Feasibility of classification of clay minerals by using PAS

Y Honda1, Y Yoshida2, Y Akiyama2, S Nishijima2

1 Institute of Scientific and Industrial Research, Osaka University, 8-1 Mihogaoka, Ibaraki, Osaka 567-0047, Japan
2 Graduate school of Engineering, Osaka University, 2-1 Yamadaoka, Suita, Osaka 565-0871, Japan

E-mail: honda@sanken.osaka-u.ac.jp

Abstract. After the nuclear power plant disaster, the evaluation of radioactive Cs kept in soil, especially in clay minerals and the elucidation of its movement are urgent subjects to promote decontamination. It is known that the extractable level of Cs depends on the sort of clay minerals. We tried to find the characteristics of clay minerals belonging to phillosilicate group using positron annihilation spectroscopy (PAS) and the relationship between the results of PAS and the amounts of substantially extracted Cs from the clay minerals. The results showed that each clay mineral was found to be distinguishable from other clay minerals by PAS and the extraction rate of Cs was different among those clay minerals, however the direct correlation between the results of PAS and the extraction rates of Cs was not found.

1. Introduction

Radioactive cesium is known as a major species of fallout due to the Fukushima nuclear power plant accident and it has been kept in soil, especially in clay minerals. The trapping mechanism of Cs for different kinds of minerals have been studied [1,2]. Phillosilicate is a group of silicate having periodic laminar structure composed of tetrahedral sheet silicate and octahedral sheet silicate minerals, and is divided into two groups. One group has a unit consisting of one octahedral sheet such as aluminosilicate and one tetrahedral silicate sheet (1:1 clay mineral). Another group is consisting of an octahedral sheet silicate minerals sandwiched with tetrahedral sheet silicates (2:1 clay mineral). Cs is hard to be leached out of such 2:1 clay even with strong acid rather than 1:1 clay, because of local strong electric field due to the exchange of trivalent aluminium with divalent cations, leading to the localization of Cs at preferable spaces such as hexagons consisting of oxygen on the silicate layer, defects called Frayed Edge Site (FES), which is a wedged defect appearing at the edge of octahedral sheet, and interlayer between silicate sheets. Condensation of Cs would progress through cation exchange process [3]. An identification of the sort of soil or clay is crucial to decide substantial decontamination process. Positron annihilation spectroscopy (PAS) seems to be a good method to detect defects such as FES, and exchanged cations with Al or Si, since positron has a high mobility and is charge sensitive. Indeed the electronic state of FES in saponite was investigated by positron annihilation spectroscopy [4]. In such a study, the samples were treated to eliminate contaminated particles prior to the measurements, however such procedure would bring about a structural change due to reduction or exchange of cations. In this work, a classification of several sorts of clay minerals was tried by using PAS and a comparison between the results of PAS and the substantial extraction rate of Cs from those clay minerals is shown without making any pre-treatments for the samples.
2. Experimental setup
The investigated samples were as follows; kaolinite which was synthesized with wet style, sintered vermiculite which was sold in a garden store, natural vermiculite which was brought from TOMOE Engineering Co., Ltd., montmorillonite which was purchased from Aquavitae Co., Ltd. and illite which was purchased from AromaFrance Co. Ltd. This illite was mixture of 65% illite and 25% kaolinite. Soil sold for the use of agriculture and indeed included much in the field of Fukushima was also prepared. No pre-treatment was made to avoid structural change. Many silver stings were included in natural vermiculite, which was observed by TEM-EDS (JEM-300F, JEOL), however there were no silver stings in the sintered vermiculite. The samples were also investigated with X-ray diffraction and the diffraction patterns were compared with the data in the PDF (Powder Diffraction File) of the ICDD (International Center for Diffraction Data). The diffraction pattern is so influenced by the presence of impurities that it is impossible to find the equivalent pattern to the measured one. However, the pattern of vermiculite was quite similar to the reference data both in peak angle and intensity profile. The measured major diffraction peaks of kaolinite and montmorillonite had almost the same peak angles as the reference data, though the intensity profiles were a little different. As the measured illite was a mixture of illite and kaolinite, the difference was larger than other samples, however the angles of the observed major diffraction peaks appeared also in the corresponding reference data of illite. Lifetime measurement of positron/positronium was carried out with a sealed Na-22 source covered with Kapton films. Its intensity was ca. 420 kBq and the time resolution was 220-240 ps. Coincidence Doppler broadening measurement (CDB), which is a simultaneous measurement of γ-rays emitted through 2 photon annihilation, was also carried out. To compare the results of PAS and the degree of Cs trapped in and extracted from the clays, all the samples were soaked in Cs solution with a concentration of 100 mg/l for 1 hour with shaking. The centrifugally separated contaminated samples were soaked in ammonium acetate solution with two different pH, 0.97 and 6.93 to extract Cs for 1 hour with shaking. The control of pH was made with nitric acid solution. The extracted Cs in solution from the sample was evaluated by an ICP-MS (Agilent7700 ;Agilent Technologies).

3. Results and discussions

3.1. Positron annihilation spectroscopy

3.1.1. Lifetime Measurements. Only kaolinite showed a small long-lived component (63 ns with ca. 2% relative intensity). Settling this lifetime, the other components were evaluated with 3 component analysis using PATFIT program as well as for other samples, where the lifetime spectrum was regarded as \( N(t) = \sum_{i=1}^{3} (I_i/t_i) \exp(-t/t_i) \). The \( t_i \)s of vermiculite and montmorillonite were similar, that of kaolinite was slightly shorter and those of illite and soil were slightly longer (Figure 1). This may reflect the structural difference among 1:1 group, 2:1 group and others. Indeed in 2:1 clay minerals, the interlayer distance varies with species of captured cation [1]. The size of hexagon on tetrahedral sheet is similar to the dimension evaluated by a lifetime of o-Ps. The \( I_i \)s of kaolinite, illite and soil were slightly higher than others, but

![Figure 1](image-url)

Figure 1(a). Lifetimes and their relative intensities.
those values were very small. Why the $I_{3s}$ were so small can be explained for 2:1 minerals by the fact that the tetrahedral sheets tend to stack as the result of Coulomb interaction between the sheet and interposed cation, reducing the interlayer gap. For 1:1 mineral, the unit layer is bound each other via hydrogen bond and the space of interlayer could be large, however the formation of $o$-Ps would be less. This is probably because the energy of electron relating to hydrogen bond is low and the space size formed with hydrated cations and the tetrahedral sheets is not enough to form positronium. In this analysis, as the source term correction of the sealed Na-22 could not be made, $I_{3s}$ included the source components, however the relative intensity still have a meaning. As the strong electric field exists between layers, positron would approach the negative site, such as hexagon mentioned above, and annihilate without forming $o$-Ps. Concerning $\tau_1$ and $\tau_2$, kaolinite showed slightly shorter lifetimes. This would be due to the presence of hydrogen bond in the interlayer. Those for natural and sintered vermiculite were almost equivalent, meaning that positron annihilated in an intrinsic structure of vermiculite without suffering from contaminants. The $\tau_1$ and $\tau_2$ of montmorillonite and illite were slightly longer than vermiculites and the soil. This would mean the interlayer gaps of montmorillonite and illite were wider than those of vermiculites.

3.1.2. CDB measurements. The profiles shown in Figure 2 are the ratios of the energy spectrum with respect to kaolinite, which was commonly measured in the different sets of measurement. The ratios for silver showed completely different profile in a higher momentum range. Kaolinite was found to have a narrower momentum distribution than other 2:1 clay minerals and silver. There was no evidence of silver in the spectrum of natural vermiculite and no significant difference between natural and sintered vermiculites. These results mean that positron approached some intrinsic structure of vermiculite and annihilated there, which was also deduced from the results of lifetime spectroscopy in the previous section. The ratio was larger in illite than those of montmorillonite and vermiculite at around normalized momentum of 0.03. Energy spread of vermiculite was slightly larger at around 0.02 than that of montmorillonite. The profile of ratio for the measured soil was quite similar to that of montmorillonite. It is said that the hydration of cation is an important process for trapping of cation at FES and diffusion of cation into interlayer [1]. The injected positron would come to the interlayer due to local electric field and annihilate with the electron relating to oxygen of tetrahedral sheet or water molecule attached to the cation or hydrogen bonding. Thus, those results would reflect the electronic status of interlayer.

3.2. Cesium extraction
The trapping ability and extraction of Cs for each clay mineral in neutral solution is shown in Figure 3. The absorption of Cs would be made at cation exchange site (CES), defects such as FES and interlayer including surfaces. Cs would be extracted easily from CES rather than from FES and interlayer. Absorption was not saturated in these experiments. The absorption rate of Cs for vermiculite and montmorillonite was rather higher than that of illite and kaolinite. Montmorillonite released about 70 % Cs, whereas vermiculite released only about 10% Cs in neutral solution regardless of whether it was sintered or not. In highly acid solution, the extraction rate for vermiculite and montmorillonite was increased a little but that for the other minerals and the soil showed no significant difference, meaning that the role of CES is not high for the sorption of Cs. Instead, the FES or fixing capacity of Cs in interlayer plays more important role for stable Cs trapping [2]. The results showed that the most stably adsorbed site of Cs was the FES and/or interlayer of vermiculite among the investigated clay minerals. The behaviour of Cs for the measured soil was similar to that of kaolinite and illite, though the ratio of CDB spectra showed quite similar profile to montmorillonite.

4. Summary
The difference between kaolinite (1:1 clay mineral) and other 2:1 clay minerals was detected by PAS. Taking into account of the results for natural and sintered vermiculite, it can be said that positron can sense its intrinsic structure. PAS could not detect the FES of 2:1 group with o-Ps. This is probably because the sites were filled with cations, and the space size was not enough for the formation of long-lived positronium. The annihilation process of positron was strongly influenced by the local electric field in the vicinity of interlayer. The annihilation γ-rays would convey the information such as the degree of hydration, binding energy of layers, hydrogen bonding, etc., leading to the difference in the CDB spectral ratio. However, there are no distinct correlation between the profile of the ratio and the extraction rate of Cs. Elucidation of the mechanism of Cs trapping in clay minerals, especially in vermiculite, seemed difficult based only on the results of PAS, however, it can be predicted that Cs cation would be preferentially exchanged at FES rather than other cations as is shown in elsewhere [1,2], and the difference of cation exchange capacity of Cs for different clay minerals might reflect on a difference around 0.02 of the normalized momentum in CDB spectral ratio. The soil bore resemblance to montmorillonite with respect to CDB results, but the behaviour of Cs in the soil through extraction process was different from that in montmorillonite and similar to kaolinite and illite, indicating that more information must be added to characterize substantial soil.

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