CATION EXCHANGE PROPERTIES OF HIGHLY CHARGED SWELLING MICAS AND TITANOSILICATES

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by

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ABSTRACT

The principal goal of this thesis work was to investigate cation exchange properties of highly charged swelling micas such as \( \text{Na}_1 \text{Si}_3 \text{AlMg}_3 \text{O}_{10} \text{F}_2 \cdot x \text{H}_2\text{O} \) (Na-2-mica), \( \text{Na}_{1.5} \text{Si}_{2.5} \text{Al}_1 \text{Mg}_3 \text{O}_{10} \text{F}_2 \cdot x \text{H}_2\text{O} \) (Na-3-mica), and \( \text{Na}_2 \text{Si}_2 \text{Al}_2 \text{Mg}_3 \text{O}_{10} \text{F}_2 \cdot x \text{H}_2\text{O} \) (Na-4-mica) and titanosilicates such as sodium Engelhard titanosilicate 4 (Na-ETS-4) and Na-titanosilicate. The three mica ion exchangers were synthesized using a NaCl melt method and the two Na titanosilicates were synthesized by hydrothermal treatment, and characterized by X-ray diffraction and scanning electron microscopy. In addition, \(^{29}\text{Si}\) and \(^{27}\text{Al}\) MAS NMR spectroscopy was used to understand layer charge properties of Na-micas and local chemical binding environment of Si and Al.

Cation exchange isotherms and Kielland plots of the above five ion exchangers were constructed in order to evaluate their selective cation exchange properties for \( \text{Sr}^{2+} \) and \( \text{Ba}^{2+} \) and heavy metals such as \( \text{Hg}^{2+} \) and \( \text{Co}^{2+} \). \( 2\text{Na}^+ \rightarrow \text{Sr}^{2+} \) exchange isotherms and Kielland plots revealed that Na-2-mica, Na-ETS-4, and Na-titanosilicate showed high selectivity for \( \text{Sr}^{2+} \). For the case of \( 2\text{Na}^+ \rightarrow \text{Ba}^{2+} \) exchange, Na-2-mica and Na-ETS-4 had high preference for \( \text{Ba}^{2+} \) over \( \text{Na}^+ \) with most of the equilibrium solutions used. Na-2-mica showed higher selectivity for \( \text{Sr}^{2+} \) and \( \text{Ba}^{2+} \) than Na-3-mica and Na-4-mica because of higher expansibility of Na-2-mica resulting in easier accessibility to exchange sites in interlayer space than the other two micas. This expansibility was limited by increasing electrostatic attraction with the increase in intercalated divalent cations. In the case of \( 2\text{Na}^+ \rightarrow \text{Hg}^{2+} \) exchange reaction, Na-ETS-4 was found to have higher distribution coefficient \( (K_d) \) value than any other ion exchangers tested. The Kielland plot for \( \text{Hg}^{2+} \)
showed that only Na-ETS-4 had selectivity for mercury (II) with most of the exchange solutions used. $2\text{Na}^+ \rightarrow \text{Co}^{2+}$ exchange equilibria revealed that Na-2-mica and Na-ETS-4 had high selectivity for cobalt ions over sodium ions at low Co equivalent fraction in the solid phase.

Two different (001) phases of ~12 Å and ~14 Å were seen in the XRD patterns of the Na-micas after $2\text{Na}^+ \rightarrow \text{M}^{2+}$ (M=Sr, Ba, Hg) exchange reactions with different exchange solutions. This difference in the $d_{001}$-value suggested the presence of adsorbed divalent cations with different hydration states in interlayer space after ion exchange reactions, because of partial dehydration of intercalated cations by strong electrostatic attraction between adsorbed cations and negatively charged layers. Both the extent of divalent cations intercalated and layer charge density affected the attractive electrostatic force. As the uptake of adsorbed divalent cations in the solid phase and the layer charge density increased, the electrostatic attraction increased contributing to the increase in the extent of the dehydration of cations intercalated. Unlike other cases, after $2\text{Na}^+ \rightarrow \text{Co}^{2+}$ exchange reaction, strong ~14 Å phase of Na-2-mica was retained even at high Co$^{2+}$ uptake, while ~12 Å phase decreased as the amount of Co$^{2+}$ increased. This is due to stronger hydration energy of Co$^{2+}$ ions than those of Sr$^{2+}$, Ba$^{2+}$ and Hg$^{2+}$ ions. The results on cation exchange properties of the above ion exchangers indicated that Na-2-mica and Na-ETS-4 could be excellent ion exchangers for separation and remediation of radioactive species such as Sr$^{2+}$ and Ba$^{2+}$ while only Na-ETS-4 would be useful for decontamination of Hg$^{2+}$. 
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CHAPTER 1
INTRODUCTION

There have been a large number of pollutants such as organic pesticides, heavy metals and radioactive species which contaminate soils and groundwater (Snedeker, 2001; Whicker et al., 1999). Among many contaminants, non-organo pollutants, particularly heavy metals and radionuclides, are not biodegradable and tend to accumulate in living organisms, causing serious problems (Bailey et al., 1999; Mollah et al., 1998) and they can be transported to uncontaminated sites through leaching into groundwater. If they are left untreated or not remediated, the pollutants may have a crucial impact not only on human health but also on the environment. Additionally, depending on the non-organo contaminants’ geochemical behavior, they can be introduced into the food chain and ecosystem, resulting in a high potential risk to human health. Therefore, although the contamination occurs even at low levels, it should be controlled and remediated to protect human health and environment.

At nuclear weapons processing facilities and weapon testing sites radionuclide-contaminated soils occur mainly by nuclear accidental spillage or leakage (e.g. Chernobyl) (Makhijani et al., 1995) and by the fallout after nuclear weapon testing (Elless et al., 2002). The radioisotopes are of concern because they have a potential risk to human health resulting from emission of ionizing radiation causing cancer, mutations, and tumors (Lubin et al., 1997; Ellegren et al., 1997). Among a variety of radioactive species, $^{90}$Sr, which has a half-life of 29.1 yr, is one of the major radioactive materials. It is released as a fission product during nuclear weapons testing and during reprocessing.
activities of spent fuel waste (Elless et al., 2002). In particular, fallout from the nuclear testing contaminated surface soils with $^{90}\text{Sr}$ to the extent of ~ 1430 Bq m$^{-2}$ in USA. If Sr is incorporated into the food chain and thus ingested, it can accumulate in the bone and skeletal tissue because of its chemical similarity to Ca (White and Broadley, 2003; Francis, 1978).

Barium (Ba) is one of the important elements because its radioactive isotope $^{133}\text{Ba}^{2+}$ has a half-life of 10.7 years. Barium affects the nervous system at high levels of exposure, resulting in cardiac irregularities, tremor, weakness, anxiety, and paralysis (Moore, 1991). Since Ba is chemically analogous to radium (Ra), Ba is used to estimate and predict the behavior of Ra in soils. $^{226}\text{Ra}$ is also a radioactive species of interest because it has a very long half-life of 1600 yr. It could be discharged from uranium processing facilities (Paschoa, 1998; Hutchinson and Toussaint, 1998). Ra has a higher activity than uranium. Its activity ratio (AR) of $^{226}\text{Ra}/^{238}\text{U}$ in soil is about 0.1, but is much higher in surface soils (~1.8) and in vegetation (~ 65) (Greeman et al., 1999).

Among many heavy metal pollutants such as Cu, Cd, Hg, Cr, Co, and Pb, mercury has received attention as a significant environmental pollutant because of its high toxicity and accumulation in organisms, even at trace levels. It is released from fossil fuel burning, mining and smelting, and natural sources (Selin, 2009). A wide variety of organisms such as fish, birds and humans are sensitive to exposure to mercury as it causes neurological disturbances and biological abnormalities. Also, Hg is easily transported in the form of vapor via the atmosphere but also transformed to organomercury which is more toxic than non-organomercury by 10 times (Boening, 2000). Therefore, it has a severe impact on the environment.
Like other heavy metals, cobalt is a toxicological element (Crosby, 1998). It is reported that cobalt may cause primarily respiratory effects, including decreased pulmonary function, asthma, interstitial lung disease, wheezing, and dyspnea (Bucher et al., 1999) and it is a possible carcinogen to humans (Bucher et al., 1999; Lison et al., 2001). Also, $^{60}$Co has a half-life of 5.3 yr and some radionuclide-contaminated sites often include $^{60}$Co (Olsen et al., 1986; Blom et al., 1991).

There are several methods to remediate metals from contaminated soils and groundwater such as vitrification, electrokinetic treatment, ion exchange, solidification, phytoremediation, and extraction (Mulligan et al., 2001). Among these remediation techniques, ion exchange is a simple and effective method to remove radionuclides and/or heavy metals from contaminated soils and groundwater. The key factors of an efficient ion exchanger are as follows: (1) selectivity for a target pollutant, (2) high exchange capacity, (3) cost effectiveness, and (4) stability during ion exchange reaction (5) environmental compatibility. In order to satisfy these conditions, many ion exchangers such as synthetic or natural clays, zeolites, and synthetic inorganic exchangers have been developed and tested. Attention has been focused on synthetic clays and inorganic ion exchangers because generally they are very stable with a well-defined and rigid structure and they can be synthesized using a variety of methods which can lead to increased ion exchange capacity.

The possible candidates to meet the above conditions are Na-swelling type-n-micas (n=2, 3, and 4), Na-ETS-4 and Na-titanosilicate because they have high exchange capacities (Table 1.1), high stability due to a rigid structure, and environmental compatibility because exchangeable cations such as Na$^+$ are relatively harmless. The ion
exchange properties of Na-synthetic micas were investigated for some radionuclides and

Table 1.1. Ideal composition and theoretical CEC of five ion exchangers.

<table>
<thead>
<tr>
<th>Name</th>
<th>Ideal formula</th>
<th>CEC (meq / 100g)$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na4-mica</td>
<td>Na$_2$Si$_2$Al$_2$Mg$<em>3$O$</em>{10}$F$_2$</td>
<td>468</td>
</tr>
<tr>
<td>Na3-mica</td>
<td>Na$<em>{1.5}$Si$</em>{2.5}$Al$_{1.5}$Mg$<em>3$O$</em>{10}$F$_2$</td>
<td>361</td>
</tr>
<tr>
<td>Na2-mica</td>
<td>Na$_1$Si$_3$AlMg$<em>3$O$</em>{10}$F$_2$</td>
<td>247</td>
</tr>
<tr>
<td>Na-ETS-4</td>
<td>Na$<em>9$Si$</em>{12}$Ti$<em>5$O$</em>{38}$(OH) • 12H$_2$O</td>
<td>639</td>
</tr>
<tr>
<td>Na-titanosilicate</td>
<td>Na$_2$Ti$_2$O$_3$SiO$_4$ • 2H$_2$O</td>
<td>710</td>
</tr>
</tbody>
</table>

$^a$ CEC was calculated on a basis of the ideal formula.

heavy metals, and they were found to be selective at low occupancy of the cation pollutants in exchange sites of the ion exchangers (Kodama et al., 2004; Paulus et al., 1992; Kodama et al., 1999). As for Na-ETS-4 and Na-titanosilicates, it has been reported that Na-ETS-4 can be changed to Sr or Ba-form (Nair et al., 2001; Marathe et al., 2005) and Na-titanosilicate has selectivity for Cs$^+$ and Sr$^{2+}$ (Solbra et al., 2001; Celestian et al., 2007). Therefore, two Na-titanosilicates (Na-ETS-4 and Na-titanosilicate) were selected for investigation and comparison of their selectivity for Sr$^{2+}$, Ba$^{2+}$, Hg$^{2+}$ and Co$^{2+}$ with the Na-swelling-type micas.

Recently, almost pure Na-4-mica was synthesized using a NaCl melt method by heat treatment at 900 °C for 15 hrs (Park et al., 2002) and this method was also successful in synthesizing Na-n-micas (n=2, 3, and 4) using kaolinite as an economical source of Si and Al (Komarneni et al., 2005). In order to reduce synthesis cost, I will attempt to modify the synthesis method by changing raw materials or heating-time. Ion exchange
properties of the Na-synthetic micas prepared by the modified method are investigated here because the ion exchange properties including selectivity for pollutants can differ somewhat depending on the synthesis method using different precursors, different fluxes and heating temperature/time (Kodama et al., 1999; Kodama et al., 2000; Komarneni et al., 2005).

Therefore, the detailed objectives of this thesis are as follows:

1. To synthesize Na swelling-type-n-micas (n=2, 3, and 4) with different layer charge densities using an improved NaCl melt method and to synthesize one Na-ETS-4 and one Na-titanosilicate for comparison with swelling micas.

2. To characterize all five synthetic ion exchangers with powder X-ray diffraction, scanning electron microscopy (SEM) and solid-state $^{29}$Si and $^{27}$Al magic-angle spinning nuclear magnetic resonance (MASNMR) spectroscopy.

3. To study selective Sr$^{2+}$, Ba$^{2+}$, and Co$^{2+}$ exchange properties of Na-n-micas (n=2, 3, and 4), Na-ETS-4 and Na-titanosilicate for potential application to radionuclide remediation in contaminated groundwater and soils.

4. To probe exchange properties of Hg$^{2+}$ using Na-n-micas (n=2, 3, and 4), Na-ETS-4 and Na-titanosilicate for practical cleanup in groundwater and soils contaminated with Hg$^{2+}$.

5. To investigate the effect of different layer charge density of Na-n-micas (n=2, 3, and 4) on selectivity for Sr$^{2+}$, Ba$^{2+}$ and Hg$^{2+}$.

6. To compare selectivity of five ion exchangers for radioactive species and heavy metals such as Sr$^{2+}$, Ba$^{2+}$, Hg$^{2+}$ and Co$^{2+}$.

The studies conducted for the above objectives, the structural and chemical
features of the ion exchangers, and literature review including synthesis methods will be discussed in the following chapters.
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CHAPTER 2

STRUCTURAL AND CHEMICAL CHARACTERISTICS OF Na-MICAS AND Na-TITANOSILICATES, AND PREVIOUS WORKS

2.1 Phyllosilicates Classification and their Structures

Phyllosilicate minerals have a great impact on the chemical and physical properties of soils because they have small particle sizes, high surface areas, and distinct cation exchange properties, which are associated with their structural features. Thus, understanding the structures of the phyllosilicate minerals is essential for interpreting many environmental processes in soils.

Tetrahedral sheet and octahedral sheet are structural components making up phyllosilicate minerals. The tetrahedral sheet is composed of continuously connected SiO$_4^{4-}$ tetrahedra forming six member rings which are called ditrigonal cavities (Fig. 1). Each tetrahedron is connected with one another along crystallographic ‘a’ and ‘b’ directions by sharing 3 basal oxygens, while an apical oxygen is shared with an octahedron which is a basic unit of the octahedral sheet. The octahedral sheet is formed by the endless connection between octahedra by edge-sharing. There are two types of octahedral sheets depending on the valency of cation and the extent of filling every three octahedral sites: a divalent ion such as Mg containing trioctahedral sheet (three out of three octahedral sites are filled) or a trivalent ion such as Al containing dioctahedral sheet (two out of three octahedral sites are filled and one remaining site is empty) (Fig. 2.2a and b).
Figure 2.1. Tetrahedral sheet (from Schulze, 2002).
(a) The Octahedral Sheet (trioctahedral)

(b) The Octahedral Sheet (dioctahedral)

Figure 2.2. Octahedral sheets: (a) Mg trioctahedral sheet and (b) Al dioctahedral sheet (from Schulze, 2002).
In phyllosilicate minerals, in order to construct a layer, the tetrahedral sheet (T) is combined with the octahedral sheet (O) in different T:O ratios such as 1:1, 2:1, 2:1:1, and 2:1 inverted ribbons. A 1:1 layer silicate consists of one tetrahedral sheet and one octahedral sheet, while a 2:1 layer silicate has an octahedral sheet sandwiched by two tetrahedral sheets (Fig. 2.3). A 2:1:1 layer silicate has one more positively charged octahedral sheet in the interlayer space which is between 2:1 layers. Finally, the phyllosilicates with the structure of 2:1 inverted ribbons are sepiolite and palygorskite. They have discontinuous octahedral sheet, but continuous tetrahedral sheet which has some portion inverted alternatively (Schulze, 1989) (Fig. 2.4). These phyllosilicate minerals can be classified depending on layer types, layer charge, and the types of the octahedral sheet (tri- or di-octahedral sheet) (Table 2.1). Fig. 2.4 shows structural models of representative phyllosilicate minerals.

Figure 2.3. Edge view of the 1:1 and 2:1 layer structures of phyllosilicates (from Schulze, 2002).
Table 2.1. Classification of phyllosilicates (modified from Bailey, 1980)

<table>
<thead>
<tr>
<th>Layer type</th>
<th>Group (X= Layer charge per formula unit)</th>
<th>Subgroup (Types of octahedral sheet)</th>
<th>Examples b</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:1</td>
<td>Kaolin- Serpentine (X~ 0)</td>
<td>Serpentine (Trioctahedral sheet)</td>
<td>Chrysotile, Antigorite, Lizardite</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Kaolins (Dioctahedral sheet)</td>
<td>Kaolinite, Dickite, Nontronite</td>
</tr>
<tr>
<td>2:1</td>
<td>Talc- Pyrophyllite (X~ 0)</td>
<td>Talc (Trioctahedral sheet)</td>
<td>Talc, Willemsite</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Pyrophyllite (Dioctahedral sheet)</td>
<td>Pyrophyllite</td>
</tr>
<tr>
<td></td>
<td>Smectites (X~ 0.2-0.6)</td>
<td>Saponites (Trioctahedral sheet)</td>
<td>Saponite, Hectorite, Sauconite, Stevensite</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Montmorillonites (Dioctahedral sheet)</td>
<td>Montmorillonite, Beidellite, Nontronite</td>
</tr>
<tr>
<td></td>
<td>Vermiculites (X~ 0.6-0.9)</td>
<td>Trioctahedral Vermiculites</td>
<td>Trioctahedral Vermiculite</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Dioctahedral Vermiculites</td>
<td>Dioctahedral Vermiculite</td>
</tr>
<tr>
<td></td>
<td>Micas (X~ 1.0)</td>
<td>Trioctahedral Micas</td>
<td>Phlogopite, Biotite, Lepidolite</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Dioctahedral Micas</td>
<td>Muscovite, Paragonite, Glauconite</td>
</tr>
<tr>
<td></td>
<td>Brittle Micas (X~ 2.0)</td>
<td>Trioctahedral Micas</td>
<td>Clintonite, Anandite</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Dioctahedral Micas</td>
<td>Margarite</td>
</tr>
<tr>
<td>2:1:1</td>
<td>Chlorites (X= variable)</td>
<td>Trioctahedral Chlorites</td>
<td>Clinochlore, Chamosite, Nimite</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Dioctahedral Chlorites</td>
<td>Donbassite</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Di-Trioctahedral Chlorites</td>
<td>Cookeite, Sudoite</td>
</tr>
<tr>
<td>2:1</td>
<td>Sepiolites-Palygorskites (X= variable)</td>
<td>Sepiolites</td>
<td>Sepiolite, Loughlinite, Xylotile</td>
</tr>
<tr>
<td></td>
<td>Inverted ribbons</td>
<td>Palygorskites</td>
<td>Palygorskite</td>
</tr>
</tbody>
</table>

aX refers to an O_{10}(OH)_{2} formula unit for smectite, vermiculite, mica and brittle mica.

bonly a few examples are given.
Figure 2.4. Structural models of soil minerals based on octahedral and tetrahedral sheets (from Schulze, 2002).
Figure 2.4. Continued (from Schulze, 2002).
2.2 Zeolites: Classification of Structures and a variety of Framework Atoms

The Na titanosilicates used in this thesis are analogous to zeolites in terms of their structure and ion exchange properties and hence a brief review of zeolite structures is given below. Zeolites are highly crystalline aluminosilicates with three-dimensional framework structures which consist of interconnected channels and cages containing exchangeable alkali, alkaline earth cations and adsorbed water (Boettinger et al., 2002). The framework structure is formed by connections of SiO$_4^{4-}$ tetrahedra which three-dimensionally share four oxygens of each tetrahedron with neighboring tetrahedra (Schulze, 2002). The negative charges of the framework are generated from the isomorphous substitution of Al$^{3+}$ for Si$^{4+}$ in some tetrahedra and are satisfied with the exchangeable cations. They have several important properties: ion exchange, catalysis, adsorption, high surface area, reversible hydration-dehydration, and molecular sieving. These properties are closely related to their open framework structure as well as

Figure 2.4. Continued (from Schulze, 2002).
composition of the structure. The zeolites can be classified into seven groups based on their framework topology (Meier, 1968) (Table 2.2, Fig. 2.5a). In this classification, primary units in each group are the Si and Al tetrahedra, but each group includes distinct subunits which are called secondary building units (SBUs). These SBUs are associated with characteristic arrangement of tetrahedra forming polyhedra which is involved in the zeolite structures (Fig. 2.5b). The polyhedral representations of the structures of selected zeolites are shown in Fig. 2.6.

Table 2.2 Classification of zeolites based on the framework topology of the zeolites (from Breck, 1974).

<table>
<thead>
<tr>
<th>Group</th>
<th>Secondary Building Unit (SBU)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Single 4-ring, S4R</td>
</tr>
<tr>
<td>2</td>
<td>Single 6-ring, S6R</td>
</tr>
<tr>
<td>3</td>
<td>Double 4-ring, D4R</td>
</tr>
<tr>
<td>4</td>
<td>Double 6-ring, D6R</td>
</tr>
<tr>
<td>5</td>
<td>Complex 4-1, $T_5O_{10}$ unit</td>
</tr>
<tr>
<td>6</td>
<td>Complex 5-1, $T_8O_{16}$ unit</td>
</tr>
<tr>
<td>7</td>
<td>Complex 4-4-1, $T_{10}O_{20}$ unit</td>
</tr>
</tbody>
</table>
Figure 2.5. (a) The secondary building units (SBUs) in zeolite structures. Only the positions of tetrahedral (T) silicons and aluminumas are shown. (b) Some polyhedra in zeolite frameworks: $\alpha$ (26-hedron) or truncated cuboctahedron; $\beta$ (14-hedron) or truncated octahedron; $\delta$ or double 8-ring; D6R or double 6-ring (hexagonal prism); $\gamma$ or 18-hedron; and $\epsilon$ or the 11-hedron (from Breck, 1974).
Figure 2.6. Polyhedral representations of the structures of selected zeolites: (a) faujasite (110); (b) chabazite (001), (c) erionite (001), (d) clinoptilolite (001). Water molecules and exchangeable cations are not shown for clarity. (from Boettiger and Ming, 2002).
There have been attempts to synthesize zeolites and zeolite-like materials with useful applications such as high ion exchange capacity and gas separation (Poojary et al., 1994; Kuznicki et al., 2001). The synthesis has been focused on using mixed aluminosilicate-metal oxide and mixed aluminophosphate-metal oxide framework systems due to the possibility of obtaining novel properties different from those of conventional zeolite materials. One of the approaches is to substitute Si or Al in the framework for other cations to form a wide variety of framework structures. In many zeolitic or related crystalline microporous materials, gallium (Ga\(^{3+}\)) (Yang et al., 1988), phosphorus (P\(^{5+}\)) (Ma et al., 2006), germanium (Ge\(^{4+}\)) (Bu et al., 1998), zirconium (Zr\(^{4+}\)) (Zhu et al., 2004), titanium (Ti\(^{4+}\)) (Nair et al., 2001), and iron (Fe\(^{3+}\)) (McNicol et al., 1972) ions, like Al, could be successfully incorporated for Si ions.

### 2.3 Properties and Structures of Synthetic Na-Micas, Na-ETS-4, and Na-Titanosilicate

Micas are 2:1 phyllosilicate minerals which have a layer consisting of one octahedral sheet between two tetrahedral sheets. Each layer is tightly held together by large interlayer cations via electrostatic attraction (Fanning et al., 1989; Bailey, 1984a). The layer charge due to isomorphous substitution of Al\(^{3+}\) for Si\(^{4+}\) in the tetrahedral sheet or Mg\(^{2+}\) for Al\(^{3+}\) in the octahedral sheet is high and it is approximately either -2 per unit cell for true micas or -4 for brittle micas. The interlayer cation, potassium in particular, strongly holds layers and occupies the ditrigonal holes in the interlayer. Potassium ion is non-hydrated and is not readily exchangeable, thus preventing swelling of the interlayers.
and limiting the capacity to exchange cations between the solid phase (mica mineral) and solution phase (soil solution).

The layer charge density and the extent of hydration of interlayer cations are key factors, which influence expansibility of 2:1 clays which in turn is related to ion exchange property. The clay minerals with low layer charge density and highly hydrated cations easily expand (Giese, 1978), while the clays like micas are not expansible due to their high layer charge density and non-hydrated interlayer cations. Brittle micas have exceptionally highly charged layers (~ 4 units of negative charge per unit cell) which are balanced by Ca$^{2+}$ or Ba$^{2+}$ cations in the interlayer space (Deer et al., 1962), and thus they are non-expansible. However, in 1972, Gregorkiewitz first reported a swelling-type of synthetic brittle mica, which is synthesized using augite and NaMgF$_3$ as precursors. This mica has several unique properties unlike common micas (Gregorkiewitz et al., 1987): (1) this novel mica has the capacity to exchange cations (2) swells well in spite of its high layer charge density (3) there are 4 exchangeable hydrated Na ions in the interlayer space (4) it has hydrated and anhydrous phases and (5) both phases are reversibly interchangeable (Park et al., 2002).

Like brittle micas, this new synthetic mica has 2:1 layers which are highly charged (~ 4 units of negative charge per unit cell). Four sodium ions in one unit cell compensate for this high layer charge density derived from the isomorphous substitution of Al$^{3+}$ for Si$^{4+}$ in tetrahedral sheet to a large extent, so that the new mica is informally called Na-4-mica. Almost all of octahedral cation sites are occupied with Mg$^{2+}$ to form a Mg trioctahedral sheet. Instead of a hydroxide ion, each Mg octahedron has a fluorine ion pointing vertically upward toward the center of the ditrigonal cavity. Therefore, these
structural features allow mica to be classified into sodium fluorophlogopite as well as brittle mica due to the highly charged layer.

Natural brittle micas such as Ba-micas (McCauley and Newnham, 1973; Giuseppetti and Tadini, 1972), have two divalent cations (Ca$^{2+}$, or Ba$^{2+}$) per unit cell in the interlayer, whereas Na-4-mica has 4 interlayer cations in one unit cell to compensate for the negative charges of ~ 4 per unit cell. In order to allow the accommodation of an unusually large number of hydrated or unhydrated Na$^+$, Gregorkiewitz et al. proposed models for anhydrous and hydrated Na-4-micas. The proposed model includes a unique layer stacking which is caused by a displacement of adjacent layers by $\pm b/3$ to allow every cavity above and below the central plane to accommodate 4 Na ions in one unit cell (Fig. 2.7). Na ions deeply sink into the holes to coordinate with 3 inner oxygens of the ditrigonal hole (Fig. 2.7). However, this conformation of Na ions and oxygens causes instability of this phase due to Na-Na repulsion. Therefore, the anhydrous phase changes into a hydrated one where the coordination sphere of Na$^+$ is completed by one single sheet of water molecules from the central plane (Figs. 2.8 and 2.9). A similar arrangement was reported in Na-montmorillonite and Na-beidellite by Pedro (1974), Mering (1975), and Besson (1980). Additionally, Gregorkiewitz et al. reported a change in d-spacing from 9.81 to 12.81 Å due to limited extent of hydration depending on the type of interlayer cations. For example, the d$_{001}$ spacings increase from 9.81 to 12.18 Å for hydrated Na$^+$ and 12.81 Å for K$^+$ in the interlayers.
Fig. 2.7 Proposed model for anhydrous Na-4-mica as projected on plane perpendicular to ‘a’. The displacement of the upper layer with respect to the lower one is +b/3 (from Gregorkiewitz and Rausell-Colom, 1987).
Fig. 2.8. Proposed model for hydrated Na-4-mica. The displacement of the upper layer with respect to the lower one is +b/3. The model shows a single sheet of H$_2$O molecules coordinating with Na (from Gregorkiewitz and Rausell-Colom, 1987).
Fig. 2.9. Proposed model for hydrated Na-4-mica as projected on (001). The displacement of the upper layer with respect to the lower one is +b/3. The model shows 4 Na and 6 H$_2$O sites per unit cell (from Gregorkiewitz and Rausell-Colom, 1987).
Na-Engelhard titanosilicate-4 (Na-ETS-4), which has an analogue of the mineral zorite, was first reported in 1990 by Kuznicki. It has a framework of titanosilicate consisting of mixed tetrahedral (Si)-pentahedral (Ti2)-octahedral (Ti1) units (Braunbarth et al., 2000; Nair et al., 2001). The framework of ETS-4 is composed of chains of Ti octahedra in the ‘b’ direction. Ti chains are connected together in the ‘c’ direction via a 6-ring and in the ‘a’ direction by either a 12-ring or a bridging titanosilicate unit (Cruciani et al., 1998; Nair et al., 2001) (Fig 2.10). The structure of ETS-4 shows faults in the ‘a’ and ‘c’ directions, and can be described as a random intergrowth of 4 pure polytypes, which differ in the arrangement of the titanosilicate bridging units (Fig. 2.11) (Nair et al., 2001). These faults allow access to the crystal interior of ETS-4 to occur through the relatively narrow 8-MRs. A unique structural feature of ETS-4 is the existence of pentahedra which is five-coordinated Ti with a titanyl, Ti=O, linkage to an apical oxygen. The distinct pentahedra that are connected to Si tetrahedra through only four oxygens makes ETS-4 to have a planar connectivity (Fig. 2.10a). It has been reported that ETS-4 has an exclusive ability, named ‘molecular gate’ effect, to select the size of adsorbents through tuning the effective size of the pores and giving access to the interior, depending on the extent of dehydration at various elevated temperatures (Fig. 2.12) (Kuznicki et al., 2001). So ETS-4 can separate mixture of gas molecules with size in the 3.0-4.0 Å such as N₂/CH₄, Ar/O₂ and N₂/O₂.

Na-titanosilicate with an ideal composition of Na₂Ti₂O₅SiO₄ • 2H₂O was first hydrothermally synthesized in 1994 using highly alkaline media by Poojary et al. This
Na-titanosilicate has a tunnel structure consisting of titanium clusters. One cluster is formed

Fig. 2.10. (a) The crystal structure of ETS-4 along [001]. (b) Projection of ETS-4 along [010] (from Cruciani et al., 1998).
Fig. 2.11. Schematic of the four hypothetical polymorphs of ETS-4 framework. (from Braunbarth et al., 2000).
Fig. 2.12. Reduction in the eight-membered ring proe opening with increasing dehydration temperature. Oxygen to oxygen distances in the 8MR (D1, D2 and D3) for Sr-ETS-4 at room temperature, 150, 200, 250, 300 °C. (from Kuznicki et al., 2001).
by grouping of octahedrally coordinated 4 Ti atoms in a cubane like structure (Fig 2.13) (Poojary et al., 1994; Clearfield et al., 2000; Clearfield, 2001; Celestian et al., 2007). In turn, the clusters are connected to each other by bridging Si tetrahedra forming a square of about 7.8 Å in length (Fig. 2.14). The framework enclosing a tunnel is formed by infinite linkage via oxo-groups between these squares in the ‘c’ direction. In the 6-membered ring of the framework half Na\(^+\) ions reside bonding to 4 framework oxygens and two water molecules in the octahedral coordination (Fig. 2.15), while the remaining Na\(^+\) ions are loosely held within the tunnels (8-membered ring) (Fig. 2.14), where some of the sodium ions are easily released out due to Na-Na repulsion and low coordination number of Na ions in the tunnel (Clearfield et al., 2000). Therefore, there are two types of exchange sites with different properties to influence ion exchange reactions with a variety of other cations such as Cs\(^+\), K\(^+\), and Rb\(^+\). For example, unlike Na\(^+\) and H\(^+\), Cs\(^+\), K\(^+\), and Rb\(^+\) cannot occupy the 6-ring framework sites which are smaller than tunnel sites because they are too large to fit into the 6-ring sites. This structural feature would affect the selectivity of Na-titanosilicate for cations.

In addition to two exchange sites, another structural factor affecting ion exchange is the existence of the bonding of O-Ti-O-Si-O. Functional groups of TiOH in Na-titanosilicate are involved in ion exchange reactions. It is known that a majority of titanium-based ion exchangers with Ti-OH groups are weak, or moderately acid exchangers due to its pK\(_1\) value (= 5.0±1.0). However, H-form of titanosilicate takes up Cs\(^+\) and Rb\(^+\) ions efficiently at pH lower than 1, which indicates the TiOH group is highly acidic. It is because of the existence of p\(_\pi\)-d\(_\pi\) conjugation in O-Ti-O-Si-O bonds that leads to a redistribution of electron density and specifically to a decrease of the negative charge
on the oxygen atom in Ti-OH groups (Clearfield et al., 2000). This result is supported by the distinct change in the $^{29}$Si NMR peak position of -81.7 to -99.8 ppm by the change of Na-form to H-form because the position does not change significantly if there is no $p_{π}$-$d_{π}$ conjugation in H-form of titanosilicate. One alternative explanation why protons are released at low pH is that the very large electrostatic field tends to repel the protons (Clearfield et al., 2000).

Fig. 2.13 A portion of the titanosilicate structure showing the cluster of four titanium-oxygen octahedra sharing edges to form the cubane-like Ti$_4$O$_4$ group (outlined with blue bonds). The Ti atoms are dark red, oxygens red and hydrogens gray (from Celestian et al., 2007).
Fig. 2.14 Top view of Na-titanosilicate showing the clusters for Ti-O6 (yellow) bridged by silicate groups (orange) with oxygens (red). The tunnels are filled with Na\(^+\) (green) and water molecules (red). The green Na\(^+\) on top of the orange tetrahedra symbolizes the Na\(^+\) ions sandwiched between silicate groups within the framework (from Celestian et al., 2007).
Fig. 2.15 Side view down the a-axis showing the 6 member ring cavity containing Na$^+$ ions (from Celestian et al., 2007).
2.4 Ion Exchange Theory

The cation exchange reaction between Na\(^+\) on solid exchanger and M\(^{n+}\) in solution is expressed as

\[
n\overline{Na}^+ + M^{n+} \rightleftharpoons nNa^+ + \overline{M}^{n+}
\]  (2.1)

The thermodynamic equilibrium constant, K of the cation exchange reaction (2.1) is defined by (Townsend, 1984)

\[
K = \frac{X_M[Na^+]^n f_M \gamma_Na^n}{X_Na[M^{n+}] f_Na \gamma_M^n}
\]  (2.2)

Where the bar above the characters refers to the exchanger phase. \(n\) denotes the number of charges. \([Na^+]\) and \([M^{n+}]\) are molalities of sodium and metal ion in solution, respectively. \(\gamma_{Na}^n\) and \(\gamma_M^n\) are activity coefficients of the two exchanging ions in the solution, respectively. \(f_{Na}^n\) and \(f_M\) denote activity coefficients of the ions in the exchanger, respectively. The ratio of the activity coefficient \(\frac{\gamma_{Na}^n}{\gamma_M^n}\) is considered to be 1.0 in a dilute solution (Barrer and Klinowski, 1974). \(\overline{X}^i\) \((i = Na or metal ion)\) represents an equivalent fraction of sodium and metal ion in the solid. It is defined by

\[
\overline{X}_{Na} = \frac{[Na^+]}{n[\overline{M}^{n+}] + [Na^+]}, \quad \overline{X}_M = \frac{n[\overline{M}^{n+}]}{n[\overline{M}^{n+}] + [Na^+]} \]  (2.3)

The equivalent fraction (\(X_i\)) of ions in the solution are defined by

\[
X_{Na} = \frac{[Na^+]}{n[M^{n+}] + [Na^+]}, \quad X_M = \frac{n[M^{n+}]}{n[M^{n+}] + [Na^+]} \]  (2.4)

\([Na^+] + n[M^{n+}] = TN\)  (2.5)
Where TN represents total normality in the solution. Since \([\text{Na}^+]\) and \([\text{M}^{n+}]\) can be expressed as \(X_{\text{Na}}\) and \(X_{\text{M}}\), respectively, using the equation (2.4) and (2.5), the equation (2.2) can be rewritten as

\[
K = \frac{X_{\text{Na}}^n X_{\text{M}}^n f_{M}^{n}}{X_{\text{M}} X_{\text{Na}}^n f_{\text{M}}^{n}} [n(TN)^{n-1}] = \frac{(1 - X_{\text{M}})^n X_{\text{M}}^n f_{\text{M}}^{n}}{X_{\text{M}} (1 - X_{\text{M}})^n f_{\text{M}}^{n}} [n(TN)^{n-1}]
\]

(2.6)

Using selectivity coefficient, \(K_{\text{Na}}^{M}\), \(K\) can be defined by (Barrer and Klinowski, 1974)

\[
K = K_{\text{Na}}^{M} \frac{f_{M}}{f_{\text{Na}}}
\]

(2.7)

Therefore, from the equation (6) and (7) \(K_{\text{Na}}^{M}\) is expressed as

\[
k_{\text{Na}}^{M} = \frac{X_{\text{Na}}^n X_{\text{M}}^n f_{\text{M}}^{n}}{X_{\text{M}} X_{\text{Na}}^n f_{\text{M}}^{n}} [n(TN)^{n-1}] = \frac{(1 - X_{\text{M}})^n X_{\text{M}}^n f_{\text{M}}^{n}}{X_{\text{M}} (1 - X_{\text{M}})^n f_{\text{M}}^{n}} [n(TN)^{n-1}]
\]

(2.8)

The corrected selectivity coefficient \((K_{\text{Na}}^{M})\) can be determined by plotting the logarithm of \(K_{\text{Na}}^{M}\) vs. \(\log[K_{\text{Na}}^{M}]\) versus equivalent fraction of metal ion in solid \((\overline{X}_{\text{M}})\). The plot can be expressed as

\[
\log K_{\text{Na}}^{M} = 2C_{1} \overline{X}_{\text{M}} + \log(K_{\text{Na}}^{M})_{X_{\text{M}}, \overline{X}_{\text{M}} \rightarrow 0}
\]

(2.9)

Where, \(C_{1}\) is Kielland coefficient. If \(\log K_{\text{Na}}^{M} > 0\), the solid exchanger shows a preference for metal ions, while the exchanger shows a preference for sodium ions if \(\log K_{\text{Na}}^{M} < 0\).

There is no preference between these ions if \(\log K_{\text{Na}}^{M} = 0\).
2.5 Review of Previous Works

Sodium fluorophlogopite (Na-4-mica) was first synthesized in 1972 by Gregorkiewitz, and in 1987 its structure to accommodate three to four Na ions in the interlayer region was revealed along with ion exchange properties and its crystallographic data such as cell dimensions (Gregorkiewitz et al., 1987). Much attention had been given to Na-4-mica due to its high cation exchange capacity and swelling property which are different from common micas. However, the Na-4-mica product prepared by Gregorkiewitz was in the form of large flakes suggesting it was not applicable for ion exchange due to diffusion limitations to interlayer space. The small size of ion exchangers is essential for fast exchange reaction.

The small size of Na-4-mica could be prepared by Paulus (1990) through sol-gel process where a monophasic gel, which was prepared by addition of tetraethylorthosilicate (TEOS) to mixture of Al(NO$_3$)$_3$ $\cdot$ 9H$_2$O and Mg(NO$_3$)$_2$ $\cdot$ 6H$_2$O in absolute ethanol, was dried and then the formed gel powder was heated at 890°C for 18 hrs in a furnace after mixing the powder with 50% by weight of NaF (Paulus et al., 1992). This Na-4-mica showed a high selectivity for strontium which is one of the important radioactive species. However, this method was complicated and expensive to prepare Na-4-mica, even though the synthesis was successful for the preparation of small sized crystals.

Franklin and Lee (1996) synthesized Na-4-mica using a solid state synthesis where all of the precursors were mixed and then directly calcined in a Pt crucible, so that the gel formation process could be deleted. In order to save cost for Na-4-mica synthesis in a solid state, calcined kaolinite (meta-kaolinite) was used as a source for Al and Si of
Na-4-mica because kaolinite was cheap (Komarneni et al., 1998; Kodama et al., 1999). Also, kaolinite was directly used as the aluminosilicate source to delete the calcination step to form the meta-kaolinite (Kodama et al., 2000). Kodama et al. (2004) used ultrafine Na-4-mica with the size of ~ 0.2µm to determine selectivity for alkali and alkaline earth metal cations and their uptake kinetics. The above ~ 0.2µm mica was synthesized with the direct use of kaolinite in the reaction medium.

In addition to developing the simple and economical synthesis procedure, an attempt to control the particle size of Na-4-mica was successful using different ratios of NaCl to Al₂O₃ (Park et al., 2002). They also synthesized relatively pure Na-4-mica, and identified phases of hydrated and dehydrated Na-4-mica using NaCl melt method. The procedures such as removing impurities with boric acid and resaturating with NaCl solution is not necessary for this method where fumed silica, Al-boehmite, MgF₂, and NaCl were used as precursors. Komarneni et al. (2005) and Alba et al. (2006) successfully prepared a series of Na-synthetic micas with different charge densities using NaCl melt method as well as characterized the micas using ²⁹Si and ²⁷Al NMR.

Additionally, the Kd values for Sr²⁺ and Ba²⁺ were determined. These synthetic micas are called Na-2, Na-3, and Na-4-micas depending on two, three, four interlayer Na ions per unit cell. Ravella et al. (2008) investigated selectivity of Na-micas and Mg-micas for Cu²⁺ using isotherm and Kielland plot. The high selectivity for Cu²⁺ was shown in Na-2-mica and its derivative.

Depending on the above synthesis methods, the selectivity and isotherm for radioactive species and heavy metals were found to be different, which indicates the synthesis method and precursors possibly affect selectivity of the Na-micas for
contaminants. Therefore, it is crucial to develop an effective method and precursors, and once a new method and precursors are successfully developed and employed in the synthesis of Na-micas, selectivity and ion exchange properties of Na-micas should be investigated for target ions.

As mentioned above, Kuznicki (1990) first hydrothermally synthesized Na-ETS-4 in Teflon-lined autoclaves at between 100 and 300 °C with a variety of heating times between 8 and 40 days in high pH. TiCl₄ was used as a Ti source. However, this Ti compound is very difficult to handle because it is very sensitive. So instead of that, TiO₂ solid was used (Liu et al., 1996). Various titanium (e.g., titanium trichloride, titanium tetrachloride, titanium isopropoxide, titanium butoxide, titanic sulfate and titanium dioxide) and silicon (e.g., sodium silicate, sodium disilicate, colloidal silica and tetraethyl orthosilicate) sources were employed to synthesize ETS-4 at temperatures varying between 130 and 230 °C (Xu et al., 2001; Nair et al., 2001; Braunbarth et al., 2000; Kuznicki, 1990; Mintova et al., 1997; Kuznicki et al., 2000; Chapman et al., 1990; Philippou et al., 1996; Miraglia et al., 2004; Yilmaz et al., 2004). Addition of some organic agents (e.g., tetramethylammonium), aging and seeding of the synthesis mixtures were also studied (Braunbarth et al., 2000; Yilmaz et al., 2004). The initial pH values of synthesis mixtures were 10.5 or higher (Xu et al., 2001; Kuznicki, 1990; Mintova et al., 1997; Kuznicki et al., 2000; Yilmaz et al., 2004). Coutinho (2006) reported Engelhard titanosilicate (ETS-4) was successfully synthesized by microwave heating at 235 °C within 50 min using titanium (IV) butoxide as the titanium source. Microwave irradiation considerably reduced the synthesis time to less than 1 h as compared to conventional synthesis of 36 - 48 h.
There was an attempt to substitute the framework of titanium and silicon by other elements such as vanadium (Ferdov et al., 2007). Titano-vanadium silicate with the structure of ETS-4 was hydrothermally synthesized to produce V-ETS-4. Based on $^{51}$V and $^{29}$Si MAS NMR, and diffuse reflectance ultraviolet-visible and Raman spectroscopy analyses, vanadium substituted for Ti$^{4+}$ and five- and six-coordinated V$^{4+}$ existed, which indicated the vanadium could be incorporated into TiO$_5$ square-pyramids and the chains of TiO$_6$ octahedra in the ETS-4 structure.

Na-titanosilicate, which has a tunnel structure, was hydrothermally synthesized using Titanium isopropoxide and TiCl$_4$ as a Ti source at 170 and 200$^\circ$C for 8 and 10 days, respectively (Poojary et al., 1994; Poojary et al., 1996). This ion exchanger has two different sizes of exchange sites with different properties (6 ring framework site and 8 ring tunnel site) which affect ion exchange reaction. Ion exchange properties of Na-titanosilicate were investigated for K$^+$, Rb$^+$, Li$^+$, and Cs$^+$ (Poojary et al., 1994; Poojary et al., 1996; Clearfield et al., 2000). Due to the smaller exchange sites of the framework, K$^+$, Rb$^+$, and Cs$^+$ do not fit into the framework sites, but Li$^+$ and Na$^+$ occupy the 6 membered rings. However, K$^+$ and Rb$^+$ sometimes fill the near framework sites but Cs$^+$ only exclusively occupies the tunnel sites (Poojary et al., 1994).

The Na-titanosilicate is highly selective for Cs$^+$ at pH values of 1-14 in dilute solutions due to high coordination of Cs ions with the tunnel sites when Cs ions occupy the tunnel sites. However, in high Na concentration solution, Cs uptake is not effective. Like ETS-4, the attempt to substitute Ti$^{4+}$ for other cations such as Nb$^{4+}$ was successful. This Nb-titanosilicate is more selective for Cs than the Na-titanosilicate, because Cs was found to be twelve coordinated (Tripathi et al., 2003).
REFERENCES


CHAPTER 3

Na-TITANOSILICATES AND SWELLING Na-MICAS: SYNTHESIS, CHARACTERIZATION AND Sr AND Ba ION EXCHANGE PROPERTIES

3.1 INTRODUCTION

The increase of nuclear facilities has brought attention to environmental and health concerns due to radioactive wastes containing $^{90}{\text{Sr}}$ and $^{133}{\text{Ba}}$. Strontium-90 and Barium-133 are not only highly toxic radionuclides but also have relatively long half-lives which are about 28.5 and 10.5 years, respectively (Fetters et al., 1988). The treatment of radioactive contaminants is necessary to reduce storage space requirement (Lehr et al., 2001) and to prevent their release to environment causing long-term problems. A variety of techniques such as ion exchange, solidification/stabilization, and phytoremediation have been used for decontamination of aqueous nuclear wastes or contaminated soils (Paulus et al., 1992; Glasser, 1992; Groudev et al., 2001; Entry et al., 1996). Ion exchange technique is one of the most efficient and simple methods to selectively remove radioisotopes from liquid nuclear waste (Paulus et al., 1992; Komarneni et al., 2001). A large number of natural or synthetic materials such as zeolites, modified and synthetic clays, amorphous and crystalline zirconium phosphates, microporous and layered titanosilicates, and birnessite have been examined for removal of radionuclides(Paulus et al., 1992; El-Kamash et al., 2008; Cho et al., 2009; Stout et al., 2006; Dyer et al., 1997; Al-Attar et al., 2003).

Swelling and highly-charged sodium fluorophlogopites are synthetic micas of
2:1 type with trioctahedral sheets (Gregorkiewitz and Rausell-Colom 1987; Park et al., 2002; Kodama et al., 1999; Shimizu et al., 2004; Kodama et al., 2001). The high charge density of these micas results from isomorphous substitution of Al$^{3+}$ for Si$^{4+}$ in tetrahedral sheet. They are designated as Na-2, Na-3 and Na-4-micas depending on either 2, 3 or 4 Na ions occupy interlayers, respectively in one unit cell. It is known that they are excellent ion exchangers because of their high selectivity for radioactive species (Paulus et al., 1992; Komarneni et al., 2001) and heavy metal cations as well as high cation exchange capacities of 247 to 468 mequiv (100 g)$^{-1}$ on an anhydrous basis (Shimizu et al., 2004; Kodama et al., 2001; Komarneni et al., 2005). However, their ion exchange properties including ion selectivity may be affected by synthesis condition and species of raw materials employed (Kodama et al., 1999; Komarneni et al., 2005; Kodama and Komarneni, 2000). Recently, a new method using NaCl as a fluxing agent for synthesis of Na-micas has been developed to improve purity of Na-micas (Park et al., 2002; Komarneni et al., 2005). Hence, in this study, modified NaCl melt method using different Si source and reduced heating time was employed for the synthesis of Na-micas. For a comparison of Sr$^{2+}$ and Ba$^{2+}$ exchange properties with Na-micas, two sodium titanosilicates were chosen because they have high selectivity for radioactive species (Al-Attar et al., 2003; Poojary et al., 1994) and high cation exchange capacities (Attar et al., 2003). In addition, the selectivity for Ba$^{2+}$ has not been investigated thus far on the two sodium titanosilicates.

Na-ETS-4 (Engelhard Titano-Silicate-4) has a similar framework structure as that of the mineral zorite. The Na-ETS-4 used here is a synthetic microporous titanosilicate containing tetrahedrally coordinated silicon as well as octahedrally and
pentahedrally coordinated titanium (Nair et al., 2001). Sodium titanosilicate is also a synthetic material built of tetrahedral Si as well as octahedral Ti units, forming a tunnel structure (Poojary et al., 1994). Ion exchange selectivity behavior should be investigated in order to use these three micas and two titanosilicates as ion exchangers.

Therefore, the objectives of this work were to synthesize the Na-2, Na-3 and Na-4-micas (referred to hereinafter as Na-micas), and Na-ETS-4 and sodium titanosilicate (designated from here on as Na-titanosilicates), to characterize these synthetic phases by using XRD analysis, MAS NMR spectroscopy, and SEM and to investigate their Sr$^{2+}$ and Ba$^{2+}$ exchange selectivity properties using equilibrium isotherms and Kielland plots.

### Table 3.1. Ideal composition and theoretical CEC of Na-micas and Na-titanosilicates.

<table>
<thead>
<tr>
<th>Name</th>
<th>Ideal formula</th>
<th>CEC (meq / 100g)$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na4-mica</td>
<td>Na$_2$Si$_2$Al$_2$Mg$<em>3$O$</em>{10}$F$_2$</td>
<td>468</td>
</tr>
<tr>
<td>Na3-mica</td>
<td>Na$<em>{1.5}$Si$</em>{2.5}$Al$_{1.5}$Mg$<em>3$O$</em>{10}$F$_2$</td>
<td>361</td>
</tr>
<tr>
<td>Na2-mica</td>
<td>Na$_1$Si$_3$AlMg$<em>3$O$</em>{10}$F$_2$</td>
<td>247</td>
</tr>
<tr>
<td>Na-ETS-4</td>
<td>Na$<em>9$Si$</em>{12}$Ti$<em>5$O$</em>{38}$(OH) • 12H$_2$O</td>
<td>639</td>
</tr>
<tr>
<td>Na-titanosilicate</td>
<td>Na$_2$Ti$_2$O$_3$SiO$_4$ • 2H$_2$O</td>
<td>710</td>
</tr>
</tbody>
</table>

$^a$ CEC was calculated on a basis of the ideal formula.

### 3.2 MATERIALS AND METHODS

#### 3.2.1 Synthesis of Na-micas and Na-titanosilicates

Highly charged micas, Na$_n$Si$_{(8-n)}$Al$_6$Mg$_6$O$_{20}$F$_4$ • yH$_2$O (n=2, 3 and 4) were
prepared from powder mixtures with molar compositions of (8-n)SiO$_2$ (99.9 %, Aldrich), nAlOOH, 6MgF$_2$ (98 %, Aldrich) and 3nNaCl (100.3 %, J.T. Baker), using a similar procedure previously used (Komarneni et al., 2005; Alba et al., 2006). The precursors such as silicic acid, boehmite, magnesium fluoride and sodium chloride were thoroughly homogenized using a mortar and pestle. Afterwards, the mixtures were transferred to Pt-crucibles, and subsequently heated at 900 °C/ 10 hours for synthesizing Na-2, Na-3 and Na-4-micas in a programmable furnace. After heating, the solids were cooled down to room temperature. ETS-4 was synthesized based on procedures in the literatures (Braunbarth et al., 2000; Du et al., 1996). Titanium butoxide (TBO, 98 %, Alfa Aesar), fumed silica (99.9 %, CABOT corp.), sodium hydroxide (97 %, Alfa Aesar), aqueous hydrogen peroxide (30 %, Alfa Aesar), aqueous ammonia (25 %, EMD chemicals) and tetrabutylammonium bromide (TBABr, 98 %, Avocado) were used for the synthesis of sodium ETS4. 1.75 g of TBO was mixed with 10 ml of ammonia, followed by the addition of 6 ml H$_2$O$_2$ and 0.8 g NaOH to this mixture. After stirring, 0.8 g TBABr and 1.2 g fumed silica were added to the mixture. The reactant mixture was stirred for 3 hours and then hydrothermally treated in a stainless-steel autoclave at 180 °C for 8 days. A sodium titanosilicate was prepared using the same method as previously reported (Poojary et al., 1994). It was synthesized hydrothermally using 4.56 g of titanium isopropoxide (98 %, Acros organics), 3.33 g of tetraethylorthosilicate (98 %, Aldrich) and 26 ml of 6.32 M NaOH. All the above starting materials were well mixed under constant stirring and then 15ml of deionized water was added, followed by heating in a Teflon vessel of a stainless-steel autoclave at 170 °C under autogenous pressure for 8 days. After the thermal or hydrothermal treatment of each sample, the solid products were separated
from salts or solutions by centrifugation and the solids were washed with deionized water four times before drying at 60°C.

3.2.2 Characterization of Na-micas and Na-titanosilicates

Powder X-ray diffraction (XRD) patterns were collected to check for phase purity using a Scintag diffractometer with Cu Kα radiation and a Ge solid-state detector at a scanning speed of 3° 2θ/min with a scan step of 0.02° 2θ. Scanning electron microscope (Hitachi S-3000H) was used to determine morphology and particle size of samples sputtered with gold. $^{29}$Si and $^{27}$Al MAS NMR spectroscopy was used to determine the Si and Al environments in their structures. These environments will provide information on the charge density as well as the uniformity of charge distribution of micas (Komarneni et al., 2005), which may be keys for the ion exchange capacity and selectivity of the synthetic micas for metal cations. A Bruker Avance 500 spectrometer and 4 and 5 mm Doty MAS probes spun at 10-12 kHz for Al and 6 kHz for Si were used to produce the $^{27}$Al and $^{29}$Si NMR spectra at 11.7T. A 1μs (π/10) pulse for solution with a 1s delay and a 6πs (π/10) pulse with a 30s delay were used for $^{27}$Al and $^{29}$Si, respectively. The chemical shifts were recorded relative to tetramethylsilane (TMS) for $^{29}$Si and Al[(H₂O)₆]³⁺ for $^{27}$Al. The $^{29}$Si NMR spectra were analyzed for relative populations of each Si environment using the PeakFit, a curve fitting program.

3.2.3 Ion exchange experiments

The $2\text{Na}^+ \rightarrow M^{2+} (M=\text{Sr}^{2+} \text{ and } \text{Ba}^{2+})$ exchange isotherms and selectivity of Sr²⁺ and Ba²⁺ were determined for all the synthetic ion exchangers. For equilibration, 25mg of
each exchanger was put into centrifuge tubes and shaken with 25ml of ion exchange solution prepared with different equivalent ratios (M\textsuperscript{2+}/Na\textsuperscript{+}=0.1, 0.2, 0.3, 0.5, 0.75 and 1.0) at room temperature for 4 weeks. The total normality of the solutions for each sample was kept constant at 0.00247N, 0.00361N, 0.00468N, 0.00639N and 0.00710N, each of which was chosen from the theoretical total cation-exchange capacities of Na-2-mica, Na-3-mica, Na-4-mica, Na-ETS-4 and Na-titanosilicate, respectively. After equilibration, the solid ion exchangers and solutions were separated by centrifugation, and then the concentrations of Sr\textsuperscript{2+} and Ba\textsuperscript{2+} in solutions were analyzed by atomic absorption spectroscopy. The solids were washed free of salts and dried followed by characterization with XRD. All these batch experiments were conducted in triplicates to obtain reliable data and check for reproducibility. The relative standard deviation in the triplicates was below 5%. The isotherms and Kielland plots were plotted to determine Sr\textsuperscript{2+} and Ba\textsuperscript{2+} selectivities of Na-micas, Na-ETS-4 and Na-titanosilicate. In the Kielland plot, a corrected selectivity coefficient, $K_{Na}^{M}$ is a good indication of ion selectivity (Cho et al., 2009; Stout et al., 2006; Kodama et al., 1999). If log $K_{Na}^{M}$ > 0, ion exchangers prefer metal ions, M, while Na\textsuperscript{+} ions are more preferred when log $K_{Na}^{M}$ < 0. When log $K_{Na}^{M}$ is equal to zero, no preference for either ion is indicated.

3.3 RESULTS AND DISCUSSION

3.3.1 Characterization of Na-micas, Na-ETS-4, and Na-titanosilicate

The XRD patterns of Na-2, Na-3 and Na-4-micas are shown in Fig 3.1 and these match those reported previously (Park et al., 2002; Komarneni et al., 2005; Alba et al.,
Their patterns are very similar to each other (Fig 3.1) and the Na-micas are very highly crystallized as indicated by their narrow and sharp XRD reflections. All the mica samples showed strong 001 reflections of 12.14-12.17 Å indicative of hydrated Na-mica phases, but the unhydrated phase of 9.6 Å was found in only Na-2-mica sample. Also, the 00l reflections showed high intensities, suggesting characteristics of layer structure of mica samples. Although the mica phases were highly dominant, trace impurity of neighborite (NaMgF3 PDF no. 00-013-0303) was identified in all three mica products and additionally Na-2 and Na-3-micas appeared to include trace amounts of sodalite (Na₄Al₃Si₃O₁₂Cl PDF no. 00-037-0476) and albite (NaAlSi₃O₈ PDF no. 00-009-0466). Fig 3.2 displays the X-ray powder diffraction patterns of Na-ETS-4 and Na-titanosilicate indicating that their patterns are consistent with those reported in previous studies (Braunbarth et al., 2000; Philippou and Anderson 1996; Clearfield et al., 2000). The X-ray results showed that the two synthesized titanosilicate phases were highly crystalline and phase pure materials.
Figure 3.1. XRD patterns of (a) Na-2-mica, (b) Na-3-mica and (c) Na-4-mica.
Figure 3.2. XRD patterns of (a) Na-ETS4 and (b) Na-titanosilicate.
$^{29}$Si NMR spectra show the nearest neighbor environments of Si atoms in tetrahedral sheets of Na-2, Na-3 and Na-4-micas (Fig. 3.3). Unlike their X-ray patterns, the results of the $^{29}$Si MAS NMR spectra easily distinguish the various micas by revealing the different charges of these synthetic layer silicates, because the chemical shift values are indicative of extent of Al substitution for Si. The NMR spectra of Na-micas can be well fitted by Gaussian deconvolution using 4 possible peak assignments based on previous studies (Komarneni et al., 2005; Alba et al., 2006). The chemical shift values of each Si environment of all Na-micas are presented in Table 3.2. Depending on the Si/Al ratio of Na-micas, the chemical shift values and the relative areas of local Si environments of micas are different as shown in Table 3.2 and Fig. 3.3. Full widths at half maximum are between 3.6 and 6.5 ppm, which indicates that $^{29}$Si MAS NMR spectra of Na-micas are between broad lines for highly disordered systems such as glassy materials and narrow peaks for perfectly ordered systems (Engelhardt and Michel, 1987). This moderate broadening of the spectra may be due to the presence of some glassy phase (Komarneni et al., 1999) and/or overlapping of aluminosilicate impurities such as albite and sodalite (Alba et al., 2006). Each Si(nAl) component of all Na-micas shifts toward the less negative value due to more electronic deshielding at Si atoms, as Al contents increase in the tetrahedral sheets. This shifting is consistent with the reported result (Sanz et al., 2006). The relative areas of the Si(3Al) environments of Na-micas increased with increasing Al amounts, which indicates their increasing layer charge density. Therefore, based on the comparison of the relative areas of each Si(nAl) environment, Na-4-mica had the largest layer charge density while Na-2-mica showed the least charge density.
based on the $^{29}\text{Si}$ MAS NMR spectra (Komarneni et al., 2005). Na-3-mica showed intermediate charge density, as expected from a theoretical basis.

Table 3.2. Chemical shift values, R.A.$^a$ and FWHM$^b$ of each Si(nAl) environment derived from deconvoluted $^{29}\text{Si}$ NMR spectra of Na-micas.

<table>
<thead>
<tr>
<th>Si(nAl)</th>
<th>$\delta$ (ppm)</th>
<th>R.A.</th>
<th>FWHM (ppm)</th>
<th>$\delta$ (ppm)</th>
<th>R.A.</th>
<th>FWHM (ppm)</th>
<th>$\delta$ (ppm)</th>
<th>R.A.</th>
<th>FWHM (ppm)</th>
<th>$\delta$ (ppm)</th>
<th>R.A.</th>
<th>FWHM (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si(3Al)</td>
<td>-74.1;</td>
<td>28;</td>
<td>6.54;</td>
<td>-81.8</td>
<td>86</td>
<td>3.56</td>
<td>-85.6</td>
<td>58</td>
<td>4.63</td>
<td>-90.2</td>
<td>22</td>
<td>6.04</td>
</tr>
<tr>
<td></td>
<td>-77.8</td>
<td></td>
<td>3.93</td>
<td></td>
<td></td>
<td></td>
<td></td>
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$^a$ R.A. = Relative area  
$^b$ FWHM = Full width at half maximum
Figure 3.3. $^{29}\text{Si}$ MAS NMR spectra of (a) Na-2-mica, (b) Na-3-mica, and (c) Na-4-mica. The four labeled 0, 1, 2, and 3 components correspond to Si(3Al), Si(2Al), Si(1Al) and Si(0Al) environments of Si, respectively. The solid and dotted lines represent convoluted and deconvoluted $^{29}\text{Si}$ MAS NMR spectra, respectively.
The $^{27}$Al MAS NMR spectra of Na-micas are given in Fig. 3.4, which show whether Al coordination is tetrahedral or octahedral. Consistent with the previous data (Sanz and Serratosa, 1984; Muller et al., 1981), Na-3 and Na-4-micas showed small amounts of octahedrally coordinated Al$^{3+}$ in Mg trioctahedral sheets resonating at 4.0 and 7.3 ppm, respectively and the octahedral coordination of Al increased as the Si/Al ratio decreased (Fig. 3.4). However, most of the Al was predominantly present in tetrahedral sheets of Na-3 and Na-4-micas, as evidenced by very strong tetrahedral Al resonances at 67.6 and 68.5 ppm, respectively (Fig. 3.4). The octahedral Al is expected to lead to a reduction in negative charges of layers in Na-3 and Na-4-micas because positive charges are produced by the substitution of Al$^{3+}$ for Mg$^{2+}$ in octahedral sheets, which compensates for negative charges created by the replacement of Al$^{3+}$ for Si$^{4+}$ in the tetrahedral sheets. The $^{27}$Al MAS NMR spectrum for Na-2-mica with the highest Si/Al shows only one Al resonance at 67.3 ppm, indicating the presence of only tetrahedral Al.

Na-2-mica showed only one Si(3Al) resonance at -79.2 ppm while both Na-3 and Na-4-micas showed two resonances assigned to the Si(3Al) environments at around -74 and -77.8 ppm, as has been reported previously but not explained (Komarneni et al., 2005; Alba et al., 2006). The two chemical shifts of the Si(3Al) component are likely to be related to different Si(3Al) environments resulting from Al substitution for Mg in the trioctahedral sheet. Each apical oxygen of Si tetrahedra surrounded by 3 Al$^{3+}$ is coordinated to 3 Mg$^{2+}$ in the trioctahedral sheet, if all octahedral sites are filled with Mg atoms. However, in order to compensate the high tetrahedral charge deficit caused by 3 tetrahedral Al$^{3+}$, some Al atoms occupied the octahedral sites and were coordinated to apical oxygens by their substitution for some portion of 3 Mg atoms in Na-3 and Na-4-
micas (Fig. 3.4), which apparently led to the different Si(3Al) environments resulting in the less negative values around -74 ppm. The trend of such chemical shift toward the less negative value by more Al incorporation into the octahedral sites to satisfy the tetrahedral charge deficit is in accordance with the results for other trioctahedral micas (Sanz et al., 2006).

The local binding configurations of silicon atoms in Na-ETS-4 and Na-titanosilicate were also investigated using $^{29}\text{Si}$ MAS NMR spectroscopy. Fig. 3.5 shows the $^{29}\text{Si}$ MAS NMR spectra of Na-ETS-4 and Na-titanosilicate. In the Na-ETS-4 spectrum, one major peak at -90.4 ppm and a small shoulder at -95 ppm are observed, reflecting two different Si environments. The former can be assigned to Si(2Si, 2Ti$_{\text{oct}}$) and the latter to Si(3Si, 1Ti$_{\text{penta}}$) (Philippou and Anderson 1996; Cruciani et al., 1998). The $^{29}\text{Si}$ MAS NMR spectrum of Na-titanosilicate exhibited a main peak centered at -81.5 ppm, which can be attributed to Si(4Ti) (Balmer et al., 1997; Cherry et al., 2004), indicating a local environment of tetrahedral Si connecting to two other Ti clusters in the framework of Na-titanosilicates. Thus, $^{29}\text{Si}$ MAS NMR spectroscopy of Na-titanosilicates confirms their structures in addition to XRD characterization.

Scanning electron micrographs of all samples are given in Fig. 3.6. The plate-like particles of Na-micas show pseudohexagonal morphology and their particle size is in the range of 1 to 4 μm (Fig. 3.6a, b and c). Na-ETS-4 has a particle size of approximately 1 μm showing a morphological form of rectangular prisms (Fig. 3.6d). The SEM micrograph of Na-titanosilicate is shown in Fig. 3.6e. The crystal size of Na-titanosilicate is very small (0.1-1 μm), and the morphology is of a quasi-cubic form. The small particle
sizes of Na-micas and Na-titanosilicates are expected to be useful for fast ion exchange reactions as these exchange reactions are diffusion limited.

Figure 3.4. $^{27}$Al MAS NMR spectra of (a) Na-2-mica, (b) Na-3-mica, and (c) Na-4-mica.
Figure 3.5. $^{29}$Si MAS NMR spectra of (a) Na-ETS-4 and (b) Na-titanosilicate.
Figure 3.6. Scanning electron micrographs of (a) Na-2-mica, (b) Na-3-mica, (c) Na-4-mica, (d) Na-ETS-4, and (e) Na-titanosilicate.
3.3.2 $2\text{Na}^+ \rightarrow \text{Sr}^{2+}$ exchange properties of Na-micas

The $2\text{Na}^+ \rightarrow \text{Sr}^{2+}$ exchange isotherm for Na-2-mica is given in Fig. 3.7a, which gives the equivalent fraction of $\text{Sr}^{2+}$ in the solid phase against the equivalent fraction of $\text{Sr}^{2+}$ in solution phase. This isotherm steeply increases up to $X_{\text{Sr}} < \sim 0.72$ showing that the Na-2-mica took up most of Sr ions from equilibrium solutions. It seems that Sr ions in the mica phase occupy up to 84% of the total exchange sites of the Na-2-mica. The Kielland plot for the isotherm data shows that Na-2-mica is selective for $\text{Sr}^{2+}$ at $X_{\text{Sr}} < \sim 0.84$ because log $K^M_{\text{Na}}$ is greater than zero until $X_{\text{Sr}}$ is $\sim 0.84$ (Fig. 3.7b). This type of high uptake and high selectivity of Na-2-mica was reported previously for Cu$^{2+}$, although the Cu$^{2+}$ exchange experiment was done with a different Na-2-mica (Ravella et al., 2008). The Kielland coefficient ($C_1 = -1.16$) can be calculated because the data demonstrated a good linear relationship (coefficient of determination of linear regression, $r^2 = 0.95$).

Thus, it is apparent from the negative value of $C_1$ that $2\text{Na}^+ \rightarrow \text{Sr}^{2+}$ exchange process becomes more difficult as more Sr ions occupy the exchange sites. The isotherm for Na-3-mica shows that this mica took up a large amount of Sr ions from all $\text{Sr}^{2+}$ equilibrium solutions. The uptake by Na-3-mica apparently stopped at $X_{\text{Sr}} > 0.70$. Based on the Kielland plot, Na-3-mica displays a selectivity for $\text{Sr}^{2+}$ at $X_{\text{Sr}} < \sim 0.2$. Fig. 3.7a shows that the isotherm of Na-4-mica increases more gently than those of other 2 micas and seems to reach a maximum ($X_{\text{Sr}} = \sim 0.65$), suggesting Sr ions replaced Na ions up to $\sim 65\%$ of total theoretical cation exchange capacity. Na-4-mica is likely to be selective for $\text{Sr}^{2+}$ at only $X_{\text{Sr}} < \sim 0.1$ as indicated from Fig. 3.7b.
Figure 3.7. (a) isotherms and (b) Kielland plots for $2\text{Na}^+ \rightarrow \text{Sr}^{2+}$ exchange reaction on Na-2-mica, Na-3-mica, and Na-4-mica.
3.3.3 Relationship between Sr exchange and electrostatic force

The following observations are made from the XRD patterns of the Na-2-mica after $2\text{Na}^+ \rightarrow \text{Sr}^{2+}$ exchange reaction with the equilibrium solutions containing the different equivalent ratios of Sr to Na (Fig. 3.8): (1) The expanded (001) phases of $\sim 14.3$ to $\sim 13 \, \text{Å}$, which are different from the original (001) phase of $\sim 12 \, \text{Å}$ by $\text{Na}^+$, appear by the exchange with larger $\text{Sr}^{2+}$ ions; (2) The $d_{001}$ value of the expanded phase decreases with increasing Sr amount taken up to the interlayer space, which indicates that the uptake of Sr by micas has a correlation with expansion of interlayers; (3) $\sim 12 \, \text{Å}$ phase with high intensity still remains (Fig. 3.8f), even though most of $\text{Na}^+$ ($\sim 84 \%$) was replaced with $\text{Sr}^{2+}$ at exchange sites, indicating that the phase of $\sim 12 \, \text{Å}$ is attributed to Sr occupation of exchange sites; (4) The (001) phases are broadened (Fig. 3.8b, c, and d) due to different amounts of $\text{Sr}^{2+}$, $\text{Na}^+$, and water molecules in the interlayers. Recently, it was reported that $\text{Sr}^{2+}$ adsorbed on muscovite and orthoclase (001) surfaces simultaneously as a hydrated outer-sphere (OS) and a partially hydrated inner-sphere (IS) species (Park et al., 2006; Fenter et al., 2008). From these reports (Park et al., 2006; Fenter et al., 2008) and the above observations of 14.3 and $\sim 12.3 \, \text{Å}$ phases caused by Sr exchange, it may be suggested that there are distinctly two types of adsorbed Sr ions in the interlayer of Na-2-mica: a more hydrated Sr and a less hydrated Sr, the latter may be directly coordinated to oxygens of exchange sites. This suggestion is acceptable because a $\sim 12 \, \text{Å}$ phase results from one-layer hydrate (less hydrated cation), whereas a $\sim 14$-$15 \, \text{Å}$ phase is considered as two-layer hydrate (more hydrated cation) in the interlayer space of a variety of phyllosilicates (Sato et al., 1992).
According to the above suggestion, the change in the $d_{001}$ value of the expanded phase from 14.3 to 12.3 Å results from the difference in the extent of hydration of Sr ions incorporated into the interlayer space. In the interlayer space of phyllosilicates, the hydration-dehydration process of cations may be related to two factors (Park et al., 2006): (1) electrostatic attraction between a cation and a negatively-charged layer, which keeps pulling a cation closely to the surface and consequently causes the partial hydration of the cation forming an IS species if the attraction is sufficiently strong, and (2) ion hydration strength, which keeps water sphere surrounding a cation. The hydration-dehydration process of interlayer cations, therefore, occurs from an energetic imbalance between the electrostatic attraction and ion hydration strength. The electrostatic attractive force is given roughly by

$$ E = \frac{z^+ z^- e^2}{\epsilon r_A} $$

(3.1)

where $z^+$ is the cation charge, $z^-$ is the local surface charge, $e$ is the unit of electron charge, $\epsilon$ is the dielectric constant of water, and $r_A$ is a distance separating the two charges. McBride suggested divalent cations can limit clay swelling by a large electrostatic attraction force, which is associated to the dielectric constant (McBride, 1994). The dielectric constant is affected by high-charged cations which strongly order the dipoles of water molecules around them, considerably lowering the dielectric constant of water near the highly charged cations. As a result, the electrostatic attraction increases as divalent or polyvalent cations increase in the interlayer space. There is another explanation accounting for the strong electrostatic attraction by divalent cations, which is known as ion-ion correlations (Kjellander et al., 1988). It has been used to explain the
strong electrostatic attraction between like charged surfaces in the presence of divalent counter ions (Kjellander et al., 1988; Kjellander et al., 1990; Segad et al., 2010; Guldbrand et al., 1984). Whether the increasing electrostatic attraction with the increasing adsorbed Sr\(^{2+}\) amount is due to a decrease in dielectric constant and/or ion-ion correlations, it causes the dehydration of Sr ions, which leads to the decrease in d-spacing of Na-2-mica (Fig. 3.8f).

In addition to the effect of divalent cations, the layer charge density is one of the factors affecting the electrostatic attraction between the negatively charged layers and cations. The electrostatic force increases with the increasing layer charge density. The high layer charge density, therefore, enhances the partial dehydration of an adsorbed Sr\(^{2+}\), leading to the decreased d-spacing in Na-micas. The increasing order of the layer charge density is Na-4 > Na-3 > Na-2-mica, as proved with the NMR analysis. The effect of layer charge density is well reflected in the XRD patterns of the Na-mica after 2Na\(^+\) \(\rightarrow\) Sr\(^{2+}\) exchange reactions with the different Sr equilibrating solutions (Figs. 3.8, 9 and 10). Fig. 3.9 shows that there are expanded phases of ~14 Å in Na-3-mica indicating the existence of Sr ions with different extents of hydration. However, Na-3-mica expands less than Na-2-mica by Sr exchange because Sr ions lose more of their surrounding water molecules due to the increased electrostatic attraction by the higher charge density and therefore, enhancing ~12 Å phase (Figs. 3.8 and 9). Like the Na-2-mica, the d-spacings of the expanded phases decrease from 13.8 to 12.2 Å with increasing Sr uptake in the interlayer space because of the dehydration of Sr ions by an increase in electrostatic force. In contrast to Na-2 and Na-3-micas, Na-4-mica has ~13.8 Å phases with very low intensity indicating that only a small fraction of adsorbed Sr ions holds a large water-
sphere due to its highest layer charge density. A decrease in d-spacing of the expanded phase by the increased Sr uptake is not observed in the case of Na-4-mica (Fig. 3.10) because most of Sr ions already lost many water molecules and led to ~12 Å phases by its higher layer charge density.

Figure 3.8. XRD patterns of Na-2-mica for (001) phase change after $2\text{Na}^+ \rightarrow \text{Sr}^{2+}$ exchange reaction with (a) 0.00025 N SrCl$_2$ + 0.00222 N NaCl, (b) 0.00049 N SrCl$_2$ + 0.00197 N NaCl, (c) 0.00074 N SrCl$_2$ + 0.00173 N NaCl, (d) 0.00123 N SrCl$_2$ + 0.00123 N NaCl, (e) 0.00185 N SrCl$_2$ + 0.00062 N NaCl, (f) 0.00247 N SrCl$_2$. 
Figure 3.9. XRD patterns of Na-3-mica for (001) phase change after $2\text{Na}^+ \rightarrow \text{Sr}^{2+}$ exchange reaction with (a) 0.00036 N SrCl$_2$ + 0.00324 N NaCl, (b) 0.00072 N SrCl$_2$ + 0.00288 N NaCl, (c) 0.00108 N SrCl$_2$ + 0.00252 N NaCl, (d) 0.00180 N SrCl$_2$ + 0.00180 N NaCl, (e) 0.00270 N SrCl$_2$ + 0.00090 N NaCl, (f) 0.00361 N SrCl$_2$. 
Figure 3.10. XRD patterns of Na-4-mica for (001) phase change after $2\text{Na}^+ \rightarrow \text{Sr}^{2+}$ exchange reaction with (a) 0.00047 N SrCl$_2$ + 0.00422 N NaCl, (b) 0.00094 N SrCl$_2$ + 0.00375 N NaCl, (c) 0.00141 N SrCl$_2$ + 0.00328 N NaCl, (d) 0.00234 N SrCl$_2$ + 0.00234 N NaCl, (e) 0.00351 N SrCl$_2$ + 0.00117 N NaCl, (f) 0.00468 N SrCl$_2$. 
3.3.4 Selectivity of Na-micas for $\text{Sr}^{2+}$

Na-2-mica shows the highest selectivity for $\text{Sr}^{2+}$ as compared to the other two micas. The difference in the selectivity for the $2\text{Na}^+ \rightarrow \text{Sr}^{2+}$ exchange is hypothesized to be associated with the accessibility to exchange sites as a consequence of expansibility of the interlayers based on their layer charge densities. In general, lower charge density in layers leads to greater expansion of the interlayers as can be seen by comparing Figs. 3.8, 9 and 10. The exchange of $\text{Sr}^{2+}$ in the interlayers of Na-2-mica leads to the highest expansion. This expansibility apparently results in easier and more access of exchanging ions to charged sites and consequently leads to higher selectivity of $\text{Sr}^{2+}$ in Na-2-mica than in the other two micas (Fig. 3.7b). This relationship between the expansibility and selectivity is consistent with the previous result (Ravella et al., 2008), where Na-2-mica showed higher selectivity for $\text{Cu}^{2+}$ than other micas. However, the expansion of layers is limited and the interlayer space can be reduced by the strong electrostatic attraction between the adsorbed cation and the negatively charged layers which increases with increasing $\text{Sr}$ amount in the interlayer. Because the selectivity for $\text{Sr}^{2+}$ is higher than $\text{Na}^+$ in this mica, $\text{Sr}^{2+}$ proportion in the interlayers increases at initial exchange stage for the $2\text{Na}^+ \rightarrow \text{Sr}^{2+}$ exchange and this change in the cationic composition in the interlayer causes a subsequent decrease in the interlayer space, which then affects the selectivity for $\text{Sr}^{2+}$. Hence, the effect of $\text{Sr}^{2+}$ amount on the interlayer space would be intensified as the $\text{Sr}$ amount increases. The conceptual model for this feedback interaction between expansion and cation exchange selectivity was suggested for swelling smectites with very low charge density (Laird and Shang, 1997) and this also applies to Na-micas.
3.3.5 $2\text{Na}^+ \rightarrow \text{Sr}^{2+}$ exchange properties of Na-titanosilicates

As seen in Fig. 3.11a, the $2\text{Na}^+ \rightarrow \text{Sr}^{2+}$ exchange isotherm for Na-ETS-4 shows that this exchanger took up most of the Sr ions from all Sr equilibrating solutions. Sr ions occupy all exchange sites up to ~97% because the maximum value of $X_{\text{Sr}}$ is ~0.97. According to Kielland plot of the isotherm data, Na-ETS-4 is highly selective for Sr$^{2+}$ because all data points fall above zero and the selectivity coefficient increases up to $X_{\text{Sr}} < ~0.5$ (Fig. 3.11b). This high selectivity for Sr ions may be firstly due to improved structural stability of Sr-exchanged-ETS-4 based on the thermal stability of Na-ETS-4 (Marathe et al., 2005). Secondly, it seems to be associated with Sr ions adsorbing preferentially on one of the exchange sites. The Sr$^{2+}$ preferentially occupies the cavity produced by the titania chain and the bridging titanosilicate unit because, in that exchange site, the larger Sr ions can form shorter bond with oxygen and water molecules than Na ions (Braunbarth et al., 2000). Therefore, after occupying those favorable sites, Sr ions are located at other exchange sites which are less favorable. This may be why the selectivity increases at the low Sr occupancy ($X_{\text{Sr}} < ~0.5$).

The $2\text{Na}^+ \rightarrow \text{Sr}^{2+}$ exchange isotherm for Na-titanosilicate shows a trend similar to that of Na-ETS-4. In Fig 3.11a, the high uptakes for Sr ions by Na-titanosilicate are observed at all of data points. The maximum of the equivalent fraction of Sr$^{2+}$ in solid phase is ~0.91. The Kielland plot of Na-titanosilicate shows that it has a high preference for Sr$^{2+}$ for all Sr exchange solutions (Fig. 3.11b). Na-titanosilicate has a framework structure enclosing tunnels along with the c-axis and has two exchange sites for Na$^+$. Half of the Na$^+$ ions are loosely held within the tunnels and the other half of Na$^+$ ions occupy
the framework cavities in between silicate groups (Poojary et al., 1994; Clearfield et al., 2000). However, the framework sites are too small to accommodate large ions such as K, Cs, and Rb (Clearfield et al., 2000; Tripathi et al., 2005). From $2\text{Na}^+ \rightarrow \text{Sr}^{2+}$ exchange isotherm for Na-titanosilicate, it is suggested that Sr ions can occupy both of the exchange sites, including the framework sites, because $\sim 91\%$ of Na ions were replaced with Sr ions from the exchange sites. The Na$^+$ ions within the tunnels are easily replaced with Sr ions because they are loosely held in the tunnels (Clearfield et al., 2000). This may explain the increase in selectivity at $X_{Sr} < \sim 0.5$ and the plateau at $X_{Sr} > \sim 0.5$.

Tripathi et al. suggested that a high coordination number formed by the exchange reactions leads to high selectivity of exchanger due to the increase in the bonding strength (Tripathi et al., 2005). They demonstrated that, with the increase from 25 to 55 mol% Sr$^{2+}$ exchange solutions, the structural features of H-titanosilicate such as space group and crystal system change, but the coordination number of an adsorbed Sr decreases from 10 to 8. However, our result shows that the selectivity coefficient increases up to $X_{Sr} = \sim 0.73$ by increasing the equivalent fraction of Sr in solid phase (Fig. 3.11b). This might be due to the increase in the binding affinity by the change in geometry which may be caused by the above structural changes.
Figure 3.11. (a) isotherms and (b) Kielland plots for $2\text{Na}^+ \rightarrow \text{Sr}^{2+}$ exchange reaction on Na-ETS-4 and Na-titanosilicate. Na-TS represents Na-titanosilicate.
3.3.6 $2\text{Na}^+ \rightarrow \text{Ba}^{2+}$ exchange properties of Na-micas

As shown in Fig. 3.12a, the isotherm for $2\text{Na}^+ \rightarrow \text{Ba}^{2+}$ exchange with Na-2-mica is highly steep up to $X_{\text{Ba}} < \sim0.5$, indicating that Na-2-mica took up a majority of Ba ions at all data points, which is similar to the case of its Sr exchange. $\text{Ba}^{2+}$ seems to occupy ~95% of all exchange sites (2.47 meq/g of the theoretical exchange capacity) of Na-2-mica. The Kielland plot for Na-2-mica indicates that $\text{Ba}^{2+}$ is highly preferred over $\text{Na}^+$ because all data points are above the zero after the equilibrium with all Ba exchange solutions (Fig. 3.12b). The isotherm of Na-3-mica increases very steeply up to $X_{\text{Ba}} < \sim0.5$ showing very good $\text{Ba}^{2+}$ uptake until Ba ions occupy ~50% of all exchange sites of Na-3-mica, and then immediately reaches a maximum ($X_{\text{Ba}} = \sim0.61$) indicating that the limitation for Ba uptake occurs at $X_{\text{Ba}} > \sim0.5$. According to the Kielland plot in Fig. 3.12b, Na-3-mica is selective for $\text{Ba}^{2+}$ at $X_{\text{Ba}} < \sim0.5$, but the log K value starts to decrease at $X_{\text{Ba}} > \sim0.3$. Moreover, from $X_{\text{Ba}} > \sim0.5$ the log K value decreases more rapidly to less than zero at $X_{\text{Ba}} = \sim0.61$. For Na-4-mica, the isotherm shows (Fig. 3.12a) that the mica took up most of Ba ions from solution phases at $X_{\text{Ba}} < \sim0.28$, but after this point, it reaches a plateau, suggesting no more significant Ba uptake after Ba ions occupy ~28% of all exchange sites. The Kielland plot suggests that Na-4-mica has a selectivity for $\text{Ba}^{2+}$ at $X_{\text{Ba}} < \sim0.2$ because the log K value is greater than zero in that range, but the preference of Na-4-mica drastically decreases when the Ba fraction in the mica is higher than 0.2. Unlike the Sr exchange reaction, these drastic decreases in the Ba selectivity
Figure 3.12. (a) isotherms and (b) Kielland plots for $2\text{Na}^+ \rightarrow \text{Ba}^{2+}$ exchange reaction on Na-2-mica, Na-3-mica, and Na-4-mica.
coefficients of Na-3 and Na-4-micas along with the limitation of Ba uptake, may result from the steric limitation for exchanging cations. These steric limitations are caused by adsorbed cations trapped or fixed in the ditrigonal holes in the restricted interlayer space (~2.8 Å) (Kodama et al., 2004). Therefore, it prevents further exchange reaction to the interior of the interlayer space.

### 3.3.7 Relationship between Ba exchange and electrostatic force

The XRD patterns of Na-micas after $2\text{Na}^+ \rightarrow \text{Ba}^{2+}$ exchange reaction with the equilibrium solutions with various equivalent ratios of Ba to Na are shown in Figs. 3.13, 14, and 15. Like the case of $2\text{Na}^+ \rightarrow \text{Sr}^{2+}$ exchange in all three Na-micas, two different (001) phases of ~12 Å and ~14 Å appear indicating the existence of Ba ions with the different hydration levels after $2\text{Na}^+ \rightarrow \text{Ba}^{2+}$ exchange. The decrease in the d-spacing of ~14 Å to ~12 Å is observed with increasing adsorbed Ba amount in Na-2 and Na-3-micas. As explained in the case of Sr exchange, such decrease occurs due to the decrease in the degree of hydration of an adsorbed Ba$^{2+}$ by increasing electrostatic attraction that results from the increase in Ba uptake. The effect of the difference in the layer charge density among Na-micas on the electrostatic attraction can be seen in Figs. 3.13, 14, and 15 i.e., as the layer charge density increased, the 12 Å phase related to the less hydrated Ba$^{2+}$ is enhanced, and the expanded phase of ~14 Å by more hydrated Ba$^{2+}$ is reduced by stronger electrostatic force.
Figure 3.13. XRD patterns of Na-2-mica for (001) phase change after $2\text{Na}^+ \rightarrow \text{Ba}^{2+}$ exchange reaction with (a) 0.00025 N BaCl$_2$ + 0.00222 N NaCl, (b) 0.00049 N BaCl$_2$ + 0.00197 N NaCl, (c) 0.00074 N BaCl$_2$ + 0.00173 N NaCl, (d) 0.00123 N BaCl$_2$ + 0.00123 N NaCl, (e) 0.00185 N BaCl$_2$ + 0.00062 N NaCl, (f) 0.00247 N BaCl$_2$. 
Figure 3.14. XRD patterns of Na-3-mica for (001) phase change after $2\text{Na}^+ \rightarrow \text{Ba}^{2+}$ exchange reaction with (a) $0.00036 \text{ N BaCl}_2 + 0.00324 \text{ N NaCl}$, (b) $0.00072 \text{ N BaCl}_2 + 0.00288 \text{ N NaCl}$, (c) $0.00108 \text{ N BaCl}_2 + 0.00252 \text{ N NaCl}$, (d) $0.00180 \text{ N BaCl}_2 + 0.00180 \text{ N NaCl}$, (e) $0.00270 \text{ N BaCl}_2 + 0.00090 \text{ N NaCl}$, (f) $0.00361 \text{ N BaCl}_2$. 
Figure 3.15. XRD patterns of Na-4-mica for (001) phase change after $2\text{Na}^+ \rightarrow \text{Ba}^{2+}$ exchange reaction with (a) 0.00047 N BaCl$_2$ + 0.00422 N NaCl, (b) 0.00094 N BaCl$_2$ + 0.00375 N NaCl, (c) 0.00141 N BaCl$_2$ + 0.00328 N NaCl, (d) 0.00234 N BaCl$_2$ + 0.00234 N NaCl, (e) 0.00351 N BaCl$_2$ + 0.00117 N NaCl, (f) 0.00468 N BaCl$_2$. 
3.3.8 Selectivity of Na-micas for Ba$^{2+}$

Similar to Sr exchange reaction, the accessibility to exchange sites and expansibility of layers can explain differences in the selectivity of Na-micas for Ba exchange reaction. The Na-2-mica has high expansibility because of its low charge density as determined by $^{29}$Si MAS NMR data (Fig. 3.3). This expansibility leads to higher selectivity of Na-2-mica for Ba$^{2+}$ than those of two other micas due to easier and more access of Ba ions to exchanging sites in the restricted interlayer space (~2.8 Å). The higher selectivity of Na-3-mica for Ba$^{2+}$ than that of Na-4-mica would be described by more expansibility of Na-3-mica as indicated by the comparison of the XRD patterns in Figs. 3.14 and 15, and Na-4-mica is the least expandible, which causes an extremely slow diffusion and less access to the exchanging sites. This is likely to be the reason for the lowest selectivity of Na-4-mica for Ba$^{2+}$. The additional factor affecting the expansion of layers is the amount of Ba$^{2+}$ taken up by solid phase. The interlayer space of Na-micas decreases with the increasing electrostatic attraction, which results from the increase in the portion of Ba$^{2+}$ in the interlayer. Therefore, for the $2\text{Na}^+ \rightarrow \text{Ba}^{2+}$ exchange, the selectivity for Ba$^{2+}$ is lowered through the decreased d-spacing as Ba ions are taken up by the micas.

3.3.9 Difference in exchange reaction of Na-micas for Sr$^{2+}$ and Ba$^{2+}$

Sr$^{2+}$ is a smaller ion than Ba$^{2+}$ indicating its higher ionic potential with more negative hydration enthalpy (-1445 kJ mol$^{-1}$) than that of Ba$^{2+}$ (-1305 kJ mol$^{-1}$). Thus, it is suggested that Sr$^{2+}$ tends to keep a more hydrated form and be more mobile, while Ba$^{2+}$ is more readily dehydrated and more tightly adsorbed at exchange sites. As a result, Sr$^{2+}$
needs more energy to shed water than Ba\(^{2+}\). This may explain why the selectivity for Ba\(^{2+}\) is higher than that of Sr\(^{2+}\) at low concentrations of Ba in equilibrating solutions. These results are supported by previous results which suggested that Ba\(^{2+}\) prefers to adsorb in ditrigonal cavities on muscovite (001) surface forming inner-sphere complexes (a partially hydrated form) (Lee \textit{et al.}, 2007; Schlegel \textit{et al.}, 2006). This adsorption preference of Ba\(^{2+}\) in the ditrigonal holes, high layer charge density of Na-3 and Na-4-micas, and the increasing electrostatic attraction along with the increasing Ba\(^{2+}\) amount may result in the trapped Ba\(^{2+}\) in the ditrigonal holes leading to the limitation of Ba\(^{2+}\) uptake. The drastic decrease in the selectivity of Na-3 and Na-4-micas for Ba\(^{2+}\) after equilibrations with solutions of higher Ba\(^{2+}\) concentration could also be explained by the formation of inner sphere complexes.

That Sr\(^{2+}\) holds on to more water is reflected in the XRD pattern of Na-2-mica after 2Na\(^{+}\) → Sr\(^{2+}\) exchange reaction with the exchange solution of 0.00247N (Fig. 3.8f). The remaining 13 Å phase indicates the existence of a more hydrated form with Sr\(^{2+}\) but this is not the case with Ba\(^{2+}\) (Fig. 3.13f). Also, there is a noticeable difference in the d-spacings between the expanded phases of Sr (~13.8 Å) and those of Ba (~14.1 Å) after exchange in both Na-3 and Na-4-micas. This difference seems to be because of the difference between the bonding distance of Sr-O (2.57-2.65 Å) (Chen \textit{et al.}, 1999; Sahai \textit{et al.}, 2000; Ohtaki and Radnai, 1993) and Ba-O (2.76-2.90 Å) (Zhang et al., 2001; Ohtaki and Radnai, 1993).
Table 3.3. Uptake amount of Sr\(^{2+}\) by Na-micas and Na-titanosilicates after 2Na\(^+\)→Sr\(^{2+}\) ion exchange reaction.

<table>
<thead>
<tr>
<th>Equivalent ratio of Hg: Na in exchange solution</th>
<th>Sr(^{2+}) uptake (meq/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Na-2-mica</td>
</tr>
<tr>
<td>0.1 : 0.9</td>
<td>0.247</td>
</tr>
<tr>
<td>0.2 : 0.8</td>
<td>0.493</td>
</tr>
<tr>
<td>0.3 : 0.7</td>
<td>0.739</td>
</tr>
<tr>
<td>0.5 : 0.5</td>
<td>1.227</td>
</tr>
<tr>
<td>0.75 : 0.25</td>
<td>1.794</td>
</tr>
<tr>
<td>1:00</td>
<td>2.277</td>
</tr>
</tbody>
</table>

Table 3.4. Uptake amount of Ba\(^{2+}\) by Na-micas and Na-titanosilicates after 2Na\(^+\)→Ba\(^{2+}\) ion exchange reaction.

<table>
<thead>
<tr>
<th>Equivalent ratio of Hg: Na in exchange solution</th>
<th>Ba(^{2+}) uptake (meq/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Na-2-mica</td>
</tr>
<tr>
<td>0.1 : 0.9</td>
<td>0.247</td>
</tr>
<tr>
<td>0.2 : 0.8</td>
<td>0.494</td>
</tr>
<tr>
<td>0.3 : 0.7</td>
<td>0.740</td>
</tr>
<tr>
<td>0.5 : 0.5</td>
<td>1.234</td>
</tr>
<tr>
<td>0.75 : 0.25</td>
<td>1.849</td>
</tr>
<tr>
<td>1:00</td>
<td>2.346</td>
</tr>
</tbody>
</table>
3.3.10 2Na⁺ → Ba²⁺ exchange properties of Na-titanosilicates

The isotherm for 2Na⁺ → Ba²⁺ exchange with Na-ETS-4 is shown in Fig 3.16a. It is suggested that Na-ETS-4 took up most of Ba²⁺ up to \( \bar{X}_{Ba} < \sim 0.74 \) because the isotherm is highly steep up to \( \bar{X}_{Ba} < \sim 0.74 \) and there seems to be no more meaningful uptake for barium after \( \bar{X}_{Ba} > \sim 0.74 \). Based on the Kielland plot shown in Fig. 3.16b, the log K values are greater than zero up to \( \bar{X}_{Ba} < \sim 0.74 \), indicating Na-ETS-4 is selective for Ba²⁺ in that range. When Ba ions occupy \( \sim 50\% \) of exchange sites in a structure, it seems that steric limitation is initiated at exchange sites between the exchanging cations because the selectivity of Na-ETS-4 drastically starts to decrease at \( \bar{X}_{Ba} = 0.50 \). Like Sr-exchanged-ETS-4, Ba-exchanged-ETS-4 has better structural stability than Na-ETS-4 (Marathe et al., 2005). Therefore, it may have resulted in the high selectivity coefficient for Ba²⁺.

The 2Na⁺ → Ba²⁺ exchange isotherm for Na-titanosilicate shows the uptake for Ba²⁺ is exceptionally good up to \( \bar{X}_{Ba} < \sim 0.49 \) and then the isotherm immediately flattens up to \( \bar{X}_{Ba} = \sim 0.59 \) suggesting that there is no more noticeable uptake at \( \bar{X}_{Ba} > \sim 0.49 \). As shown in Fig. 3.16b, the Kielland plot indicates that Na-titanosilicate is selective for Ba²⁺ in the range of \( \sim 0.3 \) to \( \sim 0.5 \) of \( \bar{X}_{Ba} \) but a drastic decrease in Ba selectivity occurs when Ba²⁺ ions replaced \( \sim 49\% \) of Na⁺ ions (\( \bar{X}_{Ba} = \sim 0.49 \)). This rapid reduction along with the difficulty of Ba²⁺ uptake may be associated with the steric limitation for the exchanging cations to proceed with further ion exchange (Kodama et al., 2004). Half of Na⁺, which is loosely held within the tunnels, is easily released during an exchange reaction, as
Figure 3.16. (a) Isotherms and (b) Kielland plots for $2\text{Na}^+ \rightarrow \text{Ba}^{2+}$ exchange reaction on Na-ETS-4 and Na-titanosilicate.
compared to the remainder in the small framework cavity. It is, therefore, suggested that the steric limitation may occur because the framework cavity is unable to accommodate $\text{Ba}^{2+}$ up to $\overline{X}_{\text{Ba}} > -0.49$ where Ba ions almost compensate for the charge of the tunnel sites.

### 3.4 CONCLUSIONS

We successfully synthesized Na-2-mica, Na-3-mica, and Na-4-mica with different charge densities using a modified NaCl melt method. The Na-micas with a variety of charge densities and Na-titanosilicates were characterized by $^{29}\text{Si}$ and $^{27}\text{Al}$ MAS NMR. Two different (001) phases of $\sim 12 \text{ Å}$ and $\sim 14 \text{ Å}$ indicated the existence of adsorbed $\text{Sr}^{2+}$ and $\text{Ba}^{2+}$ with different hydration levels in synthetic Na-micas after ion exchange reactions. The d-spacing decreased due to dehydration of cations by high electrostatic attraction between adsorbed cations and negatively charged layers. There are two factors affecting electrostatic force: amounts of divalent cations adsorbed and layer charge density. As the amount of adsorbed divalent cations and the layer charge density in interlayer space increased, the electrostatic attraction increased resulting in the increase in the extent of the dehydration of cations. Among synthetic micas, Na-2-mica showed the highest selectivity for $\text{Sr}^{2+}$ and $\text{Ba}^{2+}$. This high selectivity of Na-2-mica results from easy expansibility of the interlayers due to low charge density and thus more accessibility to exchanging sites. The selectivity of Na-micas for $\text{Sr}^{2+}$ and $\text{Ba}^{2+}$ was affected by the change in the expansibility as the uptake of the divalent cations increases in the interlayer. Unlike $\text{Sr}^{2+}$ exchange reaction, Na-2 and Na-3-mica showed drastic decrease in the
selectivity with no more significant uptake for Ba$^{2+}$ at $\bar{X}_{Ba} > 0.5$ and 0.28, respectively, due to the steric hindrance by the combination of adsorption preference of Ba$^{2+}$ for the ditrigonal cavities, their high layer charge densities, and an increasing electrostatic force with increasing Ba$^{2+}$ uptake. According to the isotherm for Sr exchange, Na-ETS-4 and Na-titanosilicate took up most of Sr ions from all exchange solutions and showed very high selectivity. In case of $2\text{Na}^+ \rightarrow \text{Ba}^{2+}$ exchange reaction, Ba$^{2+}$ was selective in Na-ETS-4 and Na-titanosilicate up to $\bar{X}_{Ba} < -0.74$ and in the range of $-0.3$ to $-0.5$ of $\bar{X}_{Ba}$, respectively. The high selectivity of Na-ETS-4 for Sr$^{2+}$ and Ba$^{2+}$ is likely due to the increase in structural stability of Sr- and Ba-ETS-4. The difficulty of Ba$^{2+}$ uptake and the rapid decrease in the selectivity coefficient of two titanosilicate exchangers for Ba$^{2+}$ suggests that the steric hindrance occurred at exchange sites. Therefore, Na-2-mica and Na-ETS-4 are potential candidates for the uptake of both Sr and Ba from nuclear waste solutions.
REFERENCES


CHAPTER 4

MERCURY (II) EXCHANGE PROPERTIES OF SODIUM-MICA, SODIUM-ETS-4, SODIUM-TITANOSILICATE

4.1 INTRODUCTION

Mercury is one of the major pollutants in the environment as it is released from fossil fuel burning, mining and smelting, and natural sources (Selin, 2009). It is not only easily transported in the form of vapor in the atmosphere but also transformed to organomercury which is more toxic than non-organomercury by 10 times (Boening, 2000). It has a severe impact on the environment because of its high toxicity and accumulation in organisms, even at the trace levels. Thus, in order to remediate mercury from contaminated sites and groundwater, various clean up techniques for mercury have been developed including chemical precipitation, electrokinetic treatment, ion exchange, bacteria accumulation and adsorption on activated carbon (Matlock et al., 2001; Reddy et al.; Lopes et al., 2007; Chen et al., 1997; Krishnan et al., 1994). Among several treatment technologies, ion exchange is one of the interesting processes due to its simple and efficient application. A great deal of interest has been given to natural zeolites, clays, oxides and synthetic ion exchangers for Hg removal (Chojnacki et al., 2004; Sarkar et al., 2000; Brigatti et al., 2005; Collins et al., 1999; Monteagudo et al., 2000).

The cation exchange capacity of ion exchangers and their selectivity for target ions are significant factors to consider in selecting ion exchangers. The synthetic ion exchangers described below have rigid structures, high cation exchange capacities, selectivity for some pollutants and compatibility with the environment. Synthetic highly-
charged sodium fluorophlogopites are expandable, unlike nonswelling natural micas and have high negative charge in the layers of 2:1 type with Mg trioctahedral sheets (Gregorkiewitz et al., 1987). The high charge density of these micas is due to isomorphic substitution in only tetrahedral sheets, ideally accommodating 2 to 4 exchangeable sodium ions in the interlayer spaces of one unit cell (Shimizu et al., 2004; Stout et al., 2003; Gregorkiewitz et al., 1987). They are informally called Na-2, Na-3 and Na-4-micas depending up on 2, 3 or 4 interlayer Na ions exist in one unit cell, respectively. Na-ETS-4 (Engelhard Titano-Silicate-4) is a synthetic microporous titanosilicate with a mixed octahedral and tetrahedral framework described as the random intergrowth of four hypothetical polymorphs, which differ in the arrangement of the titanosilicate bridging units (Nair et al., 2001). Sodium titanosilicate is also a synthetic ion exchanger built of tetrahedral Si and octahedral Ti units, which form a tunnel structure including exchangeable Na ions (Poojary et al., 1994). It was reported that they are good ion exchangers because of their high selectivity for radioactive species and heavy metal cations as well as high cation exchange capacities (Table 4.1) (Ravella et al., 2008; Komarneni et al., 2001; Kodama et al., 1999; Clearfield et al., 2000; Ferreira et al., 2009).

Therefore, the objective of this work was to investigate ion-exchange properties of the synthetic Na-2, Na-3 and Na-4-micas (referred to hereinafter as Na-micas), and Na-ETS-4 and sodium titanosilicate (designated from here on as Na-titanosilicate) for mercury (Hg$^{2+}$) using distribution coefficients, equilibrium isotherms, Kielland plots, and selectivity coefficients.
Table 4.1. Theoretical CEC and ideal formula of tested ion exchangers.

<table>
<thead>
<tr>
<th>Name</th>
<th>Ideal formula</th>
<th>CEC (meq / 100g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na4-mica</td>
<td>Na₂Si₂Al₂Mg₃O₁₀F₂</td>
<td>468</td>
</tr>
<tr>
<td>Na3-mica</td>
<td>Na₁.₅Si₂.₅Al₁.₅Mg₃O₁₀F₂</td>
<td>361</td>
</tr>
<tr>
<td>Na2-mica</td>
<td>Na₁Si₃AlMg₃O₁₀F₂</td>
<td>247</td>
</tr>
<tr>
<td>Na-ETS-4</td>
<td>Na₉Si₁₂Ti₅O₃₈(OH) • 12H₂O</td>
<td>639</td>
</tr>
<tr>
<td>Na-titanosilicate</td>
<td>Na₂Ti₂O₃SiO₄ • 2H₂O</td>
<td>710</td>
</tr>
</tbody>
</table>

* CEC was calculated on a basis of the ideal formula.

4.2 MATERIALS AND METHODS

4.2.1 Preparation and characterization of Na-micas and Na-titanosilicates

For the synthesis of highly charged Na-micas, NaₙSi₈-nAlₙMg₆O₂₀F₄ • yH₂O (n=2, 3 and 4), the powder mixtures with molar compositions of (8-n)SiO₂ (99.9 %, Aldrich), nAlOOH, 6MgF₂ (98 %, Aldrich) and 3nNaCl (100.3 %, J.T. Baker) were heated using Pt-crucibles in a furnace at 900 °C for 10 hours. Afterwards, the solids were slowly cooled down to room temperature. For the synthesis of Na-ETS-4, 10 ml of ammonia (25 %, EMD chemicals), 6 ml of H₂O₂ (30 %, Alfa Aesar) and 0.8 g of NaOH (97 %, Alfa Aesar) was mixed with 1.75 g of Titanium Butoxide (TBO, 98 %, Alfa Aesar). After 15 min mixing, 1.2 g of fumed silica (99.9 %, CABOT corp.) and 0.8 g of tetrabutylammonium bromide (TBABr, 98 %, Avocado) were added to the mixture and stirred further for 3 hours. The reactant mixture was hydrothermally treated in a stainless-steel autoclave at 180 °C for 8 days. For the synthesis of Na-titanosilicate, 4.56 g of titanium isopropoxide (98 %, Across organics), 3.33 g of tetraethyloorthosilicate (98 %,
Aldrich) and 26 ml of 6.32 M NaOH were well mixed and then 15 ml of deionized water was added. After that, the mixture was heated in a stainless-steel autoclave at 170 °C for 8 days. Following the thermal or hydrothermal treatment of each sample, the reactant solids were washed with deionized water and ethanol several times and dried at 60 °C. Powder X-ray diffraction (XRD) patterns were collected using a Scintag diffractometer with Cu Kα radiation and a Ge solid-state detector at a scanning speed of 3° 2θ / min with a scan step of 0.02° 2θ.

4.2.2 Distribution coefficient (Kd) determination

20 mg of each ion exchanger was equilibrated for 24 hrs with 25 ml of a 0.5 N NaNO₃ solution containing 0.0001 N Hg(NO₃)₂ at room temperature. After equilibrium, the solid and solution phases were separated by centrifugation. The solutions were analyzed for mercury by Milestone’s DMA-80 direct mercury analyzer. Triplicates were used for all the experiments. The Kd for Hg²⁺ was calculated by the following equation:

\[
K_d = \frac{\text{amount of Hg}^{2+} \text{ exchanged (meq/g)}}{\text{equilibrium concentration of Hg}^{2+} \text{ (meq/ml)}}
\]  

4.2.3 Ion exchange experiments

25 mg of each sample was placed in a polypropylene centrifuge tube and shaken with 25 ml of a Hg(NO₃)₂ and NaNO₃ solution prepared with different equivalent ratios (Hg²⁺/ Na⁺ = 0.1, 0.2, 0.3, 0.5, 0.75 and 1.0) at room temperature for 4 weeks. The total normalities of the solutions for each sample were kept constant at 0.00247N, 0.00361N,
0.00468N, 0.00639N and 0.00710N. Each of these normalities were chosen from theoretical total cation-exchange capacities of Na-2-mica, Na-3-mica, Na-4-mica, Na-ETS-4 and Na-titanosilicate, respectively. In order to avoid precipitation of Hg\(^{2+}\) during the exchange process, the initial pH of the equilibration solutions was set to 2.5 using HNO\(_3\) solution. Separation of solid ion exchangers and solution were done by centrifugation, and then the concentrations of Hg\(^{2+}\) were analyzed by atomic absorption spectroscopy using Milestone’s DMA-80 direct mercury analyzer. All these batch experiments were conducted in duplicate. The initial and final pH values of the exchange reactions were measured using a pH meter (Orion Research INC., Beverly, Massachusetts). Powder XRD analysis of the solid phases of Na-micas was conducted to check changes in the \(d_{001}\) spacings after equilibrium. The equivalent fraction of ion in solution and solid phase was calculated using data obtained through the exchange experiment in order to prepare isotherms and Kielland plots. As explained in chapter 2 of this thesis, a corrected selectivity coefficient, \(K_{\text{Na}}^M\) in a Kielland plot gives a good indication for ion selectivity. If \(\log K_{\text{Na}}^M\) is greater than zero, ion exchangers prefer metal (M) ions over Na\(^+\) ions whereas Na\(^+\) ions are more preferred over M ions when \(\log K_{\text{Na}}^M\) is less than zero. When \(\log K_{\text{Na}}^M = 0\), no preference for either ion is indicated.

4.3 RESULTS AND DISCUSSION

4.3.1 Characterization of Na-micas, Na-ETS-4, and Na-titanosilicate

The XRD patterns of Na-2, Na-3 and Na-4-micas are shown in Fig. 4.1, corresponding to previous reports (Shimizu et al., 2004; Stout et al., 2003; Park et al.,
All the mica samples have strong 001 reflections of 12.1-12.2 Å indicating the existence of Na\(^+\) and one layer of water molecules in the interlayers (Gregorkiewitz et al., 1987). Fig. 4.2 displays the X-ray powder diffraction patterns of Na-ETS-4 and Na-titanosilicate indicating that their patterns are consistent with previous studies (Cruciani et al., 1998; Poojary et al., 1994). The obtained X-ray results show that the phases of five synthesized ion exchangers are highly crystalline and phase pure materials.

Figure 4.1. Original XRD patterns of (a) Na-2-mica, (b) Na-3-mica and (c) Na-4-mica.
Figure 4.2. XRD patterns of (a) Na-ETS4 and (b) Sodium titanosilicate.
4.3.2 pH change after $2\text{Na}^+ \rightarrow \text{Hg}^{2+}$ exchange reaction

Initial and final pH values of solutions for the $2\text{Na}^+ \rightarrow \text{Hg}^{2+}$ exchange reaction are shown in Table 4.2. Initial pH was adjusted to 2.5. The pH increased to 5.8-6.5, after Na-micas were equilibrated with exchange solutions containing different Hg concentrations. This pH increase may be related to buffering capacity of the Na-micas, since soil pH is buffered by clay minerals through cation exchange reaction in the intermediate pH range (5.5 to 7.0) (McBride, 1994; Brady and Weil, 2002). During the $2\text{Na}^+ \rightarrow \text{Hg}^{2+}$ exchange process, the pH increase resulted from $\text{H}^+$ consumption of the Na-micas by the $\text{Na}^+ \rightarrow \text{H}^+$ exchange. With $2\text{Na}^+ \rightarrow \text{Hg}^{2+}$ exchange reactions of the two Na-titanosilicates using different concentrations of Hg$^{2+}$, the final pHs were in the range of 3.1 to 6.7. The change in pH was smaller from the initial pH, as the Hg$^{2+}$ concentration of exchange solutions increased. At the lower concentrations of Hg solutions, the pHs of Na-titanosilicates were not much different from those of Na-micas. On the other hand at the higher concentrations of Hg solutions, the pHs were much lower than those of Na-micas. This pattern for pH may be due to the competition of $\text{H}^+$ with Hg$^{2+}$. As the amount of Hg uptake increases (Table 4.3), pH values decrease because more Hg ions occupy more exchange sites, resulting in leaving protons in solution. The precipitation and the distribution of Hg$^{2+}$ species in the exchange solutions were investigated using the Visual Minteq program (Gustafsson, 2005). It was found that $[\text{Hg(OH}_2)_6]^{2+}$ was the predominant species and no precipitation was expected for all Hg exchange solutions at pH 2.5.
Table 4.2. Initial and final pH values of $2\text{Na}^+ \rightarrow \text{Hg}^{2+}$ reaction.

<table>
<thead>
<tr>
<th>Equivalent ratio of Hg: Na in exchange solution</th>
<th>initial pH</th>
<th>Na-2-mica</th>
<th>Na-3-mica</th>
<th>Na-4-mica</th>
<th>Na-ETS-4</th>
<th>Na-titanosilicate</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:00</td>
<td>2.5</td>
<td>6</td>
<td>6</td>
<td>5.8</td>
<td>3.1</td>
<td>3.2</td>
</tr>
<tr>
<td>0.75:0.25</td>
<td>2.5</td>
<td>6.1</td>
<td>6.1</td>
<td>6</td>
<td>3.8</td>
<td>3.6</td>
</tr>
<tr>
<td>0.5:0.5</td>
<td>2.5</td>
<td>6.1</td>
<td>6.2</td>
<td>6.1</td>
<td>4.4</td>
<td>4.9</td>
</tr>
<tr>
<td>0.3:0.7</td>
<td>2.5</td>
<td>6.1</td>
<td>6.2</td>
<td>6.1</td>
<td>5.1</td>
<td>6.4</td>
</tr>
<tr>
<td>0.2:0.8</td>
<td>2.5</td>
<td>6.2</td>
<td>6.3</td>
<td>6.3</td>
<td>5.7</td>
<td>6.6</td>
</tr>
<tr>
<td>0.1:0.9</td>
<td>2.5</td>
<td>6.2</td>
<td>6.3</td>
<td>6.5</td>
<td>6.3</td>
<td>6.7</td>
</tr>
</tbody>
</table>

4.3.3 Distribution coefficient for mercury by Na-micas and Na-titanosilicates

The $K_d$ values for Hg ion exchange by three Na-micas and two Na-titanosilicates are shown in Table 4.3. It can be seen from the table that among five samples the Na-ETS-4 sample showed the highest affinity for Hg$^{2+}$ in the presence of 0.5N NaNO$_3$ solution. However, the $K_d$ values of Na-micas for Hg$^{2+}$ are very low compared to two titanosilicate ion exchangers.

Table 4.3. $K_d$ values for Hg$^{2+}$ exchange by Na-micas and Na-titanosilicates.

<table>
<thead>
<tr>
<th>$K_d$ (ml/g)</th>
<th>Na-2-mica</th>
<th>Na-3-mica</th>
<th>Na-4-mica</th>
<th>Na-ETS-4</th>
<th>Na-titanosilicate</th>
</tr>
</thead>
</table>

4.3.4 $2\text{Na}^+ \rightarrow \text{Hg}^{2+}$ exchange with Na-micas

The isotherm for $2\text{Na}^+ \rightarrow \text{Hg}^{2+}$ exchange with Na-2-mica is given in Fig. 4.3a as
the equivalent fraction of Hg\(^{2+}\) in the solid phase against the equivalent fraction of Hg\(^{2+}\) in solution phase. This isotherm shows that Na-2-mica seems not to take up mercury at \(\bar{X}_{\text{Hg}} > \sim 0.19\), suggesting Na ions were exchanged with Hg ions up to \(\sim 19\%\) of total theoretical cation exchange capacity. In a Kielland plot (Fig. 4.3b) for \(2\text{Na}^+ \rightarrow \text{Hg}^{2+}\) exchange with Na-2-mica, all data points fall below x-axis, indicating thermodynamically low selectivity of Na-2-mica for Hg\(^{2+}\). The Kielland plot of the data gives a linear relationship (coefficient of determination of linear regression, \(r^2 = 0.77\)). The Kielland coefficient, \(C_1\), is estimated to be -4.362. The meaning of the negative value of \(C_1\) is that \(2\text{Na}^+ \rightarrow \text{Hg}^{2+}\) exchange process becomes more difficult as the Na ions are replaced with Hg ions. The XRD patterns of the Na-2-mica after \(2\text{Na}^+ \rightarrow \text{Hg}^{2+}\) exchange reaction with the equilibrium solutions containing the different equivalent ratios of Hg to Na (Fig. 4.4) suggest that some of Na ions were replaced with Hg ions because an expanded phase with the \(d_{001}\) spacing of 14.3 Å appeared by the exchange of Na ions with larger Hg ions in the interlayer space. In all XRD patterns of Fig. 4.4, the (001) reflections with \(\sim 14\) Å are sharp and high in intensity, compared to expanded phases of Na-3 and Na-4-micas in Fig 4.5 and 4.6. Since Na-2-mica has the lowest layer charge density among the three Na-micas, it has higher expansibility than the other two synthetic micas, so that it easily swells to \(\sim 14\) Å by the exchange reaction. In contrast, the intensities of \(\sim 12\) Å peaks are very low in Fig. 4.4b through 4.4f.
Figure 4.3. (a) Isotherms and (b) Kielland plots of Na-micas after $2Na^+ \rightarrow Hg^{2+}$ ion exchange.
Figure 4.4. XRD patterns of Na-2-mica after $2Na^+ \rightarrow Hg^{2+}$ ion exchange reaction with (a) 0.25 mN Hg(NO$_3$)$_2$ + 2.22 mN NaNO$_3$ (Hg:Na=0.1:0.9) (b) 0.49 mN Hg(NO$_3$)$_2$ + 1.97 mN NaNO$_3$ (Hg:Na=0.2:0.8) (c) 0.74 mN Hg(NO$_3$)$_2$ + 1.73 mN NaNO$_3$ (Hg:Na=0.3:0.7) (d) 1.23 mN Hg(NO$_3$)$_2$ + 1.23 mN NaNO$_3$ (Hg:Na=0.5:0.5) (e) 1.85 mN Hg(NO$_3$)$_2$ + 0.62 mN NaNO$_3$ (Hg:Na=0.75:0.25) (f) 2.47 mN Hg(NO$_3$)$_2$ (Hg:Na=1:0).
Figure 4.5. XRD patterns of Na-3-mica after $2Na^+ \rightarrow Hg^{2+}$ ion exchange reaction with (a) 0.36 mN Hg(NO$_3$)$_2$ + 3.24 mN NaNO$_3$ (Hg:Na=0.1:0.9) (b) 0.72 mN Hg(NO$_3$)$_2$ + 3.24 mN NaNO$_3$ (Hg:Na=0.2:0.8) (c) 1.08 mN Hg(NO$_3$)$_2$ + 2.52 mN NaNO$_3$ (Hg:Na=0.3:0.7) (d) 1.80 mN Hg(NO$_3$)$_2$ + 1.80 mN NaNO$_3$ (Hg:Na=0.5:0.5) (e) 2.70 mN Hg(NO$_3$)$_2$ + 0.90 mN NaNO$_3$ (Hg:Na=0.75:0.25) (f) 3.61 mN Hg(NO$_3$)$_2$ (Hg:Na=1:0).
Figure 4.6. XRD patterns of Na-4-mica after $2\text{Na}^+ \rightarrow \text{Hg}^{2+}$ ion exchange reaction with (a) 0.47 mN Hg(NO$_3$)$_2$ + 4.22 mN NaNO$_3$ (Hg:Na=0.1:0.9) (b) 0.94 mN Hg(NO$_3$)$_2$ + 3.75 mN NaNO$_3$ (Hg:Na=0.2:0.8) (c) 1.41 mN Hg(NO$_3$)$_2$ + 3.28 mN NaNO$_3$ (Hg:Na=0.3:0.7) (d) 2.34 mN Hg(NO$_3$)$_2$ + 2.34 mN NaNO$_3$ (Hg:Na=0.5:0.5) (e) 3.51 mN Hg(NO$_3$)$_2$ + 1.17 mN NaNO$_3$ (Hg:Na=0.75:0.25) (f) 4.68 mN Hg(NO$_3$)$_2$ (Hg:Na=1:0).
A ~14-15 Å phase is regarded as two-layer hydrate (more hydrated), while one-layer hydrate (less hydrated) contributes to a ~12 Å phase in 2:1 layer-type clays (Sato et al., 1992). Also, based on a simulation study using molecular dynamics and Monte Carlo techniques, clay swelling from the one-layer to the two-layer hydrate is due to transition of a partially dehydrated inner-sphere complex of an interlayer Na ion to a fully hydrated outer-sphere sodium ion in Na-montmorillonite (Hensen and Smit, 2002). Therefore, the appearance of ~12 Å phase in the d_{001}-spacing indicates the existence of less hydrated Hg ions in the interlayer space, while the ~14 Å phase results from more hydrated Hg ions. The existence of the different hydration species of Hg$^{2+}$ is supported by a study for muscovite (001) surface where Hg adsorption occurred as an inner-sphere complex and outer-sphere complex (Lee et al., 2009). This difference in the degree of the hydration of interlayer cations occurs from an energetic difference between an electrostatic attraction which keeps pulling down a cation closely to the surface and ion hydration strength which keeps water sphere surrounding a cation (Park et al., 2006). If the electrostatic attraction between a cation and a negatively-charged layer is stronger than the ion hydration strength, it causes the partial dehydration of cations, consequently producing less hydrated cations by decreasing the extent of hydration of cations. Also, in Fig. 4.4, it is noticeable that ~12 Å phase is increased as the uptake of Hg increases (Table 4.4). This is because the electrostatic attraction can be affected by the amount of intercalated divalent cations. The electrostatic attractive force is formulated roughly by

$$E = \frac{z^+ z^- e^2}{e r_A}$$  \hspace{1cm} (4.2)

where $z^+$ is the cation charge, $z^-$ is the local surface charge, $e$ is the unit of electron charge,
$\varepsilon$ is the dielectric constant of water, and $r_A$ is a distance separating the two charges. It is suggested that a divalent cation like Ca$^{2+}$ can prevent clay swelling to some degree by an increased electrostatic attraction force, as compared to Na$^+$, which is associated to the dielectric constant (McBride, 1994). The dielectric constant of water near divalent cations is lowered by the cations, which results in strong orderering of the dipoles of water molecules around them. According to Equation 4.2, the electrostatic attraction increases by the decreased dielectric constant as divalent cations increase in the interlayer space. Additionally, the strong electrostatic attraction by divalent cations can be explained by ion-ion correlations (Kjellander et al., 1988). It has been used to explain the strong electrostatic attraction between like charged surfaces in the presence of divalent counter ions (Kjellander et al., 1988; Kjellander et al., 1990; Segad et al., 2010; Guldbrand et al., 1984). Therefore, the electrostatic attraction between the negatively charged layer and Hg ions increases with the increasing adsorbed Hg$^{2+}$ amount, causing the increase in a proportion of Hg ions with the reduced hydration state, which leads to the increase of the intensity of the ~12 Å of Na-2-mica (Fig. 4.4b-f).

In Fig. 4.3a, the isotherm of Na-3-mica increases gently and seems to reach a maximum ($X_{\text{Hg}} \sim 0.59$) indicating that the $2\text{Na}^+ \rightarrow \text{Hg}^{2+}$ exchange process ceased at $X_{\text{Hg}} \sim 0.59$. Based on a Kielland plot of Na-3-mica where all log K values are less than zero, Na-3-mica does not show selectivity for Hg$^{2+}$ (Fig 4.3b). It is difficult to calculate exact Kielland coefficient because there was no good linear relationship of data because of the scattering of the data in the Kielland plot. The XRD patterns of the Na-3-mica after $2\text{Na}^+ \rightarrow \text{Hg}^{2+}$ exchange reaction using the different equilibrium solutions (Fig. 4.5) show
that, like the case of Na-2-mica, there are two types of d₀₀₁ spacings, one at ~14 Å and another at ~12 Å indicating two different hydration states. The expanded phase of ~14 Å results from the exchange of Na ions with Hg ions in the interlayer space, while the d₀₀₁ spacing of ~12 Å may be due to unexchanged Na ions or from some less hydrated Hg ions because of the strong electrostatic attraction between the negatively charged layer and Hg ions, which leads to a shedding of some water molecules surrounding Hg ions. It is found here that the intensity of ~14 Å phase changes with the Hg occupancy in Na-3-mica (Fig. 4.5 and Table 4.5). Especially, when the Hg occupancy in the interlayer space is ~52% (Fig. 4.5e), the intensity of the expanded phase significantly decreases, compared to those of Fig. 4.5a through 4.5d. This ~14 Å phase is almost completely diminished at ~59% of Hg-occupancy (Fig. 4.5f). The above result suggests a partial dehydration of large Hg ions occurred due to the increased electrostatic attraction caused by a high uptake of Hg ions (59% of Na ions were replaced by Hg ions) and this dehydration led to the decrease in d₀₀₁-spacing.

In addition to the effect of Hg ions, the layer charge density affects not only the expansibility of Na-micas but also the electrostatic attraction as expected by the equation 4.2. The electrostatic force increases with the increasing layer charge density. The high layer charge density, therefore, enhances the partial dehydration of adsorbed Hg²⁺ ions, leading to the decreased d₀₀₁-spacing in Na-micas. The increasing order of the layer charge density is Na-4 > Na-3 > Na-2-mica. Therefore, the electrostatic attraction of Na-3-mica is higher than that of Na-2-mica when only layer charge is considered. This is why the intensity of ~12 Å phase of Na-3-mica at ~6.6% of Hg-occupancy is higher than that of Na-2-mica at ~19% (Fig. 4.4f, Fig 4.5a and Table 4.5), which indicates that the
layer charge density is more influential on the electrostatic force than the Hg-occupancy.

Table 4.4. Uptake amount of Hg$^{2+}$ in Na-micas and Na-titanosilicates after $2\text{Na}^+ \rightarrow \text{Hg}^{2+}$ ion exchange reaction.

<table>
<thead>
<tr>
<th>Equivalent ratio of Hg: Na in exchange solution</th>
<th>Hg$^{2+}$ uptake (meq/g)</th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Na-2-mica</td>
<td>Na-3-mica</td>
<td>Na-4-mica</td>
<td>Na-ETS-4</td>
<td>Na-titanosilicate</td>
</tr>
<tr>
<td>0.1 : 0.9</td>
<td>0.07</td>
<td>0.24</td>
<td>0.40</td>
<td>0.63</td>
<td>0.68</td>
</tr>
<tr>
<td>0.2 : 0.8</td>
<td>0.10</td>
<td>0.58</td>
<td>0.81</td>
<td>1.27</td>
<td>1.37</td>
</tr>
<tr>
<td>0.3 : 0.7</td>
<td>0.24</td>
<td>0.71</td>
<td>0.72</td>
<td>1.90</td>
<td>2.07</td>
</tr>
<tr>
<td>0.5 : 0.5</td>
<td>0.23</td>
<td>1.37</td>
<td>0.91</td>
<td>3.17</td>
<td>3.52</td>
</tr>
<tr>
<td>0.75 : 0.25</td>
<td>0.31</td>
<td>1.89</td>
<td>1.47</td>
<td>4.54</td>
<td>4.44</td>
</tr>
<tr>
<td>1:00</td>
<td>0.47</td>
<td>2.13</td>
<td>1.29</td>
<td>5.21</td>
<td>5.14</td>
</tr>
</tbody>
</table>

Table 4.5. Occupancy of Hg$^{2+}$ in Na-micas and Na-titanosilicates after $2\text{Na}^+ \rightarrow \text{Hg}^{2+}$ ion exchange reaction.

<table>
<thead>
<tr>
<th>Equivalent ratio of Hg: Na in exchange solution</th>
<th>Hg$^{2+}$ occupancy* (%)</th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Na-2-mica</td>
<td>Na-3-mica</td>
<td>Na-4-mica</td>
<td>Na-ETS-4</td>
<td>Na-titanosilicate</td>
</tr>
<tr>
<td>0.1 : 0.9</td>
<td>2.8</td>
<td>6.6</td>
<td>8.5</td>
<td>9.9</td>
<td>9.6</td>
</tr>
<tr>
<td>0.2 : 0.8</td>
<td>4.0</td>
<td>16.1</td>
<td>17.3</td>
<td>19.9</td>
<td>19.3</td>
</tr>
<tr>
<td>0.3 : 0.7</td>
<td>9.7</td>
<td>19.7</td>
<td>15.4</td>
<td>29.8</td>
<td>29.2</td>
</tr>
<tr>
<td>0.5 : 0.5</td>
<td>9.3</td>
<td>38.0</td>
<td>19.4</td>
<td>49.6</td>
<td>49.6</td>
</tr>
<tr>
<td>0.75 : 0.25</td>
<td>12.6</td>
<td>52.4</td>
<td>31.4</td>
<td>71.1</td>
<td>62.5</td>
</tr>
<tr>
<td>1:00</td>
<td>19.0</td>
<td>59.0</td>
<td>27.6</td>
<td>81.6</td>
<td>72.4</td>
</tr>
</tbody>
</table>

* Occupancy = $\frac{\text{Hg uptake amount (meq/g)}}{\text{Cation exchange capacity (meq/g)}} \times 100$

In the case of $2\text{Na}^+ \rightarrow \text{Hg}^{2+}$ exchange with Na-4-mica, the isotherm shows an increase in uptake at initial stage ($X_{\text{Hg}} < -0.2$) but Na-4-mica seems not to take up
mercury at $\bar{X}_{\text{Hg}} > 0.3$ (Fig. 4.3a). As in the cases of Na-2 and Na-3-micas, Na-4-mica doesn’t have selectivity for Hg$^{2+}$, because all data points in the Kielland plot for Na-4-mica fall below x-axis (Fig. 4.3b). The Kielland plot of the data does not give a good linear relationship due to the scattering of data. The XRD patterns of the Na-4-mica after $2\text{Na}^+ \rightarrow \text{Hg}^{2+}$ exchange reaction with various Hg concentration solutions are shown in Fig. 4.6. The results showed that there are strong reflections of 001 phase at $\sim 12\,\text{Å}$ in all cases of Na-4-mica but expanded phases of $\sim 14\,\text{Å}$ are very weak or not shown. In contrast to XRD patterns of Na-2-mica in Fig. 4.4, the XRD patterns of Na-4-mica showed high intensity reflections of $\sim 12\,\text{Å}$ and low intensity reflections of $\sim 14\,\text{Å}$, which is due to higher layer charge density of Na-4-mica than those of Na-2 and Na-3-micas. This is because of high electrostatic attraction between the negatively charged layers and Hg ions in Na-4-mica, which leads to partial dehydration of intercalated Hg ions and as a result, the $\sim 12\,\text{Å}$ phase is enhanced in Na-4-mica.

4.3.5 $2\text{Na}^+ \rightarrow \text{Hg}^{2+}$ exchange with Na-ETS-4 and Na-titanosilicate

In Fig. 4.7a, the isotherm for $2\text{Na}^+ \rightarrow \text{Hg}^{2+}$ exchange with Na-ETS-4 increases steeply up to $\bar{X}_{\text{Hg}} < \sim 0.71$ indicating Na-ETS-4 took up most of mercury from solution at $\bar{X}_{\text{Hg}} < \sim 0.71$ (71 % of the theoretical CEC of the Na-ETS-4), although Na-ETS-4 seems to take up no more mercury at $\bar{X}_{\text{Hg}} > \sim 0.82$. All log K values in the Kielland plot (Fig. 4.7b) are greater than zero, which suggests Na-ETS-4 shows a preference for Hg ions at $\bar{X}_{\text{Hg}} < \sim 0.82$. However, the Kielland coefficient could not be calculated as the
data of Na-ETS-4 in the Kielland plot do not show a linear relationship due to the scattering of the data. The log K values overall increase until Hg ions occupy 50% of exchange sites of the structure of Na-ETS-4 ($X_{\text{Hg}} < ~ 0.5$). After that, the log K values start to decrease up to around zero at $X_{\text{Hg}} = ~ 0.82$. This pattern indicates that a steric hindrance begins to occur in the exchange sites when Hg ions occupy about 50% of the exchange sites.

The isotherm for $2\text{Na}^+ \rightarrow \text{Hg}^{2+}$ exchange with Na-titanosilicate (Fig. 4.7a) shows that Na-titanosilicate seems to take up most of mercury at $X_{\text{Hg}} < ~ 0.5$ because the isotherm is highly steep up to $X_{\text{Hg}} < ~ 0.5$ and there seems to be no more uptake for mercury at $> X_{\text{Hg}} ~ 0.72$. The Kielland plot for $2\text{Na}^+ \rightarrow \text{Hg}^{2+}$ exchange with Na-titanosilicate (Fig. 4.7b) shows that the log K values in the range of $X_{\text{Hg}}$ from 0.3 to 0.5 are greater than zero, indicating Hg is more selective than Na on Na-titanosilicate at that range. With an increase in the equivalent fraction of Hg in the solid phase, the data points continuously increase up to the break point ($X_{\text{Hg}} < ~ 0.5$). However, after the break point the log K values drastically decrease with an increase in the occupancy of Hg ions in the solid phase ($X_{\text{Hg}} > ~ 0.5$) indicating the ion exchange reaction is retarded. Based on this pattern of the data of Na-titanosilicate in the Kielland plot, it is suggested that the severe steric limitation is developed in the exchange sites after Hg ions occupy about 50% of all the exchange sites in Na-titanosilicate. Similar results have been shown previously by Kodama et al., 2004, who showed a rapid decrease in the log K values from the steric hindrance for exchanging cations with another cation exchanger.
Figure 4.7. (a) isotherms and (b) Kielland plots of Na-ETS-4 and Na-titanosilicate after $2\text{Na}^+ \rightarrow \text{Hg}^{2+}$ ion exchange.
The steric hindrance is related to several factors such as ion size, extent of hydration, and shape and the topology of a framework of an ion exchanger (Tanaka et al., 2000). The severe spatial hindrance in Na-titanosilicate seems to be related to the size of the Hg ion and the structural features of a framework of Na-titanosilicate. Na-titanosilicate has two types of exchange sites in the tunnel and the framework (Poojary et al., 1994; Clearfield et al., 2000). Ideally, half the sodium ions reside within the tunnel, so that the theoretical ion exchange capacity of the tunnel sites is 3.55 meq / g calculated from the ideal chemical formula (Table 4.1), whereas half the remainder ions are located in the framework with about 3.55 meq / g of the theoretical ion exchange capacity. The tunnel sodium ions are loosely held in the tunnel sites and can be first released during ion exchange reaction. Some large cations such as K and Rb that are too large to fit in the framework site initially occupy sites in the center of tunnels and then are located at sites near the framework (Clearfield et al., 2000). At the break point of the Na-titanosilicate in Fig. 4.7b (\(X_{\text{Hg}} \approx 0.5\)), Hg ion capacity is 3.52 meq / g which is similar to the capacity of tunnel sites. Therefore, it is suggested that Hg ions dominantly occupy the sites in the tunnels at \(X_{\text{Hg}} < 0.5\) because the tunnel sodium ions can be first released, while at \(X_{\text{Hg}} > 0.5\) probably most of the tunnel sites may be occupied by Hg ions and the sites near the framework would then be the main ones for Hg ion exchange. Accordingly, as shown in Fig. 4.7b, the steric hindrance occurs at \(X_{\text{Hg}} > 0.5\) leading to the severe decrease in the selectivity coefficient because it is difficult for the Hg ion to directly fit in the framework due to its size. Therefore, the steric hindrance could be due to the size of Hg ion and the structural properties of two types of exchange sites in Na-titanosilicate.
4.4 CONCLUSIONS

The ion exchange properties of Na-micas, Na-ETS-4, and Na-titanosilicate for Hg$^{2+}$ were investigated using the the $K_d$ values, isotherms, and Kielland plots. Na-ETS-4 showed the highest $K_d$ value for Hg. The uptake of Hg$^{2+}$ by Na-2 and Na-4-micas was ~20 and 30 % of the theoretical CEC, respectively. However, the Hg occupancies of Na-3-mica, Na-ETS-4, and Na-titanosilicate were very high showing ~60, 82, and 72 % of their theoretical CECs, respectively. The XRD patterns of Na-micas after the equilibrium indicated that there are different hydration states for Hg ions in all three micas. The Kielland plots showed that Na-ETS-4 and Na-titanosilicate were thermodynamically selective for Hg$^{2+}$ at $X_{Hg} < \sim 0.82$ and in the range of $X_{Hg}$ from 0.3 to 0.5, respectively. The log $K$ value of Na-ETS-4 and Na-titanosilicate drastically decreased, after Hg ions occupied ~50 % of all of the exchange sites suggesting a hindrance to exchange after about 50% occupancy.
REFERENCES


CHAPTER 5
COBALT (II) EXCHANGE PROPERTIES OF SODIUM-2-MICA AND SODIUM-ETS-4

5.1 INTRODUCTION

Heavy metals have a critical impact on contamination of environment because they are non-biodegradable and accumulate in soils and groundwater. Their production and releases have increased over time due to anthropogenic activities (Nriagu, 1996), possibly increasing the potential for environmental pollution. Like other heavy metals, cobalt is a toxicological element to humans and plants in case of exposure to its elevated levels (Gault et al., 2010; Aller et al., 1990; Crosby, 1998). It is known that cobalt is a possible carcinogen to humans (Bucher et al., 1999; Lison et al., 2001; Lauwery and Lison, 1994) as well as its excess application has detrimental effects on plant growth and metabolic functions (Aller et al., 1990). Also, $^{60}$Co with a radioactive half-life of 5.3 yr can be released into environment through detonation of nuclear devices or during nuclear plant operations (Hamilton, 1994). Some radionuclide-contaminated sites were shown to include $^{60}$Co (Olsen et al., 1986; Blom et al., 1991). Hence, the removal of Co ions from contaminated sites is necessary for environmental and human health.

Ion exchange has been useful to remove heavy metals from soils and groundwater (Cho and Komarneni, 2009; Kodama et al., 1999; Baker et al., 2009; Castaldi et al., 2008; Gedik and Imamoglu, 2008). In an ion exchange reaction the cation exchange capacity of ion exchangers and their selectivity for target ions and structural stability during exchange reaction are important. For these factors, some synthetic ion
exchangers have received attention including Na-2-mica and Na-ETS-4 (Camarinha et al., 2009; Qiu and Zheng, 2009; Rios et al., 2008; Khan and Alam, 2003).

The synthetic sodium fluorophlogopite (informally Na-2-mica) readily expands, unlike natural micas and has high negative charge due to isomorphic substitution of Al$^{3+}$ for Si$^{4+}$ in tetrahedral sheets of the 2:1 type layers with Mg trioctahedral sheets (Kodama et al., 2001). Na-ETS-4 (Engelhard Titano-Silicate-4) is a microporous material with a similar structure to zorite. It has a mixed octahedral and tetrahedral framework described as the random intergrowth of four hypothetical polymorphs, which differ in the arrangement of Ti-bridging units (Nair et al., 2001). It has been found that they are competent ion exchangers because of their selectivity for radioactive species and high exchange capacity for some heavy metals (Stout and Komarneni, 2003; Ravella et al., 2008; Komarneni et al., 2001; Ferreira et al., 2009; Lopes et al., 2007). For an appropriate use of ion exchangers and efficiency of decontamination, the selectivity for a target ion should be considered. However, the selectivity of Na-2-mica and Na-ETS-4 for Co$^{2+}$ was not examined and very little work was carried out for heavy metal exchange by these two ion exchangers. Therefore, the main objective of this study was to investigate ion-exchange properties of the synthetic Na-2-mica and Na-ETS-4 for Co$^{2+}$ using equilibrium isotherms and Kielland plots. The Kielland plots were used to determine selectivity coefficients.
Table 5.1. Ideal composition and theoretical CEC of Na-2-mica and Na-titanosilicate.

<table>
<thead>
<tr>
<th>Name</th>
<th>Ideal formula</th>
<th>CEC (meq / 100g)(^a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na2-mica</td>
<td>Na(_1)Si(_3)AlMg(<em>2)O(</em>{10})F(_2)</td>
<td>247</td>
</tr>
<tr>
<td>Na-ETS-4</td>
<td>Na(<em>9)Si(</em>{12})Ti(<em>3)O(</em>{38})(OH) (\bullet) 12H(_2)O</td>
<td>639</td>
</tr>
</tbody>
</table>

\(^a\) CEC was calculated on a basis of the ideal formula.

5.2 MATERIALS AND METHODS

5.2.1 Preparation and characterization of Na-2-mica and Na-ETS-4

For a typical synthesis of Na-2-mica (sodium fluorophlogopite), Na\(_2\)Si\(_6\)Al\(_2\)Mg\(_6\)O\(_{20}\)F\(_4\), all the precursors were mixed using a pestle and mortar with the stoichiometric molar composition of 6SiO\(_2\) (99.9 %, Aldrich), 2AlOOH, 6MgF\(_2\) (98 %, Aldrich) and 6NaCl (100.3 %, J.T. Baker). After that, the powder mixture was heated using Pt-crucibles in a programmable furnace at 900 °C for 10 hours and the reactants were slowly cooled down to room temperature at 2.5 °C / min. For the synthesis of Na-ETS-4, 1.75 g of titanium butoxide (TBO, 98 %, Alfa Aesar) was put into 10 ml of ammonia (25 %, EMD chemicals) in a Teflon vessel and then 6 ml of H\(_2\)O\(_2\) (30 %, Alfa Aesar) and 0.8 g of NaOH (97 %, Alfa Aesar) were added to the mixture under stirring. After mixing, 1.2 g of fumed silica (99.9 %, CABOT corp.) and 0.8 g of tetrabutylammonium bromide (TBABr, 98 %, Avocado) were added to the mixture followed by stirring for 3 hours. The reactant mixture was hydrothermally heated in a stainless-steel autoclave under autogenous pressure at 180 °C for 8 days. After the thermal or hydrothermal treatments for the synthesis of the two exchangers, the reactant solids were washed with deionized water and ethanol several times to remove remaining
salts and then dried at 60 °C. The solids were characterized by powder X-ray diffraction (XRD) analysis using a Scintag diffractometer with CuKα radiation and a Ge solid-state detector at a scanning speed of 3° 2θ / min with a scan step of 0.02° 2θ.

5.2.2 Cation exchange experiments

25 mg of each sample was placed in a polypropylene centrifuge tube followed by the addition of 25 ml of a mixed CoCl₂ and NaCl solution prepared with different equivalent ratios (Co²⁺/Na⁺ = 0.1, 0.2, 0.3, 0.5, 0.75 and 1.0). The centrifuge tubes were shaken at room temperature for 4 weeks. The total normalities of the solutions for each sample were kept constant at 0.00247N and 0.00639N and these normalities were chosen from theoretical total cation-exchange capacities of Na-2-mica and Na-ETS-4, respectively. The initial pH of the equilibration solutions was set to 4.5 using HCl solution in order to avoid precipitation of Co²⁺ during the exchange process. The visual Minteq program was used to investigate the precipitation and the distribution of Co²⁺ species in all the exchange solutions (Gustafsson, 2005). Based on the above program, [Co(H₂O)₆]²⁺ was the predominant species and no precipitation was expected for all Co exchange solutions at pH 4.5. After 4 weeks, the solid and solution phases were separated by centrifugation, and then all the solutions were analyzed by atomic absorption spectroscopy to determine the concentrations of Co²⁺. All these batch experiments were conducted in triplicates to obtain reliable data and check for reproducibility. The relative standard deviation in the triplicates was below 5%. For the solid phase of Na-2-mica, powder XRD analysis was conducted to check changes in the d₀₀₁ spacings after equilibrium. The initial and final pH values of the exchange reactions were measured
using a pH meter (Orion Research INC., Beverly, Massachusetts). The equivalent fraction of ion in solution and solid phase was calculated using data obtained through the exchange experiment. Based on the equivalent fractions, isotherms and Kielland plots were plotted to determine Co$^{2+}$ selectivity of Na-2-mica and Na-ETS-4. As explained in chapter 2 of this thesis, a corrected selectivity coefficient, $K^M_{Na}$ in a Kielland plot gives a good indication for ion selectivity. If log$K^M_{Na}$ is greater than zero, ion exchangers prefer metal (M) ions over Na$^+$ ions whereas Na$^+$ ions are more preferred over M ions when log$K^M_{Na}$ is less than zero. When log$K^M_{Na}$ = 0, no preference for either ion is indicated.

5.3 RESULTS AND DISCUSSION

5.3.1 Characterization of Na-2-mica and Na-ETS-4

The XRD pattern of Na-2-mica is shown in Fig. 5.1a, which is consistent with the previous results (Shimizu et al., 2004; Stout and Komarneni, 2003). It is shown that the synthetic mica has a strong 001 reflection of 12.2 Å which indicates the existence of Na$^+$ and one layer of water molecules in the interlayers (Gregorkiewitz et al., 1987). The presence of a small peak at 9.7 Å suggests the existence of a small portion of a dehydrated 001 phase. Fig. 5.2b displays the X-ray powder diffraction patterns of Na-ETS-4 and this pattern is well matched with that reported in a previous study (Cruciani et al., 1998). The obtained X-ray results reveal that two synthesized ion exchangers are highly crystalline and nearly phase pure materials.
Figure 5.1. XRD patterns of (a) Na-2-mica and (b) Na-ETS4.
5.3.2 pH change after $2\text{Na}^+ \rightarrow \text{Co}^{2+}$ exchange reaction

Table 5.2 shows initial and final pH values of solutions for the $2\text{Na}^+ \rightarrow \text{Co}^{2+}$ exchange reaction. The initial pH (pH=4.5) increased to 6.4-6.9 in all solutions after Na-2-mica was equilibrated with exchange solutions containing different Co concentrations. Such an increase in pH may be related with the buffering capacity because clay minerals can prevent any drastic change in pH via cation exchange reaction (McBride, 1994; Brady and Weil, 2002). Therefore, during the $2\text{Na}^+ \rightarrow \text{Co}^{2+}$ exchange process, the increase in pH was caused by H$^+$ adsorption into interlayer space of Na-2-mica through the $\text{Na}^+ \rightarrow \text{H}^+$ exchange lowering H$^+$ concentration in solution phase. For $2\text{Na}^+ \rightarrow \text{Co}^{2+}$ exchange reaction with Na-ETS-4, the final pH was in the range of 7.0 to 8.8 depending on the different concentrations of Co$^{2+}$. Like Na-2-mica this increase in pH may be due to the exchange of H$^+$ with Na$^+$ at exchange sites.

In cases of both of the ion exchangers the change in pH was smaller from the initial pH, as the Co$^{2+}$ concentration of exchange solutions increased. This pattern is associated with the competition of H$^+$ with Co$^{2+}$ for same exchange sites. As the Co$^{2+}$ concentration of exchange solutions increased, the amount of Co uptake increased (Table 5.3). With the exchange from solutions of high Co concentrations, therefore, the degree of the increase in pH decreased because Co ions occupied more exchange sites leaving more protons in the solutions.
Table 5.2. Initial and final pH values of 2Na⁺→Co²⁺ reaction.

<table>
<thead>
<tr>
<th>Equivalent ratio of Co: Na in exchange solution</th>
<th>initial pH</th>
<th>Final pH</th>
<th>Na-2-mica</th>
<th>Na-ETS-4</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1:0.9</td>
<td>4.5</td>
<td>6.9</td>
<td>8.8</td>
<td></td>
</tr>
<tr>
<td>0.2:0.8</td>
<td>4.5</td>
<td>6.9</td>
<td>8.1</td>
<td></td>
</tr>
<tr>
<td>0.3:0.7</td>
<td>4.5</td>
<td>6.8</td>
<td>7.4</td>
<td></td>
</tr>
<tr>
<td>0.5:0.5</td>
<td>4.5</td>
<td>6.6</td>
<td>7.4</td>
<td></td>
</tr>
<tr>
<td>0.75:0.25</td>
<td>4.5</td>
<td>6.5</td>
<td>7.2</td>
<td></td>
</tr>
<tr>
<td>1:0</td>
<td>4.5</td>
<td>6.4</td>
<td>7.0</td>
<td></td>
</tr>
</tbody>
</table>

Table 5.3. Amount and occupancy of Co²⁺ in Na-micas and Na-titanosilicates after 2Na⁺→Co²⁺ ion exchange reaction.

<table>
<thead>
<tr>
<th>Equivalent ratio of Co: Na in exchange solution</th>
<th>Na-2-mica</th>
<th>Na-ETS-4</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Co²⁺ uptake (meq/g)</td>
<td>Co²⁺ occupancy* (%)</td>
</tr>
<tr>
<td>0.1 : 0.9</td>
<td>0.25</td>
<td>9.97</td>
</tr>
<tr>
<td>0.2 : 0.8</td>
<td>0.49</td>
<td>19.9</td>
</tr>
<tr>
<td>0.3 : 0.7</td>
<td>0.74</td>
<td>29.9</td>
</tr>
<tr>
<td>0.5 : 0.5</td>
<td>1.21</td>
<td>49.0</td>
</tr>
<tr>
<td>0.75 : 0.25</td>
<td>1.72</td>
<td>69.6</td>
</tr>
<tr>
<td>1:0</td>
<td>1.98</td>
<td>80.2</td>
</tr>
</tbody>
</table>

* Occupancy = \( \frac{\text{Co uptake amount (meq/g)}}{\text{Cation exchange capacity (meq/g)}} \times 100 \)
5.3.3 $2\text{Na}^+ \rightarrow \text{Co}^{2+}$ exchange with Na-micas and Na-ETS-4

Fig. 5.2a shows the isotherm for $2\text{Na}^+ \rightarrow \text{Co}^{2+}$ exchange with Na-2-mica as the equivalent fraction of $\text{Co}^{2+}$ in solid phase against the equivalent fraction of $\text{Co}^{2+}$ in solution phase. This isotherm steeply increased up to $\overline{X}_{\text{co}} < \sim 0.49$ suggesting that during $2\text{Na}^+ \rightarrow \text{Co}^{2+}$ exchange reaction most of Co ions from equilibrium solutions were taken up by Na-2-mica. It appears that Na-2-mica doesn’t take up cobalt ions after Co ions occupy $\sim 80\%$ of all exchange sites ($\overline{X}_{\text{co}} > \sim 0.80$). As seen in Fig. 5.2b, the Kielland plot for $2\text{Na}^+ \rightarrow \text{Co}^{2+}$ exchange with Na-2-mica reveals that three data points fall above x-axis where the selectivity coefficient is equal to one, indicating a preference of Na-2-mica for $\text{Co}^{2+}$ at $\overline{X}_{\text{co}} < \sim 0.30$. After Co ions occupy $\sim 49\%$ of all exchange sites ($\overline{X}_{\text{co}} > \sim 0.49$) the data points fall below x-axis. A good linear relationship for data is not given in the Kielland plot.

The XRD patterns of the Na-2-mica after $2\text{Na}^+ \rightarrow \text{Co}^{2+}$ exchange reaction with the equilibrium solutions containing the different equivalent ratios of Co to Na is shown in Fig. 5.3. It is found that there are two types of 001 phases at $\sim 12 \ \text{Å}$ and $14.4 \ \text{Å}$, the latter is not shown in the original XRD pattern of Na-2-mica (Fig. 1a). Therefore, the appearance of the expanded 001 phase at $\sim 14.4 \ \text{Å}$ is due to the replacement of Na ions with Co ions. In all XRD patterns of Fig. 5.3 the (001) reflections of $14.4 \ \text{Å}$ are sharp and of high intensity, while the intensity of $\sim 12 \ \text{Å}$ peak decreased, as the uptake of Co ions by Na-2-mica increased, so that the $\sim 12 \ \text{Å}$ peak almost disappeared (Fig. 5.3e and f) after the equilibrium with the high Co exchange solutions (1.85 mN CoCl$_2$ + 0.62 mN
NaCl and 2.47 mN CoCl₂). This reduction of ~12 Å phase is due to the decrease in the concentration of Na⁺ in the solid phase.

However, this trend of decreasing intensity of the ~12 Å phase as the Co²⁺ divalent target ion uptake increased is opposite to the results presented in previous chapters for Sr²⁺, Ba²⁺ and Hg²⁺. The reason for this opposite trend is associated with the layer charge density of Na-2-mica and the higher hydration strength of Co²⁺ (-1996 kJ / mol) than those of Sr²⁺ (-1443 kJ / mol), Ba²⁺ (-1305 kJ / mol) and Hg²⁺ (-1824 kJ / mol).

Based on Fig. 5.3, Co ions may not account for ~12 Å phase because this phase decreased with increasing Co ions in the interlayer space, so that partial dehydration did not occur with the intercalated Co ions. A ~14-15 Å phase is regarded as a two-layer hydrate (more hydrated), while one-layer hydrate (less hydrated) contributes to a ~12 Å phase in 2:1 layer-type clays (Sato et al., 1992). The change in the hydration state of a cation in an interlayer space may be related with the balance between an electrostatic attraction which keeps pulling down a cation closely to the surface and ion hydration strength which keeps water sphere surrounding a cation (Komarneni and Roy, 1988; Park et al., 2006). If the electrostatic attraction between a cation and a negatively-charged layer is strong enough to overcome its hydration strength, it results in the partial dehydration of the cation, consequently leading to a reduced d₀₀₁-spacing. If the electrostatic attraction is weak, the cation can keep its hydration sphere and a decrease in the d₀₀₁-spacing doesn’t occur. Therefore, the presence of ~ 14 Å phase is due to the strong hydration strength of Co²⁺, which overcomes the electrostatic attraction between cobalt ions and layer charge of Na-2-mica. This weak electrostatic attraction between Co²⁺ ions and Na-2-mica led to the X-ray patterns which are different from the case of
Sr\(^{2+}\), Ba\(^{2+}\) and Hg\(^{2+}\) where strong electrostatic attraction occurred. A similar trend of an increasing ~14 Å phase during Co\(^{2+}\) exchange reaction was also reported with a study on K-depleted natural phlogopite (Cho and Komarneni, 2009). As the proportion of divalent cations intercalated in the interlayer space increases, the electrostatic attraction between a divalent cation and a negatively charged layer can also increase due to the decrease in dielectric constant and ion-ion correlation (McBride, 1994; Kjellander et al., 1988; Kjellander et al., 1990; Segad et al., 2010). The ~14 Å phase is maintained in Na-2-mica even though the uptake of Co\(^{2+}\) increased (Fig. 5.3a to 5.3f) in contrast to Sr\(^{2+}\), Ba\(^{2+}\) and Hg\(^{2+}\) ions. This suggests that the hydration strength of Co\(^{2+}\) is higher than the increase in electrostatic attraction caused by the higher Co\(^{2+}\) uptake.

The isotherm for 2Na\(^{+}\) → Co\(^{2+}\) exchange with Na-ETS-4 is given in Fig. 5.2a, which is highly steep up to \(\bar{X}_{\text{Co}} < \sim 0.30\) indicating that Na-ETS-4 took up most of the cobalt ions from the exchange solutions until Co ions occupy almost 30% of the exchange sites. Na-ETS-4 seems to take up no more cobalt at \(\bar{X}_{\text{Co}} \geq \sim 0.75\). The Kielland plot (Fig. 4.7b) shows that three data points are above zero at \(\bar{X}_{\text{Co}} < \sim 0.30\) during 2Na\(^{+}\) → Co\(^{2+}\) exchange with Na-ETS-4, which suggests that Na-ETS-4 shows a preference for Co ions in that range. At \(\bar{X}_{\text{Co}} = \sim 0.40\), the break point occurs due to drastic decrease in the selectivity coefficient and falls below x-axis line where log\(K_{\text{Co}}^{\text{M}}\text{Na} = 0\), and then the data points fall greatly below x-axis at \(\bar{X}_{\text{Co}} \geq \sim 0.40\). This rapid decrease in the selectivity coefficient at the break point indicates that severe steric hindrance started to occur when Co ions occupy up to ~40% of exchange sites (Kodama et al., 2004). Like the case of Na-2-mica, however, the Kielland coefficient can’t be calculated since the
Figure 5.2. (a) Isotherms and (b) Kielland plots of Na-2-mica and Na-ETS-4 after $2\text{Na}^+ \rightarrow \text{Co}^{2+}$ ion exchange.
Figure 5.3. XRD patterns of Na-2-mica after $2\text{Na}^+ \rightarrow \text{Co}^{2+}$ ion exchange reaction with (a) 0.25 mN CoCl$_2$ + 2.22 mN NaCl (Co:Na=0.1:0.9) (b) 0.49 mN CoCl$_2$ + 1.97 mN NaCl (Co:Na=0.2:0.8) (c) 0.74 mN CoCl$_2$ + 1.73 mN NaCl (Co:Na=0.3:0.7) (d) 1.23 mN CoCl$_2$ + 1.23 mN NaCl (Co:Na=0.5:0.5) (e) 1.85 mN CoCl$_2$ + 0.62 mN NaCl (Co:Na=0.75:0.25) (f) 2.47 mN CoCl$_2$ (Co:Na=1:0).
data of Na-ETS-4 in the Kielland plot are not linearly related due to the scattering of the data.

5.4 CONCLUSIONS

Cation exchange isotherms and Kielland plots were used to examine Co\(^{2+}\) ion exchange properties of Na-2-mica and Na-ETS-4. After 2Na\(^+\) \(\rightarrow\) Co\(^{2+}\) exchange with Na-2-mica, the maximum uptake of Co\(^{2+}\) was \(\sim 80\) % of the theoretical CEC. In case of Na-ETS-4, the uptake was \(\sim 75.4\) %. The XRD patterns of Na-2-mica after the equilibrium suggested that Co ions replaced Na ions as evidenced by the change in the \(\sim 12\) Å phase to a 14.4 Å phase. As the uptake of Co ions increased there was no decrease in the interlayer space of Na-2-mica because of very high hydration energy of Co\(^{2+}\) ions. Based on the Kielland plots for 2Na\(^+\) \(\rightarrow\) Co\(^{2+}\) exchange, Co\(^{2+}\) was favored until Co ions occupied 30% of all exchange sites of Na-2-mica. In case of Na-ETS-4, Co\(^{2+}\) was preferred at \(\bar{X}_{Co} < \sim 30\) %. After Co ions occupied \(\sim 30\) % of all of the exchange sites the selectivity coefficient of Na-ETS-4 drastically decreased suggesting a high steric limitation at exchange sites.
REFERENCES


York.


CHAPTER 6
SUMMARY AND FUTURE STUDIES

The main objective of this research was to investigate fundamental cation exchange properties of Na-micas (Na-2, Na-3, and Na-4-micas), Na-ETS-4, and Na-titanosilicate for applications in decontaminating radioactive species (Sr$^{2+}$ and Ba$^{2+}$) and some heavy metals (Hg$^{2+}$ and Co$^{2+}$) from soils, ground water, and drinking water. To achieve this goal, the above mentioned five ion exchangers were synthesized, characterized and investigated by constructing cation exchange isotherms and Kielland plots for Sr$^{2+}$, Ba$^{2+}$, Hg$^{2+}$ and Co$^{2+}$ ions. X-ray diffraction patterns and scanning electron microscopy showed that all the ion exchangers were highly crystalline, nearly pure, and had small particle sizes. $^{29}$Si and $^{27}$Al MASNMR spectroscopy revealed different charge densities of Na-micas and their charge location i.e., where the layer charge was originated. Na-2-mica, Na-ETS-4, and Na-titanosilicate showed high selectivity for Sr$^{2+}$ based on cation exchange isotherms and Kielland plots for Sr$^{2+}$. Na-2-mica and Na-ETS-4 were found to have great preference for Ba$^{2+}$ with most of the equilibrium solutions used. These results suggested that Na-2-mica and Na-ETS-4 would be efficient ion exchangers for selective removal of Sr$^{2+}$ and Ba$^{2+}$. Compared to Na-3 and Na-4-micas, Na-2-mica showed higher selectivity for both Sr$^{2+}$ and Ba$^{2+}$. The reason for this is likely due to high expansibility of Na-2-mica resulting in easier accessibility to exchanging sites in the interlayer spaces for the incoming ions. The expansibility of the interlayer spaces was apparently affected by the increase in electrostatic attraction of the negatively charged layers and cations, which led to a decrease in selectivity as the uptake of the divalent
cations increased in the interlayer spaces.

With regard to ion exchange experiments of $\text{Hg}^{2+}$, Na-ETS-4 showed the highest distribution coefficient ($K_d$) value among the five ion exchangers tested here. Based on Kielland plots for $\text{Hg}^{2+}$ ions, only Na-ETS-4 exhibited selectivity for mercury (II) ions with most of the solutions used for exchange. These results suggested that Na-ETS-4 would be appropriate for selective Hg-removal from soils and water. Na-2-mica and Na-ETS-4 showed higher selectivity for Co$^{2+}$ ions over Na ions at low Co$^{2+}$ occupancy in the solid phase.

The XRD patterns of the Na-micas after $2\text{Na}^+ \rightarrow \text{M}^{2+}$ ($\text{M}=$Sr, Ba, Hg) exchange reaction with different equilibrium solutions showed that there were two different (001) phases i.e., an $\sim 12$ Å and an $\sim 14$ Å, which indicated the existence of adsorbed divalent cations with two different hydration states in interlayer spaces after ion exchange reactions. The smaller $d_{001}$-spacing was due to partial dehydration of cations in the interlayer spaces by strong electrostatic attraction between exchanged cations and negatively charged layers. There were two factors affecting electrostatic force: amounts of divalent cations exchanged and layer charge density. As the amount of exchanged divalent cations and the layer charge density in interlayer space increased, the electrostatic attraction increased resulting in an increase in the extent of the dehydration of cations. Unlike Sr$^{2+}$, Ba$^{2+}$ and Hg$^{2+}$ ions, Co$^{2+}$ ions did not produce $\sim 12$ Å phase of Na-2-mica because of the latter ion’s higher hydration energy.

The selectivity and the uptake amount of Hg$^{2+}$ were lower for Na-micas when compared to those of Na-ETS-4 and Na-titanosilicate. Future studies of Fe- or Al-pillaring of Na-micas followed by Hg$^{2+}$ ion exchange would probably improve the
selectivity and capacity of the Na-micas for Hg$^{2+}$ uptake. This hypothesis is based on some previous studies which showed that heavy metals such as Cu$^{2+}$ and Zn$^{2+}$ could be adsorbed through complexation on the intercalated hydroxy metal cations used for pillaring. In this thesis, the selectivity of Sr$^{2+}$, Ba$^{2+}$, Hg$^{2+}$ and Co$^{2+}$ ions over Na$^+$ ions was investigated by the five ion exchangers, which had been initially saturated with Na$^+$ ions. However, soil solution and ground water contain a wide variety of ions such as Ca$^{2+}$, Mg$^{2+}$, K$^+$ etc. Therefore, it would be useful to test the selectivity of these ion exchangers for target ions using other competing ions that would be encountered in soil solution or ground water. In addition, heavy metal ion exchange could be pursued as a function of pH in future studies because the speciation of heavy metals would be affected by pH.
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