FUNDAMENTAL FACTORS IMPACTING ON THE MICROSTRUCTURAL PERFORMANCE AND CONTAMINANT ADSORPTION OF ILLITE

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ABSTRACT
Contaminant adsorption properties of clays are markedly influenced by the type of clay minerals, the nature of the exchangeable ions, and the type of clay microstructure present. On the other hand, the different microstructures of clay soils, due to their different surface areas and the different quantity of these surfaces exposed to the water, cause different contaminant attenuation levels for clay minerals. The present study investigates the role of various types and concentrations of pore fluid on the microstructure and contaminant adsorption of illite. A series of pH measurements, a turbidity experiment, an XRD analysis, batch equilibrium testing and soil adsorption evaluation were performed to achieve the aforementioned objective. The results of this study show that although the theoretical calculation of the double layer theory does not take into account the effect of different anion types on the variation of the thickness of double layer, the anion type has a major impact on the microstructure variations of clay minerals. In addition, it is shown that the presence of potential determining ions (PDI) in pore fluid of illite is among the major fundamental factors impacting on the microstructural performance and contaminant adsorption of illite.

RÉSUMÉ
Des propriétés d'adsorption de contaminant des argiles sont nettement influencées par le type de minerais d'argile, par la nature des ions échangeables, et par le type de microstructure d'argile. D'autre part, différentes microstructures des sols d'argile, en raison du champ de surface différent et en raison de la quantité différente de surface exposée à l'eau, mettent en évidence le niveau d'atténuation différent de contaminant pour des minerais d'argile. La présente étude est consacrée sur le rôle du type de la concentration de fluide interstitiel sur la microstructure et l'adsorption de contaminant de l'illite. Une série de mesure de pH, expérience de turbidité, Analyse de XRD, l'essai d'équilibre en lots et l'évaluation d'adsorption de sol ont été réalisés pour atteindre l'objectif mentionné ci-dessus. Les résultats de cette étude montrent cela qu'le calcul théorique obtenu de la théorie de couche double ne tienne pas compte de l'effet du type différent d'anion sur la variation de l'épaisseur d'une double couche, le type d'anion a un effect important sur les variations de microstructure des mineraux d'argile. Ces résultats montrent que la présence de PDI en fluide interstitiel d'illite est des facteurs fondamentaux principaux effectuant sur l'exécution de microstructurale et de l'adsorption de contaminant de l'illite.

1. INTRODUCTION
Soils in which the clay particles will detach spontaneously from each other and go into suspension in quiet water are termed dispersive clays (Yong and Sethi 1977; Mitchell, 1993). Clay soils are very helpful material as barrier in waste disposal projects because of their high buffering capacity and low permeability (Yong et al., 1992; Yong, 2001; Ouhadi et al., 2006). On the other hand, dispersive soils are known to have greater surface areas and higher cation exchange capacities (CEC) due to the fact that more surface area is exposed to the water following the formation of the dispersive structure (Goodarzi, 2003). Therefore, they might be effectively used as a contaminant absorbent. Several indices have been proposed to characterize the interparticle forces in dispersive soils. These include: pH, sodium adsorption ratio (SAR), exchangeable sodium percentage (ESP), dielectric dispersion, and zeta potential (Yong and Warkentin, 1966; Sherard et al., 1972; Yong and Sethi, 1977). The impact of the salt fraction of clayey soils on their dispersivity behaviour has been addressed by several authors. It is reported that clay soils with low quantities of salt show a much-dispersed structure (Yong and Sethi, 1977; Chen et al., 1990; Guler and Balci, 1998). This is attributed to the repulsive forces’ overcoming of the attractive forces. With a further increase in salt concentration, the dispersivity potential decreases (Ouhadi and Goodarzi, 2006).

On the other hand, there has been some research done on the impact of anions on soil behaviour. It is reported that differences in ion activity for the sulfate and chloride systems would result in a greater percentage of adsorbed sodium on the exchange complex for the sulfate system (Babcock and Schulz, 1963; Landau and Altschaeffl 1976). Again, the recently reported research results show that the dispersive behaviour of soils is highly dependent on the type of anion present on the pore fluid of soil (Abend and Lagaly, 2000). In addition, some anions can attach to the edge of clay particle and affect theirs surface charge (van Olphen, 1977; Yong et al., 1992; Penner and Lagaly, 2000). Ions which have the ability to affect the sing of zeta potential are referred as the potential determining ions. Most of the common anions in this group are OH\(^-\), CO\(_3\)^{2-}, PO\(_3\)^{3-}, and CN\(^-\). On the other hand, some anions like Cl\(^-\), NO\(_3\)^{-}, and
SO$_4^{2-}$ are generally considered to be non-specifically adsorbed (Bohn et al., 1979). Among the anions, the behaviour of potential determining ions is particularly important. These anions adsorbed onto particle surfaces. Subsequent to adsorption, they affect both the surface charge and surface potential. These are particularly important in the development of contaminant adsorption potential of soils.

Even though up to now, the dispersivity behaviour of soils has commanded much attention from researchers, there has not been enough research done on the microstructural impact of the dispersivity performance of clay minerals and the influence of potential determining ions on the dispersivity performance of illite and its microstructural effects on contaminant adsorption. This paper focuses on pore fluid impact on the dispersivity performance of illite mainly from a microstructural evaluation of soils and aims to address the influence of PDIs on the dispersivity and microstructure variations of illite in conjunction with its contaminant adsorption impact. The results of this paper are applicable in the application of clay liner in geo-environmental projects.

2. MATERIALS AND METHODS

An illitic soil obtained from Domtar Construction Materials, Ltd. (Domtar Sealbond), which comes from pulverizing old Canadian marine shale, and which is known as a major source material of the Champlain Sea clay, was used in this study. The alkaline and metal salts used in the study are Na$_2$SO$_4$, NaCl, NaOH, Na$_2$CO$_3$, Zn(NO$_3$)$_2$.6H$_2$O and Pb(NO$_3$)$_2$. To characterize the soil sample, some physico-chemical tests were performed. Physical properties including specific gravity, particle size distribution, Atterberg limits, organic content, moisture content and hydrometer testing were determined according to ASTM methods (ASTM, 1994). For chemical analysis, soil samples were air-dried and sieved through the #200 mesh. Chemical analysis was continued according to laboratory manual of the Geotechnical Research Center of McGill University. Some of the physical and chemical properties of illite sample are given in Table 1.

In order to investigate the effect of pore fluid properties on the dispersivity behaviour and microstructure of illite, a series of illite samples were pretreated and homoionized by different salt concentrations and types, based on the method suggested in previous research (Yong and Warkentin, 1959; Mesri and Olson, 1971). Then, series of turbidity experiments was performed on these samples according to the method suggested by other authors (Yong and Sethi, 1977). For this purpose, following the proposed method by these authors, several suspensions of clay-salt mixtures at different concentrations and with a 1 to 50 soil:electrolyte ratio were placed in centrifuge tubes and agitated in a mechanical shaker for 2 hours, and subsequently centrifuged for 15 minutes at 3000 rpm. The soil fraction of the soil-electrolyte mixture was settled in the test tubes at the bottom of the tubes and some fine clay remained dispersed in the electrolyte part. This dispersion (remaining) clay in solution is identified as the supernatant.

The concentration of the remaining dispersed clay in the separated supernatant was used as a representative of degrees of turbidity. This was determined by measuring the light transmittance through the soil sample which was already placed in glass tube of turbidity meter. The turbidity measurement performed with a turbidity meter, model WTW-Turb550. It is reported that the turbidity of such a sample is representative of the ability of soil particles to stay in the suspension condition and shows the extent of the dispersivity performance of clay particles (Yong and Sethi, 1977).

To investigate the influence of pore fluid on the microstructure of illite, a series of XRD experiments were performed and the position and intensity for the major basal spacing is reported. XRD analysis was performed based on the method suggested in the study reported by Moore and Reynolds (1989), and Ouhadi and Yong (2003). A Siemens-Diffractometer D8 Advance with Cu-Kα radiation was used to obtain the x-ray diffraction patterns of samples.

Table 1: Some of the physico-chemical characteristics of illite

<table>
<thead>
<tr>
<th>Characteristics of illite</th>
<th>Quantity measured</th>
</tr>
</thead>
<tbody>
<tr>
<td>XRD analysis</td>
<td>illite, calcite, quartz</td>
</tr>
<tr>
<td>Liquid Limit, L.L. (%)</td>
<td>27.5</td>
</tr>
<tr>
<td>Plasticity Index, P.I. (%)</td>
<td>8.4</td>
</tr>
<tr>
<td>TDS (cmol/kg)</td>
<td>2.11</td>
</tr>
<tr>
<td>CEC (meq/100 g)</td>
<td>46.4</td>
</tr>
<tr>
<td>EC (ds/m)(1:10 soil:water)</td>
<td>0.2</td>
</tr>
<tr>
<td>pH (1:10 soil:water)</td>
<td>8.6</td>
</tr>
<tr>
<td>Soil Classification</td>
<td>CL</td>
</tr>
<tr>
<td>Gs</td>
<td>2.67</td>
</tr>
<tr>
<td>Carbonate (%)</td>
<td>9</td>
</tr>
<tr>
<td>Organic (%)</td>
<td>0</td>
</tr>
</tbody>
</table>

In addition, in order to investigate the impact of soil microstructure on the contaminant adsorption by illite, two different series of illite samples were pretreated and homoionized by Na$_2$CO$_3$ and 1N CaCl$_2$, separately, in the manner previously explained. Then, the soil-contaminant interaction was investigated by performing series of batch equilibrium tests. An Atomic Absorption Spectrophotometer (AAS-GBC 932, AB Plus) was used to analyze soil pore fluid of samples.

3. RESULTS AND DISCUSSION

As can be seen in Figure 1, the dispersivity behaviour of illite is a function of the anion type of salt. Sodium hydroxide and sodium carbonate show the two highest dispersivity levels in comparison with the other salts. The turbidity of illite without any salt was equal 219 NTU. It can be seen that according to the results of Figure 1, the highest dispersivity for sodium hydroxide and sodium carbonate happens at the 1 meq/l concentration. In the presence of a low concentration of salt, both double layers are compressed, and their effective charge will be reduced. In such a condition, the card-house structure breaks down and the soil structure disperses (van Olphen, 1977). As the illite sample
is exposed to a greater concentration of different salts, due to an increase in sodium concentration, a further decrease in the thickness of double layer occurs. Therefore, due to the decrease of the repulsive forces, the particles go closer to each other. At this high salt concentration, flocculation is of the face-to-face kind, giving rise to a packet floc (Yong and Warkentin, 1966).

The consequent flocculated structure causes more settlement of particles and low turbidity. However, since potential determining ions such as carbonates and hydroxides will also contribute significantly to the net repulsive activity between the particles (Yong, 2001; Pusch and Yong, 2006), due to the PDI's effect of $CO_3^{2-}$, with increasing the electrolyte concentration, still illite/Na$_2$CO$_3$ shows larger turbidity than other soil/electrolyte mixtures (impact of excess negative charge). Furthermore, since according to the Gouy-Chapman theory, the anion type does not have any impact on the variation of thickness of double layer (Yong et al., 1992), the behaviour described in the Figure 1 cannot be perfectly explained by the theoretical base of double layer theory.

The fact that illitic samples with different electrolyte have different degrees of sodium retention can be attributed to their different negative charges (Yong and Sethi, 1977). Those excess negative charges, for samples having NaOH and Na$_2$CO$_3$, come from the impact of potential determining ions. Therefore samples with the higher negative charge show the higher sodium retention. Furthermore, this retention of sodium ions causes the higher osmotic water absorption by clay particles. This is because in the presence of high salt concentrations the osmotic potential develops. Due to this osmotic potential, water tends to flow in the direction of increasing concentration (Mitchell, 1993). Therefore samples with higher adsorbed sodium will have a greater capacity for contaminant adsorption, as will be experimentally presented in this paper.

Sodium retention was measured by performing several batch equilibrium tests. The mixtures of illite and specific salt concentrations were prepared, shaken, and centrifuged according to the procedure explained previously. Then the concentrations of sodium ions were measured in the supernatant. The ratio of initially-added concentration of Na$^+$ to the pre-washed illite minus its concentration in pore fluid (the subtraction is called the retained sodium ions) over the initially-added concentration of Na$^+$ is reported as the percent of Na$^+$ retention. The results of Figure 2 show that the highest retention of sodium ions by illite happens at the concentrations of salt similar to the concentration producing the highest turbidity.

In the experiments performed, three phenomena might be responsible for the formation of the dispersivity structure. These include: (a) excess negative charge due to the impact of potential determining ions since the PDIs are no longer acting as an exchangeable counterion (Sparks1986); (b) pH effect (Yong and Warkentin, 1966; Ouhadi and Goodarzi, 2006); and (c) water adsorption in the presence of sodium ions due to osmotic effect (Mitchell, 1993; Ouhadi et al., 2006). To investigate these phenomena a series of sodium retention and pH measurements were performed. Figures 2 and 3 show results of these tests, respectively.

To fully investigate the factors controlling the previously addressed behaviour, a series of pH experiments were performed on the illite samples with different salt concentrations and different salt types (Figure 3). It is shown that, while a low pH promotes a positive edge to negative surface interaction, which creates a flocculated structure, the dispersion of clay particles often happens in high pH conditions. This increase in pH causes an increase in the repulsive force of clay particles, and consequently the clay particles detach from each other and form the dispersive soil structure (Mitchell, 1993; Ouhadi and Goodarzi, 2003). The results of Figure 3 show that the soil solutions with sodium...
hydroxide and sodium carbonate still have the higher pH, respectively. While at the concentration of 1 meq/l and less, the pH of illite/NaOH is more than the pH of other illite/electrolyte mixtures, at the concentration above 1 meq/l, the pH of illite/NaOH and illite/Na$_2$CO$_3$ gets closer to each other. It seems that the pH effect of NaOH controls the illite/NaOH behaviour at the concentration less that 1 meq/l. With an increase in concentration, due to the relatively similar pH of illite/NaOH and illite/Na$_2$CO$_3$, the PDI's impact of CO$_3^{2-}$ comes to control the soil/electrolyte interaction. The above conclusion can be confirmed by the results presented in Figure 1, in which at the concentration of 1 meq/l and less, the turbidity of illite/NaOH is more than the turbidity of illite/Na$_2$CO$_3$. In addition, in the same Figure, in an increased the concentration of NaOH and Na$_2$CO$_3$, the turbidity of illite/Na$_2$CO$_3$ is present in a larger quantity. At this high concentration, the pH of illite/NaOH and illite/Na$_2$CO$_3$ is relatively similar. Therefore, the PDI's effect causes greater turbidity for illite/Na$_2$CO$_3$ at higher ranges of concentration.

To investigate the impact of electrolyte types and concentrations on the microstructure of illite, a series of XRD experiments were performed. Samples were prepared according to the experimental methods that were addressed in the material and method section. Figure 4 shows the results of XRD basal spacing variations for the major peak of illite at different types and concentrations of electrolytes. According to the results of Figure 4, the major basal spacing of illite in the mixture of illite/Na$_2$CO$_3$ is higher only a little than that of other soil/electrolyte mixtures. At 5 meq/l of illite/Na$_2$CO$_3$ the quantity of position of major basal spacing is the highest. The sample of illite/NaOH has the next highest basal spacing position. The other two samples have relatively constant position for the major basal spacing of illite. The monitoring of XRD peak intensity variations is another tool used to investigate the effect of pore fluid on the microstructural performance of clays. Figure 5 shows the results of XRD peak intensity variations for the major peaks of different illite samples which have different types and concentrations of electrolytes. The results of this Figure show that still the highest peak intensity for the major basal spacing of illite is observed at the concentration around 1 meq/l of Na$_2$CO$_3$ and NaOH. The other illite-solution mixtures also show the highest peak intensity at low electrolyte concentration.
atoms in these planes (Cullity, 1976). Therefore, the different clay minerals are characterized by first order basal reflections at 7° (kaolinite), 10° (illite) or 14° (montmorillonite) and etc.

If one compares the impact of PDIs on the position of major peak intensity variations (results of Figure 4) with their impact on peak intensity variations (results of Figure 5), it will be observed that such an impact is noticeable on peak intensity variations, while PDIs have shown very little impact on peak position. Assuming that the ionic bond of potassium in illite clay is a relatively strong bonding, it prevents the noticeable increase in the quantity of basal spacing of illite after the water adsorption by elevated surface potential of PDIs. As the concentration of PDI increases, corresponding to the similar concentration of salt producing the highest turbidity, a noticeable increase in negative charge of clays occurs. It was already mentioned that among the several sources which give rise to negative charges of clays, the presence of OH\(^-\) and CO\(_3^{2-}\) ions also causes the development of surface charges and the electrical surface potential of clays. This is why they are called potential determining ions (Tan, 1982). At the highest dispersivity condition, the highest turbidity is observed (Figure 1). Usually a dispersed structure indicates some degree of orientations of particles (Yong and Warkentin, 1966). Such dispersed structures and detached clay particles show higher peak intensity. A further increase in the concentration of salt, due to the further increase in Na\(^+\) ions, causes a further decrease in thickness of double layer. The reduction of repulsive forces produces more flocculated structure. These flocculated particles settle quickly. Subsequently, the turbidity of the supernatant will decrease because of the lower concentration of particles in supernatant.

To investigate the influence of microstructural change due to the PDIs on the contaminant adsorption behaviour of illite, a series of illite samples were treated by 1 meq/l Na\(_2\)CO\(_3\) to have the highest dispersivity according to the turbidity and XRD results. In addition, by mixing another illite sample with 1N CaCl\(_2\) solutions, Ca-illite samples were prepared. By performing several batch equilibrium tests, the variations of heavy metals retention in these treated samples were investigated.

Figure 6 compares the retention properties of illite, Ca-illite and PDI-treated illite in samples exposed to different concentrations of zinc nitrate. The achieved results indicate that the PDIs treated illite has shown the highest adsorption/retention in comparison to other samples. In fact, the retention by PDI's treated illite is at least 15% more than untreated illite. This retention for PDI's treated sample is 32% more than Ca-illite. In other words, at the concentration of Na\(_2\)CO\(_3\) in which the highest turbidity and the highest XRD peak intensity occurs, the highest heavy metal retention is observed on the PDI's treated illite. Similar behaviour can be observed once the retention of Pb\(^{2+}\) by treated illite is investigated (Figure 7). While the higher adsorption for Pb\(^{2+}\) in comparison with that of for Zn\(^{2+}\) ions can be attributed to the either pH impact or the selectivity phenomena (Yong et al. 1993, Ouhadi et al. 2006), the higher adsorption of PDI treated illite can be explained as follows:

As was previously stated, in PDI-treated illite, chemical adsorption or chemisorption of PDI ions refers to the high affinity or specific adsorption which occurs in the inner Helmholtz layer through covalent bonding in PDI-treated illite. In specific cation adsorption, the ions penetrate the coordination shell of the structural atom and are bonded by covalent bonds via O and OH groups to the structural cations. The most important point is the fact that the chemisorbed ions can influence the sign of \(\psi\) (surface potential) (Yong 2001). In such a case the PDIs are no longer acting as an exchangeable counterion (Sparks, 1986). Therefore, because of the influence of PDIs on the surface potential of clays, the negative charge of clay particles increases, leading to an increase on the heavy metal contaminant adsorption of soil.
4. CONCLUDING REMARKS

The results of this study show that even though the theoretical calculation of double layer theory does not take into account the effect of different anion types on the variation of the thickness of the double layer, the anion type has a major impact on the microstructure variations and soil-contaminant interactions of clay minerals. It is shown that the presence of potential determining ions (PDI) in pore fluid of illite is among the major fundamental factors impacting the microstructural performance and contaminant adsorption of illite. The results of this study show that the PDI treated illite has more capacity for adsorption of heavy metal contaminant than that of illite or Ca-illite. In addition, the adsorption properties of clays are significantly affected by the type of exchangeable cations.

5. REFERENCES


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