

<Original>      **Studies on the Sorption and Fixation of  
Cesium by Vermiculite**

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**Abstract**

The sorption and fixation of cesium in dilute solutions by vermiculite saturated with Na or K were studied in order to investigate any possibility of its use in radioactive effluent treatment. The cesium sorbed by vermiculite with the increase in pH is attributed to the increase of sorption surface as a result of the dispersion. The increased cesium sorption by Na-vermiculite is due to the different sorption rates by the different exchange sites: external surface and internal surface. It is shown that the larger amount of sorbed cesium was extracted by KCl rather than with any other extractants. It is suggested that the fixation of cesium by vermiculite occurs at the crystal edge where Cs may replace K.

Domestic vermiculite is a valuable material for use in the cesium sorption and fixation, and might be useful as a good packing material outside the tank of highly radioactive liquid waste. And from these results one could suggest that the artificial alteration of the biotite to vermiculite might be occurring by treating with NaCl.

**요 약**

천연점토 광물의 이온 교환 흡착능은 비교적 낮지만, 여러가지 활성화법이 고찰되고 있음으로서 성능의 개선이 기대되고 있다. 그중에서도 교환흡착능이 크며, 많은 양이 산출되고 있는 국산 vermiculite의 NaCl 및 KCl 처리에 의한  $\text{Cs}^+$  ion의 교환 흡착 및 고착상태에 관하여 방사성 폐액 처리의 응용면에서 연구되었으며, 그 결과는 다음과 같다.

- (1) pH의 증가와 더불어  $\text{Cs}^+$  ion의 제련율도 증가하였다.
- (2) 약  $10^{-3}\text{M}$  CsCl 용액중에서  $\text{Cs}^+$  ion의 제련효율이 가장 높았다.
- (3) Na-vermiculite에 의한  $\text{Cs}^+$  ion의 교환 흡착능이 K-vermiculite에 비해 양호하였다.
- (4)  $\text{H}_2\text{O}$ , CsCl, NaCl 및 KCl 용액에 의한 추출 실험에서 80% 정도의 Cesium이 vermiculite 상에 고착되었다.

이상의 결과로 부터 국산 vermiculite도  $\text{Cs}^+$  ion의 교환흡착에 대한 친화력이 크며, NaCl 처리에 의하여 그 성능을 크게 향상시킬 수 있고, 고 준위 방사성 폐액의 지하저장에서 오는 누출현상을 저지시키기 위한 외각 충전제로서도 그 효율성을 보

여 주고 있다. 또한 X-ray 회절상에서 보여 준 바와 같이 인위적으로 NaCl 처리에 의하여 biotite를 vermiculite로 전환시킬 수 있다는 것을 암시하고 있다.

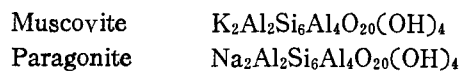
## 1. Introduction

Clay minerals have unique properties in the field of radioactive liquid waste treatment and disposal<sup>1-3</sup>. These important properties are high ionic selectivity, radiation stability, and heat stability.

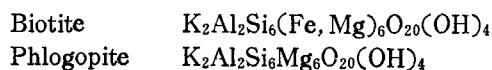
Vermiculite is a naturally occurring hydrated aluminosilicate of calcium and magnesium and like other clay minerals such as montmorillonite and illite, it is formed by the weathering of biotite schist which belongs to the precambrian stage<sup>4</sup>. Vermiculite is derived from the phlogopite or, more frequently, the biotite. This mineral looks very much like mica since it has the same physical properties and occurs as assemblages of thin sheets with the characteristic mica cleavage parallel to the sheets<sup>5</sup>.

Micas occur extensively in soils. They originate in soils primarily by inheritance from the parent rock from which the soil was formed, although an occasional suggestion has been made that, to a limited extent, micas may be formed in soils. Well-ordered micas are inherited by soils mainly from igneous and metamorphic rocks. The idealized end member micas are as the following<sup>5</sup>:

### 1) Dioctahedral

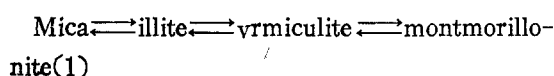


### 2) Trioctahedral



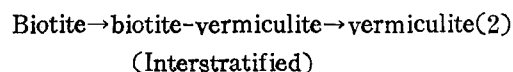
In mica weathering in soils potassium and other interlayer cations slowly diffuse out of the interlayer spaces formed by cleavage between the mica layers into the soil solution, which results in cleavage at the weathering edges of mica(Fig. 1). The K release from micas is hastened by removal of the resulting exchangeable or soluble  $K^+$  ions by roots,

by leaching, or by chemical precipitation in the laboratory. As the interlayer K is subjected to depletion through chemical equilibrium with the soil solution, there is gain that occurs in readily exchangeable ions and interlayer water, according to the equation of Jackson and other<sup>6</sup>:



The shifting of equation(1) to the right (to give lattice expansion) by the lowering of  $K^+$  activity has been demonstrated in laboratory studies.

By Mortland<sup>7</sup>, the weathering of biotite may be considered to proceed as follows:



In micas the parallel negatively charged sheets<sup>8</sup>, which is characteristic of all layer-lattice aluminosilicates, are held together by a layer of potassium ions whereas exchangeable cations and water molecules occur between the sheets in vermiculite<sup>9</sup>.

The structure<sup>5, 10</sup> is shown schematically in Fig. 2, from which it can be seen that magnesium is also present in the interlayer as well as in the sheets but only that associated with the interlayer water is exchangeable. Walker<sup>11</sup> gives the thickness of the water layer in vermiculite as shown in Table 1 and the water exists in two forms, the bound and the unbound. The two sets of value do differ in detail but there are obviously two groups. In the first group the separation is more than 5Å due to the presence of the layers of water between the sheets while in the second group the sheets are much closer together and they are separated only about a quarter of the distance that is found in the first group. Barshad<sup>12</sup> has shown that the exchange

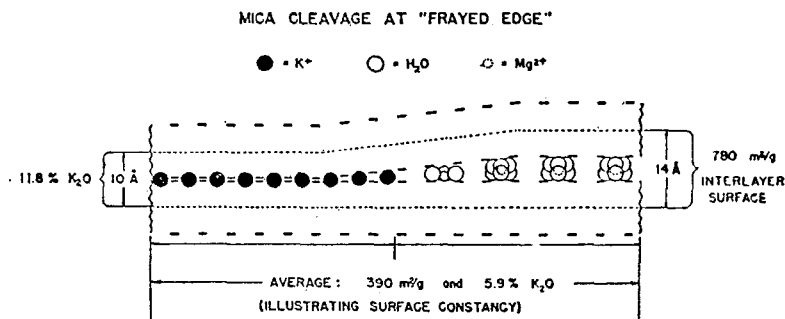


Fig. 1. "Frayed-edge" type of interlayering caused by mica weathering.

between the ions of the first group is completely reversible while the exchange between the ions of the second group is only partially reversible.

It is a well known fact that among the clay minerals cation exchange in vermiculite is often accompanied by a change in the c-axis of the unit cell and that this influences the rate of exchange<sup>13)</sup>, in addition the cesium sorbed by micaceous minerals is directly related to their cation exchange capacity<sup>14)</sup>. Vermiculite has a relatively high cation exchange capacity. The sorption and the fixation of cesium by vermiculite, especially K-saturated vermiculite, have been studied<sup>15-19)</sup>.

The clay minerals in Korea are superior in quality as well as abundant in quantity and deposited widely on the eastern and southern coastal regions of our country. Representative sample clay was taken for this study from the deposit which is located in Choongnam province. This mineral is vermiculite and belongs to the mica series<sup>5)</sup>; differs from the montmorillonite and the illite.

The aim of this work was to study the removal of the cesium by vermiculite from solution similar to those which would result from the precipitator treatment. Since the precipitator produces alkaline solutions of sodium salts, solutions of sodium nitrate at pH

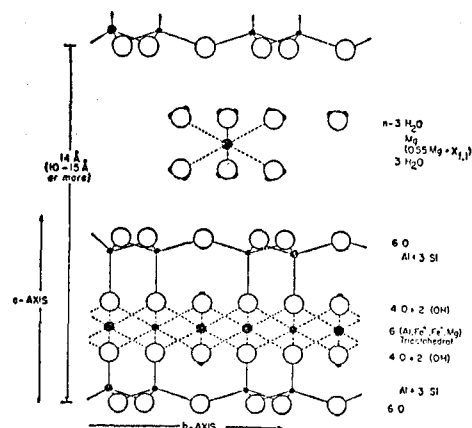


Fig. 2. Structure of vermiculite

11.5 were used and the relations to concentration of CsCl, reaction time, exchange capacity, and extractants were studied.

## 2. Experimental

Preparation of vermiculite sample was made as follows: these samples were ground into small pieces in ball mill and fractionated by sieving. The ground materials were sieved to make sure that the grains were less than 0.177mm in diameter (80 mesh sieve; U. S. standard). And the clay fraction for X-ray diffraction analysis was separated by the pipet method<sup>20)</sup> using Stoke's law. They were treated with the saturated NaCl solution for 72 hours at the room temperature. The Na-saturated vermiculites were treated with 2N KCl and 2N

Table 1. Separation between anionic sheets in ion-exchanged vermiculite

| Cation         | Mg   | Na   | K    | Cs  |
|----------------|------|------|------|-----|
| Separation (Å) | 5.11 | 5.55 | 1.34 | 2.7 |

Table 2. Chemical compositions and CEC of Vermiculites

| Reference      | SiO <sub>2</sub> | Al <sub>2</sub> O <sub>3</sub> | Fe <sub>2</sub> O <sub>3</sub> | CaO  | MgO   | Na <sub>2</sub> O | K <sub>2</sub> O | TiO <sub>2</sub> | Ignition loss | CEC meq/100g of clay |
|----------------|------------------|--------------------------------|--------------------------------|------|-------|-------------------|------------------|------------------|---------------|----------------------|
| V <sub>1</sub> | 42.16            | 20.16                          | 6.97                           | 0.69 | 8.75  | 1.51              | 12.91            | 1.01             | 5.37          | 16                   |
| V <sub>2</sub> | 39.75            | 15.87                          | 8.62                           | 1.52 | 21.37 | 2.08              | 2.63             | —                | 7.64          | 115                  |
| V <sub>3</sub> | 38.15            | 20.48                          | 6.64                           | 1.30 | 8.81  | 0.89              | 11.68            | 1.41             | 9.91          | 48                   |
| V <sub>4</sub> | 38.63            | 21.10                          | 7.26                           | 1.41 | 10.14 | 0.87              | 10.32            | 1.45             | 8.34          | 57                   |

CsCl solutions respectively for 72 hours at the room temperatures. Excess electrolyte was then rinsed with deionized water and absolute ethanol until free of chloride, and dried in an air oven at 110°C.

The samples prepared by these procedures will hereunder be called the Na- or K-vermiculite, respectively. Likewise the non-treated samples will be called the Natural-vermiculite.

The slurry tests consisted of adding 0.1–0.5g of sample to an Erlenmeyer flask (250ml) which contains 100-ml portion of the simulated waste solution. The solution was composed of 0.3M NaNO<sub>3</sub> and  $2 \times 10^{-3}$ M CsCl except the Kd change with the various concentration of CsCl (Cs-137 was used as tracer). These were adjusted with NaOH or HCl to the desired pH. The suspension was shaken for two hours, and then a 10ml portion of the suspension was taken out and then centrifuged for 1 hr at 3,000 rpm. Then a 0.5ml aliquot of the clear supernatant solution was transferred to a test tube, and Cs-137 activity was counted, in a well-type gamma scintillation counter which is equipped with a NaI(Tl) crystal (Aloka Model TDC-6)

X-ray diffraction analysis and differential thermal analysis of samples were carried out with a Shimadzu Research X-ray Goniometer

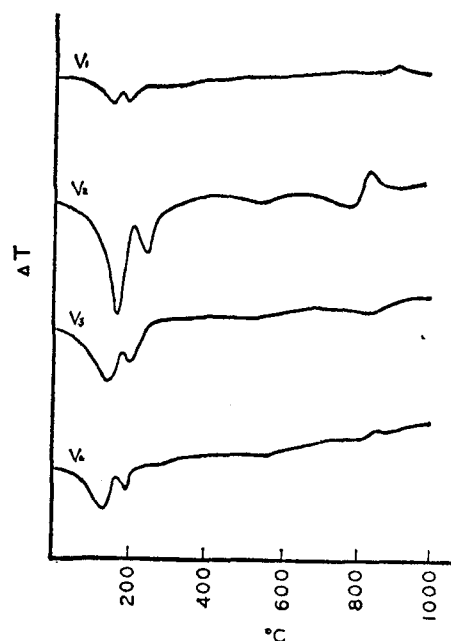


Fig. 3. Differential thermal curves of natural vermiculites

using Cu-K $\alpha$  radiation and a Shimadzu Differential Thermal Analyser, respectively.

### 3. Results and Discussion

The results of the chemical analysis, cation exchange capacity (CEC) and the differential thermal analysis are summarised in Table 2 and Fig. 3. The vermiculite samples have been found to be mostly interstratified with the exception

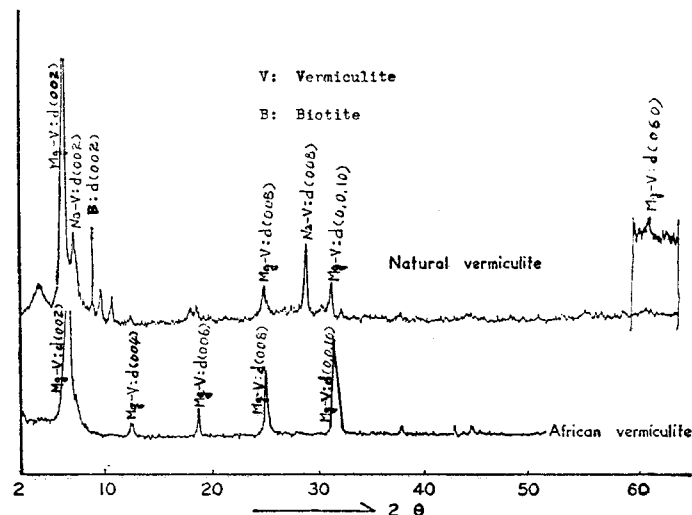


Fig. 4. X-ray diffraction curves of African vermiculite(API. pure) and Natural vermiculite(V<sub>2</sub>).

of sample V<sub>2</sub>. The ion exchange of vermiculites is reported to be in the range of 110 to 180 meq/100g according to Walker<sup>21)</sup>. The highest value in Table 2 is 115 meq/100g for sample V<sub>2</sub>. Furthermore the pure vermiculite is devoid of potassium; the presence of the potassium suggests that the specimens are mica-vermiculite assemblages. If one uses 150 meq/100g as a representative value for pure vermiculite, the approximate mineralogical compositions of these samples can be summarised as follows:

|                      |     |
|----------------------|-----|
| V <sub>1</sub> ..... | 10% |
| V <sub>2</sub> ..... | 80% |
| V <sub>3</sub> ..... | 30% |
| V <sub>4</sub> ..... | 40% |

The nature of hydration of the natural vermiculites is best clearly revealed by the differential thermal curves as shown in Fig. 3. By Barshad<sup>12)</sup>, DTA curve for natural vermiculite has two troughs, the lowest point of the first being at about 150°C. and the second at about 260°C. The curves in Fig. 3 have two troughs, the lowest points which range between 130°C.-150°C. and between 180°C.-

240°C. From the above observation it is considered that these materials are magnesium and calcium vermiculites.

According to Lim and Sim<sup>4)</sup>, Korean vermiculites are mainly of biotite origin. These minerals are considered from Fe-biotite to vermiculite and contain small or large amount of biotite, the measured capacity gives a rough idea of the degree of conversion from biotite to vermiculite.

Vermiculite samples were evaluated for cesium sorption, which was higher in Na- and K-vermiculite than the Natural-vermiculite as shown in Table 3. The K<sub>d</sub> measures the superior cesium decontaminating ability of Na- and K-vermiculite. From the above results, it is demonstrated that among these samples V<sub>2</sub> had the highest affinity which is consistent with its high capacity among the several specimens, and therefore the data reported hereafter were obtained from sample V<sub>2</sub>.

In Fig. 4, it is shown that a little sodium as well as magnesium and/or calcium is present in the sheets of the natural sample V<sub>2</sub>.

It is considered that this mineral was formed

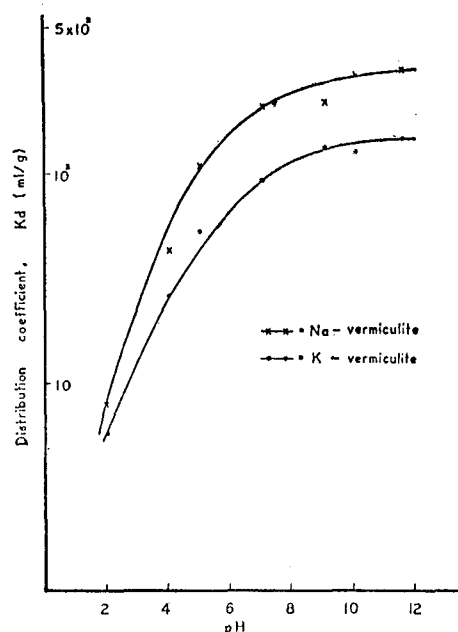


Fig. 5. Cesium sorption as a function of pH ( $V_2$ )

by the weathering of biotite schist which belongs to the precambrian stage<sup>4</sup>). From the above results, one could conclude that this mineral ( $V_2$ ) is an interstratified biotite-vermiculite which is consisted of approximately 20-80% of each component, respectively.

The sorption of cesium by vermiculite from  $2 \times 10^{-3}$  M CsCl solution at various initial pH values was evaluated in terms of the distribution coefficient. For a given cation such as Cs,  $K_d$  is expressed as follows: <sup>(22)</sup>

$$K_d = \frac{(X_1 - X_2)}{X_2} \cdot \frac{(\text{ml of solution})}{(\text{g of clay})}$$

where  $X_1$ : cpm of the initial solution, and

$X_2$ : cpm of the supernatant solution.

Results are shown in Fig. 5, where distribution coefficient  $K_d$  was plotted as a function of the initial pH of the clay suspension. The value of  $K_d$  was found to be approximately proportional to the pH range studied. The above results indicate that the affinity of the vermiculites for cesium in dilute solution increases with the increase in pH of the system

within the pH range usually encountered in nature. The decrease in  $K_d$  at pH less than 5 may be due to the slow decomposition of clays such as vermiculite in acidic media. Another possible explanation for the low  $K_d$  in the acidic range considered to be the competitive inhibition offered by  $H^+$  ions in the system.

Table 3. Cesium sorption ability of vermiculite

| Reference | Form      | Distribution coefficient<br>$K_d$ (ml/g) |
|-----------|-----------|--|
| $V_1$     | Natural   | 27                                       |
|           | Potassium | 152                                      |
|           | Sodium    | 220                                      |
| $V_2$     | Natural   | 82                                       |
|           | Potassium | 325                                      |
|           | Sodium    | 988                                      |
| $V_3$     | Natural   | 48                                       |
|           | Potassium | 224                                      |
|           | Sodium    | 426                                      |
| $V_4$     | Natural   | 64                                       |
|           | Potassium | 263                                      |
|           | Sodium    | 510                                      |

$2 \times 10^{-3}$  M CsCl, Contact time: 24 hrs.

The rapid increase of Cs sorption with the increase of pH from 2 to 7 was considered to be due to the decreasing competition of  $Na^+$  or  $K^+$  ion. However, a slight increase in  $K_d$  with the increase of pH from 7 to 12 may be attributed to the increase of sorption surface as at result of the dispersion, that is, an increase of the exchange sites in the vermiculite becomes saturated with  $Na^+$  ion. Accordingly all the data reported hereafter were obtained from the suspensions at the pH 11.5.

The study of cesium sorption was extended to the solutions containing high concentration of cesium; in this case, the ion exchange capacity is generally the most significant parameter in controlling the amount of cesium sorbed. In Fig. 6, the sorption of cesium in the solution,

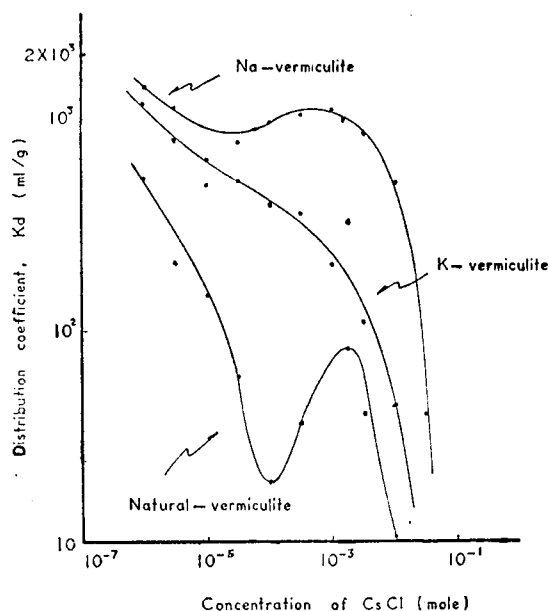


Fig. 6. Cesium sorption by vermiculite. (V<sub>2</sub>)

which was contained in 0.3M NaNO<sub>3</sub> in addition to the cesium concentrations designated, is shown for the local vermiculite. Among the vermiculites which were treated, Na-vermiculite has the highest affinity for cesium. In lower concentration range, Na-vermiculite sorbed the highest amount of cesium and K-vermiculite is also effective. But it is suggested that Na-vermiculite is more effective than K-vermiculite for cesium sorption. Note the sorption of cesium beginning at about 10<sup>-4</sup> moles of CsCl (Fig. 6). This response is due to change in the c-axis spacing of vermiculite<sup>23, 24</sup>. At this concentration, the cesium ions being sorbed are inducing the collapse of the structure. In the case of the K-vermiculite, the treatment had already induced collapse so that very little further collapse could occur. When the vermiculite is treated with K<sup>+</sup> ions prior to contact with the cesium solutions, favorable sites for cesium are formed<sup>23</sup> and it seems that when the vermiculite is treated with Na<sup>+</sup> ions prior to contact with the solutions,

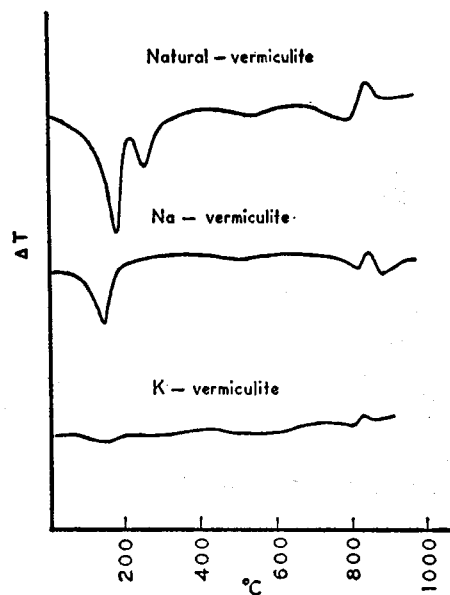


Fig. 7. Differential thermal curves of natural and treated vermiculites (V<sub>2</sub>)

favorable sites for cesium are also formed. In the clay minerals where the exchange is due to lattice substitutions, cation exchange mostly occurs in the interlayer, and the wider is the interlayer, the easier the exchange reaction<sup>10</sup>.

As shown in Fig. 7, the differential curves corresponding to the loss of interlayer water are indicated as follow: The natural-vermiculite has two endothermic trough; the Na-vermiculite has only one endothermic trough; and K-vermiculite has no trough at low temperatures. This variation is to be expected since Barshad<sup>12, 25</sup> showed that the kind of ex-

Table 4. Basal spacings d(002) for vermiculites saturated with various cations

| Interlayer cation | Air dry(Å) | In water(Å) |
|-------------------|------------|-------------|
| Mg                | 14.3       | 14.5        |
| Na                | 12.6       | 14.8        |
| K                 | 10.4       | 10.6        |
| Cs                | 11.97      | 11.97       |

changeable ion which is present between the lattice layers determines the degree of expansion of the lattice and when  $Mg^{+}$  or  $Ca^{+}$  ion is the exchangeable ion, there is a double layer of water; when  $Na^{+}$  ion is the exchangeable ion, there is a single layer of water; and when  $K^{+}$  ion is the exchangeable ion, the mineral has no interlayer water (Table 4)<sup>10, 25</sup>. Barshad<sup>12</sup> and Walker and Milne<sup>26</sup> found that the  $K^{+}$  ion tends to become fixed and relatively non replaceable when it already presents on the clay. Moreover, there are at least two diffusion path ways in the expanded Na-vermiculite: on the external surface and through the internal surface and for collapsed K-vermiculite, only the external surface is available for cationic diffusion<sup>27</sup>.

As shown in Table 4 and Fig. 6, cesium sorption by K-vermiculite is due to the high potential of the midpoint of interlayer (that is, being tightly bound) and the small exchangeable surface area, and the sorption by Na-vermiculite might be expected to have the largest exchangeable sites and altering the biotite to the vermiculite, which will be discussed in detail later (Fig. 4 and 9-1).

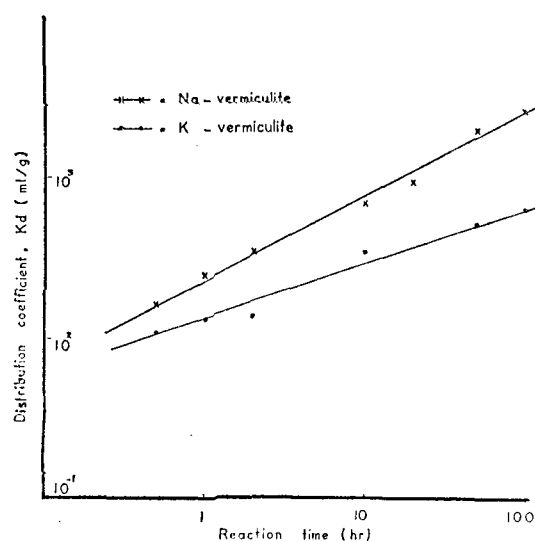


Fig. 8. The effect of reaction time on vermiculite ( $V_2$ )

Other parameter investigated according to slurry techniques was the time dependency of the cesium sorption reaction. It is necessary for the reaction to proceed with sufficient rate that the wastes are satisfactorily decontaminated. The cesium sorbed by vermiculite did not reach an equilibrium even after 100 hr (Fig. 8), whereas the cesium sorbed by montmorillonite quickly reaches an approximate equilibrium<sup>18</sup>. The cesium sorbed by K-vermiculite was only slightly increased with the increase of time as compared to Na-vermiculite. As illustrated in Fig. 9 and 10, with the increase of the reaction time a decrease in the 12.6 Å peaks and an increase in the 11.9 Å peaks occurred on cesium sorption by Na-vermiculite, while not only a decrease in the 10 Å peaks but also an increase in the 11.9 Å peaks did not almost occur on the cesium sorption by K-vermiculite. This explanation could be justified by diffusion of  $Cs^{+}$  ions through the interlayer of Na-vermiculite, that is, the increased cesium sorption by Na-vermiculite is attributed to the different sorption rates by the different exchange sites: initial fast sorption on external surfaces and edges followed by

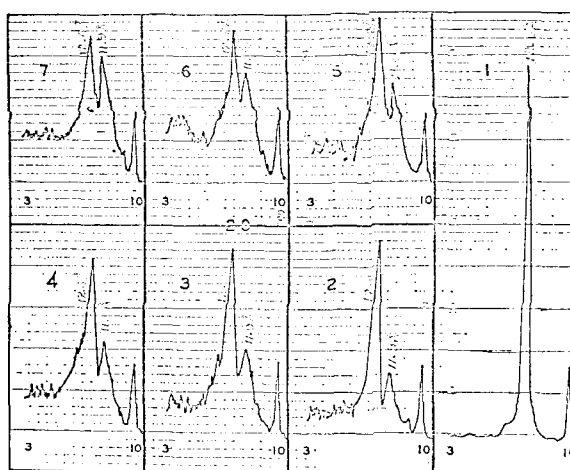


Fig. 9. X-ray diffraction patterns of Na-vermiculite(1) and vermiculite saturated with CsCl for: 2hours(2), 24hours(3), 48hours(4), 72hours(5), 100hours(6) and 169hours (7), ( $V_2$ )



slow diffusion into the interlayers. The c-axis spacing of K-vermiculite shows a collapsed structure<sup>18, 25)</sup>, with the result that only external surface is available for sorption site.

Biotite is a common constituent of many igneous and metamorphic rock types. Barshad<sup>12)</sup> studied biotite-vermiculite systems and found what appeared to be a reversible relationship between the two minerals. The conversion from biotite to vermiculite or hydrobiotite has been studied by many authors<sup>28-30)</sup>. As shown in Fig. 4 and 9-1, the 10Å peak for natural vermiculite did not almost occur on the cesium sorption by the vermiculite which was treated with NaCl. This is due to the release of potassium ion to the sodium chloride solution. This result suggests that the artificial alteration of the biotite to the vermiculite might be occurring by treating with NaCl. It seems to be one of the reasons that the cesium sorption capacity for the sample V<sub>2</sub> treated with NaCl was increased. As shown in Fig. 10-1, when K<sup>+</sup> ion is saturated the properties of vermiculite closely approximate to those of ordinary biotite<sup>12)</sup>.

Usually large sorptions by the collapsed lattices of micas in comparison to their CEC led

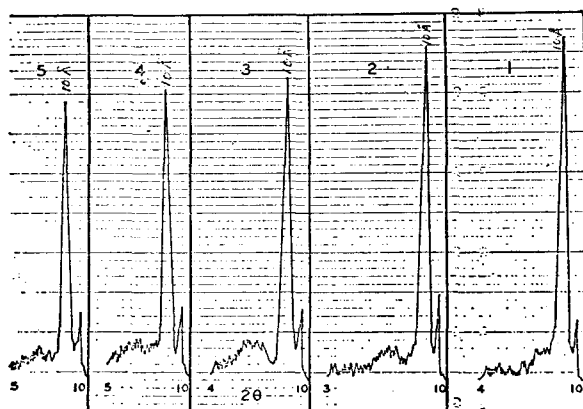


Fig. 10. X-ray diffraction patterns of K-vermiculite(1) and vermiculite saturated with CsCl for 2 hours(2), 24 hours(3), 48 hours(4), and 72 hours(5), (V<sub>2</sub>)

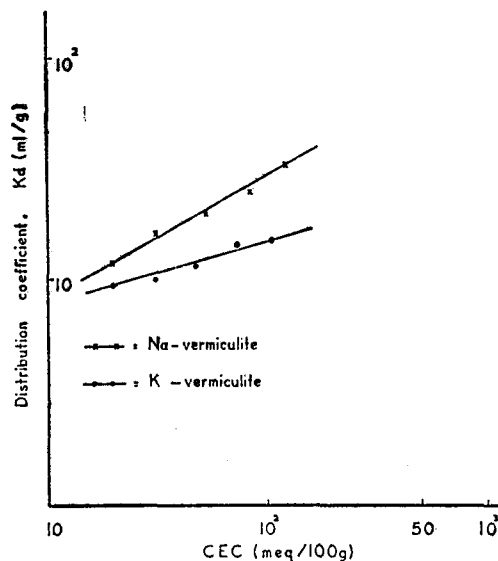


Fig. 11. The effect of CEC on vermiculite

Jacobs and Tamura<sup>24)</sup> to conclude that the edges of these lattices are highly selective for cesium, and Sawhney and Frink<sup>14)</sup> found that cesium sorbed by micaceous clay minerals is correlated with their CEC.

As shown in Fig. 11, the Na-vermiculite not only sorbs more cesium than the K-vermiculite but also the cesium sorbed by Na-vermiculite increases much rapidly with the increase of CEC. The Na-vermiculite increases the distance between the layers of vermiculite component and therefore makes all the sites available for ion exchange. The K-vermiculite, on the other hand, collapses the lattice as shown in Table 4 and Fig. 10 and then lowers the effective exchange capacity.

It is suspected that the diffusion of radionuclide ions through the interlayer lattices of clay mineral plays an important role in the fixation and exchange of ions. The cesium is the most important among the radioactive ions showing the fixation in vermiculite. Barshad and other authors had already found that a fixed ion is not necessarily unexchangeable with any kinds of cation. Also vermiculite, of which has been reported to be the high

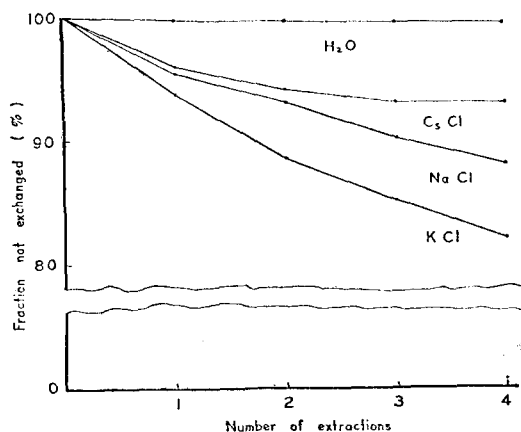


Fig. 12. Fraction of cesium retained in vermiculite after extraction by various agents. ( $V_2$ )

fixers of potassium and ammonium has been described to bind cesium strongly and no fixation of cesium was observed in montmorillonite or in kaolinite<sup>31, 32</sup>).

According to Fig. 12, the fraction of retained cesium was higher when cesium in Cs-vermiculite (100% saturated with cesium) was extracted by CsCl solution than NaCl or KCl and was higher in the case of NaCl than KCl. The most important is that in the extraction of four times more than 80% of the cesium was fixed. Levi and Miekeley<sup>31</sup>) explained this phenomenon as follows: the naked  $\text{Cs}^+$  ion surrounded by a high potential wall is very closely bound with the oxygen atoms of the silicate layer.

#### 4. Conclusion

This investigation shows that the affinity of the vermiculites for cesium in dilute solution increases with the increase in pH. This is attributed to the increase of sorption surface as a result of the dispersion.

The sorption of cesium by the vermiculite was markedly influenced by the cesium concentration, and the sorption rate of cesium for Na-vermiculite had the peak value at about  $10^{-3}\text{M}$  CsCl solution. Larger amount of cesium

sorbed from dilute solution by Na-vermiculite than K-vermiculite is related to the diffusion of  $\text{Cs}^+$  ion into the interlayer. And also it is shown that the large fraction of the cesium which is sorbed by the vermiculite is fixed.

Then the domestic vermiculite is a valuable material for applications of cesium sorption and fixation, and might be useful as a good packing material outside the storage tank of highly radioactive liquid wastes.

These results suggest that alteration of the biotite to vermiculite might be occurring by treating it with NaCl.

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