

《Original》      **Studies on the Sorption and Fixation  
of Cesium by Vermiculite (Ⅱ)**

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**Abstract**

The adsorption mechanism of Cs-137 in low level radioactive solution by vermiculite treated with Na ion is studied in order to investigate its effective utilization for the radioactive effluent treatment.

The beneficial role of Na-vermiculite is that Na ion can induce the wider c-axis spacing in which Cs ion can be sorbed in vermiculite.

Cation exchange capacity and distribution coefficient of cesium seems to be influenced by the variation of c-axis spacing of vermiculite.

Comparative identification and detection with the characteristic analyses of X-ray diffraction and electron diffraction patterns, differential thermal analysis and electron microscopy of Na-, K- and Cs-vermiculite are studied for the phenomena of Cs adsorption by vermiculite.

This importance of the utilization in terms of adsorption and fixation of cesium involving vermiculite is discussed.

It is found that the Na-vermiculite is valuable outside charging material for high level radioactive liquid waste storage tank of underground to protect the pollution of the underground water.

**요 약**

천연 점토 광물질의 ion 교환능은 비교적 낮지만, 여러가지 활성화법에 의하여 교환능의 개선이 기대된다.

본 연구에 있어서는 점토 광물질 중에서도 교환 흡착능이 비교적 큰 vermiculite를 사용하여 저준위 방사성 액체 폐기물을 처리하는데 있어서 효과적인 이용 방법을 검토하기 위하여 vermiculite의 이온교환 기능에 관한 기초 연구를 실험하였다.

Cs 이온의 교환능 및 분배계수는 Cs-137의 방사능도를 Scintillation counter로 측정하였고, 천연 및 활성화된 vermiculite에 대한 특성은 X-ray 회절과 전자회절에 의한 분석 및 열시차 분석과 아울러 전자 현미경에 의한 검사에 의거 해석하였다.

Na-vermiculite에 의한 Cs 이온의 교환 및 흡착에 있어서는 결정격자의 C-axis spacing의 수축을 초래하게 되고, Cs 이온의 교환능은 주로 C-axis spacing의 크기에 좌우된다고 본다.

Na-vermiculite 에 의한 Cs 이온의 교환 및 흡착 연구를 수행함으로써 저준위 방사성 핵종의 처리 뿐만 아니라, 고 방사성 폐액 저장 tank 의 외각 충전 물질로서 Cs-137과 같이 반감기가 긴 핵종의 leakage 로 인한 지하수 오염을 방지할 수 있는 재질로서도 적합하다.

## 1. Introduction

Many workers have reported that clay minerals have very significant use for the waste treatment and disposal of radionuclides, because of the high ionic selectivity, radiation stability and heat stability of these minerals.<sup>1-3)</sup>

Since the waste disposal plant was constructed at the Atomic Energy Research Institute in Seoul, Korea, in 1964, the author<sup>4)</sup> has investigated on clay mineral as one of the major problems of safe disposal of the radionuclide waste such as Sr-90 and Cs-137.

Several reports<sup>5-8)</sup> have shown that layer lattice minerals and clays containing these minerals sorb Cs from dilute solutions in preference to other cations. Also Tamura and Jacobs<sup>9)</sup> demonstrated that the sorption at the edge of the K-vermiculite lattice was increased with the increase of K ion, due to the collapse of vermiculite lattice, on the other hand, a large preference by these interlattice edge sites of illite and a large fixation of the added Cs-137 in soils had been demonstrated by Bolt *et al.*<sup>10)</sup> and Schulz *et al.*<sup>11)</sup>, respectively. And 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.

The object of this study is to develop the method of low level radioactive liquid waste treatment and disposal and to investigate characteristic behavior of natural vermiculite (V<sub>2</sub>) with cesium-137. For the study representative vermiculite was obtained from the

western coast in Choungnam Province, Korea. All of the vermiculites were investigated after pretreatment of excess of NaCl and KCl, so that the natural vermiculites were changed into Na- and K-vermiculite, respectively.

Investigation on the effect of natural, Na- and K-vermiculite on the adsorption of Cs-137, were carried out by distribution coefficient evaluation and X-ray diffraction analysis. These species were also identified by differential thermal analysis, electron micrography, chemical analysis and X-ray diffraction analysis.

## 2. Experimental

### 1) Sample preparation

The 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 177 $\mu$  sieve in diameter. These 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 CsCl solutions separately for 72 hours at the room temperature. Excessive electrolyte was decanted and then rinsed with deionized water, followed by absolute ethanol until free of chloride and then dried in an oven at 110°C.

The samples prepared by this procedure will hereunder be called the Na-, K-, and Cs-vermiculite respectively. Likewise the non-treated samples will be called the natural vermiculite.

### 2) Experimental procedure

From each samples, a 0.1-0.5 g aliquot was

weighed out and transferred to an Erlenmeyer flask (250ml), and then 100 ml of the simulated radioactive waste solution which was composed of 0.3 M  $\text{NaNO}_3$  and  $2 \times 10^{-3}$  M  $\text{CsCl}$  ( $\text{Cs-137}$ ), except for the  $K_d$  change measurement, was poured into the flask. The pH of the solution was adjusted with  $\text{NaOH}$  or  $\text{HCl}$  to the desired values. The suspension was shaken for two hours and a 10 ml portion of the suspension was taken out and centrifuged for one hour at 3,000 rpm. Then a 0.5 ml aliquot of the clear supernatant solution was transferred to a test tube, and activity of the  $\text{Cs-137}$  was counted in a well-type gamma scintillation counter which is equipped with a  $\text{NaI(Tl)}$  crystal (Aloka Model TDC-6).

In order to measure the release of the adsorbed cesium by various electrolyte solutions, the sample saturated with  $\text{Cs-137}$  was repeatedly extracted with solutions such as 0.1 N  $\text{NaCl}$ , 0.1 N  $\text{KCl}$ , 0.1 N  $\text{CaCl}_2$  and 0.1 N  $\text{MgCl}_2$  as described below until ten each separate extractions had been made. The 100 ml of the each extracting solutions and 10 g of the samples were added to the beaker and stirred for 2 hours. The 10 ml of these suspended solution was taken out and centrifuged for 1 hour at 3,000 rpm and then activity of  $\text{Cs-137}$  was counted as mentioned above.

X-ray diffraction, electron diffraction and differential thermal analysis of the samples were carried out with a Shimadzu Research X-ray Goniometer (Type VD-1), a Hitach Electron Microscope (Model HU-125C) and a Shimadzu Differential Thermal Analyzer (Type DT-EB), respectively.

### 3. Results and Discussion

Chemical analysis data and cation exchange capacity of Korean vermiculites located in

Ma-Suk, Bee-Bong, Dae-San, and Ye-San which are labeled as  $V_1$ ,  $V_2$ ,  $V_3$ , and  $V_4$  respectively are represented in Table 1. The contents of  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$  in each sample are quite similar. However, it was noted that Korean vermiculite had a slightly higher contents of  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$  and alkaline oxides, less  $\text{MgO}$  and ignition loss than the Kenya, Pennsylvania vermiculite.

Furthermore, the  $V_2$ -vermiculite produced in Bee-Bong district shows not only the highest  $\text{MgO}$  contents and the highest value of cation exchange capacity but also lowest contents of  $\text{K}_2\text{O}$ . From these results, it was assumed that Bee-Bong vermiculite  $V_2$  was considerably more applicable for industrial waste treatment of radionuclides. Although potassium oxide is not an essential component of pure natural vermiculite, the Bee-Bong vermiculite which the author has taken from shows 2-3% of  $\text{K}_2\text{O}$  content. This presence of the potassium probably suggests that these vermiculite belong to the biotite-vermiculite assemblages.

Recently, Dr. Lim and co-worker<sup>13)</sup> have reported that Korean vermiculites were mainly composed of biotite origin and generally accompanied by hornblende, quartz, limonite and other impurities. It was considered that the Korean vermiculites were formed by weathering of biotite schist which belongs to the precambrian stage.

Mortland<sup>14)</sup> has already suggested that the weathering of biotite would be considered to proceeded as follows:

Biotite  $\rightarrow$  Biotite-vermiculite  $\rightarrow$  vermiculite

On this process the intermediate stage of biotite-vermiculite shows interstratified system in vermiculite.

#### 1) Differential thermal analysis

The nature of hydration of the natural

Table 1. Chemical Composition and cation exchange capacity (CEC) of Korean Vermiculites

| Component                 | 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 |
|---------------------------|------------------|--------------------------------|--------------------------------|------|-------|-------------------|------------------|------------------|---------------|--------------|
| Vermiculites              |                  |                                |                                |      |       |                   |                  |                  |               |              |
| V <sub>1</sub> (Ma-Suk)   | 42.16            | 20.16                          | 6.97                           | 0.69 | 8.75  | 1.51              | 12.91            | 1.01             | 5.37          | 16           |
| V <sub>2</sub> (Bee-Bong) | 39.75            | 15.87                          | 8.62                           | 1.52 | 21.37 | 2.08              | 2.63             | —                | 10.50         | 115          |
| V <sub>3</sub> (Dae-San)  | 38.15            | 20.48                          | 6.64                           | 1.30 | 8.81  | 0.89              | 11.68            | 1.41             | 9.91          | 48           |
| V <sub>4</sub> (Ye-San)   | 38.63            | 21.10                          | 7.26                           | 1.41 | 10.14 | 0.87              | 10.32            | 1.45             | 8.34          | 57           |

vermiculite is most clearly revealed by the differential thermal curves as shown in Fig. 1. As is well known, one of the characteristic properties of vermiculite is the exfoliation which depends upon the rapid formation of water vapor between lattice layers. In general, the peak resolves into two or three distinct breaks depending on the water constituents<sup>15-17</sup>.

As shown in Fig. 1, it was found that at below 250°C the differential thermal curves of Korean natural vermiculites were broken mostly into two endothermic trough at the range of 130°-150° and 180-240°C, owing to the lattice water driven off slowly by gradual heating. The latter indicated the characteristic

second step dehydration of Mg-vermiculite. From the above observation it was considered that these materials contains a kind of Mg-vermiculite.

On the other hand, the differential thermal curves corresponding to the loss of interlayer water of Na and K-vermiculites are represented in Fig. 2. It was found that the natural, Na- and K-vermiculite had two, one, and without endothermic trough at low temperature, respectively. By Barshad<sup>15</sup>, it was seen that the curve of Cs-vermiculite was similar to that of K-vermiculite.

This variation is attributed to the different degree of hydration of interchangeable ions presented between the lattice layers, which

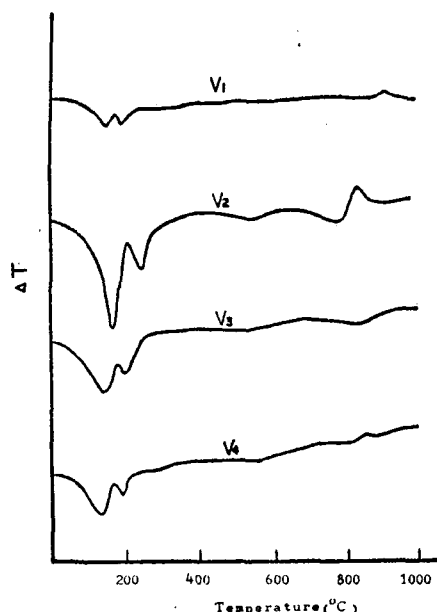


Fig. 1. Differential thermal curves of natural vermiculites

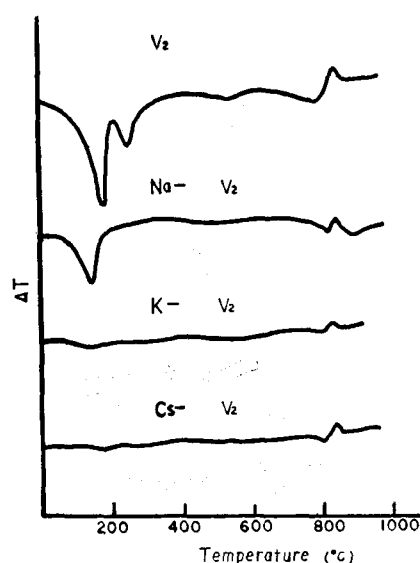


Fig. 2. Differential thermal curves of vermiculites

Table 2. Cesium sorption ability of Vermiculites

| Vermiculites   |           | Distribution coefficient, Kd (ml/g) |     |     |     |     |               | Standard deviation |
|----------------|-----------|-------------------------------------|-----|-----|-----|-----|---------------|--------------------|
|                |           | Run number                          |     |     |     |     | Average value |                    |
|                |           | 1                                   | 2   | 3   | 4   | 5   |               |                    |
| V <sub>1</sub> | Natural   | 26                                  | 22  | 28  | 30  | 29  | 27            | 2.8                |
|                | Potassium | 150                                 | 152 | 155 | 151 | 152 | 152           | 1.7                |
|                | Sodium    | 222                                 | 218 | 223 | 216 | 221 | 220           | 2.6                |
| V <sub>2</sub> | Natural   | 83                                  | 81  | 84  | 78  | 84  | 82            | 2.3                |
|                | Potassium | 327                                 | 325 | 327 | 324 | 322 | 325           | 1.9                |
|                | Sodium    | 986                                 | 988 | 990 | 985 | 991 | 988           | 2.3                |
| V <sub>3</sub> | Natural   | 48                                  | 44  | 53  | 49  | 46  | 48            | 3.0                |
|                | Potassium | 222                                 | 226 | 223 | 222 | 227 | 224           | 2.1                |
|                | Sodium    | 422                                 | 427 | 426 | 425 | 430 | 426           | 2.6                |
| V <sub>4</sub> | Natural   | 59                                  | 68  | 64  | 63  | 66  | 64            | 3.0                |
|                | Potassium | 266                                 | 263 | 261 | 264 | 261 | 263           | 1.9                |
|                | Sodium    | 510                                 | 508 | 514 | 511 | 507 | 510           | 2.4                |

Reaction period with  $2 \times 10^{-3}$  M CsCl for each run: 24hrs.

were determined by the degree of expansion of the lattice<sup>15,16)</sup>

As this, result, it is seen that the expansion of the lattice<sup>16)</sup> saturated with Na ion is equivalent to the thickness of a unimolecular layer of water.

In the case of the lattice saturated with K, however, c-axis spacing is only slightly expanded, also K ion tends to become fixed and relatively non replaceable when it already presents on clay.

## 2) Adsorbability of radioactive cesium (Cs-137)

The sorption of cesium by vermiculite from  $2 \times 10^{-3}$  M CsCl solution are evaluated in terms of the distribution coefficient(Kd). For a given cation, generally, Kd is expressed as following formula<sup>18)</sup>.

$$Kd = \frac{(\text{Activity of clay, } \mu\text{ci/g})}{(\text{Activity of solution, } \mu\text{ci/ml})} \times \frac{(\text{Vol. of soln. ml})}{(\text{wt. of clay, g})}$$

The data are represented in Table 2. It is

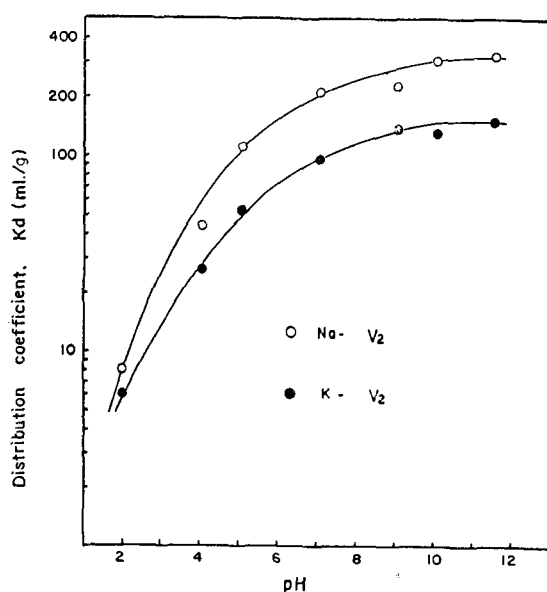


Fig. 3. Cesium sorption as a function of pH

found that the Na- and K-vermiculite which were pretreated with Na and K ion are shown higher values than natural vermiculite.

In each case of samples, we can estimate the Cs adsorption in vermiculite and the

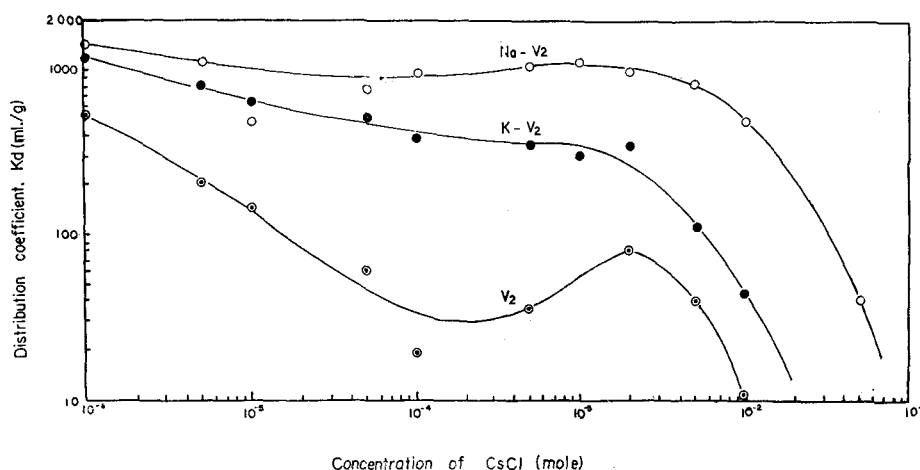


Fig. 4. Cesium sorption by  $V_2$ ,  $K-V_2$  and  $Na-V_2$ -vermiculite

cesium decontaminating ability of Na- and K-vermiculite by the measurement of Kd.

Among the specimens in Table 2, it will be assumed that  $V_2$  vermiculite has a highest affinity of Cs as it had the highest cation exchange capacity. Therefore, the data will be analysed and evaluated with  $V_2$  vermiculite hereafter.

In Fig. 3, the distribution coefficient was plotted as a function of the initial pH of the vermiculite suspension.

The decrease in Kd at pH less than 5 may be due to the slow decomposition of the vermiculite in acidic media. Also it was considered to be the competitive inhibition offered by H ions in the system.

However, a slight increase in Kd with the increase of pH from 7 to 12 may be attributed to the increase of sorption surface as a result of the dispersion, that is, the exchange site in the vermiculite becomes saturated with Na ion and then increased. Accordingly, all the data reported hereafter were obtained from the suspensions at the pH 11.5.

These studies were extended to the solutions containing high concentration of cesium.

The sorption of Cs-137 with natural, K-, and Na-vermiculite in varying amounts of cesium concentration is shown in the Fig. 4. In case of natural vermiculite, decrease of Kd curve up to about  $10^{-4}$ M of CsCl for the cesium sorption is due to the presence of Mg ion, a little amount of biotite and other impurities. However, increase of the sorption above about  $10^{-4}$ M of CsCl is attributed to the increase of penetration into the interlayer.

Among the vermiculites pretreated, Na-vermiculite has the highest adsorption affinity to cesium even in lower concentration range of cesium. As shown in Fig. 4, it is noted that Na-vermiculite is more effective than K-vermiculite for Cs sorption. This is responded to the difference in the c-axis spacing of these vermiculites<sup>6,19</sup>.

It is a well known fact that cation exchange in vermiculite is often accompanied by a change in the c-axis of the unit cell and that this influences on the rate and capacity of exchange<sup>20</sup>. In addition, the amount of sorbed cesium by micaceous minerals is directly related to their cation exchange capacity<sup>8</sup>.

By exchanging sodium ion in the Na-vermiculite with cesium ion the structure get collapse owing to c-axis spacing shortening. In case of the K-vermiculite, the structure had already shrunk by introducing K ion so that further collapse could be occurred slightly by exchanging with Cs ion.

It is assumed that when the vermiculite is treated with Na and K ions prior to contact with the Cs ion solutions, favorable sites for cesium are formed at the expanded interlayer of c-axis spacing of Na-vermiculite by introduced hydrated Na ion, and collapse of the structure of K-vermiculite by K ion would occur.

In the clay minerals where the exchange is due to lattice substitutions, the cation exchange mostly occurs in the interlayer and the wider in the interlayer, the easier the exchange reaction.<sup>17)</sup>

Barshad,<sup>15)</sup> Walker and Milne<sup>21)</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>22)</sup>

On diffusion process in ionic exchange, the rate depends on the mobility of the ions. First, the Cs ion can be adsorbed on the external surface of crystal. Secondly, the Cs ion penetrated slowly into the interlayer of unit cell and ion exchange between Na ion and Cs ion occurred in the interlayer. Thirdly, the desorption process of Na ion from the interlayer can be taken place simultaneously.

From these consideration, it may be concluded that the penetration of Cs ion into

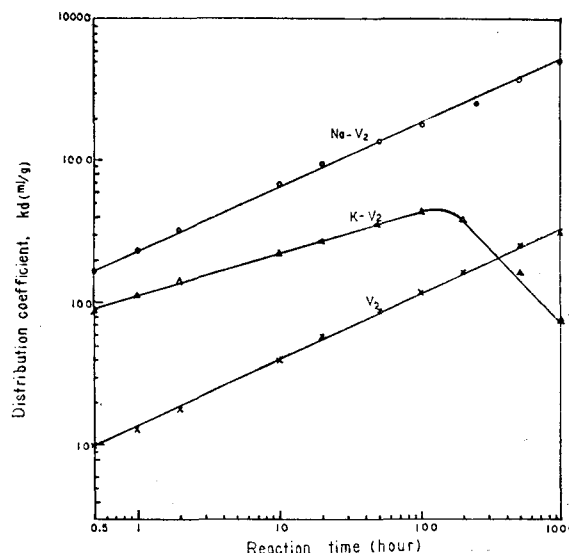


Fig. 5 Adsorption ability of vermiculite vs reaction time,

vermiculite depends largely upon the inter-layer spacing and nature of exchanging site of the vermiculite which is also the most significant parameter in controlling the amount of Cs sorbed.

At the external surface, the double layer will be developed adsorption of Cs ion on the surface of the vermiculite particle so that solid surface is positively charged, and the electrolytic solution surrounding the particles has matching negative charge, and forms fixed or diffused layer.

As we seen the data of Fig. 5, Cs ion adsorption on all the vermiculite is rather sluggish reaction. For the K-vermiculite, which believed the adsorption of Cs ion is to take place almost exclusively on the external surface, the reaction time for the equilibrium K<sub>d</sub> is about 100 hours and after equilibrium desorption of Cs ion from the vermiculite is predominant.

These facts mean that the double layer in

vermiculite CsCl solution system will be quite diffused one (so called Gouy double layer), and much less in cationic exchange reaction, which the adsorption and desorption of the ion on the surface occur simultaneously, would greatly disturb the positive layer and the zeta-potential also be frail.

Applying to the practical disposal of radioactive waste, it is important to know the relationship between adsorption ability and the reaction time on vermiculite. As reported in the previous paper, the author<sup>4)</sup> has demonstrated that the cesium was sorbed and quickly attained an equilibrium state between the adsorbate and adsorbent in case of montmorillonite. However, as shown in Fig. 5, it was found that a straight line relationship between adsorbability and reaction time on natural and Na-vermiculite was obtained even after 1,000 hours and the cesium sorbed by these was continuously increased while the cesium sorbed by K-vermiculite was increased until around 100 hours and decreased after that time. By Sawhney<sup>23)</sup>, the cesium sorbed by vermiculite did not reach an equilibrium even after 500 hours and cesium sorbed by Ca-vermiculite continued to increase while the cesium sorbed by K-vermiculite decreased.

The slope of these curves shows 0.468 and 0.448 in natural and Na-vermiculite respectively. In K-vermiculite the slope shows 0.308 from 0.5 hour to 100 hours and -1.063 from 200 hours to 1,000 hours.

This slope implies that the cesium sorption by K-vermiculite was only slightly increased with the time up to 100 hours as compared with Na-vermiculite. Many workers<sup>8,9,24)</sup> have reported that cesium sorbed by micaceous clay minerals can be correlated with the cation exchange capacity.

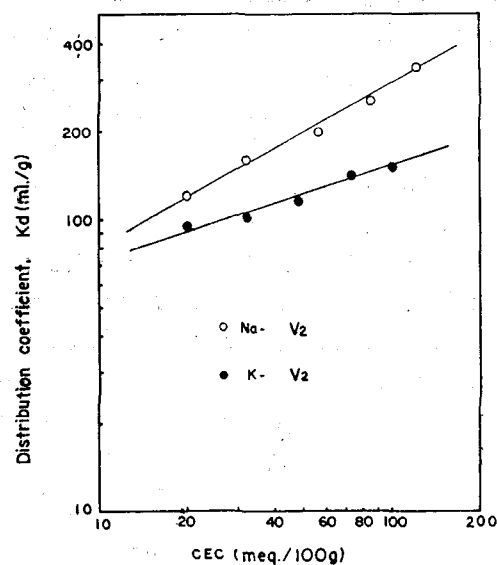


Fig. 6. Relationship between distribution coefficient and CEC on vermiculites

As shown in Fig. 6, the author also found that the linear relationship between distribution coefficients and cation exchange capacity existed.

In order to make much more effective utilization of the vermiculite in the liquid waste treatment, it is necessary to treat with NaCl rather than KCl as well as to extend the reaction time should be kept sufficiently long.

Finally, the fraction of cesium retained in vermiculite after extraction with NaCl, KCl,  $\text{CaCl}_2$  and  $\text{MgCl}_2$  is shown in Fig. 7. It was observed that at the 10th extraction of NaCl, KCl,  $\text{CaCl}_2$  and  $\text{MgCl}_2$ , the fixation of cesium was measured to be about 82%, 75%, 87%, and 85% respectively. These phenomena suggest that the cesium ions fixed in the vermiculite lattice are not able to remove and the small fraction of exchangeable cesium is bounded one at the sites close to the surface. Among these cations, the exchange-



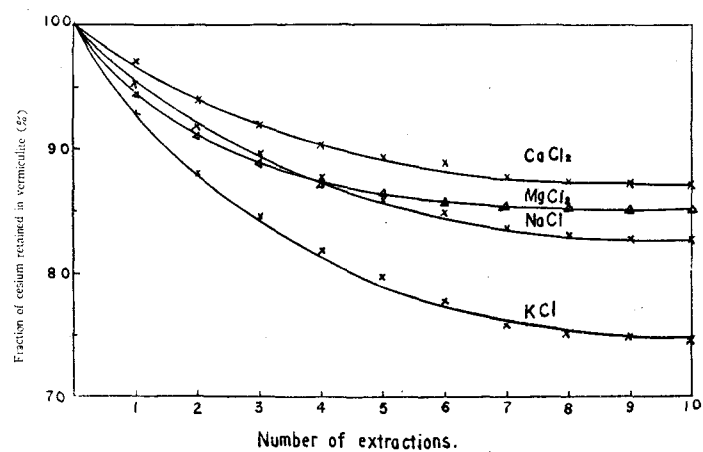
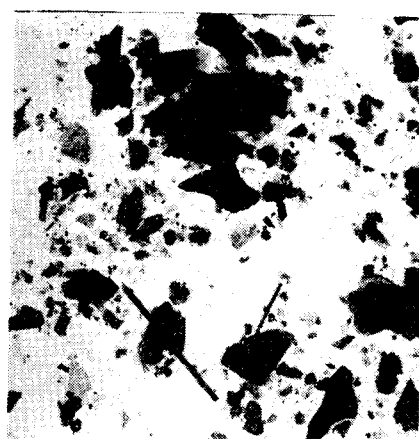
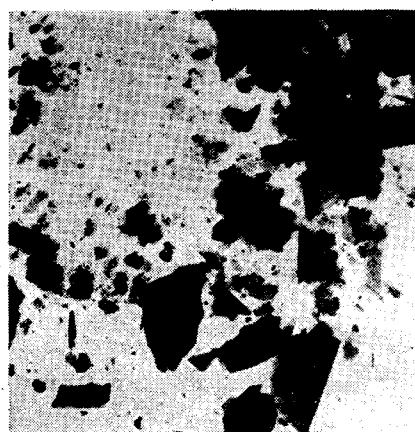


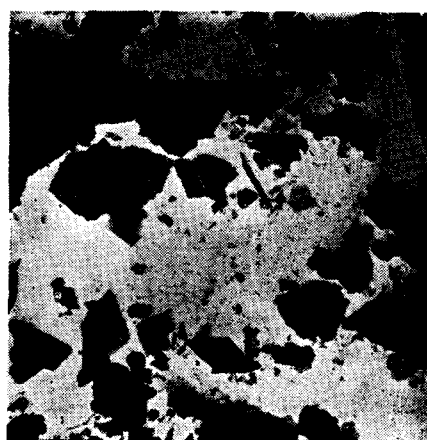
Fig. 7. Fraction curves of cesium retained in Cs-vermiculite after extraction by various agents.



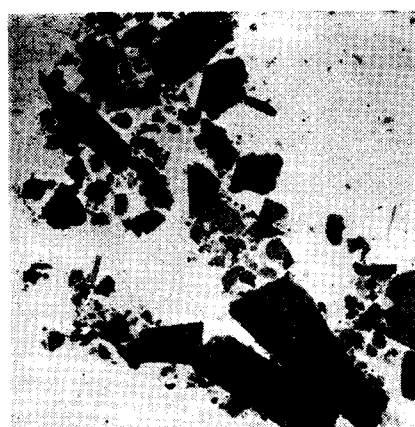
V<sub>2</sub>-Vermiculite



Na-Vermiculite



K-Vermiculite



Cs-Vermiculite

Fig. 8. Electron micrographs of vermiculites. ( $\times 4000$ )

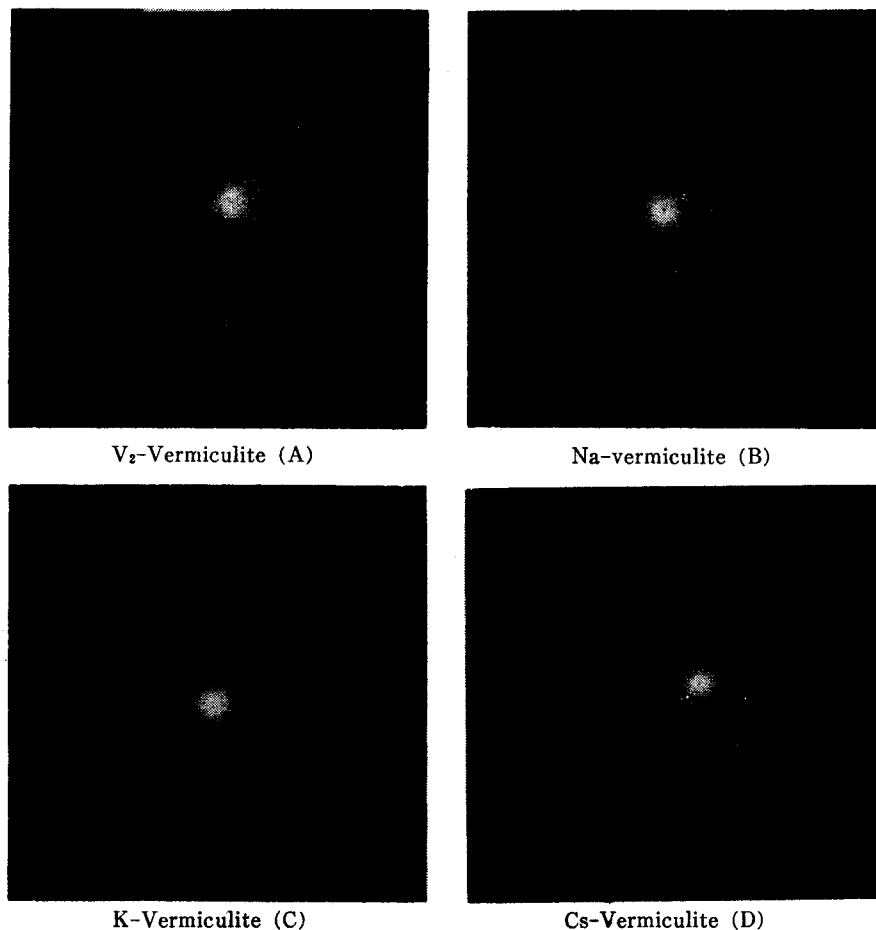


Fig. 9. Electron diffraction patterns of vermiculites( $\times 400$ )

ing effect of weakly hydrated K was greatest. By Levi and Miekeley,<sup>25)</sup> it might be explained that this effect was probably based on different defixation mechanism depending on the different degree of hydration and size of ions. However, in case of water extraction, no cesium was leached out.

### 3) Electron micrography, electron diffraction and X-ray diffraction analysis

#### (a) Electron micrography and electron diffraction

Little information is available regarding to the electron micrography of the vermiculite mineral. It appears from structural consideration, however, that electron micrographs of

the vermiculite mineral would be almost similar to those of illites except that vermiculite might occur in thinner flakes.<sup>17)</sup>

In Fig. 8, micrographs of vermiculites reveal irregular flakes and flake-shaped aggregates which appear to be stacking of units without regular outlines, and elongate flakes in one direction. Because of the similar morphology of natural sample ( $V_2$ ) to the treated samples, it was difficult to distinguish the species of these samples by micrographic method.

For the identification purpose of clay minerals electron diffraction method is not as generally useful as X-ray diffraction method because most of them consist of similar

**Table 3. Electron diffraction data of Vermiculites**

|       |                           |                |               |               |                 |                 |                 |
|-------|---------------------------|----------------|---------------|---------------|-----------------|-----------------|-----------------|
| $V_2$ | Natural-vermiculite (A)   | d (Å)<br>(hkl) | 4.62<br>(021) | 2.51<br>(202) | 1.746<br>(1312) | 1.546<br>(2014) | 1.533<br>(060)  |
|       | Sodium-vermiculite (B)    | d (Å)<br>(hkl) | 4.62<br>(021) | 2.64<br>(200) | 2.53<br>(206)   | 1.765<br>(2012) | 1.551<br>(0016) |
|       | Potassium-vermiculite (C) | d (Å)<br>(hkl) | 4.62<br>(021) | 2.64<br>(200) | 2.35<br>(206)   | 1.941<br>(0010) | 1.746<br>(0012) |
|       | Cesium-vermiculite (D)    | d (Å)<br>(hkl) | 4.62<br>(021) | 2.68<br>(008) | 2.35<br>(206)   | 1.721<br>(0014) | 1.533<br>(060)  |

Condition: 50Kv, #2, Projection current=max.

**Table 4. Interplaner spacings and Miller indices of Vermiculites**

|       |                       |                |                |               |               |                 |
|-------|-----------------------|----------------|----------------|---------------|---------------|-----------------|
| $V_2$ | Natural-vermiculite   | d (Å)<br>(hkl) | 14.47<br>(002) | 4.64<br>(021) | 3.60<br>(008) | 1.5359<br>(060) |
|       | Sodium-vermiculite    | d (Å)<br>(hkl) | 12.6<br>(002)  | 6.27<br>(004) | 4.64<br>(021) | 3.038<br>(008)  |
|       | Potassium-vermiculite | d (Å)<br>(hkl) | 10.3<br>(002)  | 5.1<br>(004)  | 4.64<br>(021) | 3.398<br>(006)  |
|       | Cesium-vermiculite    | d (Å)<br>(hkl) | 11.9<br>(002)  | 4.64<br>(021) | 3.56<br>(006) | 2.673<br>(008)  |

Condition: Cu-K $\alpha$  radiation, 30Kv, 15mA.

layer lattices and the plate-shaped particles which tend to lie on their basal planes and thus yield identical or nearly identical hexagonal spot patterns in the diffractograms.

The characteristics of electron diffraction patterns of natural, Na-, K- and Cs-vermiculite are shown in Fig. 9 and Table 3. All of the patterns show the (021) reflection and same interplaner distance of 4.62 Å. Although the differences between the samples by the diffraction data are recognized, it is considered to be not sufficient to identify the individual samples. On the other hand, it was observed that the unit cell parameters except c-axis spacing were not changed the exchange of the changeable ions.

#### (b) X-ray diffraction

The samples were identified by the X-ray

data listed in the ASTM powder diffraction file (6-0263, 7-42, 10-439, 16-613, 19-814) and given by Walker<sup>26)</sup> and other workers<sup>17)</sup>.

In Fig. 10, it is shown that the X-ray diffraction patterns of the natural vermiculite  $V_2$  is similar to the patterns of Ye San vermiculite<sup>27)</sup>. These patterns provide the strongest reflection (002) at about 14.4 Å reflection (008) at about 3.60 Å and reflection (060) at about 1.53 Å.

As mentioned previously, natural vermiculite was formed by the weathering of biotite schist which belongs to the precambrian stage. From the above X-ray results, one could assume that this mineral consist of a mixed-layer of mica-vermiculite and a trioctahedral vermiculite. By chemical analysis and X-ray diffraction data, it is considered that about 20% of mica is contained in the sample  $V_2$ .

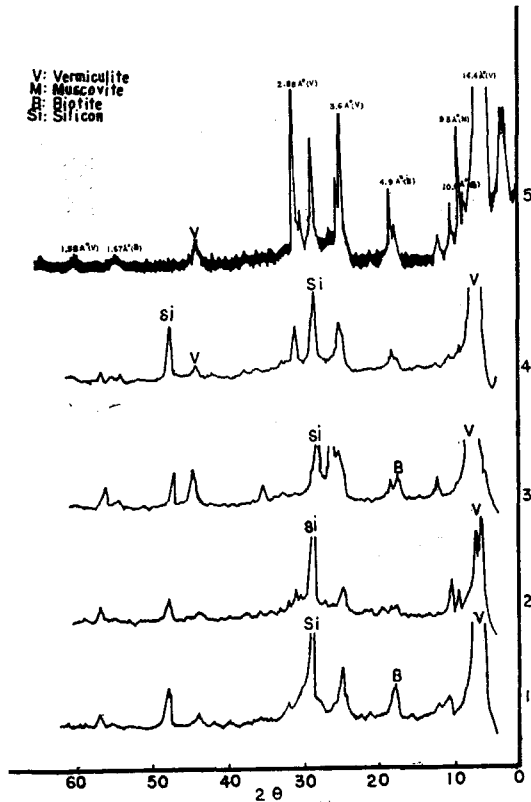


Fig. 10. X-ray diffraction patterns of Korean Vermiculites from Yong-Sa (1), Suh-San (2), Ye-San (3 & 4) and Bee-Bong (5)

The X-ray diffraction patterns of Na-, K- and Cs-vermiculite, which were treated the natural vermiculite ( $V_2$ ) with saturated NaCl, 2N KCl and 2N CsCl, and natural vermiculite ( $V_2$ ) are represented in Table 4 and Fig. 11. Only the peaks, reflection (00 $l$ ) ( $l=2, 4, 6, 8$ ), of the treated vermiculites were grown. These phenomena are due to the c-axis dimension of vermiculite with the nature of the interlayer cation. All of these patterns Fig. 11 provide the (021) reflection at about 4.64 Å as shown in electron diffraction patterns Fig. 9 and Table 3.

As represented in Fig. 12, from 2 to 7, with the increase of the reaction time, 12.6 Å

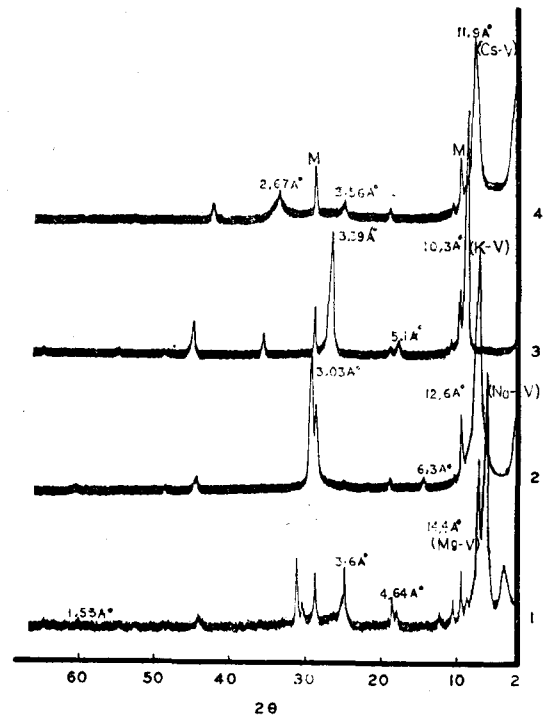


Fig. 11. X-ray diffraction patterns of the natural vermiculites (1) and the vermiculites treated with NaCl (2), KCl (3) and CsCl (4).

peak was decreased while 11.9 Å peak was increased. Also 6.27 Å, 3.038 Å, 2.089 Å and 1.536 Å peaks were disappeared and new peaks as 3.56 Å, 2.673 Å, and 2.135 Å have been growing. These changes of X-ray patterns show that sluggish transformation of the Na-vermiculite to the Cs-vermiculite structure with increasing time of reaction with Cs solution. This explanation could be justified by the penetration of Cs ions through the interlayer of Na-vermiculite. The higher cesium sorption or exchange capacity of Na-vermiculite than the other vermiculite is attributed to the higher sorption rates by the unique exchange sites: the initial fast sorption on external surfaces and edges followed by

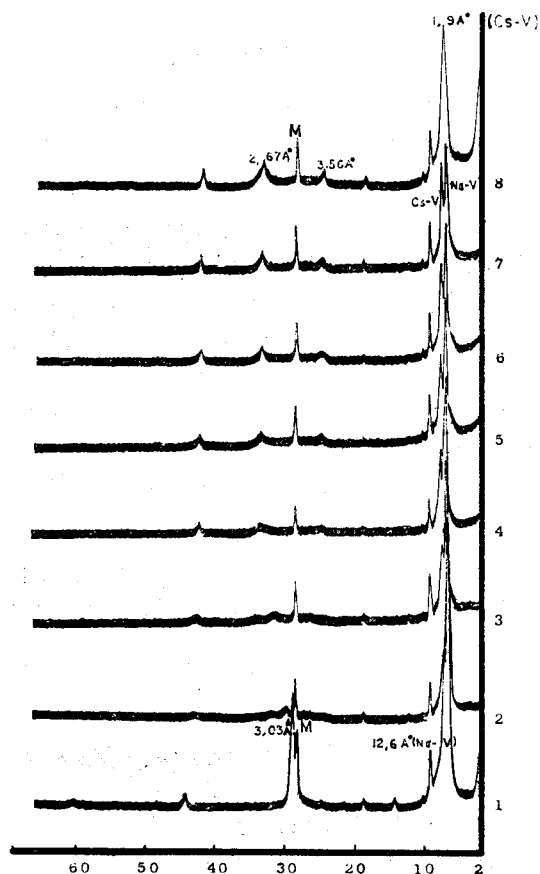


Fig. 12. X-ray diffraction patterns of vermiculite treated with CsCl for 2 hours (2), 24 hours (3), 48 hours (4), 72 hours (5), 100 hours (6) and 169 hours (7) from Na-V<sub>2</sub> vermiculite (1), and Cs-V<sub>2</sub> Vermiculite (8)

slow penetration into the interlayers. In Fig. 13, from 2 to 5, there is no sign of new peaks of Cs-vermiculite formed from K-vermiculite by treating with Cs ion, although some intensities were slightly changed. From the analysis of above X-ray diffraction patterns it can be assumed that Cs ions can not be penetrated into the interlayer of K-vermiculite.

Since the interstratified stage of weathering biotite-vermiculite would be formed during the process of bitite to vermiculite, one can expect that biotite peaks would be observed

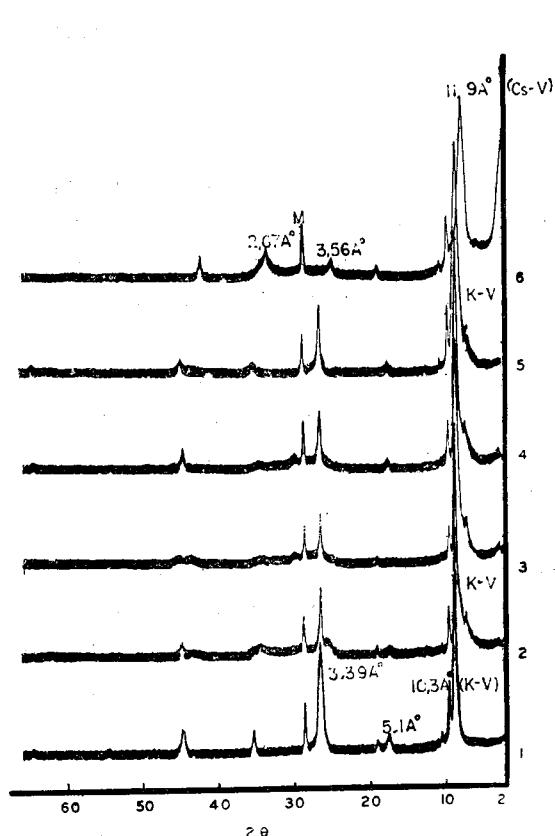


Fig. 13. X-ray diffraction patters of vermiculite treated with CsCl for 2 hours (2), 24 hours (3), 48 hours (4), and 72 hours (5) from K-V<sub>2</sub> vermiculite. (1), and Cs-V<sub>2</sub> vermiculite (6).

in the X-ray diffraction pattern of natural vermiculite and it is true as was seen in Fig. 10.

However, in pretreated vermiculite with NaCl and CsCl the patterns of biotite were not observed as shown in Fig. 11. It was considered that this was due to the release of potassium ion from interstratified system of biotite-vermiculite by the exchange process with Na ion and it would be resonable to explain that the intermediate stage of weathered biotite might be proceeded to change vermiculite by pretreatment of excess NaCl.

This weathering conversion from biotite to

vermiculite or hydrobiotite has been studied by many authors<sup>14) 28) 29)</sup> already.

#### 4. Conclusions

In order to develop the method of low level liquid waste treatment and disposal for long-lived fission products, fundamental studies on domestic vermiculite were summarized as follows:

- 1) The affinity of the vermiculite for cesium-137 in dilute solution increases with the increase in pH. This is attributed to the increase of sorption surface as a result of the dispersion
- 2) The sorption of cesium-137 by the vermiculite was markedly influenced by cesium concentration, and the sorption ability of Na-vermiculite had the maximum value at about  $10^{-3}$ M CsCl. Larger amount of cesium was sorbed from dilute solution by Na-vermiculite than K-vermiculite and this was related to the penetration of Cs ion into the interlayer of vermiculite.
- 3) From the results of X-ray diffraction analysis, it is clear that the penetration of Cs ion into the Na-vermiculite by the exchange reaction between Na and Cs ion tends to form the collapse structure due to the difference of degree of hydration and size of the ions.
- 4) From the results of extraction of Cs-vermiculite with various chloride solution it is found that more than 80 per cent of Cs ion adsorbed tends to retain into the vermiculite except extraction by KCl solution.
- 5) The domestic vermiculite is valuable material for application of fixation of long-lived fission products, and also useful as a good outside charging material in the underground tank storage for highly radioactive liquid wastes,

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