Radiocesium sorption behavior on illite, kaolinite and their mixtures

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INTRODUCTION
Cesium-135 ($^{135}$Cs) (half-life: $2 \times 10^6$ y) and $^{137}$Cs (half-life: 30 y) are produced by nuclear fission in high yield. Therefore, knowledge of the mobility of radiocesium in the natural environment is needed for the assessment of the impact of release from waste disposal sites (Japan Nuclear Cycle Development Institute, 1999). Since one of the most important pathways of radiocesium to humans from the environment is food consumption, behavior of Cs in agricultural fields should be researched.

It is well known that Cs can sorb strongly on soil, especially clay minerals (Tamura, 1964; Cornell, 1993). Clay minerals have two types of sorption sites for Cs: the Regular Exchange Complex (REC) sites which are planar and/or interlayer, and the Frayed Edge Sites (FESs) which are located at the edge and/or interlayer of the micaceous clay minerals such as illite (Delvaux et al., 2001). FESs selectively sorb Cs$^+$, K$^+$ and NH$_4^+$, and can not release these ions in soil solution. This phenomenon is called fixation. Due to the complex sorption behavior of Cs on clay minerals, it is difficult to estimate Cs sorption in soil. The objective of this study is to know quantitatively Cs sorption in a mixture of clay minerals and to estimate Cs sorption in the mixture. We use two types of clay minerals, which are kaolinite and illite. Kaolinite is a 1:1 clay mineral and has REC sites but not FESs. Illite is a 2:1 clay mineral and has both types of sites. Clarifying Cs sorption and fixation in the kaolinite-illite system could form the basis for long-term assessment of Cs mobility in soil.

MATERIALS AND METHODS

Kaolinite and illite were purchased from Iwamoto Kousan Co. Ltd. and Hayashi Shouten Co. Ltd., respectively. These clay minerals were washed with deionized water to remove excess salt and dried at room temperature prior to experiments. Table 1 summarizes their chemical compositions.

<table>
<thead>
<tr>
<th>Element</th>
<th>Illite (wt%)</th>
<th>Kaolinite (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>19.3</td>
<td>32.1</td>
</tr>
<tr>
<td>Si</td>
<td>51.4</td>
<td>60.8</td>
</tr>
<tr>
<td>S</td>
<td>0.1</td>
<td>0.3</td>
</tr>
<tr>
<td>K</td>
<td>20.4</td>
<td>0.6</td>
</tr>
<tr>
<td>Ca</td>
<td>2.4</td>
<td>0.1</td>
</tr>
<tr>
<td>Ti</td>
<td>1.5</td>
<td>2.8</td>
</tr>
<tr>
<td>Fe</td>
<td>4.2</td>
<td>2.6</td>
</tr>
<tr>
<td>Rb</td>
<td>0.1</td>
<td>not detected</td>
</tr>
<tr>
<td>Sr</td>
<td>0.2</td>
<td>0.3</td>
</tr>
</tbody>
</table>
**Batch sorption test**

Batch sorption tests using $^{137}$Cs as a tracer (half life: 30.1 y) were carried out to obtain data sets. Mixtures consisting of kaolinite and illite with a kaolinite ratio ranging from 0 to 100% were prepared and then a 100-mg amount of a mixture and 10-mL of deionized water were transferred into a 50-mL centrifuge tube. The suspension was initially shaken at 120 reciprocations per min for 1 day at 23 °C using an end-over-end shaker, and then 0.1 mL of $^{137}$Cs solution with 10 mg/L stable CsCl as a carrier (0.79 mg/L as Cs), were added to each tube. After further shaking for 7 days, the phases were separated by centrifuging at 10,000 rpm for 20 min. The supernatant was filtered through a 0.20 µm membrane filter. Radioactivity of $^{137}$Cs in the filtrate was measured with a NaI scintillation counter (Aloka, ARC-380). The pH and electric conductivity of each filtrate were measured with a pH meter and an EC meter, respectively. During the experiment, pH and EC ranged from 6.1 to 6.4 and 1.4 to 2.2 mS/m, respectively.

**Sequential extraction method**

To determine the weakly exchangeable, strongly exchangeable and fixed Cs fractions, a sequential extraction method was used. The solid part after the batch sorption test was added to 15 mL of 0.05 M calcium chloride (CaCl$_2$) and shaken for 24 h at 23 °C. The suspension was centrifuged at 10,000 rpm for 20 min, and the supernatant was filtered through a 0.20-µm membrane filter. The strongly exchangeable fraction in the residual solid phase of the sample was extracted for 24 h at 23 °C with 30 mL of 0.16 M sodium pyrophosphate (Na$_4$P$_2$O$_7$). The suspension from this extraction was processed in the same way as for the CaCl$_2$ extraction. Radioactivity of $^{137}$Cs in the filtrate was measured with the NaI scintillation counter. Cs in the residue after pyrophosphate extraction should be the fraction fixed in clay minerals. The three fractions are linked by the following relationship.

\[ Q = q_{ex} + q_{fix} \]

\[ Q: \text{the total amount of sorbed Cs} \quad q_{ex}: \text{the amount of exchangeable Cs} \quad (= q_{ex.w} + q_{ex.s}) \]

\[ q_{ex.w}: \text{the amount of weakly exchangeable Cs} \]

\[ q_{ex.s}: \text{the amount of strongly exchangeable Cs} \quad q_{fix}: \text{the amount of fixed Cs} \]
RESULTS AND CONCLUSIONS

The amount of sorbed Cs in clay mixture

Figure 1 shows the variation of the amount of sorbed Cs (Q) in the mixture with illite content. Nearly 100% of Cs was sorbed in the mixture. The Q values in the mixture did not differ with illite content. The $q_{ex}$ in the mixture decreased with increasing illite content, and the decrease ranged from 7.7 to 4.6 mg/kg. On the other hand, the $q_{fix}$ in the mixture increased with increasing illite content, and the increase ranged from 0.1 to 3.3 mg/kg. These results suggested that even though the total amount of sorbed Cs in the mixtures was not so different among illite/kaolinite ratio in them, the distribution of exchangeable and fixed Cs fractions was dependent on illite/kaolinite ratio in the mixtures. Since almost all of the sorbed Cs in kaolinite was extracted by Na$_4$P$_2$O$_7$ for pure kaolinite (100% sample), it was confirmed that 0.16 M Na$_4$P$_2$O$_7$ could extract Cs sorbed on REC sites in clay minerals. At 100% illite, $q_{ex}$ and $q_{fix}$ were 4.6 and 3.3 mg/kg, respectively. The Cs selectivity of REC sites was about 1.4 times higher than that of FESSs for illite used in this study. This indicated that REC sites were not negligible for Cs sorption compared with FESSs in clay mixture unlike in the case of soil and sediment reported by Wauters et al. (1996), because 58% of sorbed Cs was in the exchangeable fraction even on pure illite (100% sample).

Estimation of the amount of sorbed Cs in clay mixture

Clay minerals could not block each other’s sorption sites in the clay mixture because almost all surfaces in clay minerals are negatively charged. Therefore, if the abundance ratio of each clay mineral in clay mixture is known, the amount of sorbed Cs in the clay mixture can be estimated using the amounts of sorbed Cs on kaolinite and illite. Figure 2 shows $q_{ex}$ and $q_{fix}$ dependence on illite contents. $q_{ex}$ decreased linearly with increasing illite content. In addition, $q_{fix}$ increased linearly with increasing illite content. Therefore, when the amount of sorbed Cs for 100% kaolinite is $Q_{K,100,10}$ and the amount of sorbed Cs for 100% illite is $Q_{K,1100}$, the amount of sorbed Cs for the mixture of $x$% kaolinite and $y$% illite ($x + y = 100$), $Q_{K,x,y}$ can be estimated using the following equation.

$$Q_{K,x,y} = (x \times q_{K,100,10} + y \times q_{K,1100}) / 100$$
Figure 3 shows the relationship between estimated and observed $Q$ values. Correlation coefficients of these relationships were both 1.00. From these results, the amounts of exchangeable and fixed Cs can be estimated for the kaolinite-illite system if the amounts of exchangeable and fixed Cs in illite and kaolinite, and additionally the abundance ratio of illite and kaolinite are known. And then, the total amount of sorbed Cs in the mixture can be obtained. This result should provide fundamental knowledge for estimation of Cs mobility in a soil environment.

![Fig.2 $q_{ex}$ or $q_{fix}$ depending on illite contents](image1)

![Fig.3 Comparison of observed $q_{ex}$ or $q_{fix}$ with estimated values](image2)

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