

Study of Iodide Adsorption on Organobentonite using X-ray Absorption Spectroscopy

X-선 흡수분광기를 이용한 유기벤토나이트의 요오드 흡착연구

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ABSTRACT: The adsorption of iodide on untreated bentonite and bentonites modified with organic cation (i.e., hexadecylpyridinium chloride monohydrate (HDP⁺)) was investigated, and the organobentonites were characterized using uptake measurements, μ -XRD, and electrophoretic mobilities measurement. Uptake measurements indicate that bentonite has a high affinity for HDP⁺. Our μ -XRD study indicates that organobentonites significantly expanded in basal spacing and organic cations were substantially intercalated into the interlayer spaces of bentonite. The electrophoretic mobility indicates that organobentonite that is modified with organic cations in excess of the CEC of bentonite is completely different from untreated bentonite in the surface charge distribution. We found significant differences in adsorption capacities of iodide depending on the bentonite properties as follows: iodide adsorption capacities were 439 mmol/kg for the bentonite modified with HDP⁺ at an equivalent amount corresponding to 200% of the CEC of bentonite whereas no adsorption of iodide was observed for the untreated bentonite. The molecular environments of iodine adsorbed on organobentonites were further studied using I K-edge and L_{III} -edge x-ray absorption spectroscopy (XAS). The X-ray absorption near-edge structure (XANES) of iodine spectra from organobentonites was similar to that of KI reference solution. Linear combination fitting of EXAFS data suggests the fraction of iodine reacted with the organic compound increased with increasing loading of the organic compound on organobentonites. In this study, we observed significant differences in the adsorption environments of iodide depending on the modified property of bentonite and suggest that an organobentonite has potential as reactive barrier material around a nuclear waste repository containing anionic radioactive iodide.

Key words: hexadecylpyridinium chloride monohydrate (HDP), organobentonite, iodine, adsorption, XAS

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요약 : 유기양이온(hexadecylpyridinium chloride monohydrate (HDP⁺))으로 개질시킨 유기벤토나이트의 특성을 유기탄소함량 측정, 마이크로-X 선회절 분석, 전기영동 이동성 측정을 이용하여 관찰하고, 무처리 벤토나이트와 유기벤토나이트의 요오드에 대한 흡착성을 비교 조사하였다. 벤토나이트는 유기양이온인 HDP⁺에 대해서 높은 친화력을 보여주었다. 마이크로-X선 회절 분석 결과에 의하면 유기벤토나이트는 저면 간격에 있어서 현저하게 팽창을 하였고, 이는 유기 양이온이 벤토나이트의 층간에 충분히 삽입되었음을 의미한다. 전기영동 이동성 측정에 의하면 벤토나이트의 양이온 교환 용량 이상의 유기 양이온으로 치환시킨 유기벤토나이트의 경우 무처리 벤토나이트와 전혀 다른 표면 전하분포를 나타냄을 알 수 있다. 요오드의 흡착능에 있어서, 무처리 벤토나이트는 요오드를 전혀 흡착하지 못한 반면, 벤토나이트의 양이온 교환용량의 200% 양으로 개질 시킨 유기벤토나이트의 경우 요오드 439 mmol/kg를 흡착하였다. 유기 벤토나이트에 흡착된 요오드의 분자 환경은 요오드 K-edge와 L_{III}-edge X-선 흡수 분광을 이용하여 연구하였다. 유기벤토나이트의 요오드 X선 흡수 변연 구조를 통해 유기벤토나이트에 흡착된 요오드의 경우 KI 표준용액의 구조와 유사함을 알 수 있었다. 광범위 X-선 흡수 미세구조의 선형 결합 분석결과는 유기 복합체와 반응한 요오드의 비율이 벤토나이트에 흡착된 유기 복합체의 양이 증가함에 따라 같이 증가함을 나타냈다. 본 연구를 통해, 벤토나이트의 개질 특성에 의해 요오드의 흡착 환경이 현저하게 달라짐을 관찰할 수 있었으며, 음이온성 방사성 요오드를 포함하는 핵폐기물 저장소 주변의 방어벽 물질로 유기벤토나이트의 적용 가능성을 살펴 볼 수 있었다.

주요어 : HDP, 유기벤토나이트, 요오드, 흡착, X-선 흡수 분광

Introduction

Iodine exists in the environment at low concentrations; however, it is an essential element in geological and biological processes. Iodine is indispensable to most living organisms and is especially needed for the human diet, i.e., humans' thyroid glands to produce thyroid hormones that are essential for growth, the nervous system, and the metabolism. In contrast, if too much iodine enters and remains in humans' bodies, the iodine will destroy thyroid gland or can cause goiter, thyroid nodules or cancer (Risher *et al.*, 2004). Furthermore, iodine radioisotopes (¹²⁹I and ¹³¹I) generated during the processing of nuclear energy and nuclear testing and were consisted of spent nuclear fuel as a fission-product are released into the environment as contaminants, which results in a serious environmental problem (Buraglio *et al.*, 2001; Hou *et al.*, 2003; Hu *et al.*, 2005; Kodama *et al.*, 2006; Bruno and Ewing, 2006). Most radioactive forms of iodine change very quickly (seconds to days) to stable elements. However, ¹²⁹I changes very slowly ($\tau_{1/2} = 1.57 \times 10^7$ years), and its levels build up in the environment. Moreover, iodine radioisotopes are released instantaneously upon contact with water (Bruno and Ewing, 2006),

therefore they represent a potential threat to the environment and human health.

Disposal of radioactive iodine as well as other radionuclides often involves the burial of a waste form containing the radioactive materials, which is surrounded by a barrier (or backfill) material that would adsorb the radionuclides if they were released from their primary waste form. Bentonite (mainly consists of montmorillonite) is often used as a backfill material in the barrier of a nuclear waste repository, but it is an ineffective adsorbent for anionic contaminants. However, the replacement of inorganic cations in montmorillonite by organic cations via ion exchange converts the clay mineral into an effective anion adsorbent. An example of this is organo-montmorillonite, which is organic cations are substituted into the interlayer region of the montmorillonite. Montmorillonite has cation substitutions sites in both the tetrahedral and octahedral sheets, and substitutions of ions of the same valence are common in octahedral sheets. Isomorphic substitutions by ions of lesser charge, substantially Si⁴⁺ by Al³⁺ in the tetrahedral sheets and Fe³⁺ or Al³⁺ by Fe²⁺ or Mg²⁺ in the octahedral sheets, produce resultant negative charges on the sheets, which are balanced by interlayer cations, such as alkali-metal

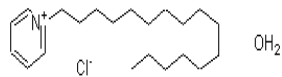
cation Na^+ , alkaline-earth-metal Ca^{2+} and Mg^{2+} ions. The replacement of inorganic cations by organic cations such as organic quaternary ammonium or pyridinium in interlayer converts the clay surfaces from hydrophilic to hydrophobic, hence the characteristics of organobentonites are remarkably different from untreated montmorillonite (Theng, 1974; Lagaly, 1981; Johnston, 1996). When organic compounds are grafted onto clay minerals, it has often been observed that minerals can adsorb more organic cations than suggested by their exchanged CEC amount. Adsorption above the exchanged CEC amount of the minerals is due to the hydrophobic bonding between the aliphatic tails of the organic compounds (Mortland, 1986; Xu and Boyd, 1995a; 1995b; Deng and Dixon, 2002). Adsorbed organic compounds in montmorillonite can be arranged in monolayers, bilayers, or in pseudo-trimolecular arrangements as well as paraffin type arrangement depending on their aliphatic chain length and mineral charge density (Deng and Dixon, 2002). Using these properties, organo-montmorillonites can be used as adsorbents for deleterious anionic radionuclides such as iodide in barriers around nuclear waste repositories (Bors *et al.*, 2000).

A considerable number of studies have been made on the use of clays and clay minerals modified with organic compounds to reduce or remove hazardous contaminants from water and soils. Organoclays has been studied as adsorbent for organic contaminants such as neutral organic contaminants (NOCs) (Sheng *et al.*, 1996; Chun *et al.*, 2003), BTEX (benzene, toluene, ethylbenzene and xylene), phenol (Mortland *et al.*, 1986; Smith and Jaffe, 1994; Koh and Dixon, 2001; Shen, 2002), acid dye (Özcan *et al.*, 2004), and anionic pollutants (Darder *et al.*, 2003; Vujakovi *et al.*, 2003; Li *et al.*, 2007; Zhu and Zhu, 2007), e.g., nitrate (Li *et al.*, 2003; Özcan *et al.*, 2005), chromate (Krishna *et al.*, 2001; Li *et al.*, 2003; Maryuk *et al.*, 2005), anionic radionuclides (Bors *et al.*, 1997, 2000; Riebe *et al.*, 2005; Dultz *et al.*, 2005; Riebe and Bunnenberg, 2007), and anionic tungsten

species (Gecol *et al.*, 2005). Furthermore, during the last several decades, considerable studies have been made to qualify suitable adsorbents that can immobilize or delay the migration of radioiodine that would be released from nuclear wastes (Strickert *et al.*, 1978; Haq *et al.*, 1980; Couture and Seitz, 1983; Gradev, 1987; Huie *et al.*, 1988; Ikeda *et al.*, 1994; Balsley *et al.*, 1996; Bors *et al.*, 1997, 2000; Kang *et al.*, 1999; Kaplan *et al.*, 2000; Riebe *et al.*, 2005). Previous iodine studies mainly have been about the significance of its speciation in iodine retention and transportation in natural environment, inorganic and organic-bound forms of iodine, and the molecular mechanism of iodine interaction with natural organic matter (NOM) (Bors *et al.*, 1988; Sheppard and Thibault, 1992; Fuge, 1996; Stipanicev and Branica, 1996; Yamada *et al.*, 1999; Radlinger and Heumann, 2000; Ashworth *et al.*, 2003; Hu *et al.*, 2005). Despite extensive investigations of organophilic clays and clay minerals as adsorbents over the past several decades, most of these types of studies have utilized only macroscopic measurements. The molecular-scale characterization of structures and compositions of reactive sites on organoclays in contact with aqueous solutions are poorly understood, mainly due to the complexities of the interfaces and scarcity of appropriate analytical tools for probing such complex systems.

X-ray absorption spectroscopy (XAS), including both X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS), is an element specific and non-destructive technique to substantiate environment of adsorbate at mineral-water interface. However, only a few studies using XAS have investigated the iodine speciation and the iodine molecular environment in natural system (Fuhrmann *et al.*, 1998; Reed *et al.*, 2002; Kodama *et al.*, 2006; Schlegel *et al.*, 2006; Yamaguchi *et al.*, 2006; Shimamoto and Takahashi, 2008) and cement-based materials (Bonhoure *et al.*, 2002), and none to organobentonite applying for nuclear waste repository. Therefore, this study is focused on investigating the properties of bento-

Table 1. Chemical formula, molecular weight, and structure of organic compound

Chemical name	Chemical formula	Molecular weight (g/mol)	Structure
Hexadecylpyridinium chloride monohydrate (HDP)	$C_{21}H_{38}ClN \cdot H_2O$	358.01	

nites modified with an organic cation (i.e., hexadecylpyridinium chloride monohydrate (HDP⁺)), noted as organobentonite hereon, and we employed XAS to elucidate the adsorption environment of iodine on organobentonite as a reactive barrier material around a nuclear waste repository at a molecular-level.

Materials and Methods

Samples

Commercial bentonite (Opazil) provided by SÜD-CHEMIE Korea Co. was used in our experiment. The bentonite was activated with NaCO₃ during the manufacturing process. The reported CEC value for this material is 101 meq/100 g. It mainly consists of Na-montmorillonite (About 98%) and minor amounts of quartz as impurities. The Na-activated bentonite was used without any further treatment for this study.

Hexadecylpyridinium chloride monohydrate (HDP) was used as an organic compound for the preparation of organobentonites. Table 1 presents the organic cation used to modify bentonite. Organic compound used in this investigation was purchased from Sigma-Aldrich Company, Inc.

Sorption Isotherms of Organic Compounds and Dissolution Measurement

The Batch equilibration isotherm was determined 0.2 g bentonite samples weighed into 15-mL centrifuge tubes; 10-mL of DDI water solutions containing quantities of HDP equivalent to 0.2~4.0 times the CEC of bentonite were added to these tubes. After then, these suspensions were shaken for 24 hr, and the mixtures were centrifuged at 6000 rpm for 30 min. Finally, the supernatants were filtered and the concentrations

of organic compounds were analyzed by a TOC analyzer (TOC-5000A, Shimadzu).

The dissolved sodium concentration was checked in filtered supernatants using inductively coupled plasma (ICP) spectrometer. A TJA IRIS Advantage/1000 Radial ICAP spectrometer equipped with a solid state CID detector was used for this measurement.

Organic Modification of the Bentonites

The organic compound solutions as three different concentrations of 101 meq/100 g, 202 meq/100 g, and 404 meq/100 g of bentonite were added in 2.0 g of bentonite. The bentonites modified with the organic cation at equivalent amount to 100%, 200%, and 400% of the CEC of bentonite, referred as organobentonite-I, organobentonite-II, and organobentonite-III, respectively. The mixtures were shaken for 24 hr and then were centrifuged at 6000 rpm for 30 min. After centrifugation, the supernatants were discarded and the solids were washed with distilled water three times. Organobentonites were frozen immediately and freeze-dried for further experiments. Synthesized organobentonites were investigated by a micro X-Ray Diffraction (μ -XRD) instrument using at beam line 11-3 at the Stanford Synchrotron Radiation Laboratory (SSRL, Stanford, CA), and surface charge of untreated bentonite and organobentonite was checked by measuring the velocity of the particles using an electrophoremeter (Malvern Instruments ZEN3601 Zetasizer Nano-ZS). For the electrophoretic mobilities measurement, the bentonite and organobentonite dispersions were prepared at concentration 1 g dm⁻³ in DDI water and mixed for 24 hr with a magnetic stirrer. Experiments were performed in pH ranging from 2 to 12 by batch experiment.

Anion Adsorption

The anion adsorption experiments were conducted for 0.2 g of untreated bentonite and bentonite treated with HDP as 200% CEC equivalent amount of bentonite with 40.0 mL of iodide solutions (KI) at various ionic strength conditions of iodide ($7.8 \times 10^{-4} \sim 7.8 \times 10^{-2}$ mol/L). The mixtures were shaken at room temperature for 24 hr. After reaction was completed, the liquid phases were separated from the solids by centrifugation at 6000 rpm for 30 min. The supernatants were filtered, and the concentrations of anion were analyzed by Ion chromatograph (DIONEXDX-500).

X-ray Absorption Spectroscopy (XAS)

Iodine L_{III} -edge XAS spectra were collected at the Stanford Synchrotron Radiation Laboratory (SSRL) using beam line 10-2 at 4557 eV. The X-ray beam was unfocused on a Si(111) monochromator crystal ($\Phi = 90^\circ$). Fluorescence-yield EXAFS data at Iodine L_{III} -edge were collected using a Ge detector. The monochromator was calibrated by using a Ti foil standard and by setting the first maximum of the Ti K-edge at 4966.8 eV. For this experiment, organobentonites were saturated with iodine equilibrating 0.2 g of organobentonites containing quantities of HDP equivalent to 1, 2, and 4.0 times the CEC of bentonite, respectively, with 40.0 mL of 0.5M KI for 48 hr. Iodine K-edge XAS spectra was collected at the Stanford Synchrotron Radiation Laboratory (SSRL), on beam line 11-2 at 33139 K, using a cryogenically cooled double-crystal Si (220) monochromator. Fluorescence-yield EXAFS data at the iodine K-edge were collected using a Lytle detector, filled with Ar gas. For this experiment, organobentonites were saturated with iodine equilibrating 0.2 g of organobentonites containing quantities of HDP equivalent to 2 times the CEC of bentonite, with 40.0 mL of 6×10^{-3} M KI for 24 hr. As reference materials of iodine L_{III} -edge and K-edge XAS spectra, 0.2 M KI and KIO_3 and 0.1 M KI and KIO_3 were used,

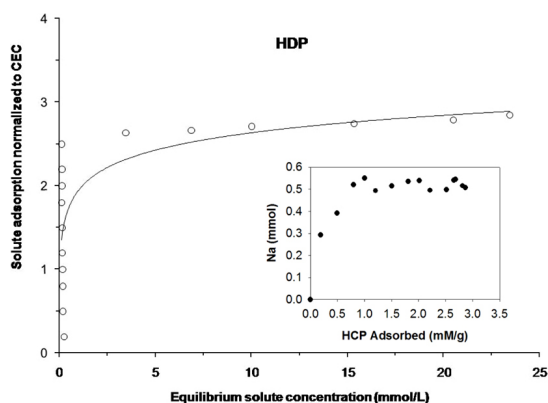


Fig. 1. Adsorption isotherm of HDP cation on bentonite. The inset shows the concentration of Na dissolved from the bentonite interlayer as a function of HDP loading.

respectively. EXAFS spectra were extracted from the averaged data files by pre-edge subtraction followed by spline fitting using Sixpack.

Results and Discussions

Organic Compound Adsorption Isotherms

HDP^+ uptake measurements indicate that bentonite has a high affinity for HDP^+ . Increasing $[HDP^+](aq)$ results in an increase in HDP^+ uptake on bentonite by up to 284% of the CEC equivalents of bentonite (Fig. 1). The large amounts of HDP^+ uptake indicate that multi-layering adsorption occurred during the reaction. In the beginning of reaction, HDP^+ adsorbed by cationic exchange in the interlayer, while the loading of HDP^+ in excess of the CEC of bentonite caused by hydrophobic bonding (Van der Waals interactions) between the hydrophobic C-chains (Theng, 1974; Lagaly, 1981; Xu and Boyd, 1995a, 1995b; Deng and Dixon, 2002). The inset of Fig. 1 shows the concentration of Na dissolved from the bentonite as a function of organic cations loading. As shown in the inset, there is a strong correlation between the amount of HDP^+ adsorbed and the amount of Na^+ released from the bentonite: an increase in HDP^+ uptake on ben-

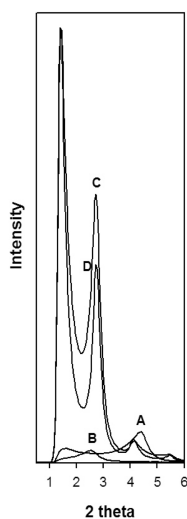


Fig. 2. μ -XRD patterns of (A) bentonite (1.27 nm), (B) organobentonite-I (2.19 nm), (C) organobentonite-II (3.93 nm), and (D) organobentonite-III (3.99 nm).

tonite causes a concomitant increase in Na released as a result of the replacement of exchangeable inorganic cations in bentonite interlayers with organic compounds.

Phase Identification of Organobentonite

The d_{001} spacing of untreated bentonite was 1.27 nm and those of organobentonite-I, organobentonite-II, and organobentonite-III showed 2.19 nm, 3.93 nm, and 3.99 nm, respectively, at room temperature based μ -XRD pattern (Fig. 2). Based on the data of Paradies and Habben (1993), though the height of pyridinium cation is different depending on the orientation of the pyridinium cation, the length of the long alkyl chain is about 2.4 nm and that of the pyridinium cation is around 0.27 nm when the HDP⁺ lies stretched out. The μ -XRD pattern implies that the organobentonites significantly expanded in basal spacing depending on the charge density of the bentonite. For organobentonite-I, the long aliphatic chain of HDP⁺ was intercalated into the interlayer of montmorillonite as a pseudotrimolecular layer or a paraffin-type monomolecular arrangement, while in case of organobentonite-II and organoben-

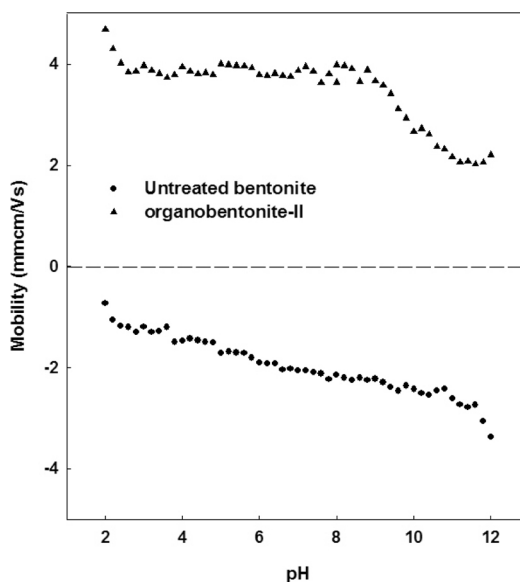


Fig. 3. Electrophoretic mobilities of untreated bentonite and organobentonite-II.

tonite-III, it was substantially inserted as an inclined or perpendicular bilayer paraffin complexes structure (Deng and Dixon, 2002). The basal spacings and intensities of the organobentonites are increased with increasing uptake amount of organic cations used in synthesis.

Electrophoretic Mobility

The results obtained for electrophoretic mobilities values measured against pH (Fig. 3). The electrophoretic mobility of untreated bentonite was negative for the whole pH range (pH 2~12). On the contrary, that of organobentonite-II was found to have the positive electrophoretic mobility in the whole pH range observed. This result supports the μ -XRD pattern of organobentonite-II. This study is important in the analysis of the electrokinetic properties of clays due to its effect on the charge distribution of the particle surface. Consequently, organobentonite that is modified with organic cations in excess of the CEC of bentonite is completely different from untreated bentonite in the surface charge distribution.

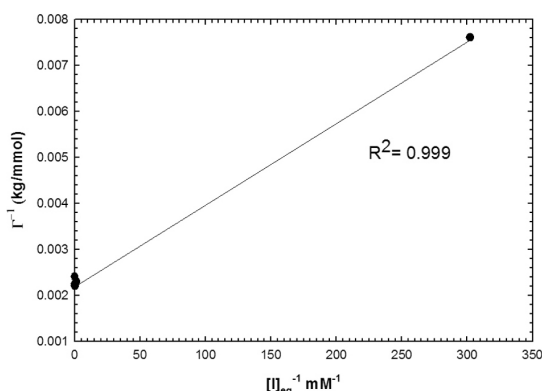


Fig. 4. Langmuir adsorption isotherm of iodide adsorption on organobentonite-II.

Table 2. Fitted langmuir parameters for adsorption of iodide by organobentonite-II

Sample	K_{ads} (L/mmol)	Γ_{max} (mmol/kg)	r^2
Iodide on organobentonite-II	127	439	0.999

Iodine adsorption Characteristics

When $A + B \rightleftharpoons AB$ means simple adsorption, the equilibrium constant, K_{ads} , is given by as below:

$$\frac{[AB]}{[A][B]} = K_{abs}$$

where A = surface site of adsorbent

B = adsorbate in solution

AB = adsorbate on surface sites

The Langmuir isotherm can be expressed as following equation (Stumm and Morgan, 1996; Kang *et al.*, 1999),

$$\Gamma = \Gamma_{max} \frac{K_{ads}[B]}{1 + K_{ads}[B]}$$

where Γ is the amount of anion adsorbed (mmol/kg), Γ_{max} is the maximum adsorption capacity (mmol/kg), K_{ads} is the equilibrium constant (L/mmol), $[B]$ is the equilibrium concentration of

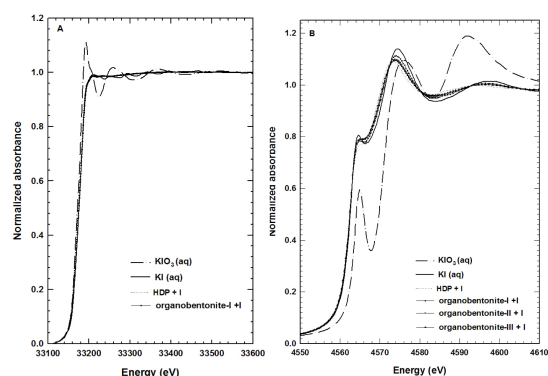


Fig. 5. Iodine K-edge (A) and L_{III} -edge (B) XANES spectra of reference compounds and samples studied.

the anion (mmol/L).

Iodine adsorption was well described by the Langmuir isotherm with correlation coefficient (r^2) exceeding 0.999 (Table 2). Iodide adsorption behavior of untreated bentonite and the organobentonite was very different: untreated bentonite did not adsorb iodide at all, whereas organobentonite-II showed excellent adsorption capacities for iodide (Fig. 4, Table 2). The maximum iodide adsorption capacities and the equilibrium constant, K_{ads} , for organobentonite-II were 439 mmol/kg and 127 L/mmol, respectively. This result signifies that bentonite was turned into a highly efficient anion adsorbent by insertion of organic cation into interlayer.

X-ray Absorption Spectroscopy (XAS)

Since the core hole lifetime increases regularly and rapidly with the increase in the atomic number for a given electronic level (Brown *et al.*, 1988), L_{III} -edge XANES could be more effective for the speciation of iodine. Even though K-edge XANES shows the featureless spectra in increasing atomic number, K-edge XANES spectra are more obvious than those of L_{III} -edge on distinguishing iodide from iodate (Fig. 5(A)) (Shimamoto and Takahashi, 2008). Fig. 5(B) depicts that XANES spectra for references and samples display peaks at 4564.5 and 4573~4576 eV. Visual inspection of Fig. 5 suggests that the main absorption edge shift to

Table 3. Fraction of HDP+KI and KI determined by linear combination fitting shown in Fig. 7

	Organobentonite-I + I	Organobentonite-II + I	Organobentonite-III + I
HDP+KI	0.491117 +/- 0.025061	0.644924 +/- 0.018977	0.772394 +/- 0.016179
KI	0.508882 +/- 0.025061	0.355075 +/- 0.018977	0.227605 +/- 0.016179
Component Sum	1.000000	1.000000	0.999999
Total residuals	4.57E-05	5.92E-07	1.46E-05

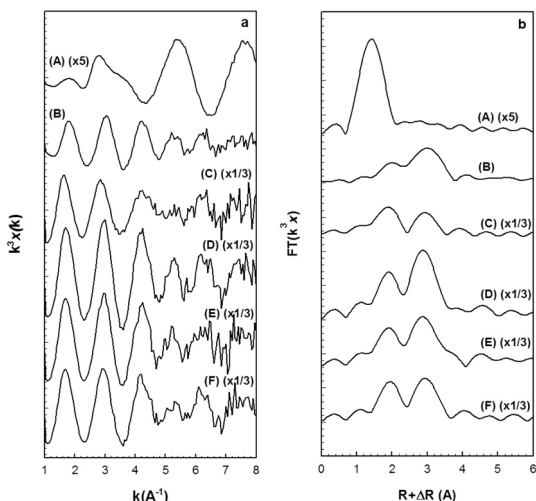


Fig. 6. (a) Iodine L_{III} -edge EXAFS spectra for references and samples studied. (b) comparison of selected Fourier transforms (FTs) for iodine in references and samples studied. (A) $KIO_3(aq)$, (B) $KI(aq)$, (C) HDP + I, (D) organobentonite-I + I, (E) organobentonite-II + I, and (F) organobentonite-III + I.

higher energies with increasing ν_I . This edge shift can be traced by the shift of the half-height of the normalized absorption edge, from 4564.5 eV in KI ($\nu_I = -1$) to 4564.9 eV in KIO_3 ($\nu_I = 5$). This reliance of the edge position with the formal oxidation state is well documented (Brown *et al.*, 1988). The XANES spectra of iodine adsorbed organobentonites were found to be similar to the spectra of KI reference solution (Fig. 5). This suggests that iodine with $\nu_I = -1$ is predominant in all of examined iodine in organobentonite. Fig. 6 presents that the iodine L_{III} -edge spectra and comparison of Fourier transform for iodine in references and samples studied. The spectral discordances observed for the X-ray adsorption edges of KIO_3 reference and iodine in organo-

bentonites and KI reference (Fig. 6a). $X(k)$ for samples and KI reference all display oscillation maxima near 1.8, 3.0, 4.2 \AA^{-1} . However, $X(k)$ for KIO_3 reference figures oscillation maxima near 1.75, 2.75, 5.35 \AA^{-1} . The FT peaks near $R + \Delta R = 1.9 \text{\AA}$ are attributed to the contribution from the carbon atom bonded to iodine and peaks near 2.9 \AA are related to contribution from oxygen atom (Fig. 6b). Iodine in the reference samples is predominately bound by oxygen molecules (I-O), 3.6 \AA for KI and 1.8 \AA for KIO_3 . Quantitative analysis of EXAFS spectra of organobentonite samples indicates that iodine is bound to carbon and the coordination number and interatomic distances between I-C varied depending on the organic concentration on bentonite. The detailed investigation into the molecular environment of adsorbed anions will be executed using FEFF EXAFS fitting. In conclusion, analysis of X-ray absorption spectra for iodine adsorbed organobentonites suggests that the presence of iodine-carbon bonds and it suggests that XANES and EXAFS spectra and FT display distinct patterns that could be used as a fingerprint of iodine molecular environment.

Linear combination fitting of EXAFS data offers an alternative method of quantifying organic compounds bonding with iodine and iodine is not bonded on organobentonites depending on different loading amount of organic compounds. 0.25 M KI reacted with 0.5 M HDP and 0.2 M KI were used as references for this fitting. Linear combination fitting of EXAFS data suggests the fraction of iodine reacted with the organic compound increased from 49% to 77% with increasing loading of the organic compound on organobentonites. (Table 3, Fig. 7).

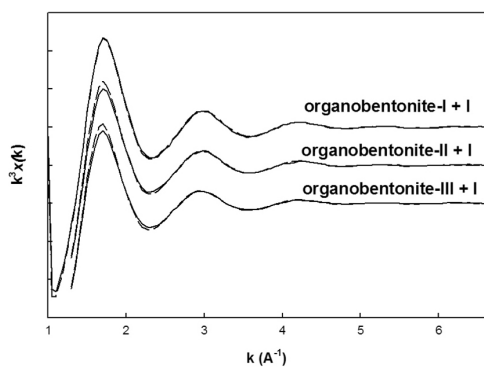


Fig. 7. Linear combination fitting of iodine L_{III} -edge EXAFS spectra for I-adsorbed organobentonites (fit data: dotted lines; experimental data: solid lines).

Conclusions

The adsorption behavior of HDP on bentonite shows a typical L-type isotherm representing continuous and stable adsorption in excess of twice the cation exchange capacity of bentonite. Results from electrophoretic mobility and μ -XRD diffraction analysis revealed that organobentonite, which is manufactured by the exchangeable inorganic cations have been replaced by organic cations in the interlayer of bentonite was completely different from untreated bentonite in the surface charge distribution and d-spacing. This means that the organobentonites significantly expanded in basal spacing, and organic cations were substantially intercalated into the interlayer spaces of bentonite. IC analysis data also showed that organobentonite has excellent adsorption efficiency for iodine. EXAFS spectroscopy measurements can explain the characteristics of organobentonite, stability and mechanism of adsorption occurring in surface and interface at the molecular level. Therefore, the precision analysis will be executed by model compound work. These stable and persistent characteristics and the relatively low price of HDP point that it is proper to apply to nuclear waste repository. These results can help explain the adsorption environment of iodide on organobentonite and also highlight the possible role of organobentonites as a reactive barrier material around a

nuclear waste repository containing radioactive iodine.

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