Cs Adsorption and CsCl Particle Formation Facilitated by Amino Talc-like Clay in Aqueous Solutions at Room Temperature

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Cite This: ACS Omega 2021, 6, 26026−26034
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ABSTRACT: Amino talc-like clay with an increased number of active sites and dispersion in a colloidal system has been synthesized and used for contaminant adsorption and support for nanoparticle formation. Amino talc-like clays having different number of layers and aminoalkyl ligands were synthesized and their Cs uptake behavior was examined. Cs uptake through Cs adsorption and CsCl particle formation facilitated by amino talc-like clay in a colloidal aqueous solution at room temperature are reported. The amino talc-like clay demonstrated better Cs uptake with a high initial Cs concentration than talc and montmorillonite. This might have been caused by a high concentration of trapped Cs and Cl ions in exfoliated amino clay, which eventually became CsCl particles. The formation of the CsCl particles in the amino clay depended on the clay concentration and ethanol treatment. The exfoliation of the basal sheets of the amino clay as a result of a high salt concentration and the protonation of amine induced by ethanol treatment was shown to be a precondition for CsCl particle formation. These results could promote amino talc-like clay for high-concentration Cs uptake and the green synthesis of Cs-halide particles in an aqueous solution.

INTRODUCTION

Clay is a well-known layered material used for various applications due to its distinct physicochemical properties such as a large surface area provided by surface, edge, and basal spacing, and relatively a nontoxic substance.1 Smectite type clays, consisting of octahedral structure sheets sandwiched between two tetrahedral structure silica sheets (2:1 type), have attracted significant interest due to their swellable basal spacing that allows for modification.2,3 However, the use of natural clay is challenging due to the presence of some contaminants and heterogeneous chemical composition.4

Synthesis of surface-functionalized clay is a better option for producing a free contaminant, homogeneous chemical composition, and well-defined properties of clay material. Amino talc-like synthetic clay, a type of synthetic smectite clay, has been developed by introducing an aminoalkyl surfactant to the clay surface. Amino talc-like clay has some different properties from talc as the parent material.3−6−10 The amino talc-like clay has a positive ζ potential, while talc has a negative ζ potential in its given pH.2,5 Additional properties by the introduction of an aminoalkyl ligand on the surface of talc result in the increase in active sites on the surface and the increase in stability in a colloidal system.5

Furthermore, the amino clay with fewer layers (delaminated amino clay) and the amino clay with more layers (lamellar amino clay) have been synthesized.6−8 However, the examination and application of these two different materials, especially for lamellar amino clay, are still limited. The delaminated amino clay has been applied for some applications such as cation adsorption,9,10 anion adsorption,11 antimicrobial agent,12 and support for nanoparticle formation. In more specific application, however, there is no research on alkali metal uptake by both types of amino talc-like clay.

The Cs ion, one of the alkali-metal elements, is known to cause adverse health effects in humans, such as fatigue, muscle weakness, palpitations, and arrhythmia.13 It is also a relatively toxic element for other organisms, such as soil microorganisms.14,15 Notably, 137Cs is a radioactive element produced in nuclear reactors. It is typically disposed of as nuclear waste and has a half-life of approximately 30.2 years. When nuclear accidents, such as the Fukushima nuclear accident, occur, 137Cs is one of the primary radionuclides released into the environment.16 137Cs may cause radiation exposure that can result in long-term radiation health effects.17 The strong interactions between the Cs ion and clay minerals have been widely studied through field studies, laboratory experiments, and computational studies.20−22 One study demonstrated the formation of the frayed edge site in the...
interlayer space caused by the insertion and subsequent dehydration of the hydrated Cs ion. It is one of the essential preconditions for the promotion of strong interaction between Cs and clay, apart from the interaction between the Cs ion and basal and edge surfaces. Therefore, some studies have aimed to utilize clay-based material, especially 2:1 type clay for a Cs adsorber.

In contrast, there is increasing interest in developing alkali-halides and alkali-metal-halide nanoparticles, such as CsCl, CsCuCl2, etc., which have unique properties such as optical property and a simple synthesis process. They are good candidates for radiation detection, optoelectronic and photovoltaic materials, and inorganic light-emitting diodes. The colloidal alkali halide and alkali-metal halide nanoparticle synthesis using organic solvents are the most studied method using some types of surfactant, including oleic acid. Research on the development of green-nanoparticle production in aqueous solutions remains limited. Therefore, research exploring water-soluble surfactants for nanoparticle production by a colloidal synthetic method is highly desirable.

In this study, the lamellar and delaminated amino talc-like clays with different aminoalkyl ligands attached on their surface have been synthesized and their Cs uptake behavior was examined. We report Cs uptake by amino talc-like clay through Cs adsorption and CsCl particle formation. Herein, we discuss the possible mechanism of CsCl particle formation to promote further development and application.

## RESULTS AND DISCUSSION

### Characterization of the Synthetic Amino Talc-like Clays. Structure of the Materials.

Two different types of amino talc-like clays were produced: lamellar amino clay and delaminated amino clay. The lamellar amino talc-like clay with the organic ligand 3-aminopropyl is denoted as LAC@1 and the lamellar amino talc-like clay with the organic ligand N-(2-aminoethyl)-3-aminopropyl is denoted as LAC@2. The delaminated amino talc-like clay with the organic ligand 3-aminopropyl is denoted as DAC@1 and the delaminated amino talc-like clay with the organic ligand N-(2-aminoethyl)-3-aminopropyl is denoted as DAC@2.

The powder X-ray diffraction (PXRD) patterns and Fourier transform infrared (FT-IR) spectra of Mmt, talc, LACs, and DACs are shown in Figure S1. The amino clays (LACs and DACs) have a typical PXRD diffraction at a low angle corresponding to the (001) plane (basal spacing), indicating a layered structure. The PXRD peaks at a higher angle that correspond to the (060, 330) plane are a characteristic of the 2:1 trioctahedral angle of Mg-phyllosilicate. The PXRD patterns of the lamellar amino clays and delaminated amino clays were in good agreement with previous reports. The PXRD patterns demonstrate that the aminoalkyl ligand expanded the basal spacing for LACs and DACs to approximately twice the size of the basal spacing of talc and Mmt (Table S1). The calculated d-spacing (001), especially for LAC@1 and LAC@2, was in good agreement with previous research.

The PXRD pattern of the synthetic amino clays clearly followed the talc PXRD pattern, demonstrating that the synthetic clay was talc-like clay. The FT-IR spectrum (Figure S1) revealed some bands corresponding to a higher degree of functionalization of amino clays than talc and Mmt. The main functional groups of the synthetic materials were −CH2, −NH2, Si−C, Si−O, and metal−O.

The elemental analysis results demonstrate that the differences in C, H, and N contents corresponded to the different aminoalkyl groups used for producing the material (Table S2). More C atoms imply a longer alkyll chain length; this was found to correlate with a bigger basal spacing in the PXRD pattern. More N atoms are an indication of more amine functional groups attached to the clay surface. There is no difference between LAC@1 and DAC@1 or between LAC@2 and DAC@2.

The transmission electron microscopy (TEM) and field emission scanning electron microscopy (FE SEM) results for LAC@2 and DAC@2 are shown in Figures 1 and S2, respectively. The TEM image indicates that the layered structure of LAC@2 was thicker than that of DAC@2. The TEM image also shows that LAC@2 was rougher than DAC@2, indicating that LAC@2 has more porous characteristics than DAC@2. The more degree of roughness and porosity of LAC@2 are probably related to its lamellar structure. In addition, The FE SEM image clearly confirmed that LAC@2 has a bigger particle size and rougher surface than DAC@2 (Figure S2). The selected area electron diffraction (SAED) patterns (inset of Figure 1) show that the amino clays were amorphous materials.

### Dispersion Degree of the Materials in the Colloid System.

The dispersion of the clays in water and ethanol is shown in Figure S3. None of the clays, even the amino clays, were dispersed in ethanol, and the only amino clays were well dispersed in water. Furthermore, the DACs were better dispersed in water than the LACs. In contrast, talc and Mmt were not dispersed in ethanol or water.

The more dispersion of the amino clays in water than Talc and Montmorillonite was not obviously related to the ζ
potential of the surface. The $\zeta$ potential of amino clays (LACs and DACs) was higher than that of montmorillonite; however, the potential value (<30 mV) was not enough to result in the electrostatic stabilization through repulsive effect among the particles in the colloid system (Table S3). The stability of LACs and DACs in water was due to the combination of electrostatic and steric stabilization by the aminoalkyl ligand attached to the clay surface. The aminoalkyl ligand on the surface caused the repulsive electrostatic forces between the pendant quaternary ammonium groups and provided a gap between the particles that weaken the van der Waals interaction between the particles.29 Moreover, the DACs were more dispersed in water than LACs. It was because the DACs have a smaller number of layers (delaminated) than LACs. Delamination of DACs caused more aminoalkyl ligand on the surface of the clay to be exposed by the medium, resulting in more steric stabilization of the colloid particles (Figure 2).

The precipitation of the amino clay particles in ethanol was probably due to the antisolvent effect of ethanol as a poorer solvent compared to water.27,30 It was not related to the $\zeta$ potential of the particles; this idea was supported by the absence of pH change effect to the stability of the particle (Table S4). The decrease of pH will increase the $\zeta$ potential and stabilization of the particle having basic group on the surface like amino clays. However, it is not the case for the present amino clays in thanol. Previous study has reported that the surface-bound ligand molecules attract each other in poor solvents but repel each other in good solvents.31 Furthermore, there was a depletion of ethanol at the interface between two ligands attached on two adjacent particles so that the ligand interaction could occur, and then eventually the precipitation of the particles occurred.31

**Cs Uptake by the Materials.** The Cs uptake by lamellar talc-like amino clay (LACs), delaminated talc-like amino clay (DACs), talc, and Mmt with various initial CsCl concentrations is presented in Figures 3 and 5. These results demonstrate a higher Cs uptake by LAC@1 than LAC@2 throughout the entire CsCl concentration range. Particularly, in the case of >50 mM initial CsCl concentration, high Cs uptake by LAC@1 may be resulted from the Cs adsorption by clay surface and a high concentration of trapped Cs and CI ions that eventually become CsCl particles, as demonstrated by the PXRD pattern (Figure 4). The formation of CsCl particles was not clearly demonstrated in the case of LAC@2 and talc and was not found in the case of Mmt.

The intensity of the (001) diffraction decreases with increasing CsCl concentration for LAC@1, while the intensity does not significantly decrease for LAC@2. This demonstrates that a high concentration of salt induced the exfoliation of LACs with different degrees of exfoliation. The presence of CsCl particles in LAC@1 was probably due to increased exfoliated basal spacing induced by a high salt concentration compared to that of LAC@2. The presence of more $-\text{NH}_2$.
was expected to create a large number of hydrogen bonds between the two \(-\text{NH}_2\) for LAC@2 than LAC@1 that may prevent the basal spacing exfoliation. The exfoliated basal spacing of LAC@1 may trap Cs\(^+\) and Cl\(^-\) ions leading to supersaturation, allowing the nucleation and formation of CsCl particles, especially during the drying process.\(^{26,32}\)

Additionally, Figure S4 shows the Cs uptake by LACs, Mmt, and talc at different contact time intervals. It shows that the Cs uptake by Mmt and talc has reached the maximum Cs uptake at 10 min contact time, while LAC@1 and LAC@2 show longer time to reach the maximum Cs uptake. It may confirm the different Cs uptake mechanisms between LACs and purchased clays (Mmt and talc). Cs uptake by Mmt and talc was probably a simpler Cs uptake mechanism resulting from their simpler surface structure than LACs. On the contrary, Cs uptake by LACs was perhaps a result of a complex process, considering their complex surface structure. This may confirm the idea that high Cs uptake by LACs, especially for LAC@1, was through the Cs adsorption and Cs-ion-trapping mechanism, leading to CsCl particle formation.

Furthermore, the results in Figure S4 show that the DACs have higher Cs uptake than the LACs throughout the entire CsCl initial concentration range. The higher Cs uptake by the DACs might be related to the higher stability of the DACs in aqueous solutions than that of the LACs (Figure S3). Furthermore, the delaminated structure of DACs caused more aminoalkyl ligand exposed to the medium, resulting in more ion–clay surface interaction than the lamellar structure of LACs. The slightly higher Cs uptake by DAC@2 than DAC@1 was probably related to the longer alkyl chain and more amine groups attached on the surface of DAC@2 than that of DAC@1.

The results in Figures 3 and 5 also indicate the more Cs uptake by amino clays (LACs and DACs) than talc throughout the entire CsCl initial concentration range. The amine functional group of the aminoalkyl attached to the amino talc-like clay was key to higher Cs uptake by amino clay than talc. The amine functional group attached on the surface of the clay through a Si–C bond provided a new Cs adsorption site, in addition to the electrostatic interaction between Cs and O in the basal, edge, and the interlayer space of the clay.\(^{23}\) However, the interaction was pH-dependent due to the protonation of \(-\text{NH}_2\) to \(-\text{NH}_3^+\) in acidic conditions. Previous research has demonstrated that the \(-\text{NH}_2/\text{NH}_3^+\) ratio was a determining factor for the contaminant adsorption of heavy metals.\(^9\)

Cs uptake was the weakest in talc among the studied clays. This might be because of the relatively less negative surface potential of talc compared to that of other clays, such as kaolinite and Mmt, based on their calculated surface potential and surface charge density from AFM measurements.\(^{35,34}\) The metal center of the octahedral sheets of the clays determined the surface potential of the clays.\(^9\) The lower negative surface potential of talc than Mmt resulted in a weaker talc surface–Cs interaction. The weaker interaction of the talc–Cs ion might have resulted in more ions being trapped rather than adsorbed, which would explain the formation of CsCl particles in a talc colloidal solution. This was not the case for Mmt, for which there was a stronger surface clay–Cs interaction (Figures 6 and 8e). However, CsCl particles in a talc colloidal solution were not observed using a TEM energy-dispersive system (TEM EDS) (Figure 8e).

Figure 5. Cs uptake (mmol/g of precipitate) by amino clays, talc, and montmorillonite with short-time ethanol treatment.

Figure 6. PXRD patterns of amino clays with different concentrations (a) and purchased clays with 30 mg/mL concentration (b) after interaction with CsCl and short-time ethanol treatment.
Figures 3 and 5 also show that Cs uptake by amino talc-like clay is different from Cs uptake by Mmt. There was more increased Cs uptake by talc-like clay than by Mmt with an initial CsCl concentration of 50 mM CsCl. Moreover, in a high concentration of CsCl, Cs uptake by amino clay surpasses Cs uptake by Mmt. This phenomenon might be somewhat influenced by Cs adsorption of the amino clay surface, and the ion-trapping phenomenon leads to the formation of CsCl particles in high concentrations of salt.

The clay recovery data are shown in Figure S5. Clay recovery is calculated using the mass of the precipitate and the initial mass of the clay. These data demonstrate that the amino clays, especially the delaminated amino clays, have lower clay recoveries than talc and Mmt. The lower recoveries may hinder the application of this material for contaminant removal. Further, these results confirmed that the presence of the aminooalkyl attached to the synthetic clay enhanced the dispersion of the clay.

Effect of the Clay Concentration and Ethanol Treatment on CsCl Particle Formation. Figure 6 shows the PXRD pattern of the amino clays (LACs and DACs) with different clay concentrations (10 and 30 mg/mL) and purchased clays (talc−Cs and Mmt−Cs) with 30 mg/mL concentration after interaction with CsCl and short-time ethanol treatment. The PXRD pattern for CsCl demonstrated marked similarities to that of the precipitate sample from the Cs uptake experiment with a high clay concentration (30 mg/mL), unlike the PXRD for the sample with a low clay concentration (10 mg/mL).

This phenomenon might be related to the increase in available amino clay that can trap and stabilize ions to form particles. With more clay to trap the ions, a greater number of CsCl particles are formed. This demonstrates that CsCl particle formation is dependent on the clay concentration.

The role of ethanol in CsCl particle formation facilitated by amino talc-like clay in colloidal aqueous solutions was investigated further. Figures 6 and 7 show the PXRD pattern of amino clay with short-time and long-time ethanol treatments, respectively. The PXRD pattern of CsCl was clearly observed in the PXRD pattern of the precipitate sample from the Cs uptake experiment with a low clay concentration (10 mg/mL) and long-time ethanol treatment. This demonstrates that CsCl particle formation is dependent on the ethanol treatment.

This phenomenon might have been caused by the sudden slight decrease in solvent polarity caused by the addition of ethanol, which changed the solubility equilibrium of the CsCl solution, resulting in the lower solubility of CsCl. The solubility equilibrium change may initiate the nucleation and formation of particles. Here, ethanol acts as an antisolvent.

The formation of nanoparticles by the antisolvent method has been reported previously.7 The injection of nanoparticle precursors dissolved in a higher polarity solvent (dimethyl sulfoxide (DMSO)) into a lower polarity solvent acting as an antisolvent (toluene) was carried out to produce alkali-metal-halide nanoparticles.

Another role of ethanol for the CsCl particle formation was revealed by the band at approximately 2000 cm⁻¹ in the FT-IR spectra of the sample after ethanol treatment (Figure S6). This band was assigned to the protonated amine (−NH₃⁺).9 Lower protonation of amine may occur in the presence of a high Cs-ion concentration without ethanol treatment so that the band corresponding to the protonated amine (−NH₄⁺) had lower intensity or was absent in the FT-IR spectra (Figure S6). Further, the protonation of −NH₃ by ethanol induced a break in the hydrogen bond between the sheets of the amino clays. The exfoliation of amino clay by ethanol treatment was confirmed by the decrease in intensity and the absence of the low-angle PXRD diffraction of the amino clay (Figure 7).

The effects of ethanol treatment on CsCl particle formation were investigated further using TEM EDS (Figures 8 and 9). The results in Figure 8d clearly indicate spherical particles of approximately 10–30 nm. The observed particles had likely escaped from the clay (Figure 8c). Notably, the highest TEM EDS peak is for Cs and the smaller peaks are for Mg, Cl, and Cu (as an impurity, this is probably coming from the TEM grid) that show the presence of Cs-rich particles (Figure 8e).

The TEM EDS data of DAC@2-Cs also show a high Cs peak, which showed adsorbed Cs on the clay surface and Cs-rich particles that were probably still trapped on the clay.

![Figure 7. PXRD patterns of synthetic amino clays (a) and purchased clays (b) after interaction with CsCl and long-time ethanol treatment.](https://doi.org/10.1021/acsomega.1c02975)
In contrast, long-time ethanol treatment may predominantly result in the production of CsCl particles (Figure 9b), although an abundance of Cs ions remained on the clay surface (Figure 9a,c). The presence of 50–200 nm-sized CsCl particles after ethanol treatment was confirmed by TEM and the SAED pattern from a CsCl single crystal (Figure 9b). The particles were confirmed to be CsCl as the TEM EDS demonstrates that the main components of the particles are Cs and Cl (Figure 9c). The presence of the O, Mg, and Si peaks from the TEM EDS data also revealed that the amino clay covered the CsCl particles. Figure 10 shows the schematic diagram of the CsCl particle formation facilitated by amino clay.

The EDS data show a decrease in the C/O peak ratio of DAC@2 before and after the Cs uptake experiment with short...
short-chain alcohol has been reported previously.35 Removal of carboxylic ligand attached on particle surface by promoted the trapped ions to form stable particles. The removal was not clear. The free aminoalkyl probably also amino clay surface. However, the mechanism of aminoalkyl possibility that the aminoalkyl was removed in some part of the deformation was not clearly con EDX measurement is a very local measurement. The dispersive X-ray (EDX) must be avoided because the TEM Si ratio could be associated with the deformation of the clay. However, the hasty judgment based only TEM energy-

Lamellar Talc-like Clay. The lamellar amino talc-like clay experiments were carried out using deionized water.

10 montmorillonite (Mmt, Aldrich) and talc (Fuji without prior puri

sodium hydroxide (Aldrich), were reagent grade and used fi

EXPERIMENTAL SECTION

Materials. The silylating agents used in the experiment, 3-aminopropyl trimethoxysilane (Fujifilm) and [N-(2-aminooethyl)-3-aminopropyl] trimethoxysilane (Shin-Etsu Chemical), were reagent grade. The other reagents, magnesium chloride hexahydrate (MgCl2·6H2O), cesium chloride (CsCl) (Fujifilm), methanol (99%) (Nacalai Tesque), ethanol (99.5%), and sodium hydroxide (Aldrich), were reagent grade and used without prior purification. The purchased clays consisted of K-10 montmorillonite (Mmt, Aldrich) and talc (Fujifilm). All experiments were carried out using deionized water.

Synthesis of Amino Talc-like Clay. Synthesis of Lamellar Talc-like Clay. The lamellar amino talc-like clay was produced according to a previously published sol–gel method.1 A magnesium chloride solution was prepared by dissolving 5.286 g of magnesium chloride hexahydrate (MgCl2·6H2O) in 150 mL of deionized water while stirring at 373 K. Then, 25 mL of a 1.39 M silylating agent in methanol was added dropwise into the solution, resulting in a white suspension. Finally, 250 mL of a 0.1 M sodium hydroxide solution was added dropwise to the white suspension to prevent the protonation of the amino clay. The suspension was aged in an oven at 323 K for 3 days until a gel was formed, and the gel was washed with 150 mL of deionized water, vortexed for 1 min, and centrifuged at 7000 rpm for 5 min. The precipitate was oven-dried at 323 K for approximately 5 days.

Synthesis of Delaminated Amino Talc-like Clay. The delaminated amino clay was produced according to previously published research.6-8 A magnesium chloride solution was prepared by dissolving 1.692 g of magnesium chloride hexahydrate (MgCl2·6H2O) in 40 mL of ethanol while stirring at room temperature (approximately 298 K). Then, 0.015 mol silylating agent (2.70 g of 3-aminopropyl trimethoxysilane or 3.35 g of [N-(2-aminoethyl)-3-aminopropyl] trimethoxysilane) was added dropwise, the solution was stirred overnight, and a white suspension was obtained. The suspension was centrifuged at 7000 rpm for 5 min, and the precipitate was washed with 40 mL of ethanol, vortexed for 1 min, and centrifuged to remove the washing solution. The white precipitate was oven-dried at 323 K for approximately 5 days.

Characterization. The synthesized materials were charac-
terized by Fourier transform infrared (FT-IR) spectrometry (Horiba, FT-720), elemental analysis (Perkin Elmer CHNS/O 2400II), powder X-ray diffraction (PXRD), transmission electron microscopy with energy dispersive X-ray analysis (TEM EDS), and field emission scanning electron microscope with energy dispersive X-ray analysis (FE-SEM EDS).

The powder X-ray diffraction pattern was acquired using a Rigaku PXRD using Cu Kα radiation (λ = 1.54059 Å) at 40 kV and 44 mA, 2θ range from 3–80°, at room temperature.

TEM EDS was conducted with a JEM 2010 (JEOL) operated at 200 kV. The sample in ethanol was dropped on a carbon-coated copper grid and dried in an oven at 323 K overnight before the analysis.

FE SEM EDS was conducted by measuring the dried precipitate using an S-5200 scanning electron microscope (Hitachi).

Figure 10. Schematic diagram of CsCl particle formation facilitated by amino clays.

and long ethanol treatment (Figures 8e and 9c). There was a possibility that the aminooalkyl was removed in some part of the amino clay surface. However, the mechanism of aminooalkyl removal was not clear. The free aminooalkyl probably also promoted the trapped ions to form stable particles. The removal of carboxylic ligand attached on particle surface by short-chain alcohol has been reported previously.35 Furthermore, the Mg/Si peak ratio of DAC@2 was increased after the Cs uptake experiment with short and long ethanol treatment (Figures 8e and 9c). The change of the Mg/Si peak ratio could be associated with the deformation of the clay. However, the hasty judgment based only TEM energy-dispersive X-ray (EDX) must be avoided because the TEM EDS measurement is a very local measurement. The deformation was not clearly confirmed by the PXRD measurement of clay after the Cs uptake experiment and ethanol addition. It only showed the change of the (001) plane and that the appearance of the PXRD pattern belongs to CsCl particles.

CONCLUSIONS

Cs adsorption and Cs⁺ and Cl⁻ ion trapping leading to particle formation are two coexisting processes in the amino talc-like clay colloidal with a high CsCl concentration solution. The surface structure and positively charged surface potential of the amino talc-like clay enabled the formation of CsCl particles from the trapped ions. The ethanol treatment decreased the solubility of CsCl and caused the exfoliation of basal sheets of amino clay, all of which led to an increase in CsCl particle formation.
The pH of 10 mg clays dispersed in 5 mL of water and 5 mL of ethanol was measured using a pH meter D-51 (Horiba).

**Examination of Cs Uptake by Clay and CsCl Particle Formation.** The following experiment was carried out using the produced lamellar amino clays (LACs) and the purchased clay (Mmt and talc). The adsorbent dosage (mg clay per mL of CsCl solution) was 60 mg/mL at the following CsCl concentrations: 5, 50, 125, and 250 mM. $^{137}$Cs was added to the CsCl solution as a tracer. The known stable Cs/$^{137}$Cs ratios for 5, 50, 125, and 250 mM CsCl solution are 0.11, 0.12, 1.19, and 1.23 $\mu$mol/Bq, respectively. The clay–CsCl solution was shaken by a vortex shaker for approximately 24 h at room temperature and centrifuged at 7000 rpm for 5 min. In the case of LAC@1, centrifugation up to 15 000 rpm was required to remove sufficient liquid from the solid particle. The precipitate was oven-dried at 363 K for approximately 2 days. The $^{137}$Cs concentration in the precipitate was measured using a $\gamma$ spectrometer with a HP Ge detector and multichannel analyzer (GEM 30-70, ORTEC), at an energy peak of 662 keV for $^{137}$Cs. The $\gamma$ spectrometer was calibrated using a set of standard sources (MX033U8PP) manufactured by the Japan Radioisotope Association. The stable Cs concentration was calculated using the stable Cs/$^{137}$Cs ratio. The clay recovery was calculated based on the mass of precipitate and the initial clay used in the experiment.

The same experimental procedure for examining the Cs uptake by delaminated amino clay (DACs) was conducted with the addition of ethanol treatment after 24 h shaking, for which 2.5 mL of ethanol was added to 1.25 mL Clay and CsCl solution mixture. The ethanol treatment aimed to recover the delaminated clay from the solution. The ethanol-treated solution was shaken for approximately 3 h. Cs uptake experiments by LACs, Talc, and Mmt with addition of ethanol were also performed for comparison.

The Cs uptake experiment with the similar experimental condition by LACs, talc, and Mmt without ethanol treatment at different contact time intervals was further conducted. An adsorbent dosage of 60 mg clay/mL of 250 mM CsCl was used. The Cs uptake by clays was analyzed during some contact time intervals: 10 min, 30 min, 1 h, 2 h, 6 h, and 15 h.

Separate experiments using a stirring method at two adsorbent dosages (10 and 30 mg/mL of 0.25 M CsCl) and various ethanol treatments were conducted to examine the effects of the clay concentration and the ethanol treatment on the CsCl particle formation. In some cases, ethanol was added to the clay–CsCl solution at the end of the experiment (short-time ethanol treatment), and ethanol was added at the beginning of the experiment (long-time ethanol treatment). The formation of CsCl particles was observed in the precipitate of the clay–CsCl solution using PXRD and TEM EDS.

**Data Analysis.** Data were analyzed using Origin pro software. The Cs uptake experiment was conducted in triplicate, and the data are expressed as the mean of the triplicate. The error value was derived from the standard deviation of the triplicate.

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