

CESIUM SELECTIVITY OF A LIGNITE
ASSOCIATED SHALE STRATA IN TEXAS

by

DAVID CARTY

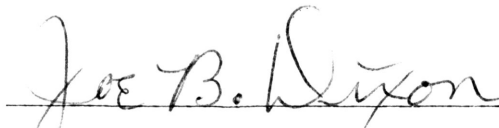
Department of Soil and Crop Sciences

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Approved by:

A handwritten signature in cursive script that reads "Joe B. Dixon". The signature is written in dark ink and is positioned above a horizontal line.

J. B. Dixon

Faculty Advisor

ABSTRACT

Cesium selectivity (k_d) exponentially increased as Cs saturation decreased in the $<0.2\mu\text{m}$ clay fraction and possibly in the $2-0.2\mu\text{m}$ clay and $20-2\mu\text{m}$ silt fractions of the lignite associated shale. The $<0.2\mu\text{m}$ clay fraction had a high selectivity up to about 10% Cs saturation. Larger particle sizes had the highest selectivity. The total number of Cs ions fixed was higher in the smaller size fractions. Additional analyses must be performed to accurately determine the mineralogical composition of the shale and the ultimate disposition of the Cs ions introduced into the mineral system.

To

My Parents

ACKNOWLEDGEMENTS

My deepest appreciation is expressed to Dr. Joe B. Dixon for introducing me to the wonderful world of research science, and for providing continual guidance and support. Ever ready assistance was available from Dr. Harpal Arora, C. D. Carson, Frank Hons, Darrell Schulze, and Robert Wiedenfield specifically, and on one occasion or another each of the resident graduate students in soil mineralogy and soil chemistry.

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INTRODUCTION

The removal of Cesium-137 from nuclear reactor fuel residues is a problem of concern to the nuclear scientist (Glasstone, 1958), and to the environment conscious public. Measurements at Oak Ridge National Laboratories in 1956 showed Cs-137, with a half-life of 30 years and a high fission yield, to contribute 85 percent of the gross β -activity in the waste liquids (Jacobs, 1960). Isaacson et al. (1975) reminds us that the accidental, unexpected release of cesium is also of concern, and that the selection of a nuclear reactor site may be influenced by the ability of a soil to retard the migration of cesium. Jacobs and Tamura (1960), who have done extensive cesium sorption work on Conasauga shale at ORNL, report that the ion exchange capacity of soil is used extensively in the decontamination of waste streams produced by Atomic Energy Installations. Many researchers have concluded that mica, and to a lesser degree vermiculite, are the soil minerals most responsible for the high degree of cesium selectivity shown by some soils.

A United States Atomic Energy Commission map (1974) showed two of the proposed nuclear reactor sites in Texas to be on or near areas underlain by near-surface lignite. Also, since electrical power transmission equipment exists at presently operating lignite fueled power plants, which are located above the lignite deposits, it is possible that conversion from lignite to nuclear power may occur for economic reasons once the local

The citations on the following pages follow the style of the Soil Science Society of America Proceedings.

lignite is depleted. The shale studied in this experiment was obtained from such a lignite shale zone. As Tamura and Jacobs (1960) point out, "Irrespective of the ultimate mode of disposing of radioactive fission product wastes, knowledge of the possible interactions between fission products and soils is of prime importance."

MATERIALS AND METHODS

An undisturbed shale sample from approximately 30 meters depth was obtained in an interbedded lignite, shale, sand, and sandstone deposit in central Texas.

Clay Preparation

The shale was fractionated according to size and the values, assuming 100% recovery, are recorded in Table 1. The 20-2 μ m, 2-0.2 μ m, and <0.2 μ m fractions were the categories of major interest and subsequently received the following treatments: The shale was ground to pass a 2mm sieve CaCO_3 was removed with pH 5 N NaOAc and the organic matter was oxidized with H_2O_2 according to the method described by Jackson (1956). Dispersion for fractionation was done by mechanical mixing in a pH 10 Na_2CO_3 solution at room temperature. Sand was removed by sieving and silt and clay by centrifugation. Clays were then separated at 0.2 μ m using the centrifuge, and HCl additions lowered the pH to 4.5 to promote flocculation. The 20-2 μ m silt fraction was washed twice with deionized water and the two clay fractions were washed chloride free with alcohol. The three fractions were then stored in a solution of 50:50 ethanol and water. Concentrations in the storage containers were determined by oven dried aliquot. The pH was established to be 7.95 by saturated solution, and the gravimetric moisture percent was 5.78 in a mechanically ground air dry sample.

Table 1

Particle size distribution and CaEC values of lignite associated shale.

Fraction	Amount*	CaEC
	%	meq/100gm
>50 μ m	0.00	N.D.
50-20 μ m	0.10	N.D.
20-2 μ m	41.74	5.59
2-0.2 μ m	35.43	34.32
<0.2 μ m	22.72	56.68
whole soil	99.99	26.57

* Assuming 100% recovery

N.D. = not determined

Mineral Determinations

Chloride free 70mg samples of each size fraction were x-rayed (Figures 1, 2, and 3) with a goniometer (Norelco, 1.54Å, Copper K α , 1000cps, 14ma, 35kV, TC2, 1°/min). Slides were prepared from soil fractions which were saturated with magnesium (solvated with glycerol), and with potassium. Potassium saturated samples were x-rayed at room temperature and after heating at 300°C and 550°C. The 2-0.2 μ m K 550°C slide material separated from the slide surface and had to be x-rayed with the inverted clay aggregate using two sided Scotch tape such that the more dense particles became farther from the new slide surface than the less dense particles. Hence, interpretation of the 2-0.2 μ m K 550°C slide rests on the inverted display.

Cation Exchange Capacity

CaEC (Table 1) was determined according to Alexiades and Jackson (1965) and interstitial cations in interlayer solution were corrected for. The CaEC of a whole soil specimen in which no organic matter was removed was also determined. Cation exchange values are expressed in meq/100gm unless otherwise noted.

Selectivity Determinations

Fractionated suspended samples containing 70mg of mineral material were pipetted into tared 40ml test tubes. Specimens were again washed in

Figure 1. X-ray diffraction pattern for the $<0.2\mu\text{m}$ fraction of a lignite associated shale.

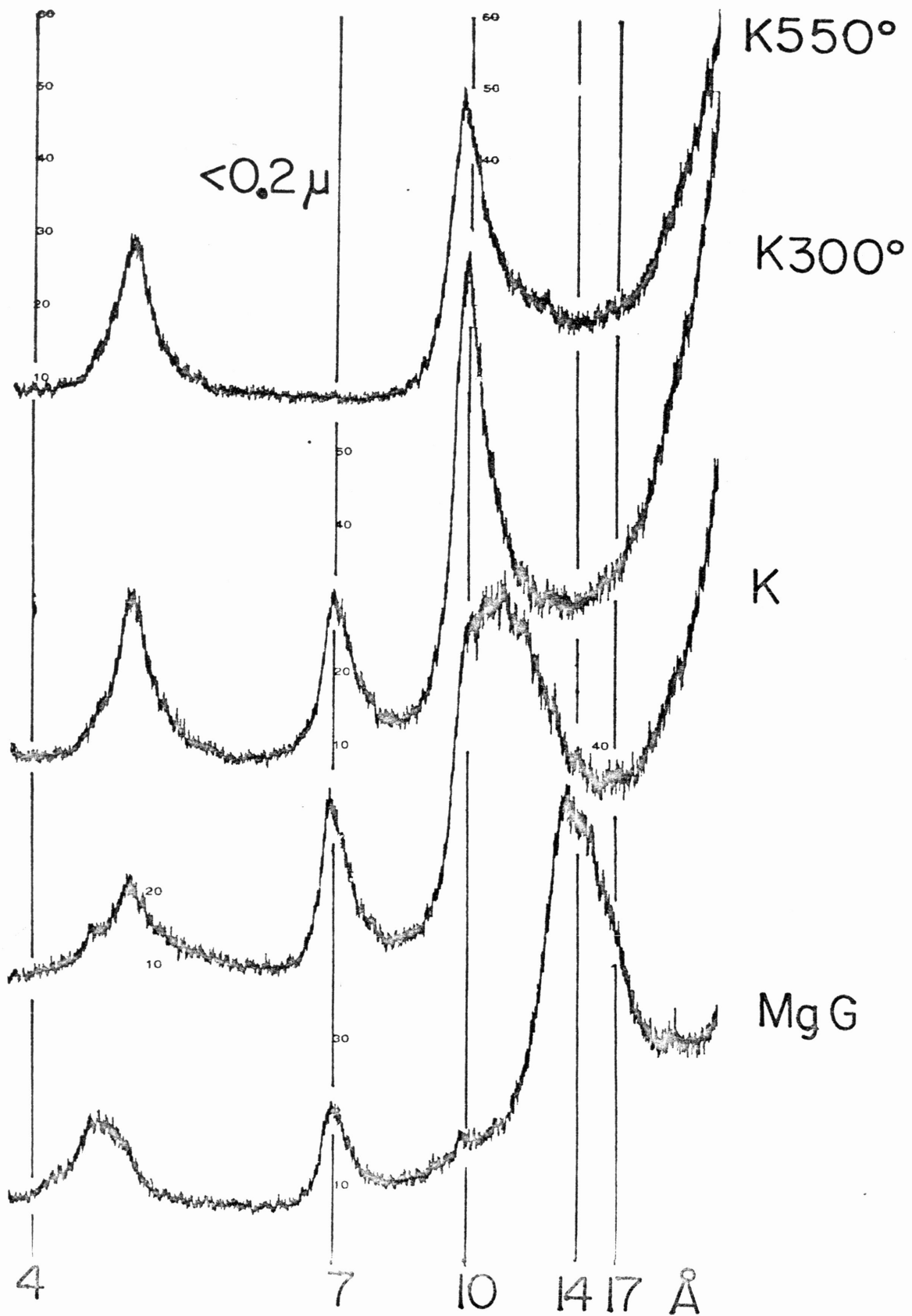


Figure 2. X-ray diffraction pattern for the 2-0.2 μ m fraction of a lignite associated shale.

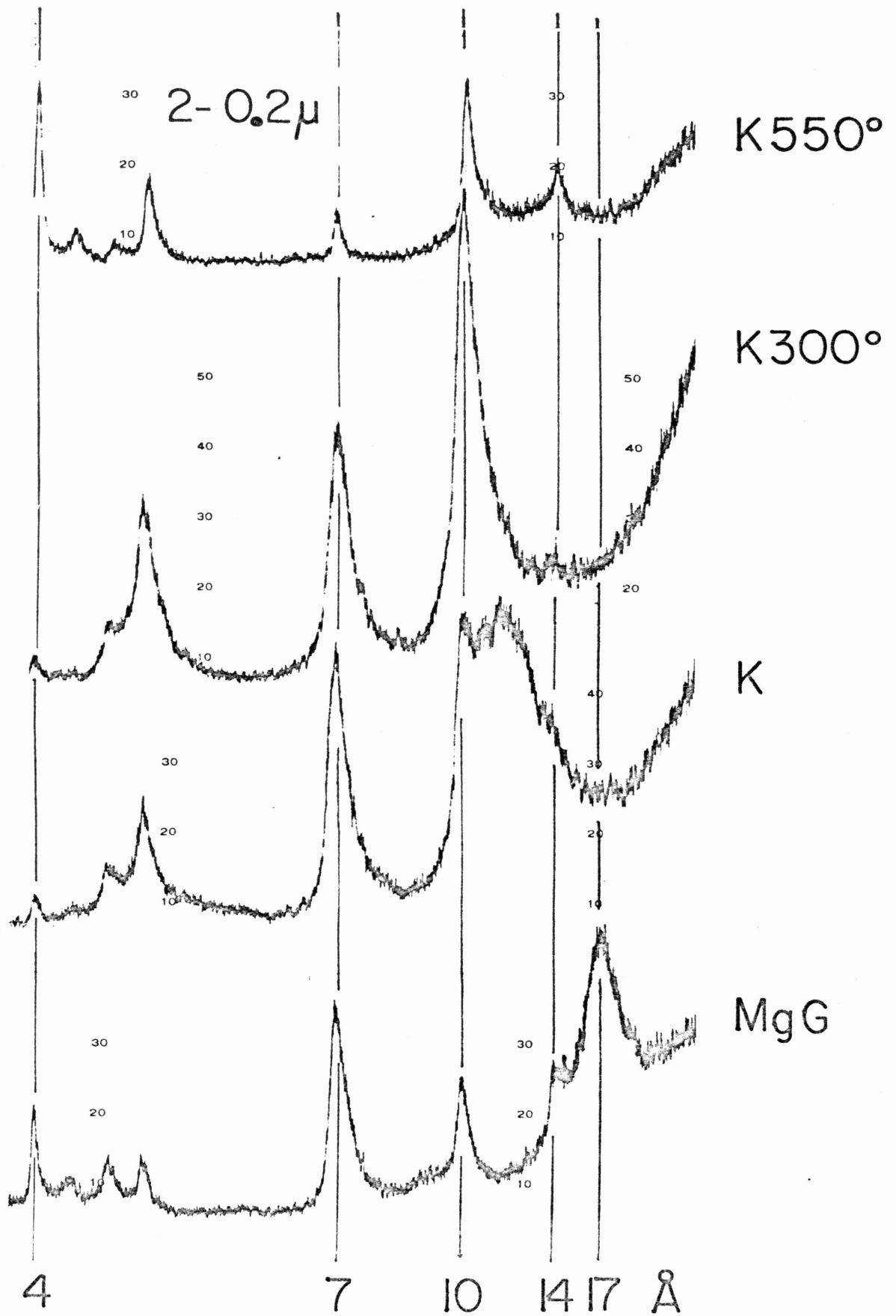
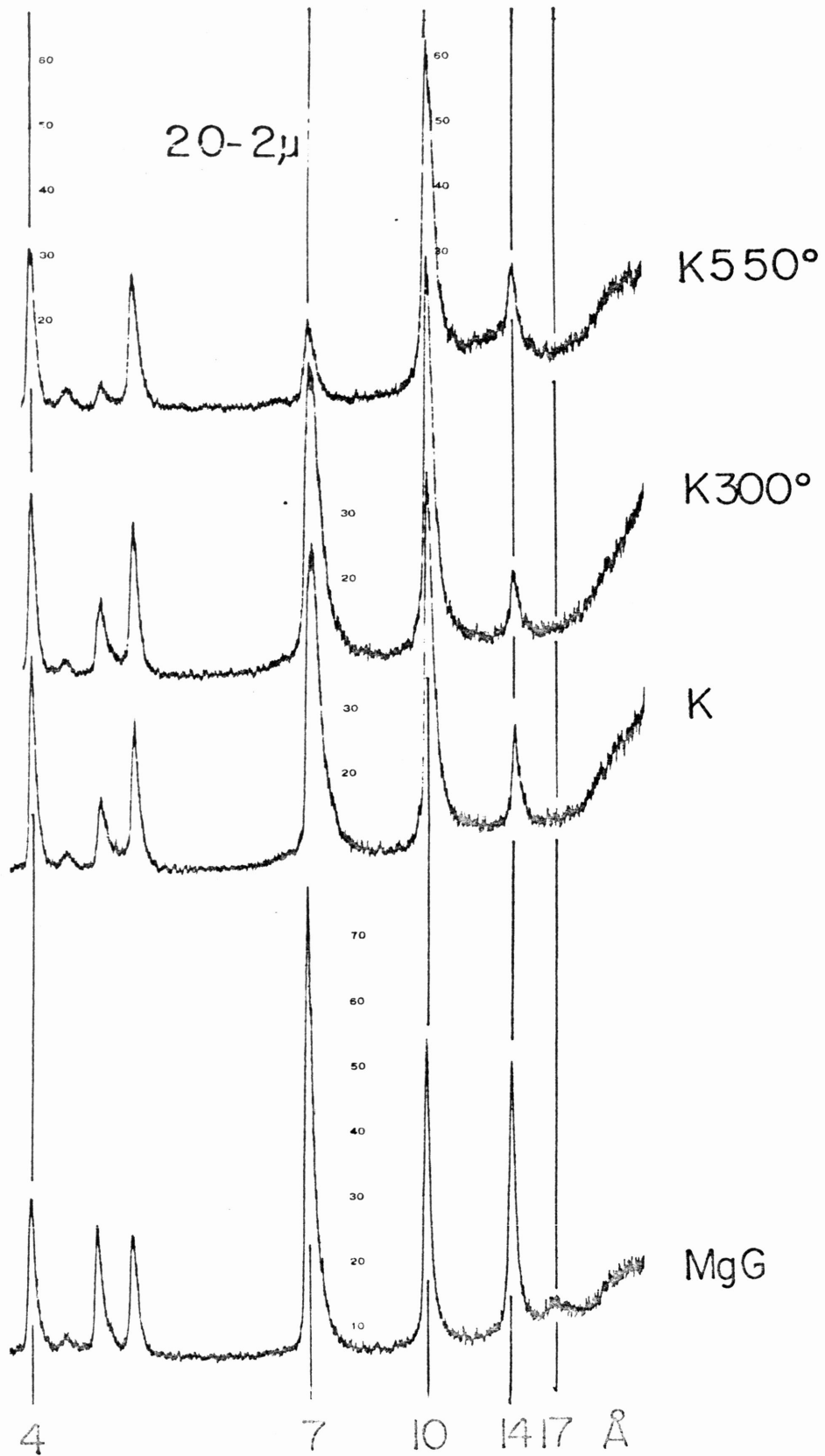


Figure 3. X-ray diffraction pattern for the 20-2 μ m fraction of a lignite associated shale.



pH 5 N NaOAC, and H_2O_2 was applied a second time. Methanol was added after decantation of the previous solution and the specimens were stored air tight in the glass test tubes for 20 days. A series of tests were run on Cs and Ca to determine the relationship of inter-ion interference. Within the concentration range of interest, Cs did not interfere with Ca readings on Atomic Absorption Spectrophotometry. Ca did interfere substantially with Cs concentration analysis using the emission mode of the same machine (Perkin-Elmer model 403). Samples were washed 5 times with 15ml of N $CaCl_2$ and mixed on a reciprocating shaker for 15 minutes each wash. Five 0.01N (Cs + Ca combined) equilibrium solutions with approximate concentrations ranging from [0.0001N Cs/0.0099N Ca] in solution A to [0.006N Cs/0.004N Ca] in solution E were used to saturate the five replicated samples in each fraction. Three 10ml equilibrium solution washes with a 15 minute shaking duration per wash were performed on the specimens. A fourth and final equilibrium solution wash of 25ml endured continuous shaking for 24 hours. The final equilibrium solution decantate was analyzed for Ca and Cs concentrations. For accurate Cs determination, the addition of 1000ppm K as a chloride salt and the addition of some Ca in most cases was required to provide a uniform matrix for the Cs. The amount of Ca required was calculated from the previously measured Ca concentrations in each equilibrium solution. Cesium standards were also analyzed in 1000ppm K and in a uniformly equal ppm Ca matrix.

Averages were made of the replicated Cs and Ca concentrations and the results are shown in Tables 2, 3, and 4 in equilibrium solution context. Three 30ml washes with pH 7 N NH_4OAC were then performed on the equilibrated minerals with a 15 minute shaking period for each wash. A final

Table 2

Cation exchange data and Cs disposition after washing with NH_4 with respect to equilibrium solution for $<0.2\mu\text{m}$ clay from a lignite associated shale.*

Equilibrium solution	CaEC	CsEC	<u>nCs sorbed</u>		<u>nCs fixed</u>	
			max.	min.	max.	min.
normal	----- meq/100gm -----					
A $\frac{0.0001 \text{ Cs}}{0.0099 \text{ Ca}}$	56.8	0.1	4.7	2.2	4.6	2.1
B $\frac{0.0004 \text{ Cs}}{0.0096 \text{ Ca}}$	55.1	0.5	6.4	3.9	5.9	3.4
C $\frac{0.0009 \text{ Cs}}{0.0094 \text{ Ca}}$	49.7	1.9	11.8	9.3	9.9	7.4
D $\frac{0.0026 \text{ Cs}}{0.0083 \text{ Ca}}$	37.6	1.0	23.9	21.4	22.9	20.4
E $\frac{0.0087 \text{ Cs}}{0.0044 \text{ Ca}}$	18.4	0.2	43.1	40.6	42.9	40.4

* All values are averages of duplicates.

Table 3

Cation exchange data and Cs disposition after washing with NH_4 with respect to equilibrium solution for 2-0.2 μm clay from a lignite associated shale.*

Equilibrium solution	CaEC	CsEC	<u>nCs sorbed</u>		<u>nCs fixed</u>	
			max.	min.	max.	min.
normal	meq/100gm					
A $\frac{0.0001 \text{ Cs}}{0.0099 \text{ Ca}}$	29.8	0.1	4.8	0.8	4.7	0.7
B $\frac{0.0003 \text{ Cs}}{0.0098 \text{ Ca}}$	28.1	0.5	6.5	2.5	6.0	2.0
C $\frac{0.0009 \text{ Cs}}{0.0096 \text{ Ca}}$	23.2	0.5	11.4	7.0	10.5	6.5
D** $\frac{0.0024 \text{ Cs}}{0.0082 \text{ Ca}}$	19.1	1.9	15.5	11.5	13.6	9.6
E $\frac{0.0074 \text{ Cs}}{0.0042 \text{ Ca}}$	10.1	3.2	24.5	20.5	21.3	17.3

* All values are averages of duplicates except **.

** The duplicate was spilled.

Table 4

Cation exchange data and Cs disposition after washing with NH_4 with respect to equilibrium solution for 20-2 μm silt from a lignite associated shale.*

Equilibrium solution	CaEC	CsEC	<u>nCs sorbed</u>		<u>nCs fixed</u>	
			max.	min.	max.	min.
normal	----- meq/100gm -----					
A $\frac{0.0001 \text{ Cs}}{0.0099 \text{ Ca}}$	6.0	0	4.8	0.8	4.8	0.8
B $\frac{0.0004 \text{ Cs}}{0.0097 \text{ Ca}}$	4.4	0	6.4	2.4	6.4	2.4
C $\frac{0.0010 \text{ Cs}}{0.0094 \text{ Ca}}$	4.6**	0.1	6.2	2.2	6.1	2.1
D $\frac{0.0025 \text{ Cs}}{0.0082 \text{ Ca}}$	3.4	0	7.4	3.4	7.4	3.4
E $\frac{0.0077 \text{ Cs}}{0.0041 \text{ Ca}}$	3.2	0.1	7.6	3.6	7.5	3.5

* All values are averages of duplicates except **.

** The duplicate seemed in error and was discarded.

100ml volume of decantate was obtained with the NH_4OAC matrix. Cs and Ca extract concentrations were analyzed analogous to the equilibrium solutions except that no Ca was added to the solutions to be analyzed for Cs concentration. The Ca interference factor was corrected for by running three standard curves, each at a different Ca concentration chosen to represent the field of Ca values known to be in the solutions awaiting Cs concentration analysis. Fairly accurate Cs concentrations were then obtained by interpolating between the three Ca related standard curves.

TREATMENT OF DATA

Mineralogical data- Determination of the percent contribution of each component in the mineral suite was deemed essential for this study and could only be approximated. The CaEC was measured for each fraction and values of the CEC for individual minerals were provided by literature. X-ray patterns were used to denote the presence of given minerals, and by coordination with known approximate attenuation factors inherent in the process, a gross first approximation of the percent contribution of each mineral was made. X-ray attenuation factors considered were gravimetric stratification of minerals on the slides, and the target angle of the goniometer.

A second approximation was made by multiplying the rough percent contribution of each mineral by the published value for the CEC of that mineral. A summation of these cation exchange capacities was compared with the measured CaEC. Disagreement forced reconsideration of the individual percentages which were carefully orchestrated with the CaEC to give a final approximation (Table 5). In the event of vermiculite structural collapse the exchange capacity of vermiculite would approximate the exchange capacity of mica in meq/100gm and the system CEC would also be reduced.

Cs sorption data- Data collected failed to measure the Cs sorbed by the minerals. Due to the variety of unknowns in the system, "maximum possible" and "minimum possible" values for Cs sorbed were calculated thereby confining the limits of the real value (Tables 2, 3, and 4). The Cs

Table 5
Estimated % mineral contribution and CaEC for a lignite associated shale.

	Mt	Ch	V	Mi	K	Q	Total	CaEC (measured)
Mineral contribution (%)*	12.0	0.0	26.0	43.0	19.0	0.0	100.0	
Mineral CEC (meq/100gm)**	80	10	136	25	5	0		
CEC contribution (meq/100gm)	9.6	0.0	35.4	10.8	0.9	0	56.7	56.7
CEC (vermiculite collapsed)	9.6	0.0	6.5	10.8	0.9	0	27.8	
				<u><0.2µm</u>				
Mineral contribution (%)*	13.8	2.0	9.5	41.9	19.2	13.6	100.0	
Mineral CEC (meq/100gm)**	80	10	136	22	5	0		
CEC contribution (meq/100gm)	11.0	0.2	12.9	9.2	0.9	0	34.2	34.3
CEC (vermiculite collapsed)	11.0	0.2	2.4	9.2	0.9	0	23.7	
				<u>2-0.2µm</u>				
Mineral contribution (%)*	0.5	1.6	1.4	16.2	12.2	68.1	100.0	
Mineral CEC (meq/100gm)**	80	10	136	16	5	0		
CEC contribution (meq/100gm)	0.4	0.2	1.9	2.6	0.6	0	5.7	5.6
CEC (vermiculite collapsed)	0.4	0.2	0.4	2.6	0.6	0	4.2	

* Basis of estimates given in Treatment of Data section.

** CEC ranges and trends given by Grim (1953), vermiculite by Sawhney (1970), and mica (illite) by Gaudette, et al. (1966), and Tamura and Jacobs (1960).

Mt=montmorillonite; Ch=chlorite; V=vermiculite; Mi=mica; K=kaolinite; Q=quartz

sorbed includes the Cs "fixed" (sorbed by selective minerals and not displaced by NH_4) as well as the Cs "exchanged" (held by less selective exchange sites such that replacement by NH_4 occurred).

The maximum possible Cs sorbed is the total number of Cs ions introduced into the mineral system minus the number of Cs ions decanted in the final 25ml equilibrium solution wash, and is expressed per 100gm. The estimate of the minimum possible Cs sorbed is assumed to be no lower than the K sorbed in the Victoria montmorillonitic clay (12% mica, 5% vermiculite) in a similar experiment using K/Ca equilibrium solutions (Carson and Dixon, 1972). Unpublished K sorbed data for the [0.0001N K/0.0099N Ca] equilibrium solutions were furnished by the authors. Their K sorbed for the 2-0.2 μm fraction was used for Cs sorbed by the 20-2 μm size fraction as well as the 2-0.2 μm fraction in this experiment since there was no basis upon which to select a different number.

Results from the lowest Cs concentrations \sim [0.0001N Cs] in solution A showed Ca sorbed to agree with the CaEC except for the 2-0.2 μm fraction (cause unknown). The maximum and minimum possible estimates of Cs sorbed were added to the measured Ca sorbed values to provide an estimate of the maximum and minimum possible sites available for both cations. This was done by fraction using CaEC values corresponding to the lowest Cs equilibrium concentrations. Some of these sites were selective for Cs and some were not.

Maximum and minimum values for Cs sorbed for equilibrium solutions B, C, D, and E were calculated by subtracting the CaEC from the maximum and minimum CEC figures. The Cs fixed is considered to be the Cs sorbed on selective sites and is calculated by subtracting the measured Cs exchanged

by NH_4 from the maximum and minimum possible values of Cs sorbed.

Selectivity data- Gapon selectivity coefficients (kg) are mathematical expressions relating the preference for a given cation species from a mixed species solution by soil minerals. Higher kg values (liters/mole)^{1/2} reflect an increased preference for the species in question (Cs). The mathematical relationship is:

$$kg \text{ (liters/mole)}^{1/2} = \frac{n\text{Cs sorbed}}{n\text{Ca sorbed}} \div \frac{m\text{Cs solution}}{(m)^{1/2} \text{ Ca solution}}$$

$$n = \text{meq/100gm}$$

$$m = \text{moles/liter}$$

Percent Cs saturation was calculated by dividing Cs sorbed by the total available sites for both ions thereby giving maximum and minimum possible % Cs saturation. Replicated determinations are averaged except where noted, and the values of kg and % Cs saturation are given in Table 6, and are graphically related in Figures 4, 5, and 6.

Table 6

Cesium saturation and selectivity coefficient (*kg*)
for a lignite associated shale.

Equilibrium solution	<u>% Cs saturation</u>		<u>Selectivity coefficient</u>	
	max.	min.	max.	min.
	%		(liters/mole) ^{1/2}	
		<u><0.2μm</u>		
A	7.6	3.7	58.2	27.3
B	10.6	6.6	23.0	14.0
C	19.2	15.8	18.2	14.4
D	35.1	32.5	14.2	12.7
E	70.1	68.8	12.6	11.9
		<u>2-0.2μm</u>		
A	13.9	2.6	119.3	19.9
B	18.8	8.2	50.6	19.5
C	32.9	22.9	39.6	24.3
D	44.7	37.6	21.7	16.1
E	70.7	66.9	15.0	12.4
		<u>20-2μm</u>		
A	44.4	11.8	511.7	85.3
B	59.2	35.3	259.7	97.4
C	57.4	32.4	92.4	32.8
D	68.5	50.1	55.6	25.5
E	70.3	53.0	14.1	6.6

$$\% \text{ Cs saturation} = \frac{n\text{Cs sorbed}}{\text{CEC}} (100)$$

All values are averages of duplicated samples except for solution D in the 2-0.2 μ m fraction - the duplicate was spilled; and solution C in the 20-2 μ m fraction - the duplicate seemed in error and was discarded.

FIGURE 4

CESIUM SELECTIVITY (kg) VS % CESIUM SATURATION IN
THE $<0.2\mu$ FRACTION OF A LIGNITE ASSOCIATED SHALE

- CALCULATED USING MAXIMUM POSSIBLE Cs SORBED
- △ CALCULATED USING MINIMUM POSSIBLE Cs SORBED

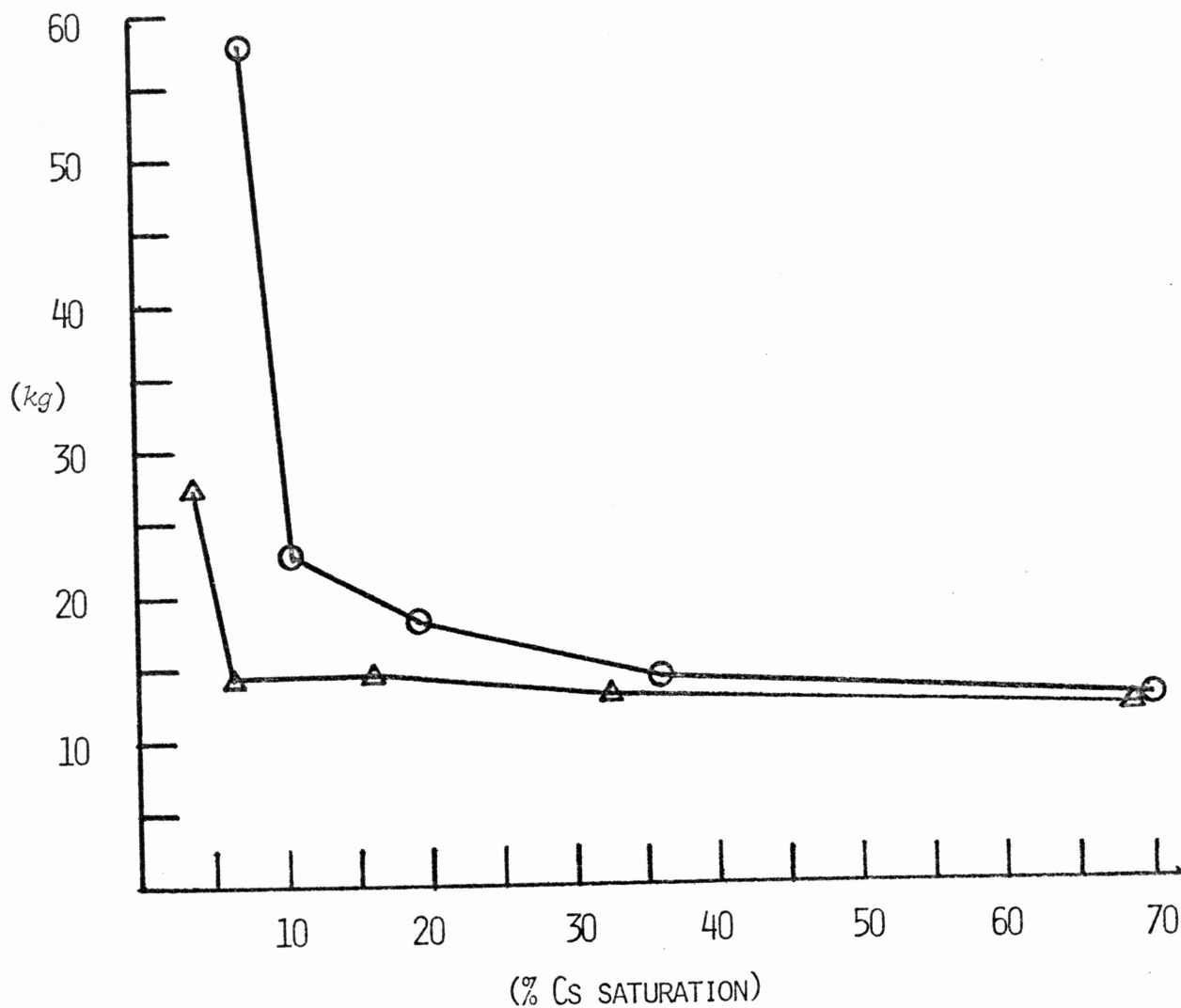


FIGURE 5

CESIUM SELECTIVITY (kg) VS % CESIUM SATURATION IN
THE 2-0.2 μ m FRACTION OF A LIGNITE ASSOCIATED SHALE

○ CALCULATED USING MAXIMUM POSSIBLE Cs SORBED

△ CALCULATED USING MINIMUM POSSIBLE Cs SORBED

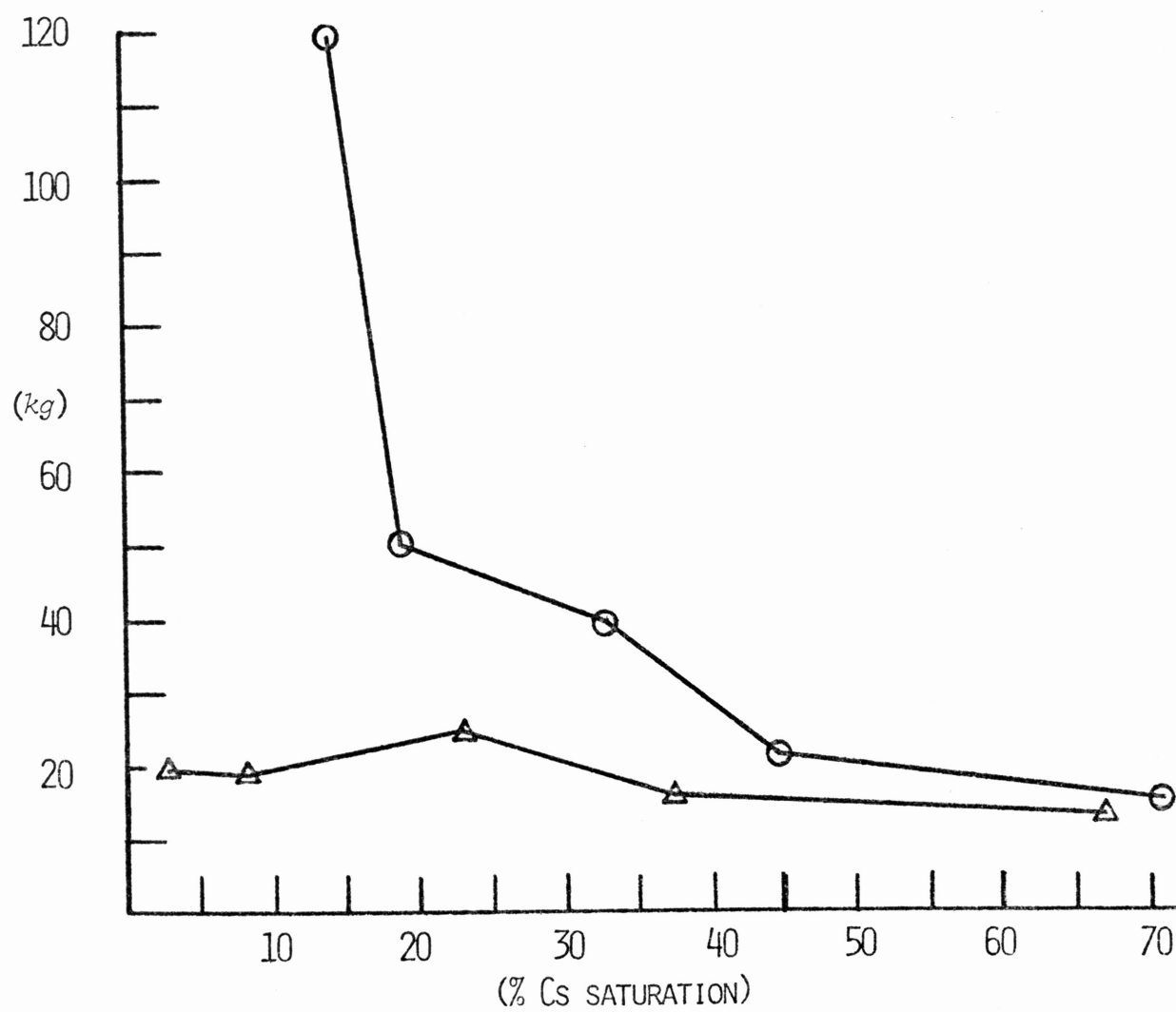
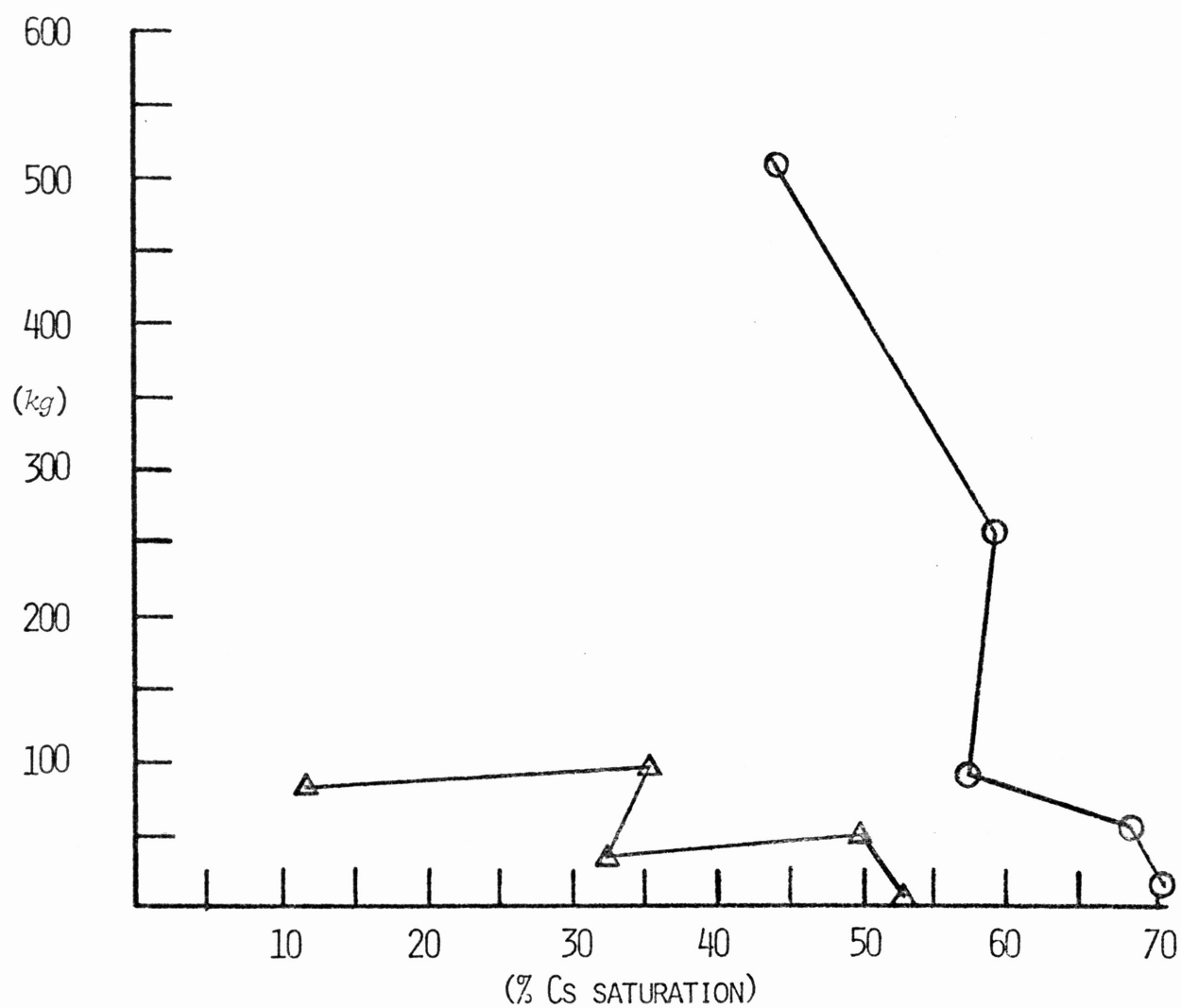


FIGURE 6

CESIUM SELECTIVITY (kg) VS % CESIUM SATURATION IN
THE 20-2 μ m FRACTION OF A LIGNITE ASSOCIATED SHALE

- CALCULATED USING MAXIMUM POSSIBLE Cs SORBED
- △ CALCULATED USING MINIMUM POSSIBLE Cs SORBED



DISCUSSION

Thorough analysis of the mineral suite was not performed, and digestion of data obtained is incomplete. Adequate understanding of the minerals involved would have required additional x-ray analysis and determination of the chemical analysis of the specimens. Consequently, the mechanisms and mineral components responsible for the results can only be surmised from other related findings in literature, and the data are inconclusive beyond the facts that for this shale: (1) There is a substantial preference for Cs over Ca. (2) Cs selectivity exponentially increases with a decrease in Cs solution concentration and with a decrease in % Cs saturation for the clay size fractions and possibly for the silt size fraction. (3) Total Cs fixation increases as particle size decreases. (4) Cs selectivity (kg) increases as particle size increases.

Mineralogical Characteristics- There is general literature agreement that mica and the hydrous mica group of soil minerals are primarily responsible for the Cs selectivity reaction, (Jacobs and Tamura, 1960, Wahlberg and Fishman, 1962, and Sawhney, 1965). Two main groups of hydrous micas are the illite group which has less K and more water than muscovite, and the vermiculite and hydrobiotite group (Marshall, 1964) which is typically quite hydrated. Hydrobiotite consists of interstratified layers of biotite and vermiculite. Cation exchange capacities (CEC expressed as meq/100gm) for some of these minerals are shown in Table 5. Which combination of the above reactive species exist in the specimen shale has not been established and henceforth their broad range of characteristics is meant

to be included by the mention of "mica" at one extreme and "vermiculite" at the other extreme except where references are given. The selective adsorption of NH_4 , K, and Cs ions with respect to other cations by these clay minerals has been established by many investigators.

There are several factors governing ion selectivity in a soil. Because Cs, K, and NH_4 have similar ionic radii they are fixed similarly in 2:1 layer silicates. Various methods of approach for determining cation selectivity have been proposed, and the use of the Gapon selectivity expression (k_g) with an approximation of the methodology used by Schwertmann(1962), Rich and Black (1964), Dolcater et al. (1968), and Carson and Dixon (1972) is used in this experiment.

Selectivity of mica- Micas display the highest selectivity for K [or Cs] for two reasons: first, the greater charge density of mica over montmorillonites and vermiculites (Sawhney, 1970). Second, mica interlayers are frayed at the edges (Jackson, 1963, and Rich and Black, 1964).

The differences in selectivity between vermiculite and montmorillonite is due to the difference in layer charge density while the differences in selectivity between mica and vermiculite is due to the frayed edges in addition to the layer charge density (Sawhney, 1970). Sawhney also points out that frayed edges in mica may be produced by removal of interlayer K during clay separation, but that natural weathering should also form frayed edges in micaceous particles. The degree to which frayed edges are produced due to clay separation, especially by mixing with a blender, is of interest here and would tend to increase the k_g contribution of mica as the number of frayed edges increased. For a comprehensive discussion of mineralogical (and other) factors influencing K and Cs selectivity see

Rich (1968).

Sawhney (1970) attributes the limitation of the K selectivity of mica to low K concentrations because an appreciable number of exchange sites on micas are on planar surfaces and broken bond edges which are not selective for K sorption. At greater concentrations, Sawhney continues, the selectivity of mica is reduced due to sorption on these non-selective sites. Thus, the process of fixation begins to occur here as Sawhney (1970) implies by noting that the frayed interlayer edges of mica collapse readily on Cs or K adsorption, and as the area of the frayed edges in micas is increased, the selectivity for K also increases.

Calculating from Gaudette, Grim, and Metzger (1966), a 1gm illite clay sample saturated with a 0.0001N CsNO_3 solution would adsorb about 30% of the Cs from 100ml solution or 0.003 meq/gm. Assuming 43% mica in 0.06656gm (average oven dry weight for $<0.2\mu\text{m}$ size fraction), the mica component of the shale fraction studied here would adsorb only 8.6×10^{-5} meq Cs or 1.6% of the Cs introduced to it in the $1 \times 10^{-4}\text{N}$ Cs solution. Tamura (1963) similarly mentions that the minimal exchange capacity of 1.38gm biotite cannot remove Cs greater than 5×10^{-4} meq. This calculates to 3.6×10^{-4} meq Cs/gm which indicates the biotite component in this shale specimen would remove only 0.2% of the Cs introduced by the $1 \times 10^{-4}\text{N}$ Cs solution. Sawhney (1970) on the other hand, shows 100mg biotite with the characteristic exponential selectivity curve for K (as % K saturation) in the 0.01N to 1N KCl concentration range which would require continued selectivity by the mineral at concentrations $>0.01\text{N}$ although the solution volume is not mentioned. Additionally, Carson and Dixon (1972) attribute the wide K saturation range over which the $2g$ vs. % K saturation showed

its exponential rise in a montmorillonitic clay to the 13% mica content. Their equilibrium solutions ranged from 0.0001N K to 0.006N K and 40ml was used. The acknowledged 10-40 meq/100gm CEC of mica would imply an ability to sorb Cs by that amount, a few of which Cs ions would be fixed while the majority of Cs ions would be held on exchange sites. Although mica is highly Cs selective at microconcentrations of Cs, its total contribution to Cs adsorption at the concentrations used in this experiment is open to question as indicated above.

Selectivity of vermiculite- There is evidence that vermiculite plays the most meaningful role in the selectivity data. In all fractions the CEC decreased as the equilibrium Cs concentration increased. A lowering of the CEC is an indication of "blockage" of exchange sites such that normal cation exchange is hindered. Aside from the steric favorability of the Cs ion in the tetrahedral sheets and its subsequent difficulty of replacement by other cations, it is likely that its power to collapse the vermiculite structure is the cause of the CEC decrease as indicated by data from all three fractions. Such a collapse would reduce the system CEC representing the transformation of vermiculite into a mica-like mineral, i.e. a decrease of 28.9 meq/100gm in the <0.2 μ m fraction. Sawhney (1969) and Mackenzie (1963) show almost no CEC reduction in montmorillonite due to Cs at much higher Cs concentrations indicating that collapse in montmorillonite would not occur at the concentrations used in this experiment.

The decrease in CEC as evidence for vermiculite collapse is supported by Jacobs (1963) who showed that high concentrations of Cs reduce vermiculite lattice spacing to 10Å causing physical entrapment of interlayer

cations approximating 45 meq/100gm. He proposes that interlayer fixation in vermiculite can be evidenced by a drop in CEC. The maximum CEC reduction in this experiment was 42.9 meq/100gm in the $<0.2\mu\text{m}$ fraction. The gradual decrease in CEC indicates that each set of adjacent vermiculite layers will collapse according to the individual forces in the interlayer space. All layers would not necessarily collapse together as a unified group. If the collapsing ion concentration is very high, all layers may appear to collapse at once, but this experiment indicates that simultaneous collapse does not occur at these lower Cs concentrations.

Evidence from the x-ray charts seems to show that collapse occurs to varying degrees for each interlayer. The migration of the 14\AA peak to 10\AA with the substitution of K for Mg (Figure 1 and 2) continues with heating to 300°C . In effect the vermiculite still had room to collapse with added influence from heat (a collapsing force). Also, the breadth of the continuous peak from 10\AA to 14\AA with ambient K shows a continuum of interlayer spacings to be present. The inference is that each interlayer unit does not necessarily have to collapse completely if it collapses at all, but rather the interlayer space is gradually reduced from 14\AA to 10\AA as Cs saturation increases. Such a mechanism would be in accord with reduction of CEC and the broad peak from 14\AA to 10\AA shown by the x-ray patterns.

The fixation capability of vermiculite has frequently been shown to be greater than that of mica, primarily because nearly all of the CEC sites are available for fixation prior to collapse whereas only the outer edges of mica are similarly available (Jacobs and Tamura, 1960). If the mica in this experiment could only remove 2% of the Cs introduced to it at the

lowest Cs concentration, then vermiculite would account for the remainder of the Cs sorbed at that concentration excepting some removal by montmorillonite and other minerals. There is evidence to support this contention: (1) In all fractions the CEC began to decrease beginning with the lowest Cs concentrations. (2) The estimated decrease in CEC which would result by collapsing vermiculite to a mica-like particle is 28.9 meq/100gm in the <0.2 μ m fraction and 10.5 meq/100gm in the 2-0.2 μ m fraction. (3) Although mica could sorb about 10 meq/100gm in the clay fractions, it is very unlikely to suffer any appreciable decrease in CEC if it has very few interlayer selective sites and has most of its exchangeable surface on the outer perimeter of the particle. That the sorption of the microconcentrations of Cs differs from the fixation reaction associated with interlayer collapse has also been noted by a number of observers (Tamura, 1962).

Cation exchange considerations- As Jacobs (1960) points out, the marked sorption of Cs by vermiculite seems to be dependent on the presence of collapsed lattices. As shown previously, the decline in CEC parallels the ability of vermiculite to collapse thereby reducing its CEC accordingly. As the CEC decreases, Cs sorbed increases and the mechanism responsible for both functions is most likely vermiculite collapse. Investigation of data reveals only one alternative possibility - that the vermiculite remained expanded and the lower bonding energy of NH_4 was yet unable to replace the sterically favored Cs ions which had occupied the hexagonal selection sites. This theory is untenable on two counts: (1) The unselected Cs ions would still be available for NH_4 exchange, yet they did not appear in the decantate, and (2) even if the up to 0.006N Cs did not

collapse the vermiculite, the $1N$ NH_4 almost certainly would have done so. That NH_4 will collapse expanding layer silicates was shown by Barshad (1950).

The anomaly of the decrease in CSEC from solutions D and E of the $<0.2\mu m$ fraction may be partially due to the dispersive effect of Cs on the particles. Work done on the flocculating ability of various cations by Jenny and Reitemeier (1935) shows Cs to tend to disperse clays by 8:1 more than Ca. As the Cs/Ca equilibrium concentration ratio increased in the $<0.2\mu m$ fraction, the interstitial solution rose from an average 0.63gm in solutions A, B, and C to 1.65gm in D, and 2.2gm in solution E. Since the particles had dispersed the danger of decanting them had increased and less complete decanting was the result. Although the Cs exchanged measurements are designed to eliminate unadsorbed Cs ions in solution from the final value, if the concentration was sufficiently large it is possible that three washes of 30ml $1N$ NH_4 did not remove all of the exchangeable and unadsorbed Cs in solution. The result would cause a decrease in Cs exchanged by NH_4 .

The decrease in CEC is more than can be accounted for by the collapse of vermiculite. Cesium which was introduced into the system and which was not replaced by NH_4 must have been retained by the system. Although the replacement of structural potassium in mica is accomplished only with considerable time and energy in most cases, the 24 hour agitation, the expanding pressure of Ca, and the increased concentrations of the competitor ion (Cs) may have caused some structural exchange. Various investigators have shown the time dependency and competing cation concentration to be influential factors in structural K replacement, and

Sumner and Bolt (1962) show the influence of Ca.

Once vermiculite collapse is induced by a given concentration of interlayer Cs ions, there may still be additional sites ready for fixation. Jacobs (1962) has shown that pretreatment of vermiculite by K until collapse is induced increases the Cs selectivity of the mineral. In an analogous way the sorbed Cs would be expected to increase if Cs collapsed the vermiculite layers, and k_g would also increase.

Selectivity related to particle size- The lignite associated shale shows selectivity coefficients which increase as particle size increases except where they converge at 12 (liters/mole)^{1/2} and 70% Cs saturation. Conversely, the Cs fixed increases as particle size decreases. The immediate inference is that while the specific surface (m^2/gm) increases with decreasing particle size (Baver et al., 1972) allowing a greater total number of Cs ions to be fixed. The Cs selective sites may not be directly related since there is apparently a higher percentage of selective sites with an increase in particle size.

Since the Cs ion is smaller it may more easily migrate farther into the vermiculite than the hydrated Ca which may encounter obstructions to its water shell. This may be especially significant if interlayer collapse were beginning and the water were being forced out. The larger the particle diameter, the more acute this phenomenon would become due to the increased interlayer length.

On the surface it would appear that the percent mica to vermiculite ratio might explain the increased k_g and lower Cs fixed, but the Victoria soil of Carson and Dixon (1972) indicates a different mechanism is operative when particle size varies. If the displacement of a crystal surface

increased as its distance from the site of a structural or interlayer abnormality increased, then the surface irregularity of a particle would increase as particle size increased. The dimensions of the octahedral and tetrahedral sheets vary with the occupancy or non-occupancy of the octahedral cation sites and by the size and charge of the octahedral cation as Bailey (1966) points out, and twisting and tilting of the tetrahedra results (Rich, 1968). Therefore a greater gross effect on particles with increased mean diameter might occur analogous to a fulcrum effect. A clear picture emerges if the location of an interlayer "wedge" is considered; the farther into the interlayer the "wedge" moves internally, the greater the arc of displacement of the crystal unit near the edge-interlayer interface. The net effect would be to greatly increase the edge-interlayer surface area where the available selective sites are located. The selectivity of the particle would increase substantially, especially if the interlamellar space were not large enough to accommodate the calcium ion. The greater capacity to fix large quantities of Cs shown by vermiculite with respect to mica may obscure any increase in the Cs fixed by mica due to this mechanism. Information provided by Carson and Dixon (1972) also showed an increase in kg with respect to % K saturation as particle size increased in a variety of montmorillonitic clays having mica and vermiculite impurities. This was especially true at low K concentrations, and occurred when there was no change in the percent mica and vermiculite in the Victoria soil. Information from Schwertmann (1962) and Rich and Black (1964) tend to support the findings of Carson and Dixon, and this paper.

Additional considerations- The specimens in this experiment were agitated

in equilibrium solution for more than 24 hours which should be long enough to complete the Cs sorption reactions (Gaudette, Grim, and Metzger, 1966). However, in a column test run by Jacobs (1962), the reaction for Cs in illite and vermiculite still showed increasing Cs sorption after 500 hours. The complexities of percolation rate, degree of aeration, and other physical soil properties make it difficult to assess the correlation of this laboratory experiment with regard to in situ situations.

Once Cs is fixed it is very difficult to remove. A series of experiments by Frysinger (1960) showed the difficulty of removing Cs from vermiculite once it is fixed. After saturating the vermiculite column with Cs-134, only 0.3% was subsequently removed by the addition of a full column volume of 0.01N Cs-133. He calculated that it would require 7,750 liters to completely elute the Cs-134 from his 6 x 1 cm column at a flow rate of 180ml/hr. Evidence of Cs exchange in a whole soil comes from Nishita et al. (1961) who reported an increased availability of radioactive Cs to plants when stable Cs was added to a soil previously contaminated with radioactive Cs. Tamura (1962) attributes this to Cs competition for the edge fixation sites.

CONCLUSIONS

In the lignite associated shale examined here, a substantial preference for Cs over Ca is exhibited. Cs selectivity exponentially increases with a decrease in Cs solution concentration, and with a decrease in % Cs saturation for the clay size fractions, and possibly for the silt size fraction. Total Cs fixation (such that NH_4 did not replace Cs) increases as particle size decreases indicating a dependence on CEC surfaces. Cesium selectivity (kg) increases as particle size increases indicating dependence on selective sites. Although it is beyond the scope of this research to evaluate the possible siting of a nuclear reactor over this shale, this study shows that it would remove Cs from solution preferentially over other cations to an increasing degree as the concentration of Cs decreased. The presence of vermiculite enhances the ability of the shale to remove Cs at higher Cs concentrations. This lignite associated shale in its natural state is therefore expected to initially adsorb Cs at a fast rate which will then decline. Once the Cs is adsorbed and fixed, it will not be easily replaced.

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