

**GEOCHEMICAL DYNAMICS OF CESIUM SORPTION
BY SELECTED CLAY MINERALS**

**By
Mark Richard Noll**

**A dissertation submitted to the Faculty of the University of Delaware
in partial fulfillment of the requirements for the degree of Doctor of Philosophy
in Plant Science**

May 1989

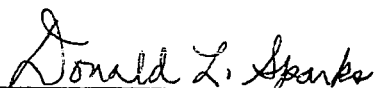
**© 89 Mark Richard Noll
All Rights Reserved**

**GEOCHEMICAL DYNAMICS OF CESIUM SORPTION
BY SELECTED CLAY MINERALS**

By

Mark Richard Noll

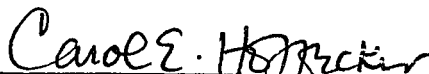
Approved:



Donald L. Sparks, Ph.D.

Chairman of the Department of Plant and Soil Science

Approved:



Carol E. Hoffecker, Ph.D.

Acting Associate Provost for Graduate Studies

I certify that I have read this dissertation and that in my opinion it meets the academic and professional standard required by the University as a dissertation for the degree of Doctor of Philosophy.

Signed:

Donald L. Sparks
Donald L. Sparks, Ph.D.
Professor in charge of dissertation

I certify that I have read this dissertation and that in my opinion it meets the academic and professional standard required by the University as a dissertation for the degree of Doctor of Philosophy.

Signed:

Paul M. Bertsch
Paul M. Bertsch, Ph.D.
Member of dissertation committee

I certify that I have read this dissertation and that in my opinion it meets the academic and professional standard required by the University as a dissertation for the degree of Doctor of Philosophy.

Signed:

Allan M. Thompson
Allan M. Thompson, Ph.D.
Member of dissertation committee

I certify that I have read this dissertation and that in my opinion it meets the academic and professional standard required by the University as a dissertation for the degree of Doctor of Philosophy.

Signed:

Ronald J. Gibbs
Ronald J. Gibbs, Ph.D.
Member of dissertation committee

I certify that I have read this dissertation and that in my opinion it meets the academic and professional standard required by the University as a dissertation for the degree of Doctor of Philosophy.

Signed:

J. Thomas Sims
J. Thomas Sims, Ph.D.
Member of dissertation committee

ACKNOWLEDGEMENTS

I would like to take this opportunity to express my thanks and appreciation to the many people who have assisted me with this project. In particular Dr. Sparks who provided me with this opportunity and who has always been ready and willing to lend his support. To the members of my dissertation committee Dr. Bertsch, Dr. Thompson, Dr. Gibbs, and Dr. Sims for their thoughtful comments and assistance in preparation of this manuscript. And to the many other people who have assisted me in various ways but are too numerous to name here. Finally, I would like to thank my parents, Richard and Josephine, and my brothers, Keith and Matthew, for their love and support. They deserve and receive my greatest thanks, admiration and love.

Dedicated to Boots and Penny.

CONTENTS

CHAPTER

1	INTRODUCTION	1
1.1	Introduction	1
1.2	Purpose	3
1.3	Previous Work	4
	1.3.1 Kaolinite Studies	7
	1.3.2 Illite Studies	9
	1.3.3 Vermiculite Studies	11
2	MATERIALS AND METHODS	13
2.1	Introduction	13
2.2	Materials and Methods	13
3	RESULTS AND DISCUSSION	17
3.1	Thermodynamic Studies	17
	3.1.1 Selectivity Coefficients and Isotherms	17
	3.1.2 Conclusions	23
3.2	Kinetics of Cs Adsorption on Kaolinite	33
	3.2.1 Adsorption Kinetics	33
	3.2.2 Desorption	34
	3.2.3 Size Fractions	35
	3.2.4 Conclusion	36
3.3	Kinetics of Cs Adsorption on Illite	44
	3.3.1 Adsorption Kinetics	44
	3.3.2 Desorption Kinetics	48
	3.3.3 Conclusion	50
3.4	Kinetics of Cs Adsorption on Vermiculite	57
	3.4.1 Adsorption Kinetics	57

3.4.2	Desorption Kinetics	61
3.4.3	Conclusion	65
4	CONCLUSION	72
4.1	Summary	72
4.2	Conclusion	74
	REFERENCES	76

TABLES

3.1	Cation Exchange Capacity (CEC)	25
3.2	Vanselow Selectivity Coefficients	26
3.3	Vanselow Selectivity Coefficients (cont.)	27
3.4	Vanselow Selectivity Coefficients (cont.)	28
3.5	Equilibrium Constants and Standard Free Energies of Exchange	29
3.6	Kaolinite Kinetics Models	38
3.7	Kaolinite Adsorption Data	39
3.8	Kaolinite Desorption Data	40
3.9	Comparison of Kinetic Models	52
3.10	Illite Adsorption Data	53
3.11	Illite Desorption Data	54
3.12	Comparison of Vermiculite Kinetics Models	66
3.13	Vermiculite Adsorption Data	67
3.14	Vermiculite Desorption Data	68

FIGURES

3.1	Kaolinite Exchange Isotherms	30
3.2	Illite Exchange Isotherms	31
3.3	Vermiculite Exchange Isotherms	32
3.4	Kaolinite Adsorption Kinetics	41
3.5	Kaolinite Desorption Kinetics	42
3.6	Unfractionated Kaolinite Adsorption	43
3.7	Illite Adsorption Kinetics	55
3.8	Illite Desorption Kinetics	56
3.9	Vermiculite Adsorption Kinetics at 298K	69
3.10	Vermiculite Adsorption Kinetics at 348K	70
3.11	Vermiculite Desorption Kinetics at 298K	71

ABSTRACT

This study focuses on the interactions of cesium with selected clay minerals. Cesium is of interest as it is a chief component of high level radioactive waste. Primarily, the thermodynamics and kinetics of Cs exchange reactions were investigated to determine the preference for Cs of a kaolinite, illite, and vermiculite.

Thermodynamic studies indicated that Cs was most strongly preferred by Ca saturated clays. Of the three minerals studied, illite proved to be the most effective in adsorbing Cs as indicated by the Vanselow Selectivity Coefficients (k_V). The k_V values for illite ranged from 5.87 to over 10^{10} , depending on the mineral and saturating cation.

Kinetics experiments proved to be the most interesting. On 2:1 clay minerals (illite and vermiculite), two simultaneous reactions are postulated. The first, and faster of the two reactions, is believed to correspond to Cs adsorption on surface planar sites. The second reaction may be the adsorption of Cs on interlayer and wedge exchange sites. Kaolinite only show a single reaction since it is a 1:1 clay mineral. Rate coefficients were calculated and the first reaction was found to be on the order of one magnitude greater than the second reaction. The reactions on kaolinite were similar to this faster reaction. Desorption data indicated that the rate of desorption was one or more orders of magnitude less than the corresponding adsorption rate. It is important to note, however, that

studies on the effect of temperature indicated that Arrhenius behavior is not followed in many of these experiments. It is postulated that changes in cation radius ratio, or the availability of exchange sites is causing this Anti-Arrhenius behavior.

Finally, it is concluded that illite exhibits the greatest preference for the adsorption of Cs. This would propose illite as a likely adsorbent material to be used in the disposal of high level radioactive wastes.

CHAPTER 1

INTRODUCTION

1.1 Introduction

Because of its status as one of the major long-lived isotopes of nuclear reactions, there is interest in the geochemical behavior of ^{137}Cs in surface and near-surface environments. Processes regulating the mobility of ^{137}Cs in soils and sediments ultimately influence its fate and bioavailability. Due to its high fission yield, moderately long half-life (30yr), high solubility, and metabolic similarity to K, ^{137}Cs is of major environmental concern.

Studies on the geochemistry of ^{137}Cs in sediments and soils has focused on the interactions of Cs^+ with the different surfaces and physical chemical phases. Among those of importance are the surface planar, interlayer and wedge sites of clay minerals, Fe- and Mn-oxyhydroxides, organic matter, and carbonates.

Many investigators (Coleman et al., 1963; Coleman and LeRoux, 1965; Eberl, 1980; Francis and Brinkley, 1976; Sawhney, 1964, 1965, 1966, 1970, 1972; Schulz et al., 1960; Tamura, 1964a,b; and Tamura and Jacobs, 1960, 1961) have reported on and reviewed the adsorptive behavior of Cs on silicate clays, in particular kaolinites, smectites, vermiculites, and illites (hydrous mica). It has been

found that Cs, like K (Bolt, et al. 1963; Rich and Black, 1963), is selectively adsorbed and strongly bound on the interlayer and wedge sites of 2:1 clay minerals, particularly illite and vermiculite (Eberl, 1980; Francis and Brinkley, 1976; Sawhney, 1970; Tamura and Jacobs, 1960; Tamura, 1964a).

Recently, however, Alberts, et al. (1979) and Evans, et al. (1983) have shown that ^{137}Cs may be remobilized from lake sediments during summer thermal stratification and hypolimnetic anoxia. The anoxic conditions result in the reduction of oxides which may occur as coatings on clay minerals, and in an increase in NH_4^+ levels due to inhibition of nitrification. The NH_4^+ ion is sufficiently small to diffuse through clay interlayers and exchange with Cs, and thus, it was proposed that the mobilization resulted via $\text{NH}_4\text{-Cs}$ ion exchange processes.

In terrestrial environments, the similarity between Cs and K is instrumental in the uptake and accumulation of ^{137}Cs . Soils on Bikini Atoll, the Marshall Islands, were contaminated by nuclear weapons testing fallout during the 1940s and 1950s. Even though background radiation has dropped to safe levels, plant uptake of ^{137}Cs makes consumption of local crops hazardous (Ellis, 1986). The mobility of ^{137}Cs in these soils, dominated by CaCO_3 and organic matter, presents an interesting problem.

More recently, the nuclear reactor accident at Chernobyl, USSR has resulted in the abandonment of the facilities and nearby town. Because of the long half-life of ^{137}Cs , a large area has been made useless. Additionally, fallout from Chernobyl was spread over a large part of Eastern and Western Europe.

Areas which were affected have ^{137}Cs in the soils which may remain for a long time, resulting in the uptake of ^{137}Cs and contamination of crops.

1.2 Purpose

As the world moves into the twenty-first century, more demands for energy are created. To satisfy this need, nuclear energy will play an increasing role and present an increasing problem to society. Once thought to be the cheap and clean power source for the future, the problem of nuclear waste has emerged as a stumbling block to the use of this energy resource.

Cesium is one of the chief by-products of nuclear reactions. Disposal of this radioisotope has presented scientists and engineers with a problem as the high solubility of Cs makes it highly mobile. Isolation of radioactive wastes containing Cs for long periods of time are the critical issues now being addressed. Clay minerals have been shown to adsorb many ions from solution including Cs. The preference or selectivity of a specific clay mineral for a particular ion and the speed or rate at which the ion is adsorbed may provide the basis for decisions on materials to be used to store and isolate nuclear waste.

This study has investigated the thermodynamics and kinetics of Cs adsorption to clay minerals in an effort to better understand the geochemistry of ^{137}Cs in surface and near-surface environments. Thermodynamic values are calculated to provide information on the preference or selectivity of a particular ion in solution for a given surface. Although these data give no information on

reaction mechanisms or pathways, the direction a reaction will move and its final equilibrium conditions are important parameters. Reaction mechanisms or pathways may be ascertained from kinetics investigations. Kinetic data are important in determining the rapidity of a reaction(s). As many reactions on clay minerals are slow, this type of information is critical when assessing the mobility of a particular element.

1.3 Previous Work

Argersinger, et al. (1950) were the first to apply rigorous thermodynamic principles to the study of cation exchange on clays and soils. The methods developed have been used to obtain selectivity coefficients, the thermodynamic equilibrium constant, and the standard free energy.

The preference of a given ion for a surface may be determined from the selectivity coefficient. Those with thermodynamic significance are those of Vanselow (1932), Gapon (1933), and Gaines and Thomas (1953). The Vanselow selectivity coefficient, k_v , which is used in this study relates the mole fraction of adsorbed cations to solution activities of the same cations as:

$$k_v = \frac{N_x [a_y]^m}{N_y [a_x]^n}$$

Where 'N' is the mole fraction of the adsorbed cation, 'a' is the activity of the cation in solution, and 'x' and 'y' are the competing cations with a valence of 'm' and 'n' respectively.

Schulz, et al. (1960) summarized to date the knowledge on Cs interactions with soil minerals. In their review, they found that Cs was more tightly bound on clay minerals than any other alkali cation. Additionally, from the results of work with carrier free ^{137}Cs , it was postulated that Cs may be irreversibly adsorbed in a manner similar to the way K is fixed by many clay minerals.

Cesium is chemically very similar to K. Both are alkali elements and their atomic radii are nearly identical (0.329 and 0.331nm, respectively). Because of this, Cs is expected to behave like K in ion exchange reactions. Bolt, et al. (1963) and Rich and Black (1963) described the behavior of K adsorption by clay minerals. They found that the adsorption preference of K was different for surface planar sites and interlayer sites. Also, they determined that K could be fixed in the interlayer of micaceous clay minerals such as illite and vermiculite.

Tamura and Jacobs (1960, 1961) found this to be true for Cs as well. They conducted experiments to explain the effectiveness of the Conasauga shale for removing Cs from radioactive waste solutions, and determined that clay mineral structure was a critical factor in adsorption behavior. The shale which is high in illitic clay has a high affinity for Cs.

Sawhney's results (1964, 1965, 1970) concurred with this earlier work. His investigations focused on the sorption and fixation of Cs by clay minerals. His results led him to conclude that Cs was highly selective for the interlayer sites of micaceous clay minerals. Once adsorbed onto these sites, only ions of similar ionic radius could exchange for them. Sawhney (1964) found that 25% to

50% more Cs was adsorbed by illite and vermiculite from a Ca solution than a K solution. This is a result of less competition for the available exchange sites.

Coleman and Le Roux (1965) found there to be two reactions operative when displacing Cs from micaceous clay minerals. The rapid initial release of Cs by $MgCl_2$ extraction was attributed to exchange from easily accessible Cs on surface sites. The slow which release followed was thought to be Cs exchange out of the interlayer sites. Exchange coefficients were found to be on the order of 10^3 for adsorption experiments with Cs preferred. Additionally, KCl solutions were better at displacing Cs than $MgCl_2$ solutions.

Brouwer, et al. (1983) found there to be three sites of decreasing selectivity for Cs on an illitic clay. Sites corresponding to 0.5, 3.0, and 96.5% of the exchange capacity were determined to have a characteristic exchange selectivity for Cs. They concluded that ions in the most highly selective sites (0.5%) were to a large extent dehydrated and that the driving force for the selectivity difference is the difference in the free energies of hydration. Maes and Cremers (1986) also found this to be true, and postulated that the sites with the greatest affinity for Cs were found along the edges of collapsed interlayer regions.

Komarneni (1979) and Oscarson, et al. (1987) investigated the effect of temperature on Cs exchange reactions with clay minerals. Both studies showed that an increase in temperature resulted in a decrease in the selectivity of the clay minerals for Cs. Komarneni (1979) concluded that the decreased selectivity was a function of the change in the ratios of the hydrated radii of the cations in solution.

1.3.1 Kaolinite Studies

Wahlberg and Fishman (1962) conducted an extensive study on the equilibrium distribution of Cs on kaolinite and other clay minerals. The study focussed on the effect of varying the concentration of Cs and the concentration of the competing cation on the distribution coefficient (K_d). At the lowest concentration of the competing cation (0.002M), the relative ability of the cations to compete with Cs was $\text{Ca}=\text{Mg}>\text{K}=\text{Na}$.

Sawhney (1964) found that more Cs was adsorbed by a K-kaolinite than a Ca-kaolinite, and that an increase in the concentration of the competing cation resulted in a decrease in the amount of Cs adsorbed. Further studies of desorption showed that a small amount of Cs remained "fixed" when Ca was the extracting cation while nearly all of the adsorbed Cs was removed when K was the extracting cation. This may indicate the presence of some exchange sites in the kaolinite sample which have a high selectivity for Cs even though Ca is preferred overall. Exchange sites with a high selectivity for Cs are not likely found on pure kaolinites and may be due to impurities in the sample. Sposito (1981) suggested that cation exchange capacities (CEC) for kaolinite in excess of 2 $\text{cmol}(+) \text{kg}^{-1}$ are probably due to 2:1 clay impurities.

An excellent example of impure kaolinites is the work of Tamura and Jacobs (1960). In their study on the adsorption of Cs from radioactive waste solutions, they found that Cs was preferentially adsorbed by kaolinite. The kaolinite sample used was from Macon, Georgia and had a CEC of 8.7 $\text{cmol}(+) \text{kg}^{-1}$. Lim, et al. (1980) used a number of Georgia kaolinites in their study and found

one sample with a similar CEC ($8.17\text{cmol}(+) \text{kg}^{-1}$) that contained only 89.5% kaolinite, the remainder being composed of montmorillonite, mica, and vermiculite.

Lim, et al. (1980) also found that there were discrepancies in the exchange capacity when Ca (Ca CEC) or Cs (Cs CEC) was used in the CEC determinations. The Cs CEC was always found to be greater than the Ca CEC. Additionally, more Cs was removed from the kaolinite when NH_4 was the extracting cation than when Ca was used. Cesium has been demonstrated to be selectively adsorbed by vermiculite (Sawhney, 1964), and cations of similar charge, size, and hydration to Cs (K, NH_4) more readily desorb Cs from all available exchange sites than Ca (Schulz, et al. 1960; Coleman, et al. 1963; Sawhney, 1964), resulting in the retention of Cs (Lim, et al. 1980). Statistical analysis of their data showed a significant correlation between Ca CEC and montmorillonite content, and the Cs retention and vermiculite content of the kaolinite.

Komarneni (1978), in a study on the sorptive behavior of kaolinites, found similar results. He found a strong correlation between the CaEC and impurities in the samples. A Yaro kaolinite, with a CaEC of $2.4\text{cmol}(+) \text{kg}^{-1}$, released all of the adsorbed Cs when either K or Na was the extracting cation. The remaining samples, with a CaEC of 6.5 and $7.8\text{cmol}(+) \text{kg}^{-1}$, did not release all of the adsorbed Cs and retained between 1 and 3.5% even when K was the extracting cation. Their results indicate that pure kaolinites do not retain any significant amounts of Cs, and observed fixation of Cs by kaolinite is due to 2:1 clay impurities.

In another study Komarneni (1979) investigated the effect of temperature on the adsorption of Cs by clay minerals. The total amount of Cs adsorbed, and therefore the selectivity coefficient, decreased with increased temperature from 298K to 353K. More Cs was adsorbed by and the decrease in selectivity was less for a Na-kaolinite than for a Ca-kaolinite.

1.3.2 Illite Studies

Tamura and Jacobs (1960) showed the importance of the c-axis dimension in determining the selectivity of Cs for a particular clay. Bentonite which was K saturated and heated to induce collapse of the expandable interlayer was found to have a greater preference for Cs than untreated bentonite (Tamura and Jacobs, 1961).

In studies on the adsorption of Cs from dilute solutions by an illitic clay, Sawhney (1965) found a single slope for adsorption isotherms in the presence of K, but two slopes when Ca was the competing cation. These different slopes were postulated to represent two exchange sites on illite. The single slope in K-Cs exchange experiments may be the result of interlayer collapse and fixation (Sawhney, 1964). Sawhney (1966) also investigated the adsorption kinetics of Cs onto a variety of clay minerals using a batch equilibration method. Results showed a rapid adsorption of Cs by a Ca-illite with an adsorption maximum being reached within 2 h. This was followed by a slight decrease in the total amount of Cs sorbed. Sawhney (1970) showed the importance of the high layer charge and the frayed edges on illite in Cs and K adsorption. This combination results in a high selectivity for collapse inducing ions such as Cs and K.

Eberl (1980) used a "weak force" fixation to explain the high preference of Cs for illite. This model suggests a strong attraction for the unhydrated Cs^+ from bonds that are so weak the other water-insulated cations are not attracted. The weak bonds originate at edge sites, which dominate the CEC of illite, that have a low but uniform surface charge density from charge imbalance in the crystal. Other investigators have shown that this model has not been effective in predicting ion exchange reactions on other clays and in the interpretation of the data from other studies (Laudelot, 1985; Maes and Cremers, 1986).

Brouwer et al. (1983) and Maes et al. (1985) showed that illite and heat treated montmorillonite behaved similarly. Sites of variable selectivity, covering an almost continuous spectrum, were quantified and the selectivity was found to correspond to reversible ion exchange reactions rather than to irreversible fixation. This is in agreement with data presented by Rich and Black (1964) and Bolt, et al. (1964) for the exchange of K on micaceous clay minerals. It does, however, suggest a complicated adsorption process involving multiple adsorption sites of different selectivities which was not seen by Sawhney (1966).

Most recently, Oscarson et al. (1987) found that increasing temperature resulted in a decrease in the total amounts of Cs sorbed in the range of 298 to 348 K. These results suggest that the sorption of Cs is an exothermic reaction. Illite was also found to fix some Cs and is therefore proposed as an effective barrier to the migration of Cs from radioactive waste burial sites.

1.3.3 Vermiculite Studies

In studies on the adsorption of Cs from dilute solutions by a vermiculitic clay, Sawhney (1965) found that in the presence of K, adsorption isotherms showed a single slope, but two slopes were present when Ca was the competing cation. These different slopes were postulated to represent at least two distinct exchange sites on vermiculite. Calcium-vermiculite was found to adsorb more Cs than K-vermiculite and a larger fraction of the adsorbed Cs was also fixed by Ca-vermiculite. The lower amounts of Cs adsorbed on K-vermiculite and the single slope shown on isotherms has been attributed to collapse of the interlayer to a 1.01nm spacing (Sawhney, 1964). Sawhney (1966) also investigated the adsorption kinetics of Cs on a variety of clay minerals using a batch equilibration method. Results showed an initial rapid adsorption of Cs on Ca-vermiculite followed by a slower reaction which was not complete even after 500 h. When the adsorption data were plotted using first-order kinetics, two linear segments with distinctly different slopes were found. This may be attributed to adsorption on external surface and interlayer exchange sites, and is analogous to the different exchange sites for K proposed by Rich and Black (1964) and Bolt, et al. (1964). Furthermore, Sawhney (1966) found that slightly more Cs was adsorbed at 278K than at room temperature.

Klobe and Gast (1970) investigated Cs fixation and Na entrapment by hydrobiotite and vermiculite. Their results indicated that a threshold value of Cs saturation is needed before edge collapse is induced. The threshold value may be reached by incremental additions. In an earlier paper, Klobe and Gast (1967)

found that vermiculite would fix Cs but not Sr. X-ray diffraction analysis showed major lattice collapse when Cs saturation exceeded 8.7% of the total exchange capacity.

CHAPTER 2

MATERIALS AND METHODS

2.1 Introduction

The objective of this study is to ascertain the effect of temperature and initial Cs concentration on the selective adsorption of Cs by kaolinite, illite, and vermiculite. Each mineral represents a different set of structural parameters and exchange capacities. It is important to determine the effectiveness of each mineral for Cs adsorption as these materials are commonly used in radioactive waste disposal scenarios.

2.2 Materials and Methods

Batch equilibrium and continuous flow miscible displacement kinetic studies were conducted on a well crystallized Georgia kaolinite (KGa-1) and Silver Hill illite (IMt-1) from the University of Missouri Source Clays Depository, and a Libby vermiculite from Wards Scientific.

The $<2\mu\text{m}$ fraction was separated by suspension in pH 10 Na_2CO_3 water followed by centrifugation in 250mL bottles at 500rpm for approximately 10 min. depending on room temperature conditions. Further fractionation to remove the $<0.2\mu\text{m}$ fraction of kaolinite was completed by centrifugation as above, but at 2500rpm for approximately 10min. The supernatant containing the

<0.2 μ m fraction was discarded. The clay samples were then saturated with either K^+ , NH_4^+ , or Ca^{+2} by a series of five 24 h washings with 1M Cl^- salt solutions. After saturation, the clays were washed free of excess salt with deionized water and aliquots of the slurry were dried to determine the density of the clay suspension.

Solutions used in the experiments had initial Cs concentrations (Cs_0) ranging from $10^{-4}M$ to $10^{-12}M$ and an ionic strength of 0.001M with the remaining salt being the same as the saturating cation. Solutions with Cs concentrations of 10^{-4} and 10^{-6} were spiked with ^{137}Cs while solutions with lower Cs concentrations used carrier-free ^{137}Cs .

Experiments to determine Vanselow selectivity coefficients (k_V), equilibrium constants (K_{eq}), and the standard free energy (ΔG^0) consisted of a single batch equilibration. A 0.01g sample of clay was added to 10ml of solution and placed on a reciprocating shaker for 48h.

Following equilibration, the samples were centrifuged, and an aliquot of the supernatant was analyzed for ^{137}Cs using gamma emission spectroscopy. The activity of the supernatant was compared to the activity of the corresponding stock solution and the concentrations of adsorbed Cs and Cs in the equilibrium solution were calculated. The concentration of the competing cation is determined using the cation exchange capacity (CEC) of each clay. The CEC values (see Table 3.1) were determined previously by saturation with a spiked Cs solution. The initial adsorbed cation and solution concentrations are known, and the equilibrium values may be calculated. The adsorbed cation concentration is

equal to the CEC minus the adsorbed Cs concentration, while the solution concentration is equal to the initial concentration in solution plus the amount desorbed which is the same as the amount of Cs adsorbed. In all cases, an equivalent amount of charge is assumed to be exchanged.

Kinetics experiments were conducted using a continuous flow technique (Sparks, et al. 1980). The clay sample (0.05g) was loaded onto a 47 mm Nuclepore filter by means of vacuum filtration to produce a thin evenly distributed clay film. All solutions used in both the adsorption and desorption experiments were held at a total ionic strength of 0.001M and a pH of 7. The adsorptive solutions had a Cs concentration of 0.0001M and were spiked with approximately 7.7 μCi of carrier-free ^{137}Cs L^{-1} solution. Solutions were pumped through the clay by means of a peristaltic pump to maintain a constant flow rate of 0.5mL min^{-1} and the leachate was collected in 10 mL (20 min) aliquots using an ISCO Foxy fraction collector. Each aliquot was analyzed for Cs content by gamma emission of the ^{137}Cs spike and the final concentration of each aliquot was determined by a ratio of sample activity to the activity of the initial standard solution.

Experiments were conducted at 298, 323 and 348K (illite and vermiculite only) by placing solutions in a water bath and insulating the filter unit with Al foil. Desorption experiments were conducted in a similar fashion.

Experimental data were evaluated using a computer program designed to calculate and plot first-order, second-order, parabolic diffusion, and Elovich equations. The apparent adsorption and desorption rate coefficients (k_a' and

k_d , respectively) and conformity of the data to a particular rate equation were assessed using R^2 values and standard errors of the estimate (SEE).

CHAPTER 3

RESULTS AND DISCUSSION

3.1 Thermodynamic Studies

3.1.1 Selectivity Coefficients and Isotherms

Many general trends are observed for Cs adsorption by the three minerals under study, regardless of the competing cation. The effect of temperature and Cs concentration on the k_v are similar in all cases (Table 3.2-3.4).

Increasing temperature from 298 to 323K results in a decrease in the k_v of Cs for each mineral. In some instances, particularly at the higher Cs_0 , the change in the k_v value is negligible or a slight increase is seen, but this is not the norm. Additionally, at the lowest Cs_0 , many k_v values are the same as the total amount of Cs in solution was adsorbed, and a true equilibrium was not reached. A decrease in selectivity with increasing temperature was also observed by Komarneni (1979). This may be the result of a change in the radius ratio of the competing cation to Cs. The increase in temperature will cause a greater decrease in the hydrated radii of the more strongly hydrated Ca, K, and NH_4 ions. This would result in a decrease in the radius ratio making Cs less competitive for the available exchange sites (Komarneni, 1979).

As might be expected, a decrease in the Cs_0 results in an increase in the k_v values. It has been shown that Cs is selectively adsorbed on certain types of exchange sites. As the amount of Cs available for adsorption decreases, these sites will compete more effectively for the Cs in solution. Tamura (1964), Sawhney (1965), and Brouwer, et al.(1983), among others, also drew similar conclusions from adsorption experiments on various clay minerals.

Cesium adsorption on kaolinite shows the previously described effects of temperature and concentration. A distinct difference is observed in comparing the K-Cs and Ca-Cs exchange. In both cases, Cs is preferred over the competing cation; however, the degree of preference as indicated by the k_v values (Table 3.2-3.4) is markedly different. Exchange on K-kaolinite gives k_v values ranging from 8.53 to 196.69, and K_{eq} values of 2.21 and 2.09 at 298 and 323K, respectively. The high k_v values observed at the lowest Cs_0 may indicate the presence of adsorption sites which are highly selective for Cs. The k_v values for the remaining Cs_0 increase only slightly as Cs_0 decreases. Observed k_v values for exchange on Ca-kaolinite are in the range of 10^4 to 10^7 . Again we see a sharp increase in the k_v value at the lowest Cs_0 . Values for K_{eq} (Table 3.5) are 10.13 and 9.33 at 298 and 323K, respectively. The large values observed for k_v and K_{eq} indicate a strong preference for Cs adsorption. This is not expected as the divalent Ca ion should be preferred over the monovalent Cs ion. These data may be explained by the presence of adsorption sites which are highly selective for Cs, and the preference of Cs due to its weakly hydrated nature.

Komarneni (1978) and Lim, et al.(1980) have shown that even small amounts of 2:1 clay impurities in a kaolinite may cause a significant increase in the CEC and the retention or fixation of Cs. Although the kaolinite was fractionated to obtain the 2.0 to 0.2 μ m fraction in an effort to eliminate the impurities, some may remain. This would include exchange sites from 2:1 clays, in particular the interlayer exchange sites, which have a high preference for Cs in the kaolinite sample. Komarneni (1979) observed a decrease in selectivity for Cs as temperature was increased and correlated this to the change in the hydrated radius of the competing cations. As described above, this was also observed in this study.

Exchange isotherms (Fig. 3.1) for both the K-Cs and Ca-Cs reactions on kaolinite are similar. It is possible to define various slopes on each isotherm at both 298 and 323K. At high values of Cs_0 , the isotherm has a slightly less than unit slope indicating a increase in the selectivity for Cs with decreasing concentration. The intermediate range of Cs_0 shows a slope with unit slope indicating a preference for Cs over the entire segment. At the lowest values of Cs_0 , the isotherm again exhibits a less than unit slope indicating an increase in Cs selectivity as concentration decreases. The observed isotherms concur with the assumption that some exchange sites with a high selectivity for Cs exist on the kaolinite, and at low concentrations of Cs they strongly influence the k_v values.

Cesium exchange on illite shows the importance of cation radius on the reaction. Data from K-Cs and NH_4 -Cs exchange reactions are similar, but

differ dramatically from data for Ca-Cs exchange. All cation pairs conform to the effects of temperature and concentration as previously discussed; however, the k_v values are significantly different.

Reactions involving K-, and NH_4 -illite produce similar results. Values for k_v range from 5.87 to 331.85 and 6.19 to 120.28 for K-Cs and NH_4 -Cs exchange, respectively (Table 3.2-3.4). The K_{eq} values are also similar (Table 3.5) at both 298 and 323K. In general, however, as indicated by the k_v values, Cs is more selectively adsorbed by the K-illite. The cation radius may produce this result with NH_4 being closer in size to Cs than K (Hazen and Wones, 1972). In the case of the K-illite, adsorption of Cs will promote collapse of the expanded edges of the illite crystal lattice resulting in fixation of the adsorbed Cs (Sawhney, 1965, 1970; Klobe and Gast, 1970). Since NH_4 is closer in size to Cs, the expanded edges of the illite will be propped-open allowing a free exchange to occur.

The reactions on Ca-illite produce a much different set of data (Table 3.4). Values of k_v range from 10^4 to 10^{12} showing an enormous preference for Cs on illite. This is a function of the radius of the strongly hydrated Ca ion and the presence of high energy exchange sites along collapsed edges (Maes and Cremers, 1986). Due to its large size, the Ca ion is unable to fit into the wedge and interlayer exchange sites. Cesium which fits well in these sites is therefore strongly preferred, resulting in the high selectivity of Cs on illite.

Isotherms for Cs exchange on K-, NH_4 , and Ca-illite confirm the strong selectivity of illite for Cs and the presence of various exchange sites (Fig.

3.2). The adsorption data for Cs in the presence of K produces a straight line isotherm with less than unit slope, similar to that found by Sawhney (1965). The increase in selectivity with decreasing concentration indicates the presence of different exchange sites with varying selectivities for Cs. This may include the replacement of interlayer K and fixation of Cs. Adsorption of Cs on NH_4 -illite produced a straight line isotherm of unit slope, and a preference for Cs is exhibited over the entire range of Cs_0 studied. The unchanging selectivity may be the result of the closeness in size of the c-axis of the Cs and NH_4 illites (Hazen and Wones, 1972). Even upon collapse, the NH_4 ion would prop open the wedge sites, allowing exchange to continue. Additionally, the difference in selectivity of illite for Cs and NH_4 may be insignificant. Similar results have been seen by Brouwer, et al. (1983) for Cs-Rb exchange on illite. Isotherms for Ca-illite show a curvilinear trend with Cs selectivity decreasing with increasing Cs_0 . This further confirms the existence of Cs selective sites on illite. At the lower Cs_0 values the Cs selective sites compete more effectively for the decreasing amount of Cs in solution.

Cesium adsorption on vermiculite is similar to that on illite. The k_v values are in all cases much lower and indicate in some cases that Cs is not preferred in the adsorbed phase (Table 3.2-3.4). The k_v values range from 0.70 to 10.54 for K-Cs exchange, 0.23 to 3.02 for NH_4 -Cs exchange, and 10^4 to 10^6 for Ca-Cs exchange.

The data for Cs exchange on K-vermiculite indicates a preference for Cs when Cs_0 values drop to 10^{-6}M and below (Table 3.2). Sawhney (1965) and

Klobe and Gast (1970) found that small amounts of Cs would induce collapse of crystal edges, trapping ions in the interlayer space and making them unavailable for exchange. Klobe and Gast (1967) determined that this would occur when approximately 8.7% of the exchange sites were filled with Cs. Sawhney (1965) observed this to occur at only 1% Cs saturation. At Cs_0 of $10^{-4}M$, Cs occupies 3.5% of the exchange sites in this study. If collapse does occur at this level of Cs saturation, the remaining exchange sites do not play an active role in the equilibrium between K and Cs. This gives the appearance of Cs selectivity being low on vermiculite. As the Cs_0 value decreases, so does the level of Cs saturation. The crystal lattice will not collapse and exchange on interlayer sites may proceed uninhibited. The k_v values rise in response, indicating the preference of Cs for the adsorbed phase.

The collapsing interlayer hypothesis also holds true for NH_4 -Cs exchange as the ions are much closer in size. Cesium saturation at Cs_0 of $10^{-4}M$ is 1.8% and drops off rapidly as Cs_0 decreases. The k_v values range from 0.23 to 3.02 (Table 3.3), and only exceed 1.0, above which indicates a preference for Cs, at the lowest values of Cs_0 . These data suggest that NH_4 is more strongly adsorbed by vermiculite than Cs except at very low concentrations of Cs. This again may be the result of reaction on a limited number of sites due to Cs induced collapse of the interlayer space.

Adsorption on Ca-vermiculite is controlled by the hydrated radius of Ca and Cs. Because of its large size, Ca will be excluded from exchange on interlayer exchange sites. Since Cs is the only ion competing for these sites,

very high k_v values are produced for Ca-Cs exchange. As Cs_0 decreases, the competition of the interlayer sites for the available Cs increases the k_v values.

Exchange isotherms (Fig. 3.3) for Ca-Cs and K-Cs exchange are similar, showing two segments both with less than unit slope. For K-Cs exchange, the isotherm shows a preference for Cs at lower Cs concentrations but crosses the homovalent non-preference line at higher Cs concentrations suggesting a preference for K. The isotherm for NH_4 -Cs exchange (Fig. 3.3) is a single linear segment with slightly less than unit slope which is superimposed over the homovalent non-preference line, suggesting that vermiculite is not selective between NH_4 and Cs.

3.1.2 Conclusions

This study demonstrated the strong preference for the adsorption of Cs by the clay minerals studied. In particular, the Ca-Cs exchange resulted in extremely high k_v values. This is due to the difference in size between the strongly hydrated Ca ion and the weakly hydrated Cs. This was shown by the decrease in k_v with increasing temperature, and by the high k_v values for adsorption on illite and vermiculite where interlayer exchange sites are important to the overall equilibrium. On kaolinite, however, the high k_v values were not expected. This may indicate the presence of 2:1 clay impurities which would have a significant effect on the equilibrium at the dilute concentrations studied.

The k_v values for K-Cs and NH_4 -Cs were much less than for Ca-Cs, but still indicated a strong preference for Cs, particularly on illite. The weak adsorption of Cs by the vermiculite may be the result of Cs induced collapse of the interlayer which effectively reduces the exchange capacity of the clay. This was observed the most on NH_4 -vermiculite and may also be the result of little preference of vermiculite for Cs or NH_4 .

Isotherms confirmed the strong selectivity of the clays for Cs. The observation on many isotherms of multiple slopes and the general decrease in the selectivity of Cs with increasing Cs_0 suggests the existence of multiple types of exchange sites with varying degrees of selectivity for Cs.

It is important to note here, however, that these experiments were conducted over a forty-eight hour period. This time may not be long enough to accurately study the very slow diffusion controlled reaction which may occur particularly on vermiculite. They do confirm the strong selectivity of clay minerals for Cs, especially illite. Even in competition with similar cations, illite exhibited a high selectivity for Cs over the concentration and temperature ranges studied. Despite having a lower exchange capacity than the vermiculite, illite has the ability to adsorb similar quantities of Cs. This is in part due to the collapse-inducing nature of Cs which effectively reduces the number of exchange sites available on vermiculite. Additionally, the frayed edges and wedge sites on illite may be the most highly selective sites for Cs.

Table 3.1: Cation Exchange Capacity (CEC)

Cation exchange capacity as measured by Cs saturation for each of the reference clay minerals studied.

	Kaolinite (KGa-1)	Illite (IMt-1)	Vermiculite (Libby)
	----- (cmol kg ⁻¹) -----		
CEC	1.2	15.0	140.0

Table 3.2: Vanselow Selectivity Coefficients

Vanselow selectivity coefficients (k_V) for Cs-K exchange on the reference clays, where Cs_0 is the initial Cs concentration.

Cs_0 (mol L ⁻¹)	Kaolinite	Illite	Vermiculite
		298K	
10 ⁻⁴	10.10	5.87	0.70
10 ⁻⁶	11.63	9.95	0.98
10 ⁻⁸	12.38	81.61	2.77
10 ⁻¹⁰	13.45	113.29	3.82
10 ⁻¹²	196.69	331.85	10.54
		323K	
10 ⁻⁴	8.53	7.90	0.78
10 ⁻⁶	10.58	8.11	0.88
10 ⁻⁸	8.82	26.66	1.77
10 ⁻¹⁰	13.41	32.08	2.29
10 ⁻¹²	196.69	120.28	5.69

Table 3.3: Vanselow Selectivity Coefficients (cont.)

Vanselow selectivity coefficients (k_V) for Cs-NH₄ exchange on the reference clays, where Cs_0 is the initial Cs concentration.

Cs_0 (mol L ⁻¹)	Kaolinite	Illite	Vermiculite
		298K	
10 ⁻⁴	---	6.19	0.26
10 ⁻⁶	---	10.06	0.45
10 ⁻⁸	---	16.81	0.70
10 ⁻¹⁰	---	22.83	0.75
10 ⁻¹²	---	78.79	2.46
		323K	
10 ⁻⁴	---	6.40	0.23
10 ⁻⁶	---	7.01	0.33
10 ⁻⁸	---	14.69	0.43
10 ⁻¹⁰	---	15.41	0.50
10 ⁻¹²	---	73.33	3.02

Table 3.4: Vanselow Selectivity Coefficients (cont.)

Vanselow selectivity coefficients (k_v) for Cs-Ca exchange on the reference clays, where Cs_0 is the initial Cs concentration.

Cs_0 (mol L ⁻¹)	Kaolinite	Illite	Vermiculite
		298K	
10 ⁻⁴	4.7*10 ⁴	1.3*10 ⁵	1.3*10 ⁵
10 ⁻⁶	7.5*10 ⁴	1.8*10 ⁷	1.1*10 ⁵
10 ⁻⁸	4.7*10 ⁴	1.6*10 ⁹	7.1*10 ⁵
10 ⁻¹⁰	1.2*10 ⁵	3.3*10 ¹⁰	1.4*10 ⁶
10 ⁻¹²	2.6*10 ⁷	2.5*10 ¹²	2.8*10 ⁶
		323K	
10 ⁻⁴	2.7*10 ⁴	6.9*10 ⁴	6.5*10 ⁴
10 ⁻⁶	2.1*10 ⁴	9.6*10 ⁵	3.9*10 ⁴
10 ⁻⁸	1.4*10 ⁴	4.6*10 ⁸	2.4*10 ⁵
10 ⁻¹⁰	5.1*10 ⁴	2.7*10 ⁸	9.0*10 ⁵
10 ⁻¹²	2.6*10 ⁷	9.9*10 ¹⁰	3.6*10 ⁵

Table 3.5: Equilibrium Constants and Standard Free Energies of Exchange

The equilibrium constant (K_{eq}) and standard free energy of exchange (ΔG^0) for Cs-K, Cs-NH₄, and Cs-Ca exchange on kaolinite, illite, and vermiculite.

		Kaolinite	Illite	Vermiculite
298K				
Cs-K	K_{eq}	2.21	1.78	-0.51
	G^0	-1.97	-1.43	---
Cs-NH ₄	K_{eq}	---	1.73	-1.47
	G^0	---	-1.36	---
Cs-Ca	K_{eq}	10.13	11.81	9.60
	G^0	-5.74	-6.12	-5.60
323K				
Cs-K	K_{eq}	2.09	2.03	-0.46
	G^0	-1.99	-1.90	---
Cs-NH ₄	K_{eq}	---	1.69	-1.54
	G^0	---	-1.42	---
Cs-Ca	K_{eq}	9.33	11.72	9.22
	G^0	-5.99	-6.10	-5.96

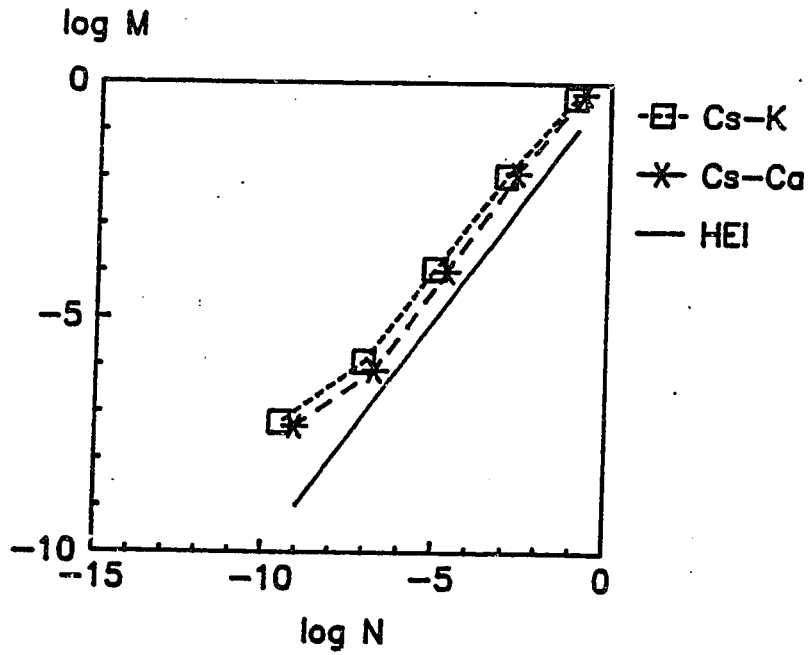


Figure 3.1: Kaolinite Exchange Isotherms. Isotherms for Cs-K and Cs-Ca exchange on kaolinite at 298K, where M is adsorbed Cs concentration and N is the Cs concentration in solution. The heavy line indicates the no preference isotherm for homovalent exchange. Results at 323K are similar.

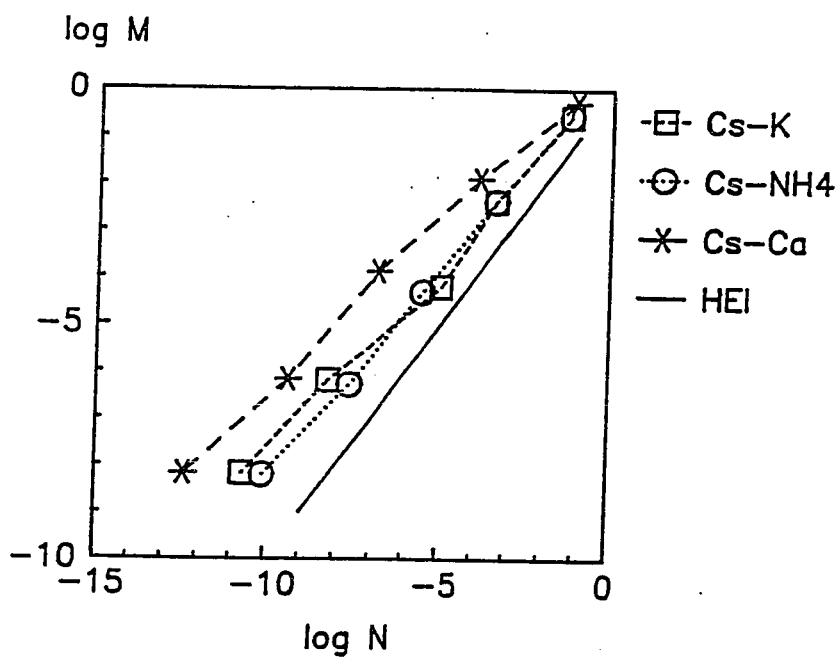


Figure 3.2: Illite Exchange Isotherms. Isotherms for Cs-K, Cs-NH₄, and Cs-Ca exchange on illite at 298K, where M is adsorbed Cs concentration and N is the Cs concentration in solution. The heavy line indicates the no preference isotherm for homovalent exchange. Results at 323K are similar.

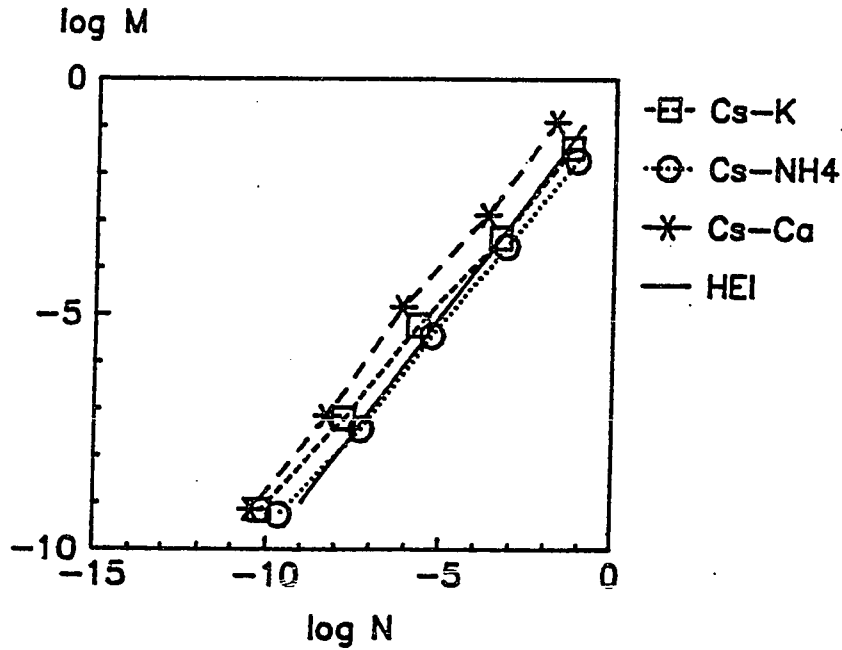


Figure 3.3: Vermiculite Exchange Isotherms. Isotherms for Cs-K, Cs-NH₄, and Cs-Ca exchange on vermiculite at 298K, where M is adsorbed Cs concentration and N is the Cs concentration in solution. The heavy line indicates the no preference isotherm for homovalent exchange. Results at 323K are similar.

3.2 Kinetics of Cs Adsorption on Kaolinite

3.2.1 Adsorption Kinetics

Adsorption of Cs by K- and Ca-kaolinite is best described by first-order kinetics (Fig. 3.4) with R^2 and SEE values ranging from 0.93 to 0.99 and 0.002 to 0.0002, respectively. Parabolic diffusion, Elovich, and second order rate equations were also used to evaluate the data, but in all cases proved to be inadequate (Table 3.6).

The K-kaolinite adsorbed more Cs than the Ca-kaolinite with the total amount not being significantly affected by temperature (Table 3.7). An equilibrium in Cs adsorption was reached within 100 to 120 min and the total amount adsorbed compared favorably with that obtained from batch equilibrium studies (discussed earlier), and a strong preference for Cs over K on kaolinite was observed.

The k_a' values were 0.44 and 0.70 h^{-1} for Cs adsorption on K-kaolinite at 298K and 323K respectively (Table 3.7). These data conform to the expected Arrhenius behavior for a simple ion exchange reaction. An increase in temperature does not appear to alter the selectivity, as nearly identical amounts of Cs are adsorbed at both 298K and 323K (Table 3.7).

Cesium adsorption on Ca-kaolinite is similar to adsorption on K-kaolinite in that Arrhenius behavior (Barrow, 1979) is observed as temperature changes (Table 3.7). Total Cs adsorbed is markedly less on Ca-kaolinite than on K-kaolinite with a total of 46 and 36 cmol kg^{-1} being adsorbed at 298K and

323K, respectively (Table 3.7). Even though this is significantly less than the total Cs adsorbed by the K-kaolinite, a slight preference for Cs is still observed. The selectivity is, however, affected by increases in temperature, as is evident from the decrease in Cs adsorbed at equilibrium (Table 3.7). Increases in temperature may result in a decrease in the hydration sphere of the divalent Ca ion, increasing its selectivity over Cs (Komarneni, 1979).

As was observed with K-kaolinite, the adsorption data were best described by first-order kinetics with the k_a' values (Table 3.7) being similar to those found with K-Cs exchange. The single slope may suggest adsorption on one type of site and the rapidity of the reaction would indicate easily accessible sites for exchange. The k_a' values for Ca-Cs exchange are similar in magnitude to values found by Sparks and Jardine (1984) for Ca-K exchange on kaolinite.

3.2.2 Desorption

The desorption of Cs from both K- and Ca-kaolinite appears to be a reversible reaction. In the Ca-kaolinite system, 94% and 80% of the total Cs adsorbed is desorbed after 120 min at 298 and 323K, respectively (Table 3.8). The percentage of adsorbed Cs desorbed from the K-kaolinite is slightly less with 66% desorbed at 298K and 83% desorbed at 323K. The greater reversibility at 323K for the K-kaolinite is due to the faster rate of desorption at 323K (Table 3.8). Plots of cumulative Cs desorbed versus time for K-kaolinite suggest that the reaction has not attained equilibrium and the remaining Cs may be desorbed. The Ca-kaolinite shows the opposite trend at higher temperature with a slight

decrease in both the percentage desorbed and the desorption rate. In all cases, kinetics data (Fig. 3.5) are best fit to a first-order equation.

3.2.3 Size Fractions

Cesium adsorption experiments on unfractionated ($<2\mu\text{m}$) kaolinitic clay were distinctly different than what was observed with fractionated ($2.0\mu\text{m}$ to $0.2\mu\text{m}$) clay sample. Adsorption experiments on the unfractionated clay were identical to those previously described for the fractionated clay except that a 25 mg L^{-1} Cs adsorptive solution was used. Cesium adsorption by the unfractionated K-kaolinite showed two distinct slopes (Fig. 3.6) similar to what was observed in reactions for K-vermiculite (see section 3.4). Equilibrium had not been attained even after 400 min, and the total amount of adsorbed Cs gave a cation exchange capacity (CEC) for the kaolinite of approximately $10\text{cmol}(+)/\text{kg}$. This is far in excess of the measured value of $1.2\text{cmol}(+)/\text{kg}$ (Sparks and Jardine, 1984; and this study).

The high CEC observed in the unfractionated K-kaolinite may suggest the inclusion of impurities as previously discussed. In our study, separating and discarding the $<0.2\mu\text{m}$ fraction resulted in a lower CEC which was comparable to reported values and the kinetics data fit a single first-order reaction. Smectites, which generally form small crystals, may be the impurity in this sample. Given an average CEC of $100\text{cmol}(+)/\text{kg}$, only an 8% inclusion of smectite would result in a total CEC for the sample of greater than $9\text{cmol}(+)/\text{kg}$. This small amount of impurity would be difficult to detect using most standard methods of clay analysis such as X-ray diffraction, etc. Komarneni (1978) and Lim, et al.(1980) had

similar elevated CEC values and were able to correlate this with smectite and vermiculite content.

Desorption of Cs from the unfractionated kaolinitic clay also suggested there were 2:1 clay impurities. Cumulative desorption plots (Fig. 3.6) show an initial rapid desorption after which little additional Cs was removed. Cesium is known to have a strong preference for interlayer exchange sites and is a strong collapse-inducing cation. Collapse and possible fixation of Cs adsorbed onto the interlayer exchange sites of the smectite or vermiculite inclusions could yield the observed desorption curve. The total amount of Cs desorbed in the initial rapid reaction corresponds to the amount adsorbed during the initial rapid reaction. These reactions are most likely cation exchange reactions on the surface planar sites of the kaolinite. Jardine and Sparks (1984) were able to delineate two types of exchange sites on soil clays using CTAB. This large organic molecule effectively blocked adsorption on surface exchange sites which resulted in a single slope on kinetics plots. These data corresponded to adsorption on interlayer exchange sites. In our study, we have shown the converse to be true. The elimination of 2:1 impurities resulted in a single slope on first-order plots corresponding to adsorption on surface planar exchange sites.

3.2.4 Conclusion

It has been shown here that the data for the sorption of Cs by kaolinite is best fit to a single first-order reaction. The observed changes in the apparent reaction rate with temperature indicated that the ion exchange reac-

tion conforms to the expected Arrhenius behavior, but an increase in temperature was significant in changing the selectivity of Cs relative to Ca by a change in the hydrated radius ratio.

Both adsorption and desorption data are best fit to single first-order equations. The k_a' values for adsorption are in the range of those found by other investigators for similar ion pairs, and suggest a rapid reaction on surface planar exchange sites. Desorption data gave k_d' values which are generally half to one order of magnitude less than the k_a' values suggesting that Cs may be strongly held on the exchanger phase.

Temperature had little effect on the selectivity for the Cs-K exchange pair. Total amounts of Cs adsorbed varied little with the increase in temperature. This was not the case for Cs-Ca exchange as the increase in temperature resulted in a large decrease in the total amount of Cs adsorbed. This is most likely due to a change in the radius of the strongly hydrated Ca ion. The inclusion of impurities had the greatest effect on Cs adsorption by kaolinite. Evidence from experiments conducted on the unfractionated sample indicate the presence of a 2:1 clay impurity, as supported by the resultant high CEC and the presence of two slopes on adsorption curves. The presence of even small amounts of the impurity, undetectable by common analytical methods, would be important in any adsorption equilibrium or kinetic study using the kaolinite used here.

Table 3.6: Kaolinite Kinetics Models

Comparison of kinetics models for Cs-K and Cs-Ca adsorption on Georgia kaolinite at 298K.

	R ²	SEE
1 st Order		
K	0.99	2.2×10^{-4}
Ca	0.98	2.8×10^{-4}
2 nd Order		
K	0.95	4.2×10^{-3}
Ca	0.97	4.4×10^{-3}
Parabolic Diffusion		
K	0.98	3.2×10^{-3}
Ca	0.97	3.0×10^{-3}
Elovich		
K	0.97	1.2×10^0
Ca	0.97	1.8×10^{-1}

Table 3.7: Kaolinite Adsorption DataCumulative Cs adsorbed (CCA) and k_a' for K- and Ca-kaolinite at 298 and 323K.

T		Competing Cations		
		K	Ca	
298	k_a' (CCA)	0.445 (0.96)	0.425 (0.46)	h^{-1} $cmol\ kg^{-1}$
323	k_a' (CCA)	0.699 (0.94)	1.188 (0.36)	h^{-1} $cmol\ kg^{-1}$

Table 3.8: Kaolinite Desorption Data

Cumulative Cs desorbed (CCD) and k_d' for K-, and Ca-kaolinite at 298 and 323K.

T		Competing Cations		
		K	Ca	
298	k_d'	0.154	0.512	h^{-1}
	(CCD)	(0.62)	(0.44)	$cmol\ kg^{-1}$
323	k_d'	0.264	0.291	h^{-1}
	(CCD)	(0.78)	(0.30)	$cmol\ kg^{-1}$

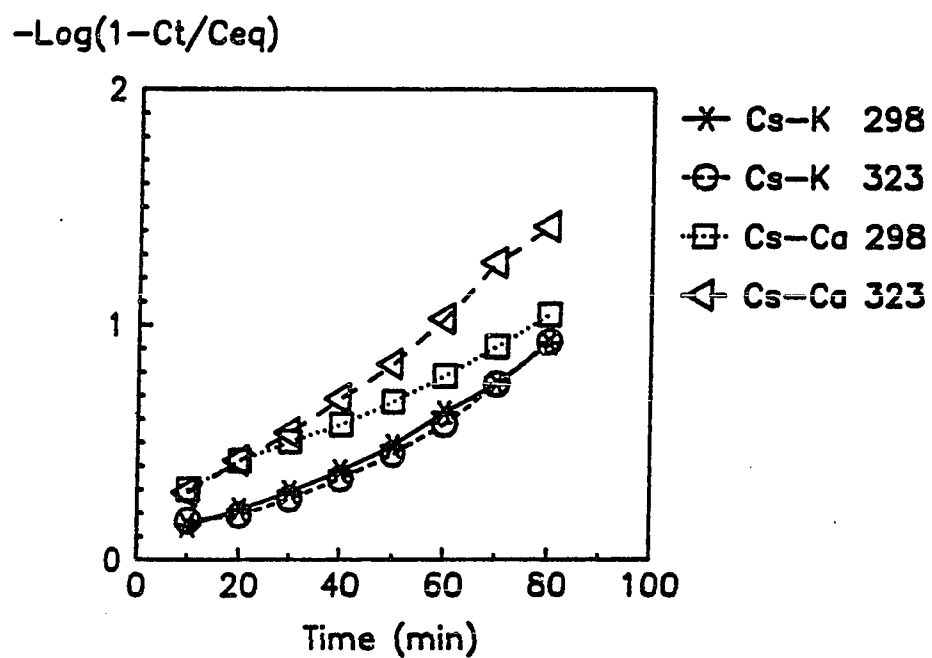


Figure 3.4: Kaolinite Adsorption Kinetics. First-order kinetics plots for Cs adsorption by K- and Ca-kaolinite at 298K and 323K, where C_t is the amount of Cs adsorbed at time t (min) and C is the amount of Cs adsorbed at Equilibrium.

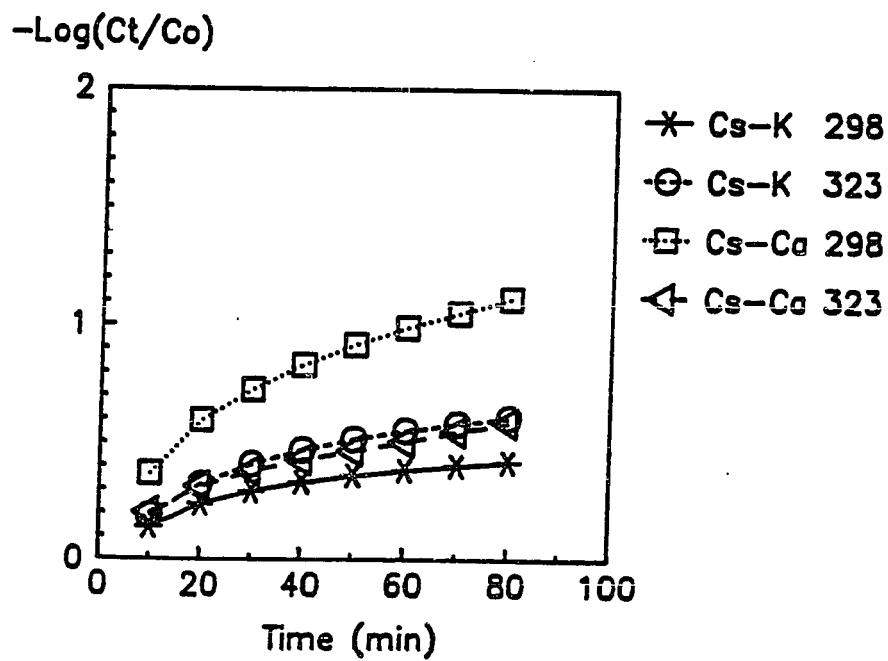


Figure 3.5: Kaolinite Desorption Kinetics. First-order kinetics plots for Cs desorption by K- and Ca-kaolinite at 298K and 323K, where C_t is the amount of Cs desorbed at time t (min) and C_0 is the initial amount of Cs adsorbed on the clay before desorption begins.

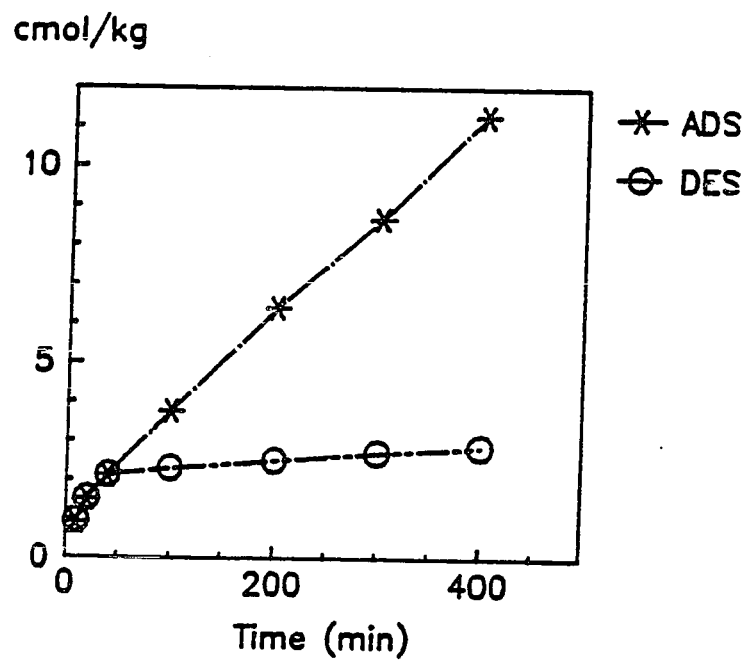


Figure 3.6: Unfractionated Kaolinite Adsorption. Cumulative Cs adsorbed and desorbed by an unfractionated K-kaolinite.

3.3 Kinetics of Cs Adsorption on Illite

The effects of temperature on the sorption of Cs by illite show that the process does not always conform to Arrhenius behavior. Results of these experiments suggest a physical and/or chemical change in the system as temperature is varied. The change in the system may be due to the inducement of collapse of the interlayer on the adsorption of Cs or a change in the selectivity of the Cs-cation pair with changing temperature. Results from the K-Cs, NH_4 -Cs, and Ca-Cs exchange experiments are different for each cation pair, and emphasize the importance of hydrated and crystalline ionic radii and cation charge.

3.3.1 Adsorption Kinetics

The adsorption of Cs by K-illite strongly suggests the importance of interlayer collapse in the overall rate of cation exchange. A comparison of data from the four kinetics models shows that the data are best fit to a first-order kinetics equation (Table 3.9). Comparison of the first order rate coefficient and cumulative adsorption values (Table 3.10) show that the rate of Cs adsorption by K-illite is not affected by increased temperature. However, the cumulative amount of Cs adsorbed (CCA) decreased with increasing temperature. Additionally, although not shown, Cs adsorption reaches a maximum value between 100 and 120 min after which Cs is spontaneously desorbed since the effluent has a higher Cs concentration than the influent. Sawhney (1966) had similar results in batch kinetic studies. Following the adsorption maximum, the adsorption curve is undulatory indicating a shifting equilibrium state which continues beyond 1000 min. Although no significant increase in adsorbed Cs is observed, it may be con-

cluded that further adsorption, if any, is being controlled by an extremely slow, tortuous diffusion controlled reaction. Since adsorption beyond 120 min is negligible, further discussion will center on the first 2 h reaction period.

Figure 3.7 shows a plot of the first-order rate equation for the K-Cs exchange at 323 K. This is similar to plots at 298 K and 348 K and the resultant k_a' values are similar at each temperature (Table 3.10). If the reaction conforms to Arrhenius behavior, k_a' values should increase with temperature. Since this is not the case, we may conclude that the system is in some way changing as a function of temperature. The spontaneous desorption of Cs seen in this experiment, was also seen by Sawhney (1966) for Cs adsorption by vermiculite. Sawhney (1966) suggested that this was due to collapse of the interlayer and the difference in the crystalline ionic radii of Cs and K (0.167 and 0.133 nm, respectively). Cesium adsorption would induce the collapse due to its weakly hydrated status and larger crystalline ionic radius. Upon collapse to a mica structure with a basal spacing of approximately 1.08 nm, the electrostatic attractive forces between the aluminosilicate layer and the K in interlayer exchange sites exceeds the hydration energy of the interlayer K ions and collapse continues, resulting in a basal spacing of 1.00 to 1.01 nm. Consequently, Cs on interlayer or more likely edge sites is too large to be accommodated in the K-mica structure and is "squeezed out." The resultant equilibrium situation would be for Cs adsorbed onto easily accessible surface planar exchange sites.

First-order kinetic plots for K-Cs exchange (Fig. 3.7) show a rapid reaction with a single slope. The single slope suggests that the reaction involves

only one group of sites with similar selectivities for Cs. The rapidity of the reaction is shown by k_a' values of approximately 1.2 h^{-1} which are on the same order of magnitude as similar ion exchange reactions on kaolinites (Sparks and Jardine, 1984).

Cesium adsorption by Ca-illite shows evidence for a change in the selectivity coefficient with temperature. As in the case for K-illite, the total amount of Cs adsorbed is inversely proportional to the change in temperature. The reaction appears to reach an equilibrium condition after approximately 100 to 120 min, but beyond that there is little change as the Cs concentration of the effluent is equal to that of the influent. These data are again best described by the first-order rate equation, but the k_a' values (Table 3.10) are not constant as in the K-illite case, nor do they show a regular variation with temperature.

The variability in the total Cs adsorbed may be a function of a change in selectivity for the Ca-Cs ion pair with temperature. The divalent Ca ion is known to have a greater selectivity for easily exchangeable surface planar sites over the monovalent alkali elements. This is evident from the overall lower amounts of Cs adsorbed by the Ca-illite compared to the K-illite or NH_4 -illite. The decrease in Cs adsorption with temperature may be a result of a decrease in the selectivity of Cs with an increase in temperature which has been observed in equilibrium studies (Komarneni, 1979; Oscarson, et al. 1987). Further evidence for this is shown in the desorption experiments and will be discussed later.

Again we see the first order rate equation fitting the data to a single slope (Fig.3.71). This supports the idea of Cs adsorption onto only the more easily exchangeable sites, those which are also available to Ca for exchange.

Ammonium saturated illite presents yet a third set of data for Cs adsorption, but may also be explained by physical changes in the system. These data are again best described by a first-order rate equation. In this case, the apparent rate coefficient varies with temperature but is inversely related to the temperature change.

The effect of temperature on Cs adsorption by the NH_4 -illite is to decrease the rate coefficient, but there is little effect on the total amount of Cs adsorbed (Table 3.10). After 360 minutes, at which time an apparent equilibrium has been reached, the total amount of Cs adsorbed varies from 384ug at 298K to 372ug at 348K, a change of approximately 3%. This is, however, a significantly larger quantity of Cs adsorbed than in either the K-illite or Ca-illite systems. The decrease in the rate of adsorption may be explained by a collapse of inter-layer spaces similar to the K-illite system. One important difference is in the degree of collapse and the basal spacing of the NH_4 -illite. Juster, et al.(1987) and Hazen and Wones (1972) have shown ammonium saturated illites and micas to have a basal spacing of approximately 10.4A. They concluded that this size difference between the K-bearing species and the NH_4 -bearing species limited the amount of natural NH_4 substitution in naturally occurring illites and micas, similar to what was found in the K-Cs system. This may also explain the greater amounts of Cs adsorption by the NH_4 -illite and the inverse relationship between temperature and the apparent rate coefficient. The NH_4 -illite structure will collapse upon Cs adsorption in the same fashion as in the K-Cs case. In the NH_4 -illite, however, the difference in the size of the Cs and NH_4 ions may not have a significant effect on adsorption into interlayer and wedge exchange sites, or the ammonium ion remains hydrated and the exchange process is not inhibited.

These data best fit a single slope when described by the first-order rate equation (Fig. 3.7), but the rate coefficient is less than those seen in the K-illite or Ca-illite systems. This may be the result of a more open interlayer space which is accessible to ion exchange reactions resulting in an overall slower rate of adsorption due to the larger influence of interlayer diffusion.

3.3.2 Desorption Kinetics

In all cases the desorption reactions proved to be fairly simple and support the interpretations of the data for the adsorption reactions. First-order kinetics again provided the best interpretation of the data of the four equations tested using the R^2 and standard error of estimate values.

Desorption from the K-illite followed a single first-order slope (Fig. 3.8); however, the k_d' values are an order of magnitude slower than the k_a' values. This confirms the proposal that, in this case, Cs is occupying only the most easily accessible exchange sites but it is also more strongly preferred on these surfaces than the K. The reaction also shows a high recovery rate of adsorbed Cs suggesting a reversible reaction (Table 3.11).

The Ca-illite first-order desorption plots show evidence for two slopes (Fig. 3.8), possibly relating to rapid desorption from surface planar sites where Ca would have a higher selectivity followed by desorption from edge and interlayer sites. The rate coefficients are again slower than those for the adsorption showing a preference for Cs on some of the surfaces. An important feature to note is the magnitude and duration of the initial rapid slope. This initial rapid

reaction decreases in importance with increasing temperature. This explains the decrease in the total amount of Cs adsorbed and may be the result of a change in the selectivity of Ca-Cs for the surface planar sites which contribute a large portion of the exchange capacity in illite.

Desorption of Cs from the NH_4 -illite is similar to the reactions found on the Ca-illite as opposed to the K-illite. Desorption reactions fit first order kinetic models with evidence of two distinct slopes indicating desorption from different exchange sites. The total amount of Cs desorbed remains fairly constant with increasing temperature in the range of 3.65 to 3.82 cmol kg^{-1} desorbed after 360 min (Table 3.11). This represents between 65% and 68% of the total Cs adsorbed indicating a significant amount of the Cs is being strongly held or may have become fixed. This may be a function of the size of the NH_4 ion being similar in size to the Cs ion. The available interlayer exchange sites would be easily accessible for exchange and collapse of the interlayer space would not preclude Cs from being incorporated into the mica structure. If collapse is induced, the adsorbed Cs would be very tightly held and difficult to remove.

First-order kinetic plots (Fig. 3.8) show a somewhat curvilinear trend and may be broken into two linear segments. Overall rate coefficients range from 0.063 to 0.071 h^{-1} with R-square values of 0.93 and SEE values of approximately 5×10^{-5} . Second order kinetics also do a good job of describing the desorption reaction. The plots have R^2 values of 0.98 and SEE values of 1×10^{-4} . They also show an indication of two simultaneous reactions in the first 40 min of the experiment.

3.3.3 Conclusion

It is evident from the data presented here and from previous studies that Cs adsorption by illite is strongly influenced by the illite structure and the hydrated and crystalline radii of the competing cations. It is also important to note that the reactions studied here do not strictly adhere to Arrhenius behavior, i.e., an increase in reaction rate with an increase in temperature. This further supports the implication that the reaction is being controlled by physical and chemical properties which are changing, thus altering the system under study.

Because of the strong collapse-inducing nature of the poorly hydrated Cs ion Maes and Cremers (1986), the c-axis dimension is of critical importance (Tamura and Jacobs, 1960). Cations with similar radii such as crystalline NH_4 , or the strongly hydrated Ca will prop open the expansible edges of the illite making interlayer sites available for exchange. Because only the edges are expansible, diffusion through the interlayer space is not rate-limiting, resulting in a single slope on first-order kinetic plots. Availability of the interlayer sites also enables some of the adsorbed Cs to become very strongly bound or fixed, resulting in lower recovery percentages in desorption reactions and multiple slopes on first-order kinetic plots. When K is the competing cation, the collapse inducing ability of Cs results in additional collapse of the illite to a K-mica structure which may exclude Cs. In reactions with Ca, the increase in temperature will result in a decrease in the hydration status of the Ca thus increasing the selectivity of the divalent species over the monovalent Cs.

Because of these physical and chemical changes in the system under study, total Cs adsorbed generally decreases with increasing temperature, and the k_g' values show no distinctive trend with temperature. This anti-Arrhenius behavior is likely due to the physical and/or chemical changes in the system which make a comparison of data at different temperatures difficult to understand with conventional reaction rate theory.

Table 3.9: Comparison of Kinetic Models

Comparison of kinetic rate equation models for K-, NH₄-, and Ca-illite at 298K using the R² and Standard Error of Estimate (SEE) values to evaluate the usefulness of each equation.

	R ²	SEE
1 st Order		
K	0.99	3.4*10 ⁻⁵
Ca	0.97	5.9*10 ⁻⁴
NH ₄	0.95	1.6*10 ⁻⁴
2 nd Order		
K	0.94	1.1*10 ⁻³
Ca	0.71	5.8*10 ⁻²
NH ₄	0.46	1.8*10 ⁻²
Parabolic Diffusion		
K	0.96	1.6*10 ⁻³
Ca	0.96	3.8*10 ⁻³
NH ₄	0.97	1.6*10 ⁻³
Elovich		
K	0.99	6.4*10 ⁻¹
Ca	0.99	4.7*10 ⁻¹
NH ₄	0.98	2.1*10 ⁰

Table 3.10: Illite Adsorption Data

Cumulative Cs adsorbed (CCA) and apparent first order rate coefficients (k_a') for K-, NH₄-, and Ca-illite at 298, 323, and 348K.

T	CCA cmol kg ⁻¹	k_a' h ⁻¹
K-Illite		
298	4.20	1.20
323	3.13	1.17
348	2.77	1.14
NH ₄ -Illite		
298	5.77	0.50
323	5.64	0.25
348	5.59	0.22
Ca-Illite		
298	2.14	0.78
323	1.85	0.96
348	1.10	0.55

Table 3.11: Illite Desorption Data

Cumulative Cs desorbed (CCD), recovery percentage(Rec), and apparent first order rate coefficients (k_d') for K-, NH_4 -, and Ca-illite at 298, 323, and 248K.

T	CCA cmol kg^{-1}	REC %	k_a' h^{-1}
K-Illite			
298	3.28	78	0.11
323	2.86	91	0.16
348	2.29	83	0.08
NH_4 -Illite			
298	3.80	66	0.06
323	3.65	65	0.06
348	3.82	68	0.07
Ca-Illite			
298	1.23	58	0.06
323	1.20	65	0.08
348	1.02	93	0.20

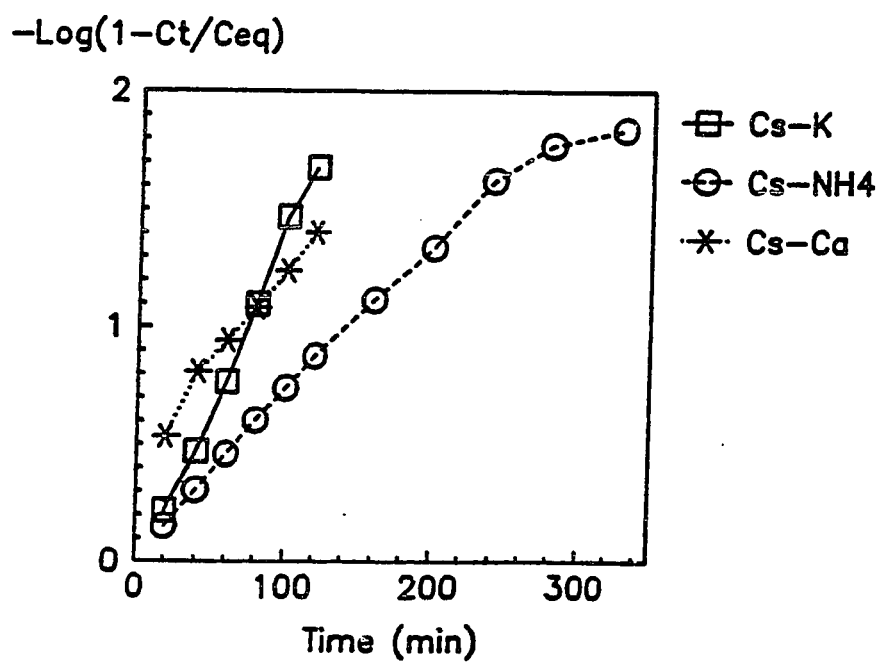


Figure 3.7: Illite Adsorption Kinetics. First-order kinetic plots of Cs adsorption on K-, NH₄- and Ca-illite at 298K.

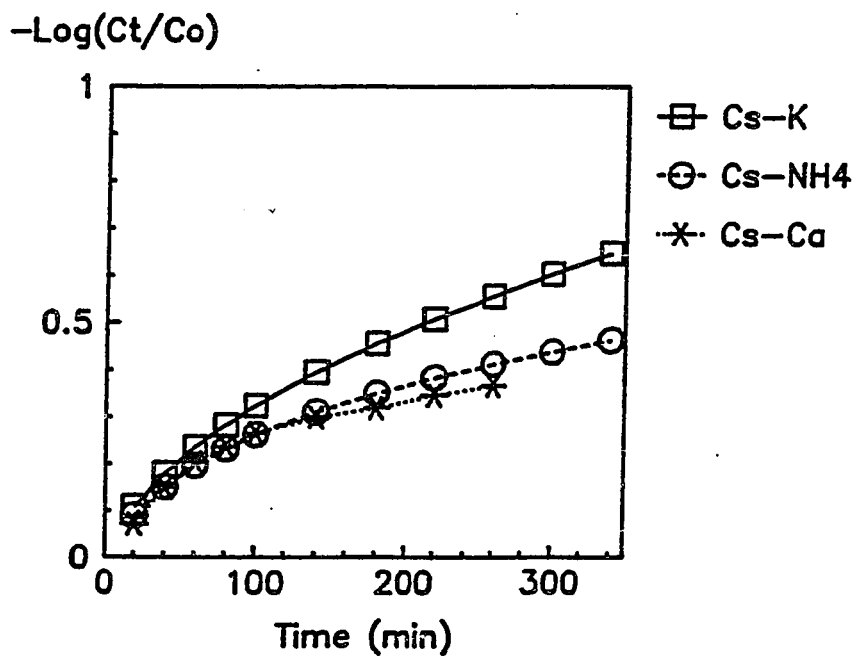


Figure 3.8: Illite Desorption Kinetics. First-order kinetic plots of Cs desorption on K-, NH₄- and Ca-illite at 298K.

3.4 Kinetics of Cs Adsorption on Vermiculite

Cesium sorption by a Libby vermiculite in this study is characterized by a relatively high selectivity which results in a large amount of Cs adsorbed per mass of clay. Results, however, vary widely and depend heavily on the competing cation and the structural implications of their ionic radii and hydration status. Adsorption and desorption data were evaluated using the four kinetics models and found to best fit first-order kinetics (Table 3.12). In some isolated cases, other equations do a good job of describing the data, but the first-order equation is the most consistent. Many of the reactions do not however, fit to a single slope but are best described by two or more simultaneous first-order reactions.

3.4.1 Adsorption Kinetics

Potassium-vermiculite shows a complicated temperature dependence on adsorbed Cs. While the total amount of Cs adsorbed (Table 3.13) decreases from 298K to 348K, it does not follow a regular pattern. Potassium-vermiculite adsorbs $7.29 \text{ cmolCs kg}^{-1}$ at 298K. With an increase in temperature to 323K, the amount of Cs adsorbed decreased to $4.66 \text{ cmolCs kg}^{-1}$. A further increase in temperature to 348K results in only a slight drop in Cs adsorption to $4.48 \text{ cmolCs kg}^{-1}$. This pattern is also observed in the kinetics data.

Adsorption data for Cs-K exchange on vermiculite are best fit to the first-order model. The effect of temperature is significant and results in two

different interpretations for the exchange kinetics data. At 298K, the data are best fit to a single first-order reaction. First-order plots (Fig. 3.9) show a single linear trend and give an apparent adsorption rate coefficient (k_a') of 0.165 h^{-1} . Adsorption reactions at the higher temperatures (Fig. 3.10) show a distinctly different reaction with first-order plots showing two slopes corresponding to two simultaneous reactions. This is similar to the results of Sawhney (1966) in work on K and Ca vermiculite. The initial rapid reaction which is complete in approximately the first 100 min gives a k_a' of 0.320 h^{-1} . The second slower reaction which reaches equilibrium within the 800 min time frame of the experiment has a k_a' of 0.150 h^{-1} . The k_a' values for both reactions are the same at both 323K and 348K.

The single slope at 298K is due to a more open exchange of Cs for K on the interlayer exchange sites, and a slower overall rate of adsorption is the result. The difference in the rates of adsorption for potential adsorption on surface planar sites and interlayer sites which is seen at higher temperatures is not observed here as is evident by the similarity in k_a' values for various segments of the first-order adsorption plot. The much higher total amount of adsorbed Cs at 298K ($7.29 \text{ cmolCs kg}^{-1}$) indicates a greater availability of interlayer exchange sites. As the reaction temperature is increased, the k_a' for the surface planar exchange sites increases as would be expected if the reaction is following Arrhenius behavior. The total amount of adsorbed Cs decreases sharply (Table 3.13) as interlayer collapse and fixation may be limiting the number of interlayer exchange sites available (Sawhney, 1964; Klobe and Gast, 1970). The second slope which corresponds to interlayer exchange gives a constant k_a' of 0.15 h^{-1} .

number of interlayer exchange sites available (Sawhney, 1964; Klobe and Gast, 1970). The second slope which corresponds to interlayer exchange gives a constant k_a' of 0.15 h^{-1} . This indicates a slowing of the reaction with increasing temperature as fewer sites are being exchanged in the same amount of time. This provides further evidence to support the collapse of the interlayer space making diffusion through this space follow a more tortuous and slower path.

Adsorption of Cs on the NH_4 -vermiculite is similar to that on the K-vermiculite. These results are not surprising as the chemistry of K and NH_4 are similar. As was seen in K-Cs exchange, adsorption data are best fit to first-order kinetics. At both 298K and 323K (Fig. 3.9) a single slope is observed when data are plotted according to first-order kinetics. At 348K, however, there are two distinct linear segments representing two simultaneous reactions which may correspond to adsorption on surface planar and interlayer exchange sites (Fig. 3.10).

The single slopes observed for the first-order plots at 298K and 323K may be explained similarly to the data observed for K-Cs exchange at 298K. The interlayer exchange sites are open and available for exchange with the solution phase. This persists to a higher temperature in the NH_4 -Cs system because of the larger ionic radius NH_4 compared to K. Even if partial collapse has been initiated, the difference in the c-axis dimension of the NH_4 and Cs clays is less than that for the K and Cs clays (Hazen and Wones, 1972). This is also evident in the k_a' values. The k_a' at 298K is 0.194 h^{-1} and it increase to 0.207 h^{-1} at 323K. This follows the expected Arrhenius behavior with changing

A definite change occurs, however, between 323K and 348K. The total amount of Cs adsorbed drops to $3.59 \text{ cmol Cs kg}^{-1}$ and first-order plots show evidence of two simultaneous reactions. The first reaction which appears to be complete within the first 100 min is attributed to adsorption on the surface planar sites, while the second reaction which reaches equilibrium in approximately 580 min involves interlayer exchange sites. Sawhney (1966) also attributed the two linear segments on kinetic plots to surface planar and interlayer exchange sites. These sites are analogous to those proposed by Rich and Black (1964) and Bolt, et al.(1964) for K exchange. The k_a' values for the two reactions are 0.103 and 0.034 h^{-1} respectively. This is a sharp decrease in the k_a' values from 323K to 348K and may be the result of collapse of the interlayer space making diffusion more difficult. This decrease was also observed in the K-Cs system and again is expected because of the similarity of the K-Cs and NH_4 -Cs exchange systems.

Cesium adsorption by Ca-vermiculite gives the strongest evidence for the occurrence of two simultaneous first-order reactions. At all temperatures, there is evidence of two distinct slopes when the data are plotted according to first-order kinetics. The difference between the k_a' values of the two simultaneous reactions decreases with temperature (Table 3.13). At 298K, the k_a' value is 0.070 h^{-1} , but it drops to 0.015 h^{-1} at 348K. At 348K the difference in the k_a' values for the first and second reaction is only 0.004 h^{-1} .

A decrease in k_a' values is seen for both the first and second reactions as temperature is increased. This goes against the expected Arrhenius behavior

which predicts an increase in rate with temperature. The k_a' for the first reaction decreases steadily from 298K to 348K, and may indicate a change in the selectivity for Ca-Cs exchange on surface planar and accessible edge sites. As temperature is increased, the strongly hydrated Ca^{+2} ion will begin to lose some of its bound water molecules making it more strongly preferred because of its higher valence. The greater competition for the surface sites will not only decrease the total amount of Cs adsorbed, but it may also decrease the rate of Cs adsorption as Cs will be preferentially adsorbed onto interlayer sites making less Cs available to the surface exchange sites. This can be shown by the difference in the k_a' values for the first and second reactions. At 298K, the k_a' of the first reaction is 2.5 times as great as that for the second reaction (Table 3.13). At 348K, however, the k_a' values for the two simultaneous reactions are nearly equal (Table 3.13).

The change in k_a' for the second slower reaction does not follow a regular pattern. At 298K, the k_a' is 0.027 h^{-1} , but this drops to 0.011 h^{-1} at 323 and 348K. The sharp drop between 298K and 323K may be the result of collapse of the interlayer space as temperature increases. The collapse would result in a slower diffusion of ions into the interlayer as they would have to follow a more tortuous path.

3.4.2 Desorption Kinetics

Desorption of Cs from the equilibrated vermiculite sample by K indicates a reversible reaction that adheres to the predicted Arrhenius behavior with

changing temperatures. Total amounts of Cs desorbed range from 5.47 cmol Cs kg^{-1} at 298K to 3.98 cmol Cs kg^{-1} at 348K (Table 3.14). The percentage of adsorbed Cs which is subsequently desorbed shows an inverse relationship with the total amounts desorbed. At 298K, 75% of the Cs is desorbed, increasing to 87% at 323K and 89% at 348K. Total cumulative desorption versus time plots indicate, however, that the reaction is not complete after 800 min, and if continued to equilibrium, may result in a nearly complete recovery of the adsorbed Cs.

Data are again best described by a first-order model and the apparent first-order desorption rate coefficient (k_d') follows Arrhenius behavior, increasing with temperature. The k_d' values are on average a half an order of magnitude less than the k_a' values, and range from 0.058 h^{-1} at 298K to 0.096 h^{-1} at 348K for the overall reaction (Table 3.14). Again, however, and at all temperatures, there is evidence for two simultaneous reactions taking place. Values of k_d' for the faster reaction range from 0.139 h^{-1} to 0.203 h^{-1} (Table 3.14). The second slower reaction gives k_d' values from 0.049 h^{-1} to 0.089 h^{-1} (Table 3.14). These two slopes may be attributed to exchange reactions on surface planar sites and interlayer sites, respectively. The second slower reaction also shows some interesting results which concur with adsorption data. The k_d' for the slower reaction is substantially lower at 298K (0.049 h^{-1}) than at 323K (0.079 h^{-1}) or 348K (0.089 h^{-1}). This may be indicative of the greater availability of interlayer exchange sites at 298K. With Cs being adsorbed onto sites much deeper into the interlayer, diffusion outward upon desorption would be slower, exaggerating the difference in the observed k_d' . Cesium may still have a slight preference for the

interlayer sites, since the greater distance the ion must travel will cause it to come in contact with and be affected by a greater number of exchange sites.

Desorption of Cs by NH_4 gives a more complicated picture than desorption by K, yet the interpretations are similar. At all temperatures, Cs desorption by NH_4 shows three distinct linear trends when data are plotted according to first-order kinetics (Fig. 3.11). One may suggest that these segments correspond to desorption from three different sets of sites. Maes, et al.(1985) found a continuous spectrum of sites of varying selectivity for Cs on a heat treated montmorillonite. It is not unlikely, therefore, to assume that a similar spectrum of sites may exist on vermiculite. Evidence from this study indicates that desorption is occurring from surface planar, edge and crystal rim interlayer, and crystal core interlayer exchange sites, which correspond to k_{d1}' , k_{d2}' , and k_{d3}' values, respectively. The k_d' values range up to two orders of magnitude from k_{d1}' to k_{d3}' , but vary only slightly with temperature (Table 3.14).

At 298 and 323K, results are similar. The total amount of Cs desorbed drops from $3.47 \text{ cmol Cs kg}^{-1}$ at 298K to $3.02 \text{ cmol Cs kg}^{-1}$ at 323K, but the percentage of adsorbed Cs which is recovered varies only slightly from 59% to 56%. The k_a' values also vary only slightly. Values for k_{a1}' increase with temperature from 0.117 h^{-1} to 0.126 h^{-1} . This follows the expected Arrhenius behavior as is expected for desorption from surface planar exchange sites. The k_{a2}' values decrease slightly with an increase in temperature from 0.024 h^{-1} to 0.019 h^{-1} , while the k_{a3}' values remain constant at 0.004 h^{-1} . The observed

deviation from Arrhenius behavior may be the result of partial interlayer collapse which results in tenacious retention of Cs on interlayer exchange sites; in particular on the edge and crystal rim interlayer sites. The increase in temperature may cause a slight decrease in the hydration of the interlayer space causing a tighter bonding of the Cs and NH_4 ions. Desorption from the crystal core interlayer exchange sites will always be a slow process as the Cs must diffuse outward along a tortuous path.

Results from data at 348K show three distinct slopes, but the difference between k_{a1}' and k_{a3}' is only one order of magnitude. The k_{a1}' value is 0.139 h^{-1} which is slightly higher than values at 298 or 323K. This is expected according to Arrhenius behavior which is followed for desorption from surface planar sites. The k_{a2}' and k_{a3}' values (0.055 and 0.012 h^{-1} respectively) are significantly higher than corresponding values at 298 and 323K. The k_{a2}' value is more than twice as large and the k_{a3}' value is tripled. It is important to note that the k_{a3}' value at 348K is similar to the k_{a2}' values at 298 and 323K. This observation is consistent with the Cs adsorption data. At 348K, less Cs was adsorbed and evidence pointed toward interlayer collapse, preventing Cs adsorption onto crystal core interlayer sites. If this is the case, the very slow desorption seen at 298 and 323K would not be observed at 348K. This observation, which could be predicted from adsorption data, is seen in the desorption data.

Desorption of Cs by Ca shows a simple relationship with temperature conforming to Arrhenius behavior. Data are best fit to first-order kinetics with a single slope resulting. Desorption proceeds at a very slow rate with k_d' values

ranging from 0.004 h^{-1} at 298K to 0.008 h^{-1} at 348K (Table 3.5). This confirms the strong preference of Cs for vermiculite. Based on the k_d' values, the Cs desorbed is probably coming from interlayer exchange sites. Cesium adsorbed on surface planar sites would be desorbed very rapidly and was not observed in these experiments.

3.4.3 Conclusion

Cesium adsorption by vermiculite was found to be a complex process dependent of the ionic radius of the exchanging cation, the degree of collapse induced by Cs adsorption, and the existence of exchange sites with various affinities for Cs. The different exchange sites have been described (Rich and Black, 1964; Bolt, et al. 1964) and well characterized (Brouwer, et al. 1983; Maes, et al. 1985; Maes and Cremers, 1986). Sites with the highest selectivity for Cs exist in interlayers near areas of collapse.

The steric exclusion of large hydrated cations (Ca) from interlayer exchange sites only increases the availability of sites open to Cs adsorption. Ions of similar size (K, NH_4) compete more favorably with Cs. Ammonium being closer in size to Cs than K will prop open interlayer spaces allowing freer exchange. Both K and Cs will induce collapse of the interlayer space, causing an effective decrease in the CEC, but also producing exchange sites with higher selectivities for Cs (Maes and Cremers, 1986).

Table 3.12: Comparison of Vermiculite Kinetics Models

Comparison of kinetic rate equation models for K-, NH₄-, and Ca-illite at 298K using the R² and SEE to evaluate the usefulness of each equation.

	R ²	SEE
First-Order		
K	0.99	4.6*10 ⁻⁵ .
Ca	0.97	1.5*10 ⁻⁵ .
NH ₄	0.99	6.9*10 ⁻⁵ .
Second-Order		
K	0.85	6.1*10 ⁻³ .
Ca	0.99	2.4*10 ⁻⁵ .
NH ₄	0.85	9.2*10 ⁻³ .
Parabolic Diffusion		
K	0.94	1.6*10 ⁻³ .
Ca	0.99	4.7*10 ⁻⁴ .
NH ₄	0.91	2.1*10 ⁻³ .
Elovich		
K	0.99	1.9*10 ⁰
Ca	0.98	7.6*10 ⁰
NH ₄	0.98	2.8*10 ⁰

Table 3.13: Vermiculite Adsorption Data

Cumulative Cs adsorbed (CCA) and k_g' for K-, Ca-, and NH_4 -vermiculite at 298, 323, and 348K. Where "x" represents the first or second of the two simultaneous reactions.

		Competing Cations			
		K	Ca	NH_4	
298K					
k_{ax}'	1	0.165	0.070	0.197	h^{-1}
	2	-----	0.027	-----	
(CCA)		(7.29)	(18.34)	(5.94)	cmol kg^{-1}
323K					
k_{ax}'	1	0.320	0.047	0.240	
	2	0.150	0.011	-----	
(CCA)		(4.66)	(11.97)	(5.34)	
348K					
k_{ax}'	1	0.320	0.015	0.103	
	2	0.150	0.011	0.034	
(CCA)		(4.48)	(9.71)	(3.59)	

Table 3.14: Vermiculite Desorption Data

Cumulative Cs desorbed (CCD) and k_d for K-, Ca-, and NH_4 -vermiculite at 298, 323, and 348K. Where "x" represents the first, second, or third of the simultaneous reactions.

		Competing Cations			
		K	Ca	NH_4	
298K					
k_{dx}'	1	0.186	0.004	0.117	h^{-1}
	2	0.049	-----	0.024	
	3	-----	-----	0.004	
(CCD)		(5.47)	(2.39)	(3.47)	cmol kg^{-1}
323K					
k_{dx}'	1	0.139	0.007	0.126	
	2	0.079	-----	0.019	
	3	-----	-----	0.004	
(CCD)		(4.04)	(2.71)	(3.02)	
348K					
k_{dx}'	1	0.203	0.008	0.139	
	2	0.089	-----	0.055	
	3	-----	-----	0.012	
(CCD)		(3.98)	(2.27)	(2.84)	

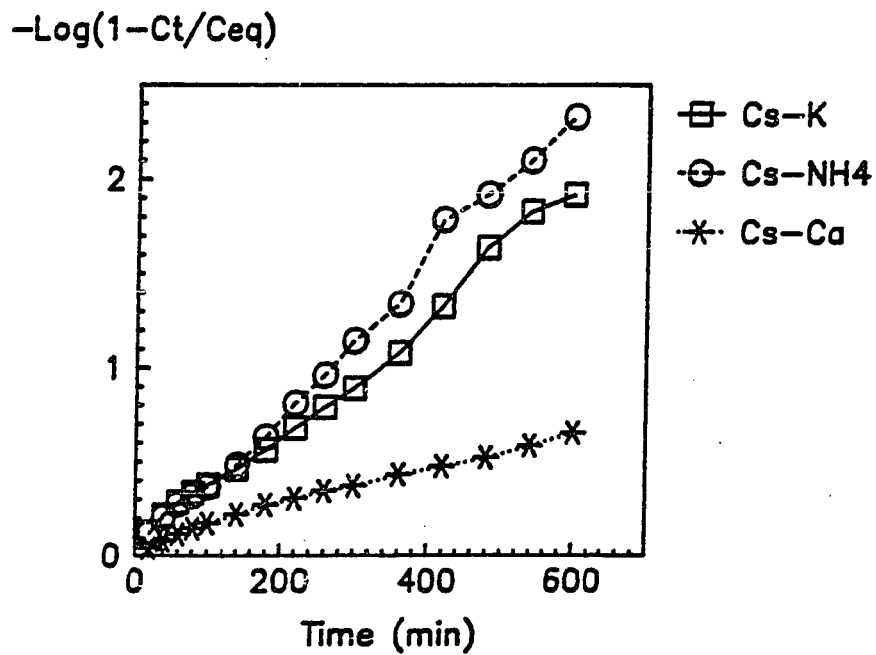


Figure 3.9: Vermiculite Adsorption Kinetics at 298K. First-order kinetic plots of Cs adsorption on K-, NH₄-, and Ca-vermiculite at 298K.

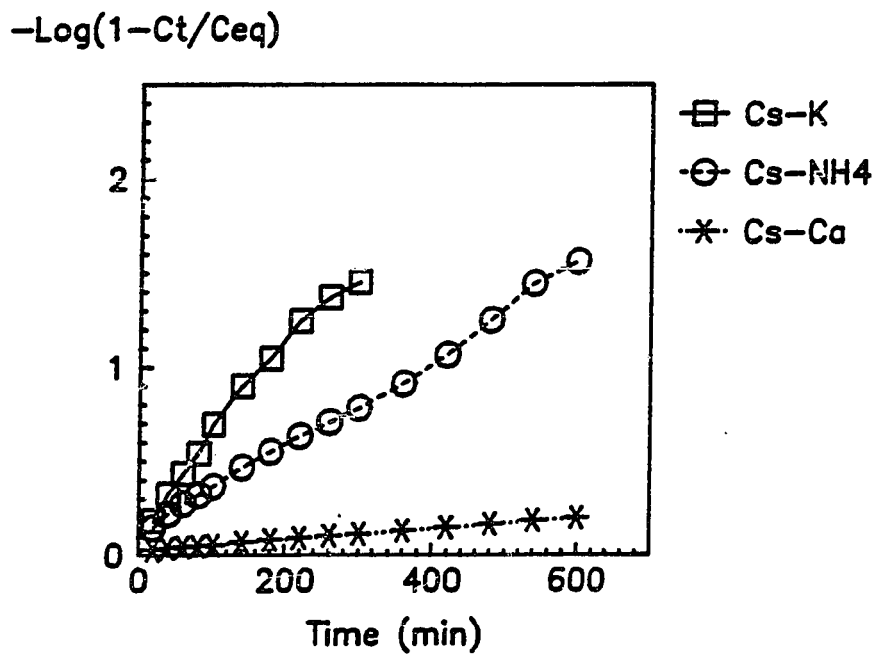


Figure 3.10: Vermiculite Adsorption Kinetics at 348K. First-order kinetic plots of Cs adsorption on K-, NH_4^- , and Ca-vermiculite at 348K.

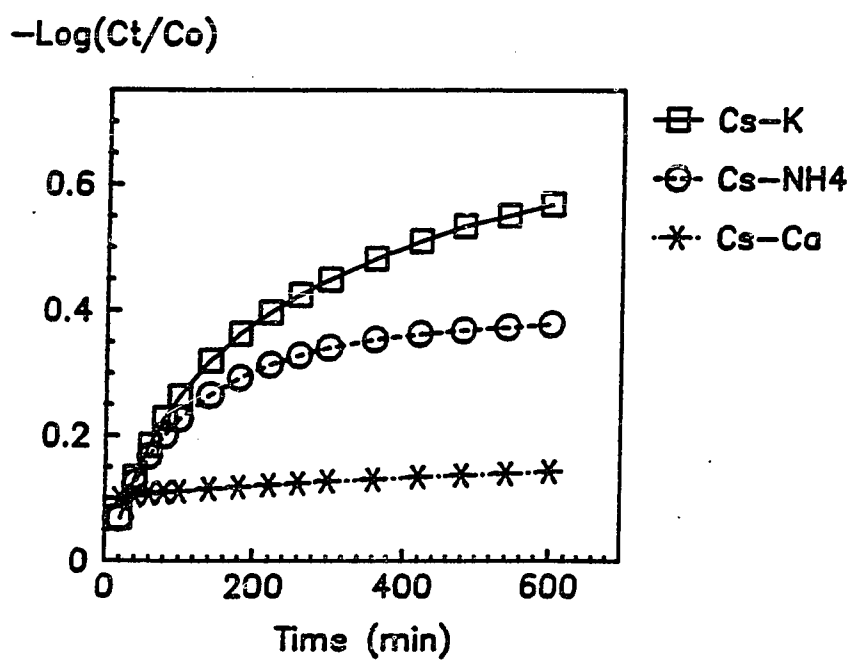


Figure 3.11: Vermiculite Desorption Kinetics at 298K. First-order kinetic plots of Cs desorption on K-, NH₄-, and Ca-vermiculite at 298K.

CHAPTER 4

CONCLUSION

4.1 Summary

This study has focused on the interaction of Cs with selected clay minerals. It was found that one of the primary factors controlling Cs adsorption-desorption reactions was the clay mineral structure, and that ion exchange reactions were best described by first-order kinetics. Additionally, the effects of temperature, Cs concentration, and competing cations were studied, and found to be significant in many cases. Experiments which determined thermodynamic and kinetic parameters have given a great deal of useful information in dealing with this potentially dangerous radionuclide.

Illite, a 2:1 clay mineral, was found to be the most effective clay studied for adsorbing Cs. Thermodynamic experiments showed that illite is highly selective for Cs. Illite contains exchange sites which are Cs specific and decreasing the solution concentration of Cs sharply increases the selectivity coefficients (k_v). Temperature has an inverse relationship with k_v . This is postulated to be the result of a change in the hydrated radius ratio of Cs and the competing cation, and a greater inducement of collapse by Cs at higher temperatures. Illites preference for Cs over the cations studied is $Cs \gg Ca$, $Cs > K$, and $Cs > NH_4$.

Kinetics data shows that Cs is rapidly adsorbed by illite with data best fitting to first-order kinetics. Apparent first-order rate coefficients for adsorption and desorption (k_a' and k_d' , respectively) vary by a half to one order of magnitude with the adsorption reaction being the faster. Arrhenius behavior is not observed as temperature increases and it is suggested that this is due to a greater collapse of the interlayer space at higher temperatures thus altering the system under study. The reaction was shown to be reversible; however, Ca was least effective in desorbing Cs.

Reactions involving vermiculite are similar to those with illite as they are both 2:1 clay minerals. There is strong evidence for the collapse inducing nature of Cs as the amount of Cs adsorbed is not significantly different than that adsorbed by illite, yet vermiculites CEC is an order of magnitude greater. The selectivity of vermiculite for Cs is similar to that of illite except k_v values are slightly less, and there appears to be no preference between Cs and NH_4 .

Kinetics data for Cs adsorption by vermiculite shows two distinct first-order reactions. These correspond to adsorption on surface planar and interlayer exchange sites. Values for k_v vary up to a half an order of magnitude between the two reactions. Desorption reactions show similar results with up to three distinct first-order reaction. The k_v values may vary up to two orders of magnitude between the different reactions. As with illite, we again do not see an adherence to Arrhenius behavior and interlayer collapse is thought to be the primary factor controlling the exchange reaction.

Kaolinite was the only 1:1 clay mineral studied and results were distinctly different as a result of the structure. Although Cs was found to be strongly adsorbed by kaolinite, some of the observed selectivity may be due to 2:1 clay impurities which are commonly found in kaolinite. Kinetics experiments adhere to the expected Arrhenius behavior. This is expected as the collapse mechanism proposed for illite and vermiculite would not have an effect on kaolinite.

4.2 Conclusion

As we face an ever increasing problem of disposal of radioactive waste products of which Cs is an important component, the selection of disposal sites and schemes is of great importance. From the observations made in this study, some conclusions may be drawn about the effectiveness of the clays studied.

Although illite has a relatively low CEC as compared to vermiculite, it has been shown that it will adsorb similar amounts of Cs. In applying this to problems of waste disposal, illite would appear to be the most effective clay mineral in this study at retarding the migration of Cs in surface or subsurface environments. It is important to note, however, that vermiculite with a greater amount of interlayer exchange sites is better at retaining adsorbed Cs. Calcium was the least effective of the competing cations in desorbing Cs from either illite or vermiculite, and the Ca saturated clays were more effective in adsorbing Cs.

Kaolinite was the only 1:1 clay mineral studied and results were distinctly different as a result of the structure. Although Cs was found to be strongly adsorbed by kaolinite, some of the observed selectivity may be due to 2:1 clay impurities which are commonly found in kaolinite. Kinetics experiments adhere to the expected Arrhenius behavior. This is expected as the collapse mechanism proposed for illite and vermiculite would not have an effect on kaolinite.

4.2 Conclusion

As we face an ever increasing problem of disposal of radioactive waste products of which Cs is an important component, the selection of disposal sites and schemes is of great importance. From the observations made in this study, some conclusions may be drawn about the effectiveness of the clays studied.

Although illite has a relatively low CEC as compared to vermiculite, it has been shown that it will adsorb similar amounts of Cs. In applying this to problems of waste disposal, illite would appear to be the most effective clay mineral in this study at retarding the migration of Cs in surface or subsurface environments. It is important to note, however, that vermiculite with a greater amount of interlayer exchange sites is better at retaining adsorbed Cs. Calcium was the least effective of the competing cations in desorbing Cs from either illite or vermiculite, and the Ca saturated clays were more effective in adsorbing Cs.

It may be possible to conclude from this study that a mixture of Ca-illite and Ca-vermiculite would be the best material for the prevention of the migration of Cs away from disposal sites by groundwater. Temperature should be as low as possible as an increase was shown to decrease the selectivity of the clays for Cs. Overall, the 2:1 clay mineral structure was shown to be the most important factor in Cs adsorption.

REFERENCES

1. Alberts, J.J., Tilly, L.J., and Vigerstad, T.J. 1979. Seasonal cycling of cesium-137 in a reservoir. Science 203:643-651.
2. Argesinger, W.J., Davidson, A.W., and Bonner, O.D. 1950. Thermodynamics and ion exchange phenomena. Kansas Acad. Sci. Trans. 53:404-410.
3. Bolt, G.H., Sumner, M.E., and Kamphorst, A. 1963. A study of the equilibria between three categories of potassium in an illitic soil. SSSA Proc. 27:294-299.
4. Brouwer, E., Baeyens, B., Maes, A., and Cremers, A. 1983. Cesium and rubidium ion equilibria in illite clay. J. Phys. Chem. v.87, n.7, pp.1213-1219.
5. Coleman, N.T., and LeRoux, F.H. 1965. Ion-exchange displacement of cesium from soil vermiculite. Soil Sci. v.99, no.4, 243-250.
6. Coleman, N.T., Lewis, R.J., and Craig, Doris. 1963. Sorption of cesium by soils and its displacement by salt solutions. SSSA Proc. 27:290-294
7. Eberl, Dennis D. 1980. Alkali cation selectivity and fixation by clay minerals. Clays Clay Min. v.28, no.3, 161-172.
8. Ellis, W.S. 1986. Bikini: A way of life lost. National Geographic v.169 no.6 pp.813-834.
9. Evans, David W., Alberts, James J., and Clark, Roy A. III. 1983. Reversible ion-fixation of cesium-137 leading to mobilization from reservoir sediments. Geochemica Et Cosmochemica Acta 47:1041-1049.
10. Francis, C.W., and Brinkley, F.S. 1976. Preferential adsorption of Cs-137 to micaceous minerals in contaminated freshwater sediments. Nature 260:511-513.
11. Gaines, G.L. Jr., and Thomas, H.C. 1953. Adsorption studies on clay minerals. II. A formulation of the thermodynamics of exchange adsorption. J. Chem. Phys. 21:714-718.
12. Gapon, Ye N. 1933. On the theory of exchange adsorption in soils. J. Gen. Chem. USSR 3:144-160.

13. Gaudette, H.E., Grim, R.E., and Metzger, C.F. 1966. Illite: A model based on the sorption of cesium. Am. Min. 51:1649-1656.
14. Hazen, R.M., and Wones, D.R. 1972. The effect of cation substitutions on the physical properties of trioctahedral micas. Am. Min. 57:103-129.
15. Jardine, P.M., and Sparks, D.L. 1984. Potassium-Calcium exchange in a multireactive soil system: II. Thermodynamics. Soil Sci. Soc. Am. J. 48:45-50.
16. Klobe, W.D., and Gast, R.G. 1967. Reactions affecting cation exchange kinetics in vermiculite. Soil Sci. Soc. Am. Proc. 31:744-749.
17. Klobe, W.D., and Gast, R.G. 1970. Conditions affecting cesium fixation and sodium entrapment in hydrobiotite and vermiculite. Soil Sci. Soc. Am. Proc. 34:746-750.
18. Komarneni, S. 1978. Cesium sorption and desorption behavior of kaolinites. Soil Sci. Soc. Am. J. 42:531-532.
19. Komarneni, S. 1979. Cesium sorption by clay minerals and shales at elevated temperatures. J. Inorg. Nucl. Chem., 41:397-400.
20. Lim, C.H., Jackson, M.L., Koons, R.D., and Helmke, P.A. 1980. Kaolins: Sources of differences in cation-exchange capacities and cesium retention. Clays Clay Min. v.28, n.3, pp.223-229.
21. Lomenick, T.F., and Tamura, T. 1965. Naturally occurring fixation of Cs-137 on sediments of lacustrine origin. SSSA Proc. 29:383-387.
22. Miller, J.R., and Reitemeier, R.F. 1963. The leaching of radiostrontium and radiocesium through soils. Soil Sci. Soc. Am. Proc. 27:141-144.
23. Maes, A., Verheyden, D., and Cremers, A. 1985. Formation of highly selective exchange sites in montmorillonite. Clays Clay Min. v.33, no.3, pp.251-257.
24. Maes, A., and Cremers, A. 1986. Highly selective ion exchange in clay minerals and zeolites. Geochemical Processes at Mineral Surfaces, James A. Davis and Kim F. Hayes, ed., Am Chem Soc., Wash., D.C.
25. Oscarson, D.W., Watson, R.L., and Miller, H.G. 1987. The interaction of trace levels of cesium with montmorillonitic and illitic clays. Applied Clay Sci. 2:29-39.
26. Rich, C.I. 1964. Effect of cation size and pH on potassium exchange in Nason Soil. Soil Sci. v.98, no.2, pp.100-106.

27. Rich, C.I., and Black, W.R. 1964. Potassium exchange as affected by cation size, pH, and mineral structure. Soil Sci. 97:384-390.
28. Sawhney, B.L. 1964. Sorption and fixation of microquantities of cesium by clay minerals: Effect of saturating cations. Soil Sci. Soc. Am. Proc. 28:183-186.
29. Sawhney, B.L. 1965. Sorption of cesium from dilute solutions. Soil Sci. Soc. Am. Proc. 29:25-28.
30. Sawhney, B.L. 1966. Kinetics of cesium adsorption by clay minerals. Soil Sci. Soc. Am. Proc. 30:565-569.
31. Sawhney, B.L. 1970. Potassium and cesium ion selectivity in relation to clay mineral structure. Clays Clay Min. 18:47-52.
32. Sawhney, B.L. 1972. Selective sorption and fixation of cations by clay minerals: a review. Clays Clay Min. 20:93-100.
33. Schulz, R.K., Overstreet, R., and Barshad, I. 1960. On the soil chemistry of cesium-137. Soil Sci. 89:16-27.
34. Sparks, D.L. 1985. Kinetics of ionic reactions in clay minerals and soils. Adv. Agron. v.38.
35. Sparks, D.L., and Jardine, P.M. 1981. Thermodynamics of potassium exchange in soils using a kinetics approach. Soil Sci. Soc. Am. J. 45:1094-1099.
36. Tamura, T. 1964a. Selective sorption reactions of cesium with soil minerals. Nuclear Safety, v.5 no.3 pp.262-268.
37. Tamura, T. 1964b. Reactions of cesium-137 and strontium-90 with soil minerals and sesquioxides. 8th Intern. Congress of Soil Sci., Bucharest, Romania.
38. Tamura, T., and Jacobs, D.G. 1960. Structural implications in cesium sorption. Health Phys. 2:391-398.
39. Tamura, T., and Jacob, D.G. 1961. Improving cesium selectivity of bentonites by heat treatment. Health Phys. 5:149-154.
40. Vanselow, A.P. 1932. Equilibria of the base exchange reactions of bentonites, permutites, colloids, and zeolites. Soil Sci. 33:95-113.
41. Wahlberg, J.S., and Fishman, M.J. 1962. Adsorption of cesium on clay minerals. Geol. Survey Bull. 1140-A.