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Kathleen M. Polgar
University of Massachusetts Amherst

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RELATIVE IMPORTANCE OF MANGANESE AND IRON OXIDES IN COBALT ADSORPTION

A Dissertation Presented
by
Kathleen M. Polgar

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RELATIVE IMPORTANCE OF
MANGANESE AND IRON OXIDES IN COBALT ADSORPTION

A dissertation

by

Kathleen M. Polyar

Approved as to style and content by:

J.H. Baker

(John H. Baker), Chairman of Committee

Ronald D Archer

(Ronald D. Archer), Member

(Mack Drake), Member

Martin E. Weeks

(Martin E. Weeks), Member

F.W. Southwick

(Franklin W. Southwick), Department Head

September 1975

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Abstract

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September 1975

Kathleen M. Polgar
Ph.D., University of Massachusetts

Directed by: Dr. John H. Baker

Fixation of heavy metal ions by soil components has been observed since the earliest use of micronutrient fertilizers. Multiple evidence indicates that oxides and hydrous oxides of manganese and iron are active adsorbents of cobalt and other metal ions of the first transition series. Knowledge of the behavior of various manganese and iron oxides in cobalt adsorption is necessary to understand the influence of such oxides on cobalt chemistry in soils.

Cobalt(II) adsorption by five manganese and two iron oxides was measured as a function of pH and cobalt concentration and related to properties of the minerals such as chemical composition, surface area, crystallinity and point of zero charge (PZC).

Manganous manganite, Mn_3O_4, amorphous $Fe(OH)_3$ and $\gamma FeOOH$ were prepared as hydrated suspensions, while MnO_2, Mn_2O_3 and Mn_3O_4 were prepared as dry solids. The minerals were identified by X-ray diffraction. The PZC of the minerals prepared as

hydrated suspension determined (±0.5 pH unit) by potentiometric titration and turbidity measurements were 1.9, 7.0, 8.3 and 6.1 respectively. The PZC of minerals, prepared as solids, evaluated (within ±0.5 pH unit) by observing positive and negative adsorption of K^+ as function of pH and found to be 7.1, 6.9 and 5.9 respectively. The surface area of manganous manganite, amorphous $Fe(OH)_3$ and $\gamma FeOOH$ as determined by BET on freeze-dried samples was about 200 M^2/g. The surface area of MnO_2, Mn_2O_3 and Mn_3O_4 as measured by BET and negative adsorption of K^+ was approximately $50 m^2/g$.

Under the experimental conditions employed (100 $m^2/1$ substrate, $5x10^{-5}$, 10^{-4}, $5x10^{-4}$ M initial Co^{2+} concentrations, 22-26 C°) cobalt adsorption from aqueous solution by all of the minerals increased with increasing pH and each mineral had a characteristic pH range in which adsorption increased rapidly until all the added cobalt was adsorbed. Oxides prepared as hydrated suspensions adsorbed cobalt at lower pH values than the coresonding oxides prepared as solid materials and generally the adsorption capacity of amorphous minerals was greater than that of their more crystalline counterparts. The specific surface of a mineral was the most important factor determining the amount of cobalt adsorbed per unit weight. The PZC of a mineral was not a sole factor determining the pH at which the mineral began to adsorb cobalt, but with the exception of manganous manganite and amorphous $Fe(OH)_3$, cobalt adsorption began at a pH near the PZC. Cobalt adsorption by amorphous $Fe(OH)_3$ began 2 pH units below the PZC indicating specific adsorption. Cobalt adsorption of manganous manganite did not begin until the pH was 3.2 units above the PZC indicating that possibly H_3O^+ ions compete with $[Co(H_2O)_6]^{2+}$ for double layer sites.

All of the manganese and iron oxides studied were about equally effective cobalt adsorbents if the pH was in their adsorption range and cobalt adsorption was not an exclusive property of any mineral. However, manganous manganite was the only mineral studied that could be effective in cobalt adsorption in acid soils with pH values below 6 where amorphous $Fe(OH)_3$ began to adsorb cobalt.

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CHAPTER I

INTRODUCTION

Cobalt, a component of Vitamin B_{12}, is essential for all animals. This is a relatively recent discovery, however, geographically related problems in animal health, such as poor growth and high mortality were known since colonial times in the eastern part of the United States. (Kubota, Allaway 1971). The first scientific evidence that linked disease in sheep and cattle to cobalt deficiency came from an investigation conducted in 1937 in Australia. The role of cobalt in ruminants, however, is not limited only to the synthesis of Vitamin B_{12}. When a perennial grass "phalaris tuberosa" is present in the diet, the cobalt requirement of cattle and sheep is raised significantly. Specifically, cobalt is needed to inactivate the neurotoxin of the above grass; Vitamin B_{12} was found ineffective. (Lee and Kuchel, 1953, Underwood, 1966) Davis, Jack and McCalls (1956) found, that a high level of molybdenum in the cattle ration prevents the synthesis of Vitamin B_{12} by rumen microflora. The inhibiting effect of molybdenum can only be overcome by an increased amount of cobalt. In addition, symbiotic bacteria of legume roots require cobalt for the fixation of atmospheric nitrogen. The cobalt requirement for this system is very low and cases of poor legume growth related to deficient cobalt have been reported only in Australia. (Kubota, Allaway 1971).

The fact that problems of animal disease and suboptimal plant growth are associated with a geographic region immediately connects both animal and plants to the soil. Under favorable conditions mineral deficiencies in soils are corrected by the use of fertilizers. Effective fertilizer application requires knowledge of soil composition, the significance and nature of mineral species and the reactions that occur between mineral surfaces and micronutrients. Multiple evidence indicates that oxides and hydrous oxides of iron and manganese are the active adsorbents of cobalt and other metal ions of the first transition series. Both manganese and iron oxides are common in soils and sediments. The prevalence and sensitivity of the above mineral species to changes in pH and oxidation potential enables them to control the metal ion distribution between the aqueous phase and the soil matrix. The geochemistry of cobalt, zinc, nickel, copper, manganese and iron is sufficiently similar that these elements, as a group, are designated here as micronutrients and heavy metals.

This research work was focused upon the preferential adsorption of cobalt by seven manganese and iron hydrous oxides as function of pH. Although the surface area of hydrous oxides in soils is unknown, the surface area of hydrous oxides and the concentration of cobalt, used in this study, may also be encountered in natural environments. The manganese and iron oxides as adsorbents in hydrated suspensions were selected for this study because these minerals are prevalent in the environmental systems and cobalt was chosen because it is an important plant and animal nutrient.

CHAPTER II

REVIEW OF LITERATURE

1. Cobalt deficient soils in the United States

In the northern United States potentially cobalt deficient areas extend from as far west as Wisconsin to Maine on the east coast. Other low cobalt areas occur on the Atlantic Coastal Plain and in Florida (Becker, Erwin and Henderson, 1946).

In the New England states a continuous low cobalt area extends from the Saco River in Maine to the Merrimac River in New Hampshire. A low cobalt area also starts south of Boston and extends to Rhode Island and Cape Cod. Soils of both areas were formed from granitic drifts and deposits predominantly from the White Mountains. However, in southeastern Massachusetts the low cobalt soils were formed on deposits of Dedham grandiorite and associated rocks. Sandy soils on Cape Cod and along the coast have partly glacial and partly marine origins (Kubota, 1964).

The geographical distribution of micronutrients in soils appears to relate most closely to the composition of the parent material. Cobalt deficiency problems related to parent material are most prevalent in soils developed on granitic till and outwash. Schist, composed of metamorphic sediments, contains a greater concentration of cobalt and other heavy metals than granites. Dark colored soils of Rhode Island, derived from slates and phyllites, probably inherited their character and high available cobalt from the parent material.

Krauskopf (1956) observed that the distribution of cobalt follows closest the distribution of magnesium in igneous rocks. He estimated about ten times as much cobalt and zinc in shales as in sandstones. Carbonate rocks may have 1-10% of all the cobalt found in the earth's crest. Although broad generalizations cannot be made about how the concentration of micronutrients changes during the weathering process, residual soils formed from parent material containing limestones and dolomites usually have relatively high total cobalt and other micronutrient contents. (Hodgson, 1963). In order to explain the greater concentration of cobalt and other micronutrient metals in sedimentary rocks, Hodgson (1963) suggested that redistribution of micronutrients occurs during the sedimentation process when formation of hydrolyzed aluminum silicates is thought to occur. He reasoned that metal ions released would be readsorbed on developing surfaces and then become occluded or isomorphously substituted in the newly formed mineral species. As the final result, cobalt and other micronutrients would become concentrated in the clay and silt fractions of sediment.

A general decrease in cobalt content was observed by

Kubota (1964) as soil texture becomes sandier. Fine textured soils of the same origin apparently had more of cobalt bearing minerals than coarse, sandy soils. Pyrite (FeS_2) pyrrhotite Fe_xS_{x+1}, chalcopyrite ($CuFeS_2$) and sphalerite (ZnS) which also contain cobalt are thought to be the principal cobalt bearing minerals in New Hampshire granites. Consequently, the same cobalt bearing minerals may be present in all textures of soils formed from the White Mountain granites (Kubota, 1963). Thus, soil texture alone is not adequate to predict the cobalt status of soils. Information about the probable origin of the parent material is also needed. It is likely that a coarse textured soil of high cobalt content has a high level of inherited cobalt and in the absence of other effects, soils of low cobalt content inherited a low cobalt concentration from the parent material.

An important factor that alters the micronutrient status of soils is leaching during the podzolization process. In soils of the Entisol and Spodosol groups, the surface horizons have about 2/3 as much cobalt as the underlying B horizons. The loss of cobalt during leaching is indicated by the generally larger amount of cobalt found in the horizons of alluvial soils. Therefore inherited and acquired cobalt deficiency can be differentiated. Inherited cobalt deficiency results from the lack of cobalt bearing minerals in parent material, acquired cobalt deficiency develops during the soil forming processes.

Kubota (1964) found that some degree of cobalt deficiency is associated with Entisols and Aquods in the northeastern part of the United States. Ultisols and Homaquods of southeastern United States generally have low or extremely low cobalt contents. Sand or sandy textured soils in these groups have lower cobalt content than soils that have a finer texture. The coarse textured soils in cobalt deficient areas usually have a low inherited cobalt level and the podzolization process would lower further the cobalt status in these soils. The Aquods and Humaquods of the southeastern United States are nearly stripped of all reactive forms of cobalt. The extremely low cobalt content of these soils may reflect the fate of cobalt in the podzolization process. In Aquods water has leached out all reactive form of cobalt; in Humaquods the presence of humus may have increased further the solubility of micronutrients and practically all forms of inherited cobalt have been removed.

Cobalt contents of soils and plants from representative areas of the northeastern and southeastern United States were measured by Kubota (1965). The cobalt content of soils and indurated aggregates seemed to be related to the iron content. Maximum iron and cobalt were found in the lower

B horizon (of most soils), but where the recycling effect of plants was important, cobalt content in the surface horizon increased. The black gum tree, a cobalt accumulator, increased the cobalt content in the surface horizon more effectively than other deep rooted shrubs and trees (Kubota, 1965).

In some Ultisols maximum cobalt concentration was found in a deeper horizon than maximum iron concentration. Kubota (1965) suggested that movement of cobalt may indicate a relatively greater stability of cobalt chelates compared to those of iron. Kubota (1965) also suggested that iron independent cobalt accumulation may have resulted from wind transported silt and clay from cobalt rich soils. Deposits of such cobalt rich particles may cover a comparatively large geographical area. The transported silt and clay incorporated into the surface horizon could result in increased cobalt content which is not followed by an increase in iron.

Both soil and plant analysis are essential in the studies of micronutrient deficiencies. Higher cobalt content was found in red clover grown in soils of high cobalt content than in the same plant grown in cobalt deficient soils in New England, but five fold increase of cobalt in soils resulted in only a two fold or less increase of cobalt in plants (Kubota, 1964). The deep red soils on tertiary basalt in Tasmania (Australia) are high in cobalt but plants can utilize very little or none of the cobalt. Even $CoSO_4$ fertilized soils produced cobalt deficient clovers. These soils have high manganese and iron content and added cobalt is rapidly converted to forms unavailable to plants. Only the poorly drained sites provided sufficient quantity of cobalt for plants (Leeper, 1970).

2. The roles of soil components in the cobalt adsorption.

Where areas of definite cobalt deficiency are well known, different methods have been used to alleviate the problem. However, there are also lands on which the cobalt status is marginal and difficiency is quite sporadic. Where a land of marginal cobalt status is used for agricultural production or for intensive grazing, regular application of cobalt fertilizer is required. For reasons of convenience and economy under suitable environmental conditions, cobalt deficiency is controlled by supplementing the phosphate or nitrate fertilizer with cobalt salts.

Pot experiments of Nicolls and Honeysett (1964) indicated that a very small amount of applied cobalt was taken up by plants from krasnozem and red-yellow podzolic soils.

Adams, Honeysett, Tiller and Norrish (1969) noted that effectiveness of cobalt fertilizer was a function of the manganese content of the soil.

Soil constituents controlling the availability of essential elements were investigated by many researchers. To understand the soil chemistry of micronutrients, the knowledge of the reaction type which predominates the controlling process is also necessary. Unfortunately, it is beyond present technology to follow the chemical behavior of each individual mineral species in the soil and the overlapping reactions that occur between metal ions and mineral surfaces. There is no clear distinction between surface adsorption and surface precipitation and in ion fixation the distinction between surface adsorption and solid state diffusion is mostly a matter of definition (Hodgson, 1963).

Numerous theories have been developed to interpret the roles and significance of various soil components in the controlling process of heavy metal ion concentration in soil solutions and in natural waters.

A. Role of layer silicates

It was proposed in early studies that layer silicates as main soil constituents are also the main adsorbants of cobalt and other heavy metal ions. Ion exchange, solid state diffusion and surface complex ion reactions were studied as possible adsorption mechanisms (Elgabaly, 1950; Elgabaly and Jenny, 1943).

Cailliere, Henin and Esquerin (1958) incorporated cobalt, copper and zinc into octahedral position of silicates. They concluded that the relatively open structure of layer silicates does not prevent solid state diffusion.

Hodgson (1960) studied cobalt adsorption by montmorillonite in 0.1 M $CaCl_2$ solution. He found that the reaction had a slow rate and adsorbed cobalt was not replaced by

Ca^{2+}, Mg^{2+}, K^+, Na^+ or NH_4^+. Cobalt unextractable with acetic acid was considered fixed. In all soils investigated the fixed fraction of cobalt was quite small compared to the total amount of cobalt adsorbed; furthermore, similar adsorption capacities were found for kaolinite, talc and montmorillonite.

Complex ion formation involving acetate and chloride as a cause of metal ion fixation was also investigated to some extent in the early literature (Elgabaly, 1950; Menzel and Jackson, 1950). Page and Whiting (1961) then Bingham, Page and Sims (1964) proved that a fairly high anion concentration is required for significant complex ion formation.

B. Role of $CaCO_3$

Piper (1942) then Leeper (1953) reported zinc, manganese and other micronutrient deficiencies in some calcareous soils. It raised the possibility that carbonates as soil constituents may be responsible for adsorption and fixation of micronutrients. In the adsorption process heavy metal ions were thought to occupy sites which normally are taken by calcium and magnesium.

Beeson, Gray and Hammer (1948) found that when $CaCO_3$ was added to soils the availability of inherited cobalt was not changed. Uptake of supplemented cobalt by plants decreased slightly upon $CaCO_3$ application.

Brown and Jurinak (1964) observed only a very small adsorption of cobalt and zinc by $CaCO_3$.

Jenne (1968) assumed, that the slight decrease in availability of heavy metals caused by $CaCO_3$ was mainly the effect of pH and HCO_3^- on the solubility of heavy metal oxides.

C. Role of organic matter.

The role of organic matter in the reactions of micronutrients has been the subject of investigation for a long time. When organic matter decomposes, inorganic ions are released, compounds dissolve, and elements are oxidized or reduced in response to changes in oxidation potential and pH. Organic matter is the soil component most frequently considered responsible for the overall control of heavy metal ions in soils.

The direct effect of organic matter on the availability of micronutrients is important in organic and in calcareous soils, because in both soils organic complexes may control partly the heavy metal ion concentration in soil solution. The direct effect of organic matter on cobalt availability is relatively small. As yet components of organic matter responsible for cobalt fixation in soils have not been identified. Experimental results (Kubota, 1965) indicate that addition of organic matter to soils was followed by an increase in extractable cobalt. Studies on cobalt chelated with fulvic acids show that these complexes are quite stable under laboratory conditions (Schnitzer, 1963). If they are also stable in soils, then any organic matter that provides these or other sufficiently stable chelating agents will increase the soluble cobalt content.

In contrast to total cobalt, dithionite extractable cobalt, classified as available cobalt, was found to be maximum in the surface horizon of some podzols (Kubota, 1965). The surface horizon usually has a higher organic matter content than the B or C horizons, therefore, the presence of organic matter seems to increase the availability of cobalt in these soils (Kubota, 1965). A chelate, which may keep some concentration of cobalt in soils is Vitamin B_{12}. This very stable, high molecular weight chelate is water soluble, non-exchangeable with Co^{2+}, but the complex is utilized by plants as Gray and Daniel (1959) reported.

The addition of organic matter to soils generally increases the solubility of heavy metal compounds although utilization of metal ions by plants does not necessarily increase. Gulyakin and Yudintsheva (1960) (reported by Hodgson 1963), found a reduced cobalt uptake by wheat, peas and oats when organic matter was added to soils.

Organic matter may have an indirect effect on cobalt availability through its direct effect on the solubility of manganese and iron minerals.

Fermented or aged leaf extracts, decomposition products of plant residue were found to reduce Mn^{4+} and Fe^{3+} ions. Bloomfield (1953) demonstrated that root exudates and leaf extracts dissolved ferric oxides and Fe^{2+} ions were complexed by the organic chelates. The Fe^{2+} organic matter complex was sufficiently stable to be separated from ionic Fe^{2+} by cation exchange column. The pH in this experiment was 7, therefore, dissolution of iron oxide was not a simple pH effect. The ferrous complex readily reoxidized when it was brought into contact with air and ferric oxide (Gasser and Bloomfield, 1955). The experiment gave the same results in presence of cell poison therefore the reduction and dissolution of iron mineral was not a microbial effect.

An indirect but also important influence of organic matter is enhanced microbiological activity and the subsequent change in pH and oxidation potential which profoundly alters the availability of all micronutrients.

Manganese is the element most sensitive to microbial activity. There are indications that microbiological processes control the oxidation states of manganese in soils through their effect on the oxidation potential and pH (Hodgson, 1963).

The first evidence that soil microorganisms can oxidize Mn^{2+}

came in 1913 (Hodgson, 1963). Broomfield (1954) identified five bacteria and two fungi capable of producing MnO_2 from $MnCO_3$ in agar. In well aerated acidic soils fungi and in the neutral or alkaline soils bacteria can convert manganous compounds to MnO_2. According to Gerei, Mate and Benedek (1960) microbiological activity also contributes to the formation ferruginous and manganiferrous nodules and concretions.

The availability of iron also varies with microbiological activity although the change is more complex. Mandal (1961) observed that more iron than manganese dissolved in submerged soil when green foilage was present. In the absence of organic matter very little iron and much manganese dissolved.

Tiller and Hodgson (1962) reported that organic matter had no effect on cobalt adsorption by subsoils.

In a continuous flow apparatus, designed to prevent any subsequent readsorption of the released metal ions, Hodgson (1960) attempted to determine cobalt and copper associated with the soil organic matter. He found that certain subsoils, practically free of organic matter, released substantial amounts of cobalt and copper upon H_2O_2 treatment. Therefore the released cobalt and copper probably were immobilized by some soil constituent other than organic matter.

A factor that has overall importance in the availability and immobilization of cobalt is soil drainage. Acetic acid extractable cobalt and copper in poorly drained soils was higher by a factor of ten than that in well drained soils (Mitchell, 1964). Hodgson (1963) considered the effect of drainage on cobalt to be the result of increased microbiological activity rather than direct oxidation of cobalt.

Oxidation of Co^{2+} aquacomplex is a large energy requiring process. In the presence of moderate or high field ligands though, the transformation is considerably easier or the process may even become spontaneous. For example, emf's of several cobalt complexes are given by Huheey (1972):

$$Co^{3+}(H_2O)_6 + e^- \rightleftharpoons Co^{2+}(H_2O)_6 \quad E° = +1.84$$

$$Co^{3+}(NH_3)_6 + e^- \rightleftharpoons Co^{2+}(NH_3)_6 \quad E° = +0.10$$

$$Co^{3+}(en)_3 + e^- \rightleftharpoons Co^{2+}(en)_3 \quad E° = -0.26$$

$$Co^{3+}(CN)_6 + e^- \rightleftharpoons Co^{2+}(CN)_5 + CN^- \quad E° = -0.85$$

In the absence of moderate or high field ligands, the conversion of Co^{2+} to a low spin Co^{3+} complex requires such a strong oxidizing condition that is unlikely to occur in normal soil environment. The possibility of catalytic oxidation of Co^{2+} on the surfaces of manganese minerals and the ultimate fixation of cobalt by solid state diffusion was discussed by McKenzie (1971, 1967) and Murray, Healy and Fuerstenau (1968). A more detailed understanding of processes that occur in well and poorly drained soils is necessary to explain the unusually large effect of drainage on the availability of cobalt.

D. Role of manganese and iron oxides

Adsorption studies with various metal ions and a variety of metal oxide substrates indicate that the adsorption of each metal ion is a function of the metal ion concentration and pH as well as the physical and chemical properties and the quantity of substrate. Consequently, adsorption from a solution of given concentration at fixed pH depends on the nature and the quantity of substrate. The most important substrate variable are: the surface area which relates to quantity and the point of zero charge which reflects all aspects of the solid composition, structure and the composition of the electrolyte solution in which the substrate is suspended.

Oxides and hydrous oxides in aqueous solution show ion exchange properties which arise from their pH dependent surface charge. In general under alkaline conditions, they have a negative surface charge and exchange cations and in acidic environment they have positive surface charge and exchange anions.

When the surface is uncharged, exchange capacities of oxides and hydrous oxides are very small for both cations and anions.

When a solid oxide is immersed in water, sites where the metal ions had incomplete coordination,become hydroxylated, and a coherent water layer also develops about the entire surface of the particle.

On a hydroxylated surface, charge can develop by dissociation (Parks, 1967)

$$\begin{aligned} MOH &\rightleftarrows MO^- + H^+ \\ MOH &\rightleftarrows M^+ + OH^- \\ M^+ + H_2O &\rightleftarrows MOH_2^+ \\ MOH + H^+ &\rightleftarrows MOH_2^+ \end{aligned}$$

Proton dissociation produces a negative surface; proton addition, which is equivalent to OH^- dissociation, produces a positive surface.

On a solid surface which carries a charge in aqueous solution an electrical double layer forms about the particle. The electrical double layer consists of a fixed layer of ions held at a short distance from the charged surface and a diffuse layer of ions in a small volume about the particle. Ion distribution between the fixed and the diffuse layer and also, that between the double layer and the bulk of the liquid are studied and well documented subjects.

In all mechanisms of charge formation, ions that establish the surface charge and the oxide-hydroxide electrode potential are the potential determining ions. Obviously, for such systems both the concentration of potential determining ions and the surface charge are pH dependent. If only H^+ and OH^- are the potential determining ions, the pH at which the solid particles carry no net charge, is the zero point of charge (ZPC).

The true point of zero charge can only be measured in systems where the interaction is limited to H^+, OH^- and the solid. Condition for measurement of a true point of zero charge allows the presence of Na^+, K^+, ClO_4^-, NO_3^- and perhaps that of Cl^-. (Parks 1967).

The surface charge for a reversible double layer where H^+ and OH^- are the potential determining ions is given by the equation; (Parks and DeBruyn, 1961):

$$\alpha = F\,(\Gamma_{H^+} - \Gamma_{OH^-})$$

α = surface charge density,

Γ = adsorption densities of potential determining ions

F = Faraday constant

The potential difference $\Psi_\circ$ across the double layer is equal to

$$\Psi_\circ = \frac{RT}{F} \ln \frac{H^+}{H^+_\circ}$$

R = ideal gas constant

T = temperature °K

H^+ = activity of H^+ ions

$H^+_\circ$ = activity of H^+ ions at the point of zero charge

Or, $\Psi_\circ = 0.059\ (pH_{zpc} - pH)$ volt at 25°C.

This relationship is valid only in the absence of any specific interaction between the supporting electrolyte and the solid. The $H^+_\circ$ or ZPC can be determined by potentiometric titration or by other methods which measure any property that depends on the presence of the electrical double layer. Thus, absence of suspension effect between the settled suspension and the supernatant solution may be used to evaluate the point of zero charge if specific adsorption is not important.

All ions have some tendency towards specific adsorption. It was reported that the positive charge density on hematite, in NO_3^- and ClO_4^- solutions, is independent of electrolyte concentration but it is considerably higher on hematite than on SiO_2 or Al_2O_3. (Berube and DeBruyn, 1968). The NO_3^- and ClO_4^- ions appear to be closer packed on hematite than on silica or aluminum oxide. The positive charge densities on ZrO_2 and on ThO_2 vary with both H^+ and with the electrolyte concentration in ClO_4^- , NO_3^- and Cl^- solutions (Ahmed, 1969). A similar behavior was observed with hematite and SnO_2 in Cl^- solutions. The above deviations from ideal behavior were attributed to specific adsorption of anions at the surface involving substitution of NO_3^-, ClO_4^-, and Cl^- for OH^- groups. The point of zero charge of ZnO also showed a remarkable dependence on the nature of the supporting electrolyte. This material gave a consistently higher point of zero charge (8.8 - 10.0) in $NaNO_3$ than in NaCl (8.5) Blok and DeBruyn, 1969). The negative charge density on Al_2O_3 increased with OH^- as well as with increasing K^+ concentration (Ahmed, 1969).

When specific adsorption is important, the observed point of zero charge is shifted to higher or lower pH values according to the specifically adsorbed species. Specifically adsorbed ions or molecules can reverse the charge on the solid. Hydroxy complexes of multi-valent metal ions, acting as coagulants, must be adsorbed specifically. By knowing the hydrolysis constants one can predict the pH range in which each species adsorbs strongly. The most effective ions in flotation and coagulation experiments usually are the $[M^{n+}(OH)_{n-1}]^{+}$ species (Parks, 1967). Therefore the point of zero charge as a variable shows the composition, the history and the whole surface chemistry of a solid. Variation in the preparation techniques of the solid or any change in concentration of the reacting compounds, including partial oxidation or reduction that result in structural defects all shift the point of zero charge. Dehydration, dehydroxylation, increased crystallinity and long exposure to strong acidity shift the point of zero charge to lower pH values (Parks, 1967).

The various oxides and hydroxides, prevalent in soils, concretions and sediments are carriers of the pH dependent surface charge. They adsorb ions in response to the pH and oxidation potential to the environment; adsorption capacity of the individual species depends on the surface area, the point of zero charge, and crystalinity. The manganese and iron oxides and hydroxides tend to attach to mineral surfaces as coatings and partial coatings; therefore, their reactivity and influence may be far greater than their relative concentration. It is generally thought, that the hydrous oxide coatings are mostly amorphous (Jenne, 1968).

Six variations of iron oxides have been identified in soils (Brown, 1953) but their formation and mineralogical conversion is not adequately defined. Hodgson (1963) reported 34 mineralogical variations of manganese oxides in soils but Ponnamperuma (1969) quoted that 150 modifications were described with composition of $MnO_{1.2}$ - $MnO_{2.0}$. The various oxides of manganese show strong tendency to form coprecipitates with other heavy metals. Morgan and Stunm (1964) characterized the manganese oxides as solid electrolytes with various amount and kind of cations and anions located in the lattice structures.

Birnessite is the first oxidation product of weathered carbonate rocks (Ponnamperuma, 1969) and a component of soils and concretions. Taylor, McKenzie and Norrish (1964) reported cobalt concentrations in birnessite and lithiophorites. Birnessite is the natural modification of manganous manganite (Bricker, 1965) and δ MnO_2 while lithiophorite is an ill-defined double layer manganite associated with substantial amount lithium and aluminum. Ponnaperuma (1969) suggests that in flooded soils at pH = 6.5 - 7.0, E_h = 0.2 and P_{CO_2} = 0.05 - 0.1 atmosphere, MnO_2 and Mn_2O_3 are stable as solid phase. In well aerated soils MnO_2 is the most stable modification, however at E_h lower than 0.17 or Pco_2 higher than 0.1 atmosphere both Mn_2O_3 and Mn_3O_4 are stable as solid phases.

In soils, the manganese oxides are characterized by both mineralogical and solubility tests (Hodgson, 1963). Dion and Mann (1947) recommended the use of hydroxylamine hydrochloride solution and related the solubility of different modifications to the availability of manganese in soils for plants. In their experiment pyrolusite was reduced more easily than manganite or hausmannite. Jones and Leeper (1951) found that oats utilized pyrolusite and manganite but no hausmannite. The hausmannite had a higher degree of crystallinity than the other minerals in this group; consequently the reduced solubility and availability of this mineral species may have been the effect of crystallinity.

Both manganese and iron oxides actively participate in many processes that occur in soils.

Kurbatov (1945) observed that fresh iron hydroxide precipitate adsorbed equal amounts of Sr and Ba when the precipitation occurred in the presence of either ion or when the precipitate was added to either Sr or Ba. This experiment indicates that the occlusion of metal ions may be either coprecipitation or adsorption.

Hydrous oxides of manganese and iron also participate in some catalytic reactions.

Gasser and Bloomfield, (1955) reported that natural organic matter chelated Fe^{2+} oxidized to Fe^{3+} on ferric oxide surfaces in the presence of air. Oxygenation of sludge removed Fe^{2+} more effectively from the solution than aeration.

Jenne (1968) interpreted the above effect as the catalytic action of colloidal iron oxide rather than the effect of Fe^{3+} ions.

Mehlich (1957) observed the oxidation of Mn^{2+} in the presence of fresh iron oxide precipitate at pH = 5.8. When the precipitate is not present, the oxidation occurs at a pH higher than 8.

Zapffe(1931) found that both Fe^{2+} and Mn^{2+} were oxidized and precipitated on pyrolusite surfaces.

Follett (1965) reported that colloidal iron oxide readily adhered to clay mineral surfaces. Taylor, McKenzie and Norrish (1964) observed ferruginous material on the outer surface of birnessite. Lithiophorite was coated with goethite and the hematite. Yarilova [quoted by Hodgson (1963)] measured

ΔE_h per unit pH in soils close to a theoretical value for the reaction

$$MnO_2 + 4H^+ + 2e^- \rightleftarrows Mn^{2+} + 2H_2O$$

When the pH and oxidation potential of the soils are low, as they usually are in poorly drained soils, reduction and dissolution of manganese and iron oxides are in progress. Heavy metal ions adsorbed by the oxides of manganese and iron will also be released into the aqueous phase. As the pH and the oxidation potential rise in the soil, oxidation and precipitation of hydrous oxides start, heavy metal ions may be removed from the solution by adsorption or coprecipitation and occluded into the solid phase. Most soils that are seriously deficient in cobalt and other micronutrients are deficient in manganese and iron as well.

Numerous authors reported, that cobalt, zinc and manganese uptake by plants became seriously reduced when the soil pH increased from 5.8 to about 6.5 (Mitchell, 1957 Crooke, 1956). A further increase of pH up to 7 had little effect on the cobalt uptake. Jenne (1968) interpreted the critical nature of pH - 6-6.5 as the oxidation process of Mn^{2+} to Mn^{4+} catalyzed by the manganese and iron oxides.

The occlusion of cobalt in manganese and iron minerals has been the subject of interest for a long time and investigated by numerous authors. There is no conclusive evidence though whether manganese or iron minerals are the more effective adsorbents of cobalt.

a. Evidence for cobalt adsorption by manganese oxides.

Kee and Bloomfield(1961) reported that while copper and zinc coprecipitated with iron, cobalt, nickel and manganese showed no tendency toward coprecipitation.

Pierce (1964) found no cobalt in iron oxides even in association with manganese oxides.

Jenne and Wahlberg (1965) observed that cobalt concentration was related to manganese and not iron contents in stream sediments.

Taylor and McKenzie (1966) determined cobalt, nickel and zinc contents in 66 samples of soils and concretions. Only a few samples indicated some relationship between cobalt and iron contents, but the relationship between cobalt and manganese contents was excellent in almost all soil samples.

Fleischer (1943) reported that cobalt is associated mainly with lithiophorite (Li, Mn aluminate), cryptomelane (K containing Mn mineral), psilomelane and hollandite, (Ba containing minerals). All samples of lithiophorite had about 5% cobalt content.

McKenzie (1971) studied cobalt fixation by cryptomelane, birnessite and pyrolusite. He found the maximum cobalt adsorption by birnessite and the lowest by pyrolusite at pH = 4.0.

Fukai (1966) observed 20% adsorption of total cobalt in 1 liter sea water by 10 mg MnO_2. Krauskopf (1956) reported a more rapid heavy metal uptake by microcrystaline MnO_2 than by iron oxide.

Boyle (1966) found manganese rich sediments rich in lime, cobalt and nickel. Murray, Healy and Fuerstenau (1968) reported both specific and non-specific adsorption of cobalt by manganous manganite 10Å.

b. Evidence for cobalt adsorption by iron oxides.

Electron microprobe studies showed the presence of cobalt in iron rich nodules of ocean floor. Burns' (1965) free energy calculations indicate that Co^{3+} as an isomorphous pair with Fe^{3+} may be present in the amorphous $(Fe,Co)OOH.nH_2O$ mineral. Co^{2+} oxidation to $Co(OH)_3$ is possible in certain marine environments. If Co^{2+} concentration is 1.3×10^{-8}M or higher in the sea water, the oxidation process is feasible. A suitable marine environment may be in the neighborhood of basaltic islands of the central Pacific Ocean.

Tiller and Hodgson (1962) found that clay size hematite adsorbed and fixed similar quantities of cobalt as other clay minerals. Nontronite, an analogue of montmorillonite, fixed ten times as much coablt as montmorillonite. Nontronite also has a considerable amount of free iron oxides.

Fujimoto and Sherman (1950) found cobalt concentrated in well developed and in incipient ferrugiuous layers of Hawaiian soils. Hill and Toth (1953) reported accumulation of cobalt and iron in the B horizons of podzols. Kubota (1963) found almost as much cobalt as iron in some soil concretions. Trautmann [reported by Jenne (1968)] observed, "$Fe(OH)_2$ can take up to 50% cobalt in solid solution, the unit cell dimension increasing linearly with increasing cobalt substitution".

Kubota (1958) found a closer relationship between cobalt and clay than between iron and clay. This study suggests that iron oxide coatings present on clay particles may be more effective cobalt adsorbants than are the concretionary iron oxides.

Some B horizons of podzols are enriched with iron oxides but not enriched with other heavy metals noted LaRichie and Wein, (1965). Possibly soluble phosphorous compounds, silica and organic matter slowed down goethite and hematite formation from amorphous iron oxide and inhibited heavy metal adsorption as well.

Reddy and Mehta (1961) reported a good relationship between cobalt and iron contents in soils. Gonzales and Garcia then Burriel and Galego [reported by Jenne (1968)] found a good relationship between cobalt and iron but a poor one between cobalt and manganese and iron oxides scavenged cobalt, nickel and copper in solution.

Burns and Fuerstenau (1966) reported that in ocean floor nodules, copper and nickel are concentrated in high manganese content areas; cobalt is concentrated in high iron content areas.

The adsorption of cobalt and other heavy metal ions by different species of manganese and iron oxides are different and they vary with varying conditions in soils. Therefore, results are often controversial. In several studies good correlations have been found between cobalt and iron, in other studies cobalt is clearly associated with manganese oxides. The purpose of this work is to

1. compare the effect of pH on the adsorption of cobalt by selected manganese and iron oxides,

2. characterize the cobalt adsorption in terms of mineral properties,such as, surface area, point of zero charge, crystallinity and various oxidation states of manganese present in the manganese oxides and

3. relate the above results to Massachusetts soils analyzed within this work.

CHAPTER III

DESCRIPTION, PREPARATION, IDENTIFICATION, DETERMINATION OF POINT OF ZERO CHARGE AND SURFACE AREA OF MINERALS USED IN COBALT ADSORPTION STUDIES.

Synthetic manganese and iron oxides were prepared for use as substrates in the cobalt adsorption studies.

1. A brief description of the minerals is presented in this table.

βMnO_2	Crystalline solid	Manganese dioxide, pyrolusite.
αMn_2O_3	Crystalline solid	Manganese sesquiozide, bixbyite.
Mn_3O_4	Crystalline solid	Trimanganese tetroxide, hausmannite.
$Mn_3O_4 . nH_2O$	hydrated suspension	
$MnO_{1.89} \cdot nH_2O$	hydrated suspension	Manganous manganite.
$\gamma FeOOH . nH_2O$	hydrated suspension	γIronoxide hydroxide.
$Fe(OH)_3$	hydrated suspension	Amorphous iron hydroxide.

2. Preparation of the minerals.

a. βMnO_2, reagent grade manganese dioxide was obtained from Fisher Scientific Company. This material was ground without further purification and stored in distilled water for a month before use in experiments.

b. αMn_2O_3, manganese sesquioxide forms when manganous chloride, nitrate or carbonate is heated at about 600-800C°. (Moore, Ellis and Selwood, 1950). In this work Mn_2O_3 was prepared by igniting $MnSO_4$ at 1000C° for about six hours with occasional opening of the furnace door. After six hours of ignition, the product was black with a few clusters of reddish particles. The material was ground and heated for an additional six hours at 1000C°. The homogenous black solid was ground again and stored in distilled water for a month before use in experiments.

c. Mn_3O_4, trimanganese tetroxide, hausmannite, was obtained by ignition of $MnSO_4$ at 1000C°; (Moore, Ellis and Selwood, 1950).

It was observed that the purplish dark red Mn_3O_4 results only when the furnace is closed throughout the entire preparation and cooling interval. Occasional opening of the furnace during ignition or cooling results in a mixture of Mn_3O_4 and a black solid which is Mn_2O_3.

d. Mn_3O_4, trimanganese tetroxide a tan colored hydrated suspension was prepared by slightly alkaline oxidation of $MnSO_4$ with H_2O_2. The method is described by Buser, Graf and Feitknecht (1954). The precipitated hydrous oxide was purified by repeated filtration and redispersion in distilled water. The pure product, free of sulfate ions, was stored in distilled water.

e. Manganous manganite, a dark brown hydrated suspension, was obtained by acidic oxidation of $MnSO_4$ with $KMnO_4$. The method is described by Feitknecht and Marti (1945). After preparation, the material was filtered and then redispersed in distilled water. This washing procedure was repeated until neither sulfate nor chloride ions were detected in the supernatant liquid. The pure suspension was stored in distilled water.

f. $\gamma FeOOH.nH_2O$,an orange colored hydrated suspension was prepared by reacting $FeSO_4$ with KIO_3 in presence of $Na_2S_2O_3$ and NH_4Cl as described by Schuylenborgh and Arens (1950). The precipitate was allowed to settle, the supernatant solution decanted, and the precipitate was then filtered and redispersed. This purification procedure was repeated until the supernatant liquid was free both of chloride and sulfate. The product was stored in distilled water.

g. Amorphous $Fe(OH)_3$, a reddish brown product, was precipitated from $FeCl_3$ solution with NH_4OH, as described by Schnuylenborgh and Arens (1950). The precipitated hydrous oxide was allowed to settle and purified by repeated filtration and dispersion in distilled water. The pure hydrated suspension, free of chloride was stored in distilled water.

3. Identification of the minerals.

The identity of all the seven samples was established by X-ray diffraction, using copper Kα for manganese and iron Kα for iron oxides by the Geology Department at the University of Massachusetts. Analyses for total manganese and for manganese at oxidation states higher than +2 were carried out in this laboratory. For total manganese, the samples were dissolved in hydrochloric acid and manganese determined using a Perkin Elmer model 214 Atomic Absorption spectrophotometer. Determination of manganese at oxidation states higher than +2 was done by reduction with arsenious trioxide (As_2O_3); a weighed sample was dissolved in a known volume of arsenious trioxide solution, and the excess of arsenious trioxide was titrated with standard permanganate as described by Kolthoff and Sandell (1952). Composition of samples was calculated based on the total manganese content and the manganese in oxidation states higher than +2 using the following equation,

$$E = Mn(z-2)$$

E = equivalents of As_2O_3

Mn = moles of total manganese

z = average valence of manganese in the sample

Chemical composition of samples: MnO_x

$$x = \frac{z}{2}$$

No chemical analysis was done either on $\gamma FeOOH$ or on the amorphous $Fe(OH)_3$.

a. MnO_2, manganese dioxide. The crystal interplanar spacing and the relative intensities are

MnO_2		Reference: ASTM	
d A°	I	d A°	I
absent		3.48	10
3.10	100	3.14	100
3.40	80	3.41	50
absent		2.21	10
2.11	20	2.13	25
absent		1.98	15
1.62	50	1.63	50
1.55	10	1.56	25
1.43	10	1.43	15
1.30	20	1.31	20

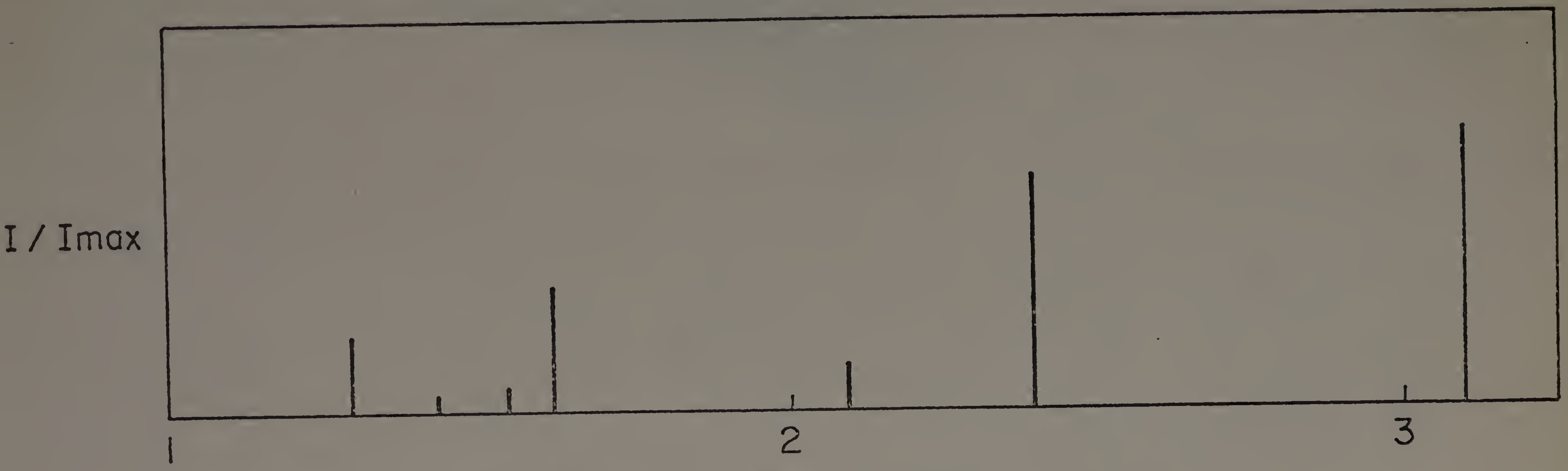
The comparative X-ray diffraction patterns are shown in Figure 1.

Chemical Analysis

Total Mn content		Chemical composition
Sample	64.4%	$MnO_{1.98}$
Theoretical	63.2%	$MnO_{2.0}$

The X-ray pattern of this material is consistent with ASTM standard but has a slightly smaller cell implying a solid solution. Many closely related manganese compounds such as hydrates give similar X-ray diffraction pattern (Morse, 1974).

Chemical analysis gave 1.2% higher total manganese content than the theoretical value; MnO_2 is usually oxygen deficient.



MnO_2 Fisher reagent

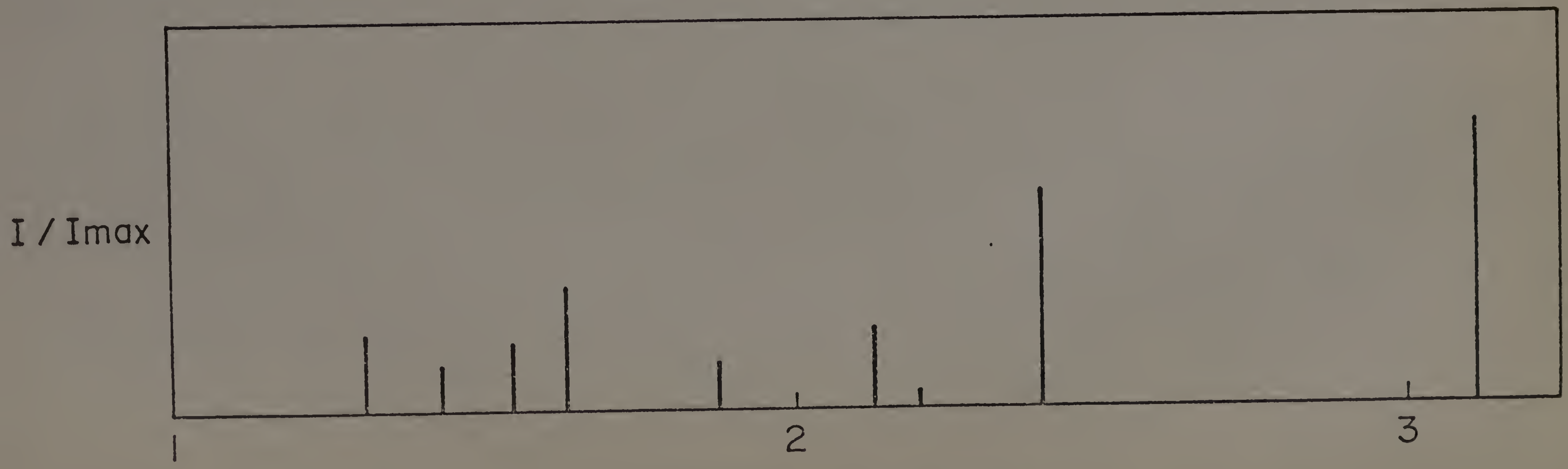


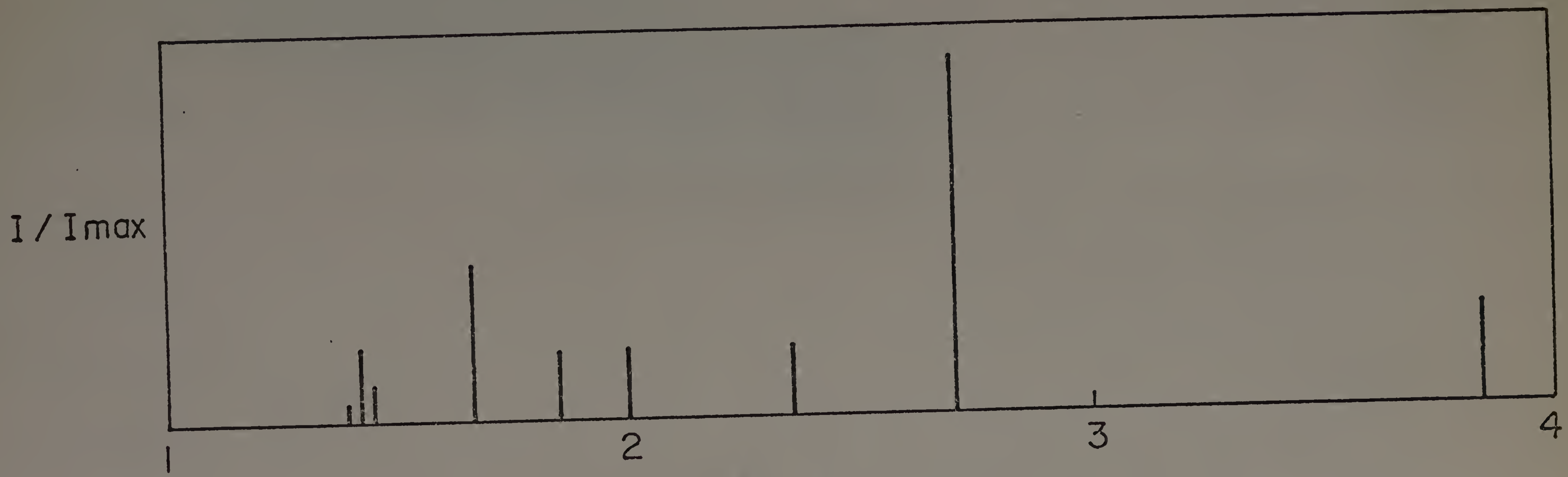
Figure 1. JCPDS Pyrolusite

b. αMn_2O_3, manganese sesquioxide. The crystal interplanar spacing and relative intensities as shown in Figure 2 are the following:

		Reference (Moore, Ellis, Selwood 1950)	
dA°	I	dA°	I
3.84	25	3.82	20
2.71	100	2.71	100
2.35	18	2.34	20
2.01	18	2.00	10
1.84	18	1.84	20
1.66	40	1.66	40
1.45	10	1.45	10
1.42	20	1.42	20
absent		1.39	1

Chemical Analysis

Total Mn content		Chemical composition
Sample	69.9%	$MnO_{1.47}$
Theoretical	69.6%	$MnO_{1.50}$



Mn_2O_3 solid

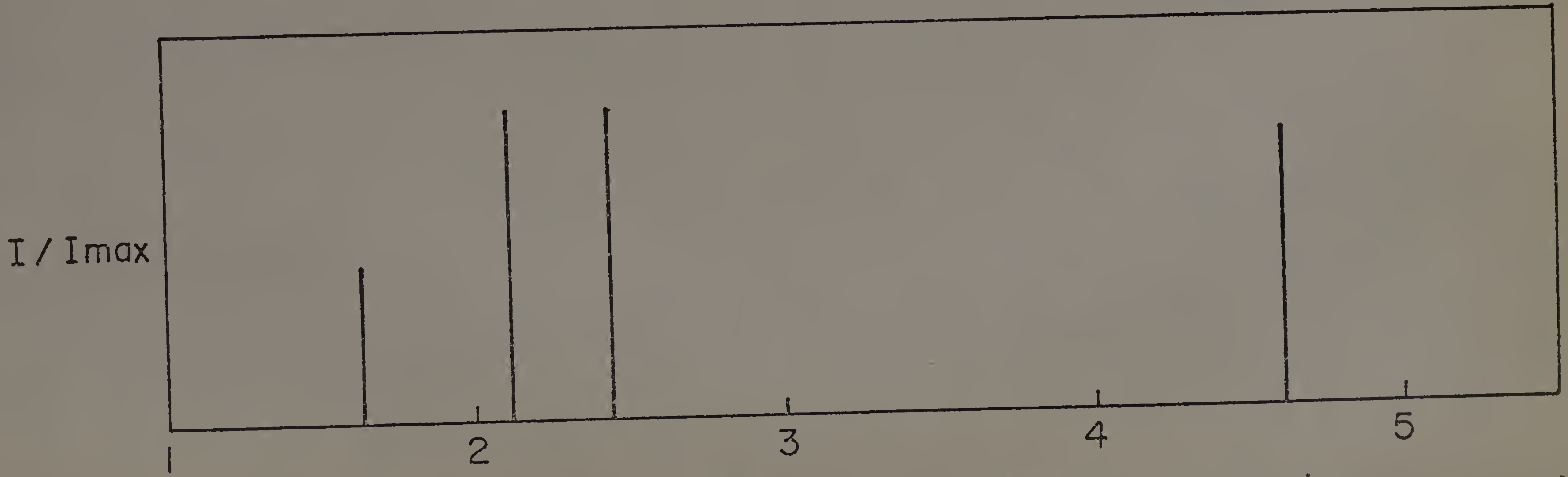


Figure 2. Manganous Manganite hydrated suspension

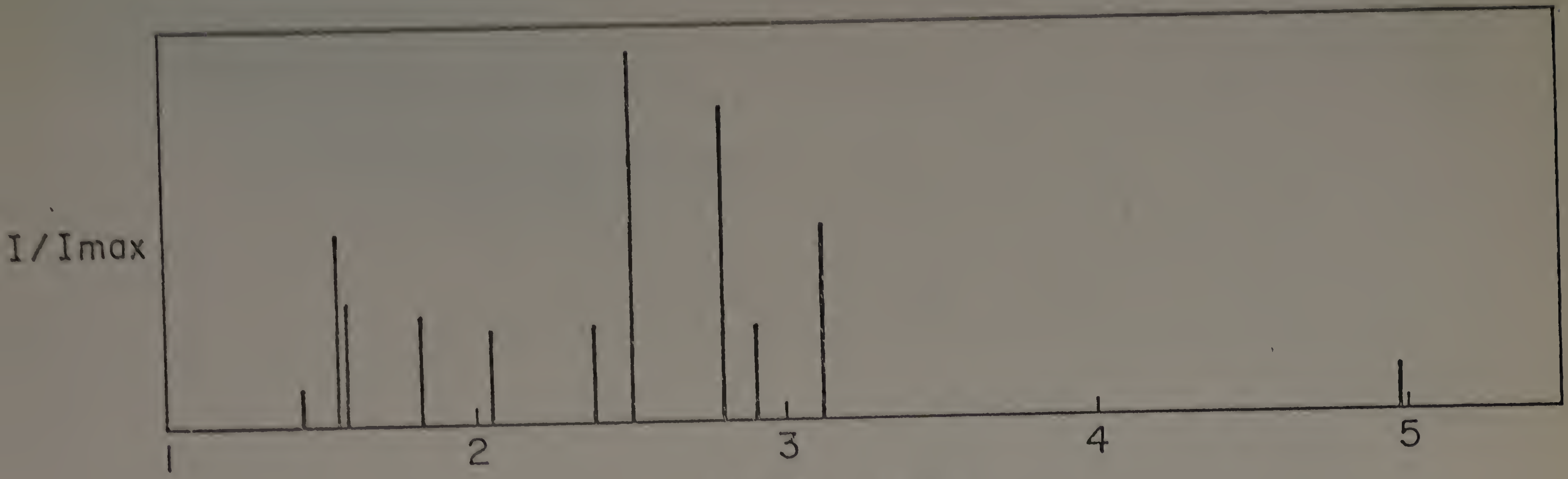
The total manganese content is close to the theoretical value. X-ray pattern of the sample has all lines of the reference Mn_2O_3 except that of the very weak high angle reflections.

c. Mn_3O_4, trimanganese tetroxide, hausmannite. The crystal interplanar spacing and relative intensities as shown in Figure 3 as the following.

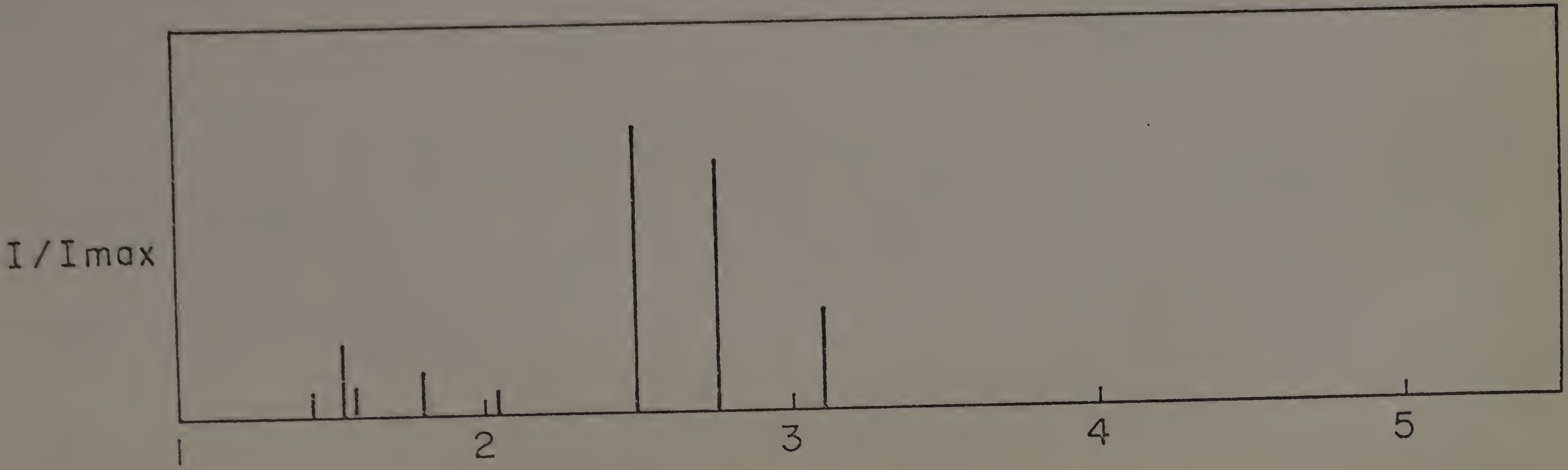
		Reference (Moore, Ellis, Selwood 1950)	
dA°	I	dA°	I
4.97	10	4.90	20
3.91	10	absent	
3.12	50	3.08	35
2.90	25	2.87	20
2.79	100	2.75	65
2.50	100	2.48	100
2.38	25	2.36	20
2.05	25	2.03	15
1.81	30	1.80	20
1.58	35	1.58	50
1.55	50	1.55	50
1.44	10	1.44	15
absent		1.28	10

Chemical Analysis

	Total Mn content	Chemical Composition
Sample	71.6%	$MnO_{1.24}$
Theoretical	72.0%	$MnO_{1.34}$



Mn_3O_4 solid



Mn_3O_4 hydrated suspension

Figure 5

Chemical analysis of product synthesized by Bricker (1965) gave composition $MnO_{1.328}$ and $MnO_{1.338}$. The sample having composition $MnO_{1.328}$ also had 1-2% water. Sample prepared by Moore, Ellis and Selwood (1950) had chemical composition of $MnO_{1.44}$. Obviously Bricker's sample had a higher grade of purity than the sample prepared here or the reference sample obtained by Moore, Ellis and Selwood (1950). Bricker reported in the X-ray pattern an additional large set of very weak reflection lines between 1.00 and 1.44A°. He also noted that a sample prepared in highly oxidizing condition had a composition of $MnO_{1.42}$ and showed weakening or absence of the high angle reflections in the X-ray pattern.

d. Mn_3O_4, trimanganese tetroxide hydrated suspension. X-ray pattern shows the following reflections and relative intensities.

dA°	I
3.11	50
2.78	100
2.49	100
2.04	8
1.80	18
1.57	8
1.54	25
1.44	8

In Figure 3 the X-ray diffraction pattern of this material and that of solid, crystalline Mn_3O_4 are shown.

Chemical Analysis

	Total Mn content	Chemical Composition
Sample	72.3%	$MnO_{1.23}$
Theoretical	72.0%	$MnO_{1.34}$

The X-ray diffraction pattern shows this material to have a significantly lower degree of crystallinity than the solid Mn_3O_4. The reflection lines are less intense than those of solid Mn_3O_4 and the less intensive lines of the latter are absent in the pattern of this sample. The slightly higher than theoretical total manganese content may indicate a relatively large fraction of total manganese in +2 oxidation state. Bricker (1965) found that during the synthesis of Mn_3O_4 and other manganese oxide suspension, the fine particles of precipitated manganous hydroxide may adsorb Mn^{2+} ions from the solution.

3. Manganous manganite, hydrated suspension X-ray diffraction pattern and intensity of lines as shown in Figure 2 are the following:

dA°	I
Absent	
4.62	80
2.74	100
2.12	50
1.64	50

Bricker (1965) observed these and 3 additional high angle reflections.

Chemical Analysis

	Total Mn content	Chemical Composition
Sample	66.2%	$MnO_{1.89}$
Theoretical	63.2%	$MnO_{2.00}$

This material was identified on the basis of X-ray diffraction and chemical analysis as microcrystalline manganous manganite following the classification by Bricker (1965) and Busar, Graf and Feitknecht (1954). A large set of compounds having composition $MnO_{1.74}$-$MnO_{1.99}$ and very similar X-ray pattern were prepared by various authors and called manganous manganite or δMnO_2. Feitknecht and Marti (1945) prepared a series of compounds by H_2O_2 oxidation of manganous hydroxide and another series by HCl reduction of $KMnO_4$. The two sets of compounds showed very similar X-ray patterns and chemical composition $MnO_{1.74}$-$MnO_{1.82}$ and $MnO_{1.82}$-$MnO_{1.99}$ respectively. Feitknecht called all the above compounds manganous manganite and attributed them a double layer structure with a varying degree of order. McMurdie synthesized two compounds, one had two, the other had four reflection lines in X-ray diffraction but called both δMnO_2. Buser, Graf and Feitknecht (1954) studied the above prepared compounds and concluded, that manganous manganite and δMnO_2 are the same phase. They recommended to retain δMnO_2 for compounds of oxidation grade of $MnO_{1.90}$ or above and manganous manganite for compounds of oxidation grade below $MnO_{1.90}$.

McMurdie and Golovato (1948) confirmed that the X-ray pattern of δMnO_2 and manganous manganite is a function of particle size as well as the preparation technique.

Bricker observed an identical X-ray pattern of compounds having composition $MnO_{1.74}$-$MnO_{1.99}$, only the intensity and width of reflection lines varied. He assumed that compositional variations were due to the presence of Mn^{2+} and Mn^{3+} ions and also an OH^- substitution for O^{2-}.

Morgan and Stumm measured the pH dependent cation exchange capacities of δMnO_2 and explained that the non-stoichiometric preparation products result from Mn^{2+} uptake by the colloidal hydrous manganese dioxide. Manganous manganite and δMnO_2 are the primary manganese compounds in deep sea nodules.

f. $\gamma FeOOH \cdot nH_2O$ hydrated dispersion X-ray diffraction pattern shows in Figure 4 this material to be a synthetic $\gamma FeOOH$. The crystal interplanar spacing and relative intensities are

		ASTM reference	
dA°	I	dA°	I
6.25	100	6.26	100
3.27	100	3.29	90
2.47	80	2.47	60
2.35	20	2.36	20
1.93	90	1.93	70
1.52	40	1.52	40
1.45	10	1.45	10

g. Amorphous $FeOOH \cdot nH_2O$ hydrated suspension.

The X-ray diffraction pattern in Figure 4 shows this material to be a synthetic amorphous ironoxide-hydroxide. Only two, weak and very diffuse, reflection lines at about 4.2 and 2.5A° were observed in the X-ray pattern after drying the

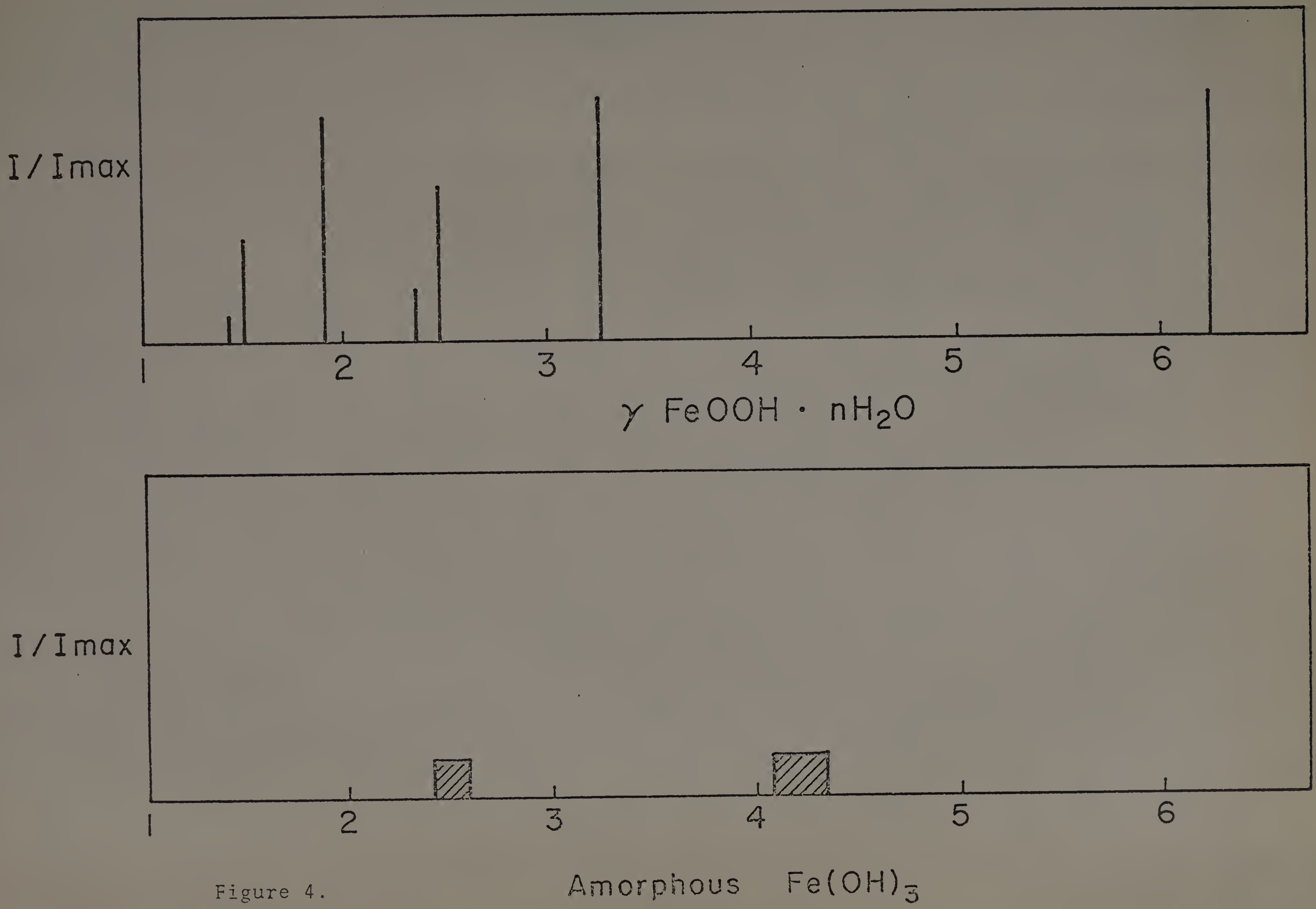

I/Imax
1
2
3
4
5
6
γ FeOOH · nH_2O
I/Imax
1
2
3
4
5
6
Amorphous $Fe(OH)_3$

Figure 4.

material at 105 C° for 20 hours. Schnyleuborgh and Arens (1950) found a compound prepared by the same method as this sample to be Rontgenographically amophous before drying. When the compound was dried at 60 and at 100 C° for a day, weak and diffused lines of the synthetic αFeOOH were observed in the X-ray pattern. The material prepared in this work produced only two approximate reflections, therefore, the structure of this sample can only be identified as amorphous. The presence of the two lines in the X-ray pattern may be accounted for as a low degree crystallinity developed only on the surface during the drying period, while the bulk of the material remained amorphous.
Figure 4. shows the X-ray diffraction pattern of both amorphous $Fe(OH)_3$ and γFeOOH.

4. Determination of point of zero charge of minerals used in cobalt adsorption studies.

Experimental: The point of zero charge of the 3 aqueous suspensions was determined by potentiometric titration in the reversible cell

glass electrode	aqueous suspension of hydrous oxides + $NaNO_3$ supporting electrolyte	saturated calomel electrode

As titrants . 1N NaOH and HNO_3 were used, the supporting electrolyte was $NaNO_3$ at 0.5M, 0.05M, 0.005M. The reason for using $NaNO_3$ as the supporting electrolyte was the very low tendency of NO_3^- ions to form complexes with ferric ions. The titration cell was a 400 ml beaker with rubber stopper and a teflon covered magnetic stirrer was used to mix the suspension. The air inlet to the cell passed through a N KOH trap in order to remove the CO_2.

The titrations were carried out on a 200 ml mixture made of 100 ml of hydrated suspension, total solid content is about 1g, and 100 ml of the supporting electrolyte. The pH range of titration was 5-10 for $Fe(OH)_3$ and γ FeOOH. 1-10 was for Mn_3O_4 and manganous manganite suspension.

The first set of adsorption curves were obtained by adding an aliquot of NaOH to the mixture of suspension and electrolyte, and the pH at equilibrium was recorded. Each aliquot of base added to the mixture was followed by a rapid increase in pH which decreased slowly to an equilibrium value. The time requirement to reach equilibrium was several hours at about pH 7, in the acidic or basic regions the equilibrium established more rapidly. The same titration was carried out on a duplicate sample but no attempt was made to obtain an equilibrium pH. Each aliquot of NaOH added to the sample was followed by 5 minutes of stirring and the pH was recorded. The hysteresis in the adsorption curves was observed here also as it was experienced at the equilibrium titration; the path of titration from acidic to alkaline pH values was different than that from alkaline to acidic pH values.

A very similar phenomena of hysteresis was observed and reported by a number of authors , Onoda and DeBruyn (1966), Berube, Onoda and DeBruyn (1967), Berube and DeBruyn (1968).

Onoda and DeBruyn (1966) explained the above observed kinetic behavior as a rapid adsorption and distribution of protons between the hydrated surface of oxides and the solution. This is followed by a slow diffusion of adsorbed protons through the interphase into the solid. The driving force in this adsorption is the chemical potential gradient across the hydrated surface layer of oxides. At the point of zero charge, the chemical potential of protons at the hydrated surface of oxides and in the solution are equal.

A similar 2 step kinetic behavior was observed and reported in the exchange reactions between D_2O and AlOOH and also in the tritium exchange processes. It was found that in all of the exchange reactions a rapid initial surface exchange preceeded a slower diffusion controlled exchange in the bulk of the solids (Onoda and DeBruyn, 1966).

The simple model of a rapid surface adsorption of protons and a slow diffusion of those into the bulk of solid fails to give a satisfactory explanation for kinetic behavior of oxides such as TiO_2, ZnO and Al_2O_3.

A combination of the adsorption - diffusion model and a surface anion exchange between OH^- and other univalent inorganic anions offers a better possibility for the overall process according to Berube and DeBruyn (1968).

Both fast and equilibrium titrations were carried out on the amorphous $Fe(OH)_3$ and on the γ FeOOH . nH_2O suspensions.

a. The potentiometric titration curves of amorphous $Fe(OH)_3$ clearly show that H^+ and OH^- are potential determining ions in this process. The best value for point of zero charge of the amorphous $Fe(OH)_3$ is 8.3 as the intersection of adsorption curves at different ionic strengths shows on Figure 5. At pH = 7.5 adsorption densities are 0.035, 0.053 and 0.079 equiv/g in 0.005 M, 0.05 M and 0.5 M $NaNO_3$ supporting electrolytes.

b. The point of zero charge of γ FeOOH . nH_2O hydrated suspension was established also by potentiometric titration at 3 different ionic strengths. The intersection of the adsorption curves is at pH=6.1 as it is shown on Figure 6; the same value was obtained by both fast and equilibrium titrations. The relative shape of the curves indicate a strong possibility that NO_3^- ions are closer packed on γ FeOOH than they are on the amorphous $Fe(OH)_3$. The same phenomena was observed by Ahmed (1969) on hematite in NO_3^- and in ClO_4^- solutions.

c. The fast titration method was used to establish the point of zero charge of Mn_3O_4 hydrated suspension. An attempt to titrate this suspension to equilibrium, showed that the time

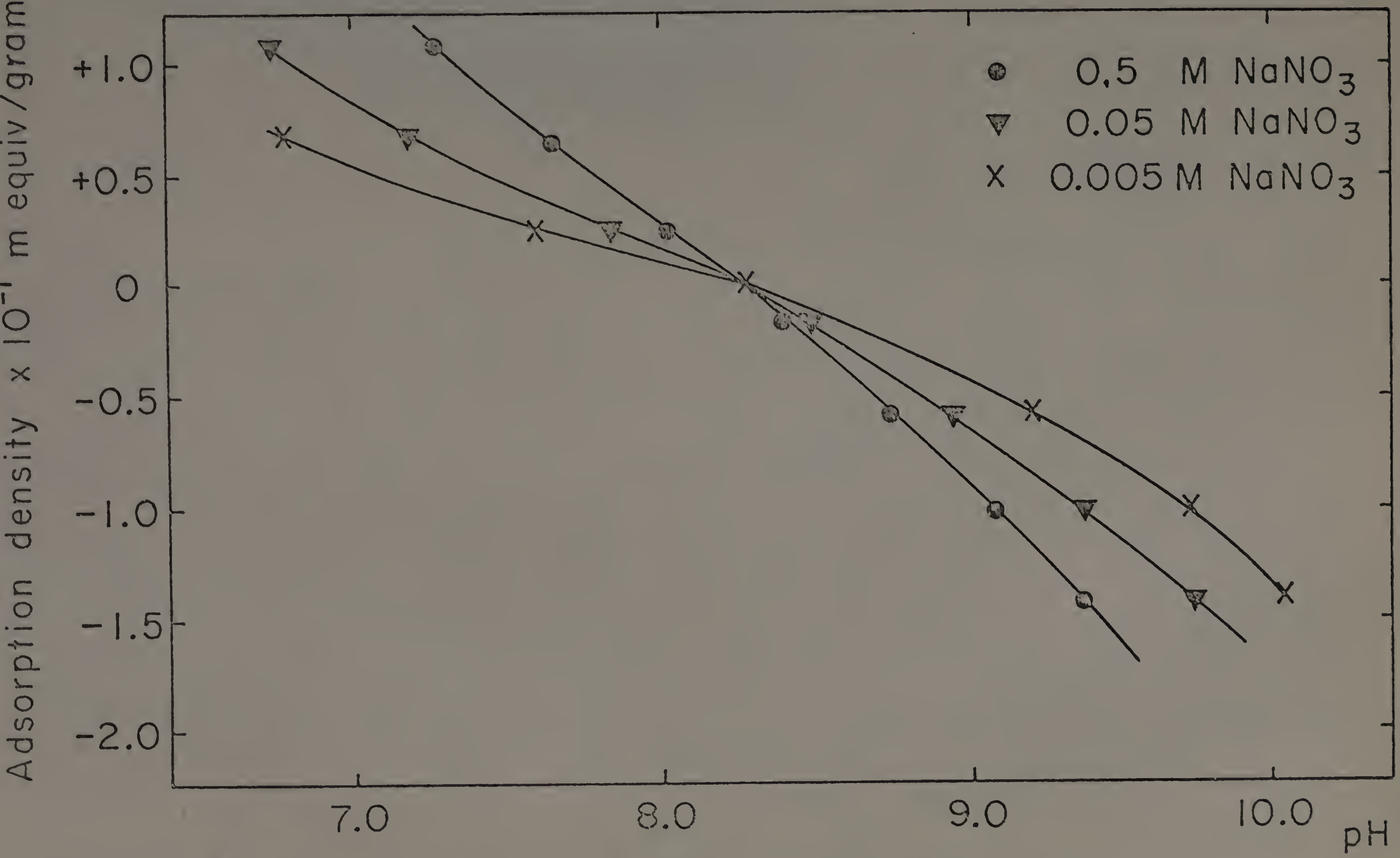


Figure 5. Adsorption isotherm of H^+ and OH^- ions on amorphous $Fe(OH)_3$. Supporting electrolyte is $NaNO_3$.

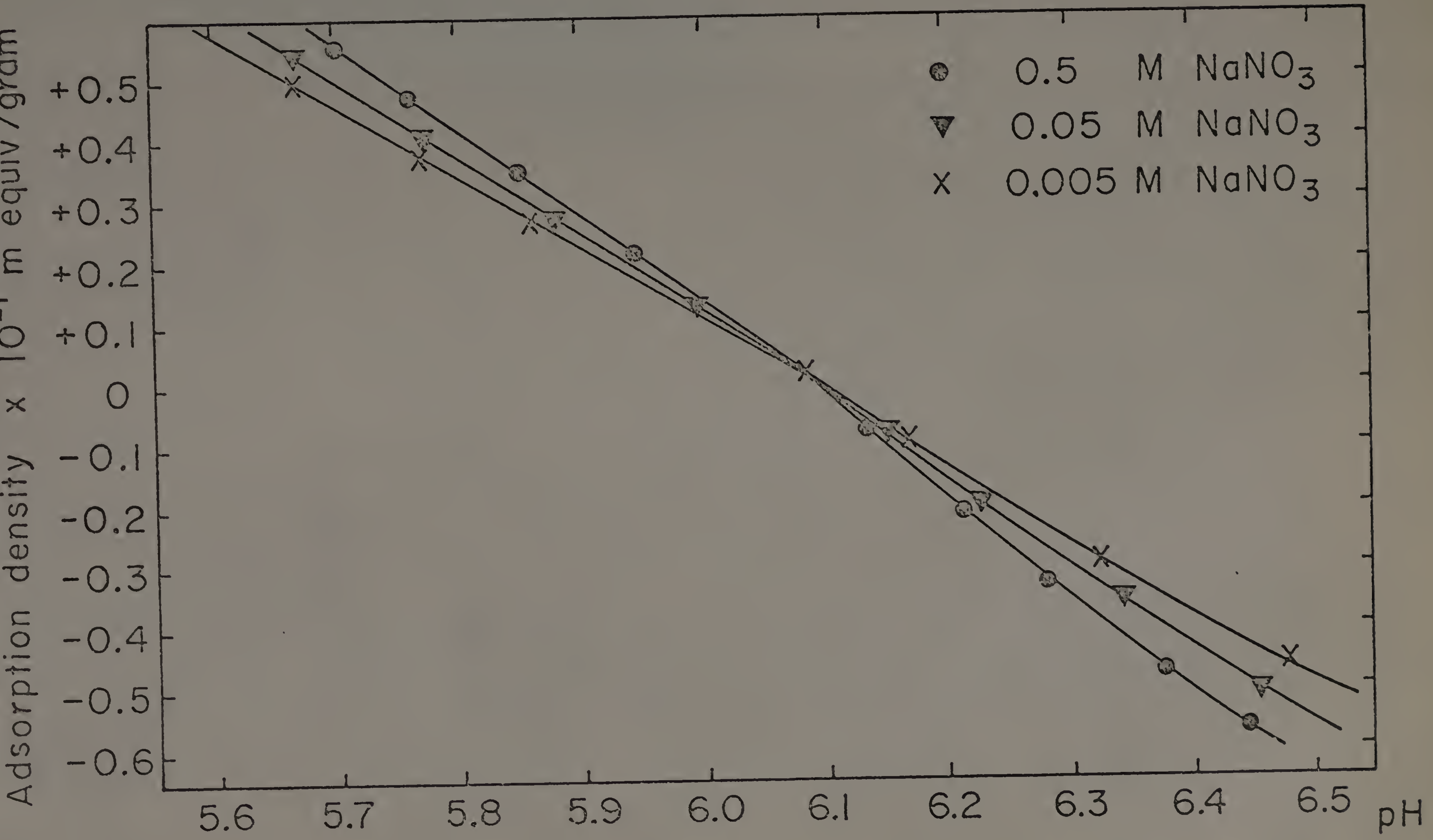


Figure 6. Adsorption isotherm of H^+ and OH^- ions on $\gamma FeOOH \cdot nH_2O$. Supporting electrolyte is $NaNO_3$

required to reach equilibrium is very long. More than 8 hours were necessary to approach a quasi equilibrium at about pH 6.5 and change in pH was observed for weeks around pH 7.

The intersection of fast titration curves show that the point of zero charge for this material is 7.0±.2. The intersection of adsorption curves is shifted to a slightly lower pH when the point of zero charge is approached from alkaline solution. As Figure 7. shows, the titration curves intersect at about pH = 6.9 when the titration proceeds from alkaline to acidic pH values and they cross at pH = 7.2 if an acidic sample is titrated toward alkaline pH. The course of the adsorption curves at acidic pH values indicate that either a specific adsorption of NO_3^- or some irreversible charges caused by the alkali occurred on the surface of Mn_3O_4.

d. Fast titration of manganous manganite suspension resulted in three non-intersecting curves at the three different ionic strength. Healy, Herring and Fuerstenau (1966) also observed that the point of zero charge of δMnO_2 and αMnO_2 increased with increasing ionic strength. To approach the point of zero charge of this material another property of aqueous suspension was considered. Since the existence of surface charge prevents coagulation in low ionic strength suspensions in absence of specific adsorption, coagulation and sedimentation is maximum

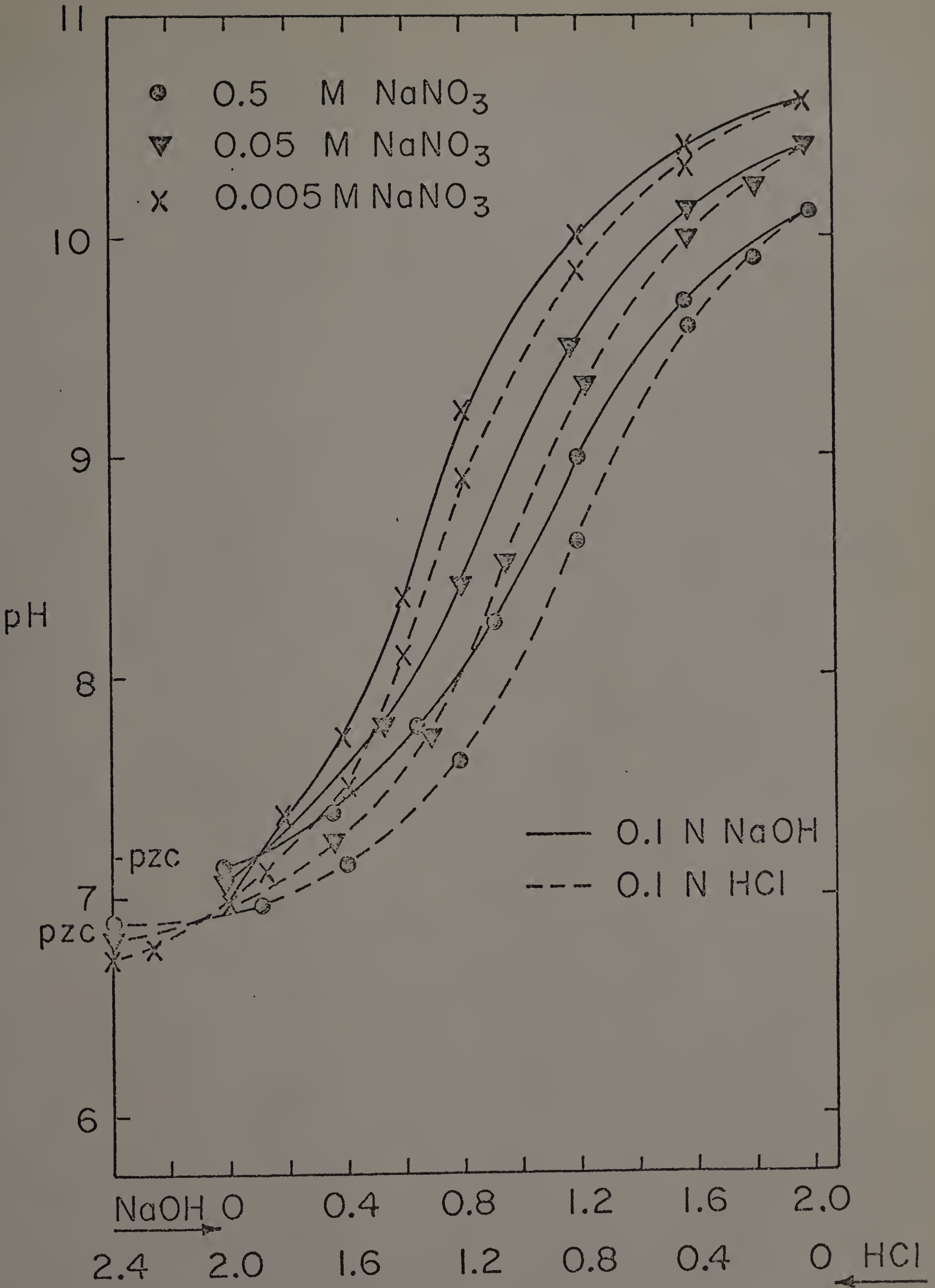


Figure 7. Adsorption isotherm of H^+ and OH^- ions on Mn_3O_4 hydrated suspension.

Supporting electrolyte is $NaNO_3$.

when the surface charge is zero. Therefore the point of zero charge of this suspension was determined by turbidity measurements at various pH values. To a measured quantity of dilute suspension a predetermined volume of HNO_3 was added and the adsorbance measured using a Bausch and Lomb Spectronic 20 spectrophotometer at 600 mu immediately after mixing.

The measurements were repeated after 15 and 30 minutes, three hours and overnight. Maximum turbidity was observed in the sample which had pH = 1.9 and the turbidity gradually decreased as the pH of samples either increased or decreased. The suspensions were sufficiently stable that it was possible to take readings after 30 minutes. When the samples were shaken, after standing three hours or overnight, and the absorbance measured, the minimum turbidity or most rapid sedimentation was observed in the sample at pH = 1.9.

The results of absorbance measurements immediately after sample preparation are shown on Figure 8. The point of zero charge of this suspension is 1.9 ± 0.5. Morgan and Stumm (1964) estimated the point of zero charge of a δMnO_2 sample to be less than three. Healy, Herring and Fuerstenau (1966) determined 1.9 ± 0.5 point of zero charge for δMnO_2 and 1.8 ± 0.5 for manganous manganite by coagulation and electrokinetic potential measurements.

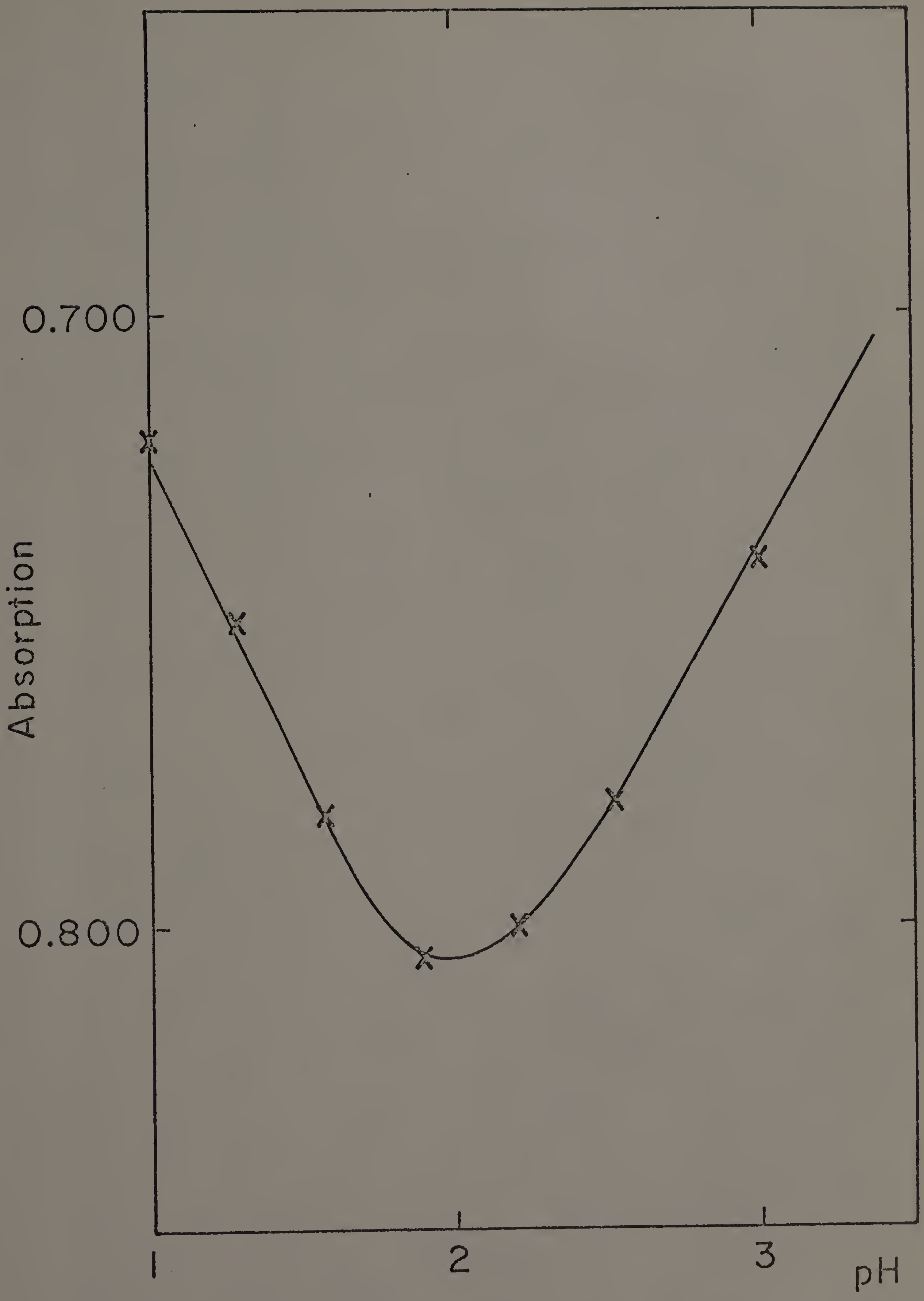


Figure 8. Turbidity measurement on Manganous manganite hydrated suspension as a function of pH.

e. Numerous attempts were made to determine the point of zero charge of the three solid samples: MnO_2, Mn_2O_3 and Mn_3O_4. Non-intersecting adsorption curves were obtained by either fast or equilibrium titrations. Turbidity measurements also failed, because the particles settled before it was possible to make any reliable measurement.

The point of zero charge of these samples was determined by the negative adsorption method. This method is based on the presence of the double layer which developes about a solid particle suspended in an aqueous environment, and on the fact that counter ions to the surface charge are deficient in the diffuse layer but they are in excess in the bulk of the solution. The concentration of K^+ ions in the bulk of the solutions were determined at various pH values. The pH, at which a slight positive adsorption of K^+ was observed, is a limit of the point of zero charge. The K^+ determinations were done using the Atomic Absorption spectrophotometer. Results of these determinations are the following:

MnO_2		Mn_2O_3		Mn_3O_4	
pH	Adsorption K^+	pH	Adsorption K^+	pH	Adsorption K^+
6.10	negative	6.00	negative	5.23	negative
6.53	negative	6.25	negative	5.41	negative
6.81	negative	6.44	negative	5.80	negative
6.95	negative	6.88	negative	5.99	negative
7.29	positive	7.11	positive	6.18	positive
Point of zero charge:		Point of zero charge:		Point of zero charge:	
7.1±0.5		6.95±0.5		5.9±0.5	

Healy, Herring and Fuerstenau (1966) reported a value of 7.3±0.5 for the point of zero charge of MnO_2 "Baker analyzed reagent" and Morimoto and Kittaka (1974) found isoelectric point of 3.5 - 5.2 for the Mn_3O_4 solid.

Experimental values of the point of zero charge of the seven adsorbing minerals are:

Material	Point of zero charge
$Fe(OH)_3$ amorphous aqueous suspension	8.3
$\gamma FeOOH.nH_2O$ aqueous suspension	6.1
Mn_3O_4 aqueous suspension	7.0±.2
Manganous manganite aqueous suspension	1.9±.5
MnO_2 solid	7.1±.5
Mn_2O_3 solid	6.95±.5
Mn_3O_4 solid	5.9±.5

5. Surface area determinations.

The efficiency or adsorption capacity of an adsorbent can be represented by two factors. One is the surface area and the other is the adsorption affinity per unit area of the adsorbent surface. A substrate may have great adsorption affinity for a given solute, the adsorbed amount per gram substrate can still be quite small if the surface area is small. Adsorption affinity is a chemical nature dependent property and the surface area is a common property of all adsorbents.

A variety of methods are available now for surface area determination of different materials. The most frequently used classical methods are based on the physical adsorption of gases, liquids and various compounds to particle surfaces. Other methods such as negative adsorption, measurement of thermal effects and particle size determination by optical or electron microscope are also used for surface area evaluation in cases where they provide the most reliable results or the best accuracy. The methods published for surface area determination have in common that they were developed for dry or nearly dry materials.

Surface area of the seven adsorbing minerals species of this work were measured by the negative adsorption and the modified BET methods.

The negative adsorption method is based on the theory of electrical double layer. The surface charge on a particle dispersed in an electrolyte solution expells the co-ions from the double layer which had developed about the particle and the method measures the concentration increase of co-ions in the bulk of the solution.

The negative adsorption of a co-ion Γ_i in moles per unit area is expressed by the equation (Lyklema and Hul; 1969).

$$\Gamma_i = \int_0^\infty [c_i - c_i(x)]\, dx$$

in which c_i is the equilibrium concentration.

The distribution of co-ions $c_i(x)$ over a distance x from the surface is given by the Boltzman equation.

$$c_i(x) = c_i e^{-z_i \varepsilon \Psi_x / kT}$$

z_i = valence of ions

Ψ_x = double layer potential

ε = electronic charge

k = Boltzman constant

T = temperature in K°

The combination of these equations and an equation developed for the diffuse double layer results in another differential equation. The charge of the diffuse part of the double layer is a parameter in the equation, however, where the charge is sufficiently high, the negative adsorption does not depend on the electrical properties of the expelling surface. When the equation is applied to an aqueous solution at 20C° in which only one electrolyte is present and infinite surface potential is considered, a number of simplications become possible. The relationship between surface area and concentration of co-ions is reduced to the following simple equation:

$$S = B \times 10^7 V_t \frac{\Delta c}{c} \sqrt{c}$$

B value depends on the charge of ions: for a 1:1 electrolyte at 20°C B = 1.64 and the equation can be rearranged to the form

$$\frac{\Delta c}{c} = \frac{S}{B \times 10^7 \times V_t} \left(\frac{1}{\sqrt{c}} \right)$$

Thus a graph relating $\frac{\Delta c}{c}$ to $\frac{1}{\sqrt{c}}$

should be a straight line through the origin with a slope equal to $\frac{S}{B\times 10^7 \times V_t}$

V_t = volume of electrolyte

c = equilibrium concentration

Δc = concentration increase of co-ions

The principal advantages of the method are that absolute areas are obtained, the surface area is directly proportional to the concentration increase of co-ions in the bulk of solution, and the size of co-ions are not involved in the calculations.

The method has several limitations as well. The measurement of a generally small increase in concentration requires accurate analytical techniques, there is a limit to the surface areas that can be measured and the determination is tedious. Furthermore, in the presence of another electrolyte the equation becomes complicated and the measurement in closely packed sediments gives a lower value for surface area. The best results are obtained when the particles are non-porous, Stern potential is greater than 150 mV and the area is greater than 1m^2/g.

BET method measures the physical adsorption of inert gases such as N_2, Ar, Kr to solid particles' surfaces. The best known interpretation of the adsorption isotherm was developed by Langmuir, assuming that the adsorbed phase is a monomolecular layer about the particle and it is in dynamic equilibrium with the vapor base. Experimental results have shown that the assumption of monomolecular adsorption is not satisfactory in all cases, and the Langmuir isotherm is a special case of a more complicated relationship. Brunauer, Emmet and Teller (1938) assumed in their equation the existence of multilayer adsorption and also the possibility that multilayer forms on some parts of the surface area while even a monomolecular layer is not complete on other parts. The relation gives good results in practical application. Huttig (1948) and Jelinek (1974) applied the equation to N_2 adsorption at liquid N_2 temperature in an apparatus which consisted of two identical halves. The adsorption cell is connected to the duplicate cell through an oil manometer and the volume of the two cells, with all the connecting parts, is equal. Under these conditions the Brunauer, Emmet and Teller equation can be reduced to a relatively simple formula.

$$S = 2 \times 10^3 \; \frac{(78.5-K_1 p_B-K_2\Delta h)\Delta h}{m} \; [K_3+K_4 \; (K_1 p_B-K_2\Delta h]$$

S = Surface area (cm^2/g)

Δh= pressure difference on the oil manometer (cm)

p_B= barometric pressure (cm)

m = sample weight (g)

This determination has several advantages: the method is simple, it can be applied to a wide variety of materials and the measurement is quick. The main limitations of the method are the relatively low accuracy, the lengthy calculation, the special apparatus that is necessary for measurement and, in the case of porous material, the values obtained for surface area are low.

Experimental: Surface areas of the three solid materials MnO_2, Mn_2O_3 and Mn_3O_4 were determined by the negative adsorption method. Four separate determinations were done on each material. 5 g of the samples and 10 ml KCl solution of the following concentrations 10^{-4}, 3×10^{-4}, 5×10^{-4} and 10^{-3}M were mixed on the automatic shaker for one hour. After standing overnight the liquid was poured off into a testtube and allowed to settle for three additional days. The almost clear solution was filtered through a Whatman #41 filter paper and the K^+ concentration measured on the Atomic Adsorption instrument. The results of determinations are given in Tables 1, 2, and 3, and in Figure 9. The average surface area of each material is about 50 m^2/g.

BET measurements indicated about the same surface area for all the three materials, but the values were smaller by a factor of 2.5 than those obtained by negative adsorption. The deviation in surface area obtained by the two methods may be the result of a greater dispersion of the particles in the electrolyte solution during the negative adsorption measurements.

Van der Hul (1967) determined the surface area of AgI by six different methods. He found that the negative adsorption and the differential capacity calculations gave the same surface areas within experimental error. Specific surfaces determined by BET and gas adsorption were about the same but the values were 3.3 times smaller than those obtained by negative adsorption.

Table 1 - Negative adsorption of K^+ by MnO_2

$c \times 10^{-4}$ M	$\Delta c \times 10^{-4}$ M	$\frac{1}{\sqrt{c}}$ $(M)^{-1/2}$	$\frac{\Delta c}{c}$	S m^2/g
1.191	1.807	91.66	1.517	54.3
3.573	3.158	52.91	0.839	52.0
5.955	3.428	40.98	0.576	46.1
11.910	5.513	28.98	0.431	48.8

Surface area of MnO_2 = 50 ± 4 m^2/g

Table 2 - Negative adsorption of K^+ by Mn_2O_3

$c \times 10^{-4}$ M	$\Delta c \times 10^{-4}$ M	$\frac{1}{\sqrt{c}}$ $M^{-1/2}$	$\frac{\Delta c}{c}$	S m^2/g
1.191	1.658	91.66	1.392	49.8
3.573	3.032	52.91	0.848	52.6
5.955	3.631	40.98	0.610	48.8
11.910	5.744	28.98	0.482	54.6

Surface area of Mn_2O_3 = 51 ± 3 m^2/g

Table 3 - Negative adsorption of K^+ by Mn_3O_4

$c \times 10^{-4}$ M	$\Delta c \times 10^{-4}$ M	$\frac{1}{\sqrt{c}}$ $M^{-1/2}$	$\frac{\Delta c}{c}$	S m^2/g
1.191	1.714	91.66	1.439	51.5
3.573	2.806	52.91	0.786	48.7
5.955	3.504	40.98	0.588	47.1
11.910	5.639	28.98	0.474	53.6

Surface area of Mn_3O_4 = 50 ± 3 m^2/g

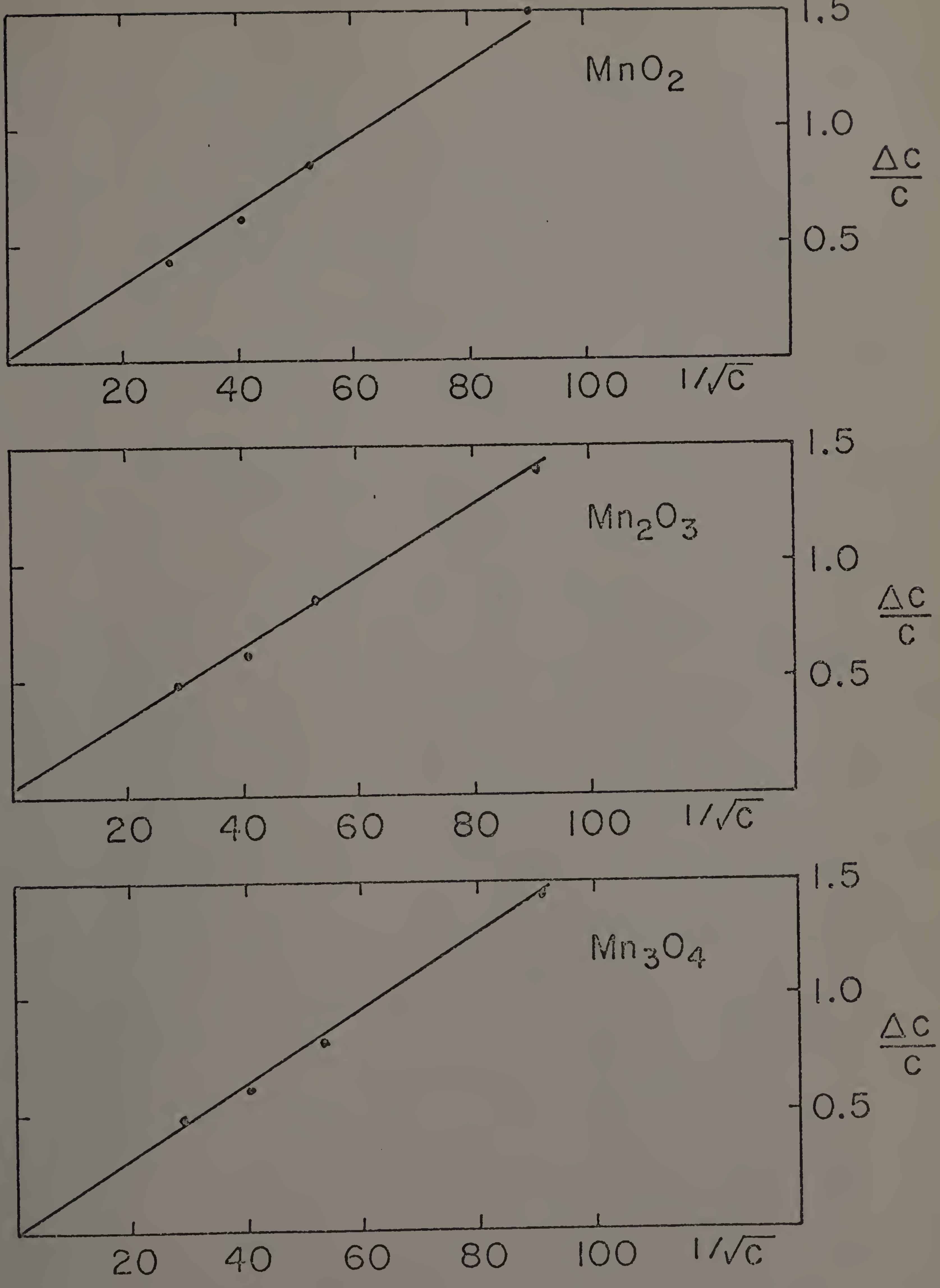


Figure 9. Negative adsorption of K^+ by MnO_2, Mn_2O_3 and Mn_3O_4.

Saturation values, in cobalt adsorption experiments, indicate that the surface area of MnO_2 and Mn_2O_3 and Mn_3O_4 are about 50 m^2/g.

Numerous attempts were made to determine the specific surface of the four hydrated suspensions.

The empirical method (Giles, D'Silva and Trivadi; 1969) of dye adsorption repeatedly failed in large numbers of experiments using methylene blue which is cationic dye. The methylene blue is known to give faulty results when the pH values are above 8. A pH 9 or 10 was needed to obtain a sufficiently large negative charge on the surfaces of γ FeOOH and amorphous $Fe(OH)_3$ and observe methylene blue adsorption. Serious interactions were observed between the manganese oxide samples and the methylene blue.

Attempts to measure the surface of the hydrated suspensions by negative adsorption were also unsuccessful. The hydrous oxide precipitates, separated from the water by ultra centrifuge, had only 17-19% total solids. 5 g. of sample and 5 ml of KCl solution gave a thick paste in which intimate mixing of the hydrous oxide and the electrolyte was impossible. The same amount of sample with 10 ml KCl solution showed positive adsorption of K^+. The apparent concentration decrease of K^+ in the bulk of solution was probably caused by dilution since more than 4 ml water was present in the hydrous oxide precipitate. An intimate mixing between the hydrous oxide and the electrolyte was not quite successful even when the volume of electrolyte was 10 ml. Photographs obtained by a scanning electron microscope show that the particle size of γ FeOOH, manganous manganite and Mn_3O_4 are approximately equal. The particles of the amorphous $Fe(OH)_3$, on the photograph, appeared as fragments in very different sizes and shapes broken off of a gel like sheet.

Acceptable values for surface area were obtained by the modified BET method and the measurements were carried out on the freeze-dried samples of γ FeOOH, amorphous $Fe(OH)_3$, manganous manganite and Mn_3O_4 hydrated suspensions. This method gave 200 m^2/g surface area for the amorphous $Fe(OH)_3$ and for the manganese manganite, 160m^2/g for the γ FeOOH and 50 m^2/g for the Mn_3O_4. The 50 m^2/g surface area obtained for Mn_3O_4 is highly questionable. This material consistently adhered to the walls of the round bottom distillation flask in which the drying was done under a vacuum. The dry sample was scrapped off the flask in flakes of various sizes and submitted for determination. The dry samples of the iron oxides and the manganous manganite were free flowing powders.

Some irreversible reaction must have occurred on the surfaces of these hydrated suspensions during the drying process, despite the fact that the temperature was always below 30C°. The freeze-dried samples have lost the hydrophillic character that the original materials had, and peptize only with difficulty.

The hydrated suspension settle only after 10 - 20 minutes of spinning in an ultra centrifuge while the freeze-dried samples dispersed in water settle almost instantaneously.

Electron microscope photographs clearly indicate that γ FeOOH and Mn_3O_4 hydrated suspensions have approximately the same particle size distribution; in cobalt adsorption experiments Mn_3O_4 followed closely the adsorption behavior of γ FeOOH and has a saturation value which corresponds to 160 m^2 specific area. Therefore, 160 m^2/g surface area is assumed for Mn_3O_4 hydrated suspension.

The collective results of surface area determinations are given in Table 4.

Table 4 - Surface area of adsorbents

Material	Surface area m^2/g	Method
MnO_2	50	negative adsorption
MnO_2	20	BET
Mn_2O_3	50	negative adsorption
Mn_2O_3	20	BET
Mn_3O_4	50	negative adsorption
Mn_3O_4	20	BET
γ FeOOH . nH_2O hydrated suspension	160	BET on freeze-dried sample
Amorphous Fe(OH) hydrated suspension	200	BET on freeze-dried sample
Manganous manganite hydrated suspension	200	BET on freeze-dried sample
Mn_3O_4 hydrated suspension	50	BET on freeze-dried sample

CHAPTER IV.

ADSORPTION OF COBALT

Experimental: The cobalt adsorption measurements were carried out on a series of samples in which the surface area of substrate was about $100 m^2/l$ and the initial cobalt concentration was 0.4285×10^{-4}, 0.857×10^{-4} and 4.285×10^{-4} M. Each determination was done on a sample of 30 ml substrate suspension plus 10 ml of cobalt solution and about 5 ml of distilled water. The required pH value was obtained by adding dilute NaOH solution (0.001 and 0.01N) slowly to the mixture while stirred with a magnetic stirrer. In order to measure the time needed to complete the cobalt adsorption, a series of preliminary determinations were carried out with each substrate. A sample made of 30 ml substrate plus 10 ml cobalt solution and water was stirred for 2 hours while the pH was continuously checked and adjusted. After 2 hours the sample was made up to a volume of 50 ml; then an aliquot was removed and used for pH and cobalt determinations. The remainder of the sample was stirred for 3 more hours without further pH adjustment. Since no apparent change occurred in cobalt adsorption during the 3 additional hours, it was assumed that under these conditions adsorption process was complete in 2 hours. Consequently an adsorption period of 2 hours was adopted and during this time the pH was checked and adjusted every 10-15 minutes. At the end of the adsorption period the sample was made up to a volume of 50 ml and mixed. Then 25 ml of the sample was centrifuged in order to remove the substrate and the liquid was filtered through a Whatman #41 filter paper. Both cobalt determination and pH measurements were done on the clear filtrate.

The second half of the sample was allowed to stand for 3 days at room temperature, then the substrate was removed and the clear filtrate used for pH and cobalt determinations.

The pH of the aqueous mixture was measured using a Beckman Model 1019 "Research" pH meter and the cobalt concentration was measured using a Perkin Elmer Model 214 Atomic Absorption spectrophotometer.

The cobalt solutions were prepared from $Co(NO_3)_2 \cdot 6H_2O$ and standardized against at 10,000 ppm cobalt standard supplied by the Fisher Scientific Company.

Preliminary Rate Determinations

The observed higher adsorption capacities of hydrated suspensions compared to those of the solid adsorbents suggest that the hydrated suspensions had higher reactivity and specific affinity for cobalt than the solid materials. Numerous attempts were made to determine the rate of cobalt adsorption by the seven manganese and iron oxides. Duplicate samples of manganous manganite and Mn_3O_4 hydrated suspensions were adjusted to 2 different pH values. One sample of each material was adjusted to pH corresponding to about 30% adsorption and the duplicate sample to pH value of 70% adsorption. In order to provide a comparable ionic strength in each sample, the pH adjustments were done in the presence of 0.01 M $NaNO_3$. A drift to lower pH values continued for several weeks. When a constant pH was observed for 12 hours, the suspension was dispersed in a blender and cobalt solution was added to the agitated sol. Samples were taken at 15 minutes, 30 minutes after mixing the hydrous oxide and the cobalt, then at 1-hour, 2-hour, 6-hour, 12-hour, 1-day, 2-day and 3-day time intervals. Very drastic pH drops were observed in the samples of both materials. One unit drop in pH was measured with manganous manganite suspension in 12 hours; then another pH unit drift occurred during the remaining time. The pH of the manganous manganite sample was adjusted to an initial value of 6.47 which is 3/10 of a unit higher than the pH of 100% adsorption. The final pH, after 3 days, was 5.11. A 15.7% cobalt adsorption was obtained for final value; in-between values varied between 5 and 20%. A similar inconsistency and continuous pH drift was observed in the rate determination experiments of Mn_3O_4 hydrated suspension. Gadde and Laitinen (1974) observed almost instantaneous adsorption of Pb^{2+}, Th^{4+}, Cd^{2+} and Zn^{2+} by manganese, iron and aluminum hydroxides. The 15.7% cobalt adsorption of the manganous manganite was first measured after one hour of reaction time. Another sample adjusted to lower pH value indicated more than 2 hours reaction time. The long reaction times observed in these adsorption processes may have been caused by the presence of electrolytes or they may have been artifacts resulting from the prolonged pH adjustments. Since the results of rate determinations were unrevealing in the case of manganous manganite and Mn_3O_4, all attempts of rate determination with other substrates were abandoned.

Results: There was an abrupt increase in cobalt adsorption at pH values characteristic for each substrate as shown in Figures 10, 11 and 12. In Figure 10, the effect of suspension pH on the percentage of the added cobalt that was adsorbed was depicted and Figure 11, shows cobalt adsorption in moles/g substrate as a function of pH. The adsorption isotherm in Figure 12 represents the cobalt adsorbed in moles/m^2 substrate plotted against the point of zero charge of the substrate minus the pH of solution. This isotherm illustrates whether cobalt adsorption occurred on positive or on negative surfaces. Curves to left from zero on the abscissa represent specific and curves to right from zero show coulombic adsorptions.

Surface coverage was also calculated for each species. If

Table 5 - Cobalt adsorption by manganous manganite hydrated suspension

	Initial Cobalt Concentration					
	0.4285×10^{-4} M		0.857×10^{-4} M		4.285×10^{-4} M	
pH	μM/g	μM/m^2	μM/g	μM/m^2	μM/g	μM/m^2
5.4	7.11	0.036	8.1	0.041		
5.5	14.4	0.072	18.1	0.091	38.9	0.195
5.6	24.3	0.121	27.6	0.138	51.6	0.258
5.7	32.2	0.161	40.1	0.201	68.1	0.341
5.8	44.4	0.222	54.1	0.271	85.7	0.429
5.9	55.5	0.278	69.1	0.346	110.0	0.550
6.0	68.1	0.340	84.5	0.423	141.2	0.706
6.1	81.9	0.410	103.2	0.516		
6.2	93.5	0.470	118.6	0.593	216.2	1.081
6.3			141.2	0.706		
6.4			157.7	0.788	321.3	1.607
6.5			179.3	0.897	521.9	2.610
6.6						
6.7					866.7	4.334

Table 6 - Cobalt adsorption by amorphous $Fe(OH)_3$ hydrated suspension

	Initial Cobalt Concentration					
	0.4285×10^{-4}M		0.857×10^{-4}M		4.285×10^{-4}M	
pH	μM/g	$\mu M/m^2$	μM/g	$\mu M/m^2$	μM/g	$\mu M/m^2$
6.2	6.49	0.032	9.27	0.046	10.2	0.051
6.3	13.1	0.065	17.6	0.088		
6.4	19.9	0.100	26.5	0.133	36.2	0.181
6.5	28.0	0.140	37.1	0.176		
6.6	36.8	0.184	48.4	0.242	74.2	0.371
6.7	47.7	0.234	61.6	0.379	97.4	0.487
6.8	62.3	0.312	83.7	0.418	135.4	0.677
6.9	79.3	0.396	108.1	0.541		
7.0			134.5	0.672	238.4	1.192
7.1			177.2	0.886		
7.2					537.9	2.690
7.3					769.8	3.849
7.4					862.6	4.313

Table 7 - Cobalt adsorption by γFeOOH hydrated suspension

	Initial Cobalt Concentration					
	0.4285×10^{-4} M		0.857×10^{-4} M		4.285×10^{-4} M	
pH	μM/g	μM/m^2	μM/g	μM/m^2	μM/g	μM/m^2
6.2	2.58	0.016	3.44	0.021	5.16	0.032
6.3	6.02	0.038	7.74	0.048		
6.4	10.4	0.065	15.5	0.097	23.2	0.145
6.5	15.9	0.099	24.4	0.153		
6.6	23.6	0.148	32.8	0.205	50.7	0.317
6.7	32.7	0.204	42.8	0.268	68.8	0.430
6.8	43.0	0.269	59.1	0.370	92.8	0.580
6.9	61.0	0.381	74.1	0.463		
7.0			90.8	0.567	154.7	0.967
7.2			146.3	0.914	236.4	1.478
7.3					286.3	1.789
7.4					351.6	2.197
7.5					429.8	2.686
7.6					790.8	4.943

Table 8 - Cobalt adsorption by Mn_3O_4 hydrated suspension

pH	Initial Cobalt Concentration					
	0.4285×10^{-4}		0.857×10^{-4} M		4.285×10^{-4} M	
	μM/g	μM/m^2	μM/g	μM/m^2	μM/g	μM/m^2
6.2	4.02	0.025	8.17	0.051		
6.3	9.23	0.058	11.9	0.074		
6.4	14.7	0.092	17.9	0.112	19.0	0.118
6.5	19.8	0.124	25.5	0.159		
6.6	26.4	0.165	33.8	0.211	41.6	0.260
6.7	33.6	0.210	42.6	0.266		
6.8	40.2	0.251	54.3	0.339	76.1	0.476
7.0	68.6	0.429	77.4	0.484	126.9	0.793
7.2			113.0	0.706	193.8	1.211
7.3			136.7	0.855		
7.4					288.2	1.802
7.6					648.4	4.052

Table 9 - Cobalt adsorption by MnO_2

Initial Cobalt Concentration

pH	0.4285×10^{-4}		0.857×10^{-4}		4.285×10^{-4} M	
	µM/g	$\mu M/m^2$	µM/g	$\mu M/m^2$	µM/g	$\mu M/m^2$
6.9			1.09	0.022	2.14	0.043
7.0	1.46	0.029	2.86	0.057	3.81	0.076
7.1	6.68	0.134	7.11	0.142	7.59	0.152
7.2	9.29	0.186	10.5	0.211	11.3	0.266
7.3	14.0	0.280	16.1	0.322	18.1	0.362
7.4			33.9	0.678	35.3	0.706
7.6					48.7	0.977
7.7					76.3	1.526
7.8					104.8	2.100
7.9					170.5	3.410

Table 10 - Cobalt adsorption by Mn_2O_3

Initial Cobalt Concentration

	0.4285×10^{-4}		0.857×10^{-4} M		4.285×10^{-4} M	
pH	µM/g	µM/m^2	µM/g	µM/m^2	µM/g	µM/m^2
6.9	1.60	0.032	1.18	0.023	2.10	0.042
7.0	6.60	0.132	2.90	0.058	3.70	0.074
7.1	9.13	0.183	7.29	0.146	7.80	0.156
7.2	14.1	0.283	10.3	0.206	11.5	0.230
7.3			16.1	0.323	17.8	0.356
7.4			33.8	0.680	35.3	0.706
7.6					48.9	0.977
7.7					77.0	1.54
7.8					104.7	2.09
7.9					178.5	3.57

Table 11 - Cobalt adsorption by Mn_3O_4 solid

pH	Initial Cobalt Concentration 0.4285×10^{-4} μM/g	 μM/m^2	 0.857×10^{-4}M μM/g	 μM/m^2	 4.285×10^{-4}M μM/g	 μM/m^2
6.9			1.27	0.026	2.04	0.041
7.0			2.94	0.059	3.94	0.079
7.1	1.75	0.035	7.13	0.143	7.82	0.156
7.2	6.51	0.130	10.4	0.209	11.2	0.260
7.3	9.23	0.185	15.9	0.318	18.3	0.366
7.4	14.3	0.286	34.0	0.680	35.0	0.700
7.6					49.2	0.984
7.7					75.9	1.52
7.8					105.3	2.11
7.9					175.5	3.51

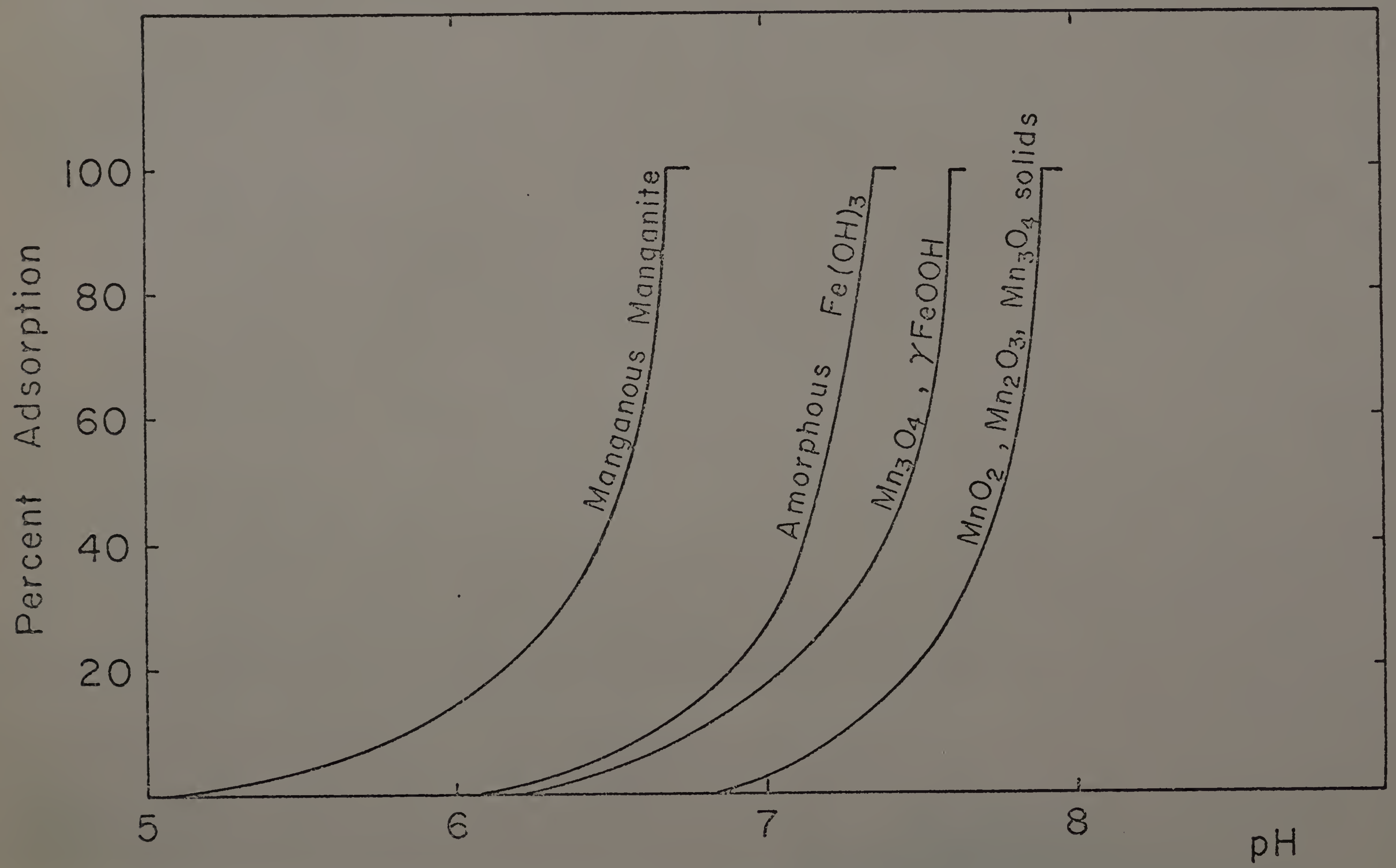


Figure 10. Percent cobalt adsorption on the various substrates as a function of

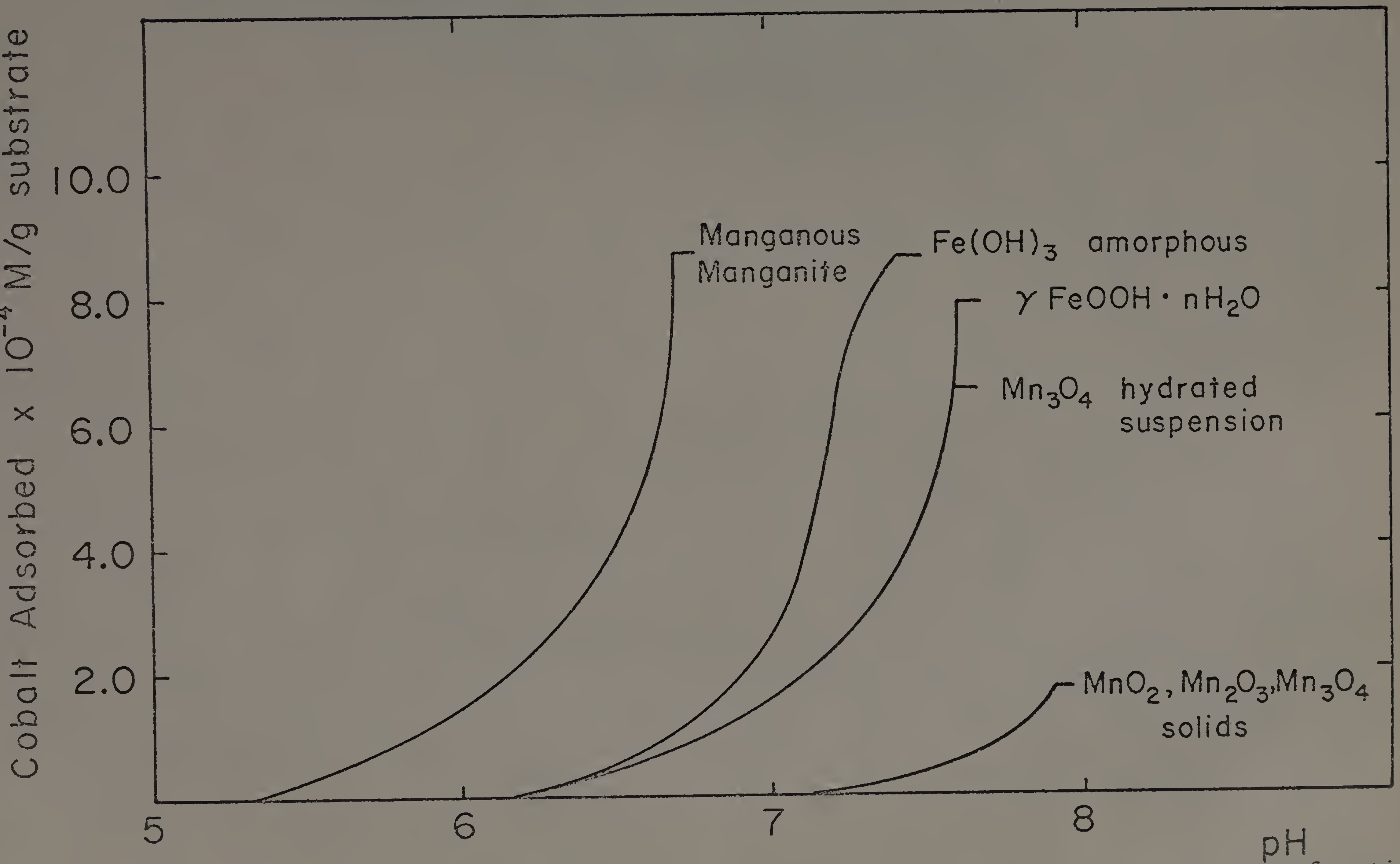


Figure 11. Adsorption of cobalt in Moles/g on the various substrates as a function of pH. Initial concentration: 4.285×10^{-4} M/1

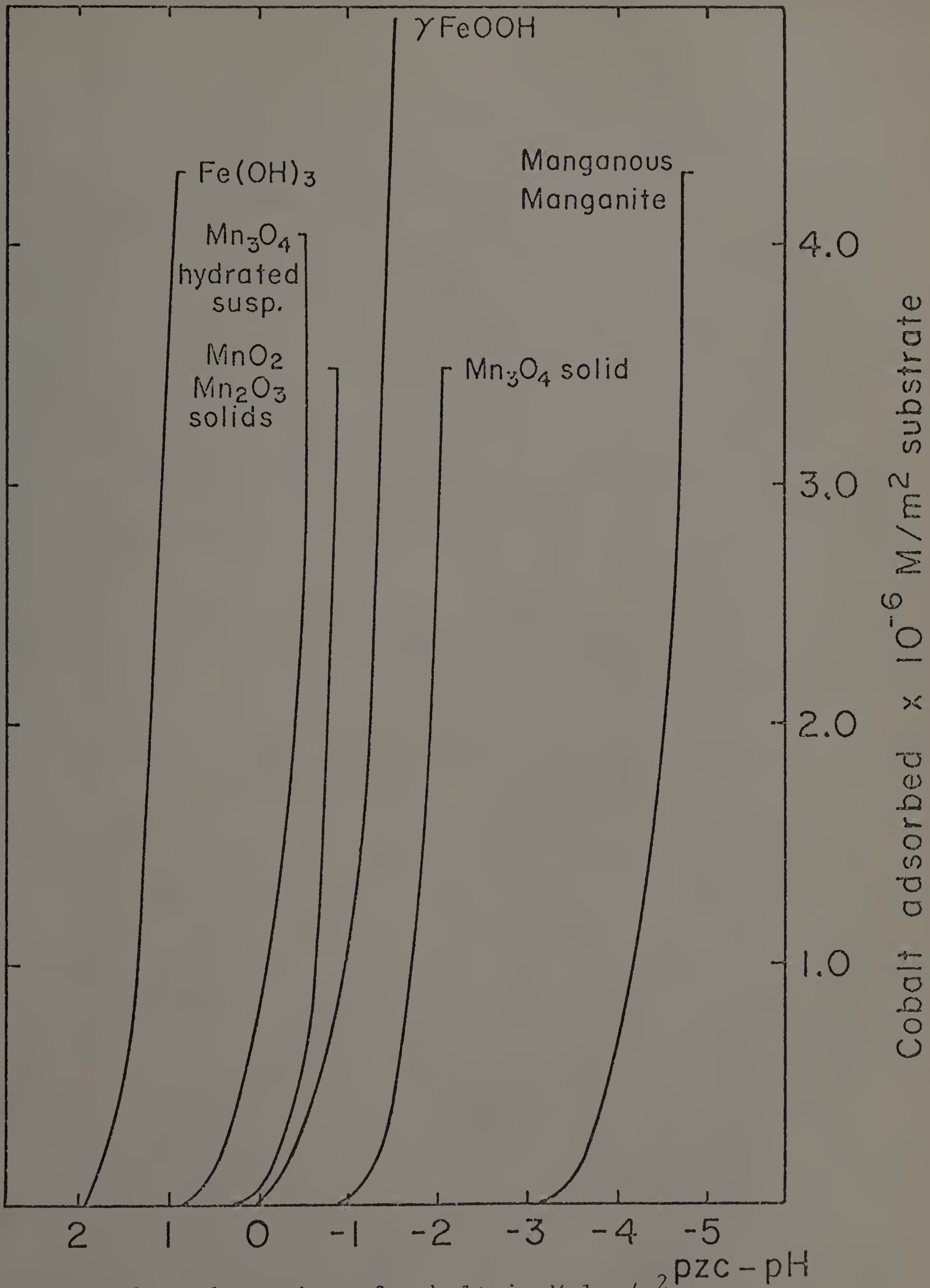


Figure 12. Adsorption of cobalt in Moles/m^2 on the various substrates as a function of PZC-pH. Initial concentration: 4.285×10^{-4} M/l

the adsorbed species is assumed to be the bare Co^{2+} ion plus a monomolecular sheath of water in hexa coordination each ion would occupy 3.935×10^{-19} m^2. Consequently a monomolecular layer of such ions would contain 4.12×10^{-6} moles Co^{2+}/m^2. The surface coverage, representing the fraction of such a monolayer occupied by adsorbed cobalt, as a function of pH at the three cobalt concentrations for each substrate is shown in Figures 13, 14, 15, 16 and 17.

Certain aspects of metal ion adsorption, such as, release of hydrogen ions, had been previously studied. Murray, Healy and Fuerstenau (1968) reported that the released hydrogen ions are in proportion to the quantity of metal ions adsorbed. In contrast Gadde and Laitinen (1974) found that the hydrous manganese oxide at pH = 6 released 1.4, 1.3, 1.1 and 0.38 H^+ for each Pb, Cd,Zn, and Tl adsorbed respectively. Gadde and Laitinen (1974) reported 10-13 minutes equilibrium time in their adsorption experiments. Murray, Healy and Fuerstenau (1968), then Healy, James and Cooper (1968) found that 3-12 hours were necessary to reach an equilibrium in cobalt adsorption by manganous manganite and SiO_2; Kurbatov, Wood and Kurbatov (1951) assumed 24 hours equilibrium time also in cobalt adsorptions by coprecipitated hydrous ferric oxides.

Equilibrium at constant pH was never attained in these experiments. The samples of hydrous oxides and cobalt required

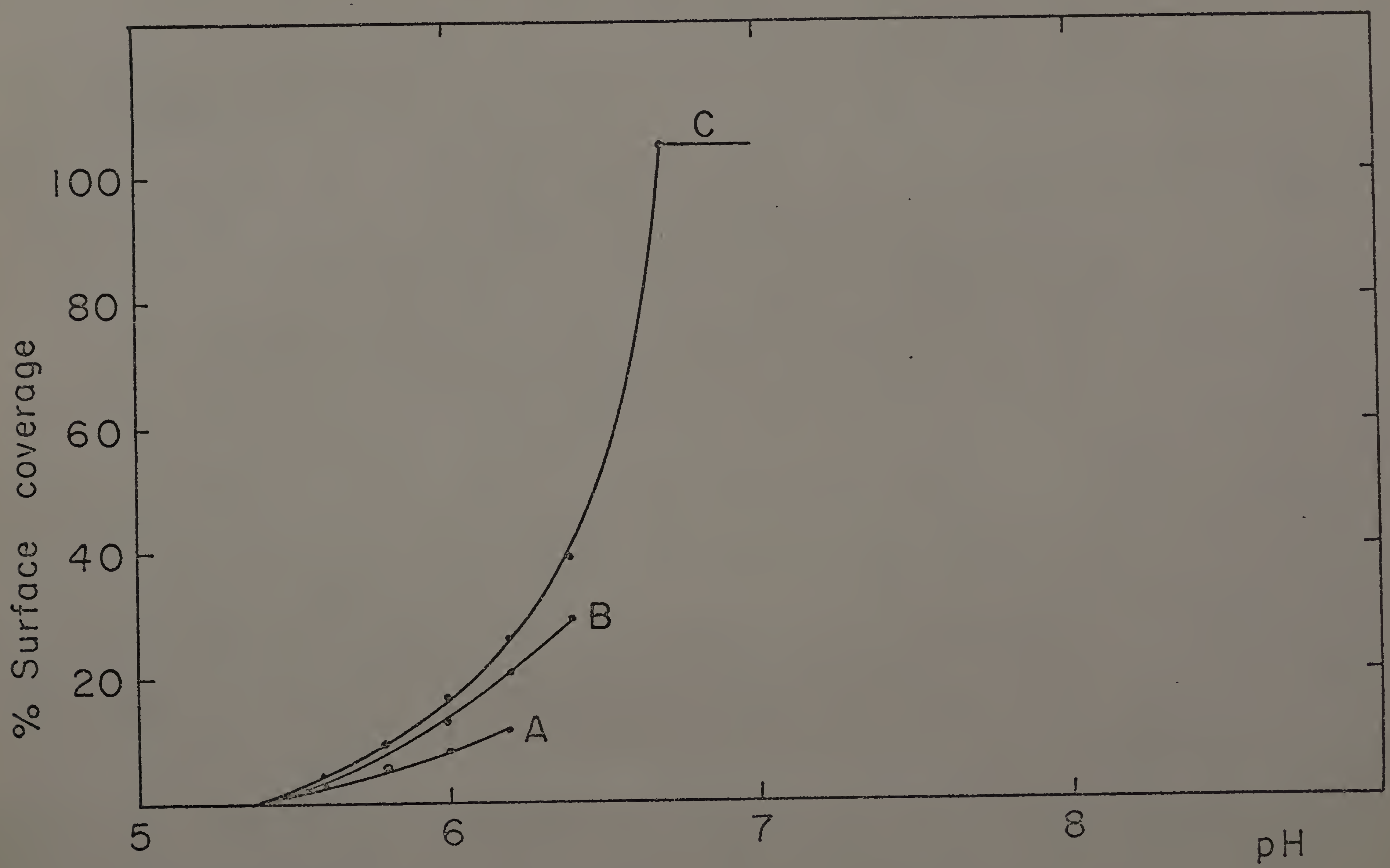


Figure 13. Monolayer coverage of $Co(H_2O)_6^{2+}$ on manganous manganite hydrated suspension. Initial concentration:

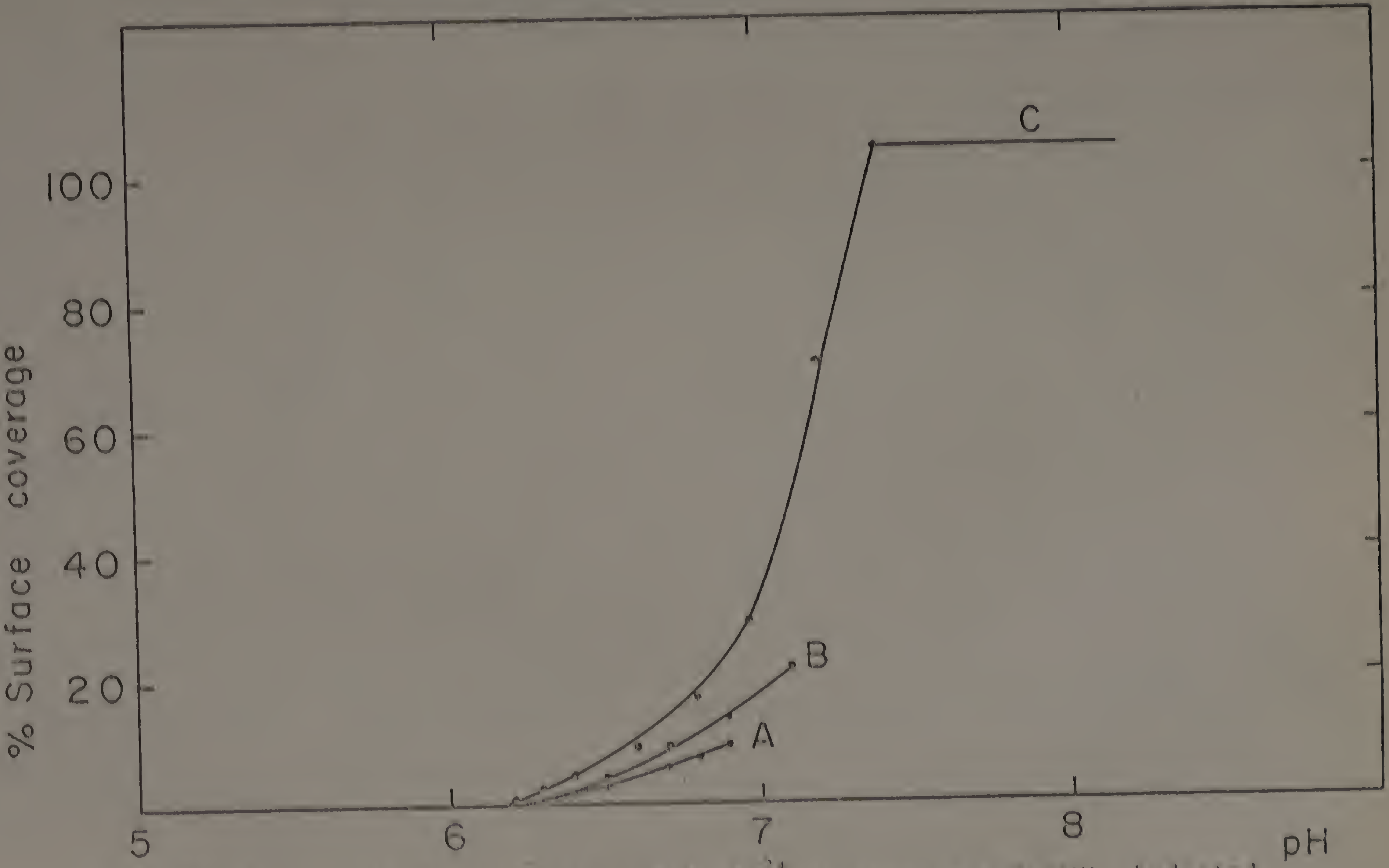


Figure 14. Monolayer coverage of $Co(H_2O)_6^{2+}$ on amorphous $Fe(OH)_3$ hydrated suspension. Initial concentration:

A= 0.4285×10^{-4} M/1, B= 0.857×10^{-4} M/1, C= 4.285×10^{-4} M/1

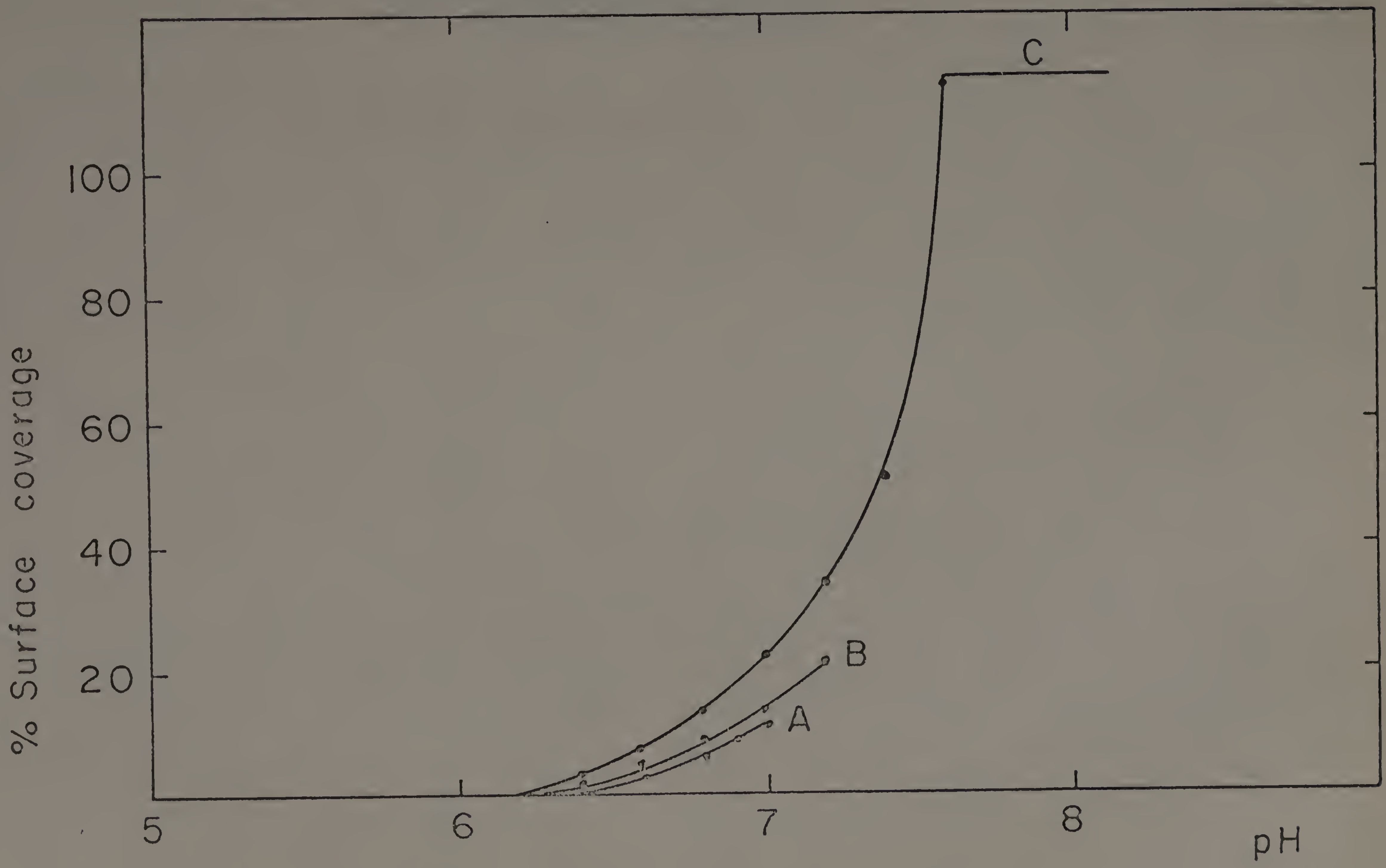


Figure 15. Monolayer coverage of $Co(H_2O)_6^{2+}$ on $\gamma FeOOH \cdot n H_2O$ hydrated suspension. Initial concentration: $A=0.4285 \times 10^{-4}$ M/1, $B= 0.857 \times 10^{-4}$ M/1, $C=4.285 \times 10^{-4}$ M/1.

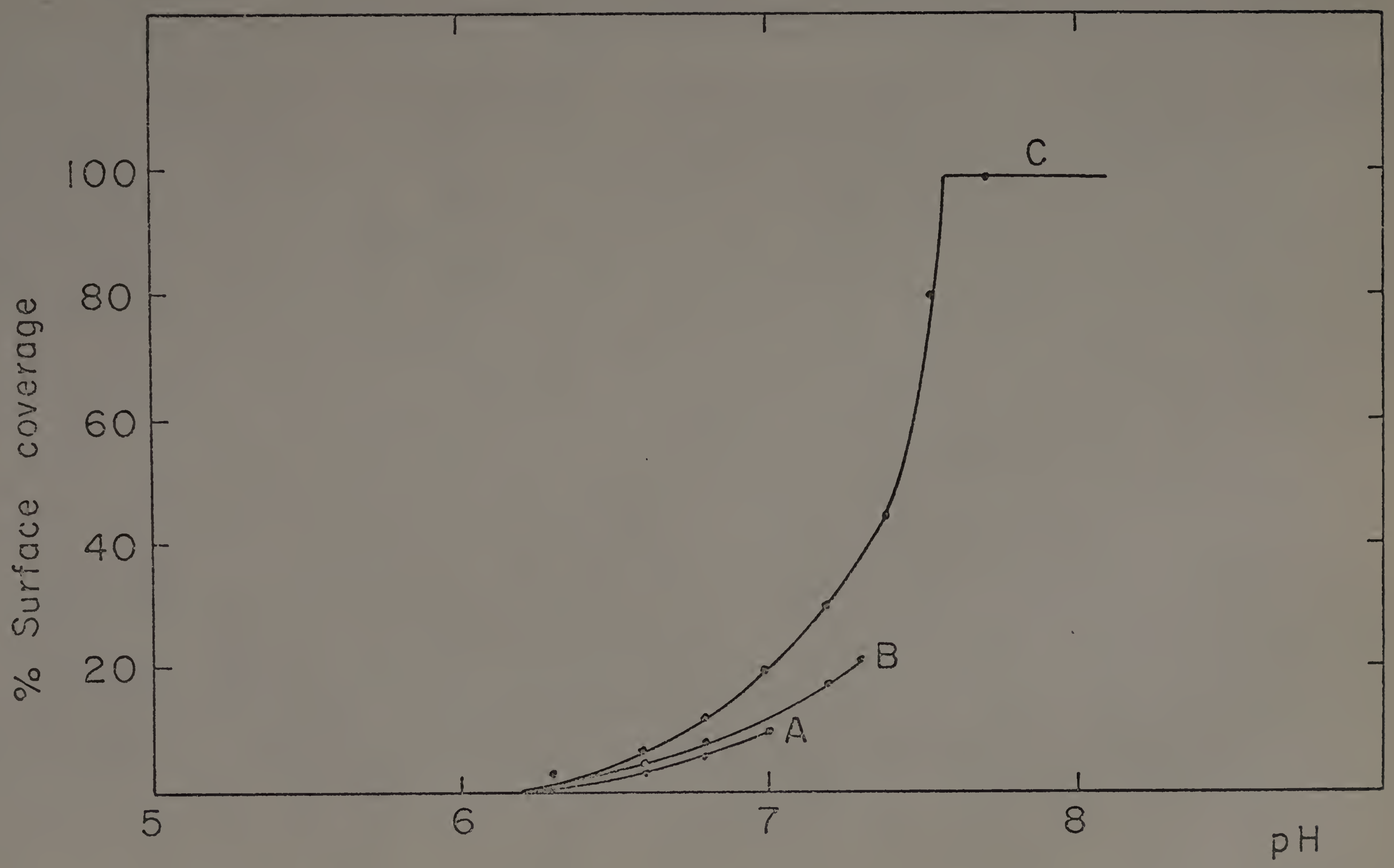


Figure 16. Monolayer coverage of $Co(H_2O)_6^{2+}$ on Mn_3O_4 hydrated suspension.

Initial concentration: A= 0.4285×10^{-4} M/1, B= 0.857×10^{-4} M/1, C+ 4.285×10^{-4} M/1.

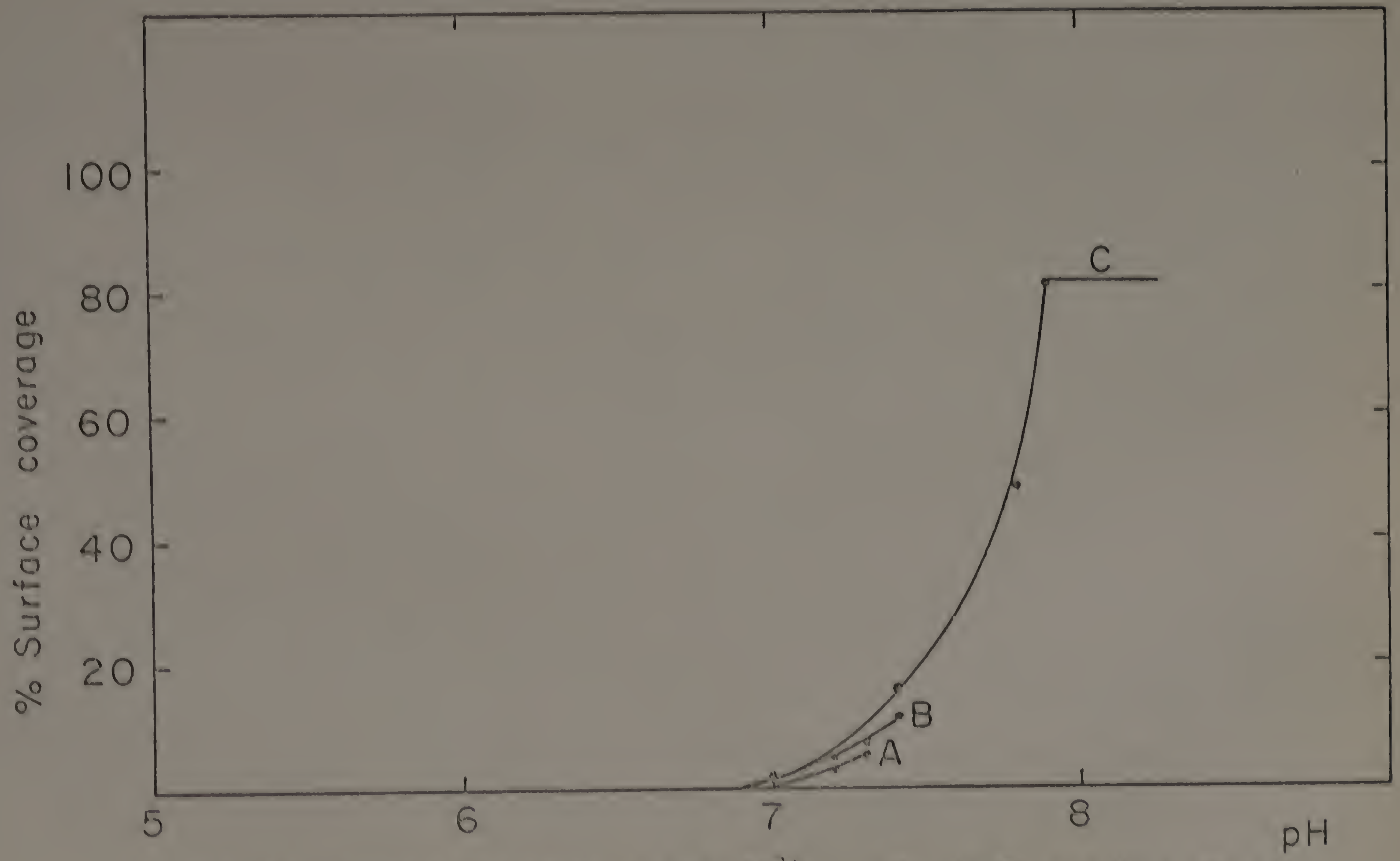


Figure 17. Monolayer coverage of $Co(H_2O)_6^{2+}$ on MnO_2, Mn_2O_3 and Mn_3O_4 solids.
Initial concentration: A= 0.4285×10^{-4} M/1, B= 0.857×10^{-4} M/1, C= 4.285×10^{-4} M/1.

almost a continuous pH readjustment in the first 15-20 minutes of adsorption and H^+ release was evident throughout the entire process.

In the preliminary experiments no change occurred in cobalt adsorption during the 3 additional hours; however, a considerable drop in pH was observed in the samples, especially where the pH was adjusted to high values. The greatest pH decrease was observed when the adsorption occurred from the most concentrated solution. All samples displayed some degree of pH decrease after standing 3 days at room temperature, but the drop in pH was seldom accompanied by an appropriate amount of released cobalt. Adsorptions over 60% were almost entirely irreversible in this respect and only a few instances at relatively low pH values indicated complete release of cobalt when the pH dropped in the sample. A varying degree of irreversibility in cobalt uptake and a characteristic adsorption behavior was displayed by each of the 7 adsorbents having different chemical composition, specific surface, crystallinity and point of zero charge.

Discussion: For each metal ion and substrate there is a critical range of pH in which the percent adsorption increases from near zero to one hundred percent. This pH range is usually 1 unit. The cobalt adsorption by the 7 adsorbing mineral species occurred between pH = 5 and 7.9. The wide pH range, in which cobalt ions adsorb to mineral surfaces of various structure and chemical composition, demonstrates that the influence of a substrate on an adsorption process is significant. The subtle yet significant role of adsorbent was studied by numerous authors. James and Healy (1971) investigated cobalt adsorption on SiO_2 and TiO_2 solids; Kurbatov, Wood and Kurbatov (1951) reported cobalt adsorption by coprecipitated iron hydroxide; Matijevic and Tezak (1953) then Matijevic, Abramson,Schultz and Kerrer (1960) studied thorium and aluminum adsorption on silver halides. Coagulation studies conducted with thorium and aluminum ions provided evidence that the hydrolyzed species of metal ion or the hydroxyl group in the counter ion complex is the main factor that causes the coagulation. These results were substantiated by adsorption studies in which thorium species adsorbed strongly on positive rather than negative silver halide sols. James and Healy's studies provided further evidence for the role of hydroxyl group in charge reversal observed on SiO_2 and TiO_2. Cobalt ions hydrolyze but the hydrolysis products are relative simple. The region of hydrolysis is around pH = 7. There is no evidence that any important polynuclear complexes form or participate in the adsorption processes.

Manganous manganite adsorbed cobalt in the region of pH = 5.4-6.7. The results of adsorption are given in Table 5. The highest quantity of cobalt on the basis of moles/g substrate was adsorbed by this material. The maximum adsorption was 4.334×10^{-6} M/m^2 at pH = 7.6 and the surface coverage obtained at the 3 cobalt concentrations were 11.4%, 38.3% and 105.2%.

The point of zero charge of manganous manganite is 1.9± 0.5 but the earliest cobalt adsorption was observed at pH = 5.3. The classical interpretation of cobalt adsorption by this material is the simple electrostatic model which places the cobalt species as counter ions in the diffuse double layer developed around the negatively charged particles. The simple coulombic attraction fails to give a satisfactory explanation for the delayed cobalt adsorption which occurred at pH - 5.3 while the surface charge on this material was negative when the pH was greater than 2.5. James and Healy (1972) suggested that the secondary solvation energy of the ion and the dielectric constant of interface are decisive factors in the adsorption processes of metal ions by various substrates. According to the theory, a bimolecular water layer envelops the ions in aqueous solution and ion adsorption can occur only if the secondary hydration sheath has been removed. The removal of the secondary solvation sheath requires a large amount of energy if the dielectric constant in the solid-liquid interface is low. The large energy requirement inhibits ion adsorption and delays the process to higher pH values where hydrolysis lowers the secondary solvation energy. A more likely possibility under these conditions is that cobalt could not be adsorbed until the H_3O^+

concentration was decreased sufficiently to allow $[Co(H_2O)_6]^{2+}$ to compete for the double layer sites, because the charge density on H_3O^+ is greater than on $[Co(H_2O)_6]^{2+}$.

Another feature of cobalt adsorption by this substrate was the relatively high degree of irreversibility. A 78.7% adsorption occurred at pH = 6.3 at cobalt concentration 0.857×10^{-4}M . Three days later the pH was 5.32 but the adsorbed cobalt remained 69.8%. An early theory was established by Murray, Healy and Fuerstenau (1968), who interpreted the extensive uptake of cobalt by manganous manganite solid in their experiments, as an ion incorporation into the disordered layers of lattice structure. They also observed that desorption of cobalt did not occur even from a strongly positive surface. It is known that certain metal ions can be oxidized on electrode surfaces, therefore the possibility of converting Co^{2+} to Co^{3+}, by surface oxidation in the solid-liquid interface region, was also proposed.

The cobalt adsorption by amorphous $Fe(OH)_3$ occurred in the region of pH = 6.2-7.4; the results are given in Table 6. This material adsorbed the second largest amount of cobalt on the basis of moles/g substrate. The point of zero charge of amorphous $Fe(OH)_3$ is 8.3, therefore the entire range of cobalt adsorption occurred on positively charged surfaces. The distinctive steep rise of the adsorption isotherm in Figures 10, 11 and 12 indicates a specific cobalt adsorption by this material. A moderate pH drop and high degree irreversibility in the adsorption was once again observed in all samples after three days.

An explanation for the irreversible nature of cobalt adsorption may be the apparently insignificant roles of electrostatic forces in this process. James and Healy (1971) proposed that this type of adsorption is governed by a negligible secondary solvation energy and a high dielectric constant in the solid-liquid interface. The low secondary solvation energy and the high dielectric constant of solid favor ion adsorption which is a specific adsorption on a positively charged substrate. Specific adsorption of zinc by ferric hydroxide gel was observed by Kinniburgh and Jackson (1974).

γ FeOOH . nH_2O adsorbed cobalt in the region of pH = 6.2-7.6. The results of adsorption measurements are shown in Table 7. Maximum adsorption with a value of 4.943×10^{-6} M/m^2 was observed at pH = 7.6 and surface coverage at the 3 cobalt concentrations were 8.8%, 21.2% and 114%. The point of zero charge of this hydrous iron oxide is 6.1, therefore the total range of cobalt adsorption occurred on negatively charged surfaces.

The most apparent feature of this adsorption was the best reversibility observed among the 7 substrates. A 54% adsorption measured at 4.285×10^{-4} M cobalt concentration at pH = 7.5. Three days later the adsorption was 29.9% while the pH dropped to 7.1 in the solution. On the adsorption isotherm pH = 7.1 corresponds to 24% adsorption. Ion uptake from the two more diluted solutions showed also good reversibility and almost ideal cobalt desorption as the pH decreased. The reversibility of adsorption and the fact that cobalt adsorption occurred exclusively on negatively charged surfaces suggest that specific contribution to the adsorption process was relatively small. Since no delay has been observed in cobalt adsorption, low secondary solvation energy and high dielectric constant in the solid-liquid interface played important roles in the process. (James and Healy, 1971)

Mn_3O_4 hydrated suspension followed very closely the γ FeOOH in the entire cobalt adsorption. The percent adsorption as Figure 10 and Table 8 show at various pH values from the 4.285×10^{-4} M solution agree with those obtained by γ FeOOH within experimental error. The maximum adsorption was 4.052×10^{-6} M/m^2 at pH = 7.6 and the values of surface coverage were 10.4%, 20.75% and 98.4%. The point of zero charge of

Mn_3O_4 hydrated suspension is estimated to 7.0. A small but definite cobalt adsorption was measured at the point of zero charge although the major part of cobalt adsorption occurred on the negatively charged substrate. The overall cobalt adsorption by this material was attributed partly to specific adsorption and partly to coulombic attraction. From 0.4285×10^{-4} M and 0.857×10^{-4} M solutions Mn_3O_4 adsorbed more cobalt but at 4.285×10^{-4} M concentration γ FeOOH was the more effective adsorbent. The actual amount of cobalt adsorbed by this substrate should have been higher at all concentrations since the adsorption was both specifically and electrostatically induced. The reduced cobalt adsorption by Mn_3O_4 may have been caused by a smaller effective surface area due to flocculation in the 4.285×10^{-4} M cobalt solution. This material displayed a noticeable tendency to flocculate even in the most dilute cobalt solution, while both iron oxides and the manganous manganite remained completely peptized under the same conditions. A small drop in pH and some irreversibility in the cobalt adsorption, observed in the samples after three days, demonstrate that the specific adsorption was probably more important here than it was in the adsorptions by the γ FeOOH.

The cobalt adsorption by the 3 solid materials MnO_2, Mn_2O_3 and

Mn_3O_4 occurred between pH = 6.5 and 7.9. These substrates adsorbed cobalt at higher pH values than any of the hydrated suspensions. The results of adsorption measurements are given in Table 9-11. The results of adsorption measurements are 3.51×10^{-6} M/m^2 and the values of surface coverage were 6.5%, 15.7% and 81.3%. The point of zero charge of MnO_2 and Mn_2O_3 is about 6.9 and 7.1 while that of Mn_3O_4 is about 5.9. Despite the difference in the point of zero charge of these materials the observed cobalt adsorption by them appears to be the same in all respects. The major part of adsorption occurred on negatively charged surfaces; however, a small per cent of specific adsorption apparently had also taken place on MnO_2 and Mn_2O_3 from $0.4285 \times 10^{-4}M$ and $0.857 \times 10^{-4}M$ solutions. A small decrease in pH and a high irreversibility in adsorption were observed with these samples. The overall cobalt adsorption by these materials was partly specific and partly coulombic attraction. Since the adsorption occurred at relatively high pH values, participation of hydrolysis products may have also been more important here than in the adsorption by the hydrated suspension.

Theory of adsorption mechanism: For the cobalt adsorption mechanism James and Healy (1972) proposed a theory supported by the results of adsorption measurements and charge reversal on SiO_2 and TiO_2. The above authors concluded that no covalent bond formation can take place between the adsorbed cobalt species and the surface. At monolaver coverage there is always one molecule of water between the adsorbed species and the surface; consequently direct chemical bond is precluded. The adsorption does not depend on any general way on any particular species such as some hydrolysis product. There is no evidence that polynuclear species had formed in response to pH or that they play any role in the cobalt adsorption processes. The cobalt aquo complex is the predominant species in all solutions at pH = 6-8. The ion uptake occurs in the interfacial region which includes adsorption and surface precipitation at pH values significantly below the bulk precipitation.

A delayed adsorption of cobalt, as was observed on manganous manganite and to some extent on M_3O_4 is the result of the effect of the secondary solvation energy according to the theory of James and Healy (1972). According to this theory, when ions are adsorbed in a liquid-solid interface the secondary solvation sheath about the ions must be removed. The energy requirement for the displacement of the secondary water layer may be quite large and a major contribution to the secondary solvation energy is made by the dielectric constant of the solid. The dielectric constant is the property of the gel-like amorphous layer in the solid-liquid interface and the value may be quite different than that obtained experimentally on a single crystal or powder. The secondary solvation energy is high when the solid has a low dielectric constant therefore both specific and coulombic attractions of ions to the surface are opposed. Metal ion adsorption by this kind of substrate will only be observed when the pH is increased enough so that the secondary solvation energy decreases in response to increased hydrolysis of the ion in solution and the coulombic attraction increases owing to the increased negative energy on the surface. In contrast, the secondary solvation energy is low if the solid has a high dielectric constant in the solid-liquid interface. Consequently significant adsorption can occur even when the surface charge on the solid is zero if there is a specific attraction and an abruptly increased adsorption will be observed as the negative charge on the solid increases. Therefore, the overall cobalt adsorption is controlled by specific and coulombic interactions when the solid has high dielectric constant, but hydrolysis is the controlling power if the dielectric constant of the substrate is low.

A relatively small effect on the secondary solvation energy is exerted by the ionic strength of the solution. As the ionic strength increases, the electrical double layer about the particles becomes compressed; in turn, the increased electrical field and secondary solvation energy result in a decrease adsorption of the cobalt ions.

Murray, Healy and Fuerstenau (1968) suggested the catalytic oxidation of Co^{2+} at the solid-liquid interface of manganese oxides and the subsequent incorporation of Co^{3+} into the crystal lattice. McKenzie (1971) interpreted his results of cobalt fixation experiments as surface oxidation process in which Co^{2+} is oxidized by Mn^{3+} and the Co^{3+} replaces the manganese ion in the octahedral lattice units. Tewari (1973) also observed specific adsorption of cobalt by ZrO_2 and Fe_3O_4 and also charge reversal with precipitation at pH> 8. However, the X-ray photoelectron spectrum of cobalt adsorbed on ZrO_2 revealed only $Co(OH)_2$ on the mineral surface. In order to understand the detailed mechanism of cobalt adsorption by various adsorbents evidently more research is necessary.

Effect of Various Factors on the Cobalt Adsorption Process

1. pH Effect: The results of cobalt adsorption on the manganese and iron oxide samples show that each mineral species has its own adsorption range of pH. In acidic soils or natural waters the most effective cobalt adsorbent by far could be minerals similar to the manganous manganite hydrated

suspension. This material adsorbs at pH = 5.4-6.7 where none of the other mineral species adsorbs appreciably. An equally effective adsorbent of slightly acidic to slightly alkaline medium is the amorphous $Fe(OH)_3$. Both manganous manganite and amorphous $Fe(OH)_3$ are prevalent in soils and sediments, and the pH range of adsorption indicates that they probably are the most important cobalt scavengers in natural environment. The slow response of cobalt desorption to pH changes may reflect the fate of cobalt fertilizers applied to soils rich in manganous manganite or amorphous $Fe(OH)_3$.

The γ FeOOH and Mn_3O_4 hydrated suspensions are effective cobalt adsorbents in slightly alkaline environments. The generally good reservibility of cobalt uptake suggests that cobalt adsorbed by these minerals in soils may be released readily as the plant roots create an acidic environment in the soils. The solid and crystalline MnO_2, Mn_2O_3 and Mn_3O_4 adsorb only under in alkaline conditions. The pH range, from 7.0 to 7.9 and the irreversible nature of adsorption indicate that these minerals may be effective scavengers in alkaline or marine environments.

2. <u>Effect of Surface Area:</u> The most predominant factor in the effectiveness of cobalt adsorption at a given pH is the

surface area of the adsorbent. These mineral species that have different chemical composition, different degree of crystallinity, different point of zero charge, but have similar surface area, showed very similar adsorption capacities on the surface area basis. At surface saturation, the adsorption capacities of the four hydrated suspensions were between 4.943×10^{-6} M/m^2 and 4.053×10^{-6} M/m^2. A slightly lower adsorption capacity of 3.5×10^{-6} M/m^2 was obtained for the three solid materials, also at surface saturation. The fact that comparable adsorption capacities were obtained for hydrated suspensions and solid materials indicate the overall importance of surface area in the cobalt adsorption processes. The similarity observed in the adsorption capacities of various mineral species also supports the theory and results of James and Healy (1972) that the adsorbed cobalt ions on all substrates retain their primary hydration sheaths at all coverage up to saturation. The 98%, 104%, 105%, 114% and the 81.3% (for solids) surface coverage at saturation indicate clearly that values obtained for surface area are also valid and reliable figures.

3. Effect of Crystallinity: Another factor that has importance in effectiveness of cobalt adsorption is the crystallinity of the adsorbent. There is considerable difference in the pH

range of adsorption for minerals of the same chemical composition and different degree of crystallinity as illustrated in Figures 10 and 11. Manganous manganite and MnO_2 displayed the most different adsorption capacities. The difference is even more noticeable when the cobalt was adsorbed from dilute solutions. Values of 0.47×10^{-6} M/m^2 and 0.90×10^{-6} M/m^2 were obtained for manganous manganite while only 0.28×10^{-6} M/m^2 and 0.68×10^{-6} M/m^2 adsorption capacities were measured for MnO_2 from 0.2485×10^{-4} M and 0.857×10^{-4} M solutions. An explanation for the spectacular difference in adsorption behavior, displayed by these minerals, may be the disordered layer structure of manganous manganite and the high degree of crystallinity of MnO_2. The presence of Mn^{2+} and Mn^{3+} ions in manganous manganite and the absence of those in MnO_2 cannot be responsible for the observed difference in adsorptions since there are manganese ions in oxidation states lower than +4 in both Mn_2O_3 and Mn_3O_4 solids and still all the three crystalline solids adsorbed the same amount of cobalt. The equal amount of cobalt adsorbed by Mn_2O_3 and Mn_3O_4 provides an additional evidence for the importance of surface area in adsorption processes because the surface area in m^2/l of both adsorbents in every sample was the same.

The difference in adsorption capacities of amorphous $Fe(OH)_3$ and γ FeOOH was small. Adsorption range in pH was very similar for both materials but maximum adsorption occurred at pH = 7.4 for amorphous $Fe(OH)_3$ and at pH = 7.6 for γ FeOOH. Perhaps a more apparent difference was displayed in the reversibility of the cobalt adsorption by these substrates and cobalt adsorbed by the crystalline γ FeOOH may be more available than that adsorbed by the amorphous $Fe(OH)_3$. It is important to remember, though, that the reversibility of cobalt uptake by a substrate was measured only over a three-day time period and predictions about the course of cobalt adsorption-desorption process cannot be made in regard to a long period of time or different conditions. Mn_3O_4 hydrated suspension and Mn_3O_4 solid showed considerable difference in adsorption capacities, and the difference was most apparent in adsorptions occurring at low cobalt concentrations. The values of maximum adsorption were 0.4285×10^{-6} M/m^2, 0.854×10^{-6} M/m^2 and 4.052×10^{-6} M/m^2 for Mn_3O_4 hydrated suspension; 0.282×10^{-6} M/m^2, 0.679×10^{-6} M/m^2 and 3.510×10^{-6} M/m^2 for solid Mn_3O_4. As these results indicate, the hydrated suspension adsorbed 10-40% more cobalt than the crystalline material. The higher reversibility of the cobalt adsorption by the hydrated suspension compared to that by the solid Mn_3O_4 cannot be explained by the effect of crystallinity.

4. Effect of pzc: The point of zero charge of the materials showed the most subtle effect on cobalt adsorption. There was no difference in adsorption capacities of substrates whether the cobalt uptake was due to either specific or coulombic attractions. Specific adsorption of cobalt occurred on the amorphous $Fe(OH)_3$ as the steep rise of adsorption isotherm and the narrow range of pH as indicated in Figures 10 and 11. A small percentage of specific cobalt uptake by Mn_3O_4 hydrated suspension was also observed. There was no difference in adsorption capacities whether the cobalt uptake was specific or coulombic as the results in Tables 4 to 8 indicate; therefore, other factors such as, the surface area and crystallinity had the controlling influence over the capacity of the minerals to adsorb cobalt.

Conclusion: Cobalt adsorption by the hydrated suspensions of manganese and iron oxides occurred in various ranges of pH while the shapes of adsorption isotherms were all similar. The general adsorption behavior of all the 7 adsorbents was also alike. The similar adsorption capacities measured at surface saturation prove that all hydrated suspensions are equally capable cobalt adsorbents at certain pH values and no preferential cobalt uptake was observed by either manganese or iron oxide sample.

In acidic environments the most reactive cobalt adsorbent of the 7 substrates is the manganous manganite. In soils or sediments, where the pH is about 5.2, only manganous manganite of the mineral species studied is capable of cobalt adsorption. With rising pH the adsorption capacity of this material increases and at pH = 6.2, 100% adsorption occurs from a 2.5 ppm cobalt solution under the experimental conditions. Amorphous $Fe(OH)_3$ shows only a 7% cobalt adsorption at pH = 6.2, but as the pH increases, this material, as a cobalt adsorbent gains importance. At pH 6.5 the manganous manganite is still 3-4 times better cobalt adsorbent than the amorphous $Fe(OH)_3$, but in the absence or in a negligible quantity of manganous manganite, the amorphous $Fe(OH)_3$ absorbs more cobalt. The Mn_3O_4 and γ FeOOH hydrated suspensions, if present, also participate with 28% and 18% adsorption values. At pH = 6.9 all hydrated suspensions adsorb with equal effectiveness, provided that all have the same surface area and the quantity of cobalt adsorbed by each substrate depends only on the relative abundance of the various mineral species. Under usual soil conditions, the more prevalent mineral species are the iron oxides. The relative amount of iron to manganese was between 10:1 and 20:1 in the soil samples analyzed here. If the pH is over 6.2 in the soil environment, irregard to the adsorption capacities of the individual minerals, iron oxides adsorb a larger quantity of cobalt than the manganese oxides in hydrated suspension. Therefore, in soil conditions where hydrated suspensions can exist, the pH and the surface area control the entire cobalt adsorption process and other properties of minerals such as chemical composition, crystallinity and point of zero charge play minor roles.

Cobalt Associated With Manganese And Iron Oxides In Massachusetts Soils

Five soil samples were used for cobalt, manganese and iron determinations with an intention to compare the amount of cobalt associated with manganese and iron oxides.

Determination of cobalt associated with manganese oxides was carried out by two methods.

1. Since manganese oxides differ from iron oxides in solubility in response to oxidation-reduction conditions Chao (1972) reported an extraction method for the selective dissolution of manganese oxides from soils and sediments. He found that manganese oxides present in soils readily dissolved in hydroxylamine hydrochloride solution with a minimal attack on coexisting iron oxides. A solution of 0.1M NH_2OH . HCl adjusted to pH=2 with 0.01 M HNO_3

dissolved synthetic α, δ, and γ manganese oxides instantly. A sample of reagent grade β MnO_2 and bog manganese oxides dissolved in 30-60 minutes. Only 8% of the total amorphous iron oxides was soluble in the hydroxylamine solution and the crystalline iron minerals such as hematite and goethite were not attacked. In a sequential extraction process the rate of dissolution of manganese oxides may relate to the reactivity of the various modifications of these minerals. Since the hydroxylamine hydrochloride both reduces and dissolves the manganese compounds, the more readily soluble fraction may represent the more reactive forms of manganese oxides.

2. Taylor and McKenzie (1966) used a 10% H_2O_2 solution in 0.001 M HNO_3 to extract the manganese oxides from soils and concretions. These authors found that birnessite and lithiophorite were the most common manganese minerals in widely different types of Australian soils. A single peroxide treatment removed about 50% of the total manganese present in the sample. Obviously the sample also contained some primary rocks and other manganese minerals insoluble in the peroxide solution. This method requires 3 days of treatment but only occasional shaking of the sample-solution mixture, a longer reaction time or continous agitation of

the rapidly settling sample could have resulted in a greater amount of dissolved manganese.

McKeague and Day (1965) and McKeague, Brydon and Miles (1971) reported that an approximate differentiation between amorphous and crystalline iron oxides can be made by selective dissolution of a sample with oxalate and dithionite-citrate solutions. The oxalate solution dissolved a large proprotion of the amorphous iron oxides but very little of the crystalline modifications. The dithionite extraction removed both amorphous and crystalline iron minerals. Therefore the oxalate values give only amorphous iron oxide content of a soil whereas dithionite values approximate the combined content of amorphous and crystalline iron modifications.

Five soil samples were extracted in sequence with hydroxylamine hydrochloride, oxalate and dithionite-citrate solutions. The results of these extractions are given in Table 12 and 14. For comparison, the soil samples were also extracted with oxalate alone; and with dithionite solution alone. The values obtained by the latter methods are shown in Table 13.

A comparison of Table 12,13 and 14 shows that sequential extraction resulted in a more complete extraction of cobalt and manganese than the single solution treatment.

TABLE 12.

Sequential extraction of soils

1. Hydroxylamine hydrochloride extract

Sample	Cobalt ppm	Manganese ppm	Iron ppm
Hadley	2.8	180	4
Sandwich	1.0	7	55
Salcum	4.4	437	75
Davidson	4.6	130	18

2. Oxalate extract (following $NH_2OH.HCl$ extraction)

Sample	Cobalt ppm	Manganese ppm	Iron %
Hadley	2.9	223	0.80
Sandwich	0.9	9	0.24
Salcum	4.4	515	0.76
Davidson	4.2	137	0.54

3. Dithionite extract (following $(NH_4COO)_2$ extraction)

Sample	Cobalt ppm	Manganese ppm	Iron %
Hadley	0.8	80	1.05
Sandwich	0	70	1.50
Salcum	0.8	150	2.00
Davidson	0.8	432	9.90

TABLE 13.

1. Oxalate extract

Sample	Cobalt ppm	Manganese ppm	Iron %
Hadley	5.4	345	0.51
Sandwich	1.3	9	0.25
Salcum	7.9	800	0.50
Davidson	7.9	240	0.23

2. Dithionite extract

Sample	Cobalt ppm	Manganese ppm	Iron %
Hadley	5.7	370	0.94
Sandwich	0.9	35	1.01
Salcum	5.2	900	2.00
Davidson	5.1	705	9.25

TABLE 14.

Sequential extraction of Berkshire soil.

1. Hydroxylamine hydrochloride extract

Horizon	Cobalt ppm	Manganese ppm	Iron ppm
A_2	1.2	45	8
B_2	3.9	19	5
B_3	1.4	26	4
C_1	1.2	28	16
C_2	3.7	151	34

2. Oxalate extract (following $NH_2OH.HCl$)

Horizon	Cobalt ppm	Manganese ppm	Iron %
A_2	2.0	130	0.22
B_2	5.1	80	0.56
B_3	1.9	31	0.35
C_1	1.9	30	0.27
C_2	3.9	162	0.19

Approximately 40-50% of the total extractable cobalt was found in the hydroxylamine hydrochloride solution. Another 50-50% of the total extractable cobalt dissolved in oxalate and the remaining 10-20% dissolved in dithionite. About the same amount of cobalt and manganese dissolved in the acidified H_2O_2 over 3 days time period as in hydroxylamine hydrochloride solution. The results of the H_2O_2 extraction are shown in Table 15.

About 40% of the total extractable manganese dissolved in the hydroxylamine hydrochloride solution. An average of 50% of the total extractable manganese was soluble in oxalate along with amorphous iron oxide, and a relatively small fraction was found to be associated with the dithionite soluble crystaline iron oxide.

Iron content was negligible in the hydroxylamine hydrochloride extracts. The relative amount of amorphous $Fe(OH)_3$ compared to crystalline iron oxide varied, although the crystalline iron oxide content was higher in every sample. In the Sandwich soil the amorphous iron oxide content was the lowest with about 20% of the total extractable iron and the remaining 80% was apparently crystalline iron oxide with no detectable cobalt.

The 40-50% of the total extractable cobalt found in the

TABLE 15.

Extraction of soils by the method of Taylor and McKenzie (1966)

1. 0.1M HNO_3 rinse

Sample	Cobalt ppm	Manganese ppm	Iron ppm
Hadley	0.4	69.5	8
Sandwich	<0.1	3.6	30
Salcum	0.4	122.5	29
Davidson	1.6	60.0	14

2. 1 hour extraction with 0.001 M HNO_3

Sample	Cobalt ppm	Manganese ppm	Iron ppm
Hadley	0.4	29.2	6
Sandwich	<0.1	4.8	14
Salcum	0.6	53.5	7
Davidson	1.8	17.5	20

3. 3 days extraction with 10% H_2O_2 in o.oolM HNO_3

Sample	Cobalt ppm	Manganese ppm	Iron ppm
Hadley	2.9	190.6	93
Sandwich	0.7	4.8	830
Salcum	4.7	475.0	310
Davidson	4.8	56.3	35

hydroxylamine hydrochloride extract, which also had about 50% of the total extractable manganese but very little iron, indicates that cobalt is associated with manganese oxides. The other 50% of the total extractable cobalt dissolved in oxalate solution following hydroxylamine hydrochloride extraction, may have been associated with both manganese and iron oxides since this solution also contained about 50% of the total extractable manganese and considerable amount of amorphous iron oxide. Unfortunately, the oxalate soluble cobalt cannot be definitely differentiated into fractions adsorbed by the manganese oxides and by the amorphous iron oxides. However, the fact that 40-50% of the total extractable cobalt dissolved with about 50% of the total extractable manganese suggests that the oxalate soluble cobalt could also be associated with manganese oxides. The oxalate soluble manganese oxides probably were of different modification and crystallinity than those dissolved in hydroxylamine hydrochloride solution.

Taylor and McKenzie (1966) noted that the principal manganese oxide was birnessite in alkaline and lithiophorite in acidic environments. Birnessite is the natural modification of manganous manganite and δMnO_2 according to Bricker's (1965) classification. Fleischer (1943) reported that four manganese minerals - lithiophorite, cryptomelane, psilomelane and hollandite - are associated with cobalt in soils. Bystrom (1950) and Wadsley (1952) characterized the above compounds as ill-defined hydrous manganese oxides with varying chemical composition and structure.

Cryptomelane, hollandite and αMnO_2 are isostructural compounds of a general formula AR_8X_{16}, in which $A=Ba^{2+}$, Pb^{2+}: $R=Mn^{4+}$, Mn^{2+} and $X=O^{2-}$, OH^-. (Bystrom 1950) Lithiophorite mineral has a layer structure with alternating octahedral sheets of MnO_6 and $(AlLi)OH_6$. Synthesis of manganese hydrous oxides by precipitation in the presence of Ba^{2+}, K^+, Pb^{2+}, and Fe^{3+}, ions resulted in a series of compounds with varying chemical compositions and structures. The manganese ions in the synthetic oxides changed position in hot water, taking up a more ordered structure and at 300°C were converted into crystaline pyrolusite (Bystrom 1950).

The outstanding adsorption capacity of manganous manganite at low pH and the tenacity to keep the cobalt adsorbed has been demonstrated in the adsorption experiments. The low degree of crystallinity and the above properties of this material suggest that in soils, where cobalt is associated with manganese oxides, the disordered and structureless modifications are probably responsible for the cobalt adsorption. A rearrangement in structure leading to various manganese minerals such as hollandite, cryptomelane and lithiophorite may have taken place at some time after cobalt adsorption when the local factors have also influenced the developing mineral species. In neutral or alkaline environment the resulting mineral may be birnessite; in the presence of Ba^{2+}, K^{+} and Pb^{2+} ions hollandite and cryptomelane may form. If the soil becomes acidic after cobalt adsorption and large concentrations of Al and Li are available, a lithiophorite type of mineral may develop.

In Massachusetts soils the cobalt appears to be associated with manganese oxides. Solubility tests carried out on these soils brought about 50% of the total extractable cobalt and manganese into solution using the hydroxylamine hydrochloride extraction procedure of Chao (1972). Since the solubility test was developed for selective dissolution of poorly crystalline α, δ and γMnO_2, cobalt may have been adsorbed in Massachusetts soils by a loose, structureless manganous manganite, δMnO_2 or the related compounds.

The results of adsorption experiments clearly indicate that cobalt may be associated with manganese oxides or with iron oxides; however, cobalt adsorption is not an exclusive property of any mineral species. All the materials prepared, as either hydrated suspension or solids studied,are capable cobalt adsorbents and the relative importance of these mineral species in an adsorption process is controlled by the pH of the aqueous phase and the surface area of the adsorbent.

CHAPTER V

SUMMARY

The adsorption of cobalt from aqueous solutions by seven manganese and iron oxides has been measured as a function of pH and cobalt concentration. The mineral species had different chemical compositions, surface areas, crystallinity and points of zero charge. From the results of adsorption experiments the following conclusions can be drawn:

1. Cobalt adsorption from an aqueous solution at all cobalt concentrations by all substrates increased with increasing pH and each substrate had a characteristic pH range in which adsorption increased rapidly until all the added cobalt was adsorbed. Oxides prepared as hydrated suspensions adsorbed cobalt at lower pH values than the corresponding oxides prepared as solid materials. As Figures 10 and 11 indicate, manganous manganite and amorphous $Fe(OH)_3$ adsorb cobalt more effectively than the other minerals in the pH range (5-7) of most soils. These results are in agreement with the studies of Taylor and McKenzie (1966) who found cobalt to be concentrated in birnessite and lithiophorite.

2. Surface area of a mineral was the most influential factor determining the amount of cobalt adsorbed per unit weight. Manganous manganite, amorphous $Fe(OH)_3$, $\gamma FeOOH$ and Mn_3O_4 hydrated suspensions had very similar adsorption capacities in moles/m^2 at surface saturation and these values were in a comparable range with the maximum adsorption in moles/m^2 of the samples prepared as crystalline solids. The similarity in the above results provides evidence to support the theory of Hahn and Stumm (1968) and James and Healy (1972) that the adsorbed metal ions retain the inner hydration sheath on a large variety of substrates.

3. Generally, the amorphous minerals adsorbed cobalt at lower pH values than the crystalline modifications and adsorption capacities of the amorphous samples were higher than those of the crystalline counterparts. The difference in the general adsorption behavior of manganous manganite and the crystalline MnO_2 was very pronounced. The difference was measurable both in adsorption capacities and in the pH interval of cobalt uptake by the Mn_3O_4 hydrated suspension and the crystalline Mn_3O_4. The amorphous $Fe(OH)_3$ also bega to adsorb cobalt at a lower pH than $\gamma FeOOH$.

4. The point of zero charge of a substrate was not the

sole factor determining the pH at which a mineral began to adsorb cobalt. However, with the exception of the amorphous $Fe(OH)_3$ and manganous manganite, cobalt adsorption did not begin until the pH was increased to near the point of zero charge. Only the amorphous $Fe(OH)_3$ adsorbed cobalt strongly when the surface was positively charged. The manganous manganite did not adsorb cobalt until the surface carried a large negative charge indicating possibly that under these conditions cobalt could not be adsorbed until the H_3O^+ concentration was decreased sufficiently to allow the $[Co(H_2O)_6]^{2+}$ to compete for the double layer sites.

5. The seven manganese and iron hydrous oxides, studied within this work, were about equally effective cobalt adsorbents if the pH of the environment was in their adsorption range and cobalt adsorption was not an exclusive property of either mineral species. At a given pH value the cobalt uptake per unit weight depended most of all on the surface area of an adsorbent.

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