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THE ADSORPTION OF COBALT IONS BY CLAY MINERALS

A Thesis

by

David Gerald Feeney

Submitted to the Graduate School of

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in partial fulfillment of the requirements for the degree of

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August 1981

Major Department: Chemistry

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ABSTRACT

THE ADSORPTION OF COBALT IONS BY
CLAY MINERALS. (August 1981)
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The importance of the ability of a clay mineral to adsorb metal ions has long been recognized, and many studies of metal ion exchange have been conducted. Koppelman and Dillard[2], as part of an ESCA study of adsorption by clay minerals, found Co(II) adsorbed on the surface of some clay minerals which had been held in contact with Co(III) solutions. The present study was designed to investigate whether the Co(II) present is due to the reduction of Co(III) in the bulk solution or whether it is due to reduction at the clay mineral surface as part of the adsorption process. A controlled-potential cell was designed and used to control the oxidation state of cobalt in solution and adsorptivity data obtained was compared to that from a control cell. These experiments were run using illite, kaolinite, and montmorillonite at pH=3 and pH=7 for Co(II) and at pH=3 for Co(III) adsorption. It was found that the clays had a greater adsorptivity at pH=7 and that they adsorbed Co(III) to a greater extent than Co(II). It was expected that since Co(III) was preferentially adsorbed, the adsorptivities of the clays would be greater in the controlled-potential cell if Co(III) was reducing in solution before

being adsorbed as Co(II). The applied potential had no effect on the adsorptivities; thus the presence of Co(II) was due to the reduction of Co(III) as part of the adsorption process. Obvious extensions of this work are included in Chapter 5.

Acknowledgements

I wish to express my sincere appreciation to my advisor, Dr. T. C. Rhyne; without his endless assistance and encouragement these pages would not be possible. I would also like to thank the members of the advisory committee who also provided both technical advice and moral support which helped in the completion of this work. The support received from all of the faculty members in the Chemistry Department is also acknowledged.

I would also like to thank my parents for their confidence in me and for all the years of support that have made the load much easier to bear.

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CHAPTER I

INTRODUCTION

The importance of the ability of a clay mineral to adsorb ions and hold them in an exchangeable state has long been known. Clays frequently play an important role in the tilth of the soil by being responsible for holding plant foods and minerals as exchangeable ions. Studies made on soils include some of the first experiments conducted on the cation exchangeability of clays, and these reports date back to about 1850.[1] The ability of a clay to exchange cations is important to geologists as part of the weathering process and as an indicator of past conditions of the environment preserved in ancient sediments. Even though these are historically the fields where the exchangeability of a clay has been the most studied, new research in recent years has dealt with a clay's ability to interact with man-made pollutants and the effects clays have on ion concentrations and pH of natural waters. Probably the largest area of clay research today is in the study of the effects of clays in holding the pH and ion concentrations of the oceans at a constant level.

Although many studies have been conducted on the subject of cation exchange in clay minerals, much work is still needed to fully understand the many conditions that surround the cation exchangeabilities of clays. Because of this need for further study, many investigators are looking for new and more efficient ways to examine clays. One such investigation used atomic absorption spectroscopy and x-ray photoelectron spectroscopy (ESCA) to detect the presence of small quantities (ppm) of adsorbed metal ions on mineral surfaces and to determine general qualitative information about the binding energies, concentration, and the oxidation states of the adsorbed ions.

Koppelman and Dillard[2] were successful in showing that ESCA is a useful tool for obtaining data about the exchangeability of cations on clay minerals and that through this technique, bonding energies and oxidation states of the adsorbed cation could indeed be determined. These workers showed that there is a direct relationship between the pH of the solution from which the ion is adsorbed and the amount of the ion adsorbed, with more adsorption being observed at increased pH. In addition, this study showed that the oxidation state of the ion is important in determining the adsorptivity. For example, the hexa-aquo cobalt(II) complex ion was adsorbed to a lesser extent than the hexa-ammine cobalt(III) complex ion. This relationship fits the expected pattern, but it was also observed that when illite or chlorite clay reacted with a solution containing only the hexaammine cobalt(III) complex ion, the clay showed the presence of cobalt(II) in some of the exchange sites. Koppelman and Dillard reasoned from this that either the cobalt was reducing spontaneously in solution before being adsorbed or that the clay contributed to reduction of the ion as it was being adsorbed.

This study is designed to reproduce a number of the experiments reported by Koppelman and Dillard in an attempt to determine the point at which cobalt(III) complexes are reduced to cobalt(II) species. Application of an appropriate potential to the solution containing the Co(III) complex should prevent the reduction of this species in the solution, and comparisons with adsorption experiments not involving the applied potential perhaps can identify whether reduction occurs in the bulk solution or at the liquid-solid interfacial boundary of the clay mineral surface.

CHAPTER II

HISTORICAL

A. General Information About Clay Minerals

The term clay mineral is used to describe a group of substances that are natural, earthy, fine-grained materials which develop plasticity when mixed with a limited amount of water. Plasticity is the ability of a moistened material to be deformed by application of an external force with the deformed shape being retained when the force is removed. It has been shown by chemical analyses that clays are composed primarily of silica, alumina, and water, and frequently with appreciable quantities of iron, alkali metal and alkaline earth metals. The term clay mineral applies to substances that are the product of weathering, have formed from hydrothermal action, or have been deposited as a sediment in a body of water.[3]

The geological term "clay fraction" is generally used to define materials with a particle size of less than about 4 micrometers.[4] Soil investigators tend to use 2 micrometers as the upper limit for a material to be classified as a clay. Although there is no steadfast boundary between the particle sizes of clays and other minerals it has been shown that non-clay minerals are usually not present in particle sizes much smaller than about 1 to 2 micrometers. In general it is usually found that clays will have a particle size of 2 micrometers or less and that clay minerals that are found with a particle size greater than 2 micrometers will break down easily to this size when placed in water.

Clay minerals are not generally found in the pure form in nature but rather are usually found as a mixture of clay and non-clay mineral components in varying relative amounts. In general, a substance will be classified as a clay if the clay grade particle size dominates and if the substance shows distinct plasticity.

B. Structure of the Clay Minerals

Clay minerals are structured compounds that have two basic building blocks or units which can be put together in various orders to define the different species of clay mineral. One of the units is made up of two sheets of oxygen atoms or hydroxyl groups between which aluminum, magnesium, or iron is held in an octahedral coordination equidistant from six oxygen atoms or hydroxyl groups (See Figure 1). When the unit contains aluminum it is the gibbsite structure in which only two-thirds of the possible bonding positions are filled giving it the formula $Al_2(OH)_6$. When magnesium is present the structure is called brucite, in which all the positions are filled and the formula is $Mg_3(OH)_6$. The OH-to-OH bond distance in these units is 0.294nm and the space available for octahedral coordination of the ions is about 0.061nm. Many of these units can be formed together to give a sheet of octahedral units with a thickness of about 0.505nm.[3]

The other unit present in the clay lattice is a silica tetrahedron. This tetrahedron has a silicon atom at the center with four equidistant oxygen atoms or hydroxyl groups at the apices. Several of these units come together to form a larger hexagonal unit which can join with others to form a sheet with the composition $Si_4O_6(OH)_4$ (See Figure 2). The O-O bond angle is found to be 120° and the bond distance is 0.255nm, giving a space for tetrahedral ion coordination of about 0.055nm. A thickness of about 0.499nm is found for this unit.[3]

The lattice structure of a clay mineral is made up of sheets of

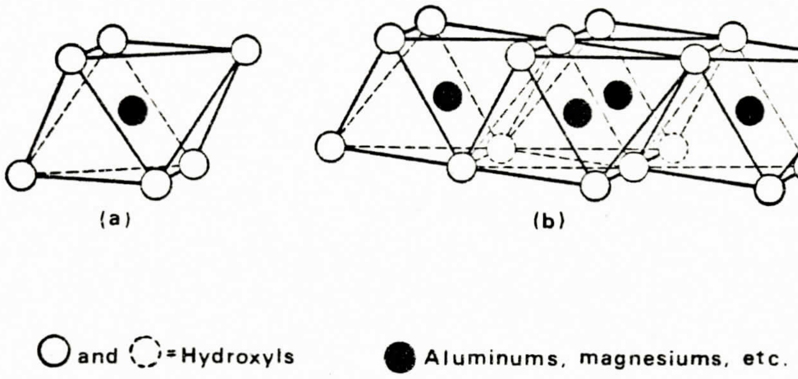

Figure 1. Diagrammatic sketch showing (a) single octahedral unit and (b) the sheet structure of the octahedral units.

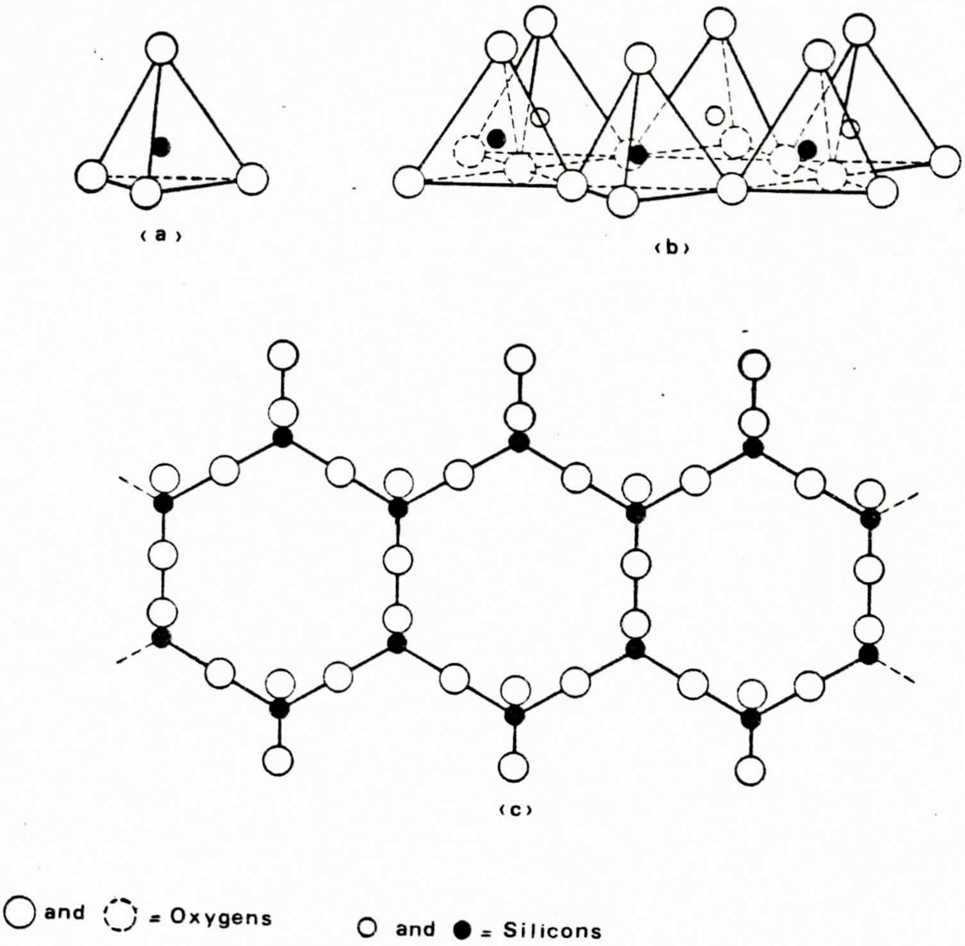

Figure 2. Diagrammatic sketch showing (a) single silica tetrahedron and (b,c) sheet structure of silica tetrahedrons arranged in a hexagonal network.

the silicon tetrahedral and gibbsite or brucite octahedral units. The orientation of these sheets and the ratio of tetrahedra to octahedra determine which clay mineral is formed (See Table 1).

C. Structural Properties of Kaolinite

Kaolinite has a crystalline two-layer structure. One layer is composed of a gibbsite octahedral sheet and the other is a silica tetrahedral sheet. The two layers are oriented in such a way that they form a unit that has the tips of the silica tetrahedra and one of the layers of the octahedral sheet forming a common layer (See Figure 3). This structure was outlined by Pauling[5] and later confirmed by Gruner.[6]

The theoretical structural formula for kaolinite is $(OH)_8Si_4O_{10}Al_4$, which gives a theoretical composition of 46.54% SiO_2, 39.50% Al_2O_2 and 13.96% H_2O.[3]

D. Structural Properties of Montmorillonite

The basic structural unit of montmorillonite is a three-layered type. This unit contains an alumina octahedral sheet with two silica tetrahedral sheets. The alumina sheet lies between the two tetrahedral silica sheets, with the tips of each of the tetrahedral sheets forming a common layer with one of the hydroxyl layers of the octahedral sheet (See Figure 4). Figure 4 shows that there is a space between the structural units that can contain water or other polar solvents. This structural feature will prove important in the ability of montmorillonite to exchange cations. The generally accepted structure of montmorillonite was suggested by Hofmann, Endell, and Wilm[7] and their findings were later modified by Maegdefrau and Hofmann,[8] Marshall,[9] and Hendricks.[10]

Table I. Classification of the Clay Minerals

- I. Amorphous
  - Allophane group
- II. Crystalline
  - A. Two-layer type (sheet structures composed of units of one layer of silica tetrahedrons and one layer of alumina octahedrons)
    - 1. Equidimensional
      - Kaolinite group
        - Kaolinite, nacrite, etc.
    - 2. Elongate
      - Halloysite group
  - B. Three-layer types (sheet structures composed of two layers of silica tetrahedrons and one central dioctahedral or trioctahedral layer)
    - 1. Expanding lattice
      - a. Equidimensional
        - Montmorillonite group
          - Montmorillonite, sauconite, etc.
        - Vermiculite
      - b. Elongate
        - Montmorillonite group
          - Nontronite, saponite, hectorite
    - 2. Nonexpanding lattice
      - Illite group
  - C. Regular mixed-layer types (ordered stacking of alternate layers of different types)
    - Chlorite group
  - D. Chain-structure types (hornblende-like chains of silica tetrahedrons linked together by octahedral groups of oxygens and hydroxyls containing Al and Mg atoms)
    - Attapulgite
    - Sepiolite
    - Palygorskite

Taken From: Grim, F. J. "Clay Minerology", 2nd ed.: McGraw-Hill: New York, 1968.

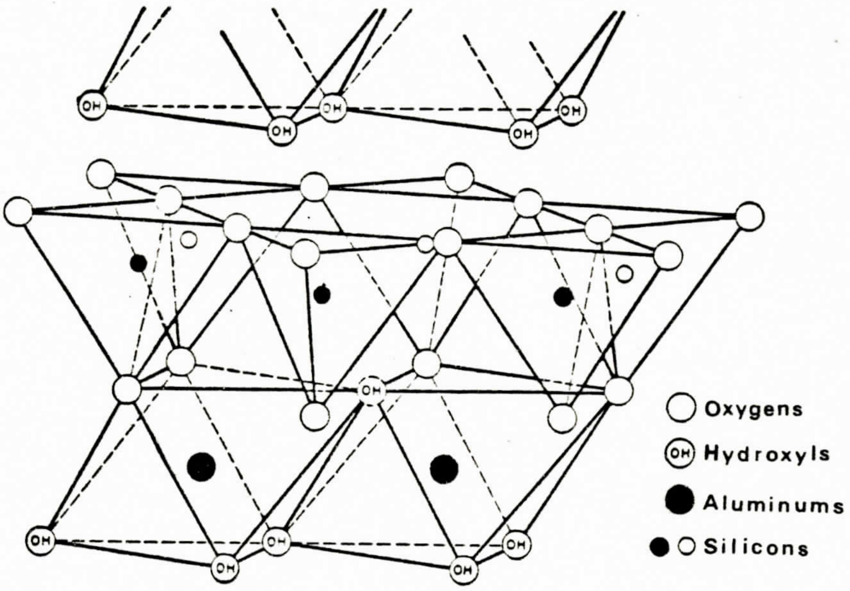

Figure 3. Diagrammatic sketch of the structure of the kaolinite layer, after Gruner.[6]

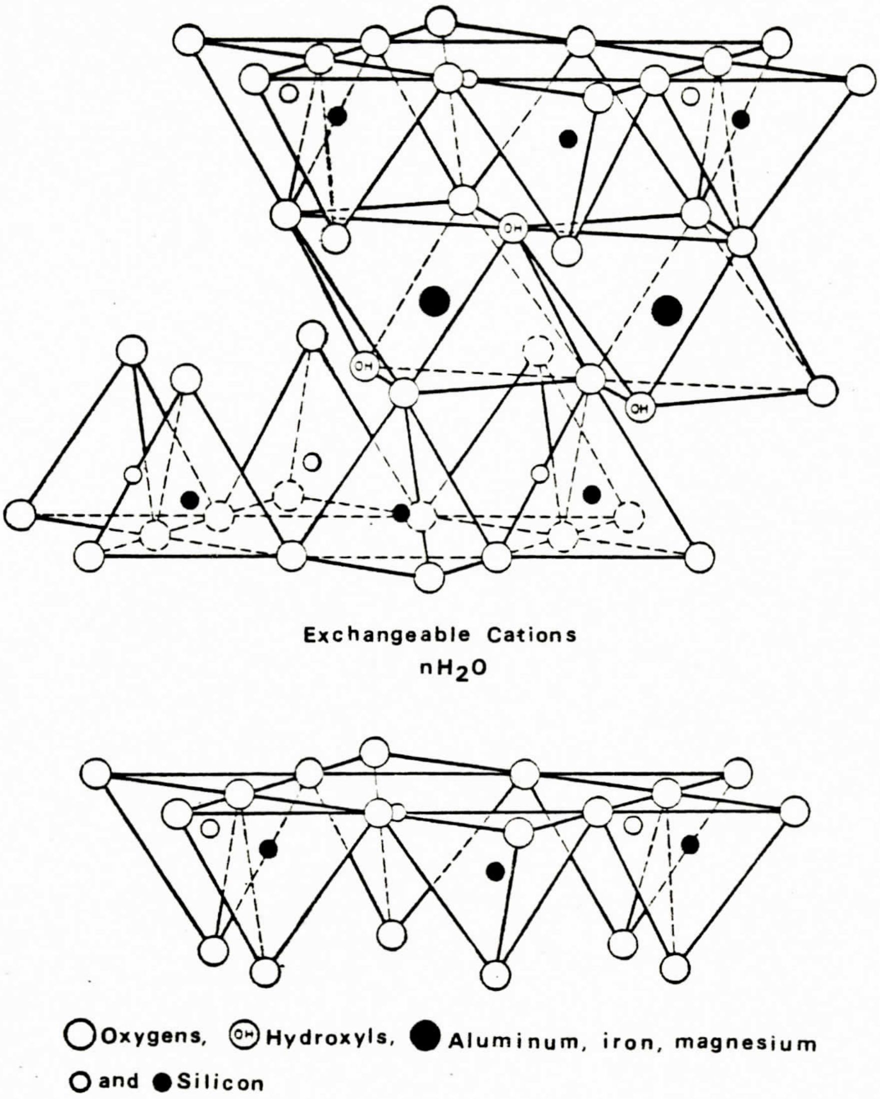

Figure 4. Diagrammatic sketch of the structure of Montmorillonite according to Hofmann, Endell, and Wilm,[7] Marshall,[9] and Hendricks.[10]

The theoretical structural formula for montmorillonite is $(OH)_4Si_8Al_4O_{20}\cdot nH_2O$, giving a theoretical composition of 66.7% SiO_2, 28.3% Al_2O_3, and 5.0% H_2O.[3]

E. Structural Properties of Illite

Illite has a structure that is almost the same as that of montmorillonite. Illite also has a three layer structural unit that contains two silica tetrahedral sheets and one alumina octahedral sheet. The orientation of these sheets is the same as that found in the montmorillonite structure. The only real structural difference between these two clays is that in illite about one sixth of the silicons are replaced by aluminum, causing a charge imbalance. This imbalance is satisfied by a potassium ion which is located between the unit layers, in perforations in the surface oxygen layer (See Figure 5). It is possible for calcium, magnesium, and hydrogen cations to replace the potassium without any change in the illite structure. The structure of illite or mica type clay minerals has been described by Pauling,[11] Mauguin,[12] Jackson and West,[13] Winchell,[14] and Hendricks and Jefferson.[15]

The theoretical structural formula for illite with 25% aluminum substitution for silicon is $K_2(Si_6Al_2)Al_4O_{20}(OH)_4$ giving a theoretical composition of 11.8% K_2O, 45.2% SiO_2, 38.5% Al_2O_3, and 4.5% H_2O.[3]

F. Adsorbtivity of Clay Minerals

Clay minerals can react in an aqueous system in three ways: cation exchange or adsorption, simple mineral dissolution and mineral phase equilibration. Since this research is only concerned with the ability of a clay mineral to adsorb metal ions only cation exchange or adsorption will be discussed in detail.

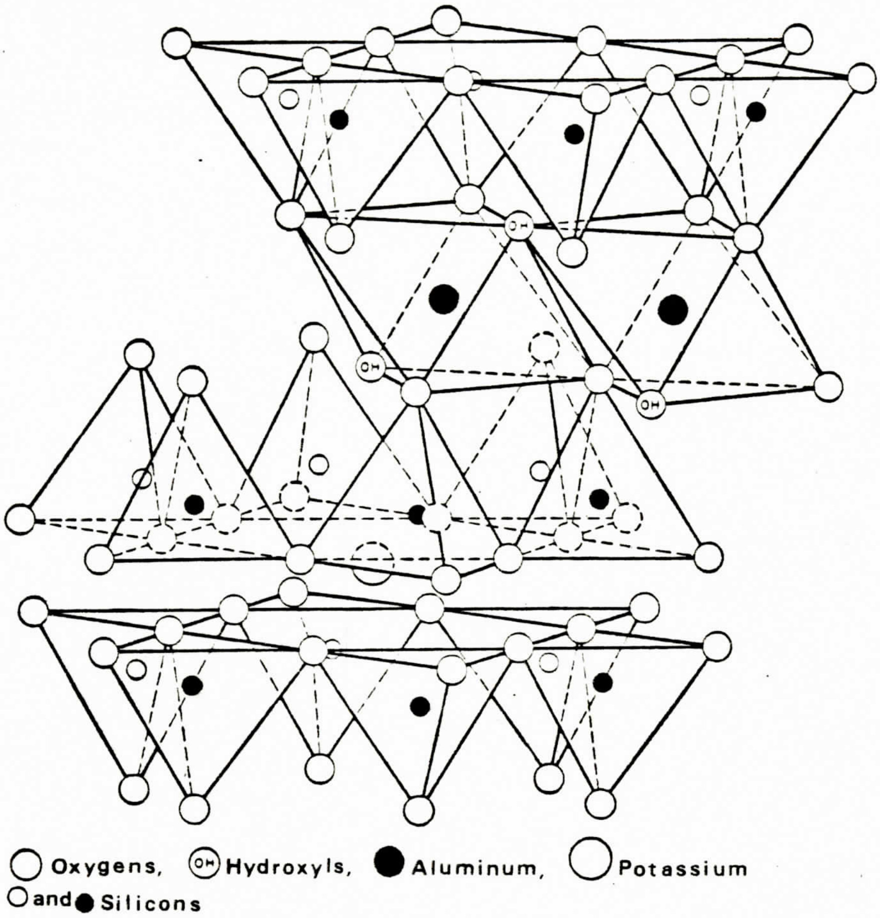

Figure 5. Diagrammatic sketch of Illite.

In the field of clay mineral research the term adsorptivity and cation or anion exchange are generally used interchangeably and denote the same process. In this paper this terminology will also hold the same meaning.

The major cause of adsorptivity in clay minerals is the formation of a net negative surface charge that forms about the faces or edges of the clay crystal units. The intensity of this net negative charge will determine the extent to which the clay mineral will adsorb cations. In general there are three possible causes for the formation of this net negative charge.

One way that this negative charge comes about is due to broken bonds around the edges of the silica-alumina units. These broken bonds will tend to form on noncleavage surfaces and the resulting net charge can be eliminated by the adsorption of a cation.

A second way that a net negative charge could be formed is by the substitution of a trivalent aluminum for a quadrivalent silicon in the tetrahedral sheet or by substitution of ions of lower valence, particularly magnesium, for aluminum in the octahedral sheet of the lattice structure. Both types of substitution cause the charge to be formed on the cleavage surfaces of the layered clay minerals and this is where exchange will occur. The net charge that is produced by substitution in the octahedral sheet has to act through a greater distance than that produced by substitution in the tetrahedral sheet and would thus produce a weaker bonding force over the cation. In general, this weak bond is the major cause of cation exchange, whereas the greater force due to substitution in the tetrahedral sheet seems to make the potassium in illite clays almost impossible to exchange.

The third way by which this negative charge may be produced is by the loss of a hydrogen from the exposed hydroxyl groups. The loss of these hydrogens can be caused by breaking the oxygen hydrogen bond or by direct cation exchange.[3]

In kaolinite the major cause of cation exchange is broken bonds. Because kaolinite has a sheet of hydroxyls on one side of the basal cleavage plane, loss of hydrogen from these hydroxyls will also be important in determining its ability to exchange. Kaolinite shows no substitution in either the octahedral or tetrahedral sheet.

In montmorillonite and illite only about 20% of the cation exchange capacity is due to broken bonds or loss of hydrogen from hydroxyl groups. The remaining 80% of the capacity is due to substitution within the lattice structure.[3]

There is a wide range of factors and conditions that can affect the cation exchange capacity of a clay mineral. The amount of nonclay mineral found in a clay will have an effect on the clay's cation exchange capacity. The particle size or amount of crystallinity can affect cation exchange with the smaller particle size and greater number of broken bonds generally giving the greater cation exchange capacity. The pH of the solution can affect the extent to which the hydrogens can be removed from the hydroxyl groups so that the higher the pH the greater the exchange capacity.[2] The period of time that the clay is exposed to the cation and the concentration of the cation itself can also affect the exchange capacity. Because there is such a wide range of factors that can effect the cation exchange capacity of the different clays, it is important to hold these variables constant whenever possible, when making comparisons. Since the exchangeability of the clay will also depend on the ratio of ionic charge to ionic size of the cation, as in any cation replacement series, it is also important that any comparison between clays be made with studies using the same cations.

Because it is a rare occasion that researchers will run an experiment under the same conditions and with the same materials, cation exchange capacities are generally reported as ranges in the literature.

CHAPTER III

EXPERIMENTAL

A. Clay Mineral Characteristics

1. Illite

The illite used in this study was from Silver Hill, Montana, and was obtained from Source Clay Minerals Repository, Dept. of Geology, University of Missouri. The clay was received as small dark blue green chunks and was ground in a mortar and pestle to a fine powder. The illite was dried in an oven at 105°C for 8 hours and then stored in a desiccator.

2. Montmorillonite

The montmorillonite used in this study is a Ca-montmorillonite from Gonzales County, Texas, and was obtained from Source Clay Minerals Repository, Dept. of Geology, University of Missouri. The clay was received as a fine white powder and was dried in an oven at 105°C for 8 hours and stored in a desiccator.

3. Kaolinite

The kaolinite used in this study is a well crystallized kaolin from Washington County, Georgia, and was obtained from Source Clay Minerals Repository, Dept. of Geology, University of Missouri. The kaolin was received as a fine white powder and was dried in an oven at 105°C for 8 hours and stored in a desiccator.

B. Preparative Procedures

1. Preparation of Hexammine Cobalt(III) Nitrate

$(Co(NH_3)_6)(NO_3)_3$ - Hexammine cobalt(III) nitrate is prepared as follows: Eighteen grams (.06mol) of cobalt nitrate 6-hydrate (Fisher, Certified) is dissolved in 100mL of H_2O, and in the order given, 20g

(.25 mol) of ammonium nitrate (Fisher, Certified), .5g activated charcoal, and 45mL of concentrated ammonia are added. This solution is air oxidized by slowly bubbling air through it for about 4 hours. The crystals produced and the charcoal were filtered by suction and washed with 100mL of ice water. The crystals were then dissolved on a steam bath in 700mL of water that was acidified with nitric acid. The charcoal was removed by filtration and the solution was treated with 50mL of concentrated nitric acid and allowed to cool. The precipitated salt was removed by filtration and washed with ice water. The salt was recrystallized by redissolving it on a steam bath in 500mL of water acidified with nitric acid, and filtered. The filtrate was treated with 25mL of concentrated nitric acid and cooled in an ice bath. The crystals were filtered by suction and washed with water and alcohol and dried at $100^{o}C$.[16]

An infrared spectrum of the crystal suspended in a KBr matrix was obtained using a Perkin-Elmer 137 (See Figure 6). The spectrum was compared to literature data and was found to be that of hexammine cobalt(III) nitrate.[17,18]

2. Test Solution Preparation

The solutions used were prepared using volumetric glassware, a Mettler Type M52A Gram Atomic balance, and distilled water. The pH of the solutions was adjusted to the desired values by the dropwise addition of very dilute sodium hydroxide and/or nitric acid.

C. Apparatus

The electrochemical apparatus used in this study consisted of two basic parts: a controlled potential dc power supply and an electrolytic cell. A 250mL Nalgene bottle was used as the reaction cell in the con-

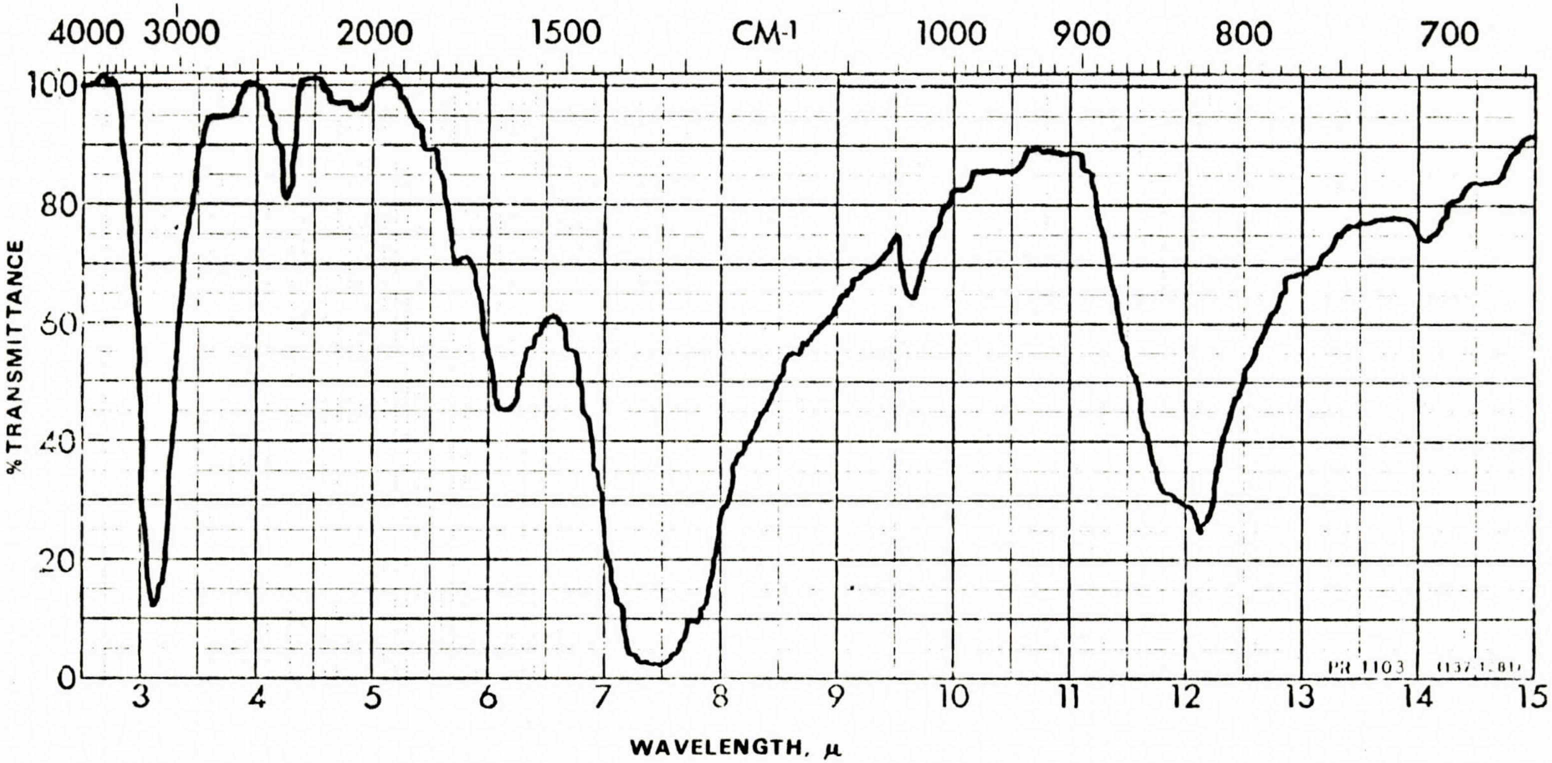

Figure 6. Infrared spectrum of the $(Co(NH_3)_6)(NO_2)_3$ sample.

trol experiments.

1. Controlled DC Power Supply

The controlled power supply is made up of a Kepco Variable DC Power Supply, Model PR-15-30M, which feeds the electrolytic cell through the control and monitoring circuit diagramed in Figure 7. The control part of this circuit is a slide wire rheostat which is a fine adjust for the dc potential that reaches the cell. The monitoring part of the circuit is made up of dc voltmeters for the power supply and for the cell and a galvanometer to sense any current which is passed through the electrolytic cell.

2. Electrolytic Cell

The electrolytic cell used in this study was constructed from a 250mL Nalgene bottle. The cell was fitted with a Number 22 cork through which a Corning Ag/AgCl reference electrode (Cat. No. 476106) and carbon rod were inserted as illustrated in Figure 8. Nalgene was chosen for the cell body and the cork was covered with Para-film M so that the cell would adsorb none of the metal ions.

The cell was tested under conditions similar to those under which it would be used in order to make sure that it would not adsorb metal ions from the test solutions and thus cause error in the adsorption studies. The cell was filled with 100mL of a 40ppm solution of cobalt ion and a 3V potential was applied across the electrodes for seven days. At the end of the seventh day the solution was tested for cobalt concentration and it was found that no change in concentration had taken place. On the basis of this test it was assumed that the cell should introduce no error in the adsorption studies.

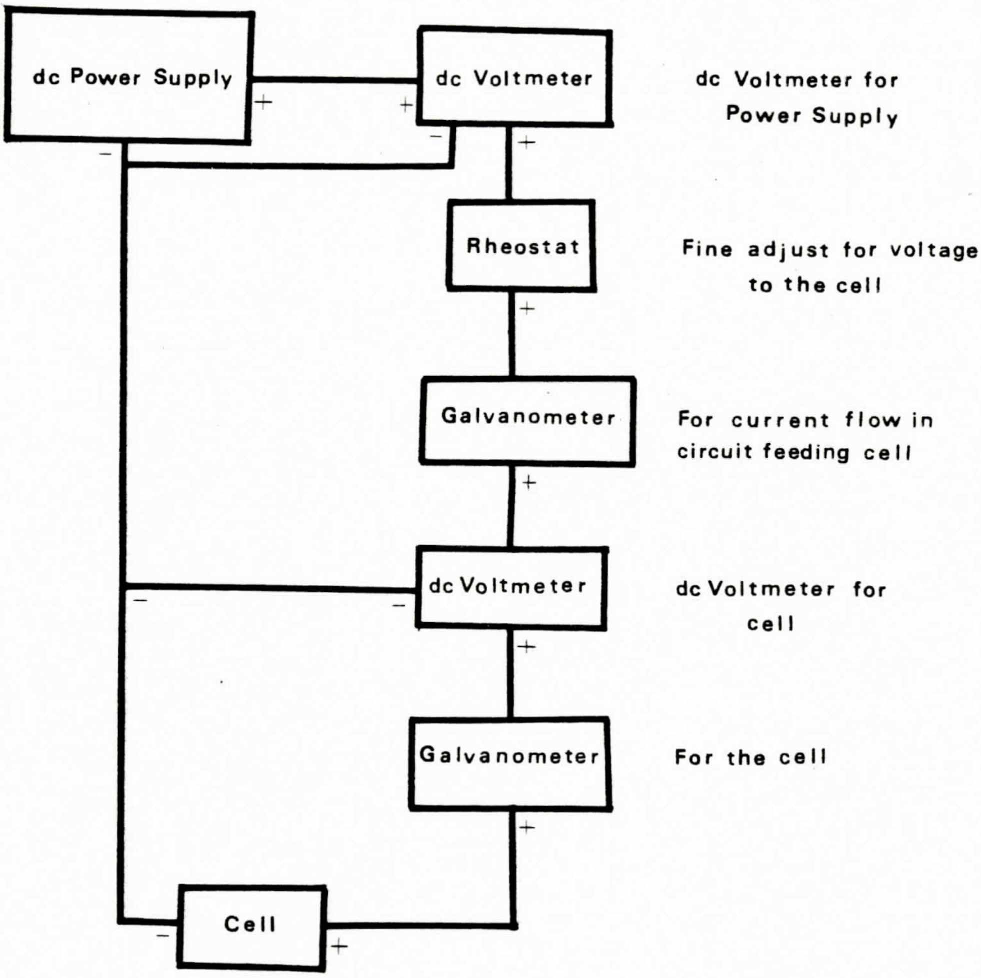

Figure 7. Block diagram of the control and monitoring circuit.

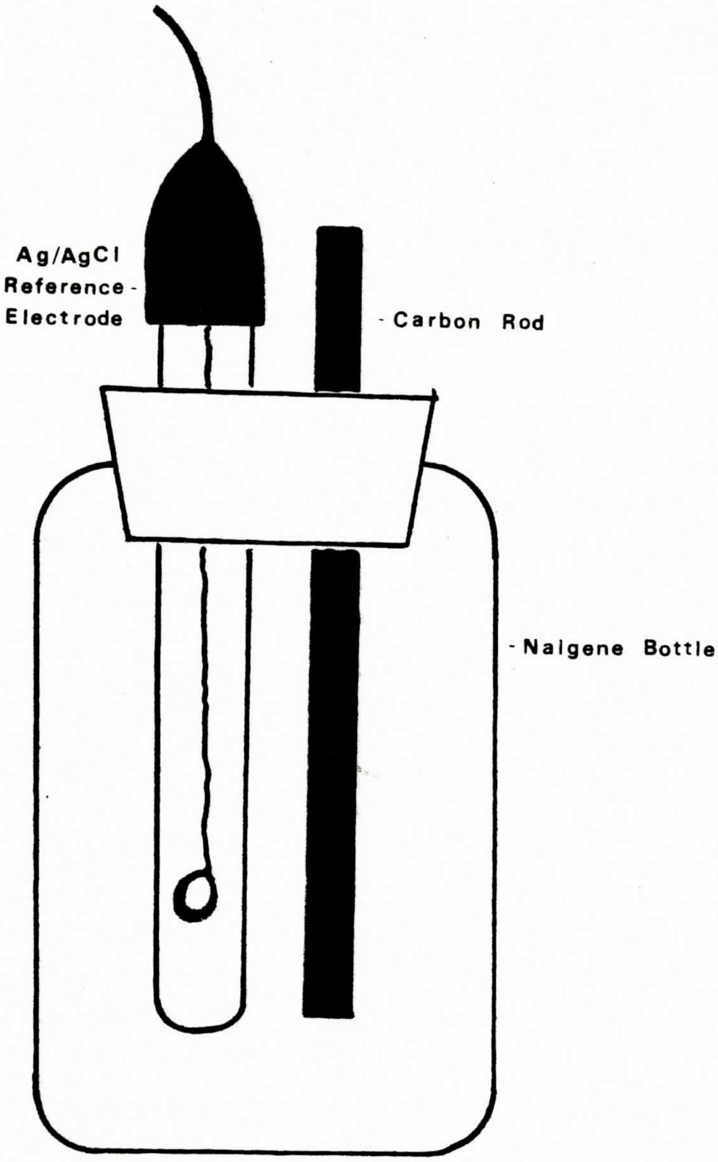

Figure 8. Cell used in applied potential studies.

D. Procedures

The experiments conducted in this study were carried out in duplicate, with one reaction cell having an applied potential and with the control reaction cell run under the same conditions but without the applied potential. Since all other conditions were held the same, any differences in the results obtained with these two reaction cells could be attributed to the applied potential.

Each cell contained 0.5g of the appropriate clay, 100mL of a 40ppm cobolt solution that had been adjusted to the proper pH, and a Teflon-coated stirring bar. This gave a 5g/L clay concentration and allowed for the adsorption of up to 0.004g of cobalt from the solution. The electrolytic cell was held at the desired potential with the carbon electrode as the anode and the cells were allowed to react for seven days during which time they were stirred twice a day with the magnetic stirring bar. At the end of the reaction time each cell was stirred for a period of 30 minutes, 15mL of the solution was placed in a centrifuge tube, and the pH of the remaining solution was determined. The 15mL aliquots were centrifuged for 15 minutes in an IEC Clinical Centrifuge at about 3000rpm. The supernatant liquid was then tested for cobalt concentration by atomic absorption spectrometry.

The seven day reaction time was chosen because Koppelman and Dillard[2] found that this was sufficient time to allow the clays to come to equilibrium with the reaction solutions. The potentials that were used in the electrochemical studies were 0.25V for the cells containing Co(II) solutions and 1.85V for the ones containing Co(III). These potentials were chosen from the half reaction potentials in order to prevent any change in oxidation state of the cobalt ion throughout the experiment. As it can be seen from the reduction potentials

$$Co^{+3} + e^- \longrightarrow Co^{+2} \qquad E^o = 1.84V \qquad (1)$$

$$Co^{+2} + 2e^- \longrightarrow Co \qquad E^o = -.28V \qquad (2)$$

$$Co(NH_3)_6{}^{+3} + e^- \longrightarrow Co(NH_3)_6{}^{+2} \qquad E^o = .1V \qquad (3)$$

the Co(II) ion is the most stable form of cobalt in an aqueous system. The 0.25V potential used in the experiments with Co(II) was chosen as a precaution to keep the Co(II) from being reduced and to determine the effect of a potential on the adsorptivity of a clay mineral. The high reduction potential of Co(III) shows that it can easily be reduced to the more stable Co(II) species and shows the need for taking precautions for preventing this reduction from occurring. The 1.85V potential used in the experiments with Co(III) was chosen because it is high enough to prevent the reduction of both $Co(NH_3)_6{}^{+3}$ and Co^{+3} and should assure the presence of only Co(III) in the reaction solutions.

E. Analytical Determinations

The concentration of cobalt in the test solutions was determined by a standard atomic absorption method using a Jarrell-Ash Model JA82-270 atomic absorption spectrometer. The spectrometer is equipped with a Triflame burner and in the determination of cobalt concentration employs an air/acetylene flame and a single element hollow cathode lamp (Co, Tekmar No. 18014).

The method used to determine cobalt concentration in the test solutions was standard in that measurements were made at 240.7nm on both unknown and standard solutions. Graphs of % absorbance vs. concentration were prepared for the standard solutions, and from these plots and the absorbance measurements of the test solutions the concentrations were obtained.

A good working range of the spectrometer for cobalt concentration was experimentally determined to be between 0 and 50ppm, so standards in this range were prepared by appropriate dilutions of a 100ppm solution of cobalt nitrate 6-hydrate. The method just described was then used to determine both final and initial test solution concentrations. The difference in these two concentrations could then be used to determine the grams of cobalt adsorbed per gram of clay.

The adsorption of metal ion by the clay is defined in terms of the ratio

$$A = \frac{C_1 - C_2}{M \times 1000} \tag{4}$$

in which A is the adsorption expressed in grams of cobalt per gram of clay, C_1 is the initial concentration of cobalt in ppm, C_2 is the final concentration of cobalt in ppm, and M is the mass of clay in the reaction cell.

F. pH Measurements

pH measurements were made by using a Corning No. 476115 combination pH electrode in conjunction with an Orion Research Model 701A pH Meter. The electrode was calibrated using pH 4.00 and 6.88 buffer solutions and all readings were taken only after there was no change in pH (±.01 units) for one minute.

CHAPTER IV

RESULTS AND DISCUSSION

The purpose for this research was to investigate the observation made by Koppelman and Dillard[2] that some clay minerals contain Co(II) in some of their exchange sites even though they were in contact with Co(III) solutions. Through this investigation it should be determined whether the presence of the Co(II) is due to the reduction of Co(III) in solution prior to adsorption or whether it is being reduced as part of the adsorption process.

A. Cobalt(II) Adsorption by Clays

The study of the adsorption of cobalt(II) from aqueous solutions by clay minerals was undertaken in order to: (1) test the relationship between the amount of Co(II) adsorbed and pH; (2) determine the effect of oxidation state on adsorptivity of the clays; and (3) determine whether an applied potential would have any effect on the adsorptivity of the clay minerals.

Figures 9 - 12 show the calibration curves which were generated for Co(II) in this study. Using these calibration curves and equation 4, the adsorptivity of each clay was determined both with and without an applied potential for control of the oxidation state of Co(II). These experiments were conducted at pH=3 and pH=7, and these data are summarized in Tables II - IV. The data reported by Koppelman are summarized in Table V for comparison with the present study.

Kaolinite, illite, and montmorillonite each showed increased adsorptivity at high pH, with illite having the most dramatic increase. These results confirm the findings of Koppelman (See Table V), who reported that increasing the pH caused an increase in cation exchange,

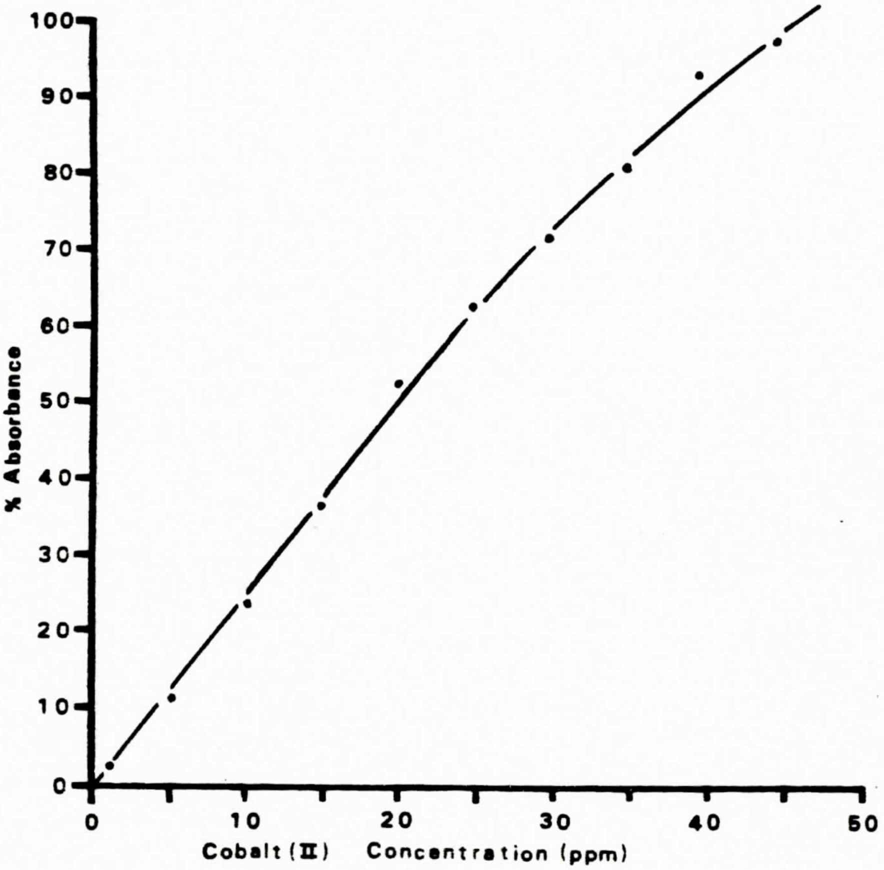

Figure 9. % Absorbance vs. Co(II) concentration at pH=3 (Run #1).

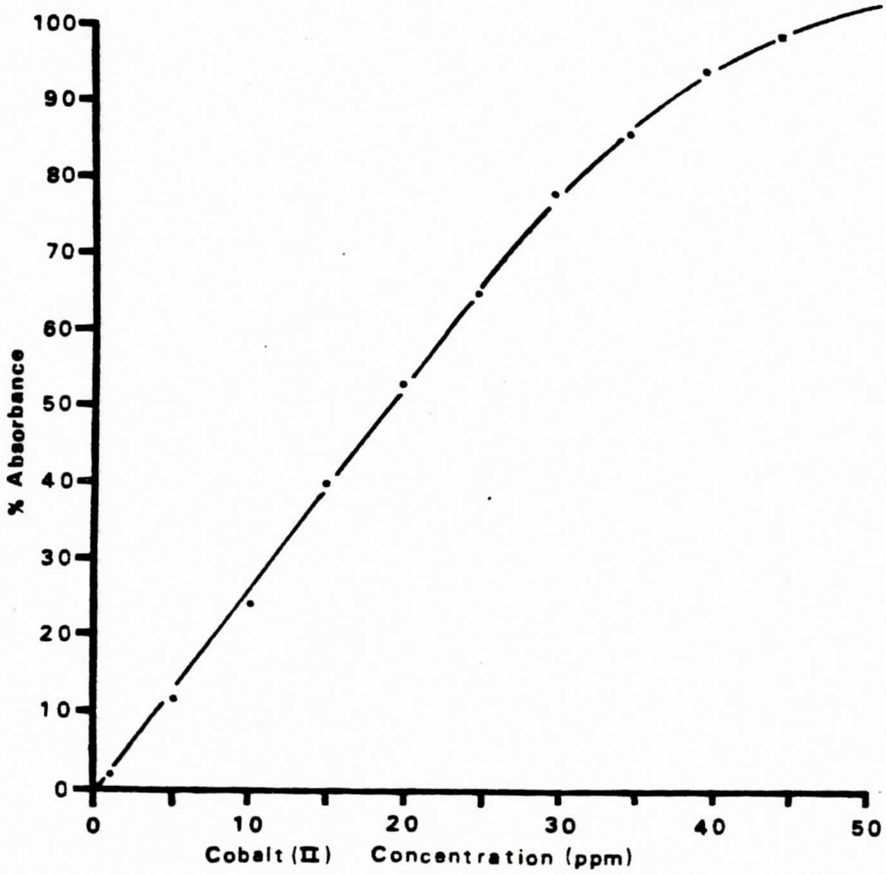

Figure 10. % Absorbance vs. Co(II) concentration at pH=3 (Run #2).

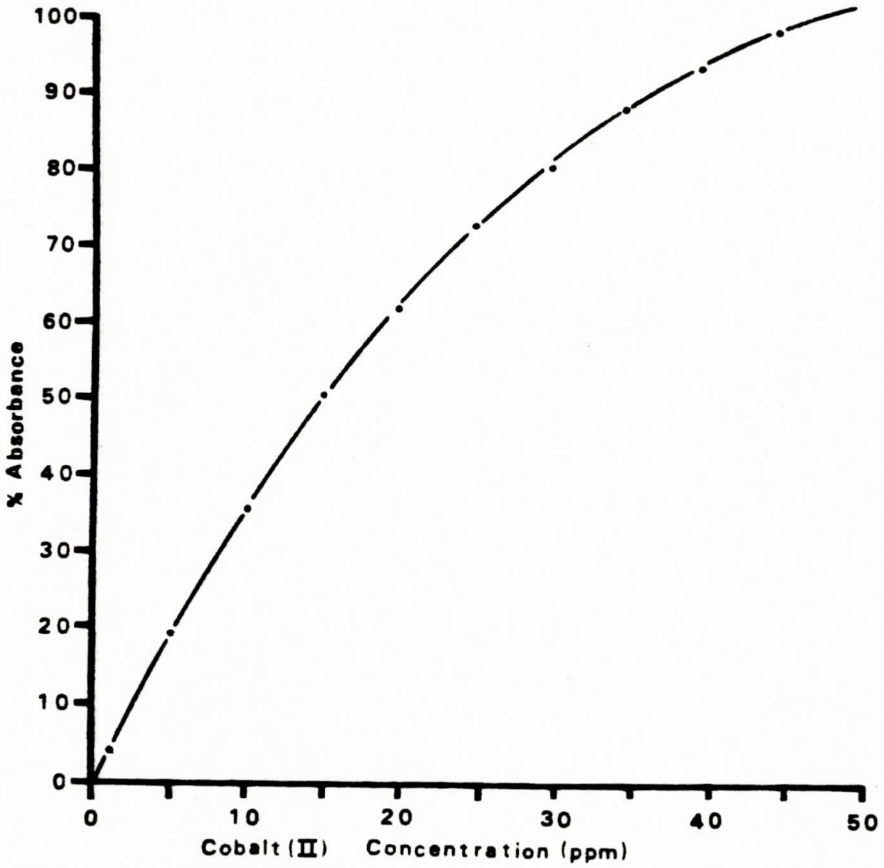

Figure 11. % Absorbance vs. Co(II) concentration at pH=7 (Run #1).

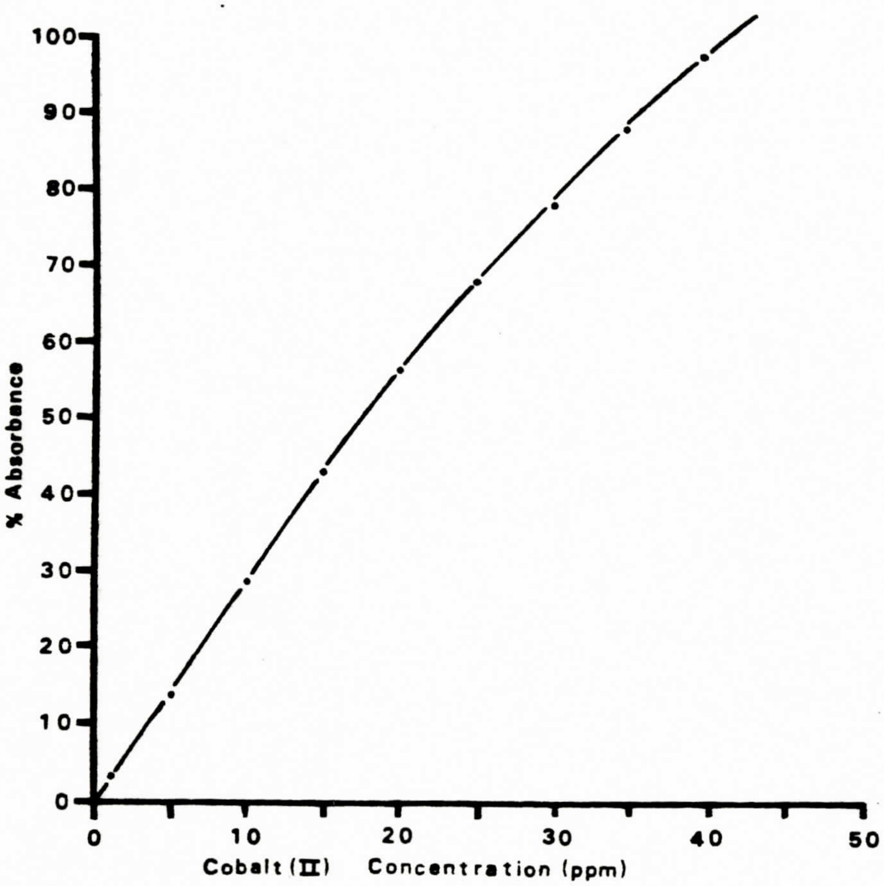

Figure 12. % Absorbance vs. Co(III) concentration at pH=7 (Run #2).

Table II. Solution Data for Co(II) and Kaolinite at pH=3 and 7.

	pH=3				pH=7			
	Applied Potential		Control		Applied Potential		Control	
Run	1	2	1	2	1	2	1	2
% Absorbance	90.5	92.5	91.0	92.5	94.2	92.0	92.5	91.5
Initial Concentration*	39.7	39.5	39.7	39.5	40.0	39.0	40.0	39.0
Final Concentration*	39.3	38.5	39.3	38.5	38.8	36.5	38.0	36.0
Initial pH	3.01	3.00	3.01	3.00	7.01	6.97	7.01	6.97
Final pH	3.00	2.98	2.99	2.97	5.04	4.70	5.06	4.83
Adsorptivity**	$9.0x10^{-5}$	$1.1x10^{-4}$	$9.0x10^{-5}$	$1.1x10^{-4}$	$2.4x10^{-4}$	$2.5x10^{-4}$	$2.0x10^{-4}$	$2.9x10^{-4}$
Average Adsorptivity**	$1.0x10^{-4}$		$1.0x10^{-4}$		$2.45x10^{-4}$		$2.45x10^{-4}$	

*All concentrations are in ppm.

**Adsorptivities are in grams of cobalt per gram of clay.

Table III. Solution Data for Co(II) and Illite at pH=3 and 7.

	pH=3				pH=7			
	Applied Potential		Control		Applied Potential		Control	
Run	1	2	1	2	1	2	1	2
% Absorbance	72.5	78.0	73.0	77.2	59.5	58.5	5.85	59.0
Initial Concentration*	39.7	39.5	39.7	39.5	40.0	39.0	40.0	39.0
Final Concentration*	29.3	29.8	29.5	29.5	23.0	20.8	22.5	21.0
Initial pH	3.01	3.00	3.01	3.00	7.01	6.97	7.01	6.97
Final pH	3.45	3.50	3.40	3.48	7.50	7.60	7.45	7.75
Adsorptivity**	$2.1\mathrm{x}10^{-3}$	$1.9\mathrm{x}10^{-3}$	$2.0\mathrm{x}10^{-3}$	$2.0\mathrm{x}10^{-3}$	$3.4\mathrm{x}10^{-3}$	$3.6\mathrm{x}10^{-3}$	$3.5\mathrm{x}10^{-3}$	$3.6\mathrm{x}10^{-3}$
Average Adsorptivity**	$2.0\mathrm{x}10^{-3}$		$2.0\mathrm{x}10^{-3}$		$3.5\mathrm{x}10^{-3}$		$3.55\mathrm{x}10^{-3}$	

*All concentrations are in ppm.

**Adsorptivities are in grams of cobalt per gram of clay.

Table IV. Solution Data for Co(II) and Montmorillonite at pH=3 and 7.

	pH=3				pH=7			
	Applied Potential		Control		Applied Potential		Control	
Run	1	2	1	2	1	2	1	2
% Absorbance	42.5	45.6	43.0	45.6	52.4	41.0	66.4	42.0
Initial Concentration*	39.7	39.5	39.7	39.5	40.0	39.0	40.0	39.0
Final Concentration*	16.8	17.5	17.0	17.5	15.0	14.5	18.8	15.0
Initial pH	3.01	3.00	3.01	3.00	7.01	6.97	7.01	6.97
Final pH	3.45	3.40	3.48	3.42	6.64	6.83	6.64	6.90
Adsorptivity**	4.6×10^{-3}	4.4×10^{-3}	4.5×10^{-3}	4.4×10^{-3}	5.0×10^{-3}	4.9×10^{-3}	4.6×10^{-3}	4.8×10^{-3}
Average Adsorptivity	4.6×10^{-3}		4.5×10^{-3}		4.95×10^{-3}		4.7×10^{-3}	

*All concentrations are in ppm.

**Adsorptivities are in grams of cobalt per gram of clay.

Table V. Solution Data for Co(II) Adsorbance Reported by Koppelman.[2]

Clay	Illite		Kaolinite	
pH	3	7	3	7
Initial Concentration*	105	102	105	102
Final Concentration*	96	86	100	97
Initial pH	3.03	6.99	3.03	6.99
Final pH	3.59	6.03	3.01	4.40
Adsorptivity**	$1.8\text{x}10^{-3}$	$3.2\text{x}10^{-3}$	$1.0\text{x}10^{-3}$	$1.0\text{x}10^{-3}$

*All concentrations are in ppm.
**Adsorptivities are in grams of cobalt per gram of clay.

especially for the illite system.

It was found that there was little or no change in adsorptivity with the application of a potential to the reaction cell. Any difference in the adsorptivities obtained from the applied potential and control systems are probably due to experimental error and not to any effect that the potential had on either the metal ions or the clays.

The changes in pH that took place in most of the solutions are due to either the cation exchange of hydrogen or to the making or breaking of hydroxyl and hydrogen bonds in the clay lattice structure.

B. Cobalt(III) Adsorption by Clays

The study of the adsorption of cobalt(III) from aqueous solution by clay minerals was undertaken in order to: (1) obtain data that can be compared with the Co(II) adsorption to determine the effect of oxidation state on adsorptivity of the clays; (2) determine whether an applied potential has any effect on the adsorptivity of the clays; and (3) determine whether Co(III) is reduced in solution to Co(II) and then adsorbed or whether it is reduced in the adsorption process.

The calibration curves for Co(III) which were generated in this study are shown in Figures 13 - 14, and the solution data for cobalt (III) adsorption on the three clays at pH=3 are summarized in Tables VI - VIII. The solution data reported by Koppelman[2] for the adsorption of Co(III) at pH=3 for illite and kaolinite are summarized in Table IX for comparison with this study. Each of the clays exhibited a larger adsorptivity for Co(III) than for Co(II). This shows, as Koppelman found, that the higher the oxidation state of a cation the higher its adsorptivity. Since the adsorption process of a clay mineral is generally a cation exchange reaction, clays would be expected to follow a

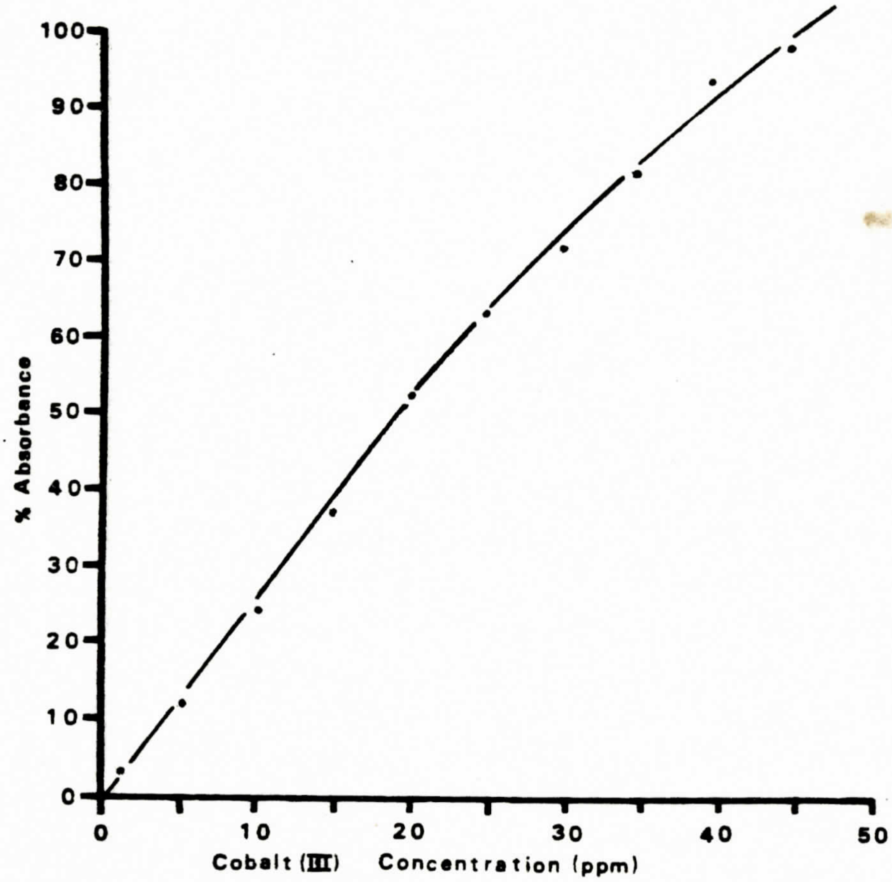

Figure 13. % Absorbance vs. Co(III) concentration at pH=3 (Run #1).

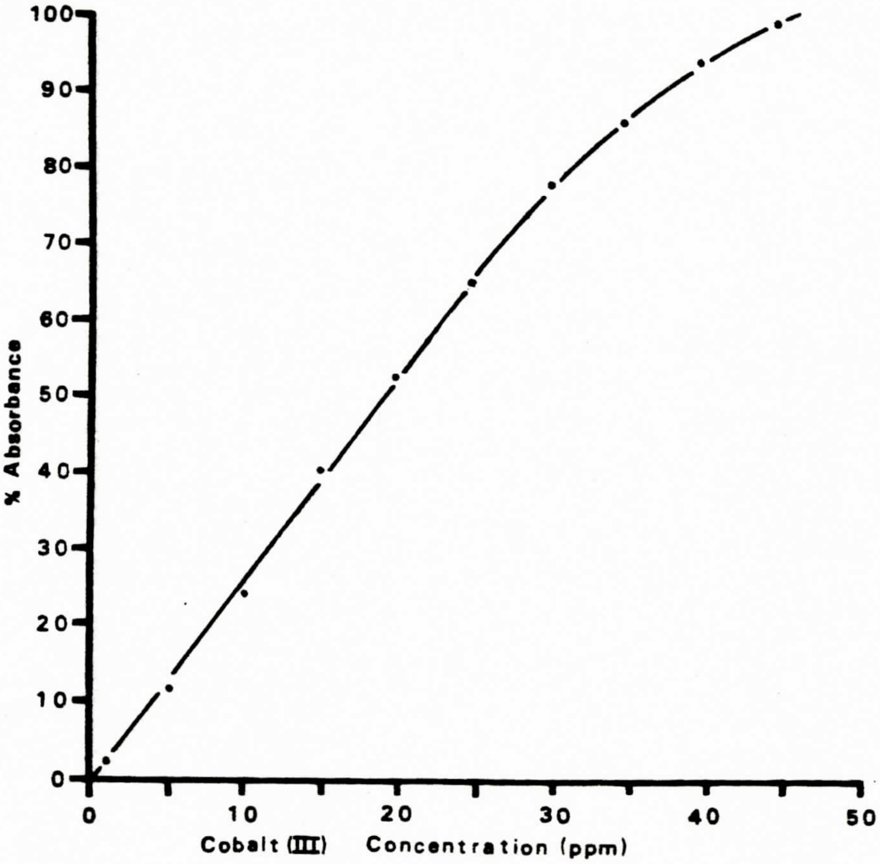

Figure 14. % Absorbance vs. Co(III) concentration at pH=3 (Run #2).

Table VI. Solution Data for Co(III) and Kaolinite.

	pH=3			
	Applied Potential		Control	
Run	1	2	1	2
% Absorbance	86.5	88.5	86.5	88.0
Initial Concentration*	41.0	39.5	41.0	39.5
Final Concentration*	36.7	35.5	36.7	35.0
Initial pH	3.01	3.00	3.01	3.00
Final pH	2.91	2.89	3.04	3.05
Adsorptivity**	$4.3\text{x}10^{-4}$	$4.0\text{x}10^{-4}$	$4.3\text{x}10^{-4}$	$4.5\text{x}10^{-4}$
Average Adsorptivity**	$4.2\text{x}10^{-4}$		$4.4\text{x}10^{-4}$	

*All concentrations are in ppm.
**Adsorptivities are in grams of cobalt per gram of clay.

Table VII. Solution Data for Co(III) and Illite.

	pH=3			
	Applied Potential		Control	
Run	1	2	1	2
% Absorbance	67.5	69.0	67.5	70.0
Initial Concentration*	41.0	39.5	41.0	39.5
Final Concentration*	27.0	26.5	27.0	26.5
Initial pH	3.01	3.00	3.01	3.00
Final pH	5.28	5.24	6.55	6.45
Adsorptivity**	$2.8x10^{-3}$	$2.6x10^{-3}$	$2.8x10^{-3}$	$2.6x10^{-3}$
Average Adsorptivity**	$2.7x10^{-3}$		$2.7x10^{-3}$	

*All concentrations are in ppm.
**Adsorptivities are in grams of cobalt per gram of clay.

Table VIII. Solution Data for Co(III) and Montmorillonite.

	pH=3			
	Applied Potential		Control	
Run	1	2	1	2
% Absorbance	18.5	17.5	18.5	15.5
Initial Concentration*	41.0	39.5	41.0	39.5
Final Concentration*	7.5	7.0	7.5	6.5
Initial pH	3.01	3.00	3.01	3.00
Final pH	2.45	2.52	3.45	3.33
Adsorptivity**	6.7x10^{-3}	6.5x10^{-3}	6.7x10^{-3}	6.6x10^{-3}
Average Adsorptivity**	6.6x10^{-3}		6.65x10^{-3}	

*All concentrations are in ppm.
**Adsorptivities are in grams of cobalt per gram of clay.

Table IX. Solution Data for Co(III) Absorbance Reported by Koppelman.[2]

Clay	Illite	Kaolinite
pH	3	3
Initial Concentration*	100	101
Final Concentration*	86	99
Initial pH	3.10	3.01
Final pH	4.50	3.30
Adsorptivity**	2.8×10^{-3}	4.0×10^{-4}

*All concentrations are in ppm.

**Adsorptivities are in grams of cobalt per gram of clay.

normal exchange series in which an ion with the highest charge-to-ionic-size ratio would have the greatest exchange ability. The ratio of charge to ionic size for Co(II) is 2.78 and for Co(III) it is 4.76; therefore, the three clays studied follow the expected pattern for cation exchange.

It was found that, as in the Co(II) study, there was little or no change in the Co(III) adsorptivity with the application of a potential to the reaction cell. In the applied potential cell there should be no possibility of the Co(III) reducing to the Co(II) ion in the solution so any cobalt adsorbed should be in the Co(III) form. Since the cobalt exists only in the Co(III) form in the reaction cells and since Co(III) is adsorbed to a greater extent than Co(II), it would be expected that the cell with the applied potential would show a greater adsorption than the control cell if Co(II) is present in the clays because of the reduction of Co(III) prior to adsorption. The differences between the adsorptivities found in the reaction cells are so small that these differences can be attributed to experimental error. This suggests that Co(III) is not being reduced to Co(II) in the solution phase, since much larger differences in adsorptivity would be expected if reduction were to occur. From the results obtained for Co(III) it can only be assumed that the Co(III) is being reduced as part of the adsorption mechanism rather than in solution prior to adsorption.

The pH of the Co(III) test solutions changed for several reasons. In the cells having an applied potential, the potential is high enough to cause the oxidation of water which would cause a lowering of the pH.

$$2H_2O \longrightarrow O_2(g) + 4H^+ + 4e^- \qquad E^o = 1.23V \qquad (5)$$

Koppelman found that the hydrolysis of a metal complex can be catalyzed by the surface Fe(II) ions of a clay and that the rate of hydrolysis is proportional to the amount of Fe(II) present. In the test solutions used in this study this hydrolysis would proceed by the reaction

$$Co(NH_3)_6^{3+} + H_2O \longrightarrow (Co(NH_3)_5H_2O)^{3+} + NH_3 \qquad (6)$$

to produce the mono-aquo substituted complex and ammonia. Dissociation of the ammonia would generate hydroxide ions

$$NH_3 + H_2O \longrightarrow NH_4^+ + OH^- \qquad (7)$$

causing an increase in the solution pH. The pH of the test solution can also change by the making or breaking of hydrogen or hydroxyl bonds or by cation exchange of hydrogen. The final pH of the test solution is probably determined by a combination of these factors.

The Co(III) studies were performed only at pH=3 because at pH=7 any large rise in pH would cause the precipitation of cobalt hydroxide giving an error in the adsorptivity. This error would be so large that a study at pH=7 would not be useful.

CHAPTER V

SUMMARY AND CONCLUSIONS

Studies of the adsorptivities of kaolinite, illite and montmorillonite were made under both applied potential and control conditions for Co(II) at pH=3 and pH=7 and for Co(III) at pH=3. These studies were conducted in order to: (1) determine the relationship between adsorptivity of a clay and the pH of the solution; (2) determine the relationship between oxidation state of the cation and adsorptivity of the clay; (3) determine the effects of an applied potential on the adsorptivity of a clay; and (4) determine whether the presence of Co(II) in clays after adsorption from Co(III) solutions is due to the reduction of Co(III) in solution or reduction as part of the adsorption process.

The studies conducted using Co(II) solutions showed that there is a relationship between the adsorptivity of a clay and the pH of the solution. It was found that the higher the pH the greater the adsorptivity and that pH did not have the same effect on each of the clays studied; rather, pH affected the clays in the following order: Illite Montmorillonite Kaolinite. It was also found that applying a potential to the solution seemed to have no effect on the adsorptivities of the clays being examined.

The Co(III) studies showed that the clays had a greater adsorptivity for Co(III) than for Co(II) and that from this it can be seen that clays follow a normal cation exchange process, whereby the cation with the highest charge-to-ionic-size ratio has the greatest exchangeability. It was also found that applying a potential to the reaction solutions had no effect on the adsorptivities of the clays. Based on this observation the conclusion was drawn that any Co(II) present in the clays after the adsorption of the cation from the Co(III) solutions was due to the reduction of Co(III) as part of the adsorption process.

There are numerous studies that could be made to give more information about the adsorption process of metal ions by clay minerals. To further prove the results found as part of this study it would be advantageous to: (1) run experiments using electrochemistry to control the oxidation state of the metal ion being adsorbed and to use a method such as ESCA to determine what species is present at the clay surface after adsorption; (2) run experiments at a greater pH range to determine the exact relationship between pH and adsorptivity; and (3) run experiments with metals other than cobalt to determine if a rise in oxidation state will cause an increase in adsorption as was found for cobalt. Although much work has already been done on the adsorption process of metal ions by clay minerals much work is still needed to fully understand this process and the implications it has in nature.

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Vita

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After graduation from high school he attended Appalachian State University in Boone, North Carolina. He received a B.A. in Chemistry from Appalachian in May 1979 after having participated in an undergraduate research project involving dipole moment studies under the direction of Dr. T. C. Rhyne.

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