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Competition of copper, lead, and cadmium adsorption to goethite

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ABSTRACT

COMPETITION OF COPPER, LEAD, AND CADMIUM ADSORPTION TO GOETHITE

by

Chris A Christophi

Competition of copper, lead, and cadmium adsorption on goethite depends on metal ion and oxide surface characteristics. Goethite was characterized via X-ray diffraction, potentiometric titrations, site density determination, particle size analysis, and optical microscopy. In this thesis, a hypothesis was tested that electronegativity is the most important factor in metal affinities and adsorption competition to goethite.

Metal affinity and site density for the goethite surface were assessed by performing adsorption edges and isotherms. Based on the results of these experiments, competition studies were designed to observe adsorption and displacement of the competing metals by limiting the number of available sites on the oxide surface. Adsorption competition was studied by conducting competition isotherms in two-metal and three-metal systems, where the temperature and pH were maintained constant. Competing metals of equivalent, below saturation, concentrations were introduced in solution in alternative orders as well as simultaneously.

In adsorption edges, ionic strength was varied and no changes were observed in the amount of metal adsorbed, suggesting that copper, lead, and cadmium were specifically adsorbed on goethite. Metal affinity and capacity for the goethite surface were found to increase with metal electronegativity:

Cu>Pb>Cd. Neutrally charged hydrolysis products of metal ions were found to slightly decrease metal affinities for goethite. Goethite posses distinct types of sites with varying affinities for adsorbates. In addition to the sites used by heavy metals (Cu, Pb, and Cd), strontium, apparently binds to another group of, possibly lower energy sites.

Modeling of copper, lead, and cadmium adsorption and competition was best described with a two-site Langmuir isotherm. From the equilibrium constants obtained from the two-site Langmuir model, more electronegative species were preferably adsorbed over less electronegative species on the high affinity sites of goethite. However, lead showed higher affinity than copper for the low energy sites.

In Cu and Cd competition studies, cadmium was completely displaced. In the Pb and Cd studies, lead displaced cadmium from the sites it required. Because sites were not limited in this experiment, unoccupied ones were then filled with cadmium.

During Cu and Pb as well as Pb, Cu, and Cd competition studies, copper preferably adsorbed over lead to the high energy sites, whereas lead showed greater affinity for the lower energy sites. During Pb, Cu and Cd competition studies, cadmium was completely desorbed. Furthermore, during the same competition study, the hydrolysis product $Cu(OH)_{2(aq)}$ decreased copper adsorption on goethite where only 30% of this species was adsorbed.

The two-site Langmuir model worked well with Cu and Cd competition and Pb and Cd competition, but it was not able to predict the Cu and Pb and the Cu, Pb, and Cd systems' results. The findings from this thesis suggest that electronegativity is an important factor in adsorption competition of pollutants on high affinity sites on the goethite surface. However, lead showed higher affinity than copper for the low energy sites. This study confirms that adsorption competition plays a crucial role in contaminant mobility in the environment.

COMPETITION OF COPPER, LEAD, AND CADMIUM ADSORPTION TO GOETHITE

by
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This thesis is dedicated to
my beloved family

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LIST OF ABBREVIATIONS

AA Atomic absorption

BET Brunauer-Emmett-Teller

HCL Hollow Cathode Lamps

IS Ionic Strength

ISE Ion Selective Electrodes

PSD Particle Size Distribution

WHH Width at Half Height

XAS X-ray Absorption Spectroscopy

XRD X-ray diffraction

ZPH Zero point of Charge

CHAPTER 1

INTRODUCTION

1.1 Objectives

The main objective of this thesis is to study adsorption competition of copper, lead, and cadmium on goethite. The important factors in adsorption are the physical and chemical characteristics of the metal which include, electronegativity, hydrated and ionic radii, polarizability, and speciation. In addition, the ionic strength and the pH of the bulk solution, the presence of complexing ligands, and metal concentration are also important factors in adsorption. One aim of this study is to determine which of the metal ion characteristic(s) is most important in adsorbate affinity and competition for the goethite surface. This study includes the following:

- Adsorption edge experiments for each of the three adsorbates to assess metal affinities for the goethite surface.
- Adsorption isotherm experiments for each adsorbate to evaluate types of sites and metal capacities for the goethite surface.
- Isotherm studies for two-metal and three-metal systems to understand and model competition.
- Determination of the most important factor(s) in competition studies.

1.2 Background Information

1.2.1 Overview

Adsorption of trace metals and organic matter on hydrous oxides is an extremely important process in the environment (1, 2, 3, 5, 6, 34). The hydrous oxides' role as sorbents for trace metals affects contaminant mobility (2, 3, 4, 18, 34). Although competitive adsorption of metal ions on hydrous iron oxides may have an significant impact in contaminant migration (3), it has not received a lot of attention. In this study, adsorption competition of Cu, Pb, and Cd on goethite are examined; these metals are contaminants in the environment at trace levels (3). Goethite was selected as the adsorbent because of its great capacity for metal ions (1, 4, 18) and its widespread abundance in the environment (3, 9, 10).

1.2.2 Goethite Occurrence and Characteristics

Goethite is one of the most common iron oxide minerals found in almost every soil type and climatic region (9, 10, 11). Under most soil conditions, goethite is a thermodynamically stable crystalline iron oxide mineral, giving a yellowish brown color to many soils and weathered material (9, 10, 11).

Goethite is structured by double chains of Fe-OH octahedra extending along the Z crystallographic axis. These octahedra are bonded to neighboring double chains by Fe-O-Fe bonds that are 0.265 nm in length (10, 12). Synthetic goethite is usually of acicularly shaped crystals, greater than 200 nm in length (10). Acicular soil goethite crystals exhibit needle lengths of 50 to 100 nm and less than 20 nm in width (10). In natural soils, however, this acicular shape is much less common where irregularly shaped aggregates are predominant (10, 13).

Pores constitute 53% of the goethite surface. Micropores usually extend into the interior region of the crystals with diameters less than 2 nm (13, 36). Goethite crystals have characteristic fissure-separated domains (10, 13). Wedged-shaped pores, greater than 100 nm in length, exist along the domain boundaries and are 20 to 30 nm wide and 4 to 6 nm deep (13). Micropores within these domains are highly ordered (10, 13, 14).

Surface area of goethite varies depending on the particle size and porosity; generally it has been observed to range from 7 to 235 m^2/gram (10, 36). A surface area of approximately 75 m^2/gram is frequently reported for laboratory synthesized goethite (13, 25).

The pH zero point of charge (zpc) of goethite, the pH at which the oxide possesses no net charge, is generally between pH 7 to 9. Because of the lack of surface impurities, synthetic goethite usually exhibits a greater pH zpc than naturally occurring goethite. In general, for a given oxide, pH zpc varies depending on the degree of hydration, contamination of the surface by other ions, and method of determination (electrophoretic mobility, potentiometric titrations, or cation and anion adsorption) (10).

As with any other oxide, the extent of metal adsorption on goethite depends on the pH (1, 2, 3, 5, 6, 34). Adsorption of heavy metals on goethite has been observed to follow the order of Cu>Pb>Zn>Cd>Co>Ni>Mn (10).

1.2.3 Adsorption Forces and Solid/Solution Interface

Many scientists have studied the adsorption process of metals and organics on various hydrous oxides (1, 3, 4, 5, 10, 11, 17, 18, 23, 26, 30-35). Ion adsorption on oxides is due to the existence of a surface charge (1, 9, 10).

The oxides and hydroxides of Al, Fe, Mn, and Si do not posses any permanent surface charge (9). The net positive or negative charge of these amphoteric oxides is dependent on pH. When the concentration of H^+ and OH^- on an oxide's surface is equal, the net surface charge is zero; this pH defines zpc. The pH zpc is very important in metal ion adsorption on hydrous iron and other oxides in aqueous environments. At pH greater than pH zpc, cation adsorption is favored whereas anion adsorption increases at lower pH values. As stated earlier, for iron oxides, the pH zpc ranges from 7 to 9 without any distinct differences between the various minerals (9, 10).

Using a double layer to describe the charged surface, adsorption in the inner layer is referred to as specific, chemical, or inner layer complexation (9, 10). Metal cations and various inorganic and organic anions are capable of being specifically adsorbed on iron oxides (9); they coordinate with surface hydroxyl groups thus forming a relatively strong, covalent bond (9). In the outer layer, however, adsorption is due to physical forces and is called outer-layer or nonspecific complexation where the excess charge on the surface is balanced by counter-ions that are held on the outer layer of the diffuse double layer. At high ionic strengths the diffused double layer is reduced, decreasing ion adsorption in the diffused layer. The ions of Cl^-, NO_3^-, and ClO_4^- and the alkali cations are generally adsorbed in this manner (10).

Adsorption onto these different types of sites on the oxide surface is usually studied by performing adsorption edge and isotherm experiments. During the former, the percent of metal adsorbed is recorded as a function of pH for different ionic strengths. In isotherms, the metal distribution between the adsorbed and the bulk aqueous phases is examined as a function of increasing initial metal concentration, while the pH and temperature are maintained constant.

1.2.4 Existing Adsorption Studies on Goethite

Numerous studies exist on the adsorption of various adsorbates on goethite. Adsorbates affinity for the goethite surface has been examined as a function of pH (3, 10, 18), temperature (3), ionic strength (11, 33, 34) as well as adsorbate and goethite concentration (19). Furthermore, adsorbate-surface complexation, kinetics, and mechanisms of adsorption were investigated by a number of researchers (2, 23, 33, 34, 35). An outline of the results from a number of these studies follows.

Coughlin and Stone (3), studied the adsorption and release of heavy metals on goethite as a function of pH. They observed typical, "S" shaped adsorption edges for all metals; with increasing pH, adsorption increased from zero to almost 100% over a narrow pH range of approximately 1.5 units. This change indicates that cation adsorption on goethite is favored as pH increases and surface charge decreases. Furthermore, they found that metal affinities for the goethite surface follows the order of Cu>Pb>Ni>Co >Mn. These results suggest that electronegativity is very important in metal adsorption on goethite; metal affinity for the goethite surface increases with increasing electronegativity. The same trend is seen in other studies (10, 23) with an interchange position of Ni and Co (10). The electronegativities of Nickel and Co are very close, with Ni being slightly greater by 0.03 units.

Johnson (18) examined the adsorption of Cd on goethite as a function of pH and temperature. The typical, "S" shaped adsorption edge was observed here as well. In addition, Johnson found that adsorption edges were shifted to higher pHs as the temperature was decreased, indicating an endothermic adsorption reaction.

A number of studies suggest that metals are specifically adsorbed on the goethite surface (33, 34, 35). Grossl et al. (33) studied the adsorption of chromate and arsenate on goethite. They observed no changes in the amount sorbed in adsorption edges of either chromate and arsenate with a tenfold increase of the ionic strength; they, therefore, concluded that chromate and arsenate were specifically adsorbed on goethite. In kinetic studies, using a pressure-jump apparatus, Grossl et al. observed a two-step adsorption process. They modeled the second step as an inner-sphere bidentate surface complex.

Similar results were reported by Manceau and Charlet (35) who investigated the mechanisms of selenate and selenite adsorption to goethite and hydrous ferric oxide using X-ray absorption spectroscopy (XAS). They found that these anions were also specifically adsorbed on goethite and reported that selenite behaved like selenate and arsenate in forming the same type of inner-sphere surface complexes with iron oxides.

Grossl et al. (34) also investigated copper adsorption on goethite. In adsorption edge studies, they observed no changes in the amount of copper adsorbed when the ionic strength was increased, suggesting that copper was specifically adsorbed on the goethite surface. Grossl et al. reported that from kinetic studies, a monodentate, inner-sphere complex was the dominant adsorption complex for copper on goethite.

A number of adsorbates, however, were observed to not be specifically adsorbed on goethite (2, 23). Gunneriusson et al. (2) questioned the presence of specific high affinity sites on the goethite surface for Hg(II) at trace concentrations. At pH 9, they found only 80% adsorption of Hg(II) and 15% adsorption of methyl mercury. The authors expected mercury to have a greater affinity for goethite at this pH. Forbes et al. (23) who studied adsorption of inorganic mercury and cobalt ions on goethite also observed that mercury has a low affinity for the goethite surface; at pH of 4.40, they found only 20% adsorption of Hg(II) and no adsorption of Co (III). They concluded that the cobalt complexes were not specifically adsorbed, because of the hydroxo cobalt complex in solution prevented the formation of hydroxo bridges between the surface and the cobalt complex.

Surface characteristics and surface coverage are also important in adsorption on goethite and were investigated in a number of studies (11, 32).

Ainsworth et al. (11) studied the adsorption of chromate on goethite as a function of aluminum substitution in the goethite, pH, sorbent concentration, and ionic strength. Their results showed that at all sorbate concentrations, chromate showed a greater affinity for pure goethite over the aluminum substituted surface. Such a difference was not attributed to the variations in adsorption capacities or to pH zpc. Ainsworth et al. concluded that aluminum substitutions altered the adsorption sites on the goethite surface, reducing chromate adsorption. Furthermore, the authors reported that a 40% decrease in chromate adsorption with a tenfold increase of the ionic strength was caused mainly by the reduced activity of the chromate ion in solution. They, therefore concluded that chromate was specifically adsorbed on goethite. However, a decrease in adsorption with an increase in ionic strength is also consistent with outer sphere complexation (9, 10).

Fendorf et al. (32) used XAS spectroscopy to examine the adsorption of chromate on goethite and found that surface coverage was important in terms of the type of complexes. Based on the oxyanion-iron distances, they concluded that at low surface coverage the monodentate complex was favored, whereas at higher surface coverage the bidentate complexes prevailed.

Adsorption competition of metals on goethite has also been examined by researchers. A number of such studies and their results are presented and discussed in the next section.

1.2.5 Existing Competition Studies

The adsorption of heavy metals on goethite and other hydrous oxides was studied by a number of researchers (3, 11, 18, 23, 26, 30-36). However, only a limited number studies dealt with heavy metal adsorption competition on hydrous oxides. In a natural setting, however, the presence of multiple competing ions is more frequent than the existence of only one contaminant (3); heavy metals along with plant nutrients are present in soil and water in trace levels. The following discussion of the results is from a number of competition studies.

In a number of studies (37, 38) adsorption competition was examined in the form of adsorption edges; the effect or the shift of a metals adsorption edge is recorded when a second metal of greater concentration is added into the system. Adsorption edge shifts are indicative of desorption of the sorbed metal. However, when competing metals are not presented with a limited number of sites on a sorbent surface, competition can not be observed. Furthermore, during edge experiments, the pH is varied; surface characteristics such as site density and net surface charge along with metal speciation and its saturation change with pH.

Benjamin and Leckie (37) studied the competitive adsorption of Cd, Cu, Pb, and Zn onto amorphous iron oxyhydroxide ($Fe_2O_3 \cdot H_2O$). They concluded that competitive interactions between metals were minimal, because of the existence of distinct types of sites for each metal on the oxide surface. The adsorption edge of a given metal, was shifted to higher pHs, in the presence of a competing metal. For example, the adsorption of cadmium was decreased by approximately 18%, in the presence of copper. The concentration of copper in solution was $5x10^{-5}$ M, 100 times greater than that of the cadmium. Such high concentrations exceeded the saturation limits of copper. In all competition experiments, as in the case of copper and cadmium, competition was not observed until the competing metal(s) were added in much higher concentrations, 10 to 100 times greater, than the other metal in solution. However, when metals exceed their saturation, both precipitation and adsorption may occur, therefore, adsorption effects cannot be distinguished from surface precipitation.

Cowan et. al (38) studied the adsorption of Cd on amorphous iron oxides in the presence of alkaline-earth metals (Ca, Mg, Sr, and Ba) using methods similar to those of Benjamin and Leckie (28). Competition was observed primarily in the Cd-Ca systems where 25% of cadmium was displaced, while less than 8% of cadmium desorbed when Mg, Sr, and Ba were the competing metals. However, cadmium was present in solution at much lower concentrations than the competing metals. For example, desorption of Cd by Ca was not observed until 2.5 mM of Ca was added, over 1000 times greater concentration than Cd. Similar observations are seen in the study by Posselt et al. (6) who reported a 66% decrease of Cd adsorption on manganese dioxide in the presence of Ca. Again, calcium concentration was, $2x10^{-3}$ M, 100 times greater in concentration than the 10^{-5} M Cd. O' Connor and Renn (22) on the other hand, found that Ca had no effect on Zn adsorption on river sediments. Zinc, however, was present in solution at 200 ppm, 3 times greater than the Ca concentration. Furthermore, such a high concentration is above the saturation limit of zinc. Therefore, adsorption effects cannot be distinguished from precipitation.

Gadde and Laitinen (17) studied heavy metal adsorption competition on hydrous manganese oxides in the form of competition isotherms. They found a 64% displacement of Cd and Zn when an equal Pb concentration, 10^{-3} M, was added to the system at pH 6. The results showed no significant variations when the order of metal introduction was reversed. However, all metal concentrations used in these experiments exceeded their saturation limits.

Zasoski and Burau (19) examined adsorption competition between Cd and Zn for the hydrous manganese oxide (δ-MnO_2) surface by conducting adsorption competition isotherms. In their studies, Zasoski and Burau reported that Cd and Zn adsorbed on two types of sites: high energy sites which were filled first, and lower energy sites. They found that the higher energy sites showed preference for Cd over Zn, whereas the reverse was true for the lower energy sites. These authors found Cd adsorption decreased by approximately 25% in the presence of equimolar concentrations of Zn. On the other hand, Zn adsorption decreased 50% in the presence of Cd. Adsorption competition was observed in this study, because site densities were evaluated first and the metals were presented with a limited number of available sites during competition. Furthermore, competing metals were added in equimolar levels and in an N_2 atmosphere, avoiding precipitation.

When examining adsorption competition, site density needs to be evaluated first. Competition studies need to be designed based on the obtained site density as to present the competing metals, of equal concentrations, with a limited number of sites. The pH needs to be maintained constant to minimize any surface changes such as site density, and net surface charge along with metal speciation and saturation. When the above requirements are met, competition among the various metals should reveal the most important factor for adsorption competition. In this research, adsorption competition is examined at constant pH and temperature, minimizing any oxide surface changes. Furthermore, the site density is evaluated prior to competition studies. In order to determine the most important factor in adsorption competition, competing metals of equal amounts are studied below their saturation limits with a limited number of sites available on the goethite surface.

CHAPTER 2

HYPOTHESIS STATEMENT

Because metal affinity to goethite tends to increase with metal electronegativity (3, 10, 17, 23), electronegativity is expected to be the most important factor in competition studies. Adsorption of less electronegative metals decreased in the presence of more electronegative metal(s) (17, 24) and have little or no effect on the adsorption of more electronegative ones (20, 22).

To test the hypothesis that electronegativity is the most important factor in adsorption competition, adsorption edge and isotherm experiments are performed to establish the order of metal affinities. Based on electronegativity, metal affinities are expected to be of the order Cu>Pb>Cd. Furthermore, given a limited amount of available sites, less electronegative metals are expected to be displaced when competing with more electronegative species. Such results are expected to be independent from the order of introduction of the competing metals in solution. In other words, results are expected to show no variation when the order of introduction of the competing metals in solution is reversed or upon simultaneous introduction.

Under the condition that the initial metal concentrations will be equivalent in all competition experiments, and that a limited number of sites will be available, the following hypotheses will be tested:

- Metal affinities are governed by electronegativity; affinities obtained from adsorption edge and isotherm experiments will, therefore, be of the order of Cu>Pb>Cd.
- Cu, Pb, and Cd adsorb on the same type of sites on the goethite surface and therefore, there is a finite number of sites for their sorption.
- Based on electronegativity, Cu will displace Pb and Cd, and Pb will displace Cd, in competition studies.

CHAPTER 3

MATERIALS and METHODS

3.1 Overview

Standard methods procedures (21) were followed throughout for standards preparation, instruments calibration, sample preparation, and sample analysis (Appendix A).

3.2 Materials

Ferric nitrate (99%) $Fe(NO_3)_3 9H_2O$ and NaOH were used in goethite synthesis. For pH adjustments, (10^{-1} N) NaOH and HNO_3 were used.

One millimolar stock solutions of lead and cadmium nitrate were used. High purity, 99.9%, $Cu(NO_3)_2 \cdot H_2O$, was used in preparing a 10^{-3} M, pH 3, stock solution. A 10^{-2} M, $^{90}Sr^{2+}$ stock solution was used for site density experiments.

A 10^{-2} M sodium nitrate stock solution was prepared for ionic strength adjustment in adsorption edge, isotherm, and competition experiments. In cases where an ionic strength greater than 10^{-2} M was desired, sodium nitrate was added directly to the water.

Nalgene polyethylene 100 ml and 1000 ml containers were used in all experiments. Metal dilutions were carried out by using 1 ml and 10^{-1} ml fixed-volume pipettes. A Labline temperature controlled shaker bath and teflon coated stirring bars with a magnetic stirrer were used for mixing. Both samples and standards were completely mixed. An Orion pH/mV meter and ion selective electrodes (ISE) were used throughout for pH and mV measurements.

3.3 Goethite Synthesis and Characterization

3.3.1 Goethite Synthesis

In this study, a slightly modified version of Atkinson's method (25) for goethite synthesis was implemented. The aging of the ferric nitrate solution was deemed unnecessary and was eliminated; ferric nitrate was observed to easily dissolve in water hence the bright yellow color. The method was developed and finalized through oxide characterization via x-ray diffraction analysis and physical examination of the goethite crystals.

Individual goethite batches of 2 and 10 gram were synthesized by adding 10^{-1} M $Fe(NO_3)_3{\cdot}9H_2O$ to deionized water. Once the ferric nitrate was dissolved, sodium hydroxide was slowly added to the solution until a pH of 12 was attained. In all batches, the molar ratio of Fe to OH^- was 1:4 with an ionic strength of 0.4. The resulting solution was mixed for 3 to 4 hours and aged in a 60^0 C oven (25). This aging period was varied between 48 to 168 hours. The 168 hour aging exhibited the greatest crystallinity, the lowest background, and was thus used when synthesizing the final five, 10 gram per liter goethite batches.

The aged solution was filtered through 10^{-1} μm membrane filters and the goethite particles were washed repeatedly with deionized water. The conductivity of the effluent was monitored to remove the concentrated electrolyte (25). Goethite crystals were then freeze-dried (29), stored in a polyethylene container, and sealed from ambient air for later use.

3.3.2 X-ray Diffraction Analysis

Goethite batches were examined for homogeneity and crystallinity via X-ray diffraction (XRD). A Philips, X-pert MPD, XRD and a PC-APD diffraction software were used in analyzing and presenting the obtained data. Table 1 shows the XRD settings implemented in all examinations.

Table 1
XRD Settings

VARIABLE	SETTINGS
Anode	Cu
Generator Voltage	40 KV
Tube Current	45 mA
Scan Type	Continuous
Scan Step time	1 Sec
Scan Step Size	0.020 (2q)
Diffraction Number	1
Divergence Slit	Fixed, 1^0
Monochromator Used	Yes

3.3.3 Optical Microscope

A Zeiss Standard 2S optical microscope with a 100x magnification was used to further investigate the goethite particles. The particles were examined after freeze-drying and resuspension in a pH 8, 10^{-3} ionic strength, and 1 gram per liter goethite solution.

3.3.4 Particle Size Analysis

Particle size distribution (PSD) was examined as a functioned of pH and ionic strength. Individual 1 gram per liter goethite solutions with a specific pH and ionic strength were prepared and used for these analyses. A MasterSizer X manufactured Version 1.2b particle size analyzer equipped with an MSX14 sampler and a 2.4 mm beam length were used in examining the goethite particle size distribution. A Polydisperse model was implemented in obtaining the PSD data; this model accounts for the two dimensional shaped goethite particles.

3.3.5 Potentiometric Titrations

Potentiometric titrations were performed by adding 1 gram of goethite per liter in an aqueous-electrolyte solution and a nitrogen gas atmosphere. Following the addition of goethite, the pH was raised to a value of 10 to 10.5, with NaOH. The titrations began by then adding 1 ml increments of 10^{-1} N HNO_3 and recording the resulting pH (25).

Two sets of titrations were performed for the determination of the pH zpc of the synthesized goethite. During the first set of titrations, 10^{-2}, 10^{-1}, and $2x10^{-1}$ ionic strengths (sodium nitrate based) were used. The solutions were allowed to equilibrate up to 20 minutes after the addition of acid or base; the pH was not recorded until a "ready" signal was given by an Orion pH meter. Equilibration period, therefore, varied from half a minute, at the extreme pH values, to 20 minutes in the vicinity of pH zpc. During the second set of titrations, equilibration time was minimized to half a minute. Ionic strengths of 10^{-1} and 10^{-2} were used during this second set of titrations.

Blank titrations with 10^{-1} and 10^{-2} ionic strengths were also carried out. The data obtained from the potentiometric and blank titrations were used to calculate goethite adsorption densities in $\mu C/m^2$ as a function of pH. The equivalents of H^+ and OH^- adsorbed by goethite was calculated by taking the difference between test suspension and blank titration volumes at each pH.

3.3.6 Surface Area Determination

Nitrogen adsorption/desorption is usually used for surface area determinations (13, 36). Atkinson (25) determined the surface area of goethite to be 70.9 m^2/gram, using the Brunauer-Emmett-Teller (BET) nitrogen adsorption method.

3.4 Analytical Techniques Theory of Operation and Implementation

3.4.1 Ion Selective Electrodes

Ion selective electrodes (ISE) consist of three components: a reference electrode, a sensing electrode, and a pH/mV meter. The reference electrode provides a steady potential, independent of any ion in the test solution. The sensing electrode, gives a potential that varies according to the activity of a specific ion in a test solution. When both electrodes are immersed in the same test solution a potential develops across the sensing element. This potential, which depends on the level of the specific free metal in solution, can be measured by using a pH/mV meter. The measured potential, corresponding to the level of the specific free metal in solution, is described by the Nernst equation:

$$E = E_0 - S^*\log(A)$$

where,

E : measured electrode potential (mV)

E_0 : reference potential (mV)

S : electrode calibration slope (mV)

A : the concentration of the free metal in solution

$$S = (2.3^*R^*T)/n^*f$$

R : gas constant, 8314 mJ/mol K

T : absolute temperature, in K

n : number of electrons transferred/mole

F : Faraday constant, 96,487 C/equivalents

ISEs were used in the analysis of samples from all experiments expect that of Cu-Pb and Cu-Pb-Cd competition because of the poisonous effect of Cu^{2+} ion on the lead ISE membrane (Table 2). Orion manufactured, filling solutions were used to fill the ISE prior to any use. In all experiments where ISEs were used at least three standards covering the expected residual metal concentration were prepared. Freshly prepared standards were used in each analysis. Calibration curves were constructed for standards by plotting the mV against the logarithm of metal concentration(s) (Appendices D to L).

Calibration curves were constructed when the samples were ready for analysis as the manufacturer recommends sample analysis within one hour of calibration. Although a steady mV signal was usually obtained in less than a minute (Table 2), the mV value was not recorded 2 to 3 minutes after electrode introduction in solution (Appendix A).

The analysis of a given set of samples was completed within the same day, in less than an hour. Such a practice eliminated any mV errors due to temperature or light variations. In the event that the analysis was not completed within an hour, the electrode was re-calibrated and the analysis of the remaining samples was continued based on the new calibration curve. Using this method, the accuracy was within 2%. In the case of competition isotherms, standards were prepared containing all competing metals present in the samples; this allowed for compensation of any interference due to the presence of the second metal in the sample (0.2% mV variations were observed when a second metal was added into the standards) (Appendices F, I, L).

3.4.2 Atomic Absorption Spectroscopy

In atomic absorption (AA) spectroscopy the sample is atomized in a thermoelectric oven. In this study, a small portion of the sample was placed in a small graphite tube which is held between two electrodes. A current is passed through the walls of the tube thus increasing the temperature in a programmed fashion. The temperature increase is usually performed in three stages with the last being a very rapid rise of the temperature over 2000^0 C.

Table 2

Ion selective electrodes characteristics

ISE	**Orion "Ionsplus" series model**	**Concentration range (M)**	**pH range**	**Temperature range (°C)**	**Response Time (min.)**[1]	**Filling solution**[2]	**Reproducibility (%)**[3]
Cu^{2+}	9629	10^{-8} - 10^{-1}	2 -12	0 - 80	0.5	D	+/- 2%
Pb^{2+}	9682	10^{-7} - 10^{-1}	4 - 8	0 - 80	0.5	B	+/- 2%
Cd^{2+}	9648 *	10^{-7} - 10^{-1}	2 - 12	0 - 80	0.5	A	+/- 2%

* Orion "Sure - Flow™ Combination Electrodes" Series

[1] minimum necessary response time for a steady mV reading.

[2] Orion manufactured, Optimum Results Series, filling solutions.

[3] reproducibility within one hour of operation.

Such an increase of the temperature volatilizes the metals into a light beam. The absorbency of this atomic vapor is then measured.

Hollow cathode lamps (HCL) were used as the light source for each metal. These lambs emit the atomic spectra of the metal analyte. A detector at the other end of the beam measures absorbency and converts absorption into a meaningful metal concentration. Beer's law describes the relation between absorbency and metal concentration. Beer's law is shown below:

$$A = \varepsilon * b * C$$

where,

A : absorbency

ε : molar absorptivity

b : length of the beam path (cm)

C : metal concentration (M)

A linear relation exists between absorption and metal concentration. Calibration curves can be constructed by using solutions of known metal concentration. The absorption of these standards is plotted against metal concentration. A Perklin Elmer 4110ZL graphite AA spectrometer unit connected to a, Gateway 2000 P5-75, PC equipped with an AAWinlab software was used in analyzing the Cu-Pb and Cu-Pb-Cd competition adsorption samples. Table 3 lists the settings implemented in these experiments. Only one 50 ppb standard was prepared for each metal. The unit was programmed to automatically dilute appropriate volumes of these standard(s) to construct the calibration curve(s). All samples were analyzed in

Table 3

Graphite AA Settings

Ion	Unit brand	Technique	Hallow Cathode Lamps	Lamp current (mA)	Wavelength (nm)	Calibration type with zero interval	Energy	Slit width (nm)	Reproducibility[1] (%)
Cu^{2+}	Perklin-Elmer	Furnace	Cu^{2+}	30	324.8	Linear	62	0.7	> 97
Pb^{2+}	Perklin-Elmer	Furnace	Pb^{2+}	10	283.3	Linear	64	0.7	> 97
Cd^{2+}	Perklin-Elmer	Furnace	Cd^{2+}	15	228.8	Linear	63	0.7	> 97

---

[1] Precision *based on results obtained from duplicate and quadruplicate analysis of samples*

duplicate and some of them in quadruplicate. Samples that exhibited absorbency greater than the standard, were automatically diluted by the unit until their adsorption was within the calibration curve range. The unit was also programmed to re-calibrate at the beginning, middle, and end of each set of samples. In all cases samples showed higher than 97% reproducibility (Appendices W, X).

3.5 Adsorption Experiments

3.5.1 Adsorption Edge Experiments

Adsorption edge experiments were carried out at 10^{-3} and 10^{-2} ionic strengths with 1 gram per liter goethite. The 1 liter solution was then divided into ten 100ml aliquots. The pH of each aliquot was adjusted to the desired value, followed by metal(s) addition. The pHs were checked and adjusted once again. A shaker was used to mix the samples for the four hour equilibration period. Every 20 to 30 minutes, the pH of the samples was checked and adjusted. No buffer was used to avoid any competing and complexing effects with the metal adsorbates. After four hours, the samples were centrifuged and the solution was used for metal analysis (Appendices P to R). A Sorvall Rc 28S was used in centrifuging the samples at 22° C and 8,000 repetitions per minute (rpm).

3.5.2 Adsorption Isotherms

Metal affinities for goethite were examined as a function of metal concentration at pH of 6, 10^{-3} ionic strength, and 1 gram per liter goethite. Both two and four hour equilibration periods were used. The same procedure used in the edge experiments was also used in conducting the isotherms, in terms of aliquot preparation, ionic strength and pH adjustment. Orion ISEs were used for the analysis of all samples (Appendices T to V).

3.5.3 Site Density

Site density was examined by flooding the sites with $^{90}Sr^{2+}$ and measuring the amount adsorbed to goethite. A Beckman LS 6000SE, liquid scintillation counter was used in measuring the site density of goethite based on $^{90}Sr^{2+}$ adsorption. The experiment was performed in quadruplicate by allowing a 10^{-3} M initial $^{90}Sr^{2+}$ concentration to equilibrate for four hours with 10^{-1} gram per liter goethite at pH 6 and 10^{-3} ionic strength. The solution was then filtered through a 0.2 μm membrane filter. Two milligrams of the filtrate were placed in a 6 ml vial with 4 ml of Beckman cocktail. After the vial was capped and mixed, the sample was then analyzed.

Adsorption isotherms were also used in calculating the site density of goethite by determining metal capacity of goethite. Nitrogen adsorption using the BET method was also employed in determining the site density and the surface area of goethite.

3.5.4 Metal Adsorption on Containers

Metal adsorption on containers was examined in triplicate for each metal individually as well as in the presence of other metals. The solutions were equilibrated for four hours at pH of 6 and 10^{-3} ionic strength in the absence of goethite. Results revealed that 2.2%, 2.0%, and 2.0% of initial metal concentration adsorbed on the containers for copper, lead, and cadmium, respectively. The percent of metal adsorption remained the same, despite increasing initial metal concentration or presence of other metals, indicating that containers do not posses a site capacity for metals.

3.5.5 Competition Adsorption Isotherms

Competition isotherms were performed at different concentrations at pH 6, 10^{-3} ionic strength, and 10^{-1} gram per liter goethite with initial metal concentrations being equal in any given experiment. The same procedure as with the edge experiments, in terms of aliquot preparation, ionic strength and pH adjustment, was used in conducting the competition isotherms as well. The metals with the lowest adsorption affinities were allowed to be adsorbed first (competition I) for two hours, the addition of the competing metal(s) followed. Both metals were then allowed to equilibrate for an additional two hour period. The order of metal introduction into the solution was then reversed (competition II) in order to further examine metal affinities. Finally both competing metals were introduced into the solution simultaneously (competition III).

During the last set of competition experiments, metal affinities were examined when all three competing metals of equal initial concentrations were introduced simultaneously (competition III) into the solution. All three metals were allowed to equilibrate for four hours. Ion Selective Electrodes were used in all competition isotherms except in the case of Cu-Pb and Cu-Pb-Cd where an atomic adsorption spectrophotometer was used (Appendices AA, AB).

CHAPTER 4

RESULTS AND DISCUSION

4.1 Overview

In this chapter, results from goethite characterization, adsorption edges, isotherms, and competition studies are presented and discussed.

4.2 Goethite Characterization

The synthesized goethite used in all experiments was characterized via XRD, potentiometric titrations, particle size analysis, site density measurements, surface area, and optical microscopy. A more detailed account of such characterization follows.

4.2.1 X-ray Diffraction Analysis

XRD analysis was used in examining the crystallinity and homogeneity of the synthesized goethite (Figure 1). Table 4A shows the goethite characteristics and Table 4B lists the diffraction angles of goethite which are also seen in Figure 1. None of the batches reveal any diffraction peaks other than those of goethite. The 48 hour sample, however, exhibits the greatest background of all three batches. Such a background is most likely due to the presence of amorphous iron oxide.

The peak width at half height (WHH) was used to determine the crystallinity of minerals. Typically, the WHH of the most intense diffraction peak of crystalline goethite varies from 0.1° to 2° with an average of 0.6° (10). As seen in Figure 1, all batches exhibit WHH within the crystalline range of goethite. The 168 hour aging batch exhibited the lowest background and the

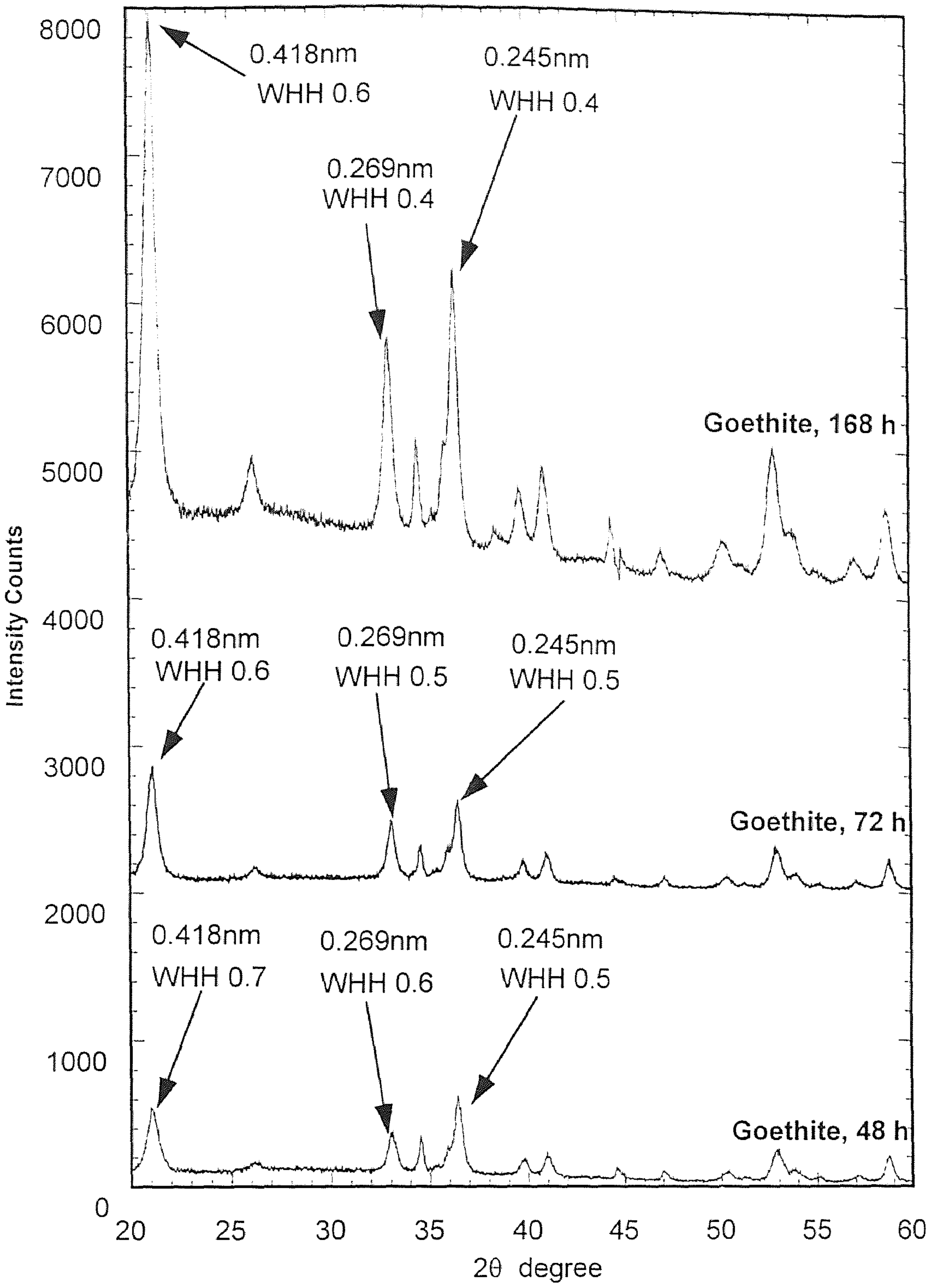


Figure 1 X-ray diffractograms of goethite as a function of aging.

Table 4A

Goethite and other iron oxide characteristics (10)

Mineral	**Chemical formula**	**Color**	**Crystal system**	**Cell dimension (nm)**	**Usual crystal shape**	**Comon ** zpc pH values**
Goethite	α–FeOOH	Yellowish - Brown	Orthorhombic	a = 0.4608 b = 0.9956 c = 0.30215	Needles Laths	7.7 - 9.0
Hematite	α–Fe_2O_3	Bright Red	Trigonal	a = 0.50340 c = 1.3752	Hexagonal Plates	8.5
Lepidocrocite	γ–FeOOH	Orange	Orthorhombic	a = 0.388 b = 1.254 c = 0.307	Laths	7.7 - 9.0
Ferrihydrite	$Fe_5HO_8*4H_2O$	Redish - Brown	Trigonal	a = 0.254 b = 0.224 c = 0.197	Spherical	7.7-9.0

** (9)

zpc is the zero point of charge

Table 4B
X-ray powder diffraction data for iron oxides (29).

Goethite			Hematite			Ferrihydrite		
d (nm)	Intensity	hkl	d (nm)	Intensity	hkl	d (nm)	Intensity	hkl
0.498	12	020	0.366	25	012	0.250	100	110
0.4183	100	110	0.269	100	104	0.221	80	112
0.3383	10	120	0.251	50	110	0.196	80	113
0.2693	35	130	0.2285	2	006	0.172	50	114
0.2583	12	021	0.2201	30	113	0.151	70	115
0.2527	4	101	0.2070	2	202	0.148	80	300
0.2489	10	040	0.1838	40	024			
0.2450	50	111	0.1690	60	116			
0.2303	1	200	0.1634	4	211			
0.2253	14	121	0.1596	16	018			
0.2190	18	140	0.1484	35	214			
0.2089	1	220	0.1452	35	300			
0.2011	2	131	0.1349	4	208			
0.1920	5	041	0.1310	20	1010,119			
0.1802	6	211	0.1258	8	220			
0.17728	1	141	0.1226	2	036			
0.17192	20	221	0.1213	4	233			
0.16906	6	240	0.1189	8	128			
0.16593	3	060	0.1162	10	0210			
0.16037	4	231	0.1141	12	134			
0.15637	10	151	0.1102	14	226			
0.15614	8	160	0.1976	2	042			
0.15091	8	002, 250	0.1055	18	2110			
0.14675	2	320	0.1042	2	1112			
0.14541	5	061	0.1038	2	404			
0.14207	2	112	0.0989	10	232, 318			
0.13936	3	330	0.0971	2	229			

hkl refers to the planes of the crystals smallest WHH. The lower background and the smaller WHH are indicative of less amorphous oxide and greater crystallinity, respectively, resulting from the longer aging period (10). A 168 hour aging period was therefore used in the final batches.

4.2.2 Potentiometric Titrations

Potentiometric titrations were performed to determine the pH of zero point of charge (zpc) of the synthesized goethite. By definition the pH zpc is the pH where the net surface charge of the oxide is zero. Surface charge varies with pH; with increasing pH the charge becomes more negative, as the ratio of bound OH^- to H^+ increases. Similarly, surface charge increases at lower pH, as the H^+ becomes the predominant species bound on the surface (6, 10). The pH zpc results when the amount of OH^- and H^+ on the oxide surface is equal.

The data obtained from the potentiometric and blank titrations were used to calculate net adsorption, $\Gamma_H^+ - \Gamma_{OH}^-$. Thus

$$\sigma = (1/A) * (\Gamma_H^+ - \Gamma_{OH}^-)$$

where,

σ : Surface density of charge ($\mu C/m^2$)

A : Surface area (m^2/g)

Γ_H^+ and Γ_{OH}^- : surface excesses ($\mu C/g$)

The titrations can be treated as adsorption isotherms, when the following approximation is implemented (25)

$\sigma A = (\Gamma_H^+ - \Gamma_{OH}^-) = \Gamma^+$ on the acid site of zpc

$\sigma A = (\Gamma_H^+ - \Gamma_{OH}^-) = \Gamma^-$ on the alkaline site of zpc

Negative surface charges are due to the excess of surface OH^-, whereas the positive surface charges are due to the excess of H^+ on the surface (25).

The results from the potentiometric titrations (Figure 2) reveal that the pH zpc of the synthesized goethite is 7.78. For goethite, pH zpc varies from pH 7.7 to 9 depending on the method of determination, degree of hydration, and method of synthesis (9, 18, 23, 25).

4.2.3 Surface Area

Atkinson et al. (25) and Mc Bride (9) found the surface area of goethite to be 70.9 m^2/gram. Others have found the surface to be in the range from 7.9 m^2/gram to 235 m^2/gram (36).

4.2.4 Particle Size Analysis

Particle size distribution (PSD) of goethite was examined as a function of pH and ionic strength (IS) after freeze-drying and resuspension in deionized water (21). The results of this PSD analysis are shown on Figure 3. A bimodal distribution (1.5 μm by 40 μm) was revealed, thus the non-spherical model was used in this analysis.

Minor aggregation occurred at pH 7.80, the pH zpc (Figure 3). At such pH, goethite net surface charge is very close to zero thus promoting aggregation due to the absence of any repulsion forces between particles. Repulsion forces are present at extreme pH values where goethite particles are similarly charged. Aggregation is also promoted with increasing ionic strength. At high ionic strengths, the diffuse double layer is compressed (9) which allows particles to come closer together, promoting aggregation. Such

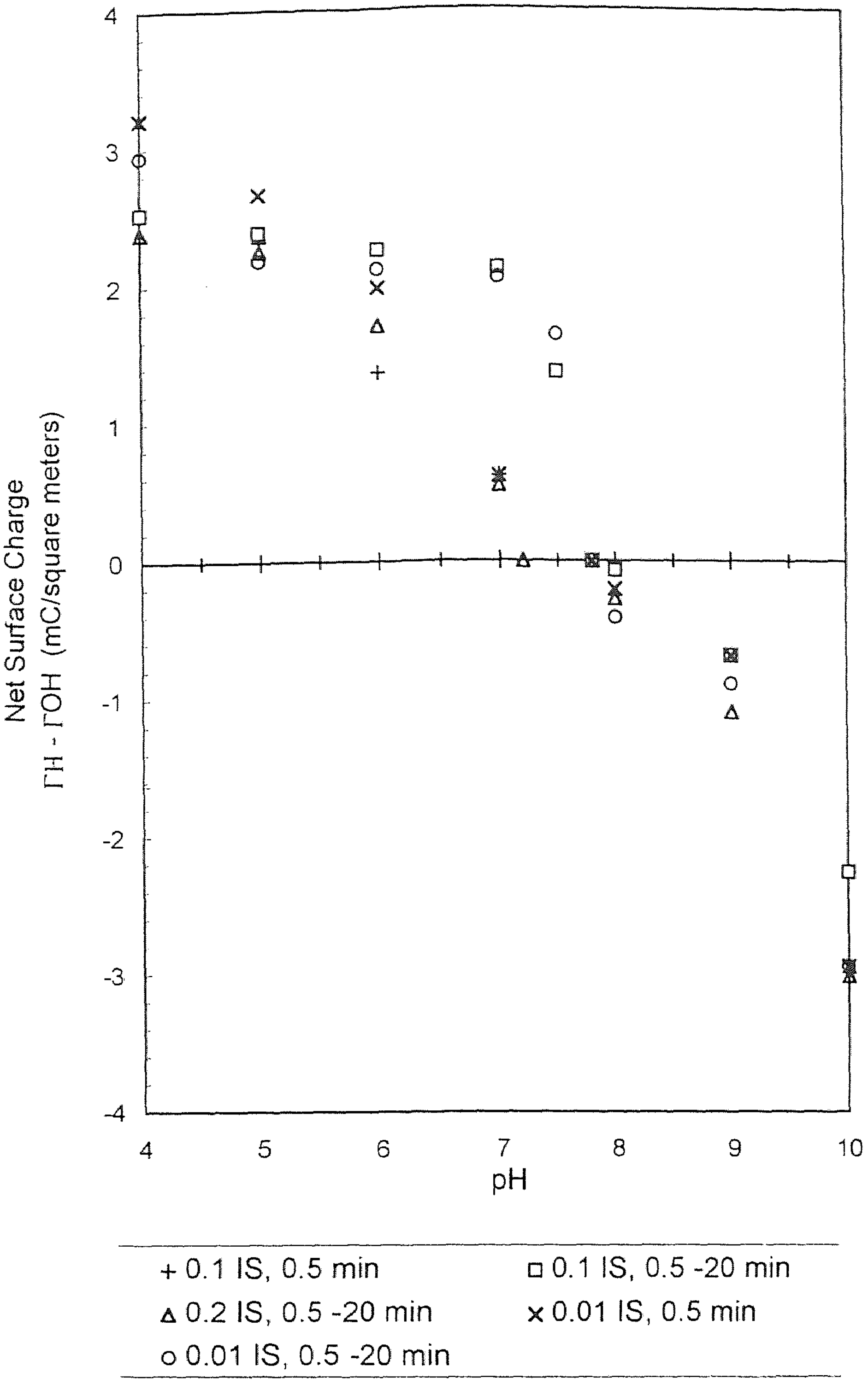


Figure 2 Net surface charge of goethite as a function of pH and ionic strength (sodium nitrate) with 1 gram per liter goethite and nitrogen atmosphere.

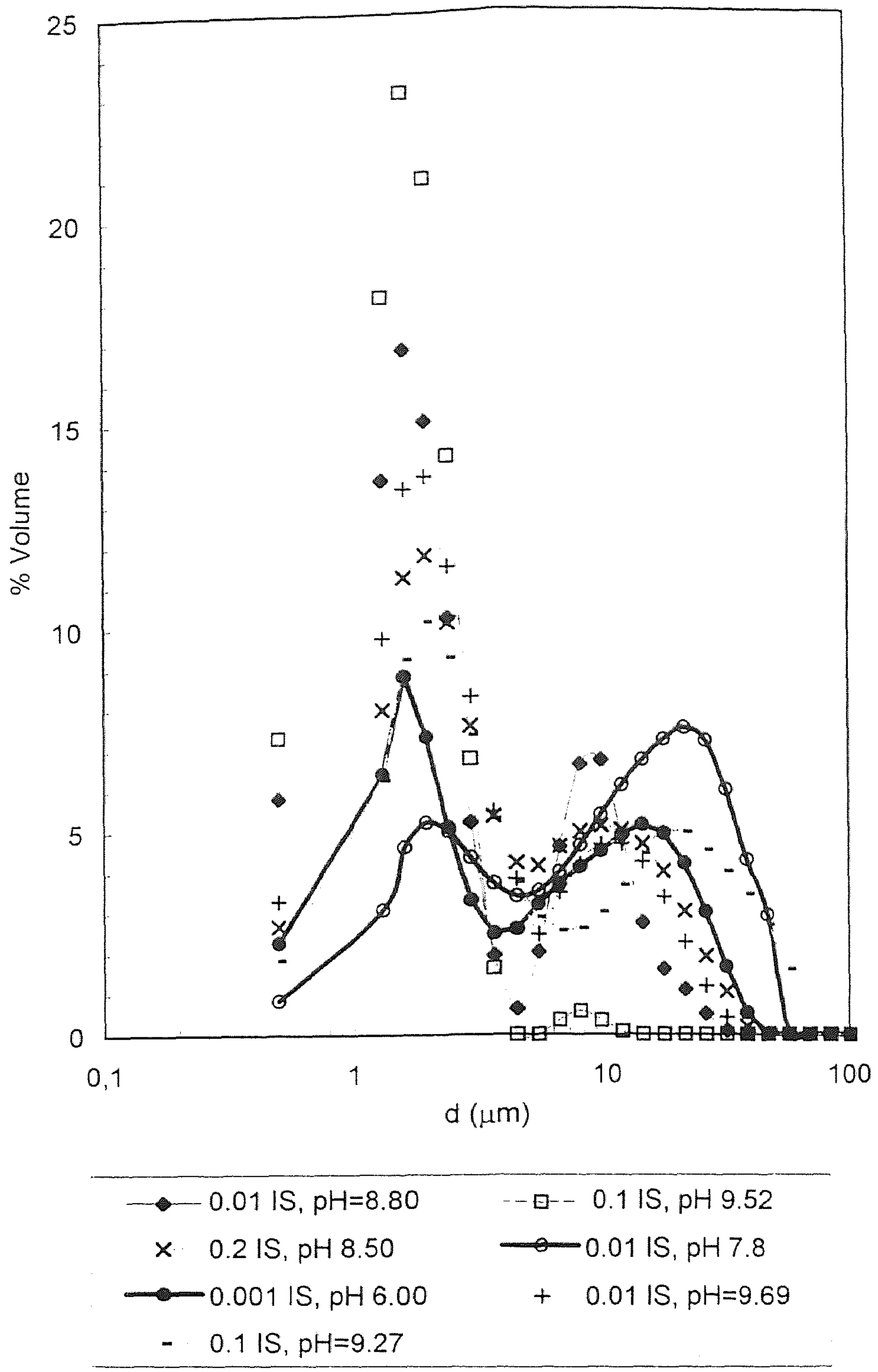


Figure 3 Particle size distribution of 1 gram per liter goethite as a function of pH and ionic strength (sodium nitrate).

a process is evident (Figure 3) when PSDs of pH 8.50 and 8.80 are compared. The PSD at pH 8.50 with an ionic strength of 0.2 showed a greater mean particle length than the pH 8.80 with ionic strength of 0.01 distribution. In this case, aggregation is thought to be due to the tenfold increase in ionic strength, despite the fact that the 0.3 pH units difference between the two distributions might be a contributing factor, as well.

Although the tendency of goethite to aggregate is, as described above, partially illustrated, it is not consistent throughout. The PSD of pH 8.80 with ionic strength of 0.01 and pH 9.69 with ionic strength of 0.01 do not follow the same trend as the other distributions. The PSD of pH 9.69 with ionic strength of 0.01 exhibits a greater mean particle length than the pH 8.80 with 0.01 ionic strength. Furthermore, the PSD of pH 9.27 with ionic strength of 0.1 and that of pH 9.52 with ionic strength of 0.1, exhibit great differences although they are of similar pH and equal ionic strength. The variations in particle length observed in Figure 3 are thought to be partially due to goethite aggregation. Such an aggregation phenomenon or its extent were not modeled here.

4.2.5 Optical Microscope

An optical microscope was used to investigate the goethite particles. An acicular shape was revealed (Figure 4) where particles were on the average50 mm by 1.5 mm. This particle shape is consistent with the PSD results and with what others have found (10, 13).

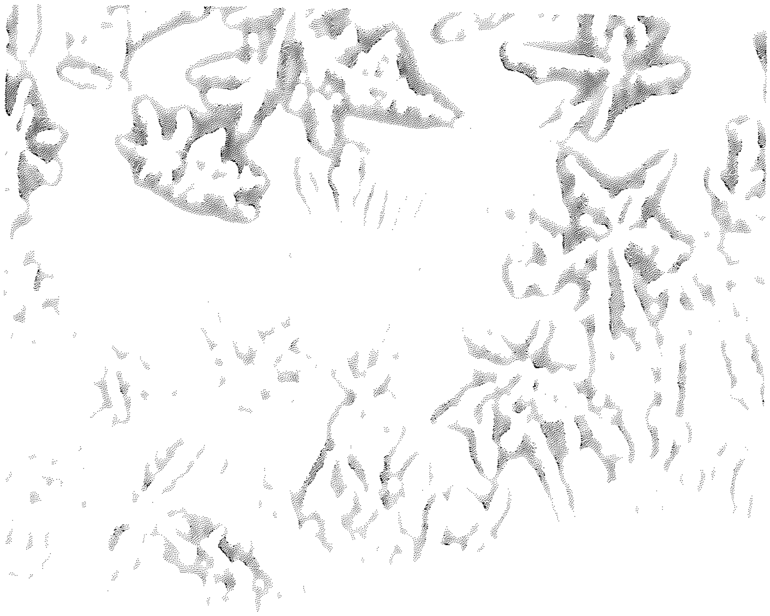


Figure 4 Goethite particles as seen through an optical petrographic microscope with x100 magnification

4.2.6 Physical Appearance

The freshly precipitated goethite was of a brown-yellow color (Table 4). A red color, indicative of ferrihydrite and possibly hematite impurities, faded away and a brown-yellow prevailed as the aging process was optimized.

4.3 Adsorption Experiments

4.3.1 Adsorption Edge Experiments

To understand metal affinities for goethite as a function of pH, adsorption edges were performed using metal concentrations below their saturation limits (Appendix M). The results from the edge experiments are shown in Figures 5, 6, 7, and 8. Metal adsorption for copper, lead, and cadmium increased with increasing pH. As pH increases the net surface charge of goethite becomes more negative. This increase in negative charge results in an increase in cation adsorption and the typical "S" shaped adsorption edge is observed (1, 3, 6, 17, 18, 23, 26). Furthermore, no changes in the amount of metal sorbed in adsorption edges of copper, lead, and cadmium were observed with a tenfold increase of the ionic strength, indicating that these metals are specifically adsorbed on goethite (34).

The adsorption edge results are consistent with what others have found (3, 10, 24). For example, studies (3, 10, 24) have revealed that copper shows high affinity for the goethite surface at a pH as low as 4. In the present study, however, copper exhibited a slightly greater affinity for goethite at a lower pH than when compared to Coughlin and Stones results (3). They

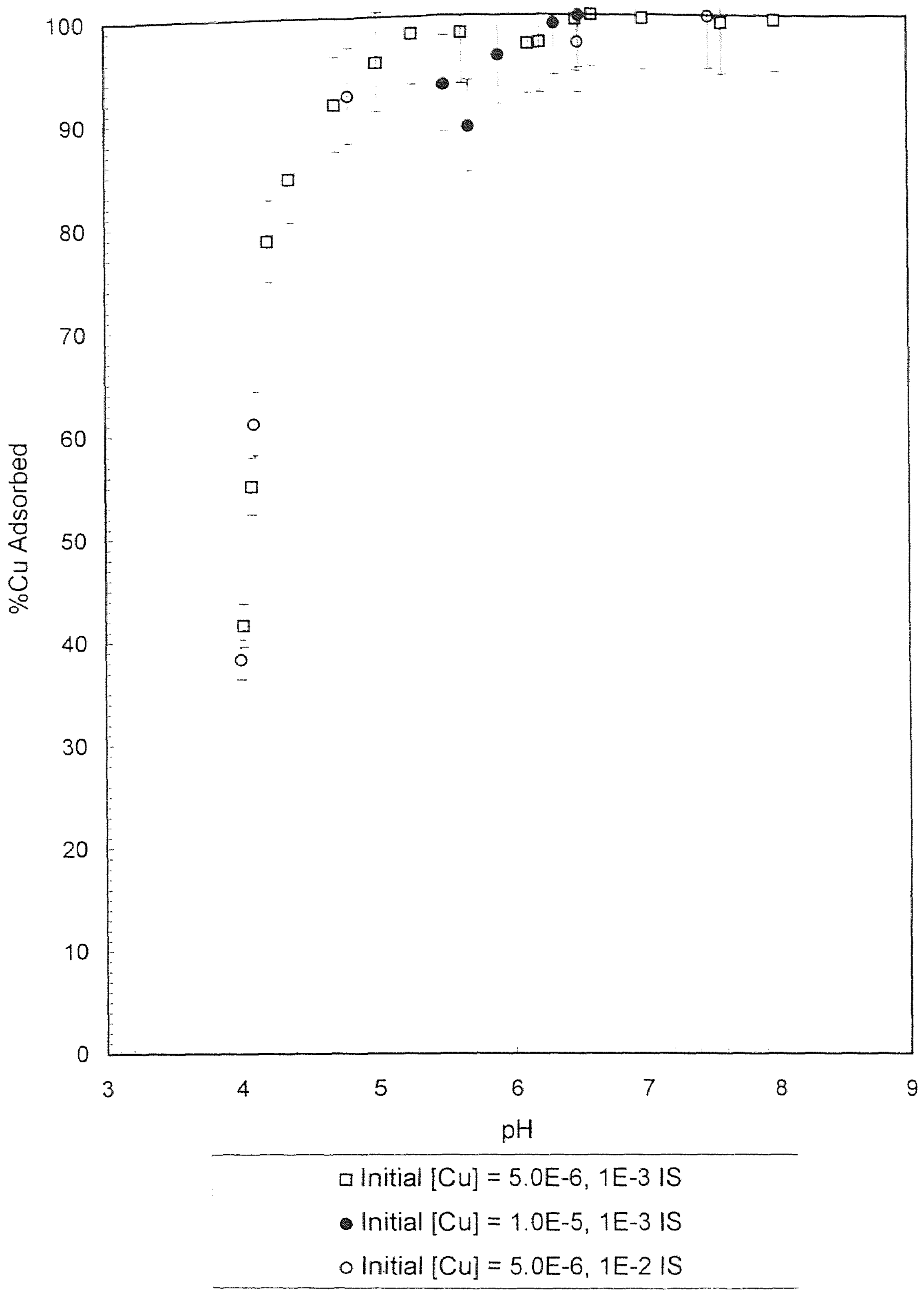


Figure 5 Adsorption edge for Cu adsorption on goethite with 1 gram/liter goethite, equilibration period 4 hours, and sodium nitrate as the ionic strength (IS) adjuster.

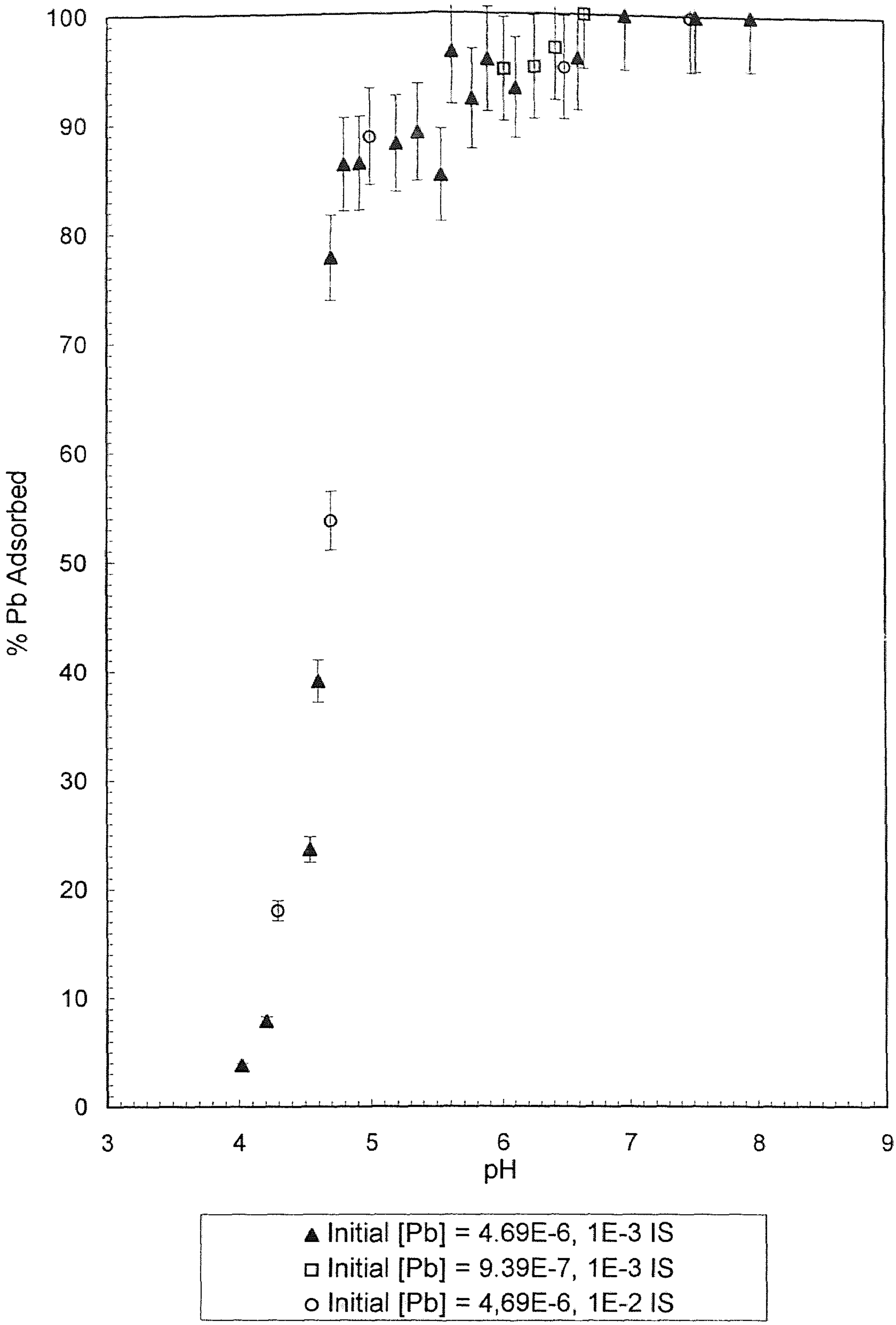
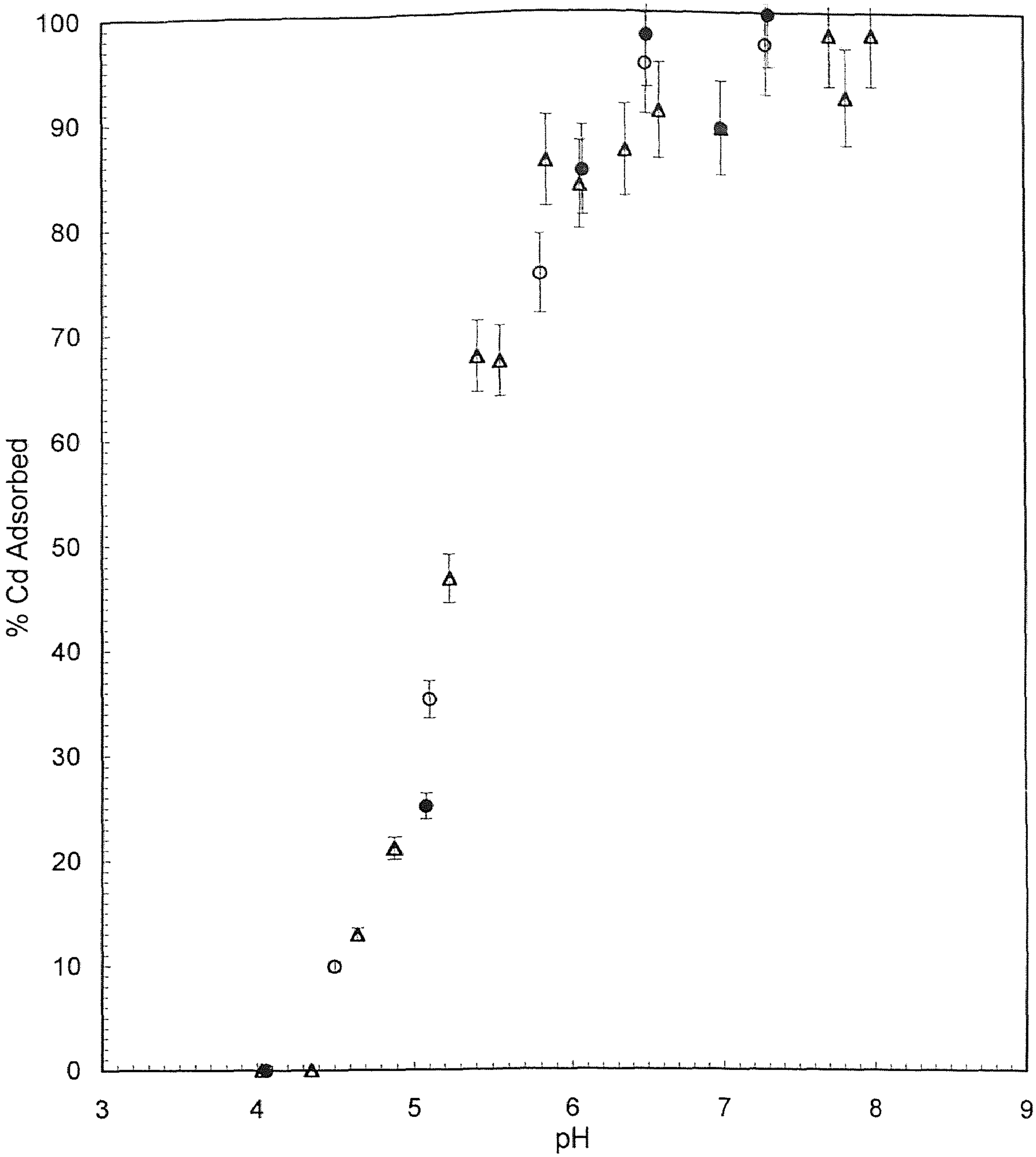


Figure 6 Adsorption edge for Pb adsorption on goethite with 1 gram/liter goethite, equilibration period 4 hours, and sodium nitrate as the ionic strength (IS) adjuster.



Δ Initial [Cd] = 4.45E-6, 1E-3 IS

● Initila [Cd] = 8.89E-7, 1E-3 IS

○ Initial [Cd] = 4,45E-6, 1E-2 IS

Figure 7 Adsorption edge for Cd adsorption on goethite with 1 gram/liter goethite, equilibration period 4 hours, and sodium nitrate as the ionic strength (IS) adjuster.

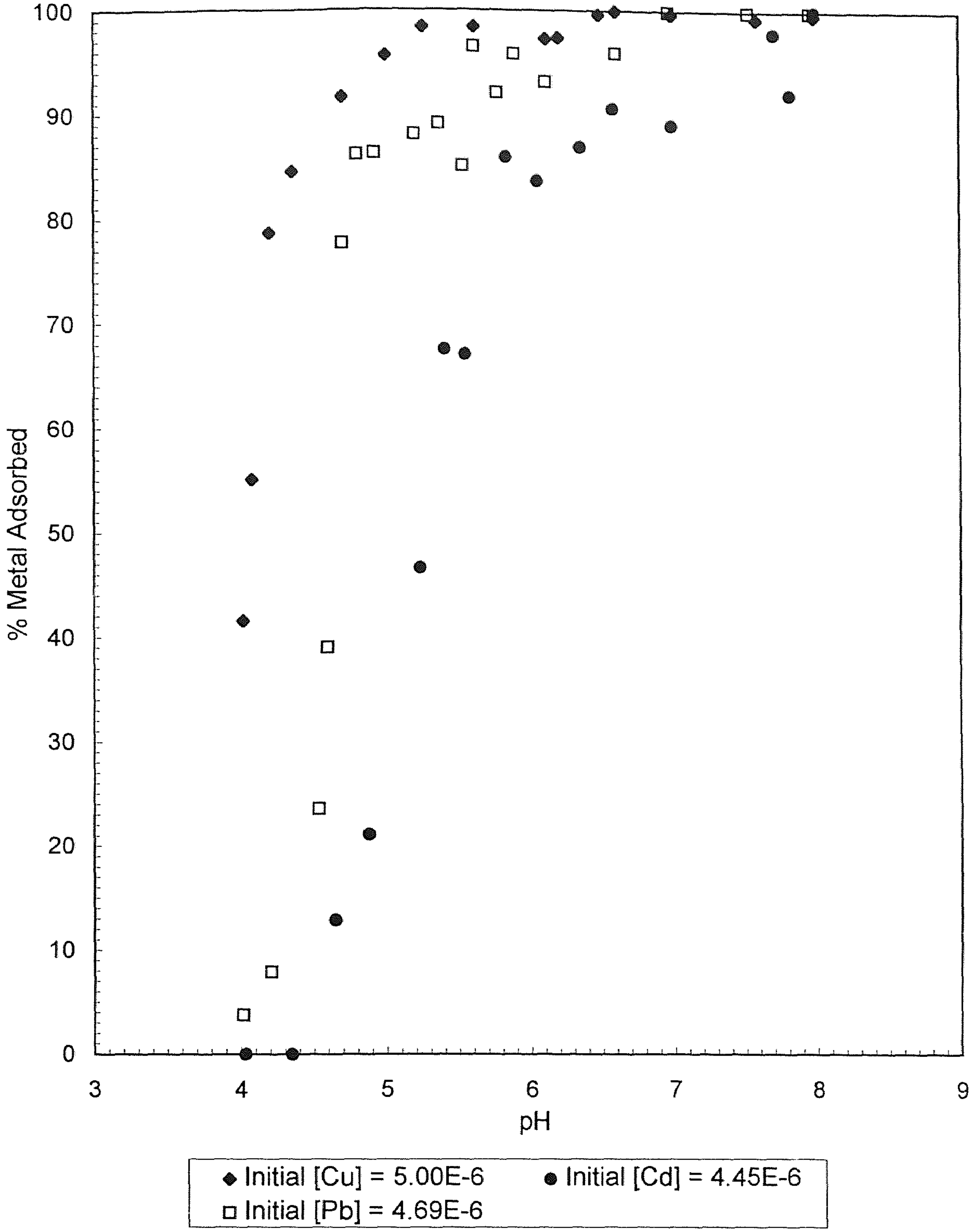


Figure 8 Adsorption edges for Cu, Pb, and Cd adsorption on goethite with 1 gram/liter goethite, equilibration period 4 hours, and 1E-3 ionic strength (sodium nitrate).

found that at pH 4.5, 75% of copper was adsorbed on goethite. In this experiment, 75% adsorption was observed at a pH of 4.3 (Figure 5). In general, results from this study show that copper has a slightly greater affinity for goethite in the pH range of 4 to 4.5. Above this range, however, little to no variation is seen when compared to others results (3, 10, 24).

Results of lead adsorption on goethite (Figure 6) are consistent with those of Schwertman and Taylor (10), Coughlin and Stone (3), and Muller and Sigg (26). Cadmium exhibits the lowest affinity of all three metals for the goethite surface (Figures 7 and 8). The results in this thesis indicate that cadmium had a greater adsorption affinity for goethite than what was observed in Johnson's study (18). This discrepancy is, however, expected as Johnson used goethite with a pH zpc of 9. The goethite used in this study was observed to have a pH zpc of 7.75, resulting in a greater negative surface charge for a given pH.

Figure 8 shows the adsorption affinity for the metals follows the order of Cu>Pb>Cd. No correlation is observed between metal affinity and its ionic or hydrated radii (Table 5 and Figure 8), suggesting that size is not a significant factor for adsorption of these heavy metals to goethite.

Metal affinities are reversibly related to the ions' polarizability (Figure 8 and Table 5). Polarizability describes the ease with which an electron cloud of a molecule or atom can be distorted by a nearby electric field (29). Polarizability is also reversibly related to the metals' ability to hydrolyze.

Hydrolysis products of metal ions include hydroxo and dihydroxo

Table 5

Metal ion characteristics

Characteristics	**Metal**		
	Cu^{2+}	Pb^{2+}	Cd^{2+}
Hydrated radius (Angstrom)[1]	4.19	4.01	4.26
Ionic radius (Angstrom)[1]	0.72	1.32	0.97
Relative electronegativity scale[1]	1.90	1.80	1.69
Polarizability (ground state) (10^{-24} cm^3)[1]	6.1	6.8	7.2
Electron configuration[2]	$4s^1 3d^{10}$	$6s^2 4f^{14} 5d^{10} 6p^2$	$5s^2 4d^{10}$
Group[2]	1B	4A	2B
Percent speciation in the absense of another metal[3]	97.0 Cu^{2+} 1.8 $Cu(OH)_{2(aq)}$	96.4 Pb^{2+} 1.7 $PbOH^+$ 1.2 $PbNO_3^+$	99.7 Cd^{2+}
In the presence of:	**Cd** 97.1 Cu^{2+} 1.8 $Cu(OH)_{2\,(aq)}$	**Cd** 97.1 Pb^{2+} 1.7 $PbOH^+$ 1.2 $PbNO_3^+$	**Pb** 99.8 Cd^{2+}
In the presence of:	**Pb** 97.1 Cu^{2+} 1.8 $Cu(OH)_{2(aq)}$	**Cu** 96.4 Pb^{2+} 1.7 $PbOH^+$ 1.2 $PbNO_3^+$	**Cu** 99.7 Cd^{2+}
In the presence of:	**Cd & Pb** 82.6 Cu^{2+} 2.3 $CuOH^+$ 15.0 $Cu(OH)_{2(aq)}$	**Cd & Cu** 93.6 Pb^{2+} 5.2 $PbOH^+$ 1.2 $PbNO_3^+$	**Pb & Cu** 99.8 Cd^{2+}

Sources:

[1] : (29)

[2] : (8)

[3] : Metal Speciation as calculated using MINTEQA2 (40) at pH 6 and 10^{-3} ionic strength (sodium nitrate).

species (Table 5). Cadmium, which exhibits the greatest polarizability of all three metals of interest, forms the least amount of hydroxo species. Some metal hydroxo species are preferably adsorbed over the divalent form of the metals when the surface has a net positive charge (23). Differences in metal adsorption of copper, lead, and cadmium to goethite range from 10% to 90% over the pH range studied (Figure 8); these differences can not, however, be accounted for by metal speciation. The predominant species (>96%) for all three metals at pH 6 is their uncomplexed divalent form.

As mentioned above, the adsorption affinity for the metals follows the order of Cu>Pb>Cd (Figure 8); this order suggests that electronegativity may be the most important factor as metal adsorption increased with increasing electronegativity (Table 5). Schwertman and Taylor (10) reported the affinity of heavy metals for goethite followed Cu>Pb>Zn>Cd>Co>Ni>Mn order which is in agreement with electronegativity being the most important factor. Similarly, Forbes and Posner et. al (23) observed metal affinities for goethite to be in the order of Cu>Pb>Zn>Cd>Co. Gadde and Laitinen (17) found that metal adsorption to hydrous Fe and Mn oxides is of the order Pb>Zn>Cd. Coughlin and Stone (3) studied the adsorption of heavy metals on goethite and found that the adsorption affinities followed Cu>Pb>Ni~Co>Mn. Contrary to other studies (10, 17, 23), in the Coughlin and Stone study Co and Ni showed similar affinities as opposed to Co being greater than Ni. Despite this discrepancy, the results from all these studies are consistent with electronegativity being the most important factor (10, 17, 23).

For isotherm and competition studies, pH 6 was chosen as it is a common pH in natural waters (15). Furthermore, this pH allows metal concentrations up to 10^{-6} M without precipitation. Dilute or trace concentrations of heavy metals are relevant with respect to contaminants existing and of concern (28). Furthermore, the metal affinities for goethite at pH 6 are great; this is expected to be helpful for saturating adsorption sites on the goethite surface in competition studies.

4.3.2 Single Ion Adsorption Isotherms

Isotherms were performed for each metal at pH of 6 and 10^{-3} ionic strength. These experiments were conducted for both two and four hour equilibration periods. The two hour equilibration period experiments were performed to verify that equilibrium is reached within two hours, as such a period was then used in competition isotherms. No variation in metal adsorption was observed between these two equilibration periods (Figures 9, 10, 11, 12) suggesting that equilibrium is reached within two hours. Data from other studies suggest that two hours, or less, is an adequate time for equilibration (6, 28).

The change in pH during each isotherm experiment was monitored and was found to be due to the addition of the metal nitrate stock. No hydrogen ions were released during metal adsorption on goethite. The adsorption reactions were observed as the following:

$$\equiv \mathrm{FeOH} + \mathrm{M}^{2+} \rightleftharpoons \equiv \mathrm{FeOHM}^{2+}$$

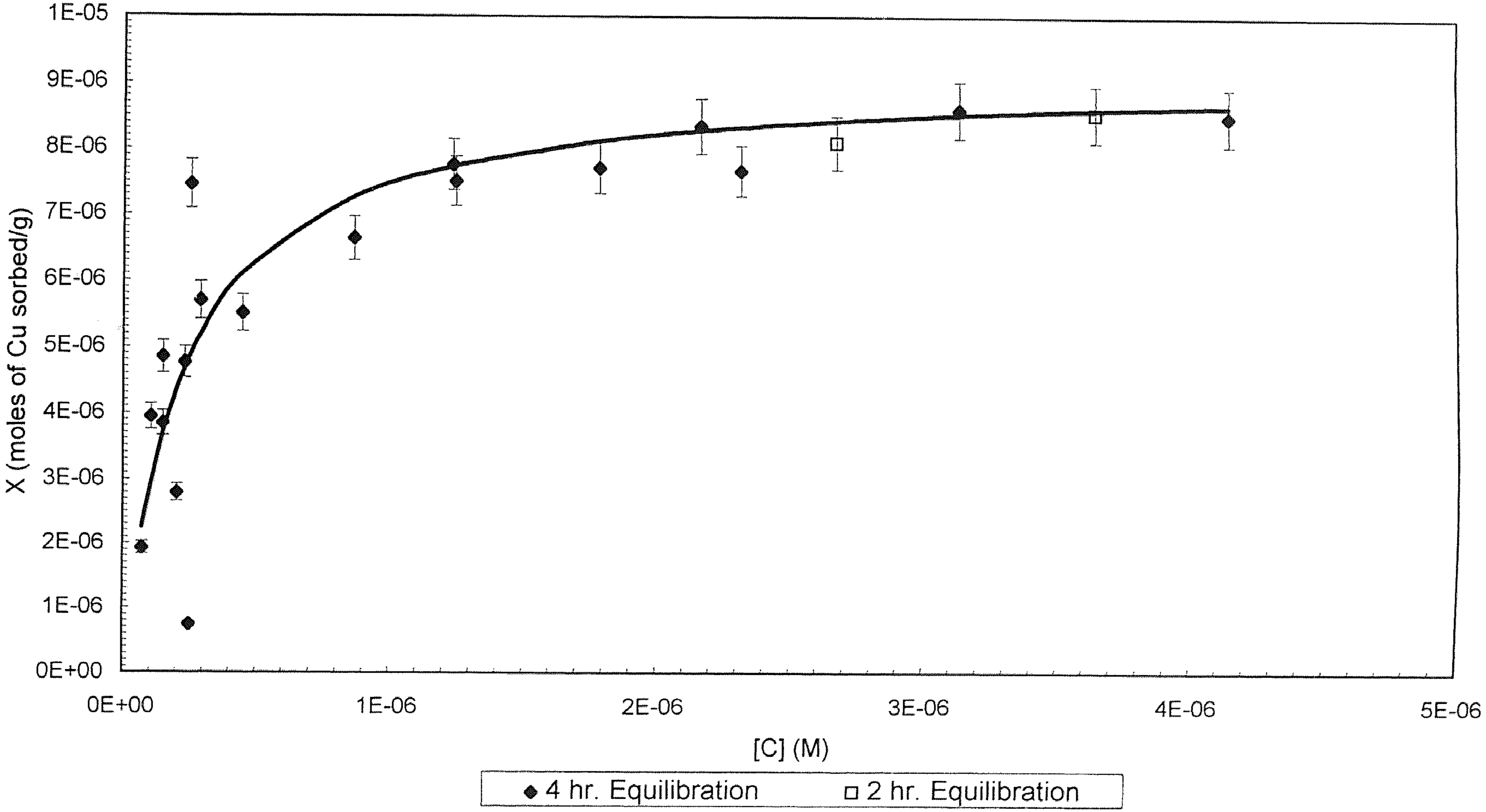


Figure 9 Isotherm for Cu adsorption to goethite with 1 gram per liter goethite, pH 6, and 1E-3 ionic strength (sodium nitrate). Solid line represents Langmuir model.

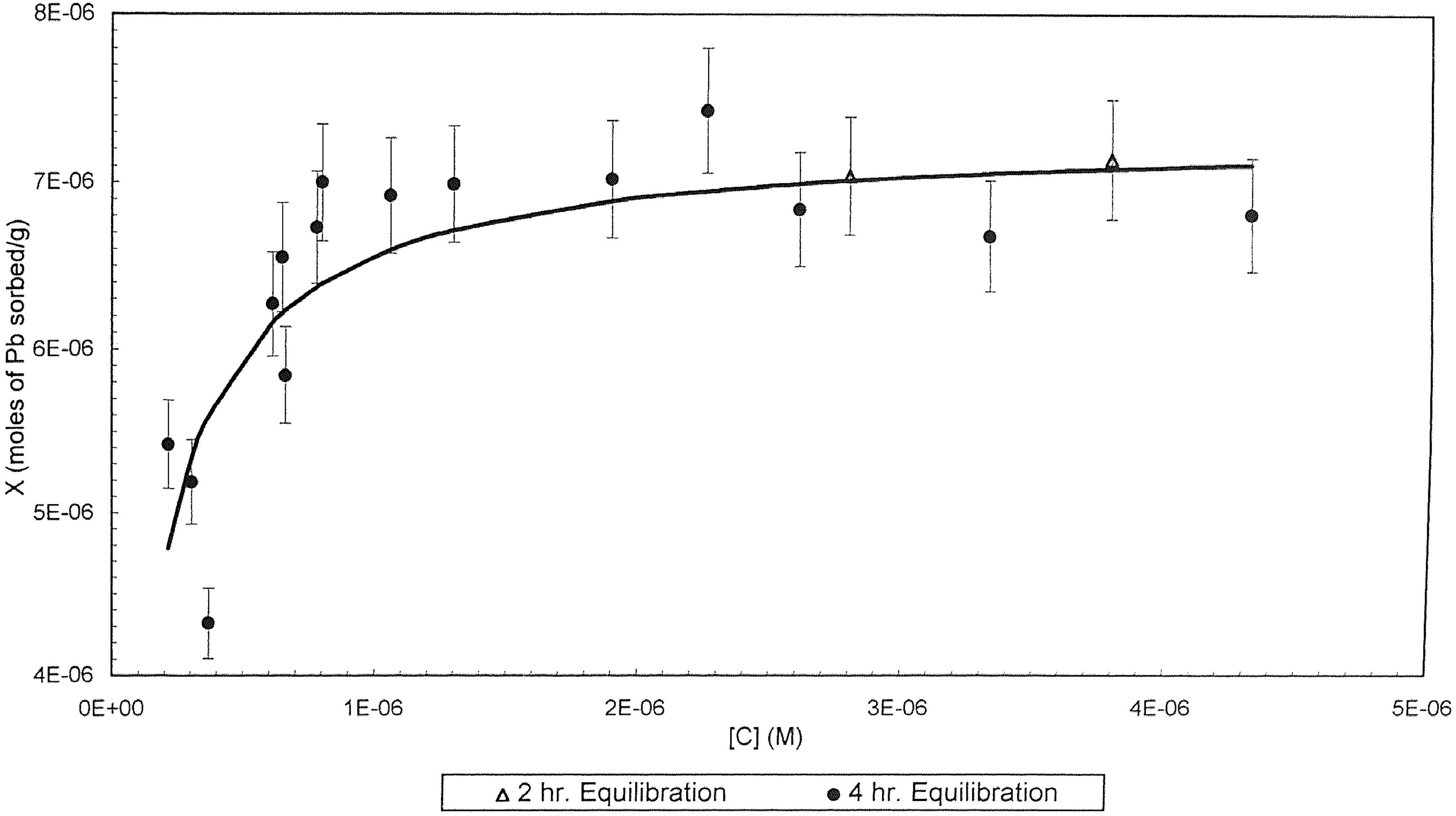


Figure 10 Isotherm for Pb adsorption to goethite with 1 gram per liter goethite, pH 6, and 1E-3 ionic strength (sodium nitrate). Solid line represents Langmuir model.

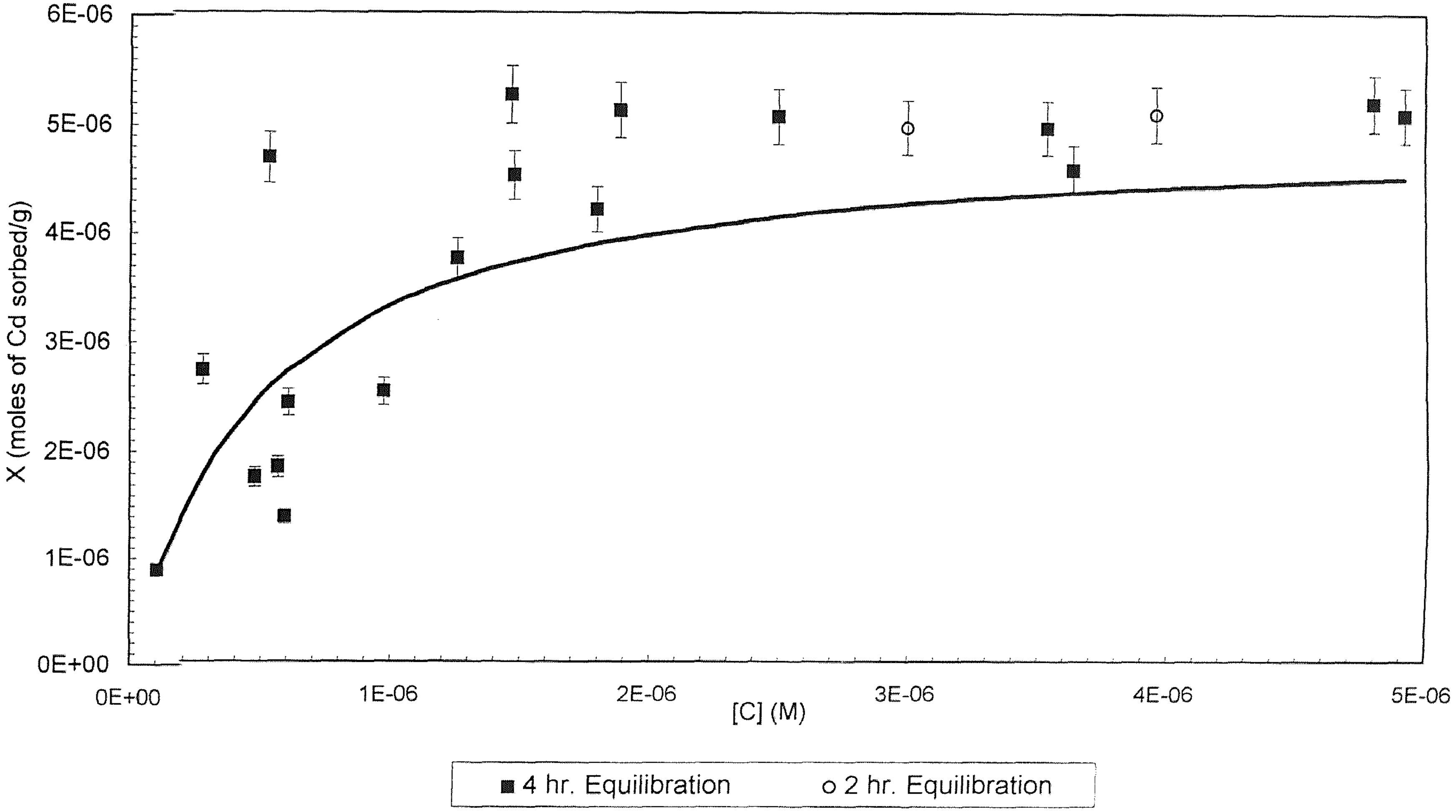


Figure 11 Isotherm for Cd adsorption to goethite with 1 gram per liter goethite, pH 6, and 1E-3 ionic strength (sodium nitrate). Solid line represents Langmuir model.

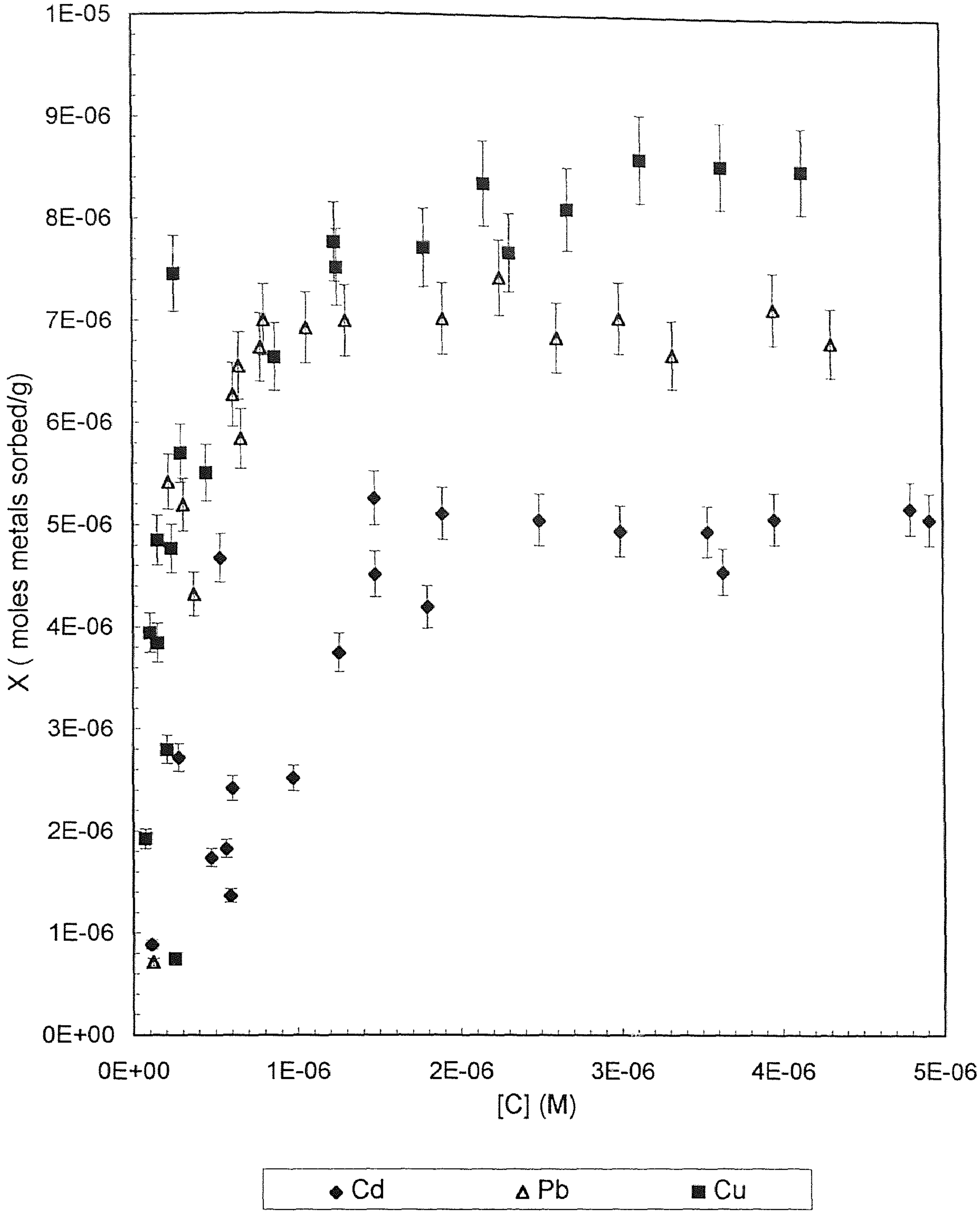


Figure 12 Adsorption isotherms for Cu, Pb, and Cd adsorption to goethite with 1 gram per liter goethite, pH 6, and 1E-3 ionic strength (sodium nitrate).

where $\equiv$FeOH represents a surface site on goethite; M^{2+} is the copper, lead or cadmium ion in the bulk aqueous phase; and $\equiv$FeOHM^{2+} is the adsorption complex.

Adsorption isotherms are graphically displayed as plots of metal adsorbed, X (moles per gram), versus residual metal concentration in the bulk aqueous phase, C (moles per liter). Isotherms describe adsorbate distribution between the bulk aqueous and adsorbed phases at equilibrium (1).

The isotherm for copper adsorption to goethite (Figure 9), indicates that metal adsorption increases with increasing metal concentration. This increase in adsorption is seen as the "rising" part of the isotherm. At the "plateau" area of the isotherm, however, the amount of copper adsorbed remains constant despite the continuous increase in initial metal concentration. This "leveling" indicates a limited number of sites, and that goethite's capacity for copper has been reached. All three isotherms exhibit the same shape as the one in Figure 9 (Figures 10 and 11).

Metal capacities for goethite follow the order of Cu>Pb>Cd (Figures 12). Because goethite exhibited a limited number of sites (Figure 12), the Langmuir model was used to fit the data. This model assumes a fixed number of total sites or a monolayer capacity, X_m, that can be occupied by a given metal. Furthermore, this model is based on the assumption that the free energy of adsorption is independent of surface coverage. That is, the driving force for adsorption is the same whether an adsorption surface is nearly filled or completely empty. This assumption leads to the development of an ideal surface solution model in which their are no interactions between adjacent surface species. Similarly, the affinity of an adsorbate for a given site is not affected by the fact that neighboring sites are occupied by water or adsorbate species (1). The Langmuir isotherm for one type of adsorption site has the form:

$$X = (X_m \cdot K \cdot C) / (1+K \cdot C)$$

where,

X : metal sorbed per mass of sorbent (moles/g)

X_m : monolayer capacity (moles/g)

K : equilibrium constant related to the energy of sorption

C : residual sorbate concentration in bulk aqueous phase (M)

Experimental data were used to calculate X_m and K by plotting $1/X$ versus $1/C$. Such a plot yields a linear trend with intercept of $1/X_m$ and a slope of $1/(X_mK)$. The fitted parameters X_m and K for these systems are presented on Table 6. The model and experimental data are shown in Figures 9, 10, and 11.

The Freundlich model was also used to model the data. This model is based on an empirical relation and has no theoretical basis (1). The mathematical expression of Freundlich isotherm is:

$$\Gamma = K \cdot C^{1/n}$$

where,

Table 6

Calculated parameters from the application of Freudlich and Langmuir models to experimental data.

	Freudlich model				Langmuir model		
Metal ion	n	K	r^2	**Metal ion**	X_m	K	r^2
Cu^{2+}	0.27	2.8×10^{-4}	0.74	Cu^{2+}	9.1×10^{-6}	44.9×10^{5}	0.8
Pb^{2+}	0.11	3.0×10^{-4}	0.56	Pb^{2+}	7.3×10^{-6}	88.4×10^{5}	0.6
Cd^{2+}	0.42	1.1×10^{-6}	0.70	Cd^{2+}	4.9×10^{-6}	19.9×10^{5}	0.7

Γ : metal sorbed per mass of sorbent (moles/g)

K : constant related to the energy of sorption

C : residual sorbate concentration in the bulk aqueous phase at equilibrium (M)

n : constant related to the distribution of the bond strength.

The average strength of surface-adsorbate bonds varies with adsorption densities. In the case of n being unity, all surface sites are equal and the Freundlich isotherm is reduced to the linear distribution. When total sites are approximately equivalent to available sites, the Langmuir model reduces to the linear distribution model (1). In the Freundlich model, the logarithm of C is plotted against the logarithm of X (metal sorption/gram of goethite); the slope is equal to 1/n and the intersection is equal to the logarithm of K.

As seen in Table 6, the Langmuir model yields a slightly better fit than

Freundlich model for all systems. Furthermore, the adsorption isotherms are consistent with the Langmuir model; adsorption initially increases with increasing metal concentration up to the point where all sites are filled and adsorption remains constant despite increasing metal concentration. Metal capacities, however, are not consistent with the obtained K values; based on the obtained K values, lead showed greater affinity than copper for the goethite surface. However, copper had greater capacity than lead. This discrepancy between the K and X_m values suggests that more than one type of sites may exist. Isotherms in Figure 12 show that the metal affinities for goethite follow the same order as electronegativity (Table 5), again suggesting that electronegativity is the most important factor in metal adsorption.

4.3.3 Site Density

Table 7 lists goethite's mole capacity per gram for various adsorbates obtained from the adsorption isotherms. Each metal revealed a slightly different site density. Strontium and N_2 adsorption indicated greater site densities than copper, lead, and cadmium adsorption.

In addition to the sites used by heavy metals (Cu, Pb, and Cd), strontium, from group IIA of the Periodic Table, apparently binds to another group of energy sites. Other researchers have identified multiple distinct groups differ from one another according to whether an oxygen is singly, doubly, or triple coordinated (5). The presence of four types of sites on the

Table 7
Goethite sorbent capacities

Sorbent	**Capacity (moles/gram) from isotherm studies pH 6, 10^{-3} ionic strength**	**Capacity (moles/gram) from Langmuir model.**	**Difference between model and experimental values**
Cu^{2+}	$8.6x10^{-6}$	$9.1x10^{-6}$	3.1%
Pb^{2+}	$7.0x10^{-6}$	$7.3x10^{-6}$	1.3%
Cd^{2+}	$5.0x10^{-6}$	$4.9x10^{-6}$	0.7%
N_2	$5.50x10^{-4}$ *	NA	NA
Sr^{2+}	$7.2x10^{-2}$	NA	NA

* calculated using the BET equation (25)
NA Not applicable

110 and 021 faces of goethite with different proton affinities was reported by Venema et al. (30). The presence of these distinct types of sites on an oxide sorbent is often used to explain different metal capacities (5). Strontium exhibited greater capacities for the goethite surface, because it most likely binds to another set of energy sites in addition to those utilized by copper, lead, and cadmium.

Nitrogen adsorption also indicated greater site densities than that of copper, lead, and cadmium adsorption. Gas-solid adsorption differs from the aqueous-solid systems for copper, lead, and cadmium. Nitrogen is most likely attracted to goethite by different forces than what is being observed in these studies with metal ion adsorption. Furthermore, nitrogen adsorption potentially includes meso- and micropore sites. Diffusion of metal ions from the adsorbed surface in micropores has been observed with amorphous iron oxides, and is known as the second, slow step of adsorption (28). In this study, however, short term studies were conducted where the fast, reversible adsorption of aqueous metal ions to the external surface sites was examined. During this step, sites located in the micropores are not utilized. The site density of nitrogen adsorption on goethite is therefore greater than that of copper, lead, and cadmium.

The three metals of interest, however, are believed to bind to the same energy sites. The difference in site densities obtained from the use of these three metal adsorbates may be due to the their different affinities for goethite. As with their metal electronegativity, site densities follow the order of Cu>Pb>Cd. These site densities are consistent with the monolayer capacity, X_m, values obtained from the Langmuir model (Table 7). The difference between experimental capacities and those obtained from the Langmuir model are, in all cases, within experimental error of the data. Overall, the metals exhibit similar capacities for the goethite surface.

4.3.4 Competition Isotherms

Competition isotherms were performed at pH 6, 10^{-3} ionic strength, and 10^{-1} gram per liter goethite with the competing metals at equivalent initial concentrations. Maximum metal concentrations were below saturation (Appendix M) and were selected based on the obtained site densities (Table 7) as to promote metal competition. Reducing goethite to 10^{-1} gram per liter, the total available sites were limited to 8.57×10^{-7} moles per liter, which is less than those needed for either one of the two metals to be completely adsorbed.

To test the hypothesis that electronegativity is the most important factor in adsorption, the metal with the smallest electronegativity was added first (competition I), with 2 hour equilibration. Subsequently, addition of the competing metal(s) followed. The system was then allowed to equilibrate for an additional 2 hours. If electronegativity is indeed the most important factor in metal affinities for goethite, the metal with greater electronegativity is expected to displace the less electronegative species. The order of metal introduction into the solution was then reversed (competition II) to further examine metal affinities. Finally both competing metals were introduced into the solution simultaneously (competition III).

The results of the Cd-Cu competition studies are shown in Figure 13 and Table 8 where copper completely displaced cadmium. The adsorbed cadmium in Figure 13 reflects the amount adsorbed to the container exclusively. The order of metal introduction in solution of the two competing pairs was then reversed (competition II). Finally, the competing metals were simultaneously introduced in the system (competition III). The results from experiments II and III revealed no variation from the first one (competition I) (Table 8 and Figure 13). Copper, which has a greater electronegativity than cadmium, displaced cadmium in all studies. The total sites occupied per gram of goethite are equal to that observed in the copper isotherm studies, suggesting that copper and cadmium bind on the same types of sites (Table 9). The experimental amount of total sites occupied is in agreement with the expected value (results from Cu adsorption isotherm); the difference is within the error of the data, indicating that metals bind on the same types of sites.

In the case of Cd-Pb competition studies, a large portion of cadmium, 97.5%, is displaced by lead (Table 10 and Figure 14). Two percent of the adsorbed fraction of cadmium is accounted for by adsorption to the containers. An average of 0.5% of the cadmium concentration remained adsorbed to goethite when competing with lead. From adsorption isotherms, lead capacity is 7.29×10^{-6} moles per gram of goethite (Table 7). Given a total

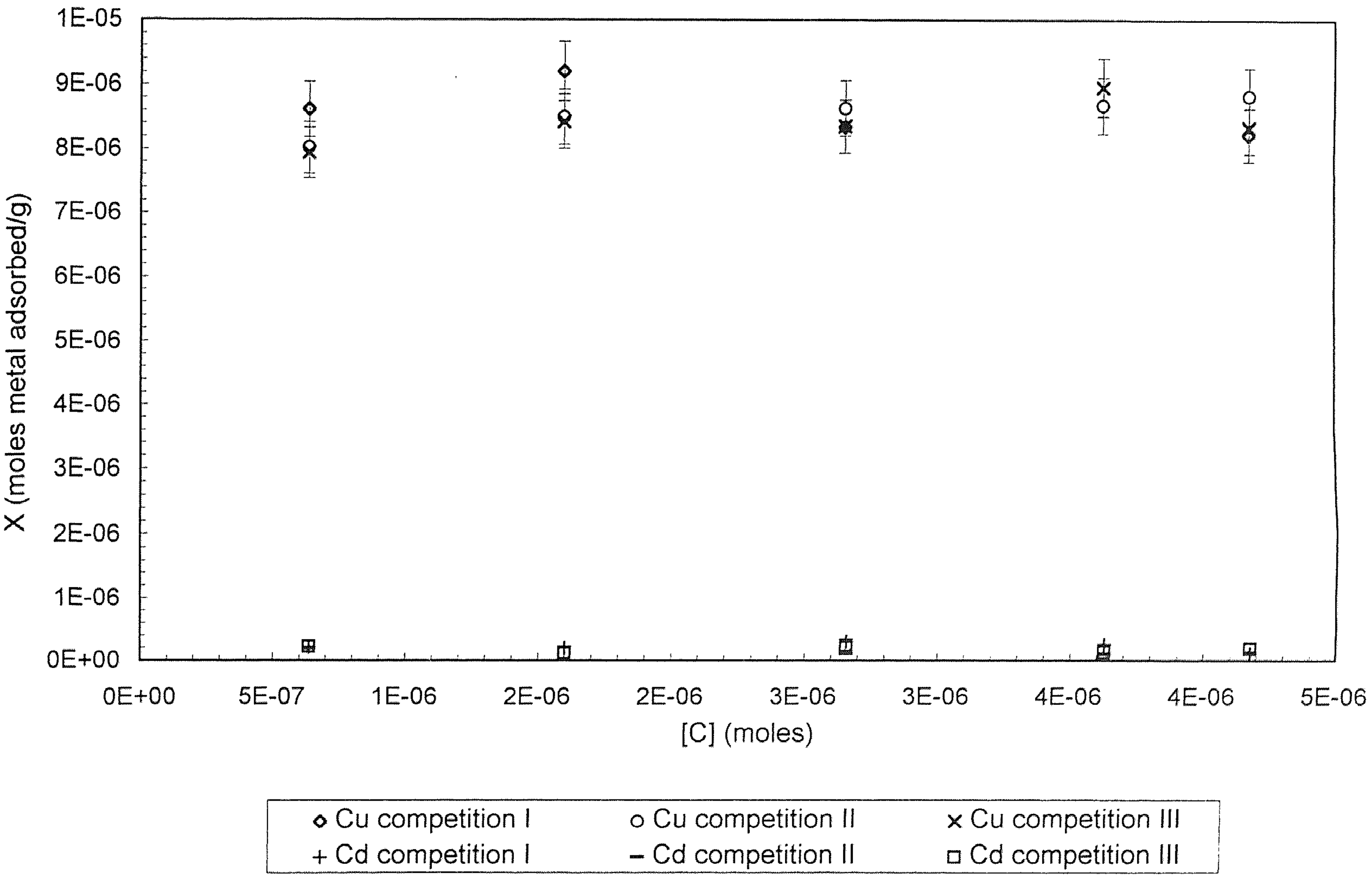


Figure 13 Cd and Cu adsorption competition isotherms with 1E-1 gram per liter goethite pH 6, and 1E-3 ionic strength (sodium nitrate).

Table 8

Metal competition results between Cd and Cu with10^{-1} gram per liter of goethite in 100ml aliquots at pH 6 and 10^{-3} ionic strength (sodium nitrate).

Competition	Metal * added (moles)	Metal added (moles)	Experimental adsorption (moles)	Experimental adsorption (moles)	Total sites occupied (moles)	Expected Total sites (moles)
I	Cd	Cu	Cd	Cu		
	1.5E-7	1.5E-7	0.21E-8	8.61E-8	8.82E-8	8.56E-8
	2.5E-7	2.5E-7	0.19E-8	9.00E-8	9.19E-8	8.56E-8
	3.5E-7	3.5E-7	0.29E-8	8.34E-8	8.63E-8	8.56E-8
	4.5E-7	4.5E-7	0.25E-8	8.68E-8	8.93E-8	8.56E-8
	5.0E-7	5.0E-7	0.10E-8	8.22E-8	8.32E-8	8.56E-8
II	Cd	Cu	Cd	Cu		
	1.5E-7	1.5E-7	0.19E-8	8.01E-8	8.20E-8	8.56E-8
	2.0E-7	2.0E-7	0.20E-8	8.49E-8	8.69E-8	8.56E-8
	3.0E-7	3.0E-7	0.11E-8	8.63E-8	8.74E-8	8.56E-8
	4.0E-7	4.0E-7	0.10E-8	8.68E-8	8.78E-8	8.56E-8
	5.0E-7	5.0E-7	0.12E-8	8.82E-8	8.94E-8	8.56E-8
III **	Cd	Cu	Cd	Cu		
	1.5E-7	1.5E-7	0.22E-8	7.93E-8	8.15E-8	8.56E-8
	2.0E-7	2.0E-7	0.12E-8	8.42E-8	8.54E-8	8.56E-8
	3.0E-7	3.0E-7	0.24E-8	8.35E-8	8.59E-8	8.56E-8
	4.0E-7	4.0E-7	0.13E-8	8.96E-8	9.09E-8	8.56E-8
	5.0E-7	5.0E-7	0.19E-8	8.34E-8	8.53E-8	8.56E-8

*** Total sites occupied based on the experimental adsorption of the competing metals.

* * In this competition both metals were introduced simultaneously in the system.

* This column shows the metal that was introduced first in the system.

Table 9

Metal competition results between Cd and Pb, Cd and Cu and Pb and Cu with 10^{-1} gram per liter of goethite, at pH 6, and 10^{-3} ionic strength (sodium nitrate).

Experiment	**Maximum adsorption Cu (moles/g)**	**Maximum adsorption Pb (moles/g)**	**Maximum adsorption Cd (moles/g)**	**Total sites occupied sites (moles/g)**	**Expected sites from Cu isotherms (moles/g)**	**Difference based on occupied and expected values % ****
Cd-Cu	8.5×10^{-6}		$1.7 \text{ X} 10^{-7}$ *	$8.7 \text{ X} 10^{-6}$	$8.6 \text{ X} 10^{-6}$	0.95
Cd-Pb		$7.1 \text{ X} 10^{-6}$	$8.8 \text{ X} 10^{-7}$	$8.1 \text{ X} 10^{-6}$	$8.6 \text{ X} 10^{-6}$	4.3
Pb-Cu	$4.5 \text{ X} 10^{-6}$	$4.4 \text{ X} 10^{-6}$		$8.9 \text{ X} 10^{-6}$	$8.6 \text{ X} 10^{-6}$	2.9
Pb-Cu-Cd	$4.3 \text{ X} 10^{-6}$	$4.2 \text{ X} 10^{-6}$	$5.5 \text{ X} 10^{-7}$ *	$9.1 \text{ X} 10^{-6}$	$8.6 \text{ X} 10^{-6}$	4.6

* Represents adsorption to containers

** All differences are within error of the data.

Table 10

Metal competition results between Cd and Pb with 10^{-1} gram per liter of goethite, in 100ml aliquots, at pH 6 and 10^{-3} ionic strength (sodium nitrate).

Competition	Metal added (moles)	Metal added (moles)	Experimental adsorption (moles)	Experimental adsorption (moles)	Total sites occupied (moles)	Expected total sites (moles)
I	**Cd**	**Pb**	**Cd**	**Pb**		
	1.5E-7	1.5E-7	0.99E-8	7.15E-8	8.14E-8	8.56E-8
	2.5E-7	2.5E-7	0.86E-8	7.23E-8	8.09E-8	8.56E-8
	3.5E-7	3.5E-7	0.92E-8	7.20E-8	8.12E-8	8.56E-8
	4.5E-7	4.5E-7	1.06E-8	7.43E-8	8.49E-8	8.56E-8
	5.0E-7	5.0E-7	1.01E-8	7.25E-8	8.26E-8	8.56E-8
II	**Pb**	**Cd**	**Cd**	**Pb**		
	1.5E-7	1.5E-7	0.88E-8	7.00E-8	7.88E-8	8.56E-8
	2.0E-7	2.0E-7	0.90E-8	7.15E-8	8.05E-8	8.56E-8
	3.0E-7	3.0E-7	0.85E-8	7.45E-8	8.30E-8	8.56E-8
	4.0E-7	4.0E-7	0.79E-8	7.32E-8	8.11E-8	8.56E-8
	5.0E-7	5.0E-7	0.70E-8	7.21E-8	7.91E-8	8.56E-8
III **	**Cd**	**Pb**	**Cd**	**Pb**		
	1.5E-7	1.5E-7	0.99E-8	6.68E-8	7.67E-8	8.56E-8
	2.0E-7	2.0E-7	0.89E-8	6.94E-8	7.83E-8	8.56E-8
	3.0E-7	3.0E-7	0.78E-8	7.24E-8	8.02E-8	8.56E-8
	4.0E-7	4.0E-7	0.80E-8	7.38E-8	8.18E-8	8.56E-8
	5.0E-7	5.0E-7	0.85E-8	6.95E-8	7.80E-8	8.56E-8

*** Total sites occupied based on the experimental adsorption of the competing metals.

** In this competition both metals were introduced simultaneously in the system.

* Column 1 shows the metal that was introduced first in the system.

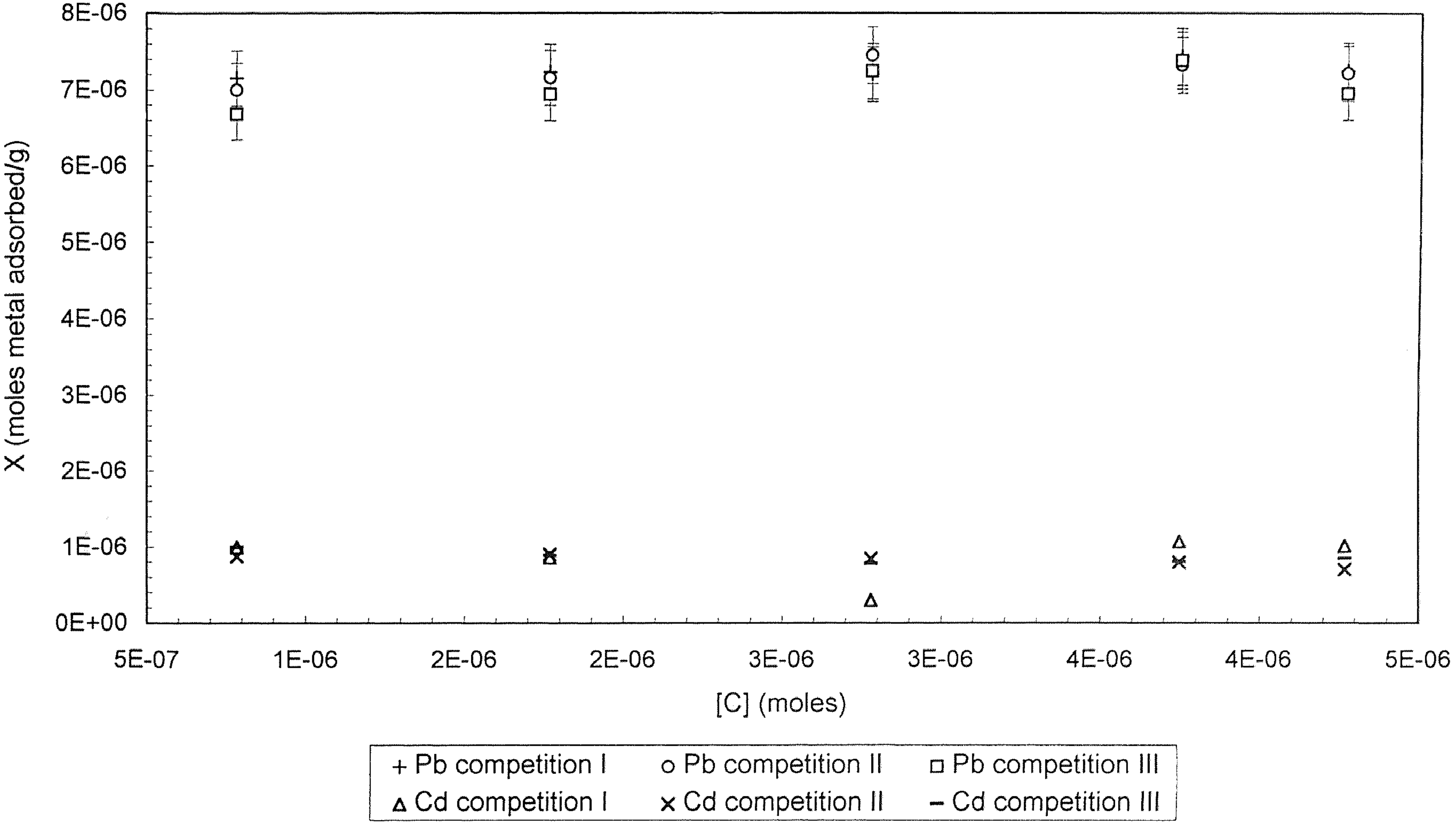


Figure 14 Cd and Pb adsorption competition isotherms with 1E-1 gram per liter goethite pH 6, and 1E-3 ionic strength (sodium nitrate).

of 8.56×10^{-6} moles per gram (from Cu isotherm) were available in this study, where 7.29×10^{-6} moles per gram are occupied by lead, the remaining 1.2×10^{-7} moles per gram are occupied by cadmium. Lead displaced cadmium from the sites it required. Because sites were not limited in this experiment, unoccupied ones could then be filled with cadmium. These results are shown in Table 9 where the percent difference between the occupied and expected site densities is 4.3%, which is within the error of the data. The order of metal introduction in solution of the two competing metals was then reversed (competition II), to further investigate metal competition. Finally, the competing metals were simultaneously introduced in the system (competition III).The results from the last two experiments showed no variation from the first one (Tables 10 and Figure 14).

In the case of Cu-Pb competition studies, 40% of lead was displaced by copper when lead was introduced first to the system (competition I) (Table 11 and Figure 15). As a result, only 50% of the sites were occupied by copper. Similar results were obtained when the order of metal introduction in solution was reversed (Table 11 competition II), where 50% of copper was actually displaced by lead, indicating that copper and lead bind on the same types of sites. When both metals were competing for the goethite sites simultaneously (competition III), identical results as with the previous competitions were obtained. Speciation in this case can not be considered as a contributing factor, as the only change is a 0.1% increase in copper ion concentration (Table 5).

Table 11

Metal competition results between Cu and Pb with 10^{-1} gram per liter of goethite in 100ml aliquots at pH 6, and 10^{-3} ionic strength (sodium nitrate).

Competition	Metal * added (moles)	Metal added (moles)	Experimental adsorption (moles)	Experimental adsorption (moles)	Total sites occupied *** (moles)	Expected total sites (moles)
I	**Pb**	**Cu**	**Pb**	**Cu**		
	1.0E-7	1.0E-7	4.22E-8	4.36E-8	8.58E-8	8.56E-8
	2.0E-7	2.0E-7	4.56E-8	4.69E-8	9.25E-8	8.56E-8
	3.0E-7	3.0E-7	4.40E-8	4.68E-8	9.08E-8	8.56E-8
	4.0E-7	4.0E-7	4.48E-8	4.59E-8	9.07E-8	8.56E-8
	5.0E-7	5.0E-7	4.49E-8	4.56E-8	9.05E-8	8.56E-8
II	**Cu**	**Pb**	**Pb**	**Cu**		
	1.0E-7	1.0E-7	4.19E-8	4.39E-8	8.58E-8	8.56E-8
	2.0E-7	2.0E-7	4.56E-8	4.78E-8	9.34E-8	8.56E-8
	3.0E-7	3.0E-7	4.10E-8	4.57E-8	8.67E-8	8.56E-8
	4.0E-7	4.0E-7	4.35E-8	4.53E-8	8.88E-8	8.56E-8
	5.0E-7	5.0E-7	4.46E-8	4.61E-8	9.07E-8	8.56E-8
III **	**Cu**	**Pb**	**Cu**	**Pb**		
	1.0E-7	1.0E-7	4.21E-8	4.12E-8	8.42E-8	8.56E-8
	2.0E-7	2.0E-7	4.53E-8	4.51E-8	9.04E-8	8.56E-8
	3.0E-7	3.0E-7	4.46E-8	4.42E-8	8.88E-8	8.56E-8
	4.0E-7	4.0E-7	4.51E-8	4.40E-8	8.91E-8	8.56E-8
	5.0E-7	5.0E-7	4.56E-8	4.59E-8	9.15E-8	8.56E-8

*** Total sites occupied based on the experimental adsorption of the competing metals.

** In this competition both metals were simultaneously in the system.

* Column 1 shows the metal that was introduced first in the system.

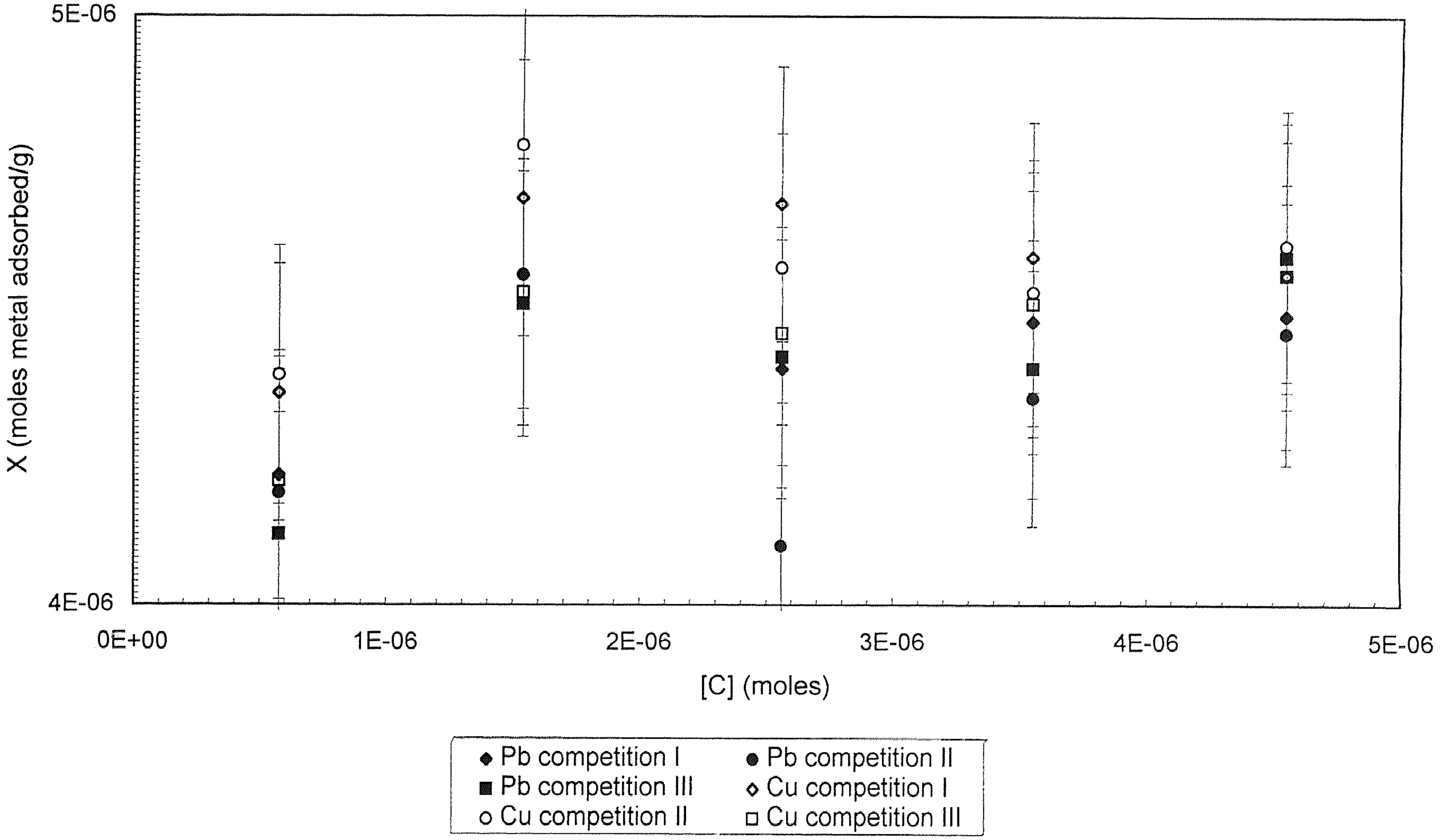


Figure 15 Cu and Pb adsorption competition isotherms with 1E-1 gram per liter goethite pH 6, and 1E-3 ionic strength (sodium nitrate).

The Langmuir model introduced earlier assumed only one average energy site for the goethite surface and was used to determine the total site capacity. Based on these competition results, the Langmuir model with two types of sites, of low and high affinity, was used to model the data:

$K_H = X_H / (C \cdot X_v)$

$K_L = X_L / (C \cdot X_v)$

$X = X_L + X_H$

$X_m = X_v + X_L + X_H$

where,

X_v : available sites per mass of sorbent (moles/g)

X : metal sorbed per mass of sorbent (moles/g)

X_m : monolayer capacity (moles/g)

X_H : metal sorbed at high affinity sites per mass of sorbent (moles/g)

X_L : metal sorbed at low affinity sites per mass of sorbent (moles/g)

K_H : equilibrium constant for high affinity sites

K_L : equilibrium constant for low affinity sites

C : metal sorbate concentration in the bulk aqueous phase (M)

The results obtained from this model are shown in Table 12. This model was applied to the experimental data (Figure 16) where both lead and copper occupy high affinity sites: 3.9×10^{-6} moles of Pb per gram of goethite and 4.5×10^{-6} moles of Cu per gram goethite. The low energy sites were occupied

Table 12

The K_H and K_L values obtained from the developed model.

Metal	K_H	X_H (moles/g)	K_L	X_L (moles/g)	r^2	Xm (moles/g)
Cu	3.0×10^{-3}	7.2×10^{-6}	1544.1	1.4×10^{-7}	0.9	8.6×10^{-6}
Pb	2.0×10^{-3}	6.5×10^{-6}	4085.5	5.0×10^{-7}	0.8	7.0×10^{-6}
Cd	1.7×10^{-3}	4.4×10^{-6}	540.00	4.9×10^{-8}	0.9	4.4×10^{-6}

by lead only and these make up approximately 5.0×10^{-7} moles per gram (Figure 16). Copper was preferably adsorbed over lead on the high affinity sites. The results in Figure 16 are consistent with those in Table 12, copper has a greater K_H than lead. In the case of low affinity sites, lead has a greater affinity than copper (Table 12). However, the model failed to predict the exact adsorption on the high energy sites (Table 12 and Figure 16) suggesting that adsorption on more than two types of sites is likely.

Interestingly, during competition II copper was desorbed by lead; copper and lead affinities for goethite are similarly high, with copper being slightly greater (Figure 8). Copper, however, showed greater affinity for the high affinity sites on the goethite surface, suggesting that electronegativity an important factor in adsorption competition.

In the last set of experiment, competition among copper, lead, and cadmium was studied. The three metals were introduced in solution

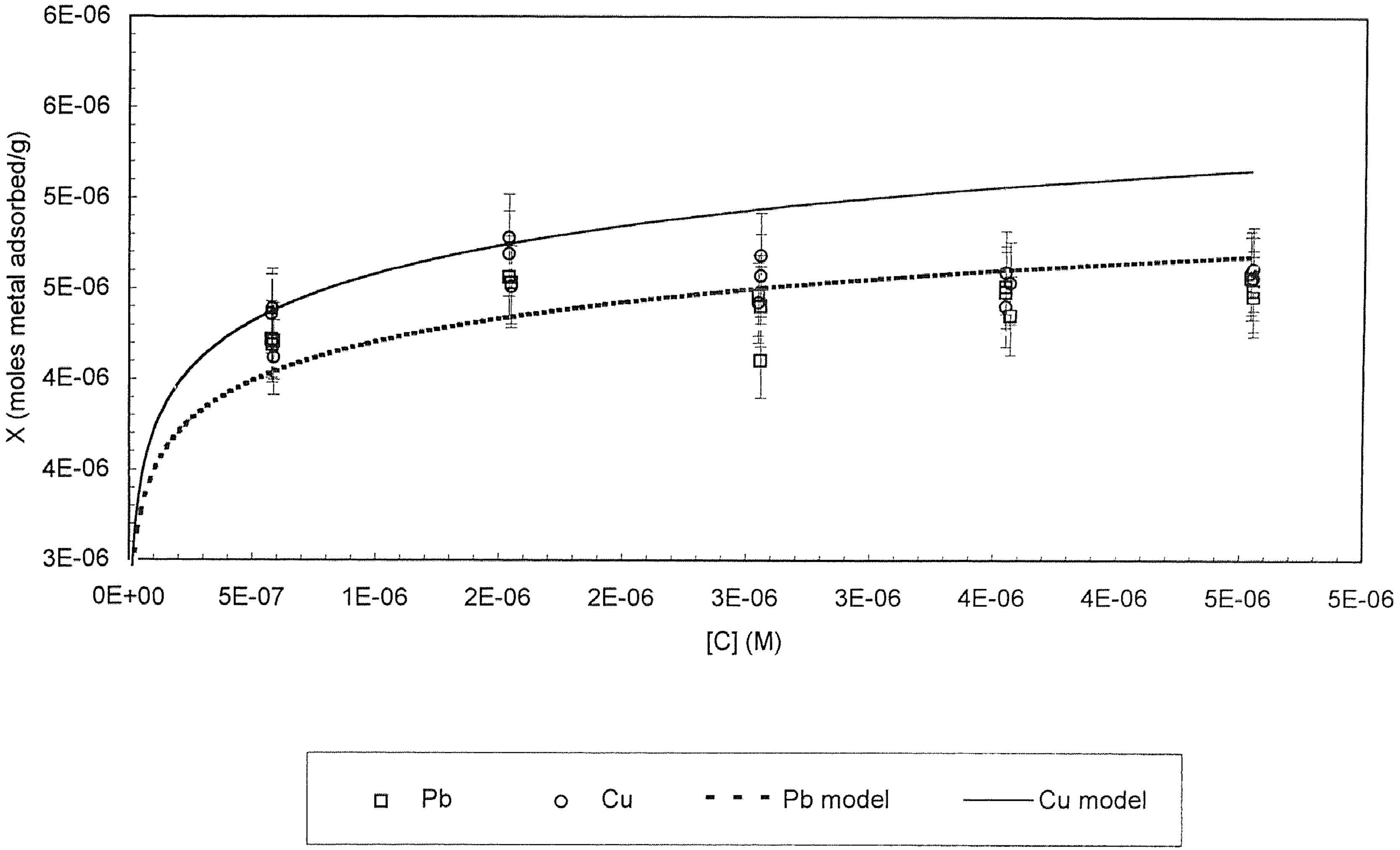


Figure 16 Modeling of Pb and Cu competition using a two site model with 1E-1 grams per liter, pH 6, 1E-3 ionic strength (sodium nitrate). Pb model includes both low and high energy sites whereas Cu model includes only high energy sites.

simultaneously. When sorption to the containers was accounted for, cadmium did not sorb on goethite. Lead and copper exhibited similarly higher affinities. The results from this competition experiment are shown in Table 13 and Figure 17, and there is little variation from the studies of Cu-Pb system (Table 11 and Figure 15). Lead adsorption showed no changes, whereas copper adsorption decreased by an average of 4.6% (~ 0.2×10^{-6} moles per grams of goethite). In the presence of cadmium and lead, 15% of the copper is present as $Cu(OH)_{2(aq)}$ (Table 5); this hydrolysis product, which is considered electrochemically inactive (31), decreases copper adsorption. A portion of this product (0.17×10^{-6} moles per gram), however, is apparently adsorbed on the goethite surface. Copper occupies 4.1×10^{-6} moles per gram of goethite high affinity sites where 0.17×10^{-6} moles per gram of goethite are occupied by $Cu(OH)_{2(aq)}$.

As discussed above, lead adsorption showed no variations from the Cu-Pb experiment; 4.3×10^{-6} moles per gram adsorbed with 3.8×10^{-6} moles per gram sorbed to high affinity sites and 5.0×10^{-7} moles per gram to low affinity sites. Cadmium adsorption, which exhibits the lowest electronegativity from all three metals, reflects sorption only to the containers (Table 9). From Table 12, the equilibrium constants for high energy sites are consistent with electronegativity where K_H follows the trend of Cu>Pb>Cd. On the other hand, the equilibrium constants for low energy sites are in agreement with the hydrated ion size; the smaller the ion the greater the K_L. These results are consistent with the physical sorption where the adsorbed species resides in the diffuse layer.

Table 13

Metal competition results between Pb, Cu, and Cd. Simultaneously addition of the metals in 10^{-1} gram per liter of goethite in 100ml aliquots at pH 6, and 10^{-3} ionic strength (sodium nitrate).

1	2	3	4	5	6	7 *	8
Metal added (moles)	**Metal added (moles)**	**Metal added (moles)**	**Experiment adsorption (moles)**	**Experiment adsorption (moles)**	**Experiment adsorption (moles)**	**Total sites occupied (moles)**	**Expected Total sites (moles)**
Cu	**Pb**	**Cd**	**Cu**	**Pb**	**Cd**		
1.0E-7	1.0E-7	1.0E-7	4.12E-8	4.09E-8	1.00E-9	8.31E-8	8.56E-8
2.0E-7	2.0E-7	2.0E-7	4.51E-8	4.43E-8	6.10E-9	9.55E-8	8.56E-8
3.0E-7	3.0E-7	3.0E-7	4.20E-8	4.31E-8	6.90E-9	9.20E-8	8.56E-8
4.0E-7	4.0E-7	4.0E-7	4.40E-8	4.20E-8	6.40E-9	9.24E-8	8.56E-8
5.0E-7	5.0E-7	5.0E-7	4.59E-8	4.52E-8	1.00E-8	10.1E-8	8.56E-8
1.0E-7	1.0E-7	1.0E-7	4.23E-8	4.03E-8	5.00E-9	8.76E-8	8.56E-8
2.0E-7	2.0E-7	2.0E-7	4.35E-8	4.38E-8	6.19E-9	9.35E-8	8.56E-8
3.0E-7	3.0E-7	3.0E-7	4.41E-8	4.11E-8	6.58E-9	9.18E-8	8.56E-8
4.0E-7	4.0E-7	4.0E-7	3.89E-8	4.23E-8	6.39E-9	8.76E-8	8.56E-8
5.0E-7	5.0E-7	5.0E-7	4.39E-8	4.47E-8	9.91E-9	9.78E-8	8.56E-8

* Total sites occupied based on the experimental adsorption of the competing metals.

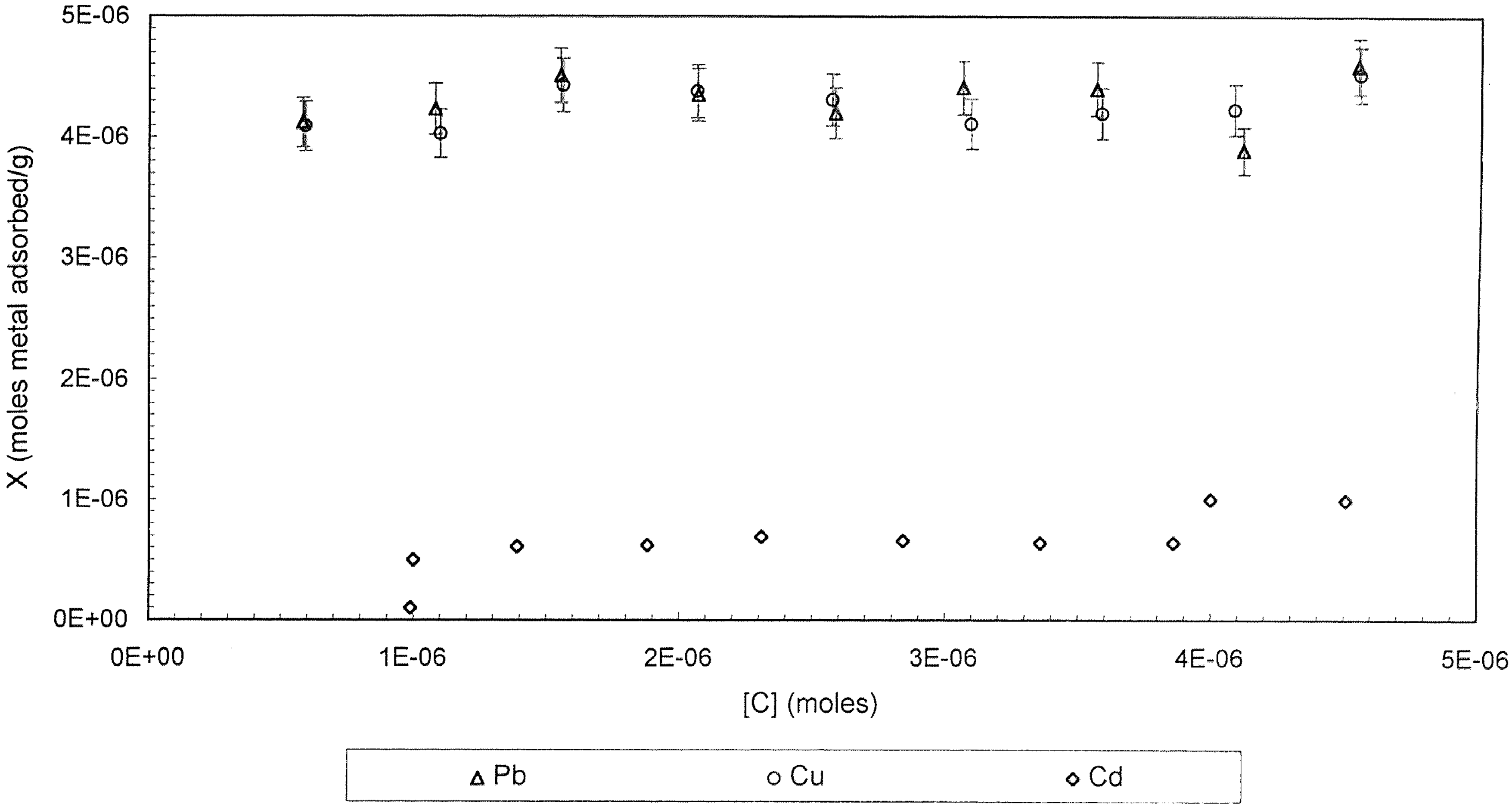


Figure 17 Pb, Cu, and Cd adsorption competition isotherms with 1E-1 gram per liter goethite pH 6, and 1E-3 ionic strength (sodium nitrate).

In Figure 18, Cu and Pb ion adsorption are modeled where again Cu adsorbed only on high affinity sites and Pb sorbed on both types of sites. As in the Cu-Pb system, copper showed greater affinity for the high affinity sites on the goethite surface, indicating that electronegativity is very important in adsorption competition. However, the model did not predict relative amounts of metal adsorption on the high energy sites (Table 12 and Figure 18) suggesting that adsorption on more than two types of sites is likely.

In all experiments metal affinity followed the same order as electronegativity. Cadmium, the least electronegative metal, was completely displaced. However, while Cu had a greater affinity than Pb for high affinity sites, both ions occupied these sites and Pb had a greater affinity for lower energy sites. Speciation is also a factor in adsorption competition, electronegativity, however, was found to be the most significant.

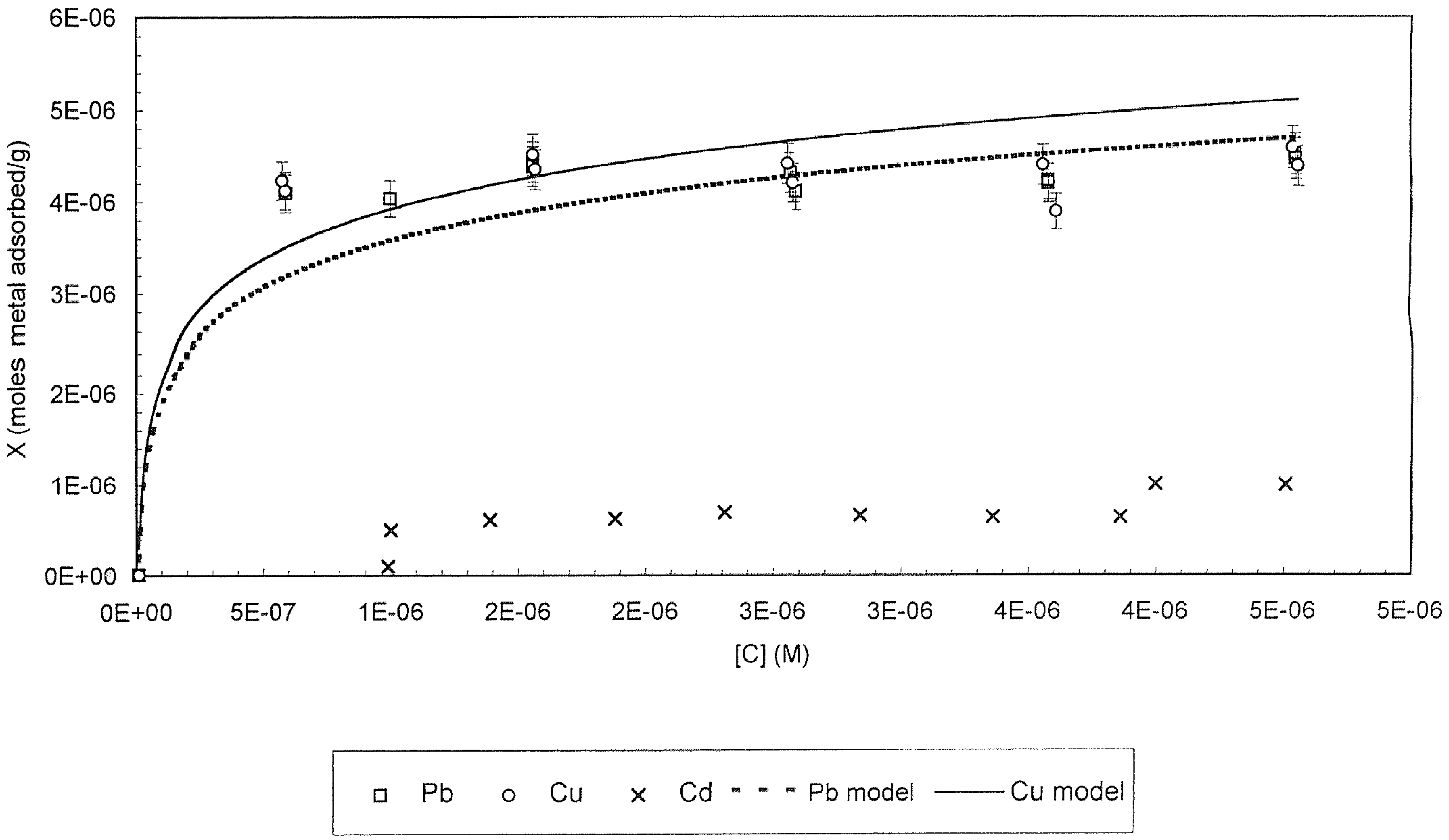


Figure 18 Modeling of Pb, Cu, and Cd competition using a two site model with 1E-1 grams per liter, pH 6, 1E-3 ionic strength (sodium nitrate). Pb model includes both low and high energy sites whereas Cu model includes only high energy sites.

CHAPTER 5

CONCLUSIONS

During this study, a number of conclusions was reached regarding goethite characteristics and sorbate adsorption to goethite. The following are the most important conclusions:

- During precipitation, goethite homogeneity and crystallinity increased with aging in the 60^0 C oven.

- Optical microscopy revealed that goethite particles are of an acicular, needle like shape. Goethite aggregation occurred at or in the vicinity of pH zpc. Data also suggest that aggregation increased with ionic strength.

- Adsorption edges revealed that Cu, Pb, and Cd are specifically adsorbed on the goethite surface. Furthermore, metal affinities for goethite are in the order of Cu>Pb>Cd, confirming what others have found (10, 23). Electronegativity is consistent with this trend where metal affinity increased with increasing electronegativity. Metal speciation affects metal adsorption; neutrally charged species are less electrochemically active than the divalent species form and deter metal adsorption on goethite.

- Goethite shows distinct types of sites with varying affinities for adsorbates. Copper, lead and cadmium adsorbed on the same types of energy sites. Strontium appears to adsorb on additional, possibly lower energy sites.

- Isotherm studies revealed a two-site Langmuir model of adsorption for copper, lead, and cadmium on goethite best fit the data. Metal capacities increased with increasing electronegativity: Cu>Pb>Cd. Equilibrium constants revealed that while Cu had a greater affinity than Pb for high affinity sites, Pb had a greater affinity for lower energy sites. Electronegativity was observed to be the most important factor in metal capacities for goethite, although speciation is a factor as well.

- During competition studies, less electronegative metals were desorbed and displaced by more electronegative species when competing for a limited number of available sites. During Cu and Cd competition and Pb, Cu and Cd competition studies, cadmium was completely desorbed. During Cu and Pb as well as Cu, Pb, and Cd competition studies, copper adsorbed on high energy sites and lead adsorbed on both high and low energy sites. However, copper was preferably adsorbed to high energy sites over lead, whereas lead showed greater affinity for the lower energy sites. In the Pb and Cd studies, lead displaced cadmium from the sites it required. Because sites were not limited in this experiment, unoccupied ones were filled then with cadmium. The two-site Langmuir model worked well with Cu and Cd competition and Pb and Cd competition, but it was not able to predict the Cu and Pb and the Cu, Pb, and Cd systems' results.

Metal affinity for potentially high affinity sites increased with increasing electronegativity indicating that electronegativity is an important factor in adsorption competition.

Appendix A

QA/QC Plan

QA/QC plan

In this study a 95% confidence factor in analyzing the samples is aimed. To assure accuracy and precision of the analytical process(es), standard methods (21) were used. The proceeding steps were followed:

- Nalgene polyethylene containers were used to hold both samples and standards to minimize any metal loss to containers.
- Fixed volume pipettes were used in all metal dilutions, acid and base additions, and sodium nitrate additions.
- All containers were washed with soap and distilled water and were soaked in 10% nitric acid overnight prior to any use in any experiment.
- The same electronic balance was used throughout in weighing all reagents.
- The pH meter was calibrated on a daily basis, prior to any experiments.
- Deionized water was used in sample and standard preparations.
- At least one process blank was competition for each experiment. This blank was subject to the same treatment as the rest of the samples with the only difference being that no metals were introduced in solution. Such blank was analyzed and used in calculating the metal ion concentration in the rest of the samples. Such a practice minimized any errors associated with the process itself such as glassware contamination or chemical interference.

- At least one replicate and a duplicate sample were also competition for every set of samples, a total of 10, and the results were used in estimating the accuracy of the analysis.
- Calibration curves ware constructed on a daily basis, where ISE are used. Such a practice eliminated any errors that are associated with temperature and light variations.
- During any analysis where ISE are used, all samples and standards are stirred in a uniformed rate to avoid errors associated with the amount of heat generated from stirring.
- During all analysis, the samples with lower metal concentrations were analyzed first to avoid cross-contamination . Where ISE were used, the ISE were cleaned repeatedly with type II water between samples.
- EPA recommended matrix modifiers were used whenever AA spectroscopy was used in the analysis of samples.
- Sodium nitrate was used as the ionic strength adjuster whenever ISE as recommended by the manufacturer.
- Orion filling solutions and membrane polishing strips were used in the conditioning of the ISE as recommended by the manufacturer.

Appendix B

Potentiometric Titration data

Potentiometric titration data of test (one gram per liter goethite) and blank solutions with 10^{-1} nitric acid, as a function of ionic strength (sodium nitrate).

IS & $2*10^{-1}$	**20 min**	**IS & 10^{-2}**	**20 min**	**IS & 10^{-1}**	**20 min**	**IS & 10^{-1}**	**0.5 min**	**IS & 10^{-2}**	**0.5 min**	**IS & 10^{-1}**	**Blank**	**IS & 10^{-2}**	**Blank**
pH	**ml. acid added**	**pH**	**ml. acid added**	**pH**	**ml. acid added**	**pH**	**ml. acid added**	**pH**	**ml. acid added**	**pH**	**ml. acid added**	**pH**	**ml. acid added**
10.51	0	10.47	0	10.29	0	10.26	0	10.25	0	10.25	0	10.13	0
10.44	1	10.37	1	10.03	1	10.15	1	10.17	1	10.06	1	9.92	1
10.37	2	10.28	2	9.86	2	10.01	2	10.08	2	9.69	2	9.49	2
10.28	3	10.16	3	9.65	3	9.85	3	9.96	3	5.58	3	5.27	3
10.17	4	10.08	4	9.38	4	9.64	4	9.83	4	4.12	4	3.92	4
10.05	5	9.84	5	8.96	5	9.36	5	9.68	5	3.82	5	3.62	5
9.90	6	9.62	6	7.70	6	8.91	6	9.50	6	3.64	6		6
9.71	7	9.27	7	7.70	7	7.75	7	9.26	7		7		7
9.48	8	8.45	8	7.45	8	6.89	8	8.89	8		8		8
9.16	9	7.72	9	7.24	9	6.18	9	7.79	9		9		9
8.59	10	7.75	10	4.98	10	5.70	10	7.01	10		10		10
7.1	11	7.65	11	4.08	11	4.84	11	6.47	11		11		11
6.4	12	7.14	12	3.72	12	4.15	12	6.07	12		12		12
7.23	13	4.34	13	3.52	13	3.85	13	5.71	13		13		13
5.89	14	3.78	14	3.30	14	3.66	14	5.29	14		14		14
4.83	15	3.54	15		15		15	4.28	15		15		15
3.99	16		16		16		16	3.7	16		16		16
3.68	17		17		17		17		17		17		17
3.49	18		18		18		18		18		18		18
3.35	19		19		19		19		19		19		19
3.25	20		20		20		20		20		20		20

Appendix C

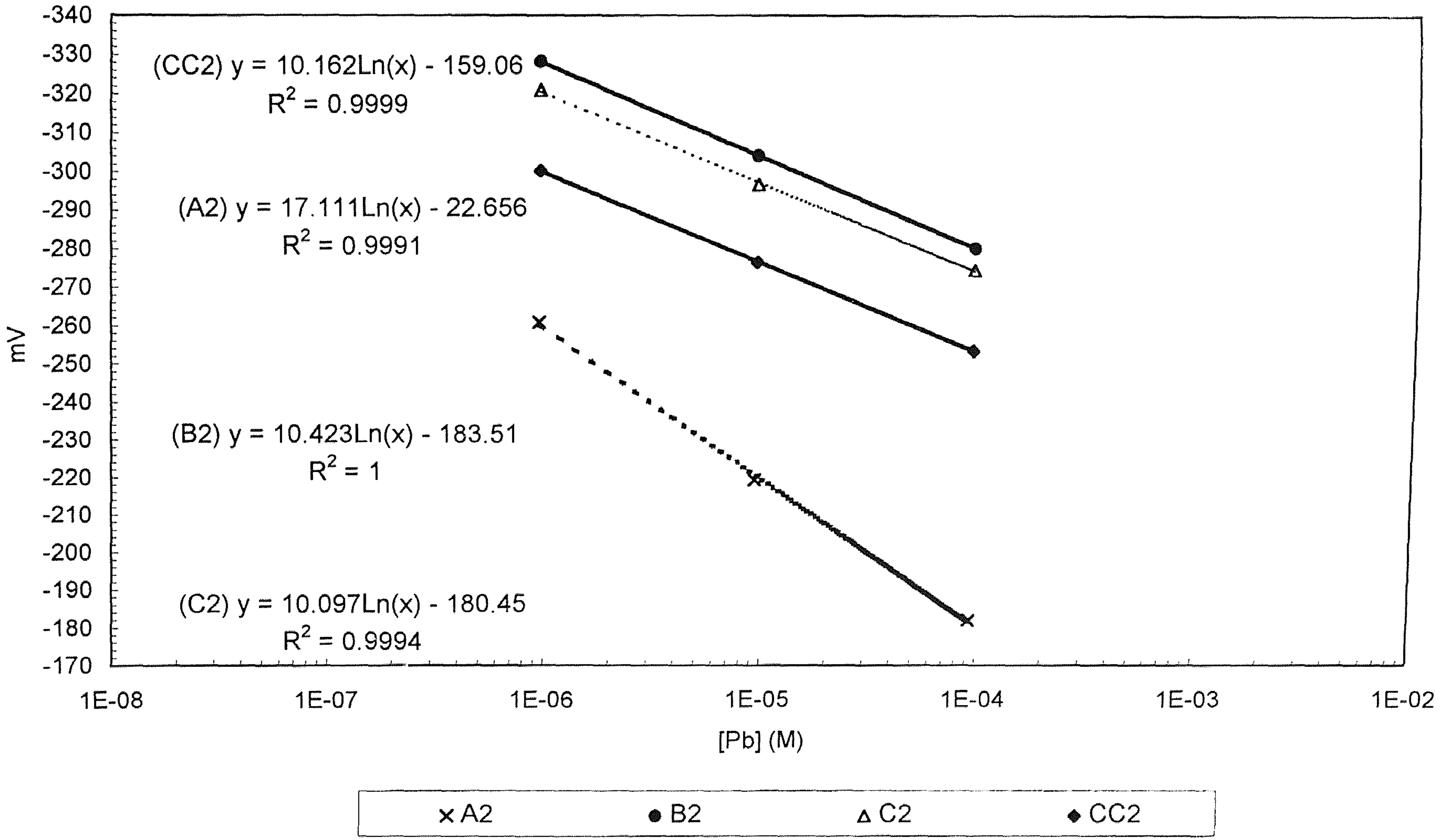
Particle Size Distribution Data

Particle size analysis of goethite as a function of pH and ionic strength (sodium nitrate).

	IS 10^{-2} pH 8.80	IS 10^{-1} pH 9.52	IS 10^{-2} pH 7.80	IS $2*10^{-1}$ pH 8.50	IS 10^{-3} pH 6.00	IS 10^{-1} pH 9.27	IS 10^{-2} pH 9.69
d (nm)	% vol.	% vol.	% vol.	% vol.	% vol.	% vol.	% vol.
0.50	5.82	7.3	0.86	1.76	2.28	1.85	3.30
1.32	13.60	18.1	3.07	5.13	6.4	6.25	9.73
1.60	16.80	23.1	4.61	7.15	8.79	9.20	13.38
1.95	15.03	20.9	5.21	7.36	7.31	10.1	13.68
2.38	10.21	14.2	4.99	6.11	5.09	9.23	11.47
2.90	5.21	6.75	4.34	4.24	3.30	7.33	8.27
3.53	1.95	1.63	3.7	2.56	2.48	5.29	5.47
4.30	0.64	0	3.38	1.56	2.59	3.73	3.80
5.24	2.04	0	3.51	1.29	3.17	2.85	2.45
6.39	4.59	0.35	3.97	1.48	3.68	2.54	3.47
7.78	6.60	0.57	4.62	1.81	4.09	2.60	4.16
9.48	6.70	0.34	5.37	2.15	4.48	2.99	4.63
1.55	4.85	0.07	6.09	2.48	4.88	3.65	4.66
14.08	2.73	0	6.7	2.88	5.12	4.42	4.22
17.15	1.61	0	7.21	3.44	4.91	4.96	3.36
20.90	1.10	0	7.49	4.18	4.18	4.94	2.25
25.46	0.51	0	7.18	5.02	3.00	4.51	1.19
31.01	0.10	0	5.98	5.92	1.66	3.98	0.42
37.79	0.01	0	4.28	6.90	0.54	3.43	0.08
46.03	0	0	2.92	7.43	0	2.68	0.01
56.09	0	0	0	6.98	0	1.59	0
68.33	0	0	0	5.53	0	0	0
83.26	0	0	0	3.51	0	0	0
101.44	0	0	0	1.72	0	0	0

Appendix D

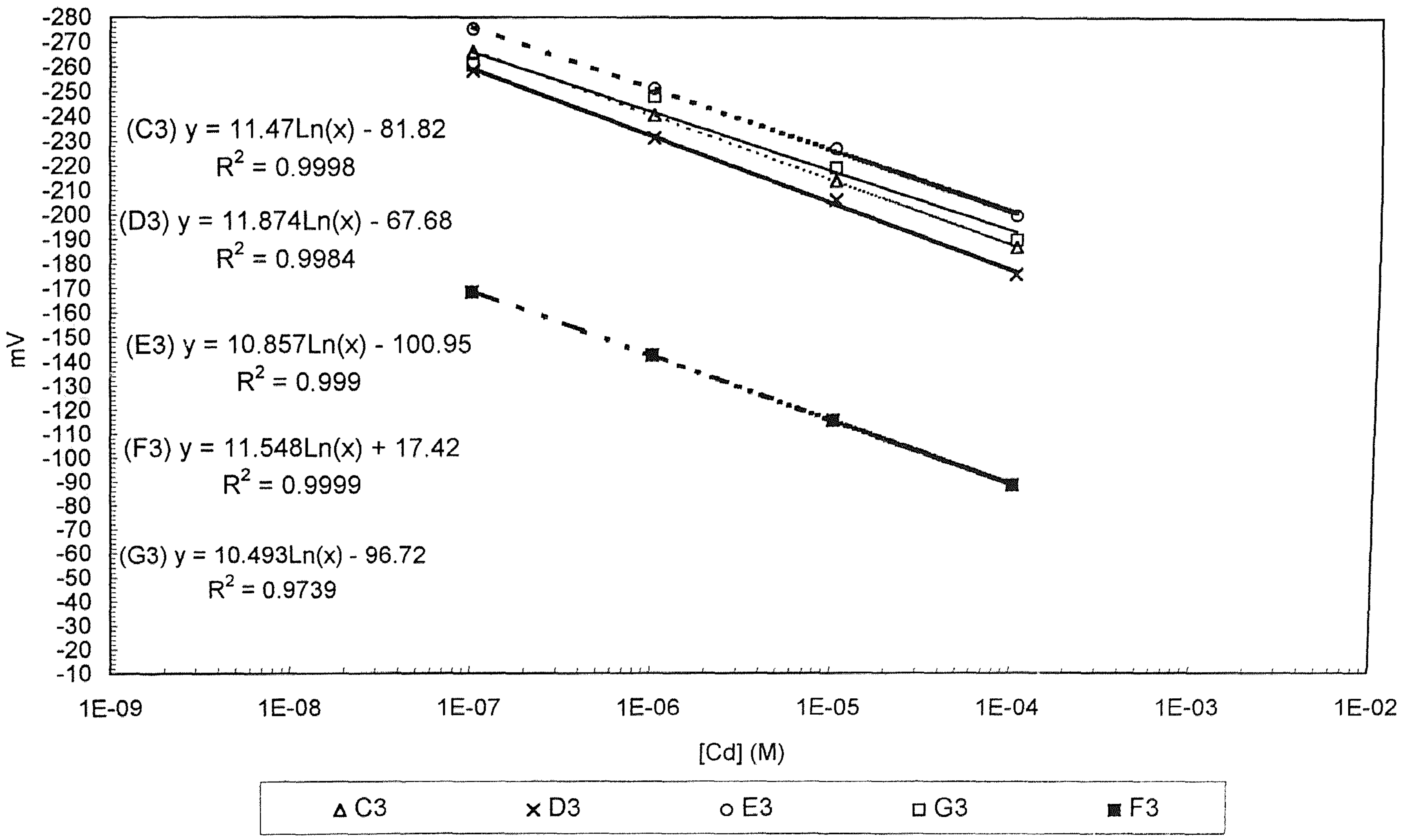
ISE Cu Calibration Curves used in Adsorption Edge Experiments



Calibration curves of the Pb ion selective electrode used in adsorption edge experiments at 0.001 ionic strength (sodium nitrate).

Appendix E

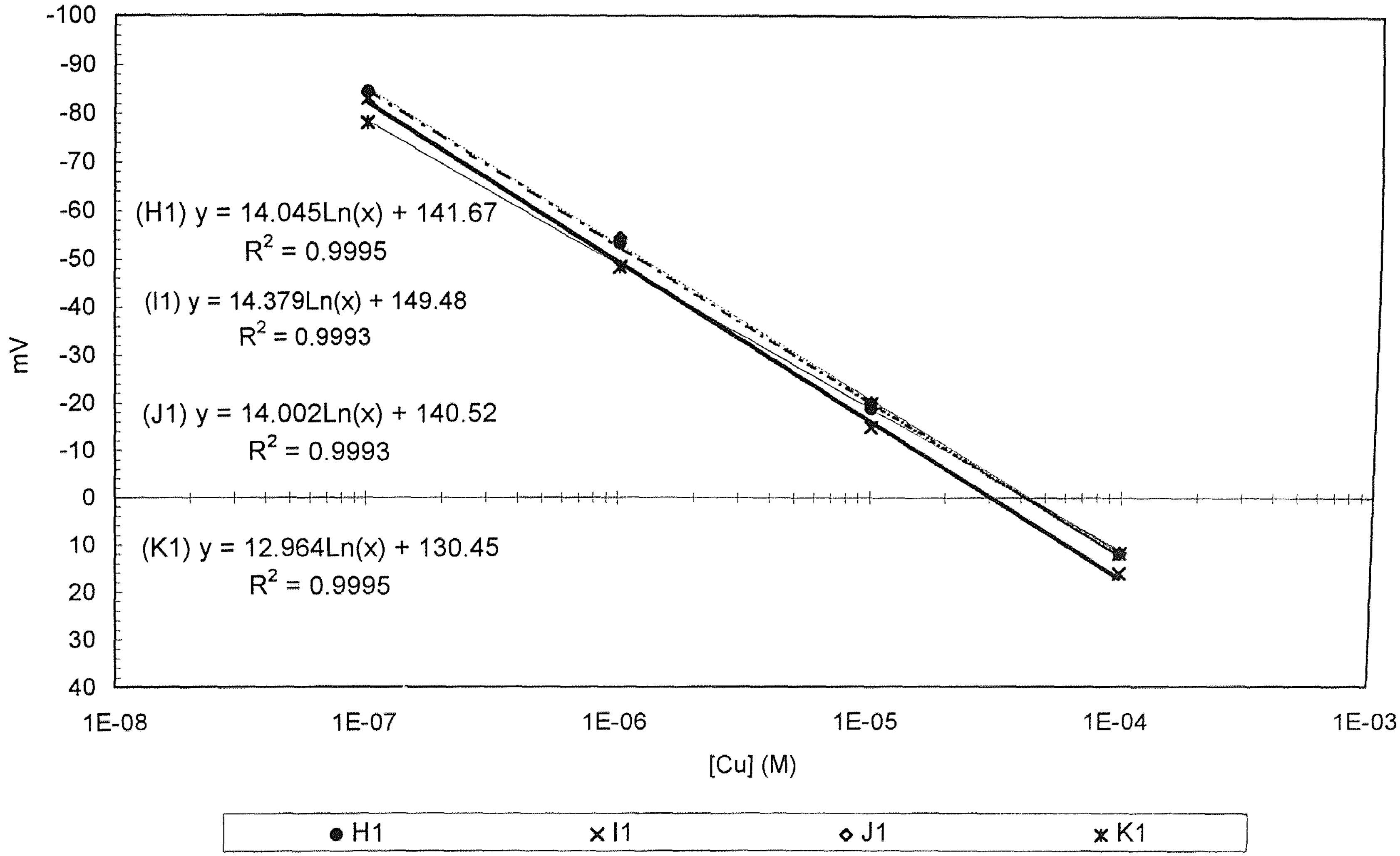
ISE Cu Calibration Curves used in Isotherm Experiments



Calibration curves of the Cd ion selective electrode used in adsorption isotherm experiments at 0.001 ionic strength (sodium nitrate).

Appendix F

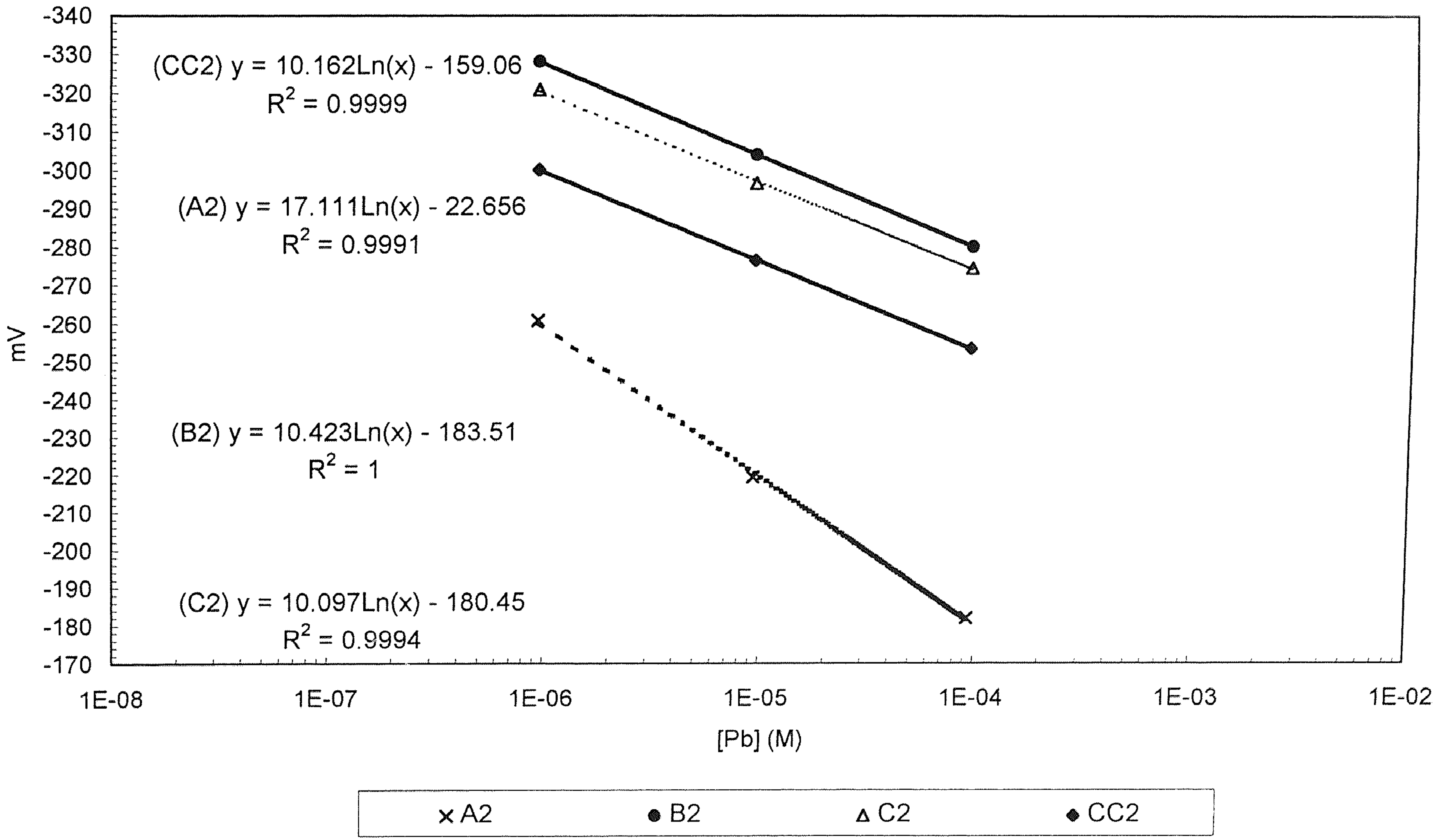
ISE Cu Calibration Curves used in Competition Adsorption Experiments



Calibration curves of the Cu ion selective electrode used in competition adsorption isotherms and wall adsorption experiments at 0.001 ionic strength (sodium nitrate).

Appendix G

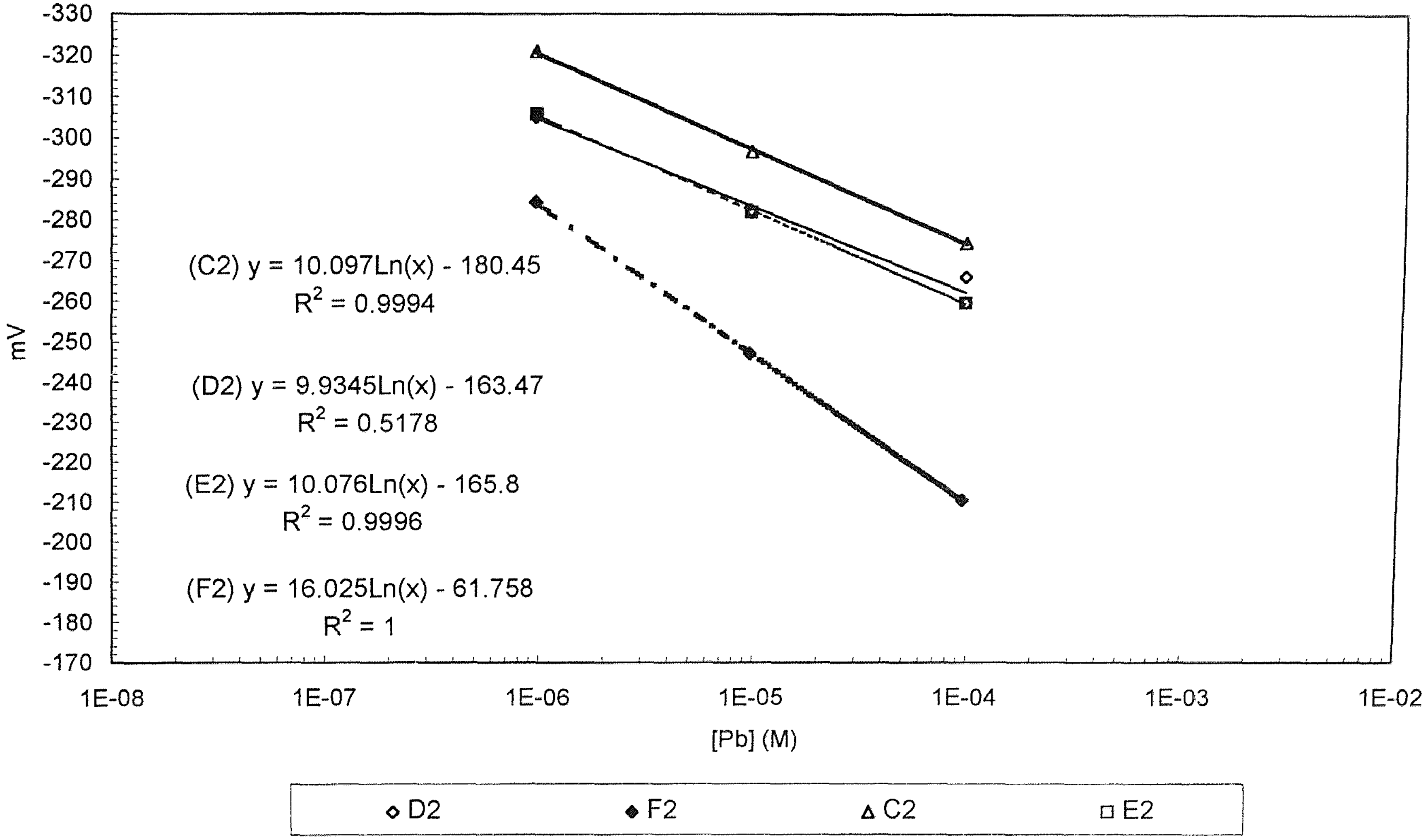
ISE Pb Calibration Curves used in Adsorption Edge Experiments



Calibration curves of the Pb ion selective electrode used in adsorption edge experiments at 0.001 ionic strength (sodium nitrate).

Appendix H

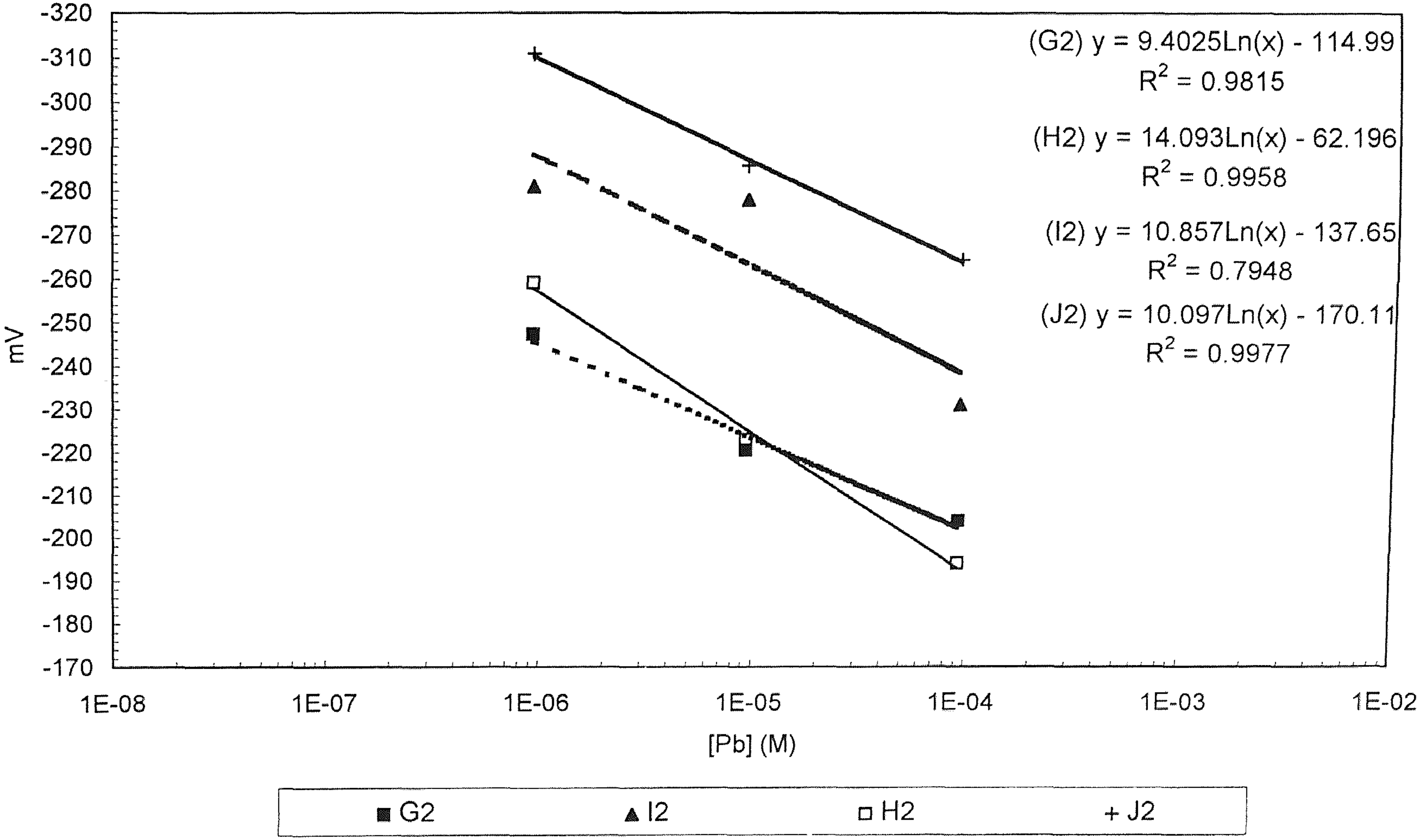
ISE Pb Calibration Curves used in Isotherm Experiments



Calibration curves of the Pb ion selective electrode used in adsorption isotherm experiments at 0.001 ionic strength (sodium nitrate).

Appendix I

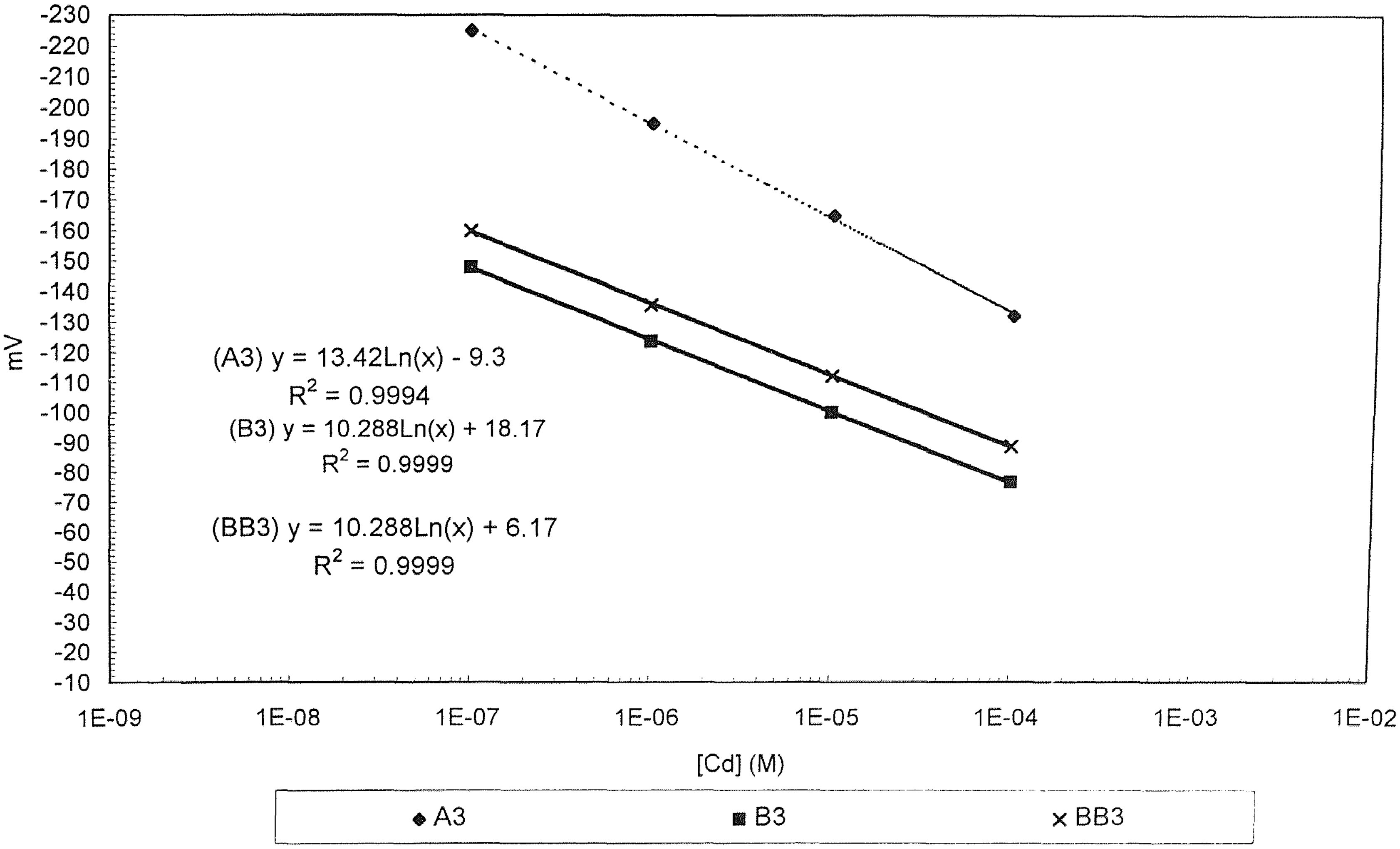
ISE Pb Calibration Curves used in Competition Adsorption Experiments



Calibration curves of the Pb ion selective electrode used in competition adsorption isotherms and container adsorption experiments at 0.001 ionic strength (sodium nitrate).

Appendix J

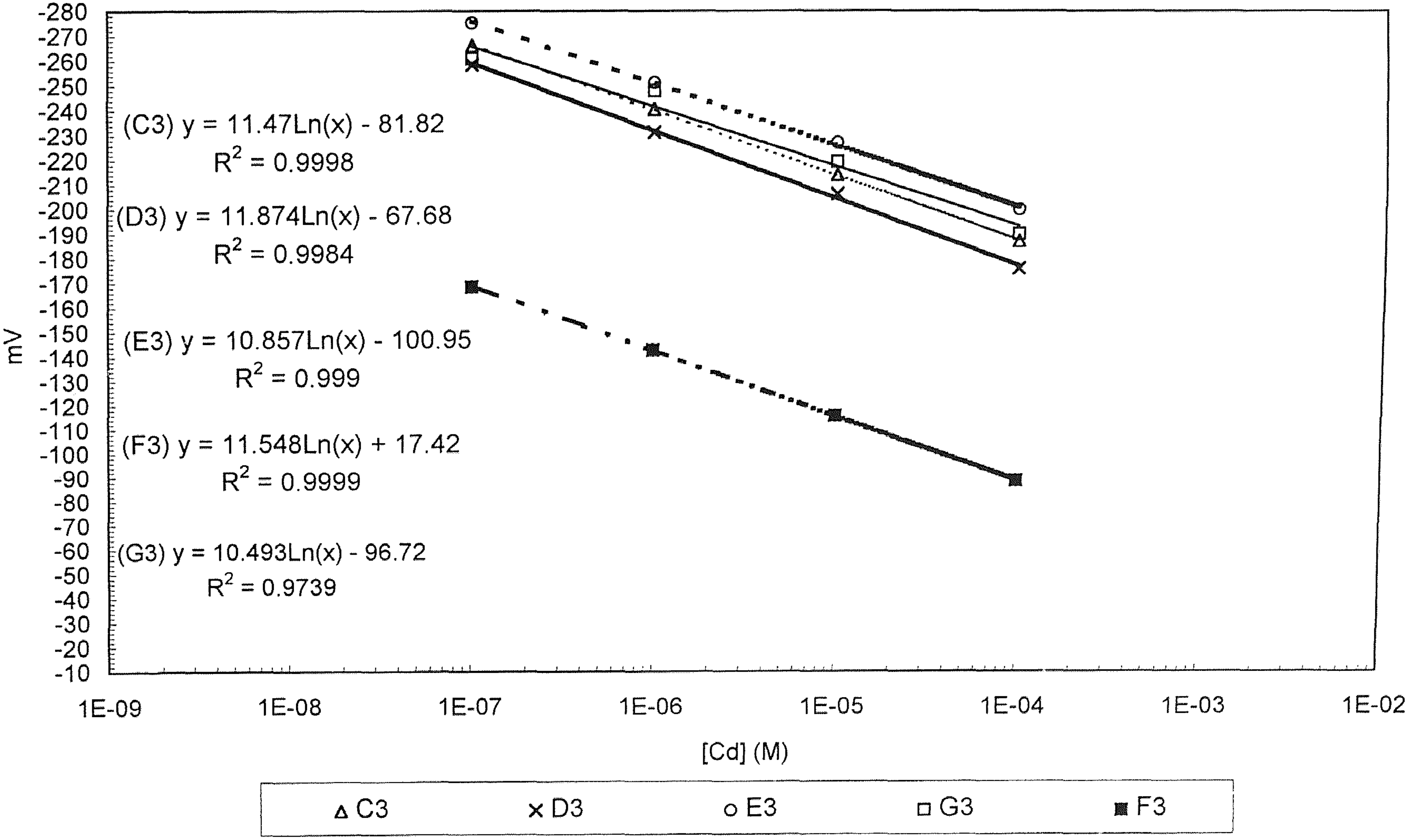
ISE Cd Calibration Curves used in Adsorption Edge Experiments



Calibration curves of the Cd ion selective electrode used in adsorption edge experiments at 0.001 ionic strength (sodium nitrate).

Appendix K

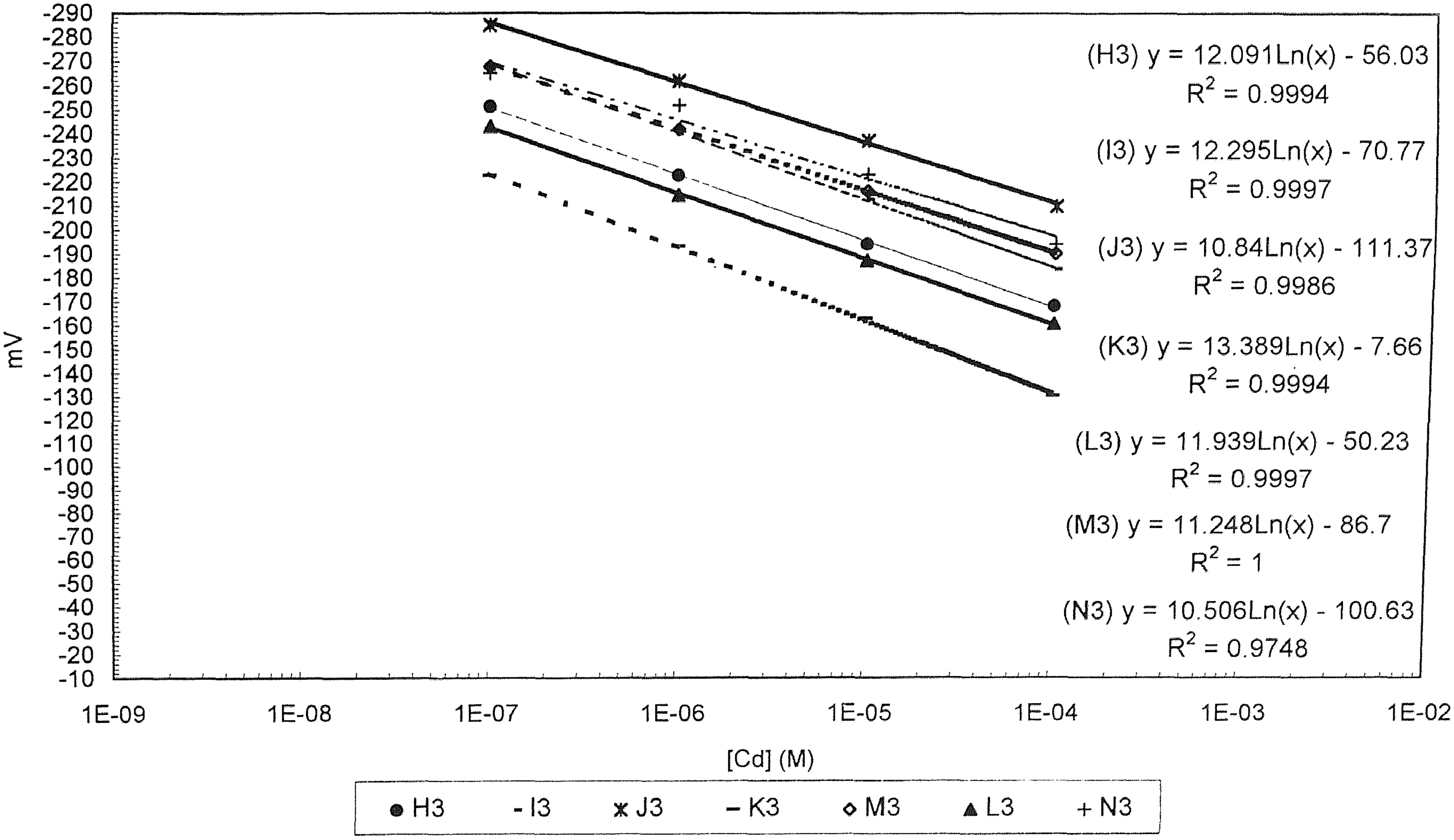
ISE Cd Calibration Curves used in Isotherm Experiments



Calibration curves of the Cd ion selective electrode used in adsorption isotherm experiments at 0.001 ionic strength (sodium nitrate).

Appendix L

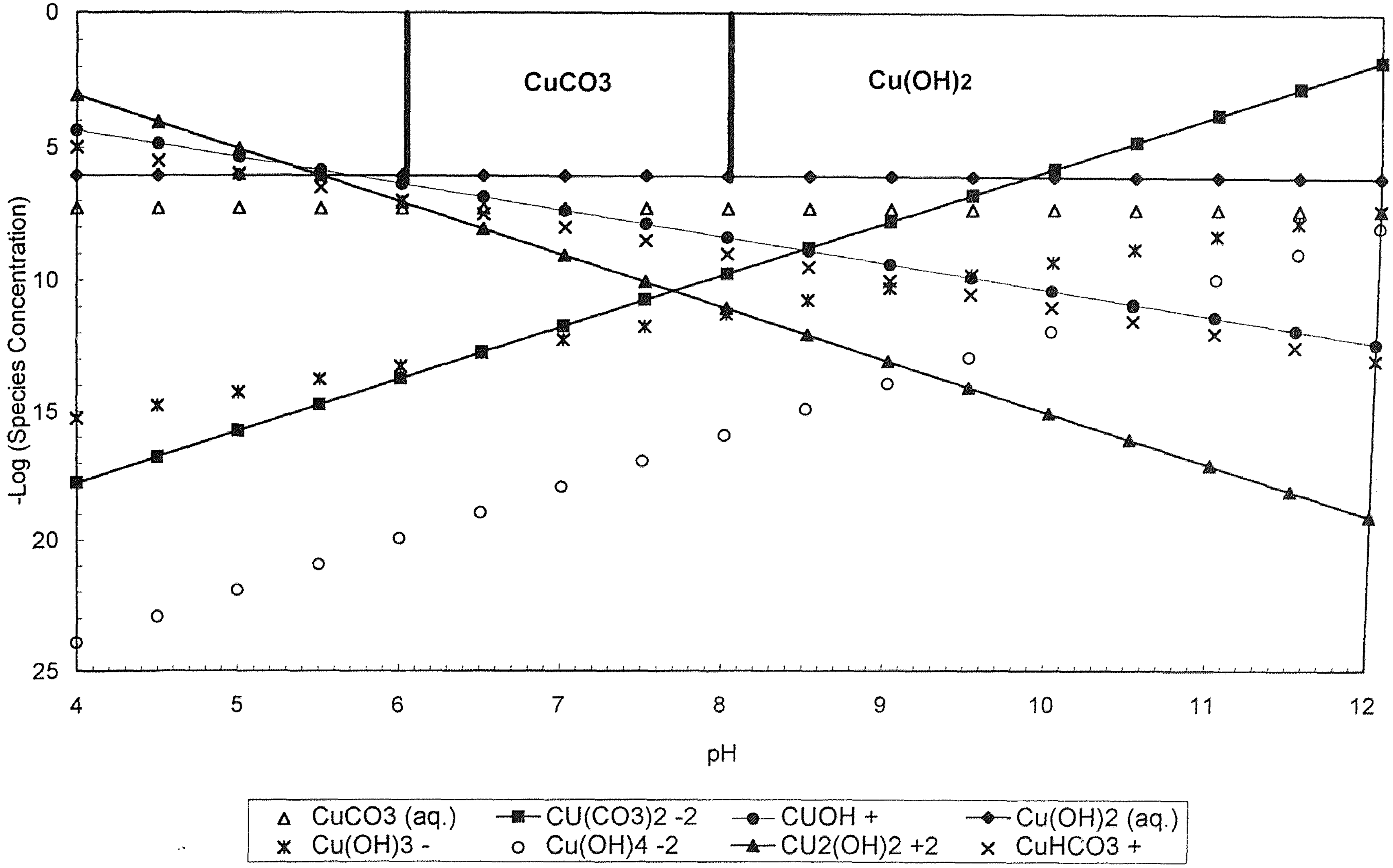
ISE Cd Calibration Curves used in Competition Adsorption Experiments



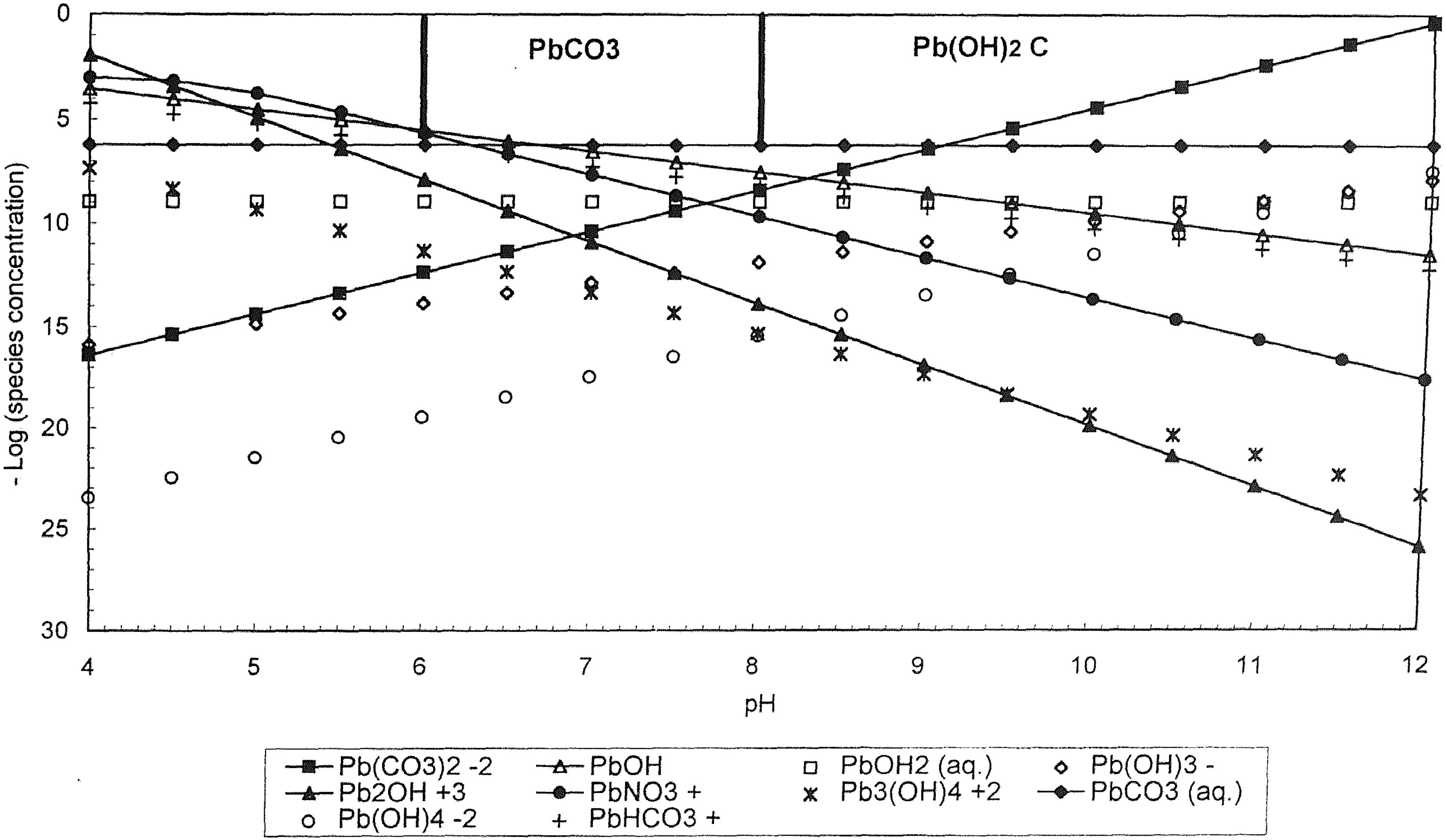
Calibration curves of the Cd ion selective electrode used in competition adsorption isotherms and container adsorption experiments at 0.001 ionic strength (sodium nitrate).

Appendix M

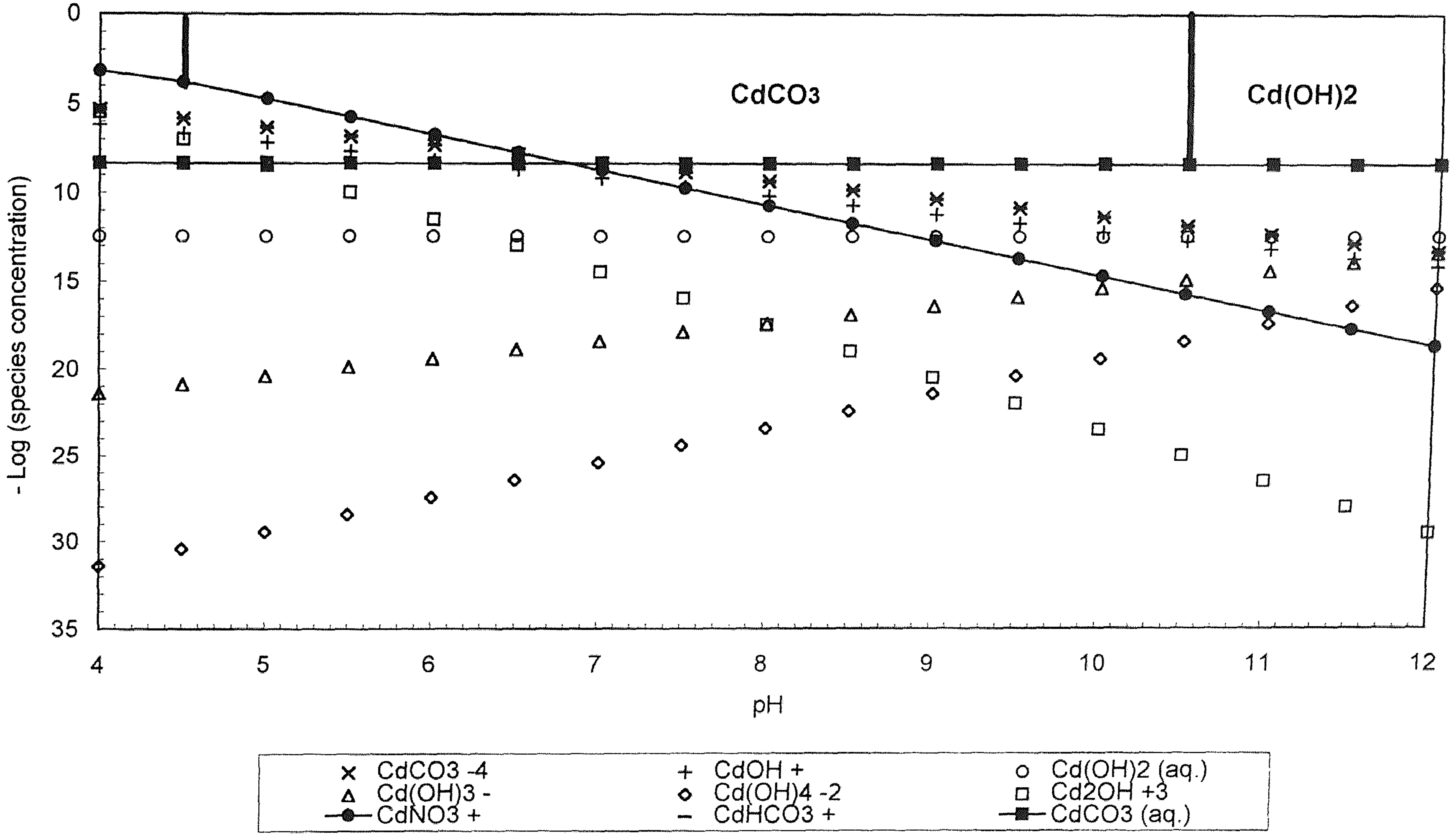
Solubility Graphs for Cu, Pb, and Cd



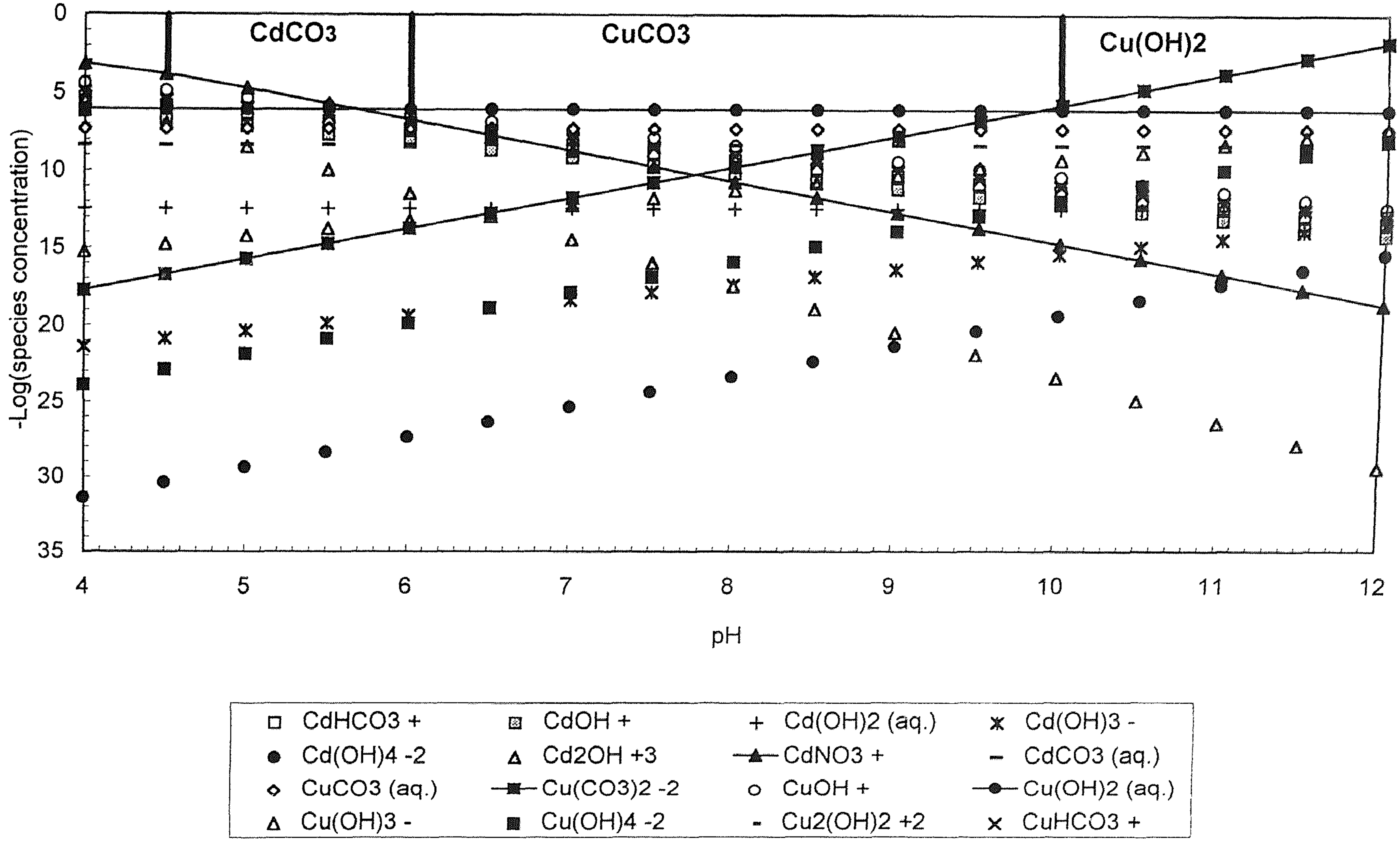
Copper solubility diagram as calculated using MINTEQA2.



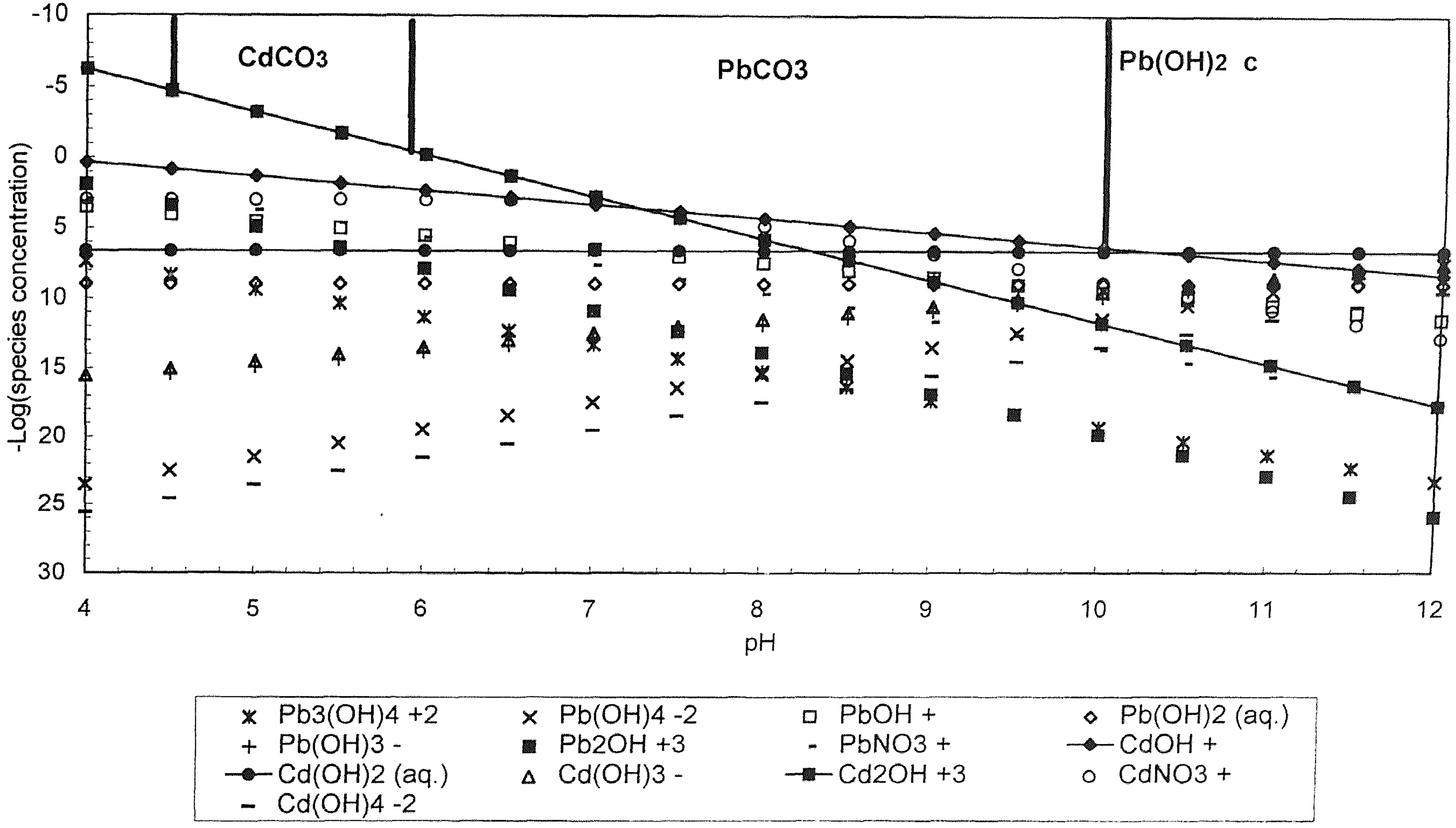
Lead solubility diagram as calculated using MINTEQA2.



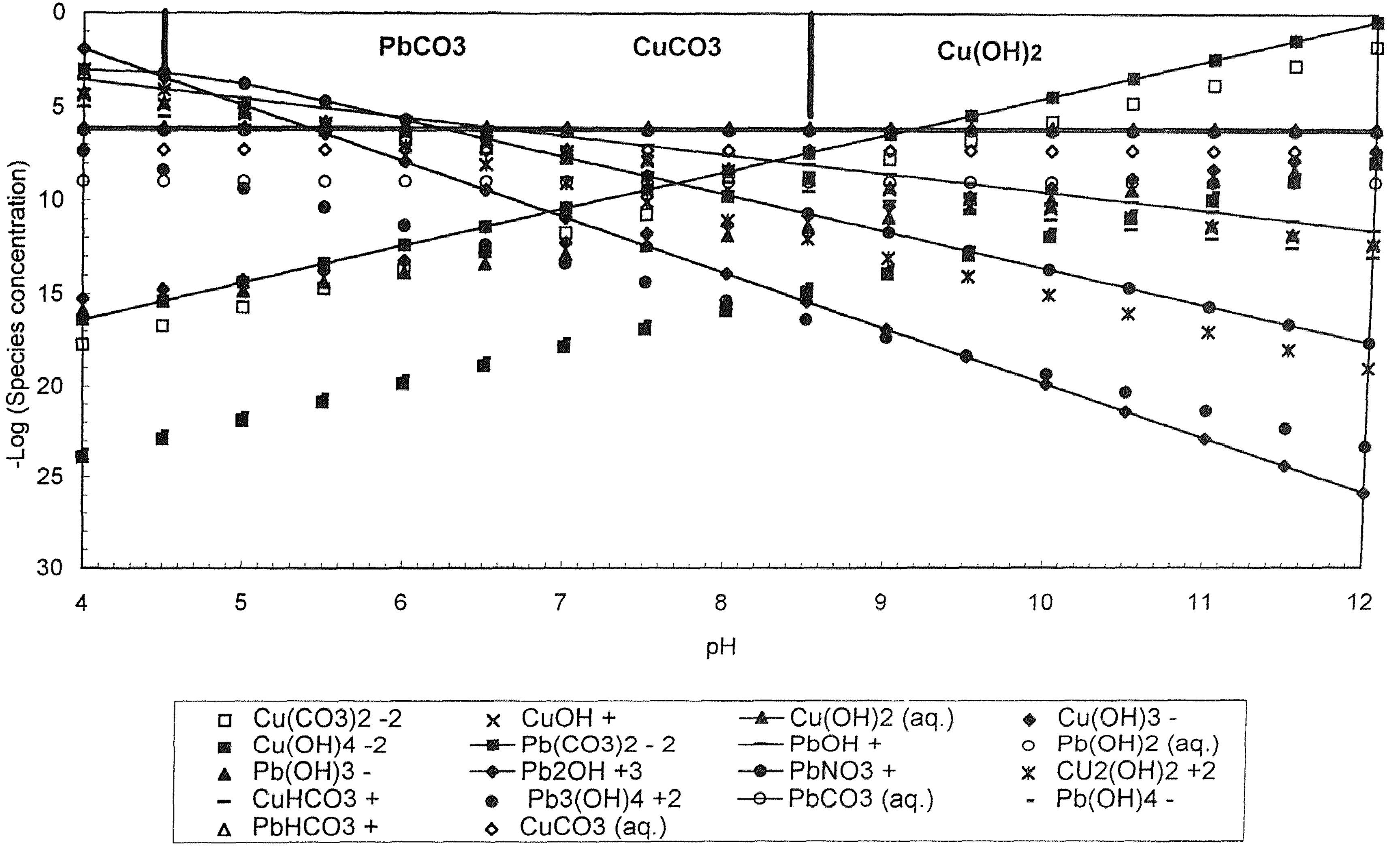
Cadmium solubility diagram as calculated using MINTEQA2.



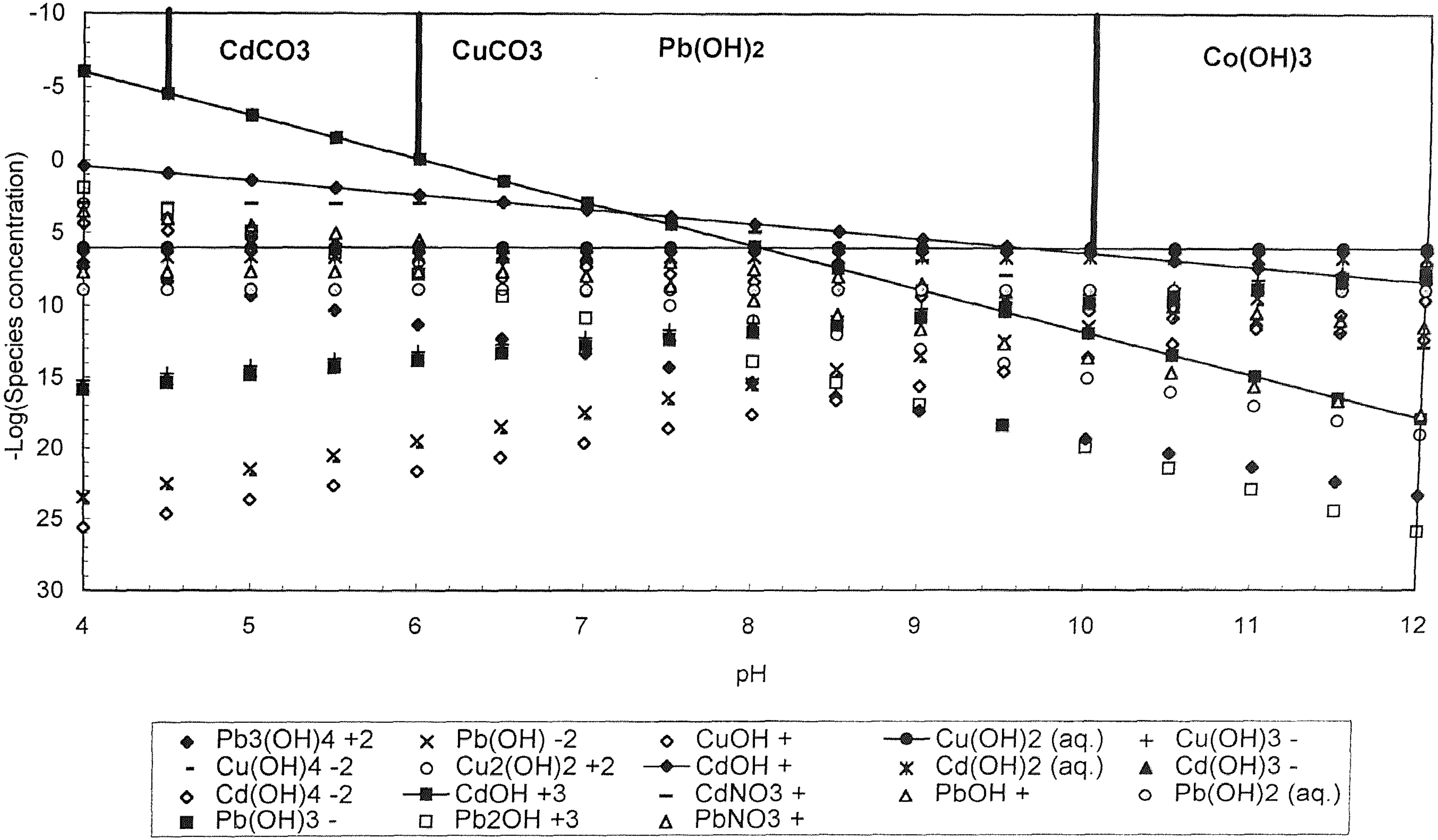
Cd and Cu solubility diagram as calculated using MINTEQA2.



Cd and Pb solubility diagram as calculated using MINTEQA2.



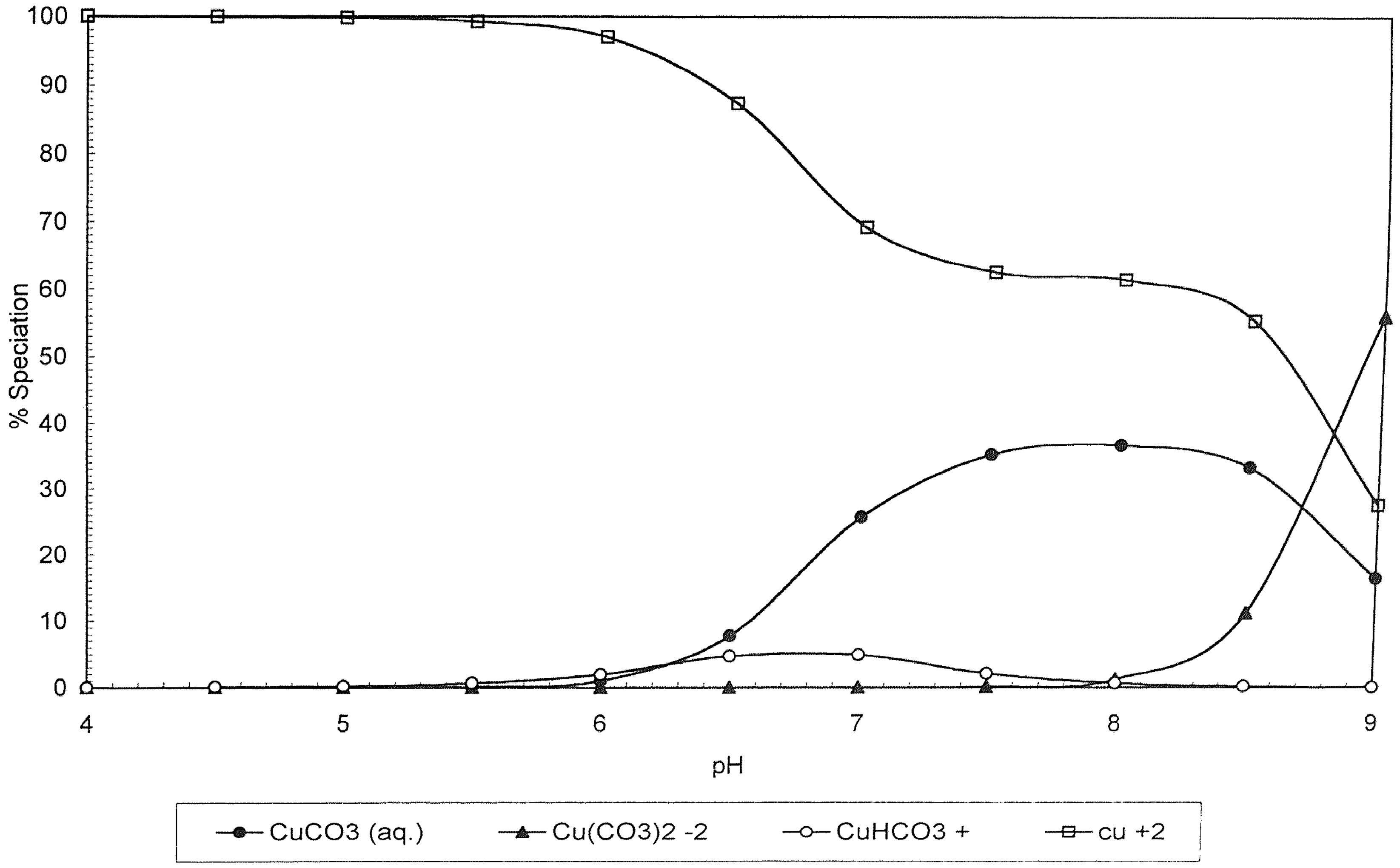
Cu and Pb solubility diagram as calculated using MINTEQA2.



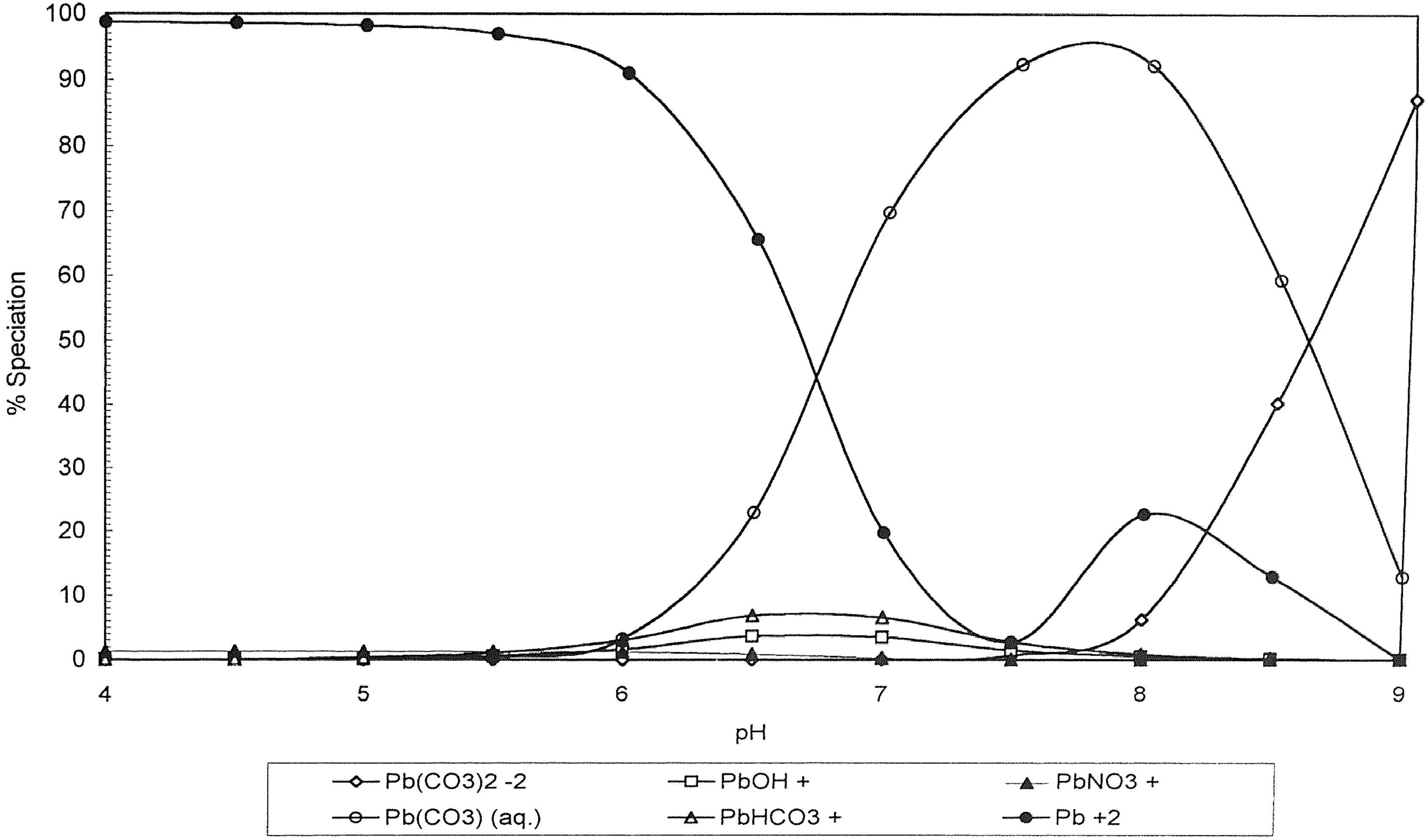
Cu, Pb, and Cd solubility diagram as calculated using MINTEQA2.

Appendix N

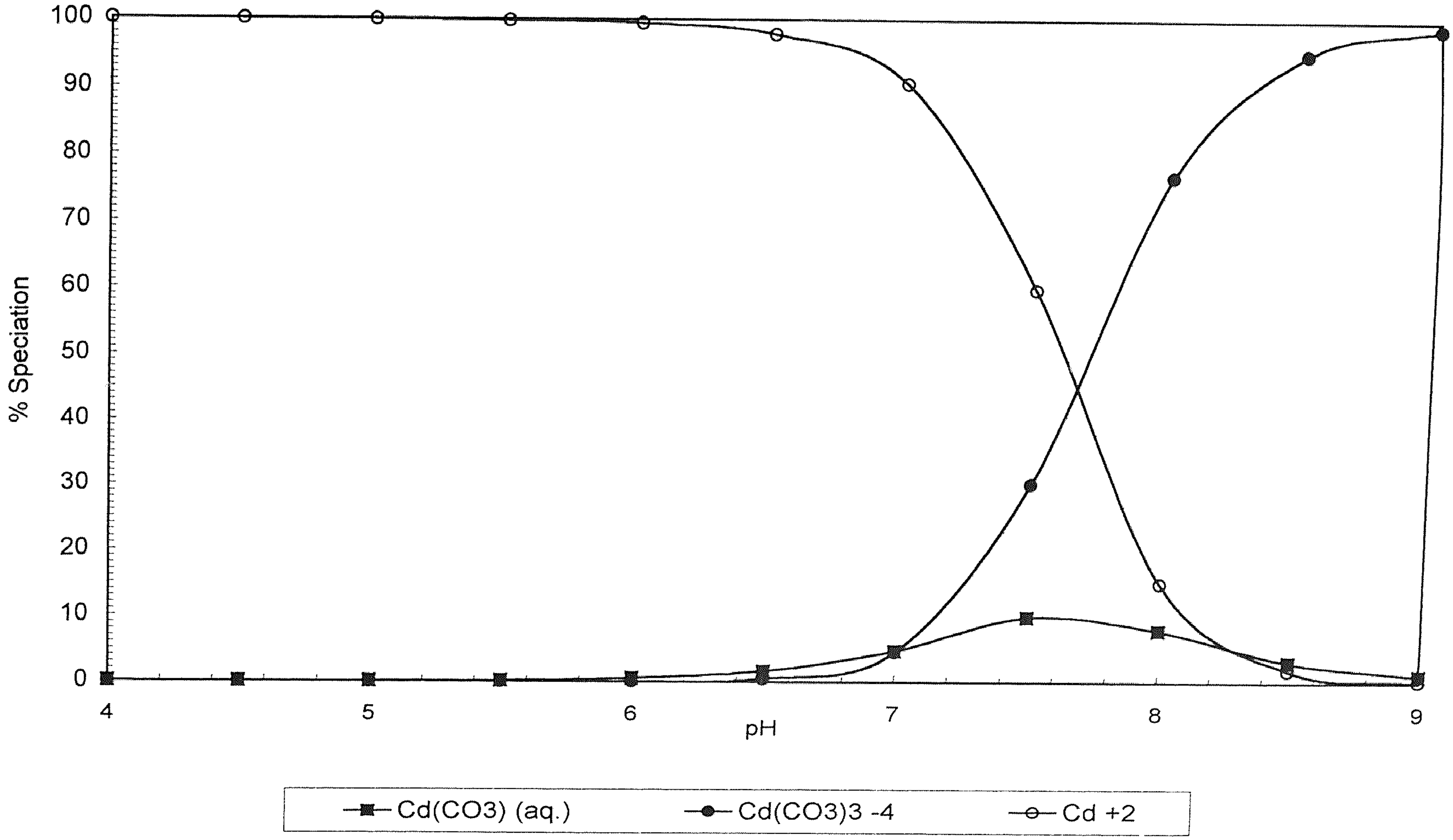
Speciation Graphs for Cu, Pb, and Cd



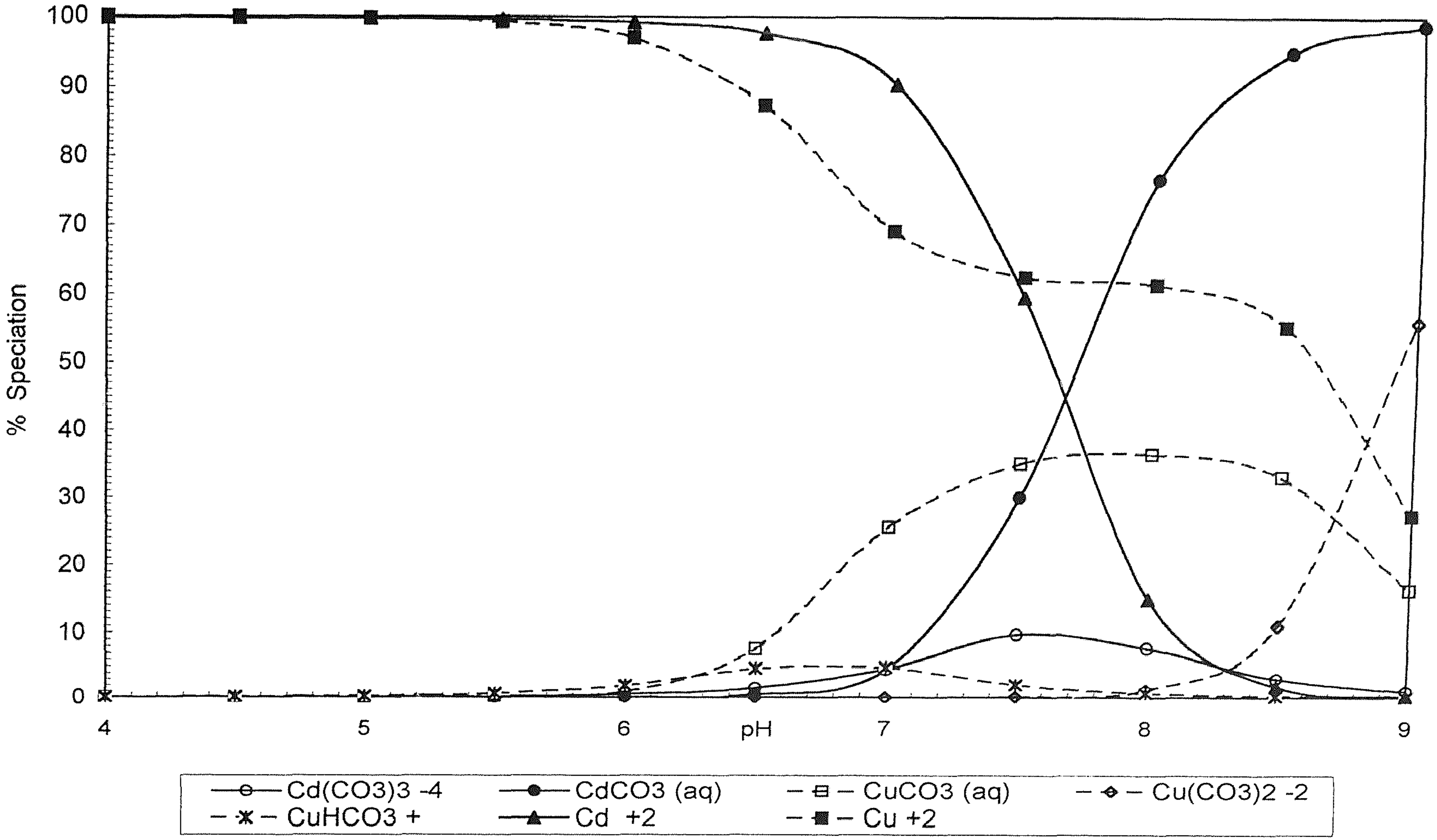
Cu speciation at 10E-3 ionic strength (sodium nitrate). Calculated using MINTEQA2.



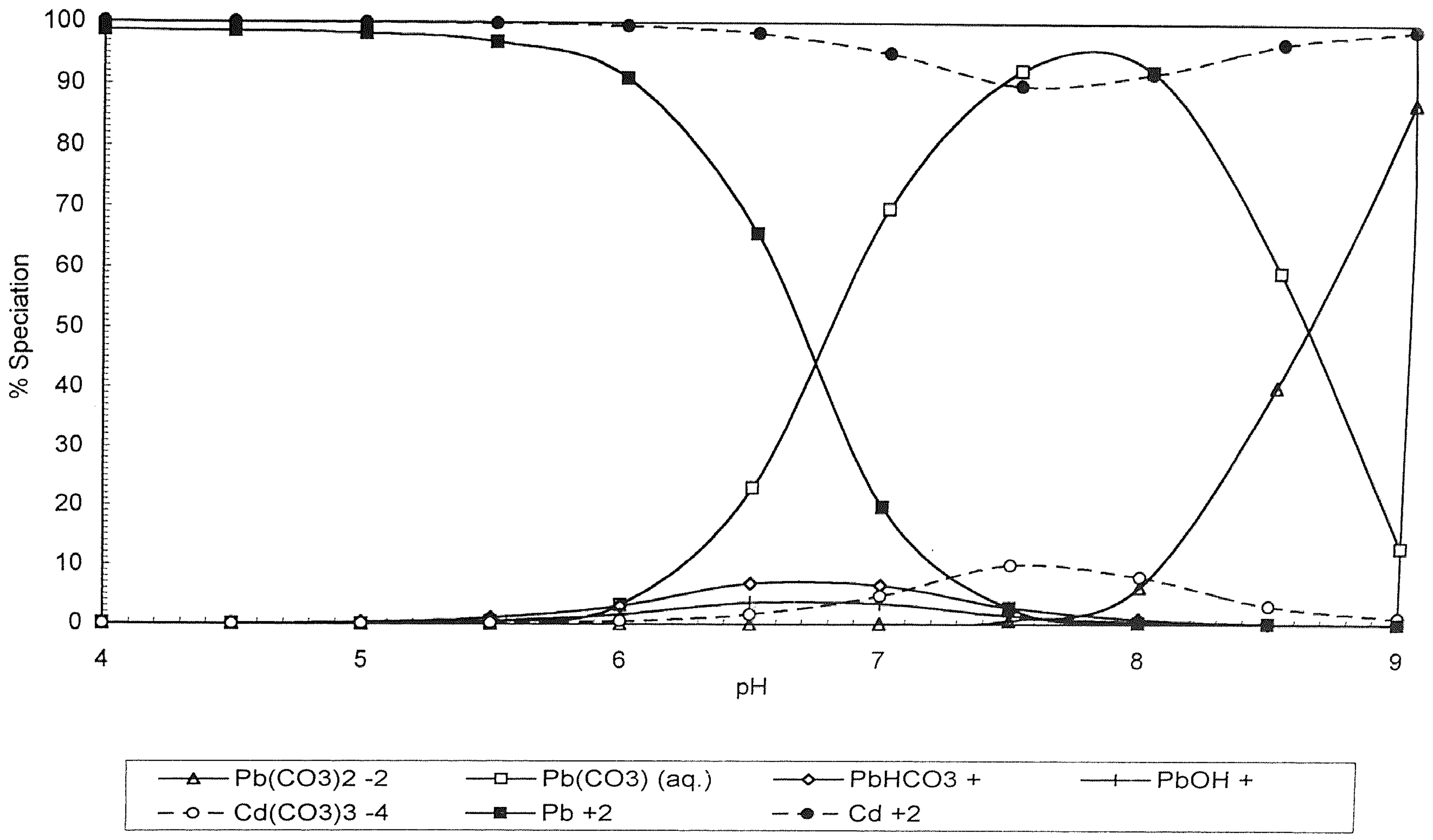
Pb speciation at 10E-3 ionic strength (sodium nitrate). Calculated using MINTEQA2.



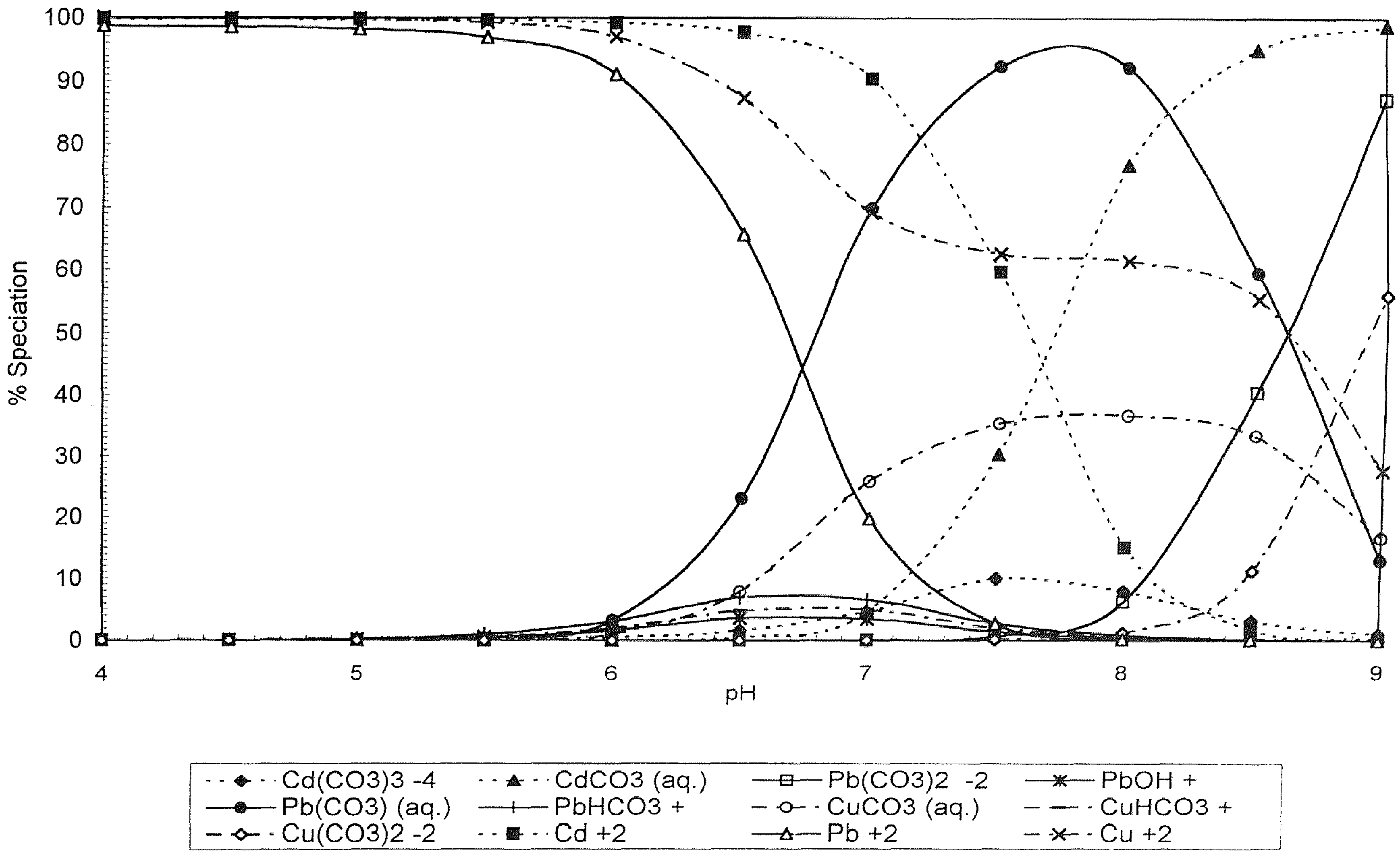
Cd speciation at 10E-3 ionic strength (sodium nitrate). Calculated using MINTEQA2.



Cd-Cu speciation at 10E-3 ionic strength (sodium nitrate). Calculated using MINTEQA2.



Cd and Pb speciation at 10E-3 ionic strength (sodium nitrate). Calculated using MINTEQA2.



Cd, Pb, and Cu speciation at 10E-3 ionic strength (sodium nitrate). Calculated using MINTEQA2.

Appendix O

Data for Metal Adsorption on Containers

Results of metal adsorption on containers in the absence of goethite: mV values and calibration curves used.

Metal added (moles)	**Metal added (moles)**	**Metal + detected (mV)**	**Metal + detected (mV)**	**Calibration curve used (#)**	**Calibration curve used (#)**
Cu	**metal 2**	**Cu**	**metal 2**	**Cu**	**metal 2**
1.0E-7	-------------	-85.50	-------------	J1	-------------
1.0E-6	-------------	-53.30	-------------	J1	-------------
1.0E-5	-------------	-20.966	-------------	J1	-------------
Pb	**metal 2**	**Pb**		**Pb**	
1.0E-7	-------------	-312.84	-------------	I2	-------------
1.0E-6	-------------	-287.88	-------------	I2	-------------
1.0E-5	-------------	-262.865	-------------	I2	-------------
Cd	**metal 2**	**Cd**		**Cd**	
1.0E-7	-------------	-242.90	-------------	L3	-------------
1.0E-6	-------------	-215.40	-------------	L3	-------------
1.0E-5	-------------	**-187.89**	-------------	L3	-------------
Cu	**Cd**	**Cu**	**Cd**	**Cu**	**Cd**
1.0E-5	[Cd]=1.0E-5	-19.10	-216.44	K1	M3
Pb	**Cd**	**Pb**	**Cd**	**Pb**	**Cd**
1.0E-5	[Cd]=1.0E-5	-286.57	-221.79	J2	N3

\+ mV obtained after 2 hour equilibration period using ISE(s).

Results of metal adsorption on containers in the absence of goethite, in 100ml aliquots, at pH 6, and 10^{-3} ionic strength (sodium nitrate).

Metal added (moles)	**Metal added (moles)**	**Metal + detected (moles)**	**Metal + Detected (moles)**	**Percent ** container adsorption**	**Percent ** container adsorption**	**Average % container adsorption**
Cu	**metal 2**	**Cu**	**metal 2**	**Cu**	**metal 2**	Cu^{2+}
1.0E-7	-------------	0.976E-7*	-------------	2.4	-------------	2.2
1.0E-6	-------------	0.973E-6	-------------	2.1	-------------	
1.0E-5	-------------	0.980E-5	-------------	2.0	-------------	
Pb	**metal 2**	**Pb**	**metal 2**	**Pb**	**metal 2**	Pb^{2+}
1.0E-7	-------------	0.982E-7 *	-------------	1.79	-------------	2.0
1.0E-6	-------------	0.978E-6	-------------	2.20	-------------	
1.0E-5	-------------	0.980E-5	-------------	2.00	-------------	
Cd	**metal 2**	**Cd**	**metal 2**	**Cd**	**metal 2**	Cd^{2+}
1.0E-7	-------------	0.980E-7 *	-------------	2.00	-------------	
1.0E-6	-------------	0.981E-6	-------------	1.90	-------------	2.0
1.0E-5	-------------	0.982E-5	-------------	1.80	-------------	
Cu	**Cd**	**Cu**	**Cd**	**Cu**	**Cd**	
1.0E-5	[Cd]=1.0E-5	0.977E-5	0.978E-5	2.3	2.2	
Pb	**Cd**	**Pb**	**Cd**	**Pb**	**Cd**	
1.0E-5	[Cd]=1.0E-5	0.979E-5	0.980E-5	2.00	1.9	

+ moles of metal detected after 2 hour equilibration period.

** percent of metal adsorbed on container walls after 2 hour equilibration period.

---- no metal added.

* value bellow detection limit.

Appendix P

Data from Cu Adsorption Edge Experiments

Copper adsorption edge experimental data. Adsorption as a function of pH, 1 gram per liter goethite, 10^{-3} ionic strength (sodium nitrate).

Initial Cd added ([M])	**pH**	**Metal ** detected (mV)**	**Calibration curve used #**	**Residual ** Cd detected ([M])**	**% Adsorption**
1.00E-5	5.49	-42.57	A1	0.600E-6	93.41
1.00E-5	6.51	-76.27	A1	0.0100 E-6	99.91
1.00E-5	5.90	-46.33	A1	0.380 E-6	96.20
1.00E-5	6.32	-59.15	A1	0.0800 E-6	99.21
1.00E-5	5.67	-37.83	A1	1.068 E-6	89.32
5.00E-6	6.21	-55.16	A1	0.130 E-6	97.40
5.00E-6	6.61	----------	A1	0 E-6	100.0
5.00E-6	6.49	-70.56	A1	0.0200 E-6	99.60
5.00E-6	6.12	-54.85	A1	0.135 E-6	97.3
5.00E-6	7.60	-65.72	A1	0.0360 E-6	99.27
5.00E-6	4.20	-39.27	B1	1.065 E-6	78.70
5.00E-6	4.02	-29.81	B1	2.92 E-6	41.60
5.00E-6	8.00	-76.56	B1	0.0200 E-6	99.60
5.00E-6	7.00	-79.26	B1	0.0150 E-6	99.70
5.00E-6	4.08	-32.30	B1	2.24 E-6	55.1
5.00E-6	4.36	-42.32	B1	0.770 E-6	84.6
5.00E-6	4.70	-48.09	B1	0.416 E-6	91.68
5.00E-6	5.62	-63.44	B1	0.0810 E-6	98.38
5.00E-6	5.26	-63.44	B1	0.0810 E-6	98.38
5.00E-6	5.00	-54.20	B1	0.217 E-6	95.65
5.00E-06 *	4.00	-26.09	BB1	3.09E-06	38.30
5.00E-06 *	4.10	-30.49	BB1	1.95E-06	61.12
5.00E-06 *	4.80	-46.18	BB1	3.75E-07	92.51
5.00E-06 *	6.50	-56.28	BB1	1.30E-07	97.41
5.00E-06 *	7.50	-87.34	BB1	5.00E-09	99.90

------ metal undetected or above detection limit.

* during these runs, 10^{-2} ionic strength (sodium nitrate) was used.

** metal detected .after 4 hour equilibration period.

Appendix Q

Data from Pb Adsorption Edge Experiments

Lead adsorption edge experimental data. Adsorption as a function of pH, 1 gram per liter goethite, 10^{-3} ionic strength (sodium nitrate).

Initial Cd added ([M])	**pH**	**Metal ** detected (mV)**	**Calibration curve used #**	**Residual ** Cd detected ([M])**	**% Adsorption**
9.39E-7	6.43	-319.61	A2	0.290E-7	96.9
9.39E-7	6.03	-310.99	A2	0.480E-7	94.88
9.39E-7	6.66	-----------	A2	0	100.00
9.39E-7	6.27	-265.07	A2	7.03E-7	25.10
1.00E-6	6.12	-278.53	A2	0.320E-6	93.16
4.69E-6	6.61	-287.54	A2	1.89 E-7	95.95
4.69E-6	5.20	-269.02	A2	0.558 E-6	88.10
4.69E-6	4.02	-233.26	A2	4.51E-6	3.80
4.69E-6	4.21	-120.56	A2	4.319	7.90
4.69E-6	4.70	-258.20	A2	1.05 E-6	77.67
4.69E-6	4.92	-332.11	B2	0.643 E-6	86.28
4.69E-6	5.54	-331.25	B2	0.698 E-6	85.10
4.69E-6	5.78	-337.87	B2	0.370 E-6	92.10
4.69E-6	5.90	-344.495	B2	0.196 E-6	95.80
4.69E-6	5.54	-326.516	B2	1.10 E-6	23.58
4.69E-6	7.97	-361.06	B2	0.0400 E-6	99.90
4.69E-6	6.98	-361.05	B2	0.0400 E-6	99.90
4.69E-6	7.54	-361.06	B2	0.0400 E-6	99.90
4.69E-6	5.62	-346.35	B2	0.164 E-6	96.50
4.69E-6	5.37	-334.50	B2	0.511 E-6	89.11
4.69E-6	4.80	-324.34	B2	0.647 E-6	86.20
4.69E-6	4.60	-309.33	B2	2.86 E-6	39.00
4.69E-06 *	4.30	-285.76	CC2	3.85E-06	18.00
4.69E-06 *	4.70	-291.52	CC2	2.18E-06	53.60
4.69E-06 *	5.01	-305.90	CC2	5.30E-07	88.71
4.69E-06 *	6.51	-314.39	CC2	2.30E-07	95.11
4.69E-06 *	7.50	-346.90	CC2	9.38E-09	99.80

------ metal undetected or above detection limit.

* during these runs, 10^{-2} ionic strength (sodium nitrate) was used.

** metal detected after 4 hour equilibration period.

Appendix R

Data from Cd Adsorption Edge Experiments

Cadmium adsorption edge experimental data. Adsorption as a function of pH, 1 gram per liter goethite, 10^{-3} ionic strength (sodium nitrate).

Initial Cd added ([M])	**pH**	**Metal ** detected (mV)**	**Calibration curve used #**	**Residual ** Cd detected ([M])**	**% Adsorption**
8.89E-7	5.84	-22.61	A3	1.25E-7	85.9
8.89E-7	7.32	-279.59	A3	0.0179E-7	99.8
8.89E-7	4.06	-196.28	A3	8.89E-7	0
8.89E-7	5.08	-200.15	A3	6.66E-7	25
8.89E-7	6.08	-221.77	A3	1.33E-7	85
8.89E-7	6.51	-247.54	A3	0.195E-7	97.8
4.45E-6	4.35	-174.67	B3	4.45E-6	0
4.45E-6	5.41	-120.21	B3	1.44E-6	67.5
4.45E-6	4.03	-108.60	B3	4.45E-6	0
4.45E-6	4.88	-111.04	B3	3.51E-6	21.07
4.45E-6	5.23	-115.08	B3	2.37E-6	46.55
4.45E-6	8.00	-148.35	A3	0.0934E-6	97.9
4.45E-6	7.72	-226.52	A3	0.0934E-6	97.9
4.45E-6	6.59	-206.47	A3	0.416E-6	90.64
4.45E-6	5.55	-189.62	A3	1.46E-6	67.00
4.45E-6	5.84	-200.96	B3	0.6274E-6	85.90
4.45E-6	6.36	-129.53	B3	0.582E-6	86.90
4.45E-6	7.83	-134.59	B3	0.356E-6	92.00
4.45E-6	6.06	-127.21	B3	0.729E-6	83.60
4.45E-6	4.65	-110.04	B3	3.87E-6	12.90
4.45E-6	7.00	-131.32	B3	0.489E-6	89.00
4.45E-6 *	4.50	-121.67	BB3	4.01E-6	9.9
4.45E-6 *	5.10	-125.05	BB3	2.89E-6	35.1
4.45E-6 *	5.80	-134.95	BB3	1.10E-6	75.2
4.45E-6 *	6.50	-151.63	BB3	2.18E-6	95.1
4.45E-6 *	7.30	-156.68	BB3	1.34E-6	97

* during these runs, 10^{-2} ionic strength (sodium nitrate) was used.

** metal detected after 4 hour equilibration period.

Appendix S

Data from Sr Adsorption Experiments

Sr adsorption experimental data with 10^{-1} gram per liter goethite, pH 6, 10^{-3} ionic strength (sodium nitrate).

Initial Sr (M)	**Equilibration period (Hours)**	**Residual Sr (counts)**	**Slope (moles/counts)**	**Residual Cu (M)**	**Adsorption (moles/gram)**
$1*10^{-3}$	4	1428	1.90	$0.272x10^{-3}$	$7.28x10^{-3}$
$1*10^{-3}$	4	1459	1.90	$0.278x10^{-3}$	$7.22x10^{-3}$
$1*10^{-3}$	4	1491	1.90	$0.284x10^{-3}$	$7.16x10^{-3}$
$1*10^{-3}$	4	1454	1.90	$0.277x10^{-3}$	$7.23x10^{-3}$

Appendix T

Data from Cu Isotherm Experiments

Cu adsorption isotherm experimental data with 1 gram per liter goethite, pH 6, 10^{-3} ionic strength (sodium nitrate).

Initial Cu (M)	**Equilibration period (Hours)**	**Residual Cu (mV)**	**Calibration curve used #**	**Residual Cu (M)**
2.00E-06	4	-61.6681	C1	3.71E-07
3.99E-06	4	-53.9737	C1	2.15E-07
5.99E-06	4	-46.8569	C1	7.79E-07
9.00E-06	4	-31.4067	C1	2.61E-06
9.99E-06	4	-24.7136	C1	6.13E-07
5.00E-06	4	-53.9028	C1	1.19E-07
9.99E-07	4	-70.0462	D1	3.06E-07
3.00E-06	4	-73.0521	D1	6.61E-07
5.00E-06	4	-71.1363	D1	6.48E-07
7.51E-06	4	-52.8326	D1	1.06E-06
9.50E-06	4	-42.7265	D1	1.90E-06
7.71E-06	4	-69.4597	E1	8.00E-07
4.05E-06	4	-80.8843	E1	1.30E-06
5.96E-06	4	-46.8751	F1	3.33E-06
8.76E-06	4	-35.2961	F1	2.26E-06
1.05E-05	4	-29.0582	F1	4.32E-06
1.17E-05	4	-24.8796	F1	2.80E-06
1.27E-05	4	-21.7257	F1	3.79E-06
1.22E-05	2	-32.7188	G1	
1.08E-05	2	-37.0482	G1	

Appendix U

Data from Pb Isotherm Experiments

Pb adsorption isotherm experimental data with 1 gram per liter goethite, pH 6, 10^{-3} ionic strength (sodium nitrate)

Initial Pb **(M)**	**Equilibration period** **(Hours)**	**Residual Pb** **(mV)**	**Calibration curve used** **#**	**Residual Pb** **(M)**
4.69E-06	4	-329.957	C2	3.71E-07
5.64E-06	4	-335.465	C2	2.15E-07
7.51E-06	4	-322.467	C2	7.79E-07
9.45E-06	4	-310.259	C2	2.61E-06
6.88E-06	4	-324.887	C2	6.13E-07
8.39E-07	4	-341.438	C2	1.19E-07
5.50E-06	4	-312.484	D2	3.06E-07
6.50E-06	4	-304.833	D2	6.61E-07
7.20E-06	4	-305.03	D2	6.48E-07
7.98E-06	4	-300.141	D2	1.06E-06
8.92E-06	4	-294.344	D2	1.90E-06
7.80E-06	4	-307.253	E2	8.00E-07
8.29E-06	4	-302.362	E2	1.30E-06
1.00E-05	4	-292.884	E2	3.33E-06
9.69E-06	4	-296.789	E2	2.26E-06
1.11E-05	4	-290.261	E2	4.32E-06
9.84E-06	2	-266.652	F2	2.80E-06
1.09E-05	2	-261.8	F2	3.79E-06

Appendix V

Data from Cd Isotherm Experiments

Cd adsorption isotherm experimental data with 1 gram per liter goethite, pH 6, 10^{-3} ionic strength (sodium nitrate).

Initial Cd (M)	**Equilibration period (Hours)**	**Residual Cd (mV)**	**Calibration curve used #**	**Residual Cd (M)**
1.96E-06	4	-246.297	C3	5.92E-07
3.50E-06	4	-240.563	C3	9.76E-07
5.99E-06	4	-233.542	C3	1.80E-06
5.99E-06	4	-235.787	C3	1.48E-06
8.20E-06	4	-225.465	C3	3.64E-06
9.99E-06	4	-222.292	C3	4.80E-06
9.99E-07	4	-258.088	D3	1.08E-07
3.00E-06	4	-246.994	D3	2.75E-07
5.00E-06	4	-228.927	D3	1.26E-06
7.00E-06	4	-224.114	D3	1.89E-06
1.00E-05	4	-212.758	D3	4.92E-06
5.20E-06	4	-149.41	F3	5.32E-07
6.72E-06	4	-137.673	F3	1.47E-06
7.55E-06	4	-131.54	F3	2.50E-06
8.49E-06	4	-127.523	F3	3.54E-06
2.22E-06	4	-259.027	E3	4.75E-07
2.40E-06	4	-257.124	E3	5.66E-07
3.03E-06	4	-256.365	E3	6.07E-07
7.95E-06	2	-230.158	G3	3.00E-06
9.04E-06	2	-227.245	G3	3.96E-06

Appendix W

Data from Cd-Cu Competition Isotherm Experiments

Metal competition results between Cd and Cu with 10^{-1} gram per liter of goethite, 100ml aliquots, at pH 6, and 10^{-3} ionic (sodium nitrate).

	1 *	2	3 **	4	5 **	6
Run	**Metal added (moles)**	**Metal added (moles)**	**Metal detected (mV)**	**Calibration curve used (#)**	**Metal detected (mV)**	**Calibration curve used (#)**
I	**Cd**	**Cu**	**Cd**	**Cd**	**Cu**	**Cu**
	1.50E-7	1.50E-7	-218,34	H3	-58,65	H1
	2.50E-7	2.50E-7	-212,08	H3	-45,76	H1
	3.50E-7	3.50E-7	-208,02	H3	-38,59	H1
	4.50E-7	4.50E-7	-204,95	H3	-34,25	H1
	5.00E-7	5.00E-7	-203,63	H3	-32,28	H1
II	**Cu**	**Cd**	**Cu**	**Cu**	**Cd**	**Cd**
	1.50E-7	1.50E-7	-57,39	H1	-218,32	H3
	2.50E-7	2.50E-7	-50,39	H1	-214,81	H3
	3.50E-7	3.50E-7	-41,70	H1	-209,83	H3
	4.50E-7	4.50E-7	-36,33	H1	-206,34	H3
	5.00E-7	5.00E-7	-32,49	H1	-203,64	H3
III **	**Cd**	**Cu**	**Cd**	**Cd**	**Cu**	**Cu**
	1.50E-7	1.50E-7	-235,82	I3	-54,15	I1
	2.50E-7	2.50E-7	-232,18	I3	-47,06	I1
	3.50E-7	3.50E-7	-227,22	I3	-38,06	I1
	4.50E-7	4.50E-7	-223,62	I3	-32,88	I1
	5.00E-7	5.00E-7	-220,89	I3	-28,65	I1

* column 1 shows the metal that was introduced first in the system.

** mV obtained after 2 hour equilibration period.

*** during this run, competing metals were introduced simultaneously in the system

Metal competition results between Cd and Cu with 10^{-1} gram per liter of goethite, 100ml aliquots, at pH 6, and 10^{-3} ionic (sodium nitrate).

	1 *	2	3 **	5 **
Run	**Metal added**	**Metal added**	**Metal detected**	**Metal detected**
	(moles)	**(moles)**	**(moles)**	**(moles)**
I	**Cd**	**Cu**	**Cd**	**Cu**
	1.50E-7	1.50E-7	1.48E-7	6.39E-8
	2.50E-7	2.50E-7	2.48E-7	1.6E-07
	3.50E-7	3.50E-7	3.47E-7	2.67E-7
	4.50E-7	4.50E-7	4.48E-7	3.63E-7
	5.00E-7	5.00E-7	4.99E-7	4.18E-7
II	**Cu**	**Cd**	**Cu**	**Cd**
	1.50E-7	1.50E-7	6.99E-8	1.48E-7
	2.50E-7	2.50E-7	1.15E-7	1.98E-7
	3.50E-7	3.50E-7	2.14E-7	2.99E-7
	4.50E-7	4.50E-7	3.13E-7	3.99E-7
	5.00E-7	5.00E-7	4.12E-7	4.99E-7
III **	**Cd**	**Cu**	**Cd**	**Cu**
	1.50E-7	1.50E-7	1.48E-7	7.07E-8
	2.50E-7	2.50E-7	1.99E-7	1.16E-7
	3.50E-7	3.50E-7	2.98E-7	2.17E-7
	4.50E-7	4.50E-7	3.99E-7	3.10E-7
	5.00E-7	5.00E-7	4.98E-7	4.17E-7

* column 1 shows the metal that was introduced first in the system.

** mV obtained after 2 hour equilibration period.

*** during this run, competing metals were introduced simultaneously in the system

Appendix X

Data from Cd-Pb Competition Isotherm Experiments

Metal competition results between Cd and Pb with 10^{-1} gram per liter of goethite, 100ml aliquots, at pH 6, and 10^{-3} ionic (sodium nitrate).

	1 *	**2**	**3 ****	**4**	**5 ****	**6**
Run	**Metal added (moles)**	**Metal added (moles)**	**Metal detected (mV)**	**Calibration curve used (#)**	**Metal detected (mV)**	**Calibration curve used (#)**
I	**Cd**	**Pb**	**Cd**	**Cd**	**Pb**	**Pb**
	1.50E-7	1.50E-7	-257,47	J3	-247,16	G2
	2.50E-7	2.50E-7	-251,57	J3	-239,48	G2
	3.50E-7	3.50E-7	-247,83	J3	-235,27	G2
	4.50E-7	4.50E-7	-245,08	J3	-232,44	G2
	5.00E-7	5.00E-7	-243,90	J3	-231,23	G2
II	**Pb**	**Cd**	**Pb**	**Pb**	**Cd**	**Cd**
	1.50E-7	1.50E-7	-246,98	G2	-257,39	J3
	2.50E-7	2.50E-7	-242,53	G2	-254,11	J3
	3.50E-7	3.50E-7	-237,24	G2	-249,53	J3
	4.50E-7	4.50E-7	-233,75	G2	-246,31	J3
	5.00E-7	5.00E-7	-231,22	G2	-243,83	J3
III *	**Cd**	**Pb**	**Cd**	**Cd**	**Pb**	**Pb**
	1.50E-7	1.50E-7	-188,12	K3	-259,49	H2
	2.50E-7	2.50E-7	-183,96	K3	-253,13	H2
	3.50E-7	3.50E-7	-178,27	K3	-245,30	H2
	4.50E-7	4.50E-7	-174,34	K3	-240,23	H2
	5.00E-7	5.00E-7	-171,31	K3	-236,32	H2

* column 1 shows the metal that was introduced first in the system.

** mV obtained after 2 hour equilibration period.

*** during this run, competing metals were introduced simultaneously in the system

Metal competition results between Cd and Pb with 10^{-1} gram per liter of goethite, 100ml aliquots, at pH 6, and 10^{-3} ionic (sodium nitrate).

Run	1 * Metal added (moles)	2 Metal added (moles)	3 ** Metal detected (moles)	5 ** Metal detected (moles)
I	**Cd**	**Pb**	**Cd**	**Pb**
	1.50E-7	1.50E-7	1.40E-07	7.85E-08
	2.50E-7	2.50E-7	2.41E-07	1.78E-07
	3.50E-7	3.50E-7	3.41E-07	2.78E-07
	4.50E-7	4.50E-7	4.39E-07	3.76E-07
	5.00E-7	5.00E-7	4.90E-07	4.28E-07
II	**Pb**	**Cd**	**Pb**	**Cd**
	1.50E-7	1.50E-7	8.0E-08	1.41E-07
	2.50E-7	2.50E-7	1.29E-7	1.91E-07
	3.50E-7	3.50E-7	2.26E-07	2.92E-07
	4.50E-7	4.50E-7	3.27E-07	3.92E-07
	5.00E-7	5.00E-7	4.28E-07	4.93E-07
III **	**Cd**	**Pb**	**Cd**	**Pb**
	1.50E-7	1.50E-7	1.40E-07	8.32E-08
	2.50E-7	2.50E-7	1.91E-07	1.31E-07
	3.50E-7	3.50E-7	2.92E-07	2.28E-07
	4.50E-7	4.50E-7	3.92E-07	3.26E-07
	5.00E-7	5.00E-7	4.92E-07	4.31E-07

* column 1 shows the metal that was introduced first in the system.

** mV obtained after 2 hour equilibration period.

*** during this run, competing metals were introduced simultaneously in the system

Appendix AA

Data from Cu-Pb Competition Isotherm Experiments

Metal competition results between Cu and Pb with 10^{-1} gram per liter of goethite, 100ml aliquots, at pH 6, and 10^{-3} ionic (sodium nitrate).

	1 *	2	3 ***	4 +	5 ***	6 +
Run	Metal added	Metal added	Metal detected	Slope of calibration used	Metal detected	Slope of calibration used
	(moles)	(moles)	(pk. area)	(mm/pk. area)	(pk. area)	(mm/pk. area)
I	Pb	Cu	Pb	Pb	Cu	Cu
	1.0E-7	1.0E-7	2.85E-02	2.031	7.21E-03	7.821
	2.0E-7	2.0E-7	7.60E-02	2.031	1.97E-02	7.821
	3.0E-7	3.0E-7	1.26E-01	2.031	3.27E-02	7.821
	4.0E-7	4.0E-7	1.75E-01	2.031	4.54E-02	7.821
	5.0E-7	5.0E-7	2.24E-01	2.031	5.82E-02	7.821
II	Cu	Pb	Cu	Cu	Pb	Pb
	1.0E-7	1.0E-7	7.17E-03	7.821	2.86E-02	2.031
	2.0E-7	2.0E-7	1.97E-02	7.821	7.60E-02	2.031
	3.0E-7	3.0E-7	3.31E-02	7.821	1.28E-01	2.031
	4.0E-7	4.0E-7	4.56E-02	7.821	1.76E-01	2.031
	5.0E-7	5.0E-7	5.82E-02	7.821	2.24E-01	2.031
III **	Pb	Cu	Pb	Pb	Cu	Cu
	1.0E-7	1.0E-7	2.90E-02	2.031	7.40E-03	7.821
	2.0E-7	2.0E-7	7.62E-02	2.031	1.98E-02	7.821
	3.0E-7	3.0E-7	1.26E-01	2.031	3.27E-02	7.821
	4.0E-7	4.0E-7	1.75E-01	2.031	4.54E-02	7.821
	5.0E-7	5.0E-7	2.24E-01	2.031	5.81E-02	7.821

* column 1 shows the metal that was introduced first in the system.

** during this run, competing metals were introduced simultaneously in the system

*** metal detected after 4 hours equilibration period using AA spectroscopy.

\+ slope of the calibration curve used in analyzing the sample using an AA spectrophotometer unit.

Metal competition results between Cu and Pb with 10^{-1} gram per liter of goethite, 100ml aliquots, at pH 6, and 10^{-3} ionic (sodium nitrate).

	1 *	**2**	**3**	**5**
Run	**Metal added**	**Metal added**	**Metal detected**	**Metal detected**
	(moles)	**(moles)**	**(moles)**	**(moles)**
I	**Pb**	**Cu**	**Pb**	**Cu**
	1.0E-7	1.0E-7	5,78E-08	5,64E-08
	2.0E-7	2.0E-7	1,54E-07	1,54E-07
	3.0E-7	3.0E-7	2,56E-07	2,56E-07
	4.0E-7	4.0E-7	3,55E-07	3,55E-07
	5.0E-7	5.0E-7	4,55E-07	4,55E-07
II	**Cu**	**Pb**	**Cu**	**Pb**
	1.0E-7	1.0E-7	5,61E-08	5,81E-08
	2.0E-7	2.0E-7	1,54E-07	1,54E-07
	3.0E-7	3.0E-7	2,59E-07	2,59E-07
	4.0E-7	4.0E-7	3,57E-07	3,57E-07
	5.0E-7	5.0E-7	4,55E-07	4,55E-07
III ***	**Cu**	**Pb**	**Cu**	**Pb**
	1.0E-7	1.0E-7	5,79E-08	5,88E-08
	2.0E-7	2.0E-7	1,55E-07	1,55E-07
	3.0E-7	3.0E-7	2,55E-07	2,55E-07
	4.0E-7	4.0E-7	3,55E-07	3,55E-07
	5.0E-7	5.0E-7	4,54E-07	4,54E-07

* column 1 shows the metal that was introduced first in the system.

*** during this run, competing metals were introduced simultaneously in the system

Appendix AB

Data from Cu-Pb-Cd Competition Isotherm Experiments

Metal competition results between Pb, Cu, and Cd with 10^{-1} gram per liter of goethite, 100ml aliquots, at pH 6, and 10^{-3} ionic (sodium nitrate).

Metal added (moles)	**Metal added (moles)**	**Metal added (moles)**	**Metal * detected (pk. area)**	**Slope of ** calibration used (µm/pk. area)**	**Metal * detected (pk. area)**	**Slope of ** calibration used (µm/pk. area)**	**Metal * detected (pk. area)**	**Slope of ** calibration used (µm/pk. area)**
Pb	**Cu**	**Cd**	**Pb**	**Pb**	**Cu**	**Cu**	**Cd**	**Cd**
1.0E-7	1.0E-7	1.0E-7	0.0494	1.195	0.0071	8.252	0.0147	6.714
2.0E-7	2.0E-7	2.0E-7	0.1302	1.195	0.0187	8.252	0.0234	6.714
3.0E-7	3.0E-7	3.0E-7	0.2149	1.195	0.0312	8.252	0.0355	6.714
4.0E-7	4.0E-7	4.0E-7	0.2995	1.195	0.0431	8.252	0.0476	6.714
5.0E-7	5.0E-7	5.0E-7	0.3805	1.195	0.0550	8.252	0.0593	6.714
1.0E-7	1.0E-7	1.0E-7	0.0836	1.195	0.0069	8.252	0.0115	6.714
2.0E-7	2.0E-7	2.0E-7	0.1307	1.195	0.0189	8.252	0.0234	6.714
3.0E-7	3.0E-7	3.0E-7	0.2166	1.195	0.0310	8.252	0.0355	6.714
4.0E-7	4.0E-7	4.0E-7	0.2993	1.195	0.0437	8.252	0.0476	6.714
5.0E-7	5.0E-7	5.0E-7	0.3810	1.195	0.0552	8.252	0.0593	6.714

* metal detected after 4 hours equilibration period using AA spectroscopy.

** slope of the calibration curve used in analyzing the sample using an AA spectrophotometer unit.

Metal competition results between Pb, Cu, and Cd with 10^{-1} gram per liter of goethite, 100ml aliquots, at pH 6, and 10^{-3} ionic strength (sodium nitrate).

Metal added (moles)	**Metal added (moles)**	**Metal added (moles)**	**Metal detected (moles)**	**Metal detected (moles)**	**Metal detected (moles)**
Cu	**Pb**	**Cd**	**Cu**	**Pb**	**Cd**
1.0E-7	1.0E-7	1.0E-7	5.88E-08	5.91E-08	9.90E-08
2.0E-7	2.0E-7	2.0E-7	1.55E-07	1.56E-07	1.94E-07
3.0E-7	3.0E-7	3.0E-7	2.58E-07	2.57E-07	2.93E-07
4.0E-7	4.0E-7	4.0E-7	3.56E-07	3.58E-07	3.94E-07
5.0E-7	5.0E-7	5.0E-7	4.54E-07	4.55E-07	4.90E-07
1.0E-7	1.0E-7	1.0E-7	5.77E-08	1.00E-07	9.50E-08
2.0E-7	2.0E-7	2.0E-7	1.57E-07	1.56E-07	1.94E-07
3.0E-7	3.0E-7	3.0E-7	2.56E-07	2.59E-07	2.93E-07
4.0E-7	4.0E-7	4.0E-7	3.61E-07	3.58E-07	3.94E-07
5.0E-7	5.0E-7	5.0E-7	4.56E-07	4.55E-07	4.90E-07

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