides also exhibit aging effects (Figures 9 and 10). For aluminum, CEC tended to be erratic but a trend towards decreasing CEC values over time is evident (Figure 9). Manganese hydrous oxide also showed a decrease in CEC with time (Figure 10). In addition, the CEC of manganese hydrous oxide was high compared to any of the other particulates in agreement with the findings of other investigators (47). These results could reflect either an increase in the crystallinity of the material or a conversion to another form.

The metal hydrous oxide-clay particulates show a variety of trends. Iron hydrous oxide-clay particulates show an increase in CEC as the percentage of iron hydrous oxide on the clay increases, and then level off at approximately 20 meq./100g. for iron concentrations above about 3 % (Figure 11). Apparently, the particulates are essentially iron hydrous oxide particulates when the percentage of iron is over about 3 %; i.e., the surface of the clay particles may no longer be accessible to solution at these iron concentrations above 3 %.

In addition, the CEC of each of the iron hydrous oxide-clay particulates varied over time (Figure 12). These variations parallel the relative variations in the CEC of the pure iron hydrous oxides, illite, and manganese hydrous oxide-clay particulates (Figure 12). The manganese hydrous oxide-clay particulates can be used, in addition to the
Figure 9. Variation in the CEC of pure aluminum hydrous oxide as a function of time after synthesis.
Figure 10. Variation in the CEC of pure manganese hydrous oxide as a function of time after synthesis.
Figure 11. Variation in the CEC of iron hydrous oxide-clay particulates as a function of the iron content.
Figure 12. Relative variations with time in the "measured" CEC for iron hydrous oxides, iron hydrous oxide-clay particulates, manganese hydrous oxide-clay particulates, and clay.

Relative Variation = $\frac{\text{Measured CEC} \times 100}{\text{Mean Measured CEC}}$
illite sample, as an indicator of systematic variations between sets of CEC measurements because of the low concentrations of manganese hydrous oxide on the clay (see below). Therefore, the results in Figure 12 may not necessarily indicate an aging effect but could be due to variations among different sets of CEC measurements. These variations are similar to the relative standard deviation calculated for illite.

The aluminum hydrous oxide-clay particulates show a consistent decrease in the "measured" CEC with increase in the percentage of aluminum (Table 14). This decrease appears to be due to the increase in mass of the particulates from the increasing amounts of aluminum (Table 4). The CEC values using the nominal clay concentrations do not vary significantly among the four aluminum hydrous oxide-clay particulates (Table 14). This implies that the surface of all four aluminum hydrous oxide-clay particulates is the same and may reflect complete coverage of the clay particles by aluminum hydrous oxides. In addition, all four particulate samples showed parallel aging effects (Figure 13). The magnitude of the variations is greater than the systematic variations between sets of CEC measurements (Figure 12). The consistency of the results for all of the aluminum hydrous oxide-clay particulates supports the view that all of the particulates had similar surfaces. The results from the aging experiment indicate that the CEC decreased during the first 2 to 5
Table 14. "Nominal" and "measured" CEC measurements of aluminum hydrous oxide-clay particulates as a function of time after synthesis.

<table>
<thead>
<tr>
<th>Particulate Sample</th>
<th>&quot;Nominal&quot; CEC (meq./100g. clay) x days after synthesis</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>5</td>
</tr>
<tr>
<td>AC1</td>
<td>13.5</td>
</tr>
<tr>
<td>AC2</td>
<td>12.7</td>
</tr>
<tr>
<td>AC3</td>
<td>13.0</td>
</tr>
<tr>
<td>AC4</td>
<td>12.8</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Particulate Sample</th>
<th>&quot;Measured&quot; CEC (meq./100g. particulate) x days after synthesis</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>5</td>
</tr>
<tr>
<td>AC1</td>
<td>13.8</td>
</tr>
<tr>
<td>AC2</td>
<td>12.6</td>
</tr>
<tr>
<td>AC3</td>
<td>12.2</td>
</tr>
<tr>
<td>AC4</td>
<td>11.9</td>
</tr>
</tbody>
</table>

1 CEC values were calculated using the nominal concentration of clay (Table 4).

2 CEC values were calculated using the measured concentration of particulates (Table 4).
Figure 13. Variation in the "nominal" CEC of aluminum hydrous oxide-clay particulates as a function of time after synthesis.
days after the particulates were made and then increased steadily for at least the next 50 days (Figure 13). This increase in CEC is in contrast to the decrease in the cation exchange capacity for the pure aluminum hydrous oxide.

The manganese hydrous oxide-clay particulates show very little variation in CEC either with concentration of manganese or with time. The mean value (18.2 ± 0.3) for these particulates is not significantly different from that for pure clay (17.8 ± 0.5). The latter value was calculated using only that data measured at the same time as the manganese hydrous oxide-clay particulates. These results suggest that the small quantities of manganese which were placed on the clay did not significantly affect CEC.

The organic matter-metal hydrous oxide-clay particulates generally had CEC's which were higher than those encountered with the other clay-based particulates (Table 13). Both the humic acid- and the fulvic acid-containing particulates show erratic increases in CEC with increasing organic carbon content (Figure 14). CEC could not be correlated with functional groups analysis (Table 2), and did not vary significantly over time.

**Summary**

In conclusion, model particulates appear to be useful in delineating variations in CEC as a function of particulate composition and aging. All of the pure metal hydrous oxides show significant decreases in CEC on aging.
Figure 14. "Measured" CEC as a function of the percentage of carbon in organic matter-containing particulates.
Iron hydrous oxide shows an apparent increase in CEC after about 5 days. However, this increase may be due to systematic variations between sets of CEC measurements and not due to aging effects. Metal hydrous oxide-clay particulates show a variety of trends. The CEC's of manganese hydrous oxide-clay mixtures were not significantly different from that of clay. This was expected since only small quantities of manganese were coated onto the clay particles. CEC of iron hydrous oxide-clay mixtures increased systematically with the percentage of iron up to approximately 3% iron. Thereafter, the CEC is relatively constant. Aluminum hydrous oxide-clay particulates did not exhibit variations in CEC as a function of the quantity of aluminum on clay. These particles showed similar aging effects, the CEC increasing over time. The results imply that the clay particles are coated entirely with aluminum hydrous oxides. The organic matter-containing particles have higher CEC's than other clay-based particulates. In general, CEC increased with percentage of carbon, but could not be correlated with functional groups. Tests of the methodology indicated that the sodium acetate method worked well for these materials. Analysis of the saturating solutions showed that a significant amount of the manganese in the manganese hydrous oxide-clay particulates was bound to cation exchange sites and was probably present as Mn(II) and not manganese dioxide.
CHAPTER V

SURFACE AREA MEASUREMENTS

Introduction

Surface area is an important parameter of particulates (105, 106, 107). It controls the exposure of reactive adsorption sites and, hence, is related to CEC and the kinetics of adsorption (47, 108). Many physical and chemical properties of soils and sediments have been correlated with surface area (106).

The purpose of this chapter is to review the methods used to measure surface area and their applicability to the measurement of the surface area of aquatic particulates. In addition, an improvement in the determination of the solution concentration of an adsorbate will be presented.

Review of Surface Area Methodology

Many methods have been used to measure specific surface area, i.e., the area per unit mass of a sample (106). Some of these include:

1. Adsorption of a gas.

This is commonly referred to as the BET method after Brunauer, Emmett, and Teller. It is the most commonly used method for determining surface area (90, 107, 109). The method depends on physical adsorption of an
inert gas, such as nitrogen, argon, krypton, ethane, ammonia, or water, and detection of the monolayer capacity (90, 105, 106, 110). From this and the area per adsorbed atom or molecule, the area of the sample can be calculated.

2. Retention of polar molecules.
This method is similar to the BET method except that the sample is contacted with a polar liquid, e.g., ethylene glycol or glycerol. Excess liquid is evaporated (90, 106, 107, 110). Evaporation either ceases or becomes much more difficult when the liquid forms a monolayer on the surface (110).

3. Heat of immersion.
This method depends on measuring the heat released when a dry particle is immersed in water (105, 106, 110). The amount of heat released is proportional to surface area.

This method is derived from electric double layer theory. When an ion is preferentially adsorbed onto a surface, its counterion concentration in solution increases relative to the adsorbed ion. This increase can be related to surface area using electric double layer theory.

5. X-ray crystallographic methods (105).


The above methods are generally unsuitable to measure
the surface area of aquatic particulates for various reasons including:

1. Almost all of the methods listed above require that the particle whose surface area is being measured be dry (106, 107). In the BET method, for example, drying of particles under high vacuum and at temperatures up to 160°C is not uncommon (90, 93). This drying, usually at elevated temperatures, irreversibly dehydrates the metal hydrous oxides on the particulates and undoubtedly causes partial decomposition of the organic matter. In addition, particulates are known to be fragile and drying may result in disaggregation of the particulates. As a consequence, the measured surface area is generally significantly different from the surface area of the particle as it exists in suspension (17, 32, 47, 67, 96, 107, 111).

2. Heats of immersion are known to vary widely and to depend on the charge density, exchangeable ions, and conditions of measurement (110). Kaolinite and bentonite, for example, had heats of immersion which varied from 320 to 500 and 50 to 140 ergs/cm\(^2\), respectively (110).

3. Adsorption of polar molecules, such as water, is dependent on the exchangeable cations and charge density (110).

4. The surface area of the adsorbate need not
necessarily be constant nor is it necessarily independent of the adsorbent (105). For example, ethylene glycol and glycerol cross-sectional areas can vary by as much as 10% (110).

5. Monolayer coverage for many adsorbates is often difficult to establish unequivocally (90).

6. Negative adsorption applies to only smooth, non-porous surfaces and is probably dependent on the model of the electric double layer adopted (111). In addition, adsorption is dependent on the ion. For example, sodium and magnesium gave surface areas of approximately 300 and 700 m$^2$/g., respectively (111), for the same material.

7. BET nitrogen adsorption cannot measure the internal surface area of swelling clays such as montmorillonite (106, 110).

8. The BET method often involves removal of organic matter by hydrogen peroxide prior to the measurement of surface area (106). Extrapolation of these measurements to particles as they exist in suspension is questionable.

If the methods listed above are excluded from consideration due to the many associated problems when they are applied to aquatic particulates, then the only methods which are left are those which depend on the adsorption of an adsorbate from solution. These "wet" techniques offer several significant advantages, including (107):
1. A dry particle is not required.
2. Equipment is generally inexpensive and widely available.
3. The methods are generally rapid.
4. Vacuums and high temperatures are not required.
5. Measurement of both internal and external surface area is possible.

Two types of methods have been proposed or used (110). They include the adsorption of polar molecules from a solution containing a non-polar solvent, and the adsorption of organic cations from a solution containing a polar solvent. In addition, the adsorption of polar organic molecules by contacting the particulate with the polar liquid may be considered a "wet" method (110), although this method usually requires a dry particle.

Counterbalancing the advantages are several problems which may occur with wet methods (107). For example, the solvent may compete effectively with the solute for adsorption sites. For this reason, no satisfactory method has been developed which involves the adsorption of a polar molecule from a non-polar solvent (110). In addition, large molecules can adopt a number of different orientations on the surface. Depending on the orientation, the surface area covered by an adsorbate can vary widely. Finally, adsorption of cations is complicated by cation exchange mechanisms.

These problems should be overcome if an accurate
determination of surface area is to be made. Competition for adsorption sites by the solvent is usually minimized by using large molecules and/or ions. The binding energy of these molecules has an energetically large component of van der Waals and/or electrostatic interactions. Complications from cation exchange processes could possibly be circumvented by choosing an appropriate adsorbate, such as an anionic or non-ionic molecule. Unfortunately, adsorption of non-ionic molecules is complicated by competition with water, and anionic molecules generally do not adsorb onto natural particulates due to electrostatic repulsion from the negatively charged surface. Therefore, adsorption of organic cations is used to measure surface area in spite of potential complications from ion exchange processes.

Two methods based on the adsorption of organic cations have been used. The adsorption of cationic surfactants, such as cetyl pyridinium bromide and dodecylamine hydrochloride (107), takes place by a combination of cation exchange processes and physical adsorption, the latter being due to van der Waals interactions and entropy effects (107). Presumably, adsorption takes place up to the point at which a monolayer of adsorbate has been formed on the adsorbent. Beyond this point, any additional surfactant will remain in solution. Detection of the amount of surfactant adsorbed can be done by using isotopes, titrating excess soap, tensiometric measurements, or conductivity detection of the critical micelle
concentration (107). The latter is based on the fact that micelles have a lower conductivity than dispersed surfactant molecules in solution (107). Given the amount of surfactant needed to form a monolayer on the particulates and the surface area per surfactant molecule, the surface area of the particulates can be calculated.

The other method of determining surface area via adsorption of an organic cation involves organic dyes. Cationic dyes are strongly adsorbed onto substances such as illite and are easily detected using absorbance measurements. Because particulates from this study are being used to study the adsorption of polynuclear aromatic hydrocarbons (PAH's) and because dyes are structurally similar to PAH's, the adsorption of dyes was used as a means of measuring surface area. Surface areas as measured by the adsorption of dyes should be approximately equal to the surface area available to PAH's for adsorption.

Surface Area Measurements based on the Adsorption of Cationic Dyes

Principles of Surface Area Measurements

The measurement of surface area via adsorption of a dye, or any other substance, has a number of requirements which must be met to achieve an accurate determination. These are:

1. The adsorbate, or dye in this case, must form a monolayer of adsorbed molecules on the particulate sample or adsorbent.
2. The point of monolayer coverage must be determined accurately.
3. The mass of the sample must be known.
4. The area per adsorbate molecule must be known.
5. The amount of adsorbate on the adsorbent at the point of monolayer of coverage must be determined.

Generally, this latter determination is made via a difference measurement in which the amount of dye which remains in solution after adsorption is subtracted from the total amount of dye which was added to the system. If all of the above requirements are met, then the surface area may be calculated as follows

\[
\text{Area (m.}^2/\text{g.}) = \frac{(A \times N \times C)}{(M \times 10^{20} \text{ A.}^2/\text{m.}^2)}
\]  

(5-1)

where \(A\) is the amount of adsorbed dye in moles, \(N\) is Avogadro's number, \(C\) is the cross-sectional area per dye molecule in square Angstroms, and \(M\) is the mass of the sample in grams.

**Method for Determining Surface Area using Dyes**

The method used to determine surface area with dyes consists of a batch method in which

1. Various amounts of a dye solution are added to samples of particulates.
2. The dye is allowed to adsorb onto the particulates until equilibrium is established.
3. The solid and solution phases are separated, usually via centrifugation or filtration.
4. The amount of dye in solution is determined, usually by an absorbance measurement.

This method imposes additional requirements on the determination (112). These are:

1. Thermodynamic equilibrium must be reached.
2. All of the sample's surface area must be available to the dye.
3. The concentration of the original dye solution must be known accurately.
4. The form of the dye which is adsorbed onto the surface must be known.
5. Separation of the solid and solution phases must be complete.
6. The concentration of dye remaining in solution after adsorption must be determined accurately.

If all of these requirements are met, then the amount of dye adsorbed per unit mass of adsorbent is plotted versus the equilibrium concentration of dye in solution. The "plateau region" of this isotherm corresponds to the point of monolayer coverage and the amount of dye adsorbed in this region is used to calculate the sample's surface area (112).

Potential Problems

There are numerous potential problems with the determination of surface area using the adsorption of cationic dyes. These include:

1. The dye or adsorbate may not form a monolayer of
coverage on the adsorbent. Adsorption of cationic dyes is generally thought to take place by an irreversible cation exchange mechanism up to the CEC and, thereafter, by simple physical adsorption. Van der Waals interactions, entropy effects, and possibly hydrogen bonding and dipole-type interactions contribute to the adsorptive force during physical adsorption (36, 48, 113). Adsorption beyond the CEC is counteracted by electrostatic repulsion between the positively charged particles and the cations. If these electrostatic forces equal the adsorptive forces before the monolayer on the adsorbent is complete, then the monolayer will not be formed.

2. Determination of the point of monolayer coverage may be difficult or impossible. This can occur if adsorption of the dye continues beyond the point of monolayer coverage, e.g., when the CEC is greater than the amount required to form the monolayer. For this reason, the point of monolayer coverage should lie in a region where physical adsorption is occurring, i.e., where the adsorptive forces are weak (81). Once the monolayer has been formed, additional adsorption will, hopefully, cease due to the much weaker contribution of entropy effects to the adsorptive energy. Alternatively, if the plateau region does not correspond to the point of monolayer coverage, then the determination of surface area will
be in error. There is some confusion in the literature over exactly what point on the adsorption isotherm corresponds to monolayer coverage. Some authors use the plateau region of the isotherm to calculate the surface area (e.g., 81) while others use the point at which optimum flocculation (coagulation) of the sample occurs (109).

3. The mass of aquatic particulates is difficult or impossible to determine accurately. Drying at 60 C. or 110 C., as is commonly done, dehydrates the sample such that its mass is less than the mass of the particle as it exists in suspension. The mass of the particulates can be expected to depend on the temperature of drying, the drying time, and on the mass of the sample. This latter factor determines the amount of water that will be trapped in the "cake" of particulates that forms as a result of drying.

4. Separation of the solid and solution phases is often incomplete. This can be particularly troublesome when colloidal particles are present. Colloids are known to remain in suspension even after prolonged centrifugation and can pass through the 0.40 or 0.45 μm. filters which are commonly used to separate solid and solution phases (24, 114, 115). These particles will scatter light (Tyndall effect) during absorbance measurements for determination of dye concentration in solution (114). In addition, dye adsorbed onto the
colloids will also absorb light. The result of these two processes will be an overestimation of the concentration of dye in solution with a attendant underestimation of the amount of dye bound to the particulates.

5. Adsorption equilibrium may not be attainable or may be approached at a prohibitively slow rate.

6. The area of a particulate suspension may be dependent on solution conditions. For example, coagulation due to high salt concentrations or the adsorption of dye (charge neutralization) may reduce the apparent surface area by making parts of the sample inaccessible. Attempts to make all of the particulate surface area available to the dye through stirring or agitation can result in an overestimation of the surface area since particulates are fragile and are likely to disaggregate under the conditions of the measurement.

7. Dyes may adsorb onto particulates in more than one form. Dyes are known to form dimers and multimers in solution (109, 116, 117, 118) and there is some indication that these aggregates compete with monomers for adsorption sites. This latter possibility is a source of controversy in the literature. Dyes, such as methylene blue and pyronin Y, dimerize in solution at relatively high concentrations. The spectrum of the monomer consists
of an alpha band due to a \( \pi \) to \( \pi^* \) transition and a shoulder or beta band at shorter wavelengths due to a vibrational component on a single electronic band (113, 119, 120). For methylene blue, these bands occur at approximately 664 and 610 nm. (10, 113, 120). When dimerization occurs, the intensity and sometimes the position of these bands is shifted (113, 120). The effect is known as metachromasy. For monomers, the alpha band is the most intense; for dimers, the beta band is. When dye is adsorbed onto clay, for example, the same sort of shifts in the spectrum are observed (109, 112, 113, 120). Some authors have attributed these shifts to the adsorption of dimers or multimers (112, 113). Other authors attribute the shifts to interactions between the benzene rings of a dye monomer and the sheet oxygens of the clay (117, 120). X-ray evidence supports the view of the latter group. Adsorption of methylene blue onto montmorillonite increased the basal \( d \) spacing from 13.0 to 14.3 Å. (48, 120). This increase of 1.3 Å. is less than the 3.25 Å. thickness of the methylene blue molecule (109) and suggests that only one layer of methylene blue molecules is being inserted in the interlayer space. Regardless of whether or not dimers adsorb onto particulates, the form of the adsorbate must be known if accurate surface area measurements are to be obtained.
8. Dimerization also affects determination of dye concentration in solution since calibration curves will be curvilinear. The extent of dimerization has been shown to be affected by the solvent \((10, 118)\) and by the counterions of the dye \((121)\). Chloride and sulfate, for example, result in the formation of dimers while iodide and perchlorate ions produce polymer formation in solution. The effect is probably related to anion size and the anion's ability to form ion pairs \((121)\). If calibration curves are constructed using dye salts of one counterion, but measurements are made in a different ionic medium in which the proportion of dimers is different, then substantial errors can occur.

9. Many dyes are notoriously impure \((122, 123, 124, 125, 126)\). Impurities arise as a result of manufacture, improper control of reaction conditions, or degradation. For example, both methylene blue and pyronin Y are marketed as the zinc chloride double salts and often contain up to 87 % dextrin, sucrose, starting material(s), and salts such as sodium chloride, sodium sulfate, and ferric chloride \((123, 124, 125, 126, 127)\). In addition, many dye impurities are formed either as the result of improper control of reaction conditions or as a result of subsequent degradation \((124)\). Methylene blue, for example, oxidizes to less methylated thionines \((116, 118, 126,\)
The reaction is possibly photo-induced (36, 113) and is catalyzed in the presence of alkali (129, 131). Pyronin Y is oxidized to acridine red and other less methylated forms (124). When these dyes are used in surface area measurements, uncertainty as to which forms adsorb onto the surface and their relative areas per molecule make accurate measurements difficult.

Orientation of dye molecules on the surface may not be known. For example, methylene blue may adsorb on its end, along its edge, or flat on a surface. These orientations have surface areas per molecule of 39.5, 75, and 115 Å², respectively (117). There is also some indication that methylene blue adsorbs flat onto glass, as micelles onto silica gel, and edgewise on silver halides (117) and can change orientation during the course of adsorption (113). This variety of possible orientations makes it difficult to assign a value for the surface area per molecule.

The surface area of the adsorbate may not be known accurately even if the orientation of the molecule on the surface is known. Obviously, the surface area per molecule is affected by the orientation of the molecule on the surface and by the form which is adsorbed (i.e., monomer versus multimer). For methylene blue, estimates of the area per molecule range from 120 to 139 Å² (103, 109, 116, 117).
12. Dye molecules can be excluded from the pores of porous solids, such as charcoal and silicas, and, therefore, give erroneously low results (116). These materials act as molecular sieves and the surface area measured will depend on the size of the adsorbate, i.e., on its ability to penetrate the pores of the solid.

13. Some dyes are precipitated under the conditions of the surface area measurement (116). This would result in an overestimation of the amount of dye adsorbed.

14. Dyes are known to adsorb strongly onto glass and other containers (105, 109). This adsorption results in "permanent" removal of the dye and can cause errors in the spectrophotometric determination of the dye concentration in solution.

These potential problems must either be minimized or eliminated if accurate determinations of surface area are to be made.

Debate over What Dye Adsorption Measures

Since the original paper by Paneth and Radu in 1924 (132) proposing the adsorption of methylene blue as a surface area technique, a controversy over exactly what the method measures has kept the literature filled with papers through at least 1980. One side contends that the method measures surface area, at least in some cases, while the other side contends that adsorption of the dye is controlled by charge properties.
Adsorption of cationic dyes, such as methylene blue and pyronin Y, is commonly thought to occur by two different mechanisms. Initially, the dye is adsorbed via a cation exchange process. This adsorption is essentially complete and irreversible due to the large electrostatic forces and usually large van der Waals interactions and entropy effects. The exchange continues up to the CEC unless some of the cation exchange sites are covered by the adsorbed dye molecules. In this latter case, ion exchange ceases at some point below the CEC.

Following ion exchange, physical adsorption occurs if the area per exchange site is greater than the area per dye molecule. This adsorption is attributed mainly to van der Waals interactions and entropy effects. Since these forces are much weaker than electrostatic interactions, this adsorption is reversible and is not as complete as during the ion exchange process. Free dye begins to appear in solution. This is the basis for measuring CEC using cationic dyes (108, 133). Generally, a sample is titrated with dye and a spot test is used to detect the first appearance of free dye in solution.

The adsorption due to ion exchange results in increasing neutralization of the charge on the particulates since most particulates are negatively charged initially. In addition, the particles become increasingly hydrophobic. At some point near the CEC, coagulation of the particulates begins to occur and is at a maximum when the amount of dye
adsorbed equals the CEC, i.e., when the charge on the surface is completely neutralized. This point is known as the "point of optimum flocculation" (109). Beyond the CEC, adsorption results in an increasing amount of positive charge on the particles. This charge development usually causes restabilization of the colloid suspension, i.e., the particulates are redispersed. The positive charge also counteracts adsorptive forces. At some point, the repulsive forces equal the adsorptive forces and adsorption ceases. This corresponds to the plateau region on many isotherms.

Support for this view of dye adsorption is extensive. For example, the idea that dye adsorption onto negatively charged surfaces occurs by two mechanisms was originally proposed by Michaelis and Ehrenreich and later elaborated by Freundlich and Poser, and Michaelis and Rona (134). The cation exchange mechanism was confirmed using Na-22 (133) and numerous authors have confirmed that an essentially irreversible adsorption occurs up to the CEC unless some special effect, such as incomplete exchange with cations in the interlayer space of montmorillonite, prevents full exchange with dye molecules (36, 107, 108, 110, 120, 133, 135). This ion exchange process has been found to be kinetically fast (133, 136), and applies to other organic cations as well, such as the pesticides paraquat and diquat, and surfactants such as long chain quaternary amines and pyridinium compounds (51, 110). Physical adsorption beyond the CEC has been shown to occur more
slowly than ion exchange (133, 136) and the reversal of charge has been demonstrated using electrophoresis (48). Undersaturation of the surface, i.e., incomplete formation of the monolayer, has been shown to occur for the adsorption of surfactants onto polystyrene lattices (110). Finally, the point of optimum flocculation has been demonstrated clearly by Yariv and Lurie (120) using percent transmittance measurements during a titration of a montmorillonite suspension with methylene blue.

Because adsorption of the dye beyond the CEC is a consequence of the balance between electrostatic repulsion and physical adsorption, and because these interactions are dependent on a large number of factors other than surface area, many of the above authors contend that the adsorption of dye either does not measure surface area or does not measure it reliably (117). These authors argue that charge interactions between the surface and the adsorbed molecules are the real factors controlling adsorption and not surface area.

An alternative view of dye adsorption is that adsorption ceases, once physical adsorption of the dye has begun, when the monolayer has been completed rather than when repulsive forces due to electrostatic interactions equal the adsorptive forces (81, 110, 116, 137). One can rationalize this view based on the contribution of entropy effects to the adsorptive forces. Prior to completion of the monolayer, the adsorption of dye molecules results in
release of water molecules from the primary hydration layer of the surface. These water molecules possess the least mobility of any water adsorbed to the surface and, therefore, the contribution to the adsorptive force from entropy effects is large. Once the monolayer has been completed, the contribution from entropy effects is much less since water in secondary and higher hydration spheres already possesses a significant amount of mobility. Therefore, once the monolayer has been completed, the adsorptive forces decrease significantly and, if the electrostatic repulsion is sufficiently large at this point, adsorption of dye molecules beyond the point of monolayer coverage is prevented.

Obviously, for such a mechanism to work, the electrostatic repulsive forces need to be strong enough to prevent adsorption beyond the amount required for monolayer coverage and yet not so strong as to prevent its completion. Likewise, the physical adsorption forces need to be strong enough to be able to complete the monolayer and not too strong to cause adsorption beyond the amount required to form the monolayer. In other words, the mechanism is likely to work only in a narrow range of charge densities (110).

Finally, Hang and Brindley (109) contend that both CEC and surface area can be measured simultaneously using methylene blue. They attribute the point of optimum flocculation to completion of the monolayer. Optimum
flocculation, in their view, is caused by a maximum in terms of the hydrophobic properties of the particulates rather than charge neutralization. The plateau region of the isotherms corresponds to the particle's CEC. Adsorption beyond the CEC is prevented due to electrostatic repulsion.

This view of dye adsorption is obviously contradictory to many of the findings by other authors. In addition, the redispersion of particles beyond the point of optimum flocculation is difficult to explain using this view of adsorption. Finally, the authors noted that the point of optimum flocculation does not change as a function of the concentration of the equilibrating methylene blue solution but that the plateau region does. It is hard to explain these experimental observations and still equate the plateau region with CEC.

**General Overview**

Despite the numerous potential experimental problems and the strong possibility that dye adsorption does not measure surface area, the method was used to measure the surface area of synthetic particulates. Surface area is a sufficiently important parameter in relation to adsorption that at least some attempt to measure it needed to be made. BET and other methods which require dry particles have significant drawbacks such that their results would be relatively meaningless.

The adsorption of dyes to measure surface area was chosen instead of the use of surfactants primarily because
dyes are structurally similar to PAH's. This investigation is connected to a project studying the adsorption of PAH's onto particulates and it was felt that the surface area measured by dye adsorption would be approximately the same surface area available to PAH's for adsorption. There is no reason to suspect that the adsorption of surfactants, especially cationic surfactants, offers any significant advantage over the use of cationic dyes.

The choice of which dye to use was based on the recommendations of Giles et al. (116). These authors recommended methylene blue, crystal violet, and victoria pure lake blue BO for use in connection with surface area measurements. All of these cationic dyes can be obtained in reasonably pure form, are adsorbed in known orientations (generally flat), and are not affected chemically by most solids (116). We chose methylene blue primarily because it has been studied more extensively than the other two dyes.

**Fluorescence Measurements**

As will be shown later, scattering from colloidal particles and absorption from dye bound to these particles resulted in significant errors in the measurement of the free concentration of dye in solution. An improvement in the measurement of the concentration of dye in solution was made using fluorescence measurements and a cationic, fluorescent dye called pyronin Y or G (97, 122). Methylene blue fluoresces, but only weakly (36). Pyronin Y, on the other hand, is a very efficient fluorophor. The structure
of pyronin Y is analogous to methylene blue.

Fluorescence measurements offer a number of distinct advantages over the use of absorbance measurements to determine the concentration of dye in solution. First, because the fluorophor is excited with light of one wavelength and the fluorescence is detected at another, usually longer, wavelength, scattering is much less of a problem in fluorescence than in absorbance measurements. Scattered radiation has the same wavelength as the incident light and most fluorescence instruments are equipped with a monochromator or filter arrangement to exclude light at the excitation wavelength from reaching the detector.

Secondly, absorption of light by dye molecules bound to the colloidal particles is not a problem. If the fluorescence of the bound dye molecules is quenched, then the fluorescence measurement will reflect only the concentration of dye in solution. If fluorescence is not quenched, then fluorescence polarization can be used to determine the concentration of dye in solution.

Finally, fluorescence measurements are much more sensitive than absorbance measurements. Therefore, measurement of much smaller concentrations of dye is possible and dimerization is much less of a problem. Additionally, it may be possible to measure the surface area of natural particulates at their in situ concentrations.
Methodology

Purification of Dye

Methylene blue was purified following the method of Hall and Marple (126). Alternative methods of purification may be found in Spencer and Sutter (10), Venkataraman (127), Marshall and Lewis (131), Tzung (138), and Russo et al. (139). Purity of the methylene blue crystals was checked by elemental analysis using a Model 240B Perkin-Elmer Elemental Analyzer and by thin layer chromatography (TLC).

Contamination of pyronin Y was indicated by emission spectroscopy, measurement of the molar absorptivity, and flame atomic absorption analysis for zinc. Emission spectroscopic analysis was done on a Baird 3-meter instrument using samples of the "raw" pyronin Y. Molar absorptivity was measured on a Model UV-200S Shimadzu Double Beam Spectrophotometer, and zinc analyses were done on a Model 951 Instrumentation Laboratory spectrophotometer.

Pyronin Y was purified by dissolving 1 g. of raw pyronin Y in 1 M sodium chloride. The solution was filtered through a 0.4 μm. filter to remove undissolved dye and placed in a continuous liquid-liquid extractor. Extraction with distilled methylene chloride removes the pyronin Y from the aqueous solution while leaving salts such as zinc chloride and sodium chloride in the aqueous layer. Sodium chloride was added to the aqueous phase to speed the
extraction of the chloride form of pyronin Y. After extraction, the methylene chloride was evaporated and the precipitate was dried in a vacuum oven at 50 C. Purified samples were stored in a dessicator. Purity of the pyronin Y was checked by measuring the carbon, nitrogen, and hydrogen content and by TLC. Samples of the pyronin Y were also digested in platinum crucibles with concentrated nitric acid and analyzed for zinc using flame atomic absorption spectrophotometry.

Thin Layer Chromatography

Analysis of the dye samples, particularly pyronin Y, for dye impurities was done using TLC after the method of Marshall and Lewis (140). Either commercially available aluminum-backed silica plates or glass plates were used. The glass plates were prepared using "Merck Silica Gel 60 PF-254-for prep LC." A slurry of the silica was spread onto the glass plates and allowed to air dry. The plates were then dried for 2 hr. in an oven at 110 C. and, finally, were allowed to equilibrate with the atmosphere overnight. Methanol or methylene chloride solutions of the dye were loaded onto the plates using capillary tubes and the plates developed for approximately 2 hr. The developing solution consisted of the butanol layer from a mixture of 12 volumes 1-butanol, 5 volumes of 1 % w/w aqueous ammonium chloride, and 2 volumes of 2 % v/v aqueous formic acid. Alternatively, a 8:2 mixture of chloroform and methanol may be used (123), although it is less effective at separating
the various components. The Rf values were calculated and fluorescent bands were observed using an ultraviolet lamp.

Because of the many components observed with pyronin Y, the methylene chloride, Nucleopore filters, sodium chloride, and water used in the purification of pyronin Y were checked for contamination using TLC. In addition, a methylene chloride solution of pyronin Y was refluxed for 6 days in the extraction apparatus and then concentrated by evaporation. Analysis of this refluxed sample and the raw pyronin Y was done by TLC to check for any possible degradation of the pyronin Y under the conditions of the extraction.

**Measurement and Calculation of Adsorption Isotherms**

Adsorption isotherms were constructed after the method of Hang and Brindley (109). Samples of the particulate suspensions, equivalent to 10 mg. of dried particulates, were placed in 50-ml. polycarbonate centrifuge tubes, followed by 1 to 20 ml. of a $3 \times 10^{-4}$ M solution of either methylene blue thiocyanate or pyronin Y chloride. The centrifuge tubes were capped and shaken on a reciprocating shaker overnight. Previous studies have indicated that equilibrium is reached in 5 minutes to 10 hours (36, 93, 109, 113, 116, 136). Following shaking, the samples were centrifuged for 5 min. and decanted into preweighed linear polyethylene (LPE) bottles. The samples were diluted as necessary and their absorbance was measured at either 665 (methylene blue) or 546 nm. (pyronin Y) using 1 cm. quartz
cuvettes in a Model UV-200S Shimadzu Double Beam Spectrophotometer. Prior to measurement, a dye solution was placed in the analytical cuvette and the dye was allowed to adsorb onto the surface (109, 118, 121, 125). The cuvette was then rinsed with deionized water and absorbance measurements made. Checks of the constancy of the baseline showed no appreciable drift due to additional adsorption of the dye onto the cuvette surface, nor was desorption of the dye into analytical blanks detected. Alternatively, dye adsorption on the cuvette could be minimized by treatment of the cuvette with dimethyldichlorosilane (116). Standards of the dye solution in the concentration range 0 to $10 \times 10^{-6}$ M were prepared from the stock dye solution and stored in the dark in polypropylene (PP) or LPE containers as suggested by Bergmann and O'Konski (113). Following the absorbance measurements, the amount of dye in solution and the amount of dye adsorbed per unit mass of adsorbent were calculated and plotted.

Adsorption isotherms were calculated using the following formula

$$\frac{x}{m} = k_1 + k_2 C^{1/n}$$  \hspace{1cm} (5-2)

where $x$, $m$, and $C$ have their usual meanings (Chapter I), and $k_1$, $k_2$, and $n$ are constants (113, 134). $k_1$ refers to the irreversible ion exchange of the dye in moles/g. and is related to the CEC as follows
CEC = k_1 \times 10^5 \quad (5-3)

where CEC is in meq./100g. The second term of the equation is simply the Freundlich isotherm equation used to describe physical adsorption of the dye. Based on the discussion from Chapter II, it should be realized that the Freundlich equation does not strictly apply to the adsorption of a cationic dye onto a charged surface. However, the equation has been used frequently to describe the adsorption of dyes and seems to fit the data reasonably well.

The constants $k_1$, $k_2$, and $n$ were calculated by first estimating a value for $k_1$ and then calculating values for $k_2$ and $n$ using statistical regression techniques and the logarithmic form of the Freundlich equation (Equation 2-16). The variance was calculated by summing the squares of the differences between predicted points and experimental data, i.e., the residuals. For data points below the CEC ($k_1$), the predicted value was taken to be the total amount of dye added to the sample. For points above the CEC, the equation as written above was used. The CEC ($k_1$) was varied iteratively until a minimum in the variance was obtained.

Calculated values for area were obtained using Equation 5-1 and experimental data points from the plateau region of the isotherm. An area of 130 Å²/molecule was assumed for both methylene blue and pyronin Y (109, 117).
Fluorescence Measurements

Fluorescence measurements were made on the same pyronin Y samples used to determine adsorption isotherms. Sample solutions were diluted until the total absorbance was less than 0.05 in order to obtain a linear response of fluorescence intensity versus concentration. Standards were prepared daily by appropriate dilution of the pyronin Y stock solution. Concentrations of the standards ranged from 0 to 6 x 10^{-7} M. Triplicate measurements of the fluorescence intensity were made for both samples and standards on a SLM 8000 fluorescence polarization instrument. Instrumental parameters were as follows:

- Sensitivity Current = 10 mA.
- Voltage = 725 to 800 V.
- Acquisition Time = 1 s.
- Excitation Polarizer = Horizontal or "9"
- Emission Polarizer = Vertical or "0"
- Excitation Wavelength = 486 nm.
- Filter = 518nm. Long Pass Filter
- Slit Opening = 1 nm.

The fluorescence measurements were made using only one of the channels on the fluorescence polarization instrument.

A variety of studies were done to determine what the instrumental parameters should be. These included:

1. Because standards and samples contained very low concentrations of pyronin Y, experiments were done to determine whether adsorption onto container walls
produced significant errors. Samples of the same pyronin Y standard were added to nitric-acid-washed PP bottles, nitric-acid-washed LPE bottles, and new LPE bottles which were never acid washed. The fluorescence of each of these samples was monitored over time.

2. Excitation and emission wavelengths of pyronin Y were determined using a Perkin-Elmer Model 204 Fluorometer. In addition, fluorescence from clay suspensions containing adsorbed pyronin Y was measured, both to check for possible degradation of the pyronin Y to other fluorescent compounds and to determine whether adsorbed pyronin Y fluoresces. These clay suspensions were compared to clay suspensions which contained no pyronin Y. The excitation and emission wavelengths for the pure hydrous oxides, both with and without pyronin Y, were also checked.

3. Since scattered radiation is polarized and the fluorescence instrument was equipped with two polarizers, each of which may polarize light either horizontally or vertically, a study was undertaken to determine the best orientation of the excitation and emission polarizers for use in fluorescence measurements. Triplicate intensity readings of a pyronin Y standard and a clay suspension were made at all four different combinations of the polarizers.
The pyronin Y standard was used to evaluate the relative sensitivity of each combination of the polarizers while the clay suspension was used to give an indication of the severity of interference from scattering. In this study, an excitation wavelength of 490 nm. was used.

4. Because the only available filter which was suitable for use in measuring pyronin Y fluorescence was a 518 nm. long pass filter, a study was undertaken to determine the excitation wavelength which would give a maximum in sensitivity yet minimize interferences from scattering. A pyronin Y standard and a clay suspension were used. The intensities from these samples were measured as a function of the excitation wavelength using the standard configuration of instrumental parameters given previously.

5. The fluorescence of pyronin Y versus pH was checked by adding acetate buffers of varying pH to pyronin Y standards and measuring the fluorescence intensity, corrected for dilution. The slope of the calibration lines is proportional to the fluorescence efficiency at a given pH.

**pH and Ionic Strength Dependence of Dye Adsorption**

If dye adsorption is dependent on charge interactions, it might be expected that adsorption would depend on the pH and ionic strength of the saturating dye solution. To check this, samples of illite and other particulates were
equilibrated with dye solutions to which various amounts of acetate buffers and/or sodium nitrate were added to vary the pH and ionic strength of the solutions. The ionic strength of the solutions was calculated taking into account the concentrations of pyronin Y and sodium nitrate, and the dissociation of the acetate buffer. Acetic acid was assumed to have a pKa of 4.75. The amount of dye added to the suspensions was such that all of the clay would be saturated with the dye and excess dye would be present in solution, i.e., all of the points corresponded to the plateau region of the isotherm.

Results

Purification of Methylene Blue

Table 15 presents the carbon, nitrogen, and hydrogen analyses for purified methylene blue thiocyanate, "raw" pyronin Y, and purified pyronin Y. For methylene blue, the percentages are very close to the predicted percentages leading to the conclusion that approximately 99% of the sample was dye. Large amounts of dye impurities were extracted from the sample as indicated by the deep red color in the chloroform extractant. These impurities are most likely trimethylthionine, also known as Azur B, which is an oxidation product of methylene blue (113, 126, 128). Trimethylthionine is probably formed as a result of excessive oxidation during the last step in the synthesis of methylene blue (141). This impurity is pink when the secondary amine is deprotonated.
Table 15. Carbon, nitrogen, and hydrogen analyses for purified methylene blue thiocyanate, "raw" pyronin Y, and purified pyronin Y.

<table>
<thead>
<tr>
<th>Dye</th>
<th>Element</th>
<th>Theoretical Percentage</th>
<th>Measured(^1) Percentage</th>
<th>Percent Dye</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methylene Blue (Purified)</td>
<td>C</td>
<td>59.62 %</td>
<td>59.0 ± 0.7</td>
<td>99.0 ± 1.2</td>
</tr>
<tr>
<td></td>
<td>N</td>
<td>16.36</td>
<td>16.2</td>
<td>99.1 ± 0.9</td>
</tr>
<tr>
<td></td>
<td>H</td>
<td>5.30</td>
<td>5.24</td>
<td>98.9 ± 2.8</td>
</tr>
<tr>
<td>Pyronin Y (&quot;raw&quot;)</td>
<td>C</td>
<td>67.43</td>
<td>49.6 ± 0.5</td>
<td>73.6 ± 0.7</td>
</tr>
<tr>
<td></td>
<td>N</td>
<td>9.25</td>
<td>6.77</td>
<td>73.2 ± 1.6</td>
</tr>
<tr>
<td></td>
<td>H</td>
<td>6.32</td>
<td>4.77</td>
<td>75.5 ± 2.4</td>
</tr>
<tr>
<td></td>
<td>Zn</td>
<td>0.00</td>
<td>11.0 ± 0.2</td>
<td>-</td>
</tr>
<tr>
<td>Pyronin Y (Purified)</td>
<td>C</td>
<td>67.43</td>
<td>67.1 ± 0.4</td>
<td>99.5 ± 0.6</td>
</tr>
<tr>
<td></td>
<td>N</td>
<td>9.25</td>
<td>9.10</td>
<td>98.4 ± 1.6</td>
</tr>
<tr>
<td></td>
<td>H</td>
<td>6.32</td>
<td>6.23</td>
<td>98.5 ± 2.4</td>
</tr>
<tr>
<td></td>
<td>Zn</td>
<td>0.00</td>
<td>0.05</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>Na</td>
<td>0.00</td>
<td>0.04</td>
<td>-</td>
</tr>
</tbody>
</table>

\(^1\) Standard deviations for carbon, nitrogen, and hydrogen analyses are ± 0.15 % except where noted.
Attempts to measure the melting point of the purified material failed because the sample decomposed at around 210 °C. This agrees with the findings of Hall and Marple (126). TLC indicated that a minor impurity remained in the purified material. The Rf value for this impurity was approximately 0.15, compared to 0.05 for the major component. These values are similar to those found for Azur B and methylene blue by Marshall and Lewis (131).

**Purification of Pyronin Y**

The carbon, nitrogen, and hydrogen data for the unpurified pyronin Y indicated that only about 73.5% of the sample was dye (Table 15). This was confirmed by molar absorptivity measurements. Using a standard calibration curve, the molar absorptivity was determined to be 58750 L/cm./mole at a concentration of approximately 5 x 10^{-6} M. This value is 72.7% of the value (80850 L/cm./mole) published in the literature (125). Emission spectroscopic analysis indicated that large quantities of zinc were present. Atomic absorption analysis confirmed that the sample contained approximately 11% zinc. Therefore, the pyronin Y sample was probably the zinc chloride double salt (122, 125).

Purification of the dye using methylene chloride resulted in a dye sample which contained approximately 99% dye (Table 15). Zinc and sodium analyses indicated that negligible quantities of these metals remained.

Results of the TLC analysis of purified pyronin Y are
given in Table 16. At least eleven different bands or components could be differentiated. Most of these bands were minor and some, e.g., components 9 and 10, could only be detected when the TLC plate was heavily loaded and with the aid of an ultraviolet lamp. Components 2 and 3 were the major components of the sample and are believed to be pyronin Y. No explanation is given for why two bands of pyronin Y were formed. The UV-visible spectra for these two components were identical and the wavelength of maximum absorbance is similar to those found by other authors (122, 123, 128). The only other components which were present in significant amounts were components 4 and 7.

These results are similar to those found by other authors. Marshall (148), using the same method, found that various commercially available pyronin Y samples contained from 4 to 14 components. Of the samples which he tested, only two had the same major component. Several other authors have reported the presence of both an orange and a violet contaminant in pyronin Y (122, 123, 124). These are suspected to be oxidation products of pyronin Y, such as acridine red, resulting from the excessive oxidation of pyronin Y during the last step in its synthesis (124, 127, 142).

Because of the large number of components in the pyronin Y sample, experiments were run to check for possible contamination from the equipment and reagents used in the purification. None were found. In addition,
Table 16. TLC analysis of pyronin Y.

<table>
<thead>
<tr>
<th>Component</th>
<th>Color</th>
<th>Fluorescence</th>
<th>Rf (^1)</th>
<th>Wavelength of Maximum Absorption</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>violet</td>
<td>--</td>
<td>0.00</td>
<td>--</td>
</tr>
<tr>
<td>1</td>
<td>violet-red</td>
<td>--</td>
<td>0.04</td>
<td>--</td>
</tr>
<tr>
<td>2</td>
<td>red</td>
<td>yellow</td>
<td>0.07</td>
<td>547 nm.</td>
</tr>
<tr>
<td>3</td>
<td>red</td>
<td>yellow</td>
<td>0.16</td>
<td>547 nm.</td>
</tr>
<tr>
<td>4</td>
<td>orange</td>
<td>yellow-green</td>
<td>0.24</td>
<td>534 nm.</td>
</tr>
<tr>
<td>5</td>
<td>red</td>
<td>--</td>
<td>0.28</td>
<td>--</td>
</tr>
<tr>
<td>6</td>
<td>red</td>
<td>--</td>
<td>0.33</td>
<td>--</td>
</tr>
<tr>
<td>7</td>
<td>violet</td>
<td>--</td>
<td>0.38</td>
<td>550 nm.</td>
</tr>
<tr>
<td>8</td>
<td>violet-red</td>
<td>--</td>
<td>0.46</td>
<td>--</td>
</tr>
<tr>
<td>9</td>
<td>yellow</td>
<td>blue</td>
<td>0.82</td>
<td>--</td>
</tr>
<tr>
<td>10</td>
<td>blue</td>
<td>yellow</td>
<td>0.91</td>
<td>--</td>
</tr>
</tbody>
</table>

\(^1\) Estimated standard deviation was ± 0.04.
degradation during the extraction procedure was checked by refluxing pyronin Y in the extraction apparatus for 6 days. No apparent shifts in the intensity of the components nor appearance of new components were observed. Heavy loading of the raw pyronin Y sample onto TLC plates indicated that all of the components listed in Table 16 were present in the original sample. Attempts to isolate only the pyronin Y components failed because the pyronin Y could not be separated from the developing solution, as indicated by excessively low nitrogen percentages in the extracted dye. Use of a 8:2 mixture of chloroform and methanol may prove successful in these attempts (123).

Because separation of dye impurities is very difficult (122), it was decided to use the purified pyronin Y dye as it was in all subsequent experiments. Even though there are many impurities in the sample, most of these were minor. In addition, those impurities which were present in significant amounts are likely to be the demethylated forms of pyronin Y. These should be cationic in the pH range used in the isotherm measurements and are also likely to have surface areas which are similar to that of pyronin Y. Finally, the spectra are similar to that of pyronin Y. Therefore, the amount of error introduced by using the pyronin Y sample after it has been purified to remove zinc salts should be small.

Fluorescence Measurements

Adsorption of pyronin Y on containers. Table 17
Table 17. Normalized intensity data for the adsorption of pyronin Y onto various plastic containers.

<table>
<thead>
<tr>
<th>Time (^1) (Minutes)</th>
<th>LPE (^2) (Saturated)</th>
<th>LPE (^2) (New)</th>
<th>LPE (^2) (Acid-washed)</th>
<th>PP (^2) (Acid-washed)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.00(^3)</td>
<td>1.00</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td></td>
<td></td>
<td>0.90</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td></td>
<td></td>
<td>0.82</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>0.98</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>0.98</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>1.00</td>
<td></td>
<td>0.75</td>
<td>0.76</td>
</tr>
<tr>
<td>54</td>
<td></td>
<td></td>
<td>0.97</td>
<td></td>
</tr>
<tr>
<td>60</td>
<td>1.01</td>
<td></td>
<td></td>
<td>0.53</td>
</tr>
<tr>
<td>222</td>
<td></td>
<td></td>
<td></td>
<td>0.98</td>
</tr>
</tbody>
</table>

\(^1\)Time after introduction of a 6 x 10^-7 M pyronin Y standard.
\(^2\)Bottles were previously saturated with pyronin Y.
\(^3\)The intensity reading for this sample was used to normalize the other intensity readings.
presents data on the adsorption of pyronin Y onto plastic containers. The results indicate a negligible amount of adsorption occurs when pyronin Y solutions are stored in LPE bottles which have been previously saturated with pyronin Y. However, significant amounts of dye were lost when the solutions were stored in nitric acid-washed containers. Because of these results, all pyronin Y fluorescence measurements were made in non-acid-washed containers. The containers were saturated with pyronin Y prior to use to ensure that no subsequent losses occurred. As indicated in Table 17, no more than 3% of a $6 \times 10^{-7}$ M pyronin Y standard was adsorbed during the saturation process, and adsorption was essentially complete within a few min. to 1 hr. Experiments to check for subsequent desorption of the adsorbed pyronin Y indicated that no significant desorption of the pyronin Y occurred.

**Excitation and emission spectra.** Figures 15, 16, and 17 present the excitation and emission spectra for a pyronin Y solution, a clay suspension to which a small amount of pyronin Y had been added, and a clay suspension blank. The spectra for the pyronin Y solution (Figure 15) show maxima at wavelengths of 540 and 560 nm. for the excitation and emission spectra, respectively. Consequently, all subsequent measurements were made at these wavelengths.

Figure 16 presents the excitation and emission spectra for pyronin Y adsorbed onto illite. The amount of pyronin Y
Figure 15. Excitation and emission spectra for pyronin Y.
Figure 16. Excitation and emission spectra for pyronin Y adsorbed on illite.
Figure 17. Excitation and emission spectra for illite.
added to the clay suspension was not sufficient to saturate the surface, i.e., free pyronin Y in solution was not present. Both the excitation and emission spectra are significantly different from the spectra for the pyronin Y solution. The peaks are symmetrical and are centered about the wavelength at which the emission or excitation monochromators were set. In other words, the peak in the excitation spectrum is centered about 560 nm., which is the wavelength to which the emission monochromator was set. Similarly, the peak in the emission spectrum is centered about 540 nm., the wavelength at which the excitation monochromator was set. In addition, the spectra are identical to those for the clay suspension blank (Figure 17). Therefore, the spectra are due to scattering by the clay. Fluorescence by pyronin Y adsorbed to the clay appears to be quenched. Because of this quenching effect, a simple fluorescence measurement will yield the concentration of pyronin Y in solution directly, eliminating the need for fluorescence polarization measurements.

Orientation of the polarizers. Table 18 presents the results of a study on the orientation of excitation and emission polarizers. Several trends are evident. First, the intensities of the pyronin Y standard when the excitation polarizer is in a horizontal position are greater than when the polarizer is vertically oriented. This greater sensitivity is probably due to polarization of the incident
Table 18. Intensity data as a function of the orientation of the emission and excitation polarizers for a pyronin Y standard and an illite suspension.

<table>
<thead>
<tr>
<th>Excitation Polarizer</th>
<th>Emission Polarizer</th>
<th>Intensity Data</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Pyronin Y Standard</td>
</tr>
<tr>
<td>Vertical</td>
<td>Vertical</td>
<td>47785</td>
</tr>
<tr>
<td>Vertical</td>
<td>Horizontal</td>
<td>45392</td>
</tr>
<tr>
<td>Horizontal</td>
<td>Vertical</td>
<td>84347</td>
</tr>
<tr>
<td>Horizontal</td>
<td>Horizontal</td>
<td>84393</td>
</tr>
</tbody>
</table>
light.

Secondly, the ability for scattered radiation to reach the detector as indicated by the intensity data for the clay suspension is much less if the polarizers are crossed, i.e., if one polarizer is in a vertical orientation while the other is oriented horizontally.

Finally, the intensity of the scattered radiation when both polarizers are in a vertical position is higher than any of the other orientations. Scattered radiation is polarized as was evident by looking down into the cell containing the clay suspension and varying the position of the excitation polarizer. When the polarizer was horizontal, a beam of light could be clearly seen in the suspension meaning that radiation was being scattered vertically or away from the detector. When the polarizer was vertical, the scattered radiation was no longer evident. In this case, the light was being scattered horizontally, i.e., towards the detector. The higher intensity observed when both polarizers were oriented vertically reflects the ability of the scattered radiation to reach the detector.

Because of the higher sensitivity when the excitation polarizer is vertical and the reduction in scattering when the polarizers are crossed, a configuration in which the excitation polarizer was vertical and the emission polarizer was horizontal was used in all of the fluorescence measurements.
**Excitation wavelength.** The only filter available for use in the fluorescence polarization instrument which had a reasonable transmissivity at the wavelength of maximum fluorescence intensity (560 nm.) was a 518 nm. long pass filter. Because of the spectral characteristics of this filter, the excitation wavelength could not be 540 nm., if interferences from scattering were to be reduced. Therefore, a study was undertaken to determine the wavelength which would give maximum sensitivity and still keep the intensity from scattering to a minimum.

The intensity data is presented as a percentage of either the scattering intensity or the intensity from a pyronin Y standard measured at 500 nm. (Figure 18). The "sensitivity factor", i.e., the ratio of the intensity measured for the pyronin Y standard and the scattered intensity from a clay suspension, is shown as a percentage of the maximum sensitivity factor measured. The results indicate that intensity from scattering is essentially constant and probably not significantly different from a water blank at wavelengths of less than 490 nm. The intensity data for the pyronin Y standard was nearly constant at wavelengths between 484 and 487 nm. Therefore, slight errors in the setting of the excitation wavelength would have less of an effect on the sensitivity of the fluorescence measurement in this region of the spectrum than at other wavelengths. Finally, the sensitivity factors were all above 94 % of the maximum between 484 and 491 nm.
Figure 18. Relative intensities of (a) a pyronin Y standard and (b) a clay suspension, and (c) the relative "sensitivity factor," as a function of the excitation wavelength.
Because of the near constancy of both the scattering and fluorescence intensities in the range of 484 to 487 nm., all measurements were made at a excitation wavelength of 486 nm.

**pH dependence of fluorescence.** Table 19 shows that the slopes of the calibration lines, and, hence, the fluorescence efficiency, decrease with increasing pH. No explanation for this is apparent. The data may indicate a sensitivity to pH or a sensitivity to ionic strength since the ionic strength increased systematically with pH for the acetate buffer system in the pH range tested. This sensitivity could possibly be due to dimerization. Narine (36) noted that dimerization increased as a function of ionic strength. Dimerization may also be facilitated by increasing the hydroxyl ion concentration. Dimers generally do not fluoresce due to internal conversion of electronic excitation energy into vibrational energy (118). However, estimates for the dimerization constant for pyronin Y indicate that no appreciable formation of dimers should occur in the concentration range tested.

Because of the sensitivity to pH, all test and standard solutions in the ionic strength experiment described below were buffered to the same pH and ionic strength. The adsorption isotherms were not, primarily because the dependence of fluorescence on pH was not discovered until after the isotherm work was completed. However, measurement of the pH of pyronin Y-clay
Table 19. Variation in the slopes of fluorescence calibration lines as a function of pH.

<table>
<thead>
<tr>
<th>pH</th>
<th>Slope x 10^{-4}</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.93</td>
<td>1.146</td>
</tr>
<tr>
<td>4.75</td>
<td>1.111</td>
</tr>
<tr>
<td>5.60</td>
<td>1.097</td>
</tr>
<tr>
<td>6.47</td>
<td>1.081</td>
</tr>
<tr>
<td>6.74</td>
<td>1.073</td>
</tr>
</tbody>
</table>
suspensions indicated that pH did not vary substantially among samples. Therefore, errors introduced due to pH variations among the samples should be small.

**Adsorption Isotherms**

Figures 19, 20, and 21 present the adsorption isotherm data for the less than 2 μm. fraction of the API illite, a 2 to 20 μm. size fraction derived from the API illite sample, and the pure metal hydrous oxides, respectively. The coarse clay fraction was prepared by sedimentation after the fine clay fraction had been separated from the suspension.

Figure 19 shows the adsorption isotherms for the less than 2 μm. clay fraction. The adsorption isotherms are typical of H-type adsorption profiles and indicate a very strong adsorbate-adsorbent interaction between the clay and both methylene blue and pyronin Y (25). Similar profiles have been found for the cationic pesticides paraquat and diquat (51). In the two isotherms (Figures 19a and 19c) in which absorbance measurements were used to determine the concentration of dye in solution, significant deviations from the y axis occur at low coverages. These deviations are due to an overestimation of the concentration of dye in solution. Colloids are normally not separated completely from the solution phase by centrifugation or filtration. These colloids scatter some of the radiation during the absorbance measurement. In addition, dye bound to the colloids adsorbed some of the radiation. The result of
Figure 19. Adsorption isotherms for the less than 2 um, fraction of the API illite. Adsorbates and methods used to determine the solution concentration of the adsorbate included; (a) methylene blue, absorbance; (b) methylene blue plus sodium chloride, absorbance; (c) pyronin Y, absorbance; (d) pyronin Y, fluorescence.
Figure 20. Adsorption isotherms for the 2 to 20 μm fraction of the API illite. Adsorbates and methods used to determine the solution concentration of the adsorbate included: (a) methylene blue, absorbance; (b) methylene blue plus sodium chloride, absorbance; (c) pyronin Y, absorbance; (d) pyronin Y, fluorescence.
Figure 21. Adsorption "isotherms" for the pure metal hydrous oxides as determined by absorbance and fluorescence measurements of pyronin Y.
these two processes was an overestimation of the concentration in solution.

This hypothesis was supported by adding a sodium chloride solution to the clay-methylene blue suspensions. If the measured concentrations were due to the presence of colloids in the solutions, then addition of a salt solution should cause the electric double layer to collapse and result in coagulation of the colloids. Centrifugation under these conditions should yield a cleaner separation of the solid and solution phases. In addition, the sodium would be expected to compete with methylene blue molecules for adsorption sites. This could be reflected in a desorption of the methylene blue or in a decrease in the selectivity coefficient for methylene blue.

The results from the addition of sodium chloride to the clay-methylene blue suspensions are shown in Figure 19b. The suspensions were some of the same suspensions used to construct the adsorption isotherms without sodium chloride. The points at lower coverages lie essentially on the y axis as is typical with H-type adsorption isotherms. Experiments to test whether or not methylene blue had been precipitated or salted out as a result of sodium chloride addition to the suspensions showed it was not affected by the addition of salt. In addition, the break between the rising portion of the isotherm and the plateau region is much more gradual than in the methylene blue isotherm in which no sodium chloride had been added to the suspensions.
This reflects a greater competition from sodium for adsorption sites. Finally, the adsorption maximum is higher than in the case in which no sodium chloride had been added to the suspensions. The explanation for this will be presented later on in this chapter.

Figure 19d presents the adsorption isotherm obtained when the concentration of pyronin Y in solution was determined by fluorescence. The same samples used to determine the adsorption isotherm via absorbance measurements were used in the fluorescence measurements. Clearly, the use of fluorescence measurements to determine the concentration of dye in solution is superior to the use of absorbance measurements. The adsorption isotherm obtained using fluorescence measurements is very similar to the isotherm obtained with methylene blue in which sodium chloride had been added to the suspensions to remove colloids.

Figure 20 presents the adsorption isotherms obtained using the 2 to 20 µm clay fraction. These isotherms were measured because complete separation of the solid and solution phases using this clay fraction should occur in all cases. Errors due to the presence of colloids in the analyte solutions, therefore, should be at a minimum. The adsorption isotherms in Figure 20 indicate that this was, in fact, the case. In addition, the isotherms using fluorescence measurements agree well with the isotherms using absorbance measurements. Finally, the isotherm
constructed from measurements of methylene blue in which sodium chloride had been added to the suspensions appears to have a slightly higher plateau region than the other isotherms.

The above findings indicate the utility of fluorescence measurements in determining the concentration of dye in solution. The similarity in the pyronin Y and methylene blue adsorption isotherms also indicates that the surface area per molecule for the two molecules is approximately the same, provided that the measurement is estimating surface area.

Table 20 presents the values for $k_1$, $k_2$, and $1/n$ used to construct the adsorption isotherms shown in Figures 19 and 20. In addition, the cation exchange capacities calculated from the values of $k_1$ and from the points of optimum flocculation are also given. The values for $1/n$ range from -0.041 to 0.483. The one negative value for $1/n$ is related to an apparent decrease in the amount of dye adsorbed as the concentration of dye in solution increases. It is probably an artifact of scatter in the measured points. The other values for $1/n$ agree reasonably well with those published elsewhere (113).

The calculated values for $k_1$ are proportional to CEC. For the coarse clay fraction, calculated values for CEC based on the values of $k_1$ range from 2.8 to 3.0 meq./100g. These are lower than the CEC of 5.1 meq./100g. measured by the sodium acetate method outlined in Chapter IV and are
Table 20. Isotherm parameters and CEC's calculated from $k_1$ and the point of optimum flocculation (POF) for the isotherms in Figures 19 and 20.

<table>
<thead>
<tr>
<th>Figure</th>
<th>Fraction</th>
<th>Adsorbate</th>
<th>$k_1 \times 10^5$</th>
<th>$k_2 \times 10^6$</th>
<th>$1/n$</th>
<th>CEC (k_1)</th>
<th>CEC (POF)</th>
<th>100g.</th>
<th>100g.</th>
</tr>
</thead>
<tbody>
<tr>
<td>19a</td>
<td>&lt;2 um.</td>
<td>MB</td>
<td>21.0</td>
<td>2.93</td>
<td>0.240</td>
<td>21.0</td>
<td>21.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>19b</td>
<td>&lt;2</td>
<td>MB+NaCl</td>
<td>20.8</td>
<td>144</td>
<td>0.483</td>
<td>20.8</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>19c</td>
<td>&lt;2</td>
<td>PY</td>
<td>21.9</td>
<td>46.6</td>
<td>0.454</td>
<td>21.9</td>
<td>21.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>19d</td>
<td>&lt;2</td>
<td>PY</td>
<td>21.9</td>
<td>34.4</td>
<td>0.432</td>
<td>21.9</td>
<td>21.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>20a</td>
<td>2-20 um.</td>
<td>MB</td>
<td>3.0</td>
<td>0.550</td>
<td>0.133</td>
<td>3.0</td>
<td>3.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>20b</td>
<td>2-20</td>
<td>MB+NaCl</td>
<td>2.8</td>
<td>0.109</td>
<td>-0.041</td>
<td>2.8</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>20c</td>
<td>2-20</td>
<td>PY</td>
<td>2.9</td>
<td>0.542</td>
<td>0.162</td>
<td>2.9</td>
<td>3.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>20d</td>
<td>2-20</td>
<td>PY</td>
<td>2.9</td>
<td>1.04</td>
<td>0.199</td>
<td>2.9</td>
<td>3.6</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^1$MB=methylene blue; PY=pyronin Y.

$^2$Standard deviations for these values were ± 0.9 for the less than 2 um. fraction and ± 0.6 for the 2 to 20 um. fraction.
slightly lower than the CEC's determined from the points of optimum flocculation. In fact, almost all of the measured amounts of dye adsorbed onto the coarse clay fraction were less than the CEC as determined by the sodium acetate method. This suggests either that the CEC as measured by the sodium acetate method was erroneously high or that some of the cation exchange sites on the coarse clay fraction were inaccessible to both methylene blue and pyronin Y. The latter could indicate a covering up of exchange sites by previously adsorbed dye molecules.

The calculated CEC values from the isotherms for the fine clay fraction range from 20.8 to 21.9 meq./100g. These values agree well with the CEC value of 22.3 ± 0.6 determined using the sodium acetate method and with CEC values calculated from the points of optimum flocculation. This data indicates that optimum flocculation corresponds to CEC and not surface area as Hang and Brindley (109) contended. Flocculation is clearly seen on the adsorption isotherms in Figure 19 (a and c) in which the dye concentrations in solution were measured by absorbance. As the CEC is approached, the charge on the clay is neutralized and coagulation occurs, resulting in cleaner separations of the solid and solution phases and, therefore, in smaller errors for the measured solution concentrations.

Figure 21 presents the data for the pure metal hydrous oxides. Adsorption isotherms were not calculated for these
substances. The data for both the iron and aluminum hydrous oxides show that little or no pyronin Y was adsorbed. The absorbance measurements for iron hydrous oxides resulted in negative values for the calculated amounts of dye adsorbed, reflecting errors due to scattering in the measurement of solution concentration of dye. All of the hydrous oxides were probably colloidal in size and, therefore, errors from scattering should be substantial. The fluorescence measurements for iron hydrous oxides were reasonably constant and resulted in positive values for the calculated amount of adsorbed dye. However, these values were well below the CEC as measured by the sodium acetate method.

These trends can best be explained in terms of the charge on the iron hydrous oxides. The iron hydrous oxide suspension had a pH somewhere between 6 and 7, which is well below its apparent pH of zero point of charge (pH(ZPC)) of 8.4 (Chapter VI). Pyronin Y solutions have a pH of around 4.4. Therefore, the surface of iron hydrous oxide during the measurement of the adsorption isotherm should be positively charged and adsorption of dye onto this surface should be negligible, as was found. CEC measurements, on the other hand, were made at a pH of 8.2. Surface charge under these conditions should be very close to neutral and adsorption of sodium ions should occur in greater amounts than did the dye during the adsorption isotherm measurements. Therefore, the measured CEC should be significantly greater than the amount of dye adsorbed.
The amount of dye adsorbed by the iron hydrous oxide may reflect adsorption of non-charged dye impurities, a small amount of adsorption due to van der Waals forces and entropy effects, or some quenching of the dye's fluorescence in solution by the iron hydrous oxides. The amounts adsorbed are well below the value which corresponds to the smallest surface area for iron hydrous oxides reported in the literature (17).

The measurements for aluminum hydrous oxides are even worse than those for iron hydrous oxides. Both absorbance and fluorescence measurements of dye concentration in solution resulted in negative values for the amount adsorbed. This data suggests that fluorescence of pyronin Y adsorbed onto aluminum hydrous oxides is not quenched, or the presence of a fluorescent contaminant. However, the most likely cause is a small error in the concentration of the pyronin Y stock solution. All of the fluorescence measurements appear to lie on a straight line indicating a systematic error. Calculations revealed that if the nominal concentration of the pyronin Y stock solution was increased by a factor of much less than 1%, all of the measured amounts adsorbed would be zero or greater. In other words, the data points on Figure 21 are not significantly different from zero. These measurements again support the view that charge interactions control dye adsorption since the pH(ZPC) for aluminum hydrous oxides is greater than the pH of the pyronin Y solution. Therefore, the surface of the
aluminum hydrous oxides had a net positive charge during the adsorption isotherm measurements.

The adsorption isotherm measurements for manganese dioxide show a wide discrepancy between fluorescence and absorbance measurements. The absorbance points lie distinctly away from the y axis, particularly at low coverages. In fact, the lowest point resulted in a negative value for the calculated amount of dye adsorbed. Observations of the solutions made at the time of measurement indicated a large portion of colloidal particles. The solutions were literally black with suspended manganese dioxide even after prolonged centrifugation. The fluorescence measurements on these same samples show a dramatic improvement in the results, at least at lower dye coverages. At higher concentrations of the dye, the fluorescence and absorbance curves intersect. The fluorescence excitation spectrum of the decantates (Figure 22) revealed a large shift in the absorption spectrum of pyronin Y. This shift is most likely due to oxidation of the pyronin Y to other fluorescent compound(s) by manganese dioxide.

All of the data points for manganese dioxide lie well below the CEC. The pH(ZPC) for manganese dioxide is very low (less than 3). Therefore, the pH of the pyronin Y solutions was greater than the pH(ZPC). Under these conditions, the surface should be negatively charged. Therefore, it is not surprising that pyronin Y would adsorb
Figure 22. Fluorescence excitation spectrum of a decantate after adsorption of pyronin Y on pure manganese hydrous oxide.
onto manganese dioxide. This and the results for illite and the other hydrous oxides indicates that dye adsorption is controlled by charge interactions between the surface and the dye molecules.

**pH and Ionic Strength Dependence of Dye Adsorption**

Figure 23 presents the data from the study of the pH and ionic strength dependence of dye adsorption on illite. The apparent area calculated from the amount of dye adsorbed onto illite is plotted versus the square root of the ionic strength. The pH of the saturating solutions is indicated by the symbols for each of the data points. Two trends are immediately discernible. First, pyronin Y adsorption onto illite is highly dependent on ionic strength. The derived area for illite can vary by up to a factor of 2 depending on the ionic strength of the saturating solution. In addition, one would expect that as the ionic strength increased, competition for adsorption sites by ions other than pyronin Y would increase. Also, coagulation of the illite suspension would occur at the higher ionic strengths. Both of these effects are expected to result in a decrease in apparent surface area as the ionic strength increased. However, the opposite trend was observed.

Secondly, a detailed analysis of the pH data indicates that dye adsorption was not pH dependent. Rather, pH affects dye adsorption by controlling dissociation of acetate ions and, hence, controls the ionic strength of the
Figure 23. Apparent surface area of illite as a function of the square root of the ionic strength of the pyronin Y solutions.
solutions.

These facts can be explained in terms of the simple model of charge distribution at the solid-solution interface. Illite is predominantly a constant charge surface in which very little specific adsorption of hydrogen or other potential determining ions occurs. Therefore, the charge densities due to specific adsorption of hydrogen ions and other potential determining ions can be ignored. In addition, pyronin Y is specifically adsorbed, as indicated by the H-type adsorption isotherms, and, therefore, is represented by the interlayer charge density \( \sigma_i \). Taking the equations for the diffuse layer charge density and for electroneutrality (Equations 2-46 and 2-47), one can derive

\[
\sigma_i = (8\varepsilon_0 RTI)^{1/2} \sinh(F\psi_d/2RT) - \sigma_s \tag{5-4}
\]

The ionic strength dependence of pyronin Y adsorption is readily apparent. The surface charge density is constant due to isomorphous substitution in the illite crystal lattice. The diffuse layer potential does not necessarily have to be constant, but apparently is.

Table 21 presents the results for adsorption of pyronin Y on other particulates as a function of pH and ionic strength. For these materials, a greater pH dependence is expected due to the higher proportion of constant potential surfaces. In fact, the variation in apparent surface area cannot be explained solely on the
Table 21. Apparent surface area of various model particulates as a function of pH and ionic strength.

<table>
<thead>
<tr>
<th>Particulate</th>
<th>Low Ionic Strength</th>
<th>High Ionic Strength</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>pH 4.75</td>
<td>pH 6.74</td>
</tr>
<tr>
<td>FCage</td>
<td>130</td>
<td>164</td>
</tr>
<tr>
<td>ACage</td>
<td>33</td>
<td>79</td>
</tr>
<tr>
<td>HFCage</td>
<td>201</td>
<td>261</td>
</tr>
<tr>
<td>HACage</td>
<td>52</td>
<td>104</td>
</tr>
</tbody>
</table>
basis of ionic strength as in the case of illite. Apparent surface area increased as the pH increased from 4.75 to 6.74. This increase could reflect an increase in the number of negatively charged sites on the surface. Area also increased in all but one of the samples as the ionic strength increased.

The above findings agree with those reported by other authors. For example, the observation that dye adsorption increases with increasing ionic strength, either due to increases in the dye concentration or due to the presence of other salts, has been made by Padday (112), van Olphen (110), Narine (36), and Hang and Brindley (109). Both Narine (36) and Giles et al. (116) found that adsorption of methylene blue onto various substances was pH dependent. In addition, many authors have made the comment that adsorption of dyes is controlled by charge interactions (e.g., 110, 112). Given the above findings, it is reasonable to conclude that the adsorption of cationic dyes does not measure surface area and appears to be controlled by charge interactions between the surface and the cationic dye. It is also unlikely that the adsorption of any ionic substance is able to measure the surface area of particulates reliably. Given the review of the various methods used to measure surface area presented earlier in this chapter, it appears that the measurement of surface area for aquatic particulates is not possible at this time.
CHAPTER VI

ZERO POINT OF CHARGE MEASUREMENTS

Introduction

The development of an electric double layer at a solid-solution interface is an important factor governing adsorption. Interfacial charge determines whether or not charged molecules adsorb and, if they do, how strongly they are bound to the surface. In addition, surface charge determines whether polar molecules adsorb and the extent of competition by the solvent for adsorption sites. Charge interactions between particles also determines colloid stability and, hence, the distribution and transport mode of particulates.

The most important property of an electric double layer, particularly for pH-dependent charged surfaces, is the pH of zero point of charge (pH(ZPC)) \((66, 143)\). It is the pH at which the net charge on the surface is zero \((66)\). At the pH(ZPC), the electric double layer is collapsed or absent, i.e., the diffuse layer charge density is zero \((50)\). Colloid stability is at a minimum due to charge neutralization, and colloids readily coagulate and settle out of suspension. When the suspension pH is either lower or higher than the pH(ZPC), the particles are either
positively or negatively charged, respectively. Therefore, given the pH of the suspension and the pH(ZPC), it is possible to predict colloid stability and whether adsorption of charged chemicals should occur.

The purpose of this chapter is to review the measurement of pH(ZPC) and to present data for the particulates described in Chapter II.

Definitions

Definitions in the Literature

The definition for the pH(ZPC) as the pH at which the net charge on the surface is zero (66) has lead to a considerable amount of confusion in the literature. This confusion stems, in part, from differences in the definition of surface charge (60). In addition, many authors have confused operationally determined parameters with the pH(ZPC) and have not stated explicitly the conditions under which the two are equivalent.

At least three definitions for the pH(ZPC) are commonly used. These are:

1. The pH(ZPC) is the pH at which the surface charge density due to adsorption of only potential determining ions (PDI's) is zero, i.e.,

\[ \sigma_H + \sigma_P = 0 \]  

(6-1)

This point has been called the zero point of charge (ZPC) or point of zero charge (PZC; 50, 58, 143), the pristine point of zero charge (PPZC; 53), the
isoelectric point (IEP; 50), or the isoelectric point of the solid (IEPS; 53, 66).

2. A second definition holds that the pH(ZPC) is the pH at which the surface charge density from all sources is zero, i.e.,

$$\sigma_s + \sigma_H + \sigma_p + \sigma_i = 0$$  \hspace{1cm} (6-2)

This point has been called either the zero point of charge or point of zero charge (53, 60, 66, 69), or the isoelectric point (60, 144).

3. The pH(ZPC) has also been defined as the pH at which the net proton charge density on the surface is invariant with changes in the ionic strength of the solution, i.e.,

$$\partial \sigma_H / \partial I = 0$$  \hspace{1cm} (6-3)

This point has been called the zero point of charge (49, 83, 111), the isoelectric point (49), or the point of zero salt effect (PZSE; 53, 60, 69).

In addition to these definitions for the pH(ZPC), some authors (e.g., 145) reserve the use of the term zero point of charge for measurements which involve the determination of charge densities and the term isoelectric point for measurements which involve determinations of electrokinetic properties.

Other terms which are commonly used in the description of surface charge measurements include
1. The zero point of titration (ZPT) is defined as the pH of the suspension (49, 83). It is the starting pH of an acid-base titration.

2. The zero proton condition, abbreviated ZPC, is the pH at which the net proton charge density is zero (60, 144), i.e.,

$$\sigma_H = 0$$  \hspace{1cm} (6-4)

This point has also been called the point of zero net proton charge (PZNPC; 69).

3. The point of zero net charge (PZNC) is defined as the pH at which the CEC equals the anion exchange capacity (66, 69).

In addition to the multitude of definitions, several other aspects of the literature cause difficulties. For example, confusion results from the use of the terms zero point of charge and point of zero charge to refer to the same point, and the use of the abbreviation ZPC to refer to both the zero point of charge and the zero proton condition. Differences in the definition of potential-determining ions add to the confusion. Most authors define PDI's to be the ions comprising the solid surface plus the hydronium and hydroxyl ions (e.g., 66). Hohl et al. (60) define PDI's to be any specifically adsorbed ion. These same authors also define any ion which reacts with a specifically adsorbed ion as a "potential determining ion of the second kind." Finally, Parks and de
Bruyn (143) contend that the surface of many solids is covered with hydroxyl groups such that the lattice ions have no active potential determining role. PDI's, in this case, are restricted to only the hydronium and hydroxyl ions.

Definitions Used in this Chapter

The concept of a zero point of charge (ZPC) stems originally from electrochemistry and the theory developed for ion-selective electrodes. Hydrogen ions, for example, are selectively, i.e., specifically, adsorbed onto the glass surface of a pH electrode. Other ions are not. In this case, the charge and potential of the electrode surface is determined solely by hydrogen ions on the surface which are in equilibrium with hydrogen ions in solution. Under these circumstances, a solution pH may exist in which the net surface charge density is zero. If the solution pH is either higher or lower than the pH at which the surface charge density is zero, then the surface will be either negatively or positively charged, respectively.

To distinguish the hydrogen ion from all other ions, it is designated as a potential determining ion. PDI's, by definition, contribute to the establishment of a charge and potential on a surface and are able to reverse the surface charge and potential through either adsorption or desorption. These ions are specifically adsorbed and are part of either the solid or the solvent. Lattice ions may
reverse the charge and potential of a surface by preferentially adsorbing or desorbing relative to their counterions. Their solution concentrations are controlled by the solubility product for the solid. Solvent ions also help to establish surface charge if they are specifically adsorbed. Their concentrations are controlled by the dissociation constant of the solvent. The distinction between specifically adsorbable ions and PDI's is that PDI's always involve a cation-anion pair whose solution concentrations are controlled by an equilibrium constant. Both the cation and anion are specifically adsorbed onto the surface. Specifically adsorbable ions are not able to reverse the charge on a surface in all cases, do not necessarily involve a counterion which is specifically adsorbed, and have concentrations which are not controlled by an equilibrium constant.

The pH at which the surface charge density is zero is distinguished from all other values of pH. For the pH electrode, where surface charge densities from permanent structural charge and specific adsorption of non-potential determining ions are zero, this pH is called the pH of the isoelectric point of the solid (pH(IEPS); 66). The isoelectric point of the solid (IEPS) is defined in terms of the concentrations of all PDI's, as in Equation 6-1. It should be noted that the IEPS is distinct from the pH(IEPS). A particle may have an IEPS which is not dependent on the hydrogen ion concentration, i.e., hydrogen
ions are not specifically adsorbed onto the surface. In this case, hydrogen ions are not PDI's and a pH(IEPS) does not exist. For the pH electrode, there is only one PDI, i.e., hydrogen. Therefore, the IEPS is equivalent to the pH(IEPS) and corresponds to a single value of pH. This pH(IEPS) is a unique property of the surface. If, however, there were other PDI's in addition to hydrogen, then the IEPS would not have a singular value of pH. In this case, the pH(IEPS) would vary depending on the concentrations of the other PDI's.

In addition to the IEPS, the point at which the surface charge density from all sources is zero (Equation 6-2) will be designated as the zero point of charge (ZPC), as suggested by Parks (66). The ZPC is equivalent to the IEPS only when the net charge density from specifically adsorbed ions and the permanent structural charge is zero. Again, a distinction should be made between the ZPC and the pH(ZPC). The ZPC is defined in terms of the charge densities from all specifically adsorbed ions and permanent structural charge. It is equivalent to the pH(ZPC) only when hydrogen ions are specifically adsorbed and when the net charge density from specifically adsorbed ions, adsorption of lattice ions, and the permanent structural charge is zero.

In addition to the definitions for PDI's, specifically adsorbable ions, IEPS, and ZPC, other definitions which will be used include:
1. The point of zero salt effect (PZSE) will be defined as the pH at which there is no change in the net proton charge density with changes in ionic strength (Equation 6-3; 69).

2. The isoelectric point (IEP) will refer to the pH at which there is no electrokinetic mobility (145). This is distinct from the IEPS which is defined in terms of charge densities.

**Methods**

A variety of techniques have been used in an attempt to measure the pH(ZPC) or the pH(IEPS) of particles. These include:

1. Electrokinetic methods including electrophoresis, electroosmosis, and streaming potential (50, 60, 146).

   The pH at which there is no electrophoretic mobility is termed the IEP. Electrophoretic mobility is related to the charge density and potential at the shear or slipping plane. These quantities may not be equivalent to the charge and potential at the "d" plane in electric double layer theory (60, 145). Adsorbed organic matter, for example, can cause the shear plane to be located much further away from the surface than the "d" plane (70). In addition, the ZPC corresponds to zero electrophoretic mobility but the IEP does not necessarily correspond to the ZPC. The IEP is dependent on ionic strength when the shear
plane is located further away from the surface than the "d" plane. For these reasons, electrokinetic measurements should be used with caution.

2. Titration data (50, 60, 66, 143).

This method usually involves the acid-base titration of a suspension at a variety of ionic strengths. Under certain conditions, which will be described below in more detail, the resultant intersection of two titration curves is equivalent to the pH(IEPS) or the pH(ZPC).

3. Other methods (58, 143).

Any property which depends on the presence of an electric double layer can be used to measure the ZPC. For example, the flocculation rate of colloids is at a maximum at the ZPC (60, 66). These methods have been used less commonly than the two methods described previously.

Because of the ease of measurement and the availability of equipment, the acid-base titration method was chosen.

**Determination of Apparent PSZE and pH(ZPC) by Acid-Base Titration Data**

**General Description of the Method**

The acid-base titration method consists of a series of acid-base titrations at different ionic strengths (143). From the quantity of acid or base added to a suspension, the concentration of particulates in the suspension, and the measured pH, the net apparent proton charge density is
calculated as follows:

\[
\sigma_H \text{ (mole/g.)} = \left( C_a - C_b + [OH^-] - [H^+] \right)/C_p \quad (6-5)
\]

where \( C_a \) and \( C_b \) are the concentrations of acid and base added to the suspension in moles/l., \([H^+]\) and \([OH^-]\) are the concentrations of the hydronium and hydroxyl ions calculated from the pH measurement in moles/l., and \( C_p \) is the concentration of the particulate suspension in g./l. It should be noted that the apparent net proton charge density equals the net proton charge density when hydronium and hydroxyl ions are only specifically adsorbed. The measured net proton charge density will not equal the net proton charge density when non-specific adsorption of these ions occurs. The apparent net proton charge density is plotted as a function of the measured pH. The pH of the intersection point between two or more curves is the apparent PZSE (Figure 24). This pH will equal the PZSE only when the apparent net proton charge density equals the net proton charge density.

**Conditions under which the apparent PZSE is equivalent to the pH(ZPC) and pH(IEPS)**

The apparent PZSE can be equated to the pH(ZPC) and the pH(IEPS) if the measured PZSE equals the PZSE and if certain other conditions are met. In the following description, it is assumed that the apparent PZSE equals the PZSE.

Consider two titration curves, each of which was
Figure 24. Example of a PZSE measurement assuming all restrictions related to the equivalence of the PZSE to the pH(IEPS) are met.
measured at a different ionic strength. For this system, the PZSE is defined as the point in which

\[ \sigma_{H1} = \sigma_{H2} \] (6-6)

where \( \sigma_{H1} \) and \( \sigma_{H2} \) are the net proton charge densities at the PZSE for each of the two titrations. Electroneutrality requires that

\[ -\sigma_{s1} - \sigma_{p1} - \sigma_{i1} - \sigma_{d1} = -\sigma_{s2} - \sigma_{p2} - \sigma_{i2} - \sigma_{d2} \] (6-7)

Since the charge density due to isomorphous substitution is constant, it can be dropped from both sides of the equation. If the charge density from lattice ions and specifically adsorbable ions is constant, then

\[ -\sigma_{d1} = -\sigma_{d2} \] (6-8)

or

\[ (8\varepsilon\varepsilon_0 RTI_1)^{1/2} \sinh(F\psi_d/2RT) = (8\varepsilon\varepsilon_0 RTI_2)^{1/2} \sinh(F\psi_d/2RT) \] (6-9)

Because the potential at the inner-most plane of the diffuse layer is a function of \( \sigma_s \), \( \sigma_H \), \( \sigma_i \), and \( \sigma_p \), and if all of these quantities are constant, then this potential is also a constant. Therefore, the diffuse layer charge densities for the two titration curves will be equivalent only when the value for the hyperbolic sine term is zero. The hyperbolic sine term is zero when the diffuse layer potential is zero which implies that the diffuse layer
charge density is also zero. Therefore, the PZSE equals the pH(ZPC), provided that the charge density from lattice ions and specifically adsorbable ions is constant with ionic strength. The PZSE will also equal the pH(IEPS) if, and only if, the charge density from isomorphous substitution and specific adsorption of ions is zero and the charge density from lattice ions is constant with ionic strength (53, 66).

**The Indifferent Electrolyte**

Because the determination of either the pH(ZPC) or the pH(IEPS) from titration data depends, in addition to other restrictions, on the interlayer charge density being constant or zero, the electrolyte used to adjust the ionic strength must be chosen carefully. Ideally, both of the ions of the electrolyte should be non-specifically adsorbed onto the surface (49, 66). However, no ion is devoid of some tendency towards specific adsorption (58, 66). Therefore, the requirement for the indifferent electrolyte is that both ions of the electrolyte must be specifically adsorbed in equal amounts (66). Under these circumstances, the charge density from specifically adsorbable ions will be zero and should not interfere with the determination of either pH(ZPC) or pH(IEPS). Ions which meet this criterion are generally those which have similar charge and hydrated radii (69). Salts of sodium, potassium, nitrate, chloride, and perchlorate are the most commonly used (49, 50, 66, 83).
Explanation of the Titration Curves

Figure 24 shows an idealized example of the determination of the PZSE. Generally, the high ionic strength curve has a steeper slope than the low ionic strength curve. This can be explained as follows. If $\sigma_s$, $\sigma_i$, and $\sigma_p$ are constant with changes in ionic strength, then the electroneutrality equation may be written as

$$\sigma_H + \sigma_d + k = 0 \quad (6-10)$$

or

$$\sigma_H - (8\varepsilon\varepsilon_0 RT)^{1/2} \sinh(F\psi_d/2RT) + k = 0 \quad (6-11)$$

where $k$ is a constant. When the solution pH is below the PZSE (which equals the pH(ZPC)), the diffuse layer potential is greater than zero, i.e., the surface is positively charged, and the hyperbolic sine term is positive. As the ionic strength increases, the diffuse layer charge density decreases, and the net proton charge density must increase to maintain electroneutrality. Therefore, at pH values below the PZSE, or pH(ZPC), the high ionic strength curve will be at more positive values of $\sigma_H$ than the low ionic strength curve. When the solution pH is higher than the PZSE, the surface is negatively charged and the hyperbolic sine term is negative. As the ionic strength increases, the diffuse layer charge density increases and the net proton charge density must decrease to maintain electroneutrality. Therefore, the high ionic
strength curve will be at more negative values of the net proton charge density than the low ionic strength curve. The result is that the high ionic strength curve has a steeper slope than the low ionic strength curve.

**Effects of Specific Adsorption**

Assume that the permanent structural charge density is zero and that the charge densities from lattice ions and specific adsorption are constant. Under these conditions, the PZSE will equal the pH(ZPC). This PZSE will also equal the pH(IEPS) only when the charge density from specific adsorption of ions is zero. In other words, the PZSE, or pH(ZPC), shifts in relation to the pH(IEPS) as a result of specific adsorption. If the interlayer charge density ($\sigma_1$) is positive due to adsorption of cations, then the net proton charge density will be less than if the interlayer charge density were zero. Therefore, the adsorption of cations shifts the pH(ZPC) to higher values of pH from the pH(IEPS) (50, 58, 60, 66, 69). If anions adsorb, the net proton charge density will be greater than when the interlayer charge density is zero. Therefore, the adsorption of anions shifts the pH(ZPC) to lower values of pH in relation to the pH(IEPS).

These shifts in pH(ZPC) relative to the pH(IEPS) apply to the charge densities from lattice ions and permanent structural charge as well (49, 66). When the charge density from lattice ions, specifically adsorbable ions, or the permanent structural charge is negative, the net proton
charge density must be greater than when the sum of these charge densities is zero in order to produce a diffuse layer charge density equal to zero. Therefore, the pH(ZPC) is shifted to lower values of pH. Similarly, if the sum of the charge densities is positive, the net proton charge density will be lower than when the sum is zero, and the pH(ZPC) will shift to higher values of pH. Because of these effects, specific adsorption has been defined as adsorption which results in a shift in the pH(ZPC) (49, 66, 145).

Other Effects

At the pH(ZPC),

\[ \sigma_H = -\sigma_s -\sigma_i -\sigma_p \]  

(6-12)

Therefore, the value of the net proton charge density at the pH(ZPC) is indicative of the net charge density from permanent structural charge, specific adsorption, and/or lattice ions other than hydronium and hydroxyl ions (49, 83). If the net proton charge density at the pH(ZPC) equals zero, then it is likely that the pH(ZPC) equals the pH(IEPS).

Application of the Titration Method to Natural Particulates

When the titration method is used in an attempt to determine the pH(ZPC) or the pH(IEPS) of natural particulates, three possible situations may occur. These are:

1. The particulates may not adsorb hydrogen ions or may adsorb hydrogen ions only non-specifically.
In this case, the ZPC and IEPS cannot be determined by the titration method and a pH(ZPC) or pH(IEPS) does not exist.

2. The particulates may adsorb hydrogen ions specifically at some sites and non-specifically at others.
   In this case, the "apparent" PZSE will not equal the PZSE and, therefore, will not equal the pH(ZPC) or the pH(IEPS). The measured PZSE will depend on the exchange capacities of the particulates and the ionic medium (66).

3. The particulates adsorb hydrogen ions specifically at all sites, i.e., non-specific adsorption is negligible.
   In this case, three possibilities exist. If the charge densities from lattice ions, specific adsorption of non-PDI's, and permanent structural charge are all zero, then the PZSE will equal the pH(IEPS). Furthermore, this pH(IEPS) will be a unique property of the surface. If other PDI's are present, then the PZSE will equal the pH(IEPS) but the pH(IEPS) may not be unique. The pH(IEPS) will be unique only when the concentrations of the other PDI's are controlled by pH. Otherwise, the pH(IEPS) will depend on the concentrations of the other PDI's. Finally, if specific adsorption of non-PDI's occurs or if the charge density from permanent structural
charge is significant, then the PZSE equals the pH(ZPC). The pH(ZPC) will not be unique and will depend on the permanent structural charge and the concentrations of all other specifically adsorbable ions.

Methodology

The titration method was used to determine the apparent PZSE. Descriptions of the method can be found in Parks and de Bruyn (143), Hendershot and Lavkulich (83), and Brown (52). A sample of a particulate suspension containing about 70 mg. of particulates was placed in a plastic container along with a magnetic stir bar, various amounts of a 2.93 M sodium nitrate solution, and distilled-deionized water. The plastic container was fitted with a plastic cap through which holes had been bored and was placed on a magnetic stirrer. A combination pH electrode, a thermometer, a nitrogen line, and a tube connected to a 5-ml. microburet were passed through the holes in the cap and placed in the sample. Nitrogen was bubbled through the suspension to purge the system of carbon dioxide, and the magnetic stirrer was turned on. The sample was titrated with either 0.0993 M nitric acid or 0.104 M carbonate-free sodium hydroxide. The sodium hydroxide was stored in a polypropylene carboy under nitrogen to avoid contamination from carbon dioxide and silicates. The base was standardized using potassium hydrogen phthalate and was then used to standardize the
acid. The pH of the sample was monitored on a strip chart recorder and was read only when the pH had stabilized. Stabilization usually occurred within 15 minutes. Each of the particulate suspensions was titrated twice: once at low ionic strength (approximately \(5 \times 10^{-4}\) M) and once at high ionic strength (approximately 0.1 M). From the pH measurements, the apparent net proton charge density was calculated using Equation 6-5. Both the hydronium and hydroxyl ion concentrations were corrected for activity coefficients using Debye-Hückel theory.

**Results**

**Pure Metal Hydrous Oxides**

Results of the determination of apparent net proton charge density versus pH for the pure metal hydrous oxides are shown in Figures 25, 26, and 27. The titration curves for iron hydrous oxides (Figure 25) are similar to the idealized curves shown in Figure 24. The high ionic strength line has a slope which is greater than that for the low ionic strength line and the apparent PZSE is at a pH of approximately 8.4.

Figure 26 shows the results for manganese dioxide. The two lines do not intersect in the pH range covered. However, using the relative position of the high and low ionic strength curves and assuming that the high ionic strength curve must have a greater slope than the low ionic strength curve at the apparent PZSE, the apparent PZSE may be inferred to be at a pH of less than 3.0.
Figure 25. Apparent net proton charge density ("$\sigma_H$") versus pH for pure iron hydrous oxide. High and low ionic strength curves are represented by circles and triangles, respectively.
Figure 26. Apparent net proton charge density ("$\sigma_H$") versus pH for pure manganese hydrous oxide. High and low ionic strength curves are represented by circles and triangles, respectively.
Figure 27. Apparent net proton charge density ("$\sigma_H$") versus pH for pure aluminum hydrous oxide. High and low ionic strength curves are represented by circles and triangles, respectively.
Figure 27 presents the results for aluminum hydrous oxides. The apparent PZSE is either at a pH of approximately 10 or at a pH somewhere between 4.25 and 4.60. Again, using the relative positions of the high and low ionic strength lines, an apparent PZSE of approximately 10 is indicated.

These results are in agreement with values reported in the literature (Table 22). The values listed in Table 22 are compiled from electrokinetic and mass balance data. The wide range in reported pH(IEPS) generally reflects variations in sample preparation and in measurement technique. Lower values usually correspond to materials which were less hydrated (50).

The apparent PZSE of 8.4 for iron hydrous oxide agrees well with the values for the pH(IEPS) of amorphous iron hydroxide and synthetic hematite. It is also within the range of values reported for goethite. The apparent PZSE for manganese hydrous oxide also agrees with reported pH(IEPS)'s. Generally, a low value for the pH(IEPS) is indicated (50). Finally, the value for aluminum hydrous oxide is most similar to those reported for boehmite and bayerite. Both boehmite and bayerite form from fresh aluminum hydrous oxide precipitates (39, 50).

Parks (50, 66) and Parks and de Bruyn (143) noted that the pH(IESP) corresponded closely to the point of minimum solubility for the solid. To test this, log concentration diagrams were constructed for both "active" amorphous iron
Table 22. Summary of reported pH(IEPS)'s for metal oxides.

<table>
<thead>
<tr>
<th>Metal Hydrous Oxide</th>
<th>Range in Reported Values</th>
<th>Mean of Reported Values</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hematite</td>
<td>5.4-9.0</td>
<td>7.8</td>
<td>50,143</td>
</tr>
<tr>
<td>Natural Hematite</td>
<td>5.4-6.9</td>
<td>6.3</td>
<td>50</td>
</tr>
<tr>
<td>Synthetic Hematite</td>
<td>6.5-9.0</td>
<td>8.4</td>
<td>50</td>
</tr>
<tr>
<td>Goethite</td>
<td>5.9-9.2</td>
<td>7.5</td>
<td>50,53,147</td>
</tr>
<tr>
<td>Lepidocrocite</td>
<td>5.4-7.4</td>
<td>n.d. ¹</td>
<td>50</td>
</tr>
<tr>
<td>Amorphous iron</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>hydroxide</td>
<td>7.9-8.6</td>
<td>8.2</td>
<td>17,50,58,96,111</td>
</tr>
<tr>
<td>Boehmite</td>
<td>6.5-9.4</td>
<td>8.2</td>
<td>50</td>
</tr>
<tr>
<td>Diaspore</td>
<td>5.4-7.5</td>
<td>6.4</td>
<td>50</td>
</tr>
<tr>
<td>Gibbsite</td>
<td>3.8-5.2</td>
<td>4.8</td>
<td>50,58</td>
</tr>
<tr>
<td>Bayerite</td>
<td>5.4-9.3</td>
<td>8.1</td>
<td>50</td>
</tr>
<tr>
<td>Amorphous aluminum</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>hydroxide</td>
<td>5.1-7.3</td>
<td>n.d. ¹</td>
<td>50</td>
</tr>
<tr>
<td>Pyrolusite</td>
<td>2.0-7.3</td>
<td>n.d. ¹</td>
<td>50,58</td>
</tr>
</tbody>
</table>

¹n.d.=not determined. Values were reported as ranges.
hydroxide and amorphous aluminum hydroxide (Figures 28 and 29). All of the equilibria used to construct these diagrams assumed excess solid in suspension. The reactions and equilibrium constants were obtained from Feitknecht and Schindler (39) and Krauskopf (22). The solubility curve was constructed by totalling the concentrations for all of the dissolved metal species. A similar diagram for manganese dioxide could not be constructed because of the lack of equilibrium data.

The results in Figures 28 and 29 show a reasonable agreement between the point of minimum solubility (pH 7.95) and the apparent PZSE (pH 8.4) for iron but a lack of agreement for aluminum. Part of the problem with aluminum is its relatively high solubility. Below pH 4.5, substantial quantities of dissolved aluminum species exist in solution relative to the hydrogen ion concentration. Dissolution of amorphous aluminum hydroxide through addition of acid results in the release of hydroxide ions to solution. These hydroxide ions neutralize some of the acid and result in a high value of the apparent net proton charge density. Similarly, addition of base causes the aluminum species to precipitate as aluminum hydroxide. The added hydroxide ions are removed from solution and the calculated net proton charge density is negative. The sharp break in Figure 27 at a pH of about 4.5 reflects this buffering action.
Figure 28. Log concentration diagram for the dissolution of "active" amorphous iron hydroxide.
Figure 29. Log concentration diagram for the dissolution of amorphous aluminum hydroxide.
Clay and Metal Hydrous Oxide-Clay Mixtures

Figure 30 shows the apparent PZSE curves for the Montana illite. Similar results were found for all of the metal hydrous oxide-clay mixtures with the possible exception of aluminum. Representative curves for these mixtures are shown in Figures 31, 32, and 33, and a summary of apparent PZSE values for all of the particulates is given in Table 23. The most significant feature of these curves is that the high and low ionic strength lines are "reversed," i.e., the low ionic strength line has a greater slope at the apparent PZSE than the high ionic strength line. The reason for this is that the clay and metal hydrous oxide-clay mixtures have a substantial amount of permanent CEC (Chapter IV). Hydrogen ions are both specifically and non-specifically adsorbed. For clay, the non-specific adsorption of the faces far outweighs the specific adsorption of the edges (48, 49, 58, 66, 69). The latter accounts for about 1% of the total surface area (49). The ions of the electrolyte compete with hydronium and hydroxyl ions for ion exchange sites (47, 66). At high electrolyte concentrations, this competition is greater than at lower electrolyte concentrations, and less hydronium and hydroxyl ions are able to adsorb onto the particulates. Therefore, the magnitude of the calculated net proton charge density is less and the high ionic strength curves have slopes which are less than the low ionic strength curves.
Figure 30. Apparent net proton charge density ("$\sigma_H$") versus pH for Montana illite. High and low ionic strength curves are represented by circles and triangles, respectively.
Figure 31. Apparent net proton charge density ("$\sigma_-$") versus pH for iron hydrous oxide-clay particulates ($\text{FeO}_4^-$). High and low ionic strength curves are represented by circles and triangles, respectively.
Figure 32. Apparent net proton charge density (\(\sigma_H\)) versus pH for manganese hydrous oxide-clay particulates (MCU). High and low ionic strength curves are represented by circles and triangles, respectively.
Figure 33. Apparent net proton charge density ("σ_H") versus pH for aluminum hydrous oxide-clay particulates ("AC3"). High and low ionic strength curves are represented by circles and triangles, respectively.
Table 23. Apparent PZSE's for the synthesized particulates.

<table>
<thead>
<tr>
<th>Particulate</th>
<th>Apparent PZSE('s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>7.2</td>
</tr>
<tr>
<td>F</td>
<td>8.4</td>
</tr>
<tr>
<td>A</td>
<td>4.2-4.6,10.0</td>
</tr>
<tr>
<td>M</td>
<td>&lt;3</td>
</tr>
<tr>
<td>FC1</td>
<td>7.4</td>
</tr>
<tr>
<td>FC2</td>
<td>7.1</td>
</tr>
<tr>
<td>FC3</td>
<td>5.5,7.0</td>
</tr>
<tr>
<td>FC4</td>
<td>6.8</td>
</tr>
<tr>
<td>AC1</td>
<td>10.0</td>
</tr>
<tr>
<td>AC2</td>
<td>5.4,9.9</td>
</tr>
<tr>
<td>AC3</td>
<td>3.7,7.2,9.7</td>
</tr>
<tr>
<td>AC4</td>
<td>5.9,9.8</td>
</tr>
<tr>
<td>MC1</td>
<td>7.2</td>
</tr>
<tr>
<td>MC2</td>
<td>7.3</td>
</tr>
<tr>
<td>MC3</td>
<td>7.4</td>
</tr>
<tr>
<td>MC4</td>
<td>7.4</td>
</tr>
<tr>
<td>HFC1</td>
<td>10.2</td>
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<tr>
<td>HFC2</td>
<td>10.0</td>
</tr>
<tr>
<td>HFC3</td>
<td>10.1</td>
</tr>
<tr>
<td>HFC4</td>
<td>9.9</td>
</tr>
<tr>
<td>FaFC1</td>
<td>9.6</td>
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<td>9.3</td>
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<tr>
<td>FaFC3</td>
<td>9.8</td>
</tr>
<tr>
<td>FaFC4</td>
<td>9.1</td>
</tr>
</tbody>
</table>

1 C=clay; F=iron hydrous oxide; A=aluminum hydrous oxide; M=manganese hydrous oxide; H=humic acid; Fa=fulvic acid.

2 Underlined values have "normal" orientations of the high and low ionic strength curves, i.e., the high ionic strength curve has a greater slope at the apparent PZSE than the low ionic strength curve. All other values are "reversed."
Because of the non-specific adsorption of hydrogen ions, the apparent PZSE's for the clay and metal hydrous oxide-clay mixtures are dependent on the CEC, the identity, concentration and ionization of exchangeable ions, the adsorptive capacity of the hydroxylated surface, and the solid-solution ratio (66). Therefore, the apparent PZSE's for these particulates are expected to be highly variable and do not represent unique properties of the surface (49, 52, 69, 83).

Results for the hydrous oxide-clay mixtures are contrary to what was expected. Adsorption of specifically adsorbable ions causes shifts in the PZSE. If these ions are adsorbed in excess, then either the surface will no longer be pH dependent or the PZSE will approach the pH(IEPS) of the adsorbed ions (50, 56, 66, 70). Whereas the manganese hydrous oxide-clay mixtures were not expected to be greatly different from pure clay due to the low quantities of manganese on the clay, both the iron and aluminum hydrous oxide-clay mixtures had enough metal adsorbed onto the surface to coat all of the clay particles. In addition, these ions would be expected to exhibit their own pH dependent charge behavior.

The results in Table 23 show that for iron, the apparent PZSE's of the metal hydrous oxide-clay mixtures are not substantially different from that for clay. In addition, the values do not approach the value for the pure metal hydrous oxide as the concentration of iron on the
For aluminum, the titration curves show an intersection point around pH 9.9 (e.g., Figure 33) which is close to the value for the pure metal hydrous oxide. However, unlike the pure hydrous oxide, all of these intersection points for the metal hydrous oxide-clay mixtures have "reversed" titration curves, i.e., the low ionic strength line has a slope which is greater than the high ionic strength line. In addition, three out of four curves had a "normal" intersection point which varied from pH 5.4 to 7.2. These values are substantially lower than the value for the pure metal hydrous oxide. Therefore, the apparent PZSE does not approach the value for the adsorbed ion for either the iron or aluminum hydrous oxide-clay particulates.

Organic Matter-Containing Particulates

Figures 34 and 35 show representative titration curves for the humic acid- and fulvic acid-containing particulates. The results for the other organic matter-containing particulates are given in Table 23. The apparent PZSE's for these particulates are reasonably constant, being approximately 10.0 and 9.5 for humic and fulvic acid particulates, respectively. However, the titration curves are once again reversed, indicating a substantial amount of non-specific adsorption. The high ionic strength curve lies below the low ionic strength curve over much of the pH range covered. This is probably
Figure 34. Apparent net proton charge density ("$\sigma_H$") versus pH for humic acid-iron hydrous oxide-clay particulates ("HFC3"). High and low ionic strength curves are represented by circles and triangles, respectively.
Figure 35. Apparent net proton charge density ($\sigma_{H}^{n}$) versus pH for fulvic acid-iron hydrous oxide-clay particulates ("FaFCl"). High and low ionic strength curves are represented by circles and triangles, respectively.
the result of greater competition for carboxylate groups at high ionic strengths than at low ionic strengths. Sodium from the ionic strength adjustor displaces hydrogen ion from the carboxylic acid groups of the organic matter. At high ionic strengths, the extent of displacement or release of hydrogen is greater than at lower ionic strengths. These extra hydrogen ions in solution result in a more negative value for the calculated net proton charge density.

These results for organic matter-containing particulates are contrary to what has been reported in the literature. Most authors have reported that adsorption of organic matter results in the development of a negative charge on the surface and a decrease in the pH(IEPS) relative to that for the particulate with no adsorbed organic matter (70, 71, 83, 146). The apparent PZSE's reported here indicate an increase relative to the apparent PZSE for iron hydrous oxide-clay particulates. In addition, these shifts in the apparent PZSE are opposite to those predicted for the development of a negative charge due to specific adsorption of ions, changes in lattice ion adsorption, and the presence of a permanent charge.

**SUMMARY**

In conclusion, the titration method for determining the apparent PZSE does not yield values which can be properly equated with the pH(IEPS) or pH(ZPC) for the particulates described in Chapter III. This non-equivalence is primarily due to interferences in the measurement from
permanent exchange capacity and the non-specific adsorption of hydrogen ions. It is doubtful whether the method yields values for the pH(ZPC) or pH(IEPS) when applied to soils and sediments, since these materials often possess substantial cation exchange capacities.
The original objective of this research was to synthesize a model particulate which would mimic natural particulates in terms of its adsorptive behavior. CEC, surface area, and the pH(ZPC) were to be used as the criteria for determining whether a model particulate simulated a natural one. It was hoped that such a model particulate could be made and, once made, could be used in sorption studies. The ability to systematically vary particulate composition and to make particulates with specified surface properties would represent a great advance in our pursuit to understand adsorptive processes. This would, in turn, contribute to our understanding of chemical speciation and, ultimately, to the factors which control biological availability of toxic chemicals.

The original objective was not met. The problem was not in synthesizing model particulates with known composition, but was due to deficiencies in the methods used in characterization. Surface area could not be measured using the adsorption of cationic dyes. The data presented herein strongly suggest that adsorption of these dyes is controlled by charge interactions between the
surface and the dye. In addition, errors in the absorbance measurement of the solution concentration of the dye proved to be substantial. These were attributed to the incomplete separation of colloids from the solution phase.

Zero point of charge measurements also proved to be deficient. Net proton charge density versus pH curves were opposite to those predicted from theory. This was attributed to the non-specific adsorption of hydronium ions.

Cation exchange capacity measurements were the only characterization measurements which appeared to be adequate for use with aquatic particulates. The model particulates showed a variety of trends, both with composition and aging. All of the pure metal hydrous oxides exhibited a decrease in CEC over time. This decrease is most likely due to an increase in crystallinity of the material. The CEC's of metal hydrous oxide-clay particulates were roughly similar to that of clay. Iron-containing mixtures showed an increase in CEC with percentage of iron, up to approximately 3% iron. Thereafter, the CEC was reasonably constant. The CEC of all aluminum-containing particles did not vary with percentage of aluminum but did increase steadily over time. These results suggested that the surfaces of aluminum hydrous oxide-clay particulates were the same in all cases. Organic matter-containing particulates exhibited an erratic increase in CEC with percentage of organic matter. The measured CEC's were
substantially higher than those for the other clay-based particulates.

The results presented here should be viewed as a preliminary attempt to synthesize and characterize multicomponent model aquatic particulates. Additional work is required. For example, the properties of particulates as a function of the method of synthesis was not investigated. Synthesis methods are likely to exert important influences over particulate properties. In addition, the adequacy of model components needs to be verified. The humic and fulvic acids used here could have been altered during the base extraction from soil. The extent of this alteration, if any, needs to be documented and kept at a minimum. The use of oxygen isotopes may prove useful in this regard. Characterization methods need to be developed in order to verify that model particulates mimic those which occur in nature. These methods must be tested rigorously to ensure their applicability to environmental samples.

The way in which model particulates are equated with natural particles also needs to be examined. The criteria used to judge whether a model particulate is similar to a natural particulate should be chosen carefully. In this respect, surface area and CEC may not be as important as some other parameters. The most important characteristics in terms of adsorption are binding capacity, binding strength, and the kinetics of adsorption. Surface area is generally correlated with all three of these
characteristics. However, it may be better to compare the relative binding strengths and capacities of two particulates rather than their surface areas. Similarly, CEC is related to the non-specific adsorption of cationic substances. However, many potentially toxic compounds are specifically adsorbed onto particulates and, therefore, would adsorb in quantities greater than the CEC. The CEC is useful as an indicator of the minimum binding capacity for cationic compounds but it is probably better to measure the adsorption capacity of the chemicals separately.

The best method(s) to equate model and natural particulates may eventually prove to be the determination of binding strength and capacity for a variety of cationic, non-ionic, and anionic compounds. In this respect, the fluorescence method for determination of the solution concentration of an adsorbate would be the method of choice. Fluorescence measurements were clearly superior to absorbance measurements for the pyronin Y-clay system. The extension of the applicability of this method should be pursued. In addition, the adsorption of various fluorescent compounds could be used to model adsorption of toxic substances. Pyronin Y, for example, should be a reasonable model for the cationic pesticides paraquat and diquat. The use of non-toxic fluorescent compounds as models of toxic chemicals avoids exposure to the latter. In addition to pyronin Y, similar systems based on anionic and non-ionic fluorescent compounds could be developed. The investigation
of the fluorescence method in conjunction with competitive binding of a non-fluorescent adsorbate would also be worthwhile.

The usefulness of model particulates has been demonstrated in connection with the variation in CEC as a function of composition and aging. In addition, model particulates should be useful in testing various environmentally related analytical procedures, such as selective extraction techniques. The data contained herein for iron and aluminum hydrous oxide-clay particulates were inconclusive due to potential interferences in the atomic absorption determination of these metals. However, the data for manganese suggested that the extraction was complicated by cation exchange processes. Model particulates, in which the amount of metal on the particle is known, could be used to test and improve available extraction techniques.

Several other aspects of the data have important implications. For example, the adsorption of methylene blue and pyronin Y on clay increased as the ionic strength increased, whereas the adsorption of hydronium ions decreased with increasing ionic strength. This differing dependence on ionic strength between specifically and non-specifically adsorbed cations has important implications in regard to environmental processes which occur in an estuary. The solution concentrations of specifically adsorbed toxic substances would be expected to decrease when rivers enter an estuarine system whereas the
solution concentrations of non-specifically adsorbed chemicals would be expected to increase. The deposition of specifically adsorbed toxic substances occurs at the same time that humic materials are precipitated out of solution. These humic substances could act to preserve any deposited toxic chemicals either by adsorption or by causing the bottom sediments to become anaerobic. Therefore, the persistence of toxic chemicals may be greatly enhanced as a result of these processes.

Finally, the titration method for determining the pH(ZPC) probably has extremely limited applicability to natural systems. Uniform terminology which is carefully defined needs to be adopted. In addition, the results presented herein should serve as a warning that extension of methodology from relatively simple systems to environmental samples is fraught with difficulties and should only be done with extreme caution.


