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Characterization of homoionic Fe^{2+}-type montmorillonite: Potential chemical species of iron contaminant

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Abstract

Fe^{2+}-montmorillonite with Fe^{2+} ions occupying cation exchange sites is an ideal transformation product in bentonite buffer material. In our previous study on preparation and characterization of Fe^{2+}-montmorillonite, the montmorillonite sample that adsorbed Fe^{2+} ions on almost all of the cation exchange sites was prepared using a $FeCl_2$ solution under an inert gas condition [N. Kozai, Y. Adachi, S. Kawamura, K. Inada, T. Kozaki, S. Sato, H. Ohashi, T. Ohnuki, T. Banba, J. Nucl. Sci. Technol. 38 (2001) 1141]. In view of the unstable nature of iron(II) chemical species, this study attempted to determine the potential contaminant iron chemical species in the sample. Nondestructive elemental analysis revealed that a small amount of chloride ions remained dispersed throughout the clay particles. The chloride ion retention may be due to the adsorption of $FeCl^+$ ion pairs in the initial $FeCl_2$ solution and the subsequent containment of the Cl^- ions that are dissociated from the $FeCl^+$ ion pairs during excess salt removal treatment. Two explanations are advanced for the second process: the slow release of the remaining Cl^- ions from the collapsed interlayer of the montmorillonite, and the transformation of a minor fraction of the remaining $FeCl^+$ ion pairs to iron(III) hydroxide chloride complexes having low solubility.

Keywords: Montmorillonite; Iron; Chloride; Corrosion product; High-level radioactive waste

1. Introduction

Montmorillonite is a layered clay mineral with high cation exchange and swelling abilities [1]. This clay adsorbs cations (called interlayer cations or exchangeable cations) on the outer and the interlayer surfaces of the layer structure to balance the permanent negative charge arising from the isomorphous substitution, the replacement of a fraction of the matrix silicon, or aluminum ions by lower valence cations. Water molecules penetrate the interlayer spaces and hydrate the interlayer cations, giving rise to swelling and plasticization. Because of these unique characteristics, montmorillonite and bentonite, the latter being an impure clay consisting mainly of montmorillonite, are valuable materials used in applications such as foundry mold materials, sealants, drilling muds, adhesives, cosmetics, and medicines.

This paper deals with homoionic Fe^{2+}- montmorillonite, which is an ideal transformation product in the bentonite used in the geological disposal sites of high-level radioactive waste (HLW) generated through the operation of nuclear power plants. For geological disposal of HLW, bentonite and carbon steel are the candidate materials of the buffer material and overpack, respectively [2–4]. The buffer material is positioned between the bedrock and the overpack encapsulating the HLW. If the carbon steel corrodes, corrosion products will diffuse into the bentonite [5–8]. Leaching of radionuclides from the HLW and their migration within the bentonite would therefore begin after a considerable fraction of the bentonite adsorbed the

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corrosion products. Under reducing geological conditions, the most probable corrosion products would be Fe^{2+} ions. Montmorillonite would be the host mineral of bentonite for the adsorption of Fe^{2+} ions due to its high content in the bentonite and its high cation exchange capacity (CEC). A well-known fact is that Fe^{2+} ions are adsorbed at the cation exchange sites of montmorillonite and related clay minerals (smectites) below a neutral pH [9–11]. Thus, adsorption of Fe^{2+} ions on montmorillonite is supposed to happen in natural process under the environment of the geological disposal sites. The montmorillonite where all the interlayer cations are ideally replaced by Fe^{2+} ions is Fe^{2+}-montmorillonite.

The adsorbed Fe^{2+} ions would be transformed into different chemical and physical forms (including oxidation state) depending upon the surrounding conditions, such as pore water pH, radiation, and heat from the HLW, since iron is sensitive to these factors [12–15]. Thus, Fe^{2+}-montmorillonite could also be a precursor of iron–clay hybrids where sub-nanoparticles of iron (oxy) hydroxides or oxides are formed in the interlayers of the montmorillonite. These iron chemical species, which include Fe^{2+} ions, would alter the migration behavior of radionuclides in bentonite by redox reactions, adsorption, and change in swelling behavior of the montmorillonite. However, few papers have been published on this subject [16–20], and thus the impact of those iron chemical species on the radionuclide migration in the buffer material has yet to be ascertained.

The simplest starting point of investigation to elucidate these impacts may be the characterization of Fe^{2+}-montmorillonite. In the previous study, which was the first paper on the characterization of Fe^{2+}-montmorillonite, preparation of Fe^{2+}-montmorillonite using $FeCl_2$ aqueous solutions under an inert gas atmosphere was attempted [19]. The amount of Fe^{2+} ions contained in the prepared sample was almost equivalent to the CEC of the host montmorillonite. However, the prepared sample may have contained contaminants (iron chemical species other than Fe^{2+} ions), since Fe^{2+} ions are likely to transform into various chemical and physical forms [12–15]. The contaminants could be of concern because they might affect various aspects of characterization of this sample, depending upon their concentration within the sample.

A nondestructive elemental analysis of the Fe^{2+}-montmorillonite sample, which was prepared using $FeCl_2$ aqueous solutions, was performed with the original purpose of investigating the behavior of the adsorbed iron chemical species during their aerial oxidation process. We found that chloride-containing iron chemical species formed as contaminant in the Fe^{2+}-montmorillonite sample. This paper mainly describes the investigation of the potential contaminant iron chemical species by destructive and nondestructive elemental analyses for the Fe^{2+}-montmorillonite sample along with some control materials. This paper also describes the examination of the behavior of chloride ions during aerial oxidation of the adsorbed iron.

2. Experimental method

2.1. Materials

All solutions used in this study were prepared using reagent-grade chemicals and purified water (18.2 MΩ).

Natural montmorillonite obtained from the Tsukinuno Mine in Yamagata Prefecture (Kunipia F, Kunimine Industries Co. Ltd., Japan) was used. Before use, the minor contaminant minerals such as quartz and calcite were removed by water elutriation. A scanning electron microscopy (SEM) image and the powder X-ray diffraction (XRD) patterns of this montmorillonite are shown in Figs. 1 and 2, respectively. The CEC of this montmorillonite was determined by exchange with NH_4^+ to be 113 cmol(+) kg^{-1} (centimoles of positive charge per

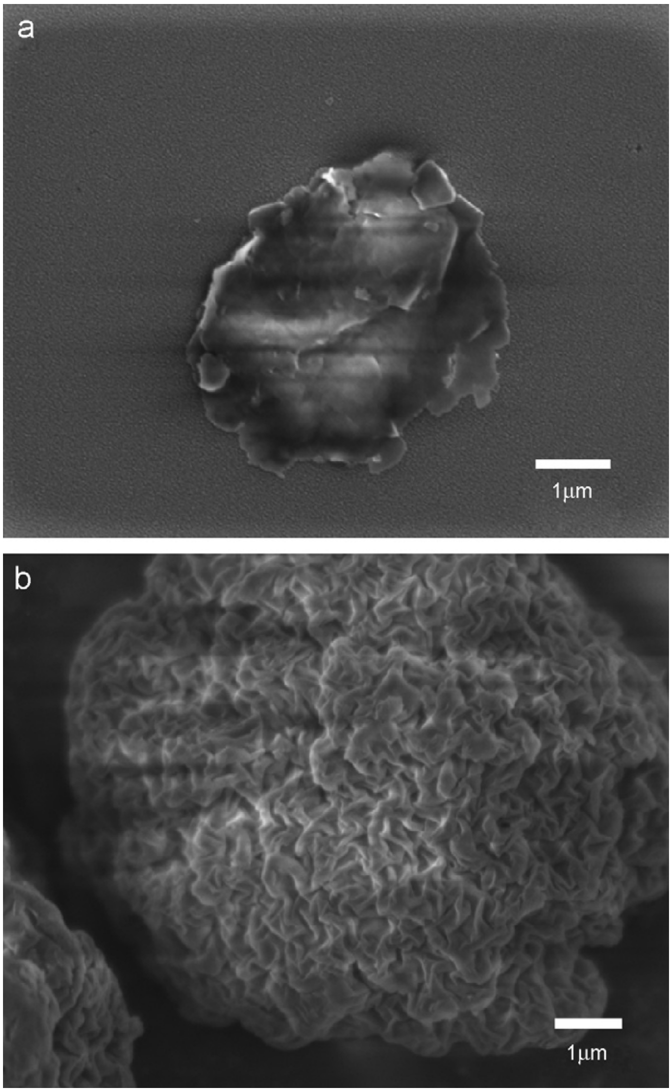

Fig. 1. SEM images of starting clay samples: (a) montmorillonite and (b) saponite.

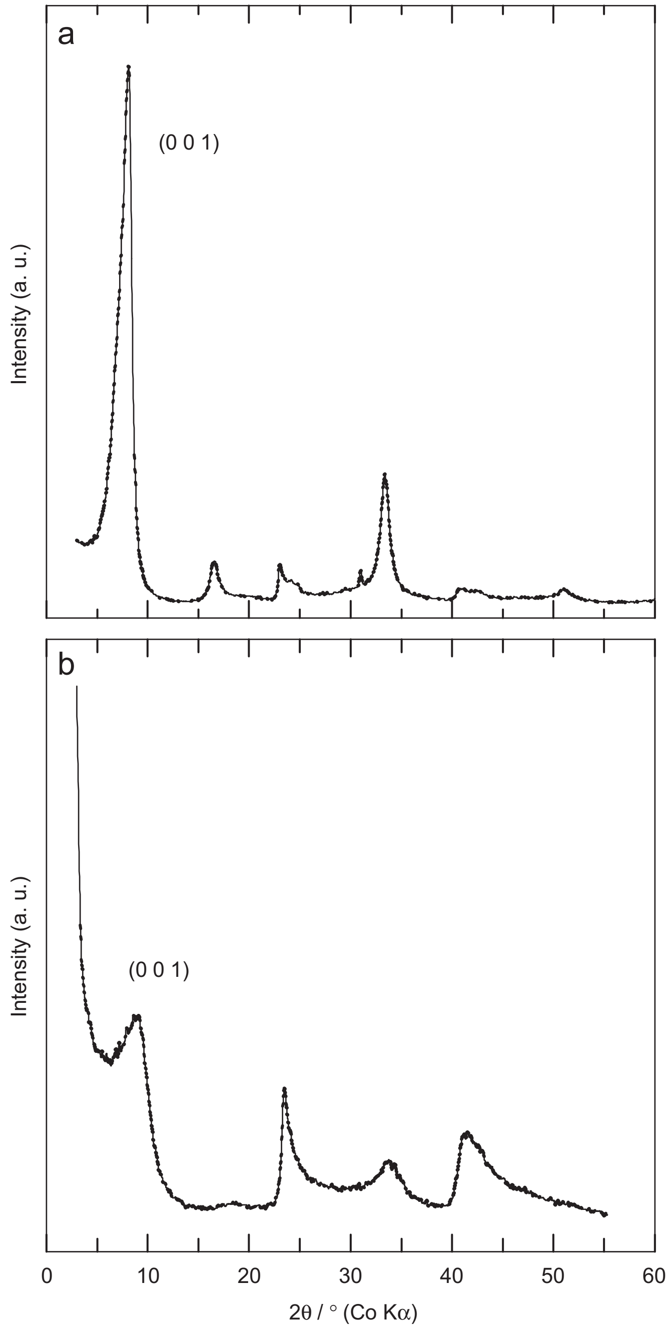

Fig. 2. Powder XRD patterns of starting clay samples: (a) montmorillonite and (b) saponite.

kilogram of solid = meq 100 g^{-1}) [21]. This montmorillonite contains a small amount of iron in the silicate matrix [22].

For comparison, a commercially available synthetic saponite (Sumecton, Kunimine Industries Co. Ltd., Japan) containing no iron in the silicate layers was also examined. Saponite and montmorillonite are similar minerals belonging to the smectite group of clay minerals [1]. Natural montmorillonite and the other natural smectites generally contain iron in the silicate matrix. Thus, analyses of iron may be composed of data from both the adsorbed iron and the iron in the matrix. If Fe^{2+} ion adsorbing clay samples that contain no iron in the silicate matrix can be prepared, these samples will provide various advantages to the characterization of the adsorbed iron. The CEC of the saponite used, measured by exchange with NH_4^+, was 79 cmol(+) kg^{-1}. The SEM image and the XRD pattern of the saponite are also shown in Figs. 1 and 2, respectively. These figures show that the saponite has a smaller crystal size (several hundred nm or less) and lower crystallinity than the montmorillonite.

2.2. Sample preparation

The following procedure to substitute Fe^{2+} ions for the interlayer cations of the montmorillonite and saponite was performed in an inert gas glove box. All solutions used were prepared with purified water deaerated by overnight inert gas bubbling. The montmorillonite and saponite samples were immersed in 0.5 M (mol dm^{-3}) or 0.1 M $FeCl_2$ aqueous solutions containing a small amount of ascorbic acid. The starting ratio of $FeCl_2$ solution, clay, and ascorbic acid was 100 cm^3:1 g:about 0.1 g, respectively. The initial pHs of the 0.5 and 0.1 M $FeCl_2$ solutions containing ascorbic acid were 2.8 and 3.1, respectively. After overnight immersion, the supernatant was removed by decantation. This treatment was repeated two more times. The solid phases were then washed with purified water until the Cl^- ions in the supernatant were undetectable with $AgNO_3$. The "Fe^{2+}-montmorillonite" and "Fe^{2+}-saponite" samples obtained were dried and stored in the glove box at room temperature. Except for the use of the inert gas glove box, the above procedure is commonly used for preparation of homoionic clay samples with cations such as Na^+ or Ca^{2+}.

This study examined four samples, "Fe^{2+}-montmorillonite H", "Fe^{2+}-montmorillonite L", "Fe^{2+}-saponite H", and "Fe^{2+}-saponite L" (Table 1). The "Fe^{2+}-montmorillonite H" sample was the same as that used in the previous study [19], while the other samples were newly prepared for this study. The colors of the samples obtained were similar to those of the original clays (gray or white), which visually indicates that the adsorbed iron was mostly divalent (+II). Mössbauer spectroscopy of the "Fe^{2+}-montmorillonite H" sample showed that the adsorbed iron chemical species were predominantly divalent [19].

Portions of the "Fe^{2+}-montmorillonite H" sample and the "Fe^{2+}-saponite L" sample were aerially oxidized for several months with the original purpose of observing a change in the adsorbed iron chemical species during one of the possible oxidation processes. These aerially oxidized samples were whitish orange (or pale brown). Mössbauer spectroscopy of the aerially oxidized "Fe^{2+}-montmorillonite H" sample indicated that the iron chemical species in this sample were trivalent (+III) [19]. The aerially oxidized montmorillonite sample examined in this study was the same as that used in the previous study [19], while the saponite sample was newly prepared for this study.

Table 1
Fe^{2+}-type samples tested

Sample	Concentration of $FeCl_2$ solutions used (M)	C_{Fe} (cmol kg^{-1})	CEC of host mineral (cmol(+) kg^{-1})
Fe^{2+}-montmorillonite H	0.5	57 [19]	113
Fe^{2+}-montmorillonite L	0.1	47.0	113
Fe^{2+}-saponite H	0.1	45.7	79
Fe^{2+}-saponite L	0.1	40.6	79

C_{Fe} is the content of the adsorbed iron on each sample. The values of C_{Fe}s for the montmorillonite samples were determined from the total amounts of the iron extracted by exchange with 1 M NH_4Cl solution. The values of C_{Fe}s for the saponite samples were determined from the total amounts of the iron extracted with 1 M NH_4Cl and 1 M HCl solutions.

For comparison, homoionic Na^+-montmorillonite was prepared in a similar manner using the elutriated montmorillonite and a 1 M NaCl aqueous solution. The montmorillonite was immersed in a 1 M NaCl solution three times. The solid phase was then washed with purified water until Cl^- ions in the supernatant were undetectable with $AgNO_3$. The Na^+-montmorillonite obtained was dried in air.

2.3. Sequential extraction of iron

To better understand the chemical form of the adsorbed iron chemical species, the adsorbed irons were sequentially extracted from Fe^{2+}-type samples using 1 M NH_4Cl (pH about 4.8) and 1 M HCl aqueous solutions. Prior to the sequential extractions, these solutions were deaerated by overnight inert gas bubbling.

To extract the exchangeable fraction of the adsorbed iron, clay samples were added to the 1 M NH_4Cl solution in centrifuge tubes at room temperature in a liquid–solid ratio of 100 cm^3:1 g. After standing overnight, the liquid phase was collected by centrifugation and then removed to another vessel. The extraction using 1 M NH_4Cl solution was repeated four more times. Then, the extraction using 1 M HCl solution to extract the residual iron by dissolution was performed three times in the same way. The amount of iron extracted in each step was determined by the method described in the analytical methods section.

As a control experiment, the elutriated montmorillonite (the starting material) was sequentially placed in 1 M NH_4Cl and 1 M HCl solutions in the same way, and the amount of iron extracted in each step was determined.

2.4. Extraction of chloride ions

To extract chloride ions from Fe^{2+}-type samples, 1 cm^3 of 95% sulfuric acid and 9 cm^3 of purified water were added to weighed samples (about 0.1 g each) in centrifuge tubes. After standing overnight at room temperature, the liquid phase was collected by centrifugation. The extraction of chloride ions was performed again. The amount of the chloride ions extracted in the liquid phase was determined by ion chromatography after diluting the collected liquid phase with purified water.

For Na^+-montmorillonite, a dilute (0.5 mM) sulfuric acid aqueous solution was used as an extracting solution to avoid dilution of the extracts to be analyzed because the amount of chloride ions in the Na^+-montmorillonite sample was very low. Except this, the extraction of chloride ions from Na^+-montmorillonite was performed in the same method as that for Fe^{2+}-type samples.

2.5. Analytical methods

2.5.1. Analysis of liquid phase

Solution pHs were measured with a pH meter (HM-30S, DKK-TOA Corporation, Tokyo, Japan) together with a combined electrode (GS-5015C, DKK-TOA Corporation, Tokyo, Japan).

The amount of iron extracted in the liquid phase was determined using an inductivity coupled plasma atomic emission spectrometer (Model SPS1200A, Seiko EG&G, Chiba, Japan).

The amount of chloride ions extracted in the liquid phase was determined using an ion chromatograph analyzer (Model IC7000, Yokogawa Electric Corporation, Musashino, Japan) together with an anion exchange column (ICS-A23, Yokogawa Electric Corporation, Musashino, Japan).

2.5.2. Analysis of solid phase

2.5.2.1. XRD. Powder XRD patterns were obtained at ambient temperatures by the use of a Rigaku diffractometer (Geigerflex, Rigaku Corporation, Tokyo, Japan) with a graphite monochromator. Monochromatic Co$K\alpha$ radiation ($\lambda\alpha_1 = 0.178897$ nm) was used for the measurement. The X-ray tube was operated at 40 kV and 20 mA.

2.5.2.2. SEM. SEM micrographs were taken at 3 kV using a field emission scanning electron microscope (FE-SEM; Model JSM-6700F, JEOL Co., Ltd., Tokyo, Japan) equipped with an energy dispersive spectrometer (EDS). The EDS analyses were performed at an operating voltage of 15 kV and a working distance of 15 mm.

2.5.2.3. Micro-PIXE. To analyze chloride ions in solid phases nondestructively, micro particle induced X-ray emission (micro-PIXE) analyses were carried out. To accomplish the micro-PIXE analysis of the Fe^{2+}-type samples, portions of the samples were gently ground in an agate mortar with a small amount of purified water, spread on graphite plates, and dried at room temperature. The sample-spread graphite plate was then attached to an acrylic holder having a 1-mmØ hole at the center. These steps were performed in the inert gas glove box. To transfer the sample-attached holders to the micro-PIXE analyzing system, the sample-attached holders were sealed in low oxygen permeability plastic bags together with oxygen absorbents. The sample-attached holders were removed from the bags just before the analysis, mounted on the system, and analyzed in a vacuum.

For micro-PIXE analysis of the other samples, portions of the samples were similarly spread on graphite plates with purified water, and dried at 333 K in air. To prevent the possible loss of the low-adhesive samples (such as the aerially oxidized clay samples) from graphite plates during transfer, mounting, and measurement, a Mylar membrane was inserted between the graphite plate and the acrylic holder.

Elements in those samples were nondestructively analyzed by the micro-PIXE analyzing system developed in the TIARA facility, JAEA. The spatial resolution of the micro-PIXE analyzing system using a proton beam with an energy of 2.6 MeV has a diameter less than 1 μm. The characteristic $K\alpha$ X-rays of Si (1.74 keV), Fe (6.40 keV), and Cl (2.62 keV) were measured using a high purity Ge detector with a 100-mm^2 crystal (ORTEC IGLET-X, Oak Ridge, TN, USA). This Ge detector is inefficient for X-rays with an energy less than about 2 keV and is unable to detect the $K\alpha$ X-rays of Na (1.04 keV) and Mg (1.25 keV). The details of this arrangement and performance of the measurement devices have been described elsewhere [23,24].

No software or measurement instrument for quantitative evaluation of elements has been developed for the micro-PIXE analyzing system in the TIARA facility. However, the following two factors are known to linearly correlate: (a) the concentration of the adsorbed element in the mineral and (b) the ratio of the net peak area of the characteristic X-ray from the adsorbed element to that from the matrix cation of the mineral [25]. This relation holds when the concentration of the matrix cations before and after the adsorption is regarded as constant. We used this relation to evaluate the results of this study. That is, the ratios of the net peak area of $K\alpha$ X-rays of the adsorbed elements (Fe and Cl) to that of $K\alpha$ X-rays of the matrix silicon (Fe/Si, and Cl/Si) were compared before and after the aerial oxidation of the Fe^{2+}-type samples.

3. Results

3.1. Fe^{2+}-type samples

3.1.1. Sequential extraction of iron

Table 2 summarizes the amount of iron extracted from three clay samples in each sequential extraction step. The amount of iron extracted with the 1 M NH_4Cl solution from the elutriated montmorillonite was negligible, but a small amount of iron was extracted with the 1 M HCl solution. The latter iron probably had originated from the iron in the silicate matrices because portions of these matrices are dissolvable under acidic conditions [26,27].

The extraction with 1 M NH_4Cl solution from the "Fe^{2+}-montmorillonite L" sample was completed in the fourth extraction step because no iron was extracted in the fifth extraction step. The amount of iron extracted with the 1 M HCl solution from this sample (0.5 cmol kg^{-1} ($=$ mmol 100 g^{-1})) was less than that of the elutriated montmorillonite (1.3 cmol kg^{-1}), indicating that the former is not adsorbed iron but is the iron in the silicate matrices. The decrease of the iron extractable with the 1 M HCl solution (about 0.8 cmol kg^{-1}) would be due to dissolution of a fraction of the iron in the silicate matrices during the triple contact of the elutriated montmorillonite with the acidic 0.1 M $FeCl_2$ solution used for the sample preparation. To confirm this hypothesis, the elutriated montmorillonite was immersed three times in 1 mM HCl solution having a pH of 3.0, which was similar to that of the 0.1 M $FeCl_2$ solution used for the preparation of the "Fe^{2+}-montmorillonite L" sample. The iron extracted by this treatment, about 0.5 cmol kg^{-1}, was comparable to the above-mentioned amount of iron (about 0.8 cmol kg^{-1}). Therefore, the sum of the iron extracted with the 1 M NH_4Cl solution is regarded as the content of the adsorbed iron (C_{Fe}) in the "Fe^{2+}-montmorillonite L" sample.

The synthetic saponite does not contain iron in the silicate matrix, so the C_{Fe} of the "Fe^{2+}-saponite L" sample is the sum of the iron extracted with the 1 M NH_4Cl and

Table 2
Amounts of the iron sequentially extracted from clay samples with 1 M NH_4Cl and 1 M HCl aqueous solutions

Sample	Iron extracted with1 M NH_4Cl (cmol kg^{-1})						Iron extracted with 1 M HCl (cmol kg^{-1})				Total
	Step 1	Step 2	Step 3	Step 4	Step 5	Sub-total	Step 6	Step 7	Step 8	Subtotal	
Fe^{2+}-montmorillonite[a]	45.7	0.9	0.2	0.1	0.0	47.0	0.3	0.2	0.1	0.5	47.5
Fe^{2+}-saponite[a]	32.3	1.6	0.7	0.5	0.3	35.3	3.5	1.6	0.2	5.3	40.6
Montmorillonite[b]	0.0	0.0	0.0	0.0	0.0	0.0	0.9	0.3	0.1	1.3	1.3

[a] These samples were prepared using 0.1 M $FeCl_2$ solution.

[b] Water-elutriated montmorillonite used for the preparation of "Fe^{2+}-montmorillonite".

1 M HCl solutions. Of all sources of the extracted iron, about 10% was not extracted with 1 M NH_4Cl solution but was extracted with the 1 M HCl solution, indicating that the saponite sample contained iron chemical species that were not ion exchangeable.

The C_{Fe} values of the "Fe^{2+}-montmorillonite H" and the "Fe^{2+}-saponite H" samples were defined similarly to those of the "Fe^{2+}-montmorillonite L" and the "Fe^{2+}-saponite L" samples, respectively. When the adsorbed iron is assumed to be in the form of divalent cations (Fe^{2+}), the C_{Fe} values of the "Fe^{2+}-montmorillonite H" sample and the "Fe^{2+}-montmorillonite L" sample (Table 1) correspond to about 101% and 83% of the CEC of the host montmorillonite, respectively. These results suggest that the cation exchange sites of the "Fe^{2+}-montmorillonite H" sample are saturated with Fe^{2+} ions, while those of the "Fe^{2+}-montmorillonite L" sample are undersaturated. The C_{Fe} values of the "Fe^{2+}-saponite H" sample and "Fe^{2+}-saponite L" sample (Table 1) correspond to 116% and 103% of the CEC of the host saponite, respectively.

3.1.2. Chloride ions in solid phases

Fig. 3 is a plot of the energy dispersive spectra of the micro-PIXE analysis of the "Fe^{2+}-montmorillonite H" sample and the "Fe^{2+}-saponite H" sample. Although the Cl was supposed to have been removed by washing with purified water, the weak but clear peaks of $K\alpha$ X-rays of Cl are seen in this figure. For reference, the Cl in the "Fe^{2+}-montmorillonite H" sample was barely detected by the FE-SEM-EDS analysis (Fig. 4). The weak $K\alpha$ X-rays of K and Ca in the Fe^{2+}-type samples are from the original interlayer cations of the host clays, which indicate that a very minor fraction of the interlayer cations were not replaced by iron. In the case of Na^+-montmorillonite (Fig. 3c), the $K\alpha$ X-ray peaks of Cl were not detected, suggesting that chloride ions were sufficiently removed from the sample by the excess salt removal procedure. However, weak $K\alpha$ X-ray peaks of K and Ca were detected, indicating that a part of the original interlayer cations of the host montmorillonite were not exchanged with Na^+ ions.

Fig. 5 shows two-dimensional elemental mapping of Si, Fe, and Cl of the "Fe^{2+}-montmorillonite H" and the "Fe^{2+}-saponite H" samples. In both samples, the regions where Fe and Cl were observed agree with those where Si (clays) were observed, which indicates that Fe and Cl are distributed throughout the clay particles. Compared to the regions where Si and Fe were observed, the boundary where Cl was observed was not clear because the net count of Cl is low and the background count is high (Fig. 3).

The amounts of chloride ions extracted with acid solution from the Na^+-montmorillonite, the "Fe^{2+}-montmorillonite H", and the "Fe^{2+}-saponite H" samples were about 1.9×10^{-2}, 2.1, and 25 cmol kg^{-1}, respectively. These quantities correspond to 1.7×10^{-2}, 1.9, and 32% of the respective CEC values of the host clays.

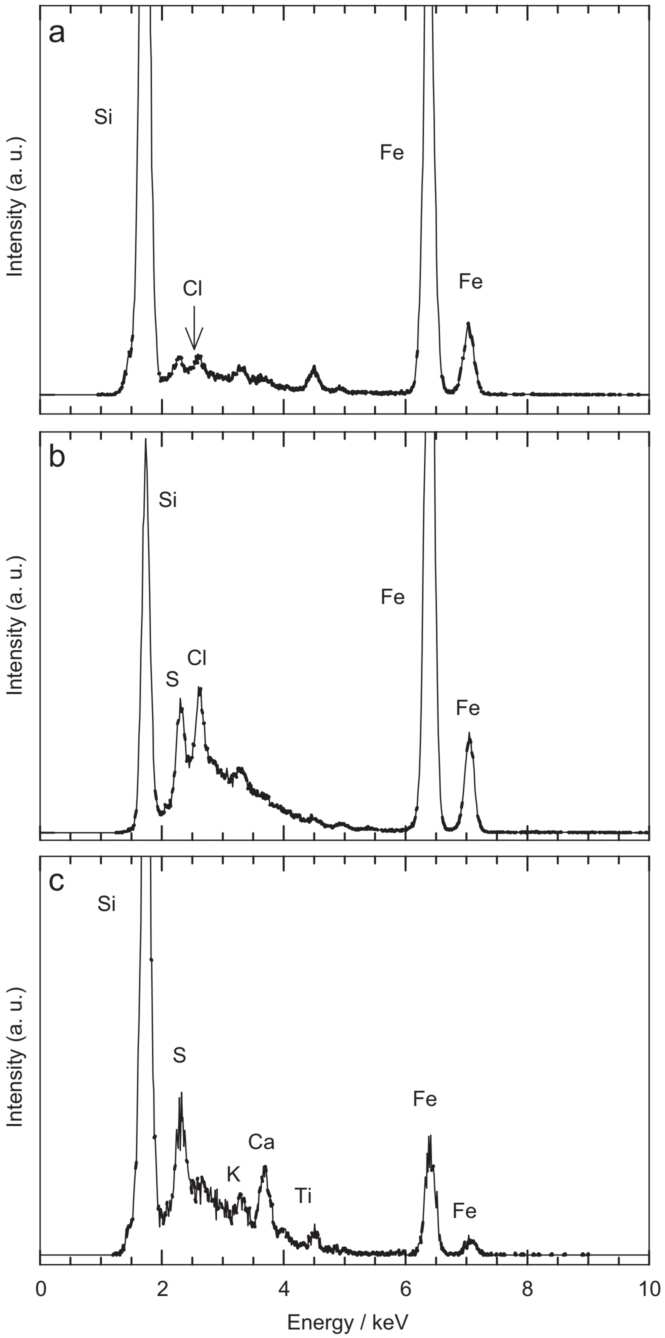

Fig. 3. Energy dispersive spectra measured by micro-PIXE: (a) the "Fe^{2+}-montmorillonite H" sample; (b) the "Fe^{2+}-saponite H" sample; (c) the Na^+-montmorillonite sample. The region of lower intensity was enlarged. The characteristic X-ray peak of sulfur in the spectrum was attributed to impure substances in the graphite plate. The $K\alpha$ X-ray peak of Fe in the Na^+-montmorillonite sample is attributed to the iron in the silicate matrix.

3.2. Aerially oxidized samples

Fig. 6a is a two-dimensional elemental mapping of Si, Fe, and Cl in the aerially oxidized sample prepared from the "Fe^{2+}-montmorillonite H" sample. The region where Fe was observed well matches the region where Si (clay) was distributed. This is consistent with the analysis of other clay particles (figure not shown). $K\alpha$ X-rays of Cl were barely detectable in the clay particles as shown in Figs. 6a and 7a, but Cl was found in small aggregates located apart from the clay particles. The EDS of two Cl bearing aggregates are shown in Figs. 8a′-1 and 8a′-2. The former contained Ca as cation, while few cations were detected in the latter.

Fig. 6b shows two-dimensional elemental mapping of Si, Fe, and Cl in the aerially oxidized sample prepared from the "Fe^{2+}-saponite H" sample. The region where Fe was observed mostly agrees with the region where Si (clay) was distributed. However, as indicated by the b-1 white arrow, a dense distribution of Fe located apart from the clay particles is observed. This suggests that part of the adsorbed iron was dissociated from the host clay during the aerial oxidation. However, this may be a rare case because no such Fe bearing aggregate was observed in other areas analyzed (figures not shown). Little Cl was detected in the clay particles but was seen as a large aggregate indicated by the b-2 white arrow. The energy dispersive spectrum of this Cl bearing aggregate measured by micro-PIXE (Fig. 8 b-2) shows that this aggregate contained K, Ca, and Fe as cations. The FE-SEM-EDS analysis for a different Cl bearing aggregate revealed that this Cl bearing aggregate contained Na and Mg (Fig. 9).

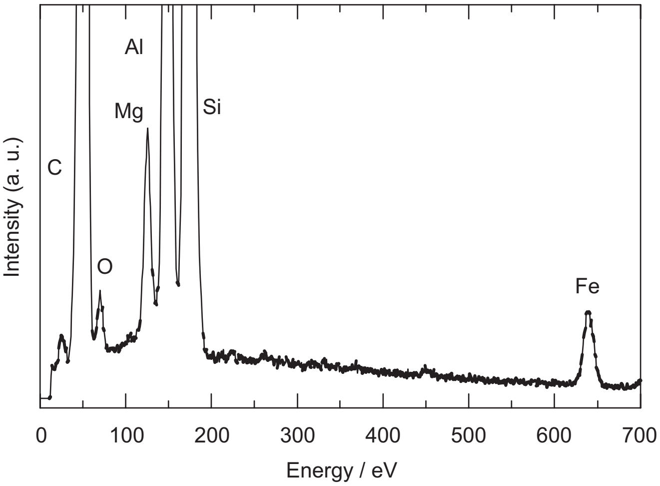

Fig. 4. Energy dispersive spectrum of the "Fe^{2+}-montmorillonite H" sample measured by FE-SEM-EDS analysis.

4. Discussion

4.1. Fe^{2+}-type samples

Aqueous solutions of chloride salts are generally employed in the preparation of homoionic cation-type clay samples because the end point of sample washing for the removal of the excess salts is easily determined using an aqueous solution of $AgNO_3$. The abundant permanent negative charge due to the isomorphous substitution in montmorillonite excludes anions. Therefore, removal of anions (Cl^-) from montmorillonite by washing has been supposed to be readily achievable. Actually, the Na^+-montmorillonite sample prepared by a conventional method using a NaCl aqueous solution was practically free from chloride ions. However, our results showed that some chloride ions remained in the Fe^{2+}-type samples, even though no AgCl precipitation was observed after the exposure of the washings to the $AgNO_3$ solution.

To explain the presence of the remaining chloride ions, the adsorption process of iron in $FeCl_2$ solutions will first be discussed. Noteworthy is the fact that the C_{Fe} of each sample prepared was comparable to the CEC of the

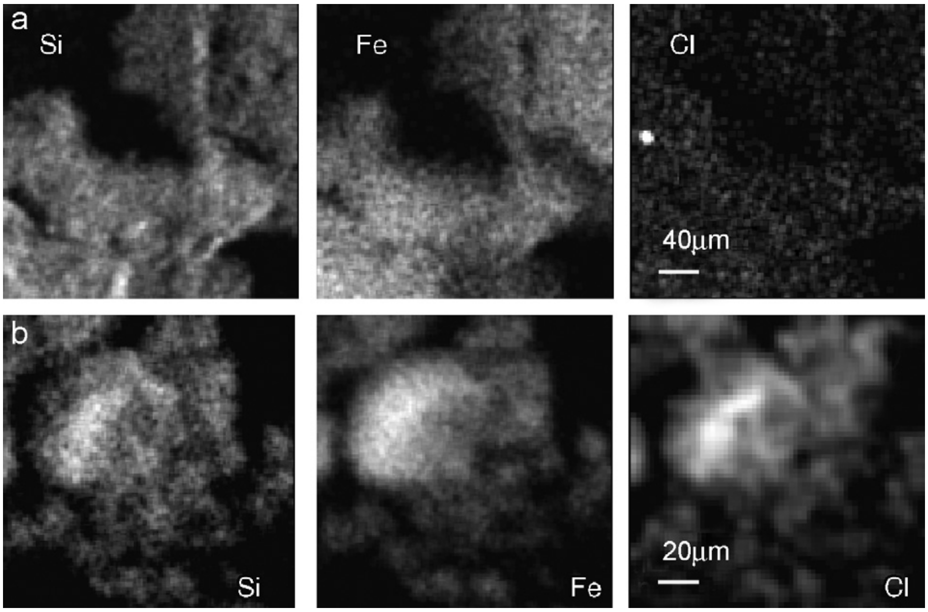

Fig. 5. Two-dimensional elemental mappings of Si, Fe, and Cl for (a) the "Fe^{2+}-montmorillonite H" sample and (b) the "Fe^{2+}-saponite H" sample. All three elemental mappings for each sample show the same region on a graphite plate. A brighter region shows a higher concentration of a given element.

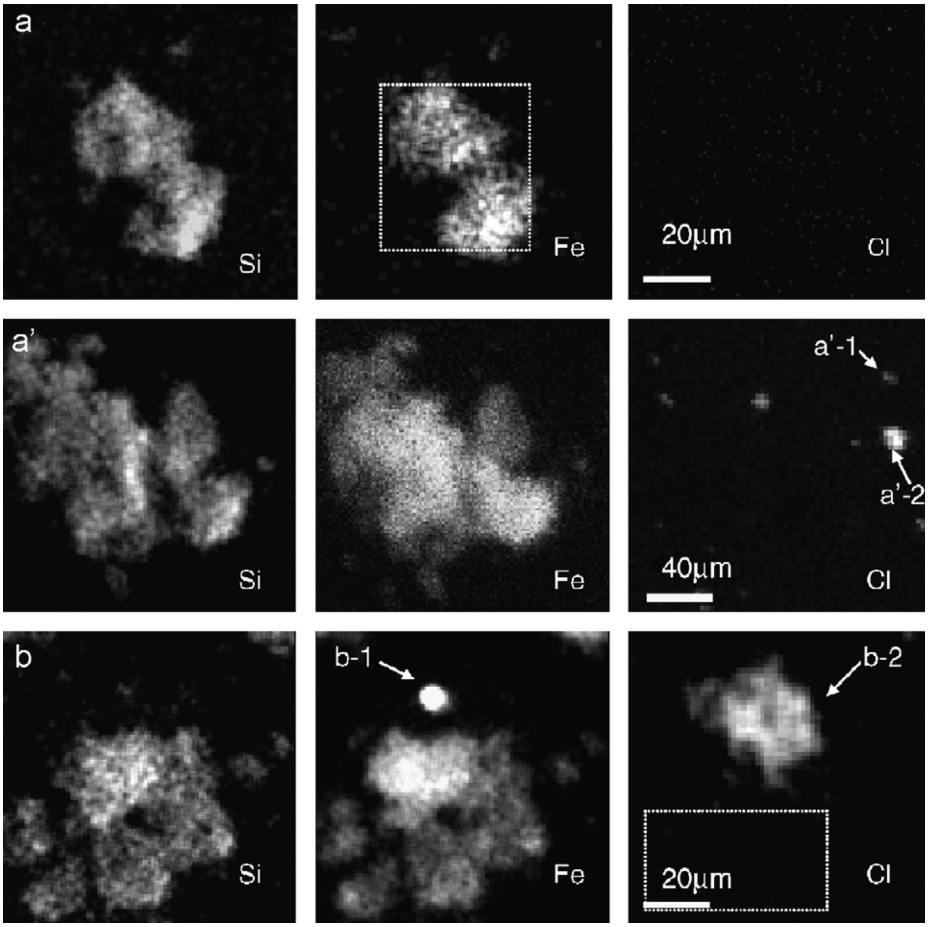

Fig. 6. Two-dimensional elemental mappings of Si, Fe, and Cl for (a, a′) the aerially oxidized “Fe^{2+}-montmorillonite H” sample, and (b) the aerially oxidized “Fe^{2+}-saponite H” sample. All three elemental mappings for each sample show the same region on a graphite plate. A brighter region shows a higher concentration of a given element. The energy dispersive spectra for the white-dotted-line enclosed rectangular areas are shown in Fig. 7.

corresponding clay. This fact suggests that the adsorption of iron on clay depends on the CEC, i.e., adsorption of cationic species of iron at cation exchange sites of the clays. Precipitation of iron hydroxides (e.g., FeOHCl), which is independent of CEC, would therefore be ruled out. A recent paper showed the possible adsorption of Fe^{2+} ions and $FeCl^{+}$ ion pairs at cation exchange sites of montmorillonite in acidic solutions containing high concentrations of $FeCl_2$ [28]. Table 3 shows estimated fractions of these iron chemical species in $FeCl_2$ aqueous solutions using thermodynamic modeling software, the Geochemist's Workbench® release 4.0.2 (The University of Illinois, IL, USA) [29,30], with the thermodynamic database, thermo minteq gwb4 (Kungliga Tekniska Högskolan, Stockholm, Sweden). The thermodynamic calculation suggests the presence of Fe^{2+} ions and $FeCl^{+}$ ion pairs as the predominant iron chemical species in high-concentration $FeCl_2$ solutions under reducing and acidic conditions. The presence of the other iron chemical species was not expected. Hydroxylation of Fe^{2+} ions does not occur below a neutral pH [12]. Therefore, the origin of the chloride ions remained in the Fe^{2+}-type samples would be the $FeCl^{+}$ ion pairs adsorbed in a high-concentration $FeCl_2$ solution.

A result of the thermodynamic calculation also suggests that Fe^{2+} ions are practically the sole iron chemical species in dilute $FeCl_2$ solutions under reducing conditions (Table 3). The association of $FeCl^{+}$ ion pairs is very unstable [31]. The once-adsorbed $FeCl^{+}$ ion pairs are believed to dissociate to Fe^{2+} and Cl^{-} ions during the excess salt removal (washing) process. Thus, the Cl^{-} ions are removed from the clays. This is, however, inconsistent with the experimental results that indicated Cl^{-} ions remained in the samples.

Two explanations have been advanced for the failure to remove chloride ions. One is that the release of chloride ions from the interlayers of the Fe^{2+}-type samples could be retarded due to the reduction of the expandability of the interlayer spacing caused by the adsorption of Fe^{2+} ions. The swelling of the smectite saturated with multivalent cations is very limited. Thus, these smectites flocculate even in water [32,33]. On the other hand, Na^{+}-smectite shows infinite swelling in water due to the high hydration energy of Na^{+}, which may allow ready departure of chloride ions

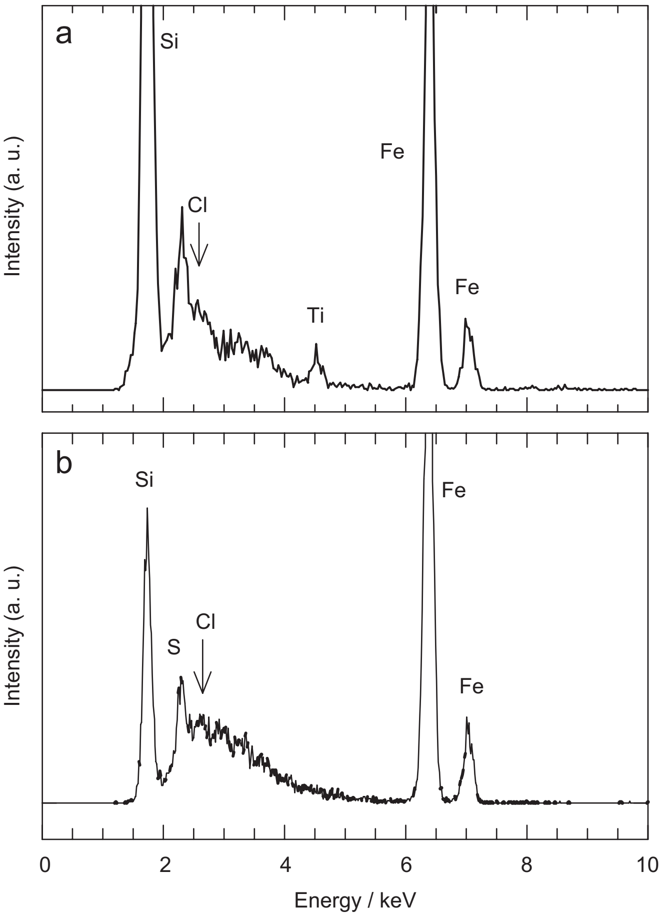

Fig. 7. Energy dispersive spectra of (a) the aerially oxidized "Fe^{2+}-montmorillonite H" sample and (b) the aerially oxidized "Fe^{2+}-saponite H" sample. The spectra are for the white-dotted-line enclosed rectangular area shown in Fig. 6. The characteristic X-ray peak of titanium results from the titanium contained in the silicate matrix of the montmorillonite. The characteristic X-ray peak of sulfur in the spectrum was attributed to the impure substances in the graphite plate.

from the interlayers. Actually, the prepared Na^+-montmorillonite was practically chloride ion free.

The other explanation for the failure of chloride ion removal is the change of the chemical form of the adsorbed iron during the excess salt removal process. This is very likely for the saponite case described below. As shown in Table 2, more than 10% of the iron on the "Fe^{2+}-saponite L" sample was not exchangeable, while almost all the iron on the "Fe^{2+}-montmorillonite L" sample was exchangeable. This difference would primarily result from the differences in the pHs of the clay slurries in the rinse water. When the starting materials of montmorillonite and saponite were suspended in purified water at a liquid–solid ratio of 100 cm^3:1 g, the pHs of the clay slurries were 5.3 and 10.1, respectively. At high pHs, as is the case for saponite, a fraction of iron(II) transforms into iron(II) hydroxides [12]. Also, chloride ions are able to replace a fraction of hydroxide ions of iron hydroxides [34–36]. Metal hydroxides tend to aggregate to form polynuclear complexes by hydroxo bridging with or without subsequent oxo-bridging [12,14,37]. Rapid dissociation of chloride ions from once-formed hydroxide complexes would not be expected except in acid solutions due to the generally low solubility of metal hydroxide complexes at a neutral or

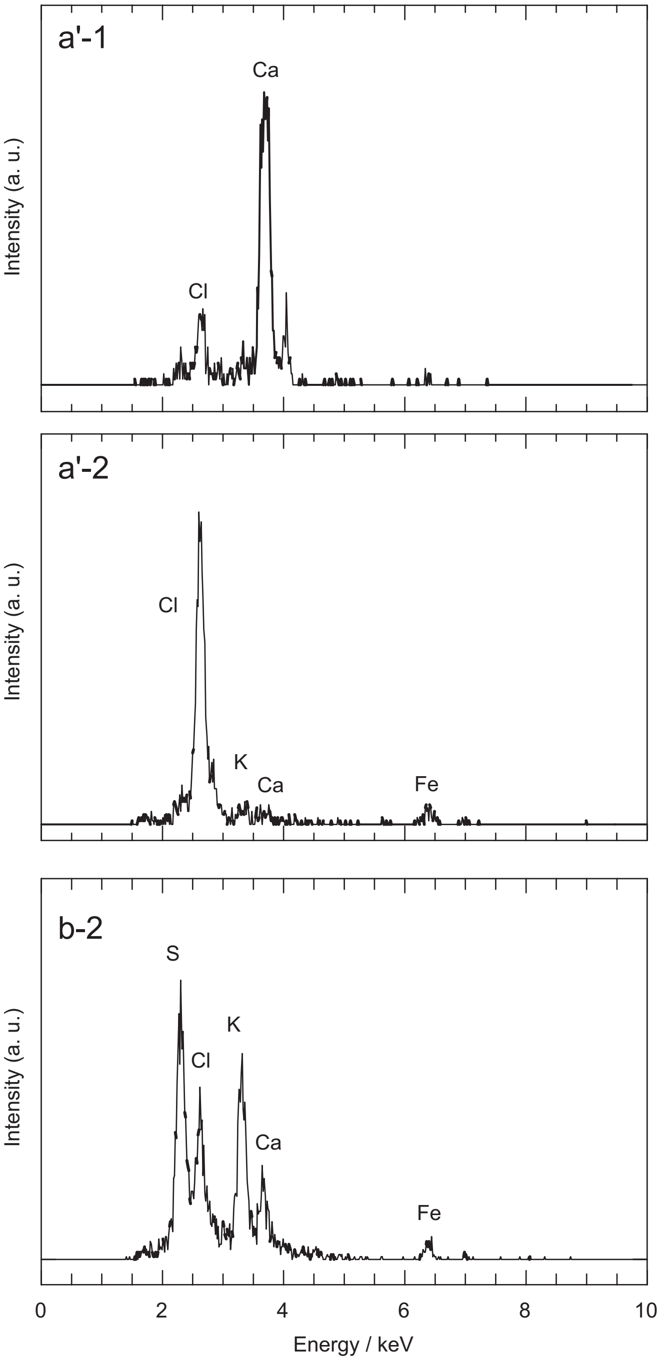

Fig. 8. Energy dispersive spectra of the Cl-bearing aggregates (a′-1, a′-2) located apart from the aerially oxidized "Fe^{2+}-montmorillonite H" sample, and that of the Cl-bearing aggregate (b-2) located apart from the aerially oxidized "Fe^{2+}-saponite H" sample. The spectra, a′-1 and a′-2, are obtained from the corresponding Cl-bearing aggregates (a′-1 and a′-2) indicated with white arrows in Fig. 6a′. The spectrum, b-2, is obtained from the corresponding Cl-bearing aggregate (b-2) in Fig. 6b, where the Fe-bearing aggregate (b-1) and the clay particles (Si) are not included. The characteristic X-ray peak of sulfur in the spectrum was attributed to the impure substances in the graphite plate.

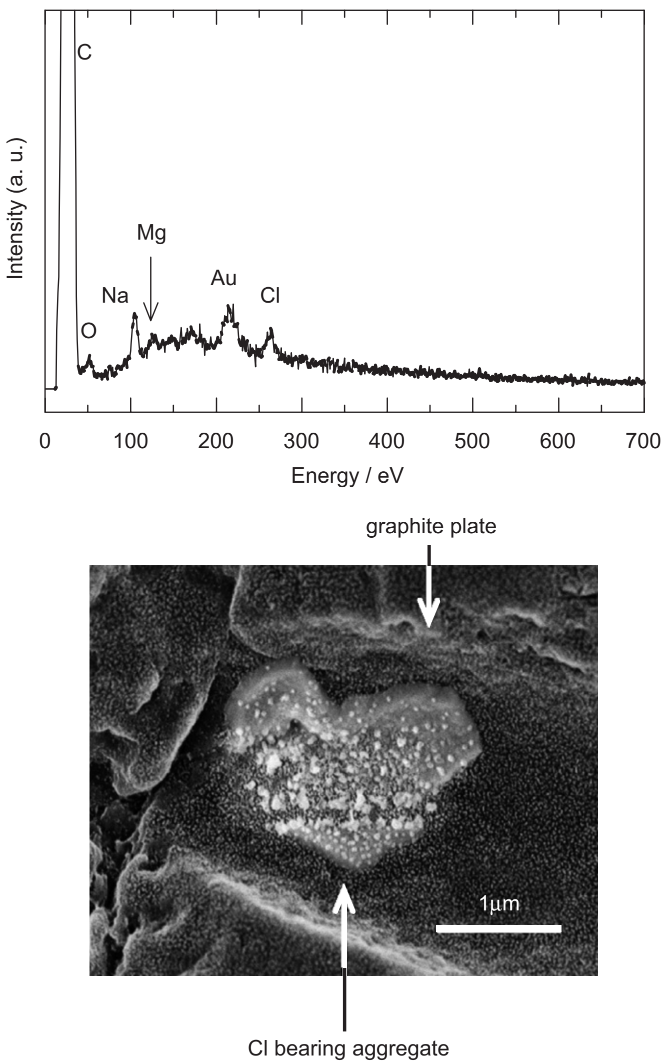

Fig. 9. SEM image and energy dispersive spectrum of a Cl-bearing aggregate in the aerially oxidized “Fe^{2+}-saponite H” sample. Prior to the analysis, the sample was coated with gold. This Cl-bearing aggregate was not the same one as that shown in Fig. 6b.

Table 3
Thermodynamic estimation of iron chemical species in $FeCl_2$ aqueous solutions

Concentration of $FeCl_2$ solution (M)	pH[a]	Fraction of iron chemical species (%)		
		Fe^{2+}	$FeCl^+$	$FeOH^+$
0.5	3.3	79.98	20.02	0.00
0.1	4.7	79.96	20.04	0.00
0.01	5.3	99.59	0.40	0.01
0.001	5.8	99.92	0.05	0.02

[a] Measured value of each solution.

higher pH [15,38]. At the pH of the montmorillonite slurry in purified water, no iron(II) hydroxides are formed [12]. However, it is possible that a minor fraction of the remaining $FeCl^+$ ion pairs on the montmorillonite and the saponite samples were transformed to iron(III) hydroxide chloride complexes since oxidation of iron(II) species in more deaerated aqueous solutions was reported previously [34,39], and Fe^{3+} ions are readily hydroxylated even in acid solutions [12].

For the preparation of homoionic Fe^{2+}-montmorillonite, removal of excess salt would be the principal process. Despite the fact that the “Fe^{2+}-montmorillonite H” sample contained a small amount of the undesirable iron chemical species, no influence of the contaminant iron chemical species on the swelling properties or Mössbauer spectroscopic characteristics of the sample was observed [19]. This indicates that the “Fe^{2+}-montmorillonite H” sample can be substantially used as a homoionic Fe^{2+}-type sample. On the other hand, the method employed in this study to prepare homoionic “Fe^{2+}-saponite” samples using the synthetic saponite failed because these samples contained many contaminant iron chemical species, which were thought to be hydroxides.

4.2. Aerially oxidized samples

As shown in Figs. 5a, 6a, and 6a′, both the iron of the “Fe^{2+}-montmorillonite H” sample and that of its aerially oxidized sample were distributed with the host montmorillonite. The ratio of the net peak area of the Fe$K\alpha$ X-ray to that of the Si$K\alpha$ X-ray (Fe/Si) of the “Fe^{2+}-montmorillonite H” sample was 0.78 ± 0.12, and that of its aerially oxidized sample where the Cl bearing aggregates were not included was 0.78 ± 0.16. These results indicate that most of the iron adsorbed on the montmorillonite remained on the clay after the iron was oxidized in air to become trivalent. The ratio of the net peak count of the Cl$K\alpha$ X-ray to that of the Si$K\alpha$ X-ray (Cl/Si) of the “Fe^{2+}-montmorillonite H” sample was $(1.5 \pm 0.3) \times 10^{-2}$, while that of its aerially oxidized sample was about 5×10^{-3} or less (this value was not determined precisely since the Cl peak in this sample (Fig. 7a) was almost indistinguishable from the background). This result indicates that the chloride ion content decreased to one-third or less during the aerial oxidation. Similarly, in the case of the “Fe^{2+}-saponite H” sample, the Cl/Si ratio decreased from $(1.9 \pm 0.5) \times 10^{-1}$ of the Fe^{2+}-type sample to $(1.7 \pm 0.3) \times 10^{-2}$ during the aerial oxidation. These results show that most chloride ions that remained on the Fe^{2+}-type samples were dissociated from the adsorbed iron during the aerial oxidation.

In the Cl-bearing aggregates located apart from clay particles, some varieties of cations were detected (Figs. 8 and 9). Except Fe, these cations are the interlayer cations that were contained in the original montmorillonite and saponite but remained unexchanged by the contact with the $FeCl_2$ solution. The Cl bearing aggregates would therefore mainly be the salts of the interlayer cations that remained unexchanged with cationic irons. It is supposed that these unexchanged original interlayer cations were replaced by the hydronium (oxonium) ions generated in the interlayers through oxidation and the subsequent hydrolysis of the adsorbed divalent iron [19], since hydronium ions have high replacing power (ability to replace interlayer cations). Water addition and the subsequent heat treatment for preparation of the samples for micro-PIXE analysis are thought to have separated the component ions of the salts from the host clays. There are two possibilities for the origin of the faintly detected iron (a′-1 and a′-2 in Fig. 8): the iron adsorbed on the montmorillonite or the iron in the silicate matrix of the montmorillonite. Both are possible. The generated hydronium ions can replace the previously adsorbed iron and separate it from the host clay. These hydronium ions also can dissolve portions of the silicate matrix [26,27], which would release iron in the matrix.

5. Conclusions

This paper describes the investigation of contaminant iron chemical species potentially formed on a homoionic Fe^{2+}-type montmorillonite (Fe^{2+}-montmorillontie) sample prepared using $FeCl_2$ solutions. The traditional preparation method was reasoned to yield a small quantity of the iron chemical species containing chloride ions as a contaminant, which could be $FeCl^+$ or, less likely, iron(III) hydroxide chloride complexes. Though the content of the contaminant was minor and its effect on the characterization of the sample could be ignored, the excess salt removal would be the crucial process for the success of the sample preparation. Preparation of Fe^{2+}-saponite using a commercial synthetic saponite was suggested to be barely attainable because of the high alkalinity of the host clay, which yields much iron (II or III) hydroxides.

We also investigated the behavior of the remaining chloride ions before and after the aerial oxidation of the prepared "Fe^{2+}-montmorillontie" and the "Fe^{2+}-saponite" samples. Most remaining chloride ions were found to be separated from the iron(III) compounds formed by the aerial oxidation.

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