

Assessing the anion type effect on the hydro-mechanical properties of smectite from macro and micro-structure aspects

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Abstract. The expansivity of clayey soils is a complicated phenomenon which may affect the stability of geotechnical structures and geo-environmental projects. In all common factors for the monitoring of soil expansion, less attention is given to anion type of pore space solutions. Therefore, this paper is concerned with the impact of various concentrations of different inorganic salts including NaCl, Na₂SO₄, and Na₂CO₃ on the macro and microstructure behavior of the expandable smectite clay. Comparison of the responses of the smectite/NaCl and smectite/Na₂SO₄ mixtures indicates that the effect of anion valance on the soil engineering properties is not very pronounced, regardless of the electrolyte concentration. However, at presence of carbonate as potential determining ions (PDIs) the swelling power increases up to 1.5 times compared to sulfate or chloride ions. The samples with Na₂CO₃ are also more deformable and show lower osmotic compressibility than the other mixtures. This demonstrates that the barrier performance of smectite greatly decreases in case of anions with the non-specific adsorption (e.g., Cl⁻ and SO₄²⁻) as the salinity of solution increases. Based on the results of the X-ray diffraction and sedimentation tests, the high soil volumetric changes upon exposure to carbonate is attributed to an increase in the repulsive forces between smectite basic unit layers due to the PDI effect of CO₃²⁻ and increasing the pH level which enhance the buffering capacity of smectite. The study concluded that the nature of anion through its influence on the re-arrangement of soil microstructure and osmotic phenomena governs the hydro-mechanical parameters of expansive clays. It seems not coinciding with the double layer theory of the Gouy-Chapman double layer model.

Keywords: smectite; anion type; microstructure; volume change behavior; barrier performance

1. Introduction

Expansive clayey soils are generally found in arid and semi-arid climates in various locations in Australia, China, Iran, Oman, USA, and many other countries (Al-Rawas and Goosen 2006, Seco *et al.* 2011). These types of soils can undergo periodic volumetric changes in the form of ground heave and settlement when subjected to moisture fluctuations. Such volumetric changes may lead to exert stress and serious problems to civil structures. On the other hand, the high swelling clayey soils are favorable material for the construction of engineered barrier system (EBS) in waste disposal projects (Katsumi *et al.* 2008, Villar *et al.* 2012). This is due to possessing very low

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permeability and large capacity for attenuation that can protect the environment by avoiding the migration of pollutant (Ouhadi *et al.* 2010, Chen and Huang 2013).

Based on the importance of the soil expansion from a geotechnical and geo-environmental point of view, it is necessary to take attention on the all factors that govern the behaviour of swelling soil. The soil expansivity is a complicated phenomenon which is affected by the numerous parameters such as mineralogy and pore fluid characteristics of soil (Lee *et al.* 2005, Kaufhold and Dohrmann 2011, Zhu *et al.* 2013). Even though up to now, the impact of pore fluid characteristics on the expansivity behavior of clayey soils have been investigated by many researchers, they mainly focused on the effect of cation nature and ions concentration and less attention is given to the role of anion type in this phenomena. Volume change behaviour of clayey soils upon exposure to concentrations of inorganic pore fluid can be usually described by the use of osmotic compressibility theory (Di Maio 1996, Yukselen-Aksoy *et al.* 2008). Theoretically the swelling capacity is strongly dependent on the salinity and major type of adsorbed cation although the recently reported research results show that the microstructure and rheological behavior of clayey soils are highly dependent on the type of anion presence on the soil pore fluid (Penner and Lagaly 2000, Ouhadi *et al.* 2007). In fact, anions through the physical adsorption (non-specific adsorption) can accumulate around the edge of the clay particles, causing neutrality on the positive charge of these edges. This will eliminate the edge to face interaction providing a decrease in shear strength of slurry and a more formation of dispersive structure. Sulfate (SO_4^{2-}), chloride (Cl^-) and nitrate (NO_3^-) are generally considered as anions that have the physical adsorption (Yong 2001). On the other hand, some anions through the chemical reaction (chemisorption/specific adsorption) have also the ability to adsorb onto the clay particles surfaces and affect their surface potential that are referred to as the potential determining ions (PDIs) (van Olphen 1977). Most of the common anions in this group are OH^- , CO_3^{2-} , and PO_4^{3-} . Subsequent to adsorption of these anions onto the clay particles, they can affect the sing of zeta potential and increase the negative charge of the clay surfaces, causing an increase in the thickness of particles' double layers (Abend and Lagaly 2000, Ouhadi and Goodarzi 2003). Such a variation might increase the tendency of swelling due to the fact that more surface area of the clay particles is exposed to the water.

With respect to the afore-mentioned anion impact on the charge of the clay particles, one may expect that any variation in anion type of solutions can be accompanied by a change in the microstructure of fine-grained soil which may in turn affect its swell-shrink performance. Therefore, the main objective of this paper is to investigate the effect of different anion fraction with similar source of cation on the microstructure of clays and on the properties at macroscopic level (hydro-mechanical parameters) of smectite as highly expansive soil. An attempt is also made to demonstrate the role of PDIs in enhancing of smectite barrier performance when is used as a part of the EBS in solid waste landfills.

2. Materials and methods

2.1 Materials

The soil expansion usually happens at presence of active clay minerals, such as montmorillonite (Al-Rawas and Goosen 2006, Kalkan 2011). The application of smectite (rich in montmorillonite) as buffer material is also very favorable in engineering barrier system for the immobilization of hazardous materials such as radioactive wastes (Mishra *et al.* 2011, Cui *et al.* 2012, Chen and Huang 2013). So in this research, smectite was used as source material for all tests.

To characterize the soil sample, its engineering properties were determined according to ASTM methods (ASTM 2006). Atterberg limits (i.e., liquid limit, *LL*, and plastic limit, *PL*) were determined in accordance with the ASTM D-4318 Standard Test (2006). The swelling test was also performed according to ASTM D-4546, for measuring the swelling potential and swelling pressure of the soil sample. A brief description of Atterberg limits and swelling tests are presented in the Section 2.2. In order to determine the compaction characteristics, the standard Proctor compaction test was performed according to ASTM D-698 on the smectite clay. Particle size distribution of the smectite sample was obtained by the hydrometer analysis (ASTM 2006, D-422). According to the grain size distribution graph and Atterberg limits, the soil has 77% clay content and was classified as CH (clay of high plasticity). The specific gravity of soil solids (G_s) was determined according to ASTM D-854. To determine the unconfined compression strength (UCS) of soil smectite sample, the UCS test was performed following ASTM D-2166, under a constant strain rate of 1.2 mm/min. The soil-chemical analyses were conducted using the procedures described in the manual of EPA (1983) and laboratory manual of the Geotechnical Research Center of McGill University. The cation exchange capacity (CEC) of soil sample was calculated by using the BaCl₂ replacement method (Hendershot and Duquette 1986). The specific surface area (SSA) was determined using the ethylene glycol monoethyl ether (EGME) adsorption method described by Heilman *et al.* (1965). The electrical conductivity (EC) of the soil sample and the soil pH was measured in 1:20 soil suspension. The X-ray diffraction (XRD) analysis was performed based on the method suggested in the studies reported by Ouhadi *et al.* (2010). The engineering and geo-environmental properties of the soil sample are given in Table 1. Mineral identification with X-ray powder diffraction technique for this sample showed that it contained high amount of montmorillonite mineral. In addition, its main exchangeable cation was sodium ions. Therefore, it can be considered as a Na-montmorillonite which has the highest degree of tendency to swell.

To investigate the effect of anion type of pore space solutions on the swell-shrink behaviour, the soil-water interaction experiments were conducted with different alkaline salts (i.e., Na₂SO₄,

Table 1 Engineering and geo-environmental properties of smectite

Characteristics	Quantity measured
Mineral composition in decreasing abundance	Montmorillonite, Quartz, Calcite
Soil-pH	9.04
EC, mS/cm	2.80
SSA, m ² /g	435
CEC, cmol /kg	81.5
Clay fraction, %	77
Specific gravity, G_s	2.81
Liquid limit (LL), %	350
Plasticity index (PI), %	309.1
Soil classification	CH
Swelling potential, %	140
Maximum dry density, gr/cm ³	1.27
Optimum moisture content, %	44.8
Unconfined compression strength, kPa	315

NaCl , and Na_2CO_3) covering a wide range of salinities (ionic concentration 0 to 1 N). To select the type of alkaline salts, the similarity of their cation with the dominant cation in the groundwater, which mostly contain sodium (Bennett and Gens 2008), is considered.

2.2 Samples preparation and experimental methods

The smectite clay samples were separately mixed with the different solutions and the soil-electrolyte homogenized mixtures were then used at different tests. For each test, the triplicate samples were prepared to verify the reproducibility of results. The average values of results employed in further computation and plotting of graphs. The following tests were conducted to evaluate different effects of various types and concentrations of solutions on the hydro-mechanical and microstructural performance of smectite as a highly expansive soil.

Generally, Atterberg limits are one of the common geotechnical tests that give a first insight into the chemical reactivity of the clay surfaces and also can be used as an indirect indicator for the swell-shrink performance of clayey soils (Montes *et al.* 2003, Mishra *et al.* 2011). This is because the Atterberg limits values depend precisely on the same physical factors which determine the swelling potential of soils, factors such as the shape of particles, effective size, uniformity, and water retention capacity. In order to investigate the effect of water chemistry on the Atterberg limits, the soil samples were exposed to the electrolytes at different concentrations then placed in plastic bags to remain for at least 96 hours. The samples in the bags were subjected to mixing before executing the tests. Following the attainment of equilibrium, the liquid limit and plastic limit tests were performed according to ASTM D-4318 (2006).

To determine the swelling characteristics variations of soil samples due to wetting with the solutions that contain different ions concentration and anion type, as a first step, appropriate amount of each solution as optimum moisture content and soil required for the maximum dry density were weighed and a hand mixing technique was employed to enhance the homogeneity of sample. Subsequently, the wet homogenized mixtures were placed in the consolidation ring of 76 mm diameter and 20 mm height. To ensure uniformed compaction, the samples were subjected to a static compression force using a hydraulic jack to achieve the desired dry density. In order to achieve equilibrium, the samples were kept in a humid chamber at temperature $22 \pm 1^\circ\text{C}$ for 96 h. The consolidation ring was immersed in the solution with the same composition as the preparation liquid, and the entire consolidation cell was enclosed within a plastic cover to minimize fluid evaporation. The swelling tests were then performed according to ASTM D-4546 (2006), for measuring the swelling potential and swelling pressure of the soil samples.

For performing consolidation tests and permeability measurement, suspensions of smectite with the various types and concentrations of each solution were loaded under 25 kPa to prepare homogenous compacted samples by an earlier described procedure of Ouhadi *et al.* (2010). For this purpose, the soil suspensions in a ratio of 1:20 were prepared in the 1000 mL laboratory flask, were shaken for 24 h on a horizontal shaker and left for a 96 h to attain equilibrium. Air from the samples in the flasks was extracted using a laboratory pump for about 2 h. After completion of air extraction, the soil-solutions were poured in plastic molds with a radius of 70 mm and 150 mm height and an incremental loading to reach pre-consolidation state at 12.5 kPa was used. The undisturbed samples were taken using a 50 mm diameter and 20 mm height consolidation ring. All the samples were initially loaded with a pressure of 12.5 kPa and increased gradually by an increment ratio of 1 to a maximum pressure of 800 kPa. The permeability of those samples was calculated from the oedometer testing data, for various stress increments. It should be noted that

consolidation test has been widely used by other investigators to determine the hydraulic conductivity of fine-grained soil (Mesri and Olson 1971, Sivapullaiah *et al.* 2000, Ouhadi and Goodarzi 2006, Yong *et al.* 2009, Sakr *et al.* 2009, Olgun and Yildiz 2010, Ouhadi *et al.* 2010, Mishra *et al.* 2011). This test as an indirect method generally provides the hydraulic conductivity comparable with the permeability test, however slightly underestimates the hydraulic conductivity compared with the permeability test (Mitchell and Madson 1987). Beside, due to flexibility of consolidation test for testing mixtures under a range of confining pressures, it is the most useful test type to measure the hydraulic conductivity of soil in different conditions. Additionally, since the ratio of soil-electrolytes for performing consolidation tests was exactly similar to that used in the sedimentation, pH and XRD tests, it is possible to compare the physico-chemical interactions and microstructure changes of treated specimens in conjunction with the hydraulic conductivity variations which are calculated from the consolidation test. On the other hand, the aim here was not to find the exact permeability coefficient (k) value of soil samples but to assess how the chemical solutions affect the coefficient of permeability when compared with DI water. Therefore, in this study, k values of soil samples were measured by application of oedometer testing apparatus.

To investigate the impact of electrolyte characteristics on the microstructure of clayey soils, the X-ray diffraction response of smectite samples with different anion types and ions concentration were also studied. Soil samples were prepared by adding solutions of Na_2SO_4 , NaCl , and Na_2CO_3 at different concentrations to the smectite sample in 1 to 20 soil-electrolyte ratios. The soil suspensions were shaken for 24 h and left for a 96 h in a closed laboratory flask in order to attain equilibrium. The volumetric flask was then placed on an ultrasound to adequately disperse the soil before XRD testing. Finally, 4 drops of the prepared solution were positioned on a glass slide by using a micro pipette. The coatings on glass slides for all samples had similar thicknesses. The glass slides were air dried and were scanned in the 2θ range of 2 to 70 degrees for their XRD spectra. A Bruker D4 apparatus with $\text{Cu-K}\alpha$ radiation was used to obtain the X-ray diffraction patterns of soil samples. On the other hand, it is well-known that the rate of sedimentation in a soil suspension is a function of the particles size. So, at a constant laboratory conditions, the variations in sedimentation rate of a series clayey soil samples with similar mineralogy can be ascribed to the changes in the clay particles arrangement (Lee *et al.* 2005). Therefore, to further evaluate the microstructure variation of smectite samples, the sedimentation tests were performed on the soil specimens with different amount of salts. The soil suspensions were prepared similar to that used for the consolidation test. After the equilibrium process, the samples were poured in the 1000 mL cylindrical hydrometer jar and their sedimentations were then monitored.

3. Results and discussion

3.1 Effect of anion types and ions concentration on the physical properties

Cations and anions transportation in expansive soil layer can happen either from groundwater or from the solubility of bedrocks. On the other hand, it has been shown in the previous studies that the physical and mechanical properties of clayey soils can be affected by the nature of pore fluid such as type of exchangeable cations and salt concentration (Ouhadi and Goodarzi 2006, Chen and Huang 2013). Based on this fact, one may expect various changes in Atterberg limits due to interaction of smectite with the solutions that contain different anion type. As can be seen in

Fig. 1, the plasticity index of smectite is a function of the concentration and anion type of solutions. For example the plasticity index of the natural smectite clay ($PI = 309.1\%$) declined to about 68% in specimen containing NaCl with a normal concentration of 0.5 N, however the further addition in the salt provided little additional decrease of the PI. Such changes can be explained in the terms of the interparticle forces between the clay particles playing an important role in determining the plasticity of clayey soils. In fact, with an increase on the salt concentration, interparticle repulsion in smectite decreases, the aggregate structure takes place (Mishra *et al.* 2011, Zhu *et al.* 2013) leading a significant decrease in the soil PI. The other studies have also shown that the plasticity of CH clayey soils generally decreases as the salinity of pore space solution increases, which is consistent with the double layer theory.

According to the presented results in Fig. 1, at similar concentration, the plasticity index values of samples containing Na_2SO_4 and NaCl solutions get very much close to each other. It means that the valancey of anions having the physical adsorption (e.g., Cl^- and SO_4^{2-}) has a minor impact on the water uptake capacity of clayey soil. However, as the smectite samples were exposed to sodium carbonate, a remarkable increase in the soil PI especially at the low electrolyte concentration was occurred in comparison with the other soil/electrolyte mixtures. Such behavior may be associated with the chemisorption of carbonates as PDIs that significantly contributes to the net repulsive activity between the clay particles and increases the thickness of particles' double layers (Penner and Lagaly 2000, Ouhadi *et al.* 2007). This increases the ability of the clay surfaces to hold water and eventually higher soil plasticity was observed. Even though a further increase in the concentration of sodium carbonate also promoted a decrease in the plasticity index, still smectite/ Na_2CO_3 mixtures show higher PI than the other soil/electrolyte mixtures as the salinity of solution increased. Its reason may be attributed to the excess negative charge on the clay particles due to the impact of carbonate as potential determining ions (Abend and Lagaly 2000). On the other side, the consistency limits of fine grained soils can be correlated with various engineering

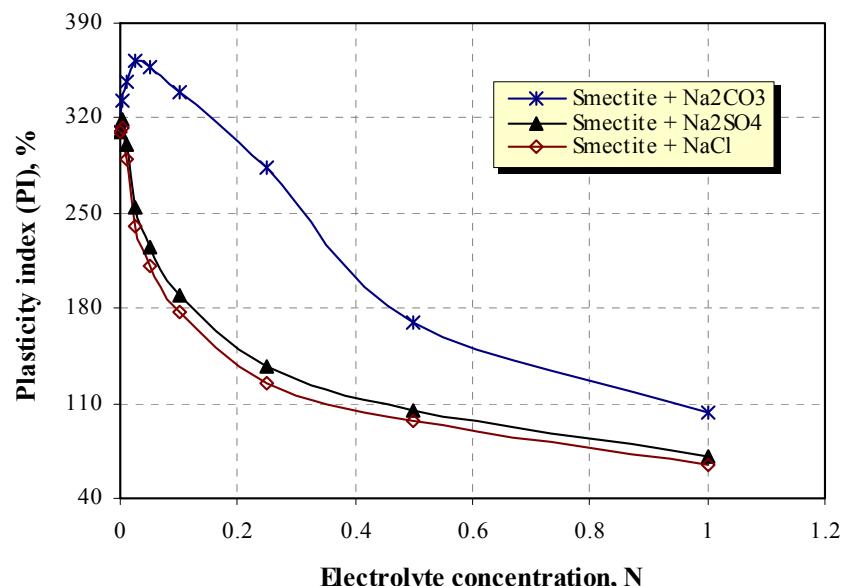


Fig. 1 Evolution of plasticity index measured using different solutions

properties, such as swell-shrinkage behavior. Therefore, based on the results of Fig. 1, one may conclude that the interaction of PDIs and clayey soils may lead to an increase in their potential for water adsorption and consequently an increase in the tendency for soil expansivity, as will be experimentally evaluated by other macro and microstructure test in this paper.

3.2 Effects of anion types and ions concentration on the expandability power

Safe and economic designs of geotechnical structures on clayey soils and performance of clay barriers for geo-environmental purposes require the knowledge of swelling characteristics such as swelling potential and swelling pressure (Kalkan 2011, Villar *et al.* 2012). So, to take into consideration the impact of anion type on the expansivity behavior of smectite, different salt solution having similar cation type and different anion type were used as electrolyte. Figs. 2 and 3 show the variation of expansivity and swelling pressure of the smectite samples with different concentrations of these electrolytes. As can be seen in these figures, the interaction of solutions with smectite influenced the soil expansion both by the type of anion and salt concentration. At the low electrolyte concentration, the quantity of the percentage of swelling increased and then decreased back as the salinity of pore fluid increases. These results confirm the occurrence of water uptake capacity increasing in the low electrolyte concentration also observing in the Atterberg limits tests. In fact, after the addition of a small amount of sodium ions the edge to face attraction has become less than the face to face repulsion (Yong and Sethi 1977), and consequently the clay particles become more hydrated (Ouhadi *et al.* 2007) and an increase in the swelling power occurs. The further addition of different salts lead to the decrease of the thickness of diffuse double layer (DDL) and decrease the distance between the particles by increasing the osmotic potential. This causes the attractive force to be dominated, hence developing of the capillary stress

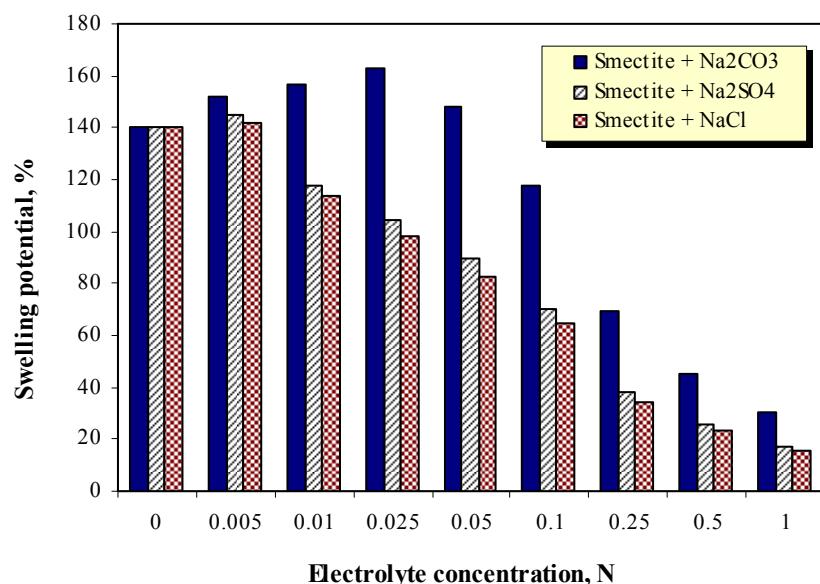


Fig. 2 Variation of swelling potential of smectite due to wetting with different solutions under a vertical stress of 1 kPa

that formed between the particles boundaries and finally giving a tighter packing or aggregation of particles (Herbert *et al.* 2008). Such microstructure changes reduce the available surface for interaction with water which negatively affects the swelling characteristics of smectite.

The results also demonstrated that the interacting of soil samples with the potential determining ions (i.e., CO_3^{2-}) increased the swelling power up to 1.5 times as compare to samples containing sulfate or chloride ions, although this difference becomes less patent as the salinity of the solution increased. On the other hand, due to physical adsorption of sulfate and chloride ions with the clay particles, one cannot observe a major change between the effects of Na_2SO_4 and NaCl solutions on the expansivity behaviour of smectite. The fact that smectite specimens with similar cation and different anion have different swelling capacity can be attributed to their different negative layer charge. As the negative layer charge increases, coming from the chemisorption of PDIs, the adsorption of water on the clay surfaces tend to become larger and consequently the swelling potential increased. This also causes the repulsive force to be dominated and thereby the samples with solution containing CO_3^{2-} have higher swelling pressure than the samples with solution containing Cl^- and SO_4^{2-} . This may indicate that the swell behavior described in the Figs. 2 and 3 cannot be completely explained by the theoretical base of double layer theory. Since according to the Gouy-Chapman double layer model, the thickness of double layer is strongly dependent on the salinity and nature of adsorbed cation, and the anion type does not have any impact on the microstructure variations of the clay particles.

To more precisely investigate on the extent of contribution of anion type on the soil behavior the sedimentation performance of smectite samples with various concentrations of NaCl , Na_2SO_4 , and Na_2CO_3 solutions was also evaluated. Fig. 4 shows that for NaCl solutions, the soil sedimentation increased considerably for an increase in the concentration from 0 to 0.5 N. However, upon the further addition of the electrolyte concentration from 0.5 to 1 N, the sedimentation was increased marginally. Similar trends were obtained for smectite samples with

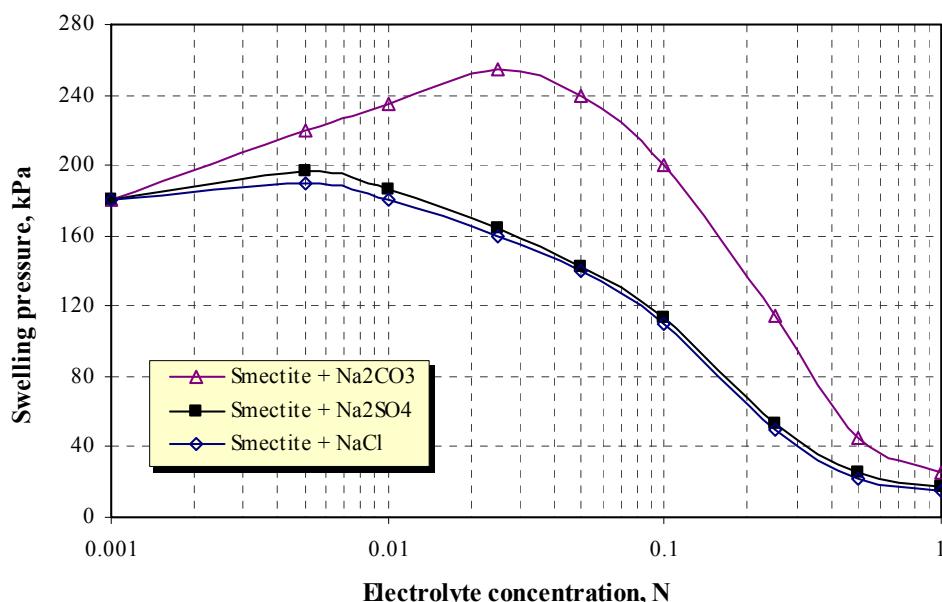


Fig. 3 Variation of swelling pressure of smectite due to interaction with different solutions

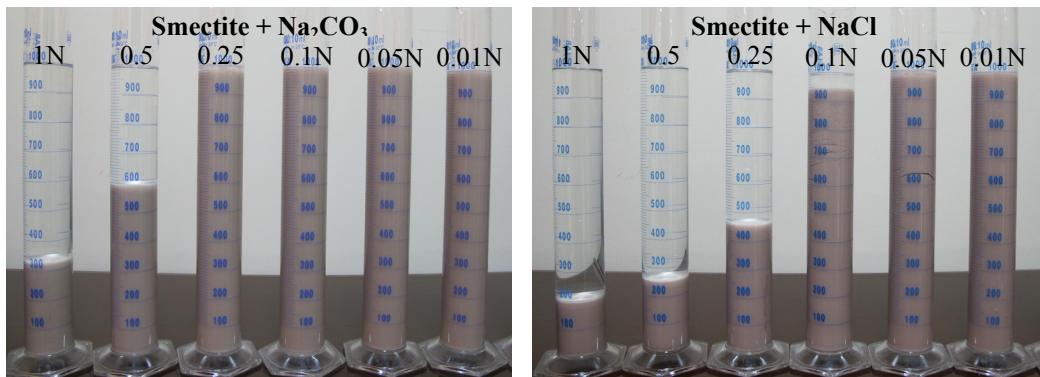


Fig. 4 Impact of different solutions on the sedimentation performance of smectite

Na_2SO_4 solutions. In contrast to this, the sedimentation of smectite samples significantly increased when the concentration reached to 0.5 N of Na_2CO_3 solutions. It is clearly observed in Fig. 4 that for same content of salt, higher sedimentation was occurred for NaCl solutions compared to Na_2CO_3 solutions. In fact, with an increase in the concentration of NaCl solutions, an increase in the van der Waals attraction take place which allows the interlayer spacing to become small, diminishing the tendency of the clay particles to go into suspension causing an increase in the sedimentation of the smectite sample. On the other side, in the presence of carbonate the attraction has become less than the repulsive force (Penner and Lagaly 2000) due to increasing the negative charge, and thereby the particles become more disengaged, resulting in less sedimentation of smectite compared to the smectite/ NaCl mixtures with a same concentration. However, at high electrolyte concentration, the anion type does not have a marked impact on the clay particles sedimentation. Indeed, based on the osmotic pressure concept, an increase in the dissolved ions in the soil pore fluid can lead to a reduction in the repulsive forces which is the result of closer of individual the clay particles (Katsumi *et al.* 2008, Yong *et al.* 2009, Kaufhold and Dohrmann 2011) that will make unstable suspension and a noticeable increase in the soil sedimentation regardless of anion type. Therefore, it may be concluded that an increase in the swelling power at presence of PDIs (Figs. 2 and 3) is the consequence of the extent negative charge, allowing the interlayer spacing to get larger, resulting in higher swelling.

3.3 Effects of anion types and ions concentration on the compressibility behavior

To further investigate on interaction process of smectite and PDIs and its consequence on volume change behavior of smectite, a series of consolidation experiments on smectite mixtures with different solutions were also performed. Fig. 5 presents the results of the compression stages in term of final void ratios after the interaction of smectite samples with the various concentrations of solutions. It was evident from this figure that at each specific applied loading, as the concentration of NaCl solutions increase, the samples face less settlement.

The lower compressibility of smectite/ NaCl samples with high-salinity solutions could be a consequence of the lower porosity and the stiffer performance they reach after the interaction with salts. For the smectite samples having Na_2SO_4 as their pore fluid, almost a similar consolidation behavior was observed. In fact, with respect to the osmotic pressure concept the thickness of the

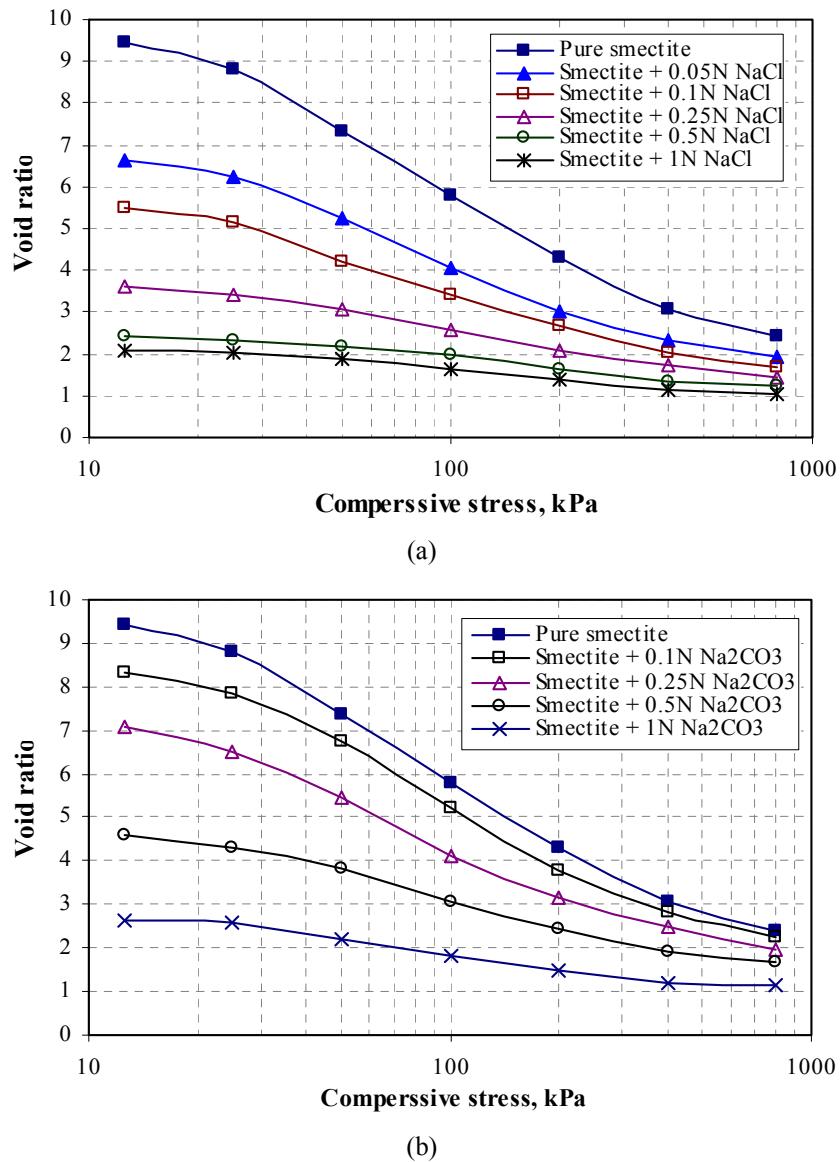


Fig. 5 Variation of the consolidation behaviour of smectite sample due to interaction with different solutions

diffuse double layer is continuously decreased with increasing the ions concentration. Once the diffuse double layer tends to depress, the smectite particles is allowed to come closer to each other (Karnland *et al.* 2007). The consequence of such an interaction will be the formation of noticeable flocculated structure. In such a case, the aggregation of particles forms which is the result of closer of individual clay particles and formation of clay clusters. Those clusters become larger and particles tend to settle even before the application of external loading which is called chemical consolidation that come from the impact of pore space solutions characteristics.

Fig. 5 also clearly exposed that the type of anion has a major impact on the volume change behavior of smectite. It can be seen that by increasing the amount of NaCl from zero to 1 N, the settlement value of smectite noticeably changes. As long as the concentration of NaCl is less than 0.1 N, the soil sample shows considerable settlement. However, as the initial concentration of salt increases more than 0.1 N, most of the settlement occurs before the application of external loading which is mainly related to chemical consolidation. In contrast, the compressibility potential of smectite + Na₂CO₃ samples significantly decreased when the concentration reached to 0.5 N of salt. It means that for same content of salt, especially at low concentration of salt, higher settlement (i.e., lower osmotic compressibility) was occurred for samples having Na₂CO₃ as compared to the other soil/solutions mixtures, assuming a specific applied loading. The explanation for this achieved result which is consistent with the results of the Atterberg limits and the swelling tests may be due to the two effects of PDIs on the process of smectite-electrolyte interactions. In one aspect, as was previously addressed, the sodium carbonate is a source of producing CO₃²⁻ ions which is known as one of the potential determining ions that can lead to increase on the repulsion force between the clay particles due to increasing their negative charge (van Olphen 1977). This causes the increase of the double layer thickness and subsequently those particles will have a tendency to settle slowly (Fig. 4). Therefore, at each specific applied loading, the mixtures of smectite + Na₂CO₃ face lower settlement than the smectite samples with NaCl solutions. In the second aspect, the lower compressibility of the smectite mixtures containing CO₃²⁻ can be explained in context of pH. Since, the presence of carbonate may increase the pH of clayey soils (Yong 2001) that may delay the soil osmotic consolidation as the electrolyte concentration increases. Based on this assumption, the pH of smectite samples with the various solutions were measured. To monitor the changes of soil-pH, the smectite suspension samples with different electrolytes in a ratio of 1:20 were prepared in the 50 mL centrifuge tubes and shaken for 24 h on a horizontal shaker for equilibrium. The pH of the each slurry was then recorded after 96 h and presented in Fig 6. As can be seen in this figure, adding NaCl and Na₂SO₄ to smectite even up to 1 N of concentration had no significant effect in term of pH. In contrast, at presence of carbonate ions, the pH increased from 9 to about 11 with

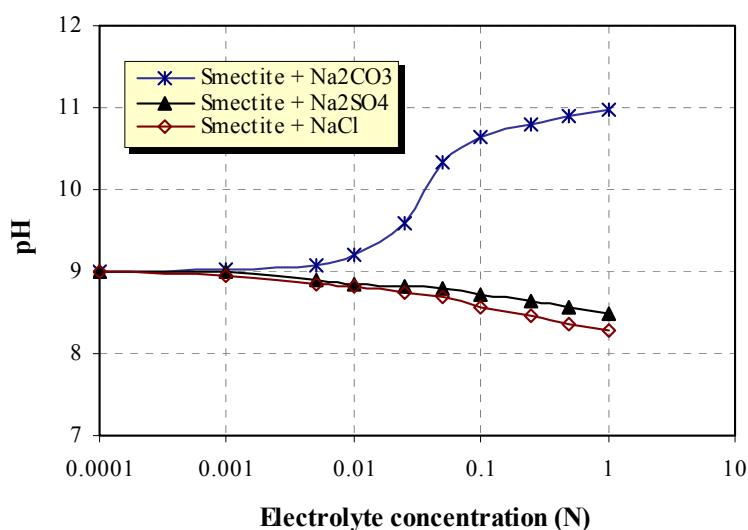


Fig. 6 pH variation of smectite due to interaction with different solutions

1 N of Na_2CO_3 solutions. This increase in pH can decrease the formation of flocculated structure with increasing the salinity of solution (Ouhadi and Goodarzi 2006). In fact, increasing the pH will make the surface charge density more negative since the surface concentration of OH^- will be increased (Herbert *et al.* 2008). Those excess negative charges lead to an increase in the ions retention by smectite which decreases the concentration of dissolved ions in pore fluid that develops the osmotic compressibility at higher salt concentration for smectite/ Na_2CO_3 mixtures as compare to samples with NaCl or Na_2SO_4 . Consequently, with increasing the ions concentration, the decrease in settlement due to chemical consolidation is much less in case of Na_2CO_3 since we are simultaneously faced with the contrasting effects of carbonate (i.e., the PDI effect and increasing the pH) and the high concentration of salts. It should be noted that the consolidation behavior of smectite samples with different anion types is almost close together at high compressive stress or low void ratios, regardless of pore fluid characteristics. The decrease of the diffuse double layer's thickness due to breaking interparticles bonding by high pressures may be the source of this trend which is consistent with the results of previous studies (Castellanos *et al.* 2008, Yong *et al.* 2009). Therefore, it can be concluded that the effects of anion type on the variation of thickness of DDL and its consequence on the soil volume change behavior decrease as the density of the clay or exterior compressive stress increases.

3.4 Effects of anion types and ions concentration on the permeability

Any variation in the pore fluid of fine-grained soil may be accompanied by a change in the soil microstructure which may in turn affect its hydraulic conductivity (Mishra *et al.* 2011, Zhu *et al.* 2013). This point has important role on the swell-shrink performance of swelling soils. This is because, increasing the hydraulic conductivity can provide the water drainage in dipping expansive layers that may be generated instability problem in their body due to develop extensive volume change. Beside, one of the applicable tests for investigation of influence of pore fluid nature on the microstructure variation of clayey soils is the permeability measurement (Ouhadi *et al.* 2010). Therefore, the variations of permeability coefficient, k , of smectite samples with different

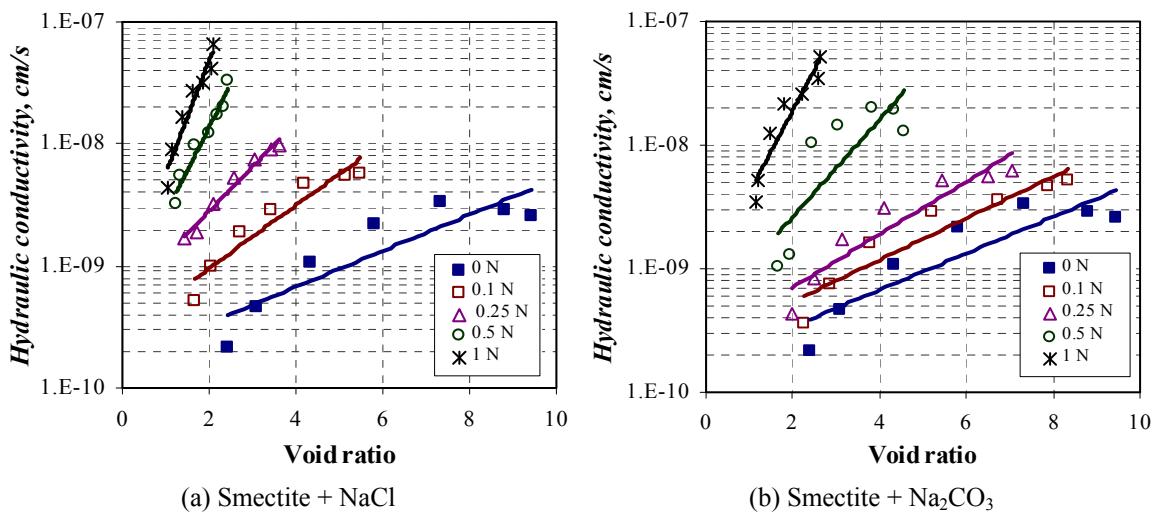


Fig. 7 Impact of void ratio and different solutions on the hydraulic conductivity of smectite

concentrations of the solutions were calculated from the results of the oedometer tests and presented in Fig. 7. There was the dependence of permeability coefficient on the anion type and electrolyte concentration. It is not uncommon to see that for each specific sample as the void ratio decreases the sample shows lesser permeability. In addition, the hydraulic conductivity values of the smectite samples with NaCl significantly decreased with increasing electrolyte concentration. Similar trends were obtained for smectite samples with Na₂SO₄ solutions. This process can reduce the performance of expandable smectite clay when is used as liquid impermeable material, especially as clay barrier surrounding geo-environmental projects such as high level nuclear waste disposal (Yong *et al.* 2009). The results of Fig. 7 demonstrate that for each specific void ratio, the sample having Na₂CO₃ as its pore fluid shows a lower permeability than that of the soil/NaCl mixture. For example at 0.25 N concentration of salt, the permeability is around one orders of magnitude lower. It should be noticed that at very high concentration of salt, almost an equal value of permeability was observed for all the soil/electrolyte mixtures and the anion type does not have any noticeable impact on changing the permeability of soil.

By and large, the results of permeability experiments show that the presence of sodium carbonate either by the PDI effect of CO₃²⁻ or by producing high pH contributes to the buffering capacity of smectite. In other words, at the presence of NaCl and Na₂SO₄ solutions, due to the physical interaction of their anion by the smectite particles the thickness of diffuse double layer can be continuously decreased as the salinity increases. This depression of the DDL allows for more aggregation to occur. In such a process, the clay particles get closer to each other which provide a flocculated structure and caused a gradual increase in the size of voids between the clusters of the clay particles. Therefore, the higher permeability owing to increasing the soil macropores was observed. On the other hand, as was previously addressed, the thickness of the DDL and consequently the wetted specific surface area become lesser at samples with similar concentration of NaCl or Na₂SO₄ solutions as compared to samples having Na₂CO₃ as their pore fluid. So, as the concentration of ions increases, the lower change in the microstructure and permeability of smectite + Na₂CO₃ mixtures are happened that promotes the barrier performance of smectite. Therefore, one may conclude that adding carbonate to the natural smectite can be considered to enhance its compatibility against the chemical attack when is used as a part of the EBS in waste disposal projects. However, in order to judge the applicability of the carbonate activated smectite as buffer material, further discussions such as the effects of the diffusion and sorption properties of buried wastes are also necessary.

3.5 Results of X-ray diffraction (XRD) analysis

Generally, montmorillonite minerals may have basal spacing of 12 to 15 Å which depends on the thickness of the water layers between the silicates unites and the nature of ions penetrating between those unites. On the other hand, some results are reported on the impact of pore fluid characteristics on the basal spacing and especially major peaks intensity of montmorillonite (Karnland *et al.* 2007). Therefore, to investigate the effect of solution nature on the microstructural performance of smectite, a series of XRD tests were performed. The present results in Fig. 8 illustrate that the solutions with similar source of cation and different types of anion have no a major influence on the major basal spacing of Na-smectite. The observed small difference between those results is less than the standard deviation which is reported for XRD analysis of clay minerals (Ouhadi *et al.* 2007) and thereby can be neglected. If fact, due to the similarity of cation (i.e., Na⁺) of the pore fluid with the exchangeable cation of soil sample which mainly contains

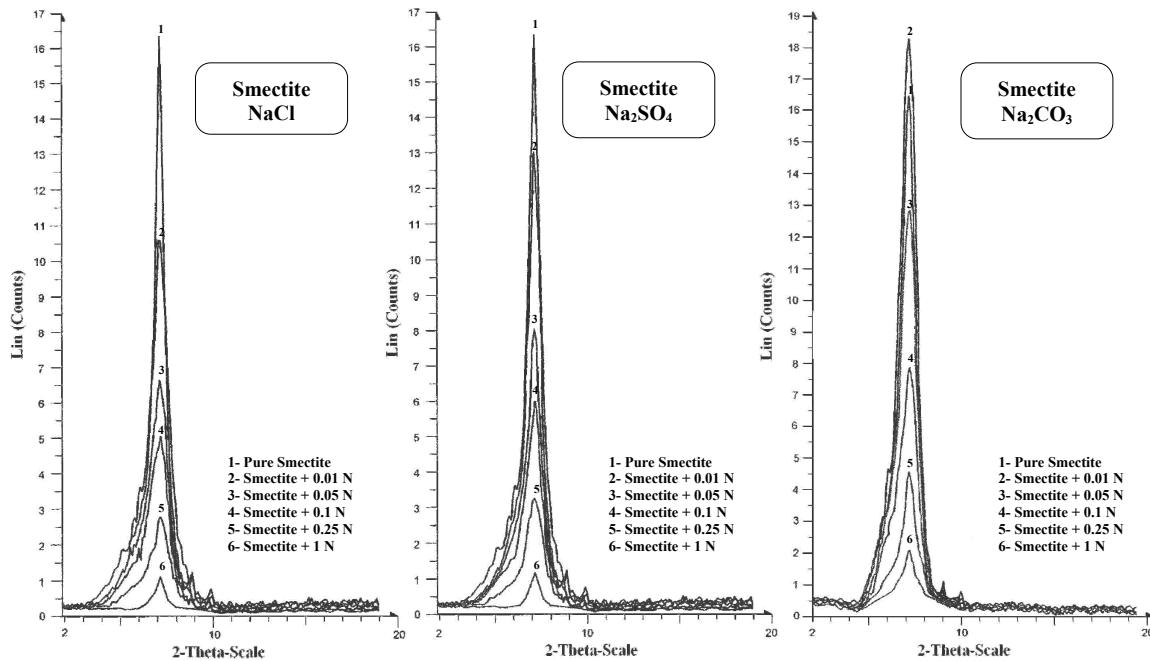


Fig. 8 Microstructural change of smectite after interaction with different solutions

sodium ions, one cannot observe any change between the effects of these solutions on the position of the major basal spacing of smectite.

On the other side, the monitoring of XRD peak intensity variations also can be used to evaluate the effect of pore space solution on the arrangement of the clay particle. Fig. 9 shows the changes of XRD peak intensity for the major peaks of smectite mixtures with different types and concentrations of electrolytes. In contrast with the peak's position, there was a remarkable dependence of peak intensity on the anion type and ions concentration. It means that the XRD peak intensity is more sensitive to the nature of pore fluid than the position of peak which mainly depends on the type of the exchangeable cation that is held in the exchange sit. As can be seen, the addition of salt generally leads to a decrease in the peak intensity although the smectite + Na_2CO_3 mixtures show the highest peak intensity at low ions concentration. Indeed, as was previously explained, the soil sample with low quantities of Na_2CO_3 exhibits a much-dispersed structure. This is attributed to the repulsive forces overcoming of the attractive forces. On the other hand, dispersed structure causes some degree of orientation of the clay particles (Yong 2001). These detached particles reflect the incident ray higher than that of the flocculated structure (Ouhadi and Goodarzi 2003) and consequently show the higher peak intensity. As the concentration of salt increases, due to a decrease in the thickness of the DDL and a more formation of flocculated structure, the clay particles settle quickly (Fig. 4) which promotes lower compressibility (Fig. 5). In such a case, those flocculated particles show lesser peak intensities owing to a decrease in the reflection of incident ray as compared to the dispersed structure. It is important to note that this type of reduction in the peak intensities is much less in case of smectite/ Na_2CO_3 mixtures. At each specific concentration, the higher intensity of these samples in comparison with that of the samples

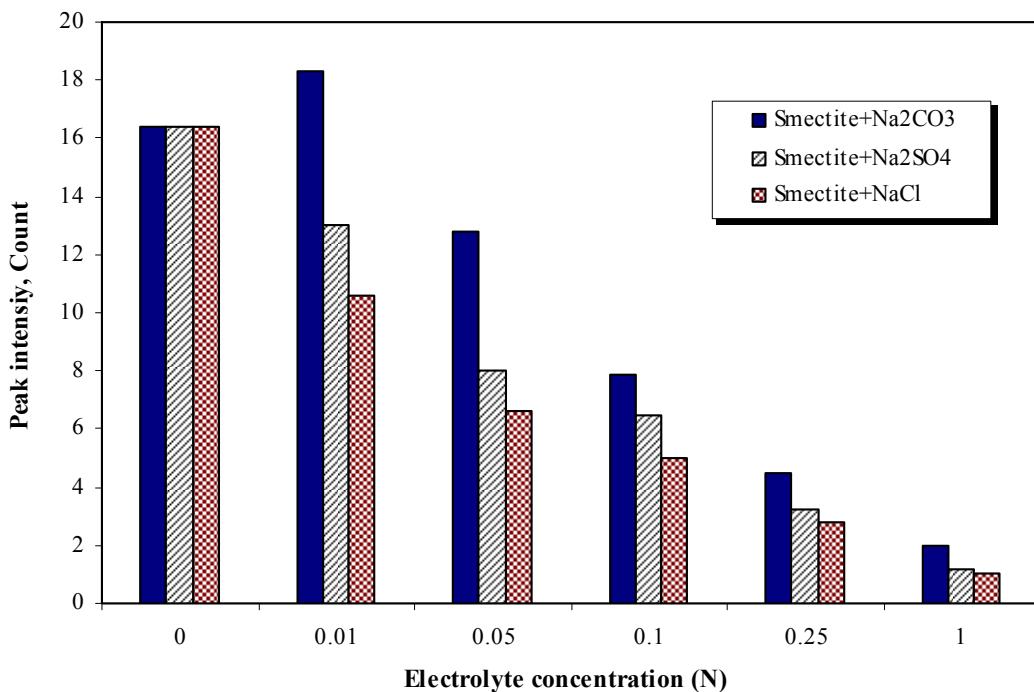


Fig. 9 Variations of XRD peak intensity for major peak of smectite having different solutions

having sodium chloride or sodium sulfate confirm the higher oriented structure once CO_3^{2-} anion presents in the soil solution. This finding is greatly consistent with the results of the macro-structure experiments.

Furthermore, even though the effect of anion valence cannot clearly be seen in the results of performed physical and mechanical tests, Fig. 9 indicates that the smectite samples with Na_2SO_4 show higher peak intensity as compared to the smectite/NaCl samples. This may be attributed to differences in ion activity for the sulfate and chloride anions resulting in a greater percentage of adsorbed sodium on the exchange complex for the sulfate system (Ouhadi *et al.* 2007). In such a case, the distance between the clay particles may increase and consequently the high peak intensity is observed.

4. Conclusions

The type of anion in the solution has a major influence on the hydro-mechanical performance of smectite. The results of micro-structure tests also confirm the alteration of soil properties due to interaction with different anion types. This may demonstrate that the double layer theory of the Gouy-Chapman double layer model does not completely take in to account the impact of all electrolyte characteristics on the variation of the thickness of DDL.

The presence of carbonate due to the PDI effect and producing high pH plays a significant role in enhancing the water uptake capacity of expansive soil. Consequently, for an equivalent concentration, the smectite/ Na_2CO_3 mixtures reveal higher swelling power and lower permeability

than that of the samples with NaCl and Na₂SO₄ solutions. Also, the soil osmotic consolidation is much less in case of Na₂CO₃. These differences are remarkable at intermediate stage of salinity whereas ions concentration dominates at high amount of salt. In addition, the volume change behavior and hydraulic conductivity depend more on the type of anion at high void ratio and when the stress level is low.

Based on the couple macro and microstructure tests results, the barrier performance of smectite is negatively affected by increasing the salinity of contacting solution-most likely due to a tighter packing of particles in microstructural units, leaving larger macropores in between them. However, the soil sample with carbonate undergoes less change in its hydro-mechanical parameters due to the permeation of salt. Therefore, adding carbonate to the natural smectite can be considered to enhance its compatibility against the chemical attack when is used as buffer material in waste disposal projects. To judge the applicability of the carbonate activated smectite, further discussions such as the effects of the diffusion and sorption properties of buried wastes are also necessary.

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References

- Abend, S. and Lagaly, G. (2000), "Sol-gel Transition of sodium montmorillonite dispersion", *Applied Clay Science*, **16**(3-4), 201-227.
- Al-Rawas, A.A. and Goosen, M.F.A. (Eds.) (2006), *Expansive Soils*, Taylor and Francis, London, UK.
- ASTM (2006), Annual Book of ASTM Standard, American Society for Testing and Materials, Philadelphia, 4.08.
- Bennett, D.G. and Gens, R. (2008), "Overview of European concepts for high-level waste and spent fuel disposal with special reference waste container corrosion", *J. Nucl. Mater.*, **379**(1-3), 1-8.
- Castellanos, E., Villar, M.V., Romero, E., Lloret, A. and Gens, A. (2008), "Chemical impact on the hydro-mechanical behaviour of high-density FEBEX bentonite", *Phys. Chem. Earth*, **33**(1), S516-S526.
- Chen, W.C. and Huang, W.H. (2013), "Effect of groundwater chemistry on the swelling behavior of a Ca-bentonite for deep geological repository", *Phys. Chem. Earth*, **65**, 42-49.
- Cui, S.L., Zhang, H.Y. and Zhang, M. (2012), "Swelling characteristics of compacted GMZ bentonite-sand mixtures as a buffer/backfill material in China", *Eng. Geol.*, **141**, 65-73.
- Di Maio, C. (1996), "Exposure of bentonite to salt solution: Osmotic and mechanical effects", *Geotechnique*, **46**(4), 695-707.
- EPA (1983), Process Design Manual: Land Application of Municipal Sludge, Municipal Environ, Research Laboratory, EPA-625/1-83-016.
- Heliman, M.D., Carter, D.L. and Gonzalez, C.L. (1965), "The EGME technique for determining soil-surface area", *Soil Sci.*, **100**, 409-413.
- Hendershot, W.H. and Duquette, M. (1986), "A simple barium chloride method for determining CEC and exchangeable cations", *Soil Sci. Soc. Am. J.*, **50**(3), 605-608.
- Herbert, H.J., Kasbohm, J., Sprenger, H., Fernndez, A.M. and Reichelt, C. (2008), "Swelling pressures of MX-80 bentonite in solutions of different ionic strength", *Phys. Chem. Earth*, **33**(1), S327-S342.
- Kalkan, E. (2011), "Impact of wetting-drying cycles on swelling behavior of clayey soils modified by silica

- fume", *Applied Clay Science*, **52**(4), 345-352.
- Karnland, O., Olsson, S., Nilsson, U. and Sellin, P. (2007), "Experimentally determined swelling pressures and geochemical interactions of compacted Wyoming bentonite with highly alkaline solutions", *Physics and Chemistry of the Earth*, **32**(1-7), 275-286.
- Katsumi, T., Ishimori, H., Onikata, M. and Fukagawa, R. (2008), "Long-term barrier performance of modified bentonite materials against sodium and calcium permeant solutions", *Geotext. Geomembr.*, **26**(1), 14-30.
- Kaufhold, S. and Dohrmann, R. (2011), "Stability of bentonites in salt solutions III-Calcium hydroxide", *Appl. Clay Sci.*, **51**(3), 300-307.
- Lee, J.M., Shackelford, C.D., Benson, C.H., Jo, H.Y. and Edil, T.B. (2005), "Correlating index properties and hydraulic conductivity of geosynthetic clay liners", *J. Geotech. Geoenvir. Eng.*, **131**(11), 1319-1329.
- Mesri, G. and Olson, R.E. (1971), "Mechanisms controlling the permeability of clays", *Clay Clay Mineral*, **19**(3), 151-158.
- Mishra, A.K., Ohtsubo, M., Li, L. and Higashi, T. (2011), "Controlling factors of the swelling of various bentonites and their correlations with the hydraulic conductivity of soil-bentonite mixtures", *Applied Clay Science*, **52**(1-2), 78-84.
- Mitchell, J.K. and Madson, F.T. (1987), "Chemical effects on the clay hydraulic conductivity", *Geotechnical Practice for Waste Disposal, ASCE*, pp. 87-116.
- Montes, H.G., Duplay, J., Martinez, L., Geraud, Y. and Tournier, R.B. (2003), "Influence of interlayer cations on the water sorption and swelling-shrinkage of MX80 bentonite", *Appl. Clay Sci.*, **23**, 309-321.
- Olgun, M. and Yildiz, M. (2010), "Effect of organic fluids on the geotechnical behavior of a highly plastic clayey soil", *Appl. Clay Sci.*, **48**(4), 615-621.
- Ouhadi, V.R. and Goodarzi, A.R. (2003), "Pore fluid characteristics effect on the dispersivity behaviour of soils from macro and micro structure aspects", *Proceedings of the 2nd International Symposium on Contaminated Sediments*, Canada, May, pp. 200-206.
- Ouhadi, V.R. and Goodarzi, A.R. (2006), "Assessment of the stability of a dispersive soil treated by alum", *Eng. Geol.*, **85**(1-2), 91-101.
- Ouhadi, V.R., Yong, R.N., Bayesteh, H. and Goodarzi, A.R. (2007), "Influence of potential determining ions on the microstructural performance and contaminant adsorption of a homoionic illitic clay", *Water, Air, Soil Pollut.*, **181**(1-4), 77-93.
- Ouhadi, V.R., Yong, R.N., Goodarzi, A.R. and Safari, M. (2010), "Effect of temperature on the re-structuring of the microstructure and geo-environmental behaviour of smectite", *Appl. Clay Sci.*, **47**(1-2), 2-9.
- Penner, D. and Lagaly, G. (2000), "Influence of anions on the rheological properties of clay mineral dispersion", *Appl. Clay Sci.*, **19**(1-6), 131-142.
- Sakr, M.A., Shahin, M.A. and Metwally, Y.M. (2009), "Utilization of lime for stabilizing soft clay soil of high organic content", *Geotech. Geol. Eng.*, **27**(1), 105-113.
- Seco, A., Ramírez, F., Miqueleiz, L. and García, B. (2011), "Stabilization of expansive soils for use in construction", *Appl. Clay Sci.*, **51**(3), 348-352.
- Sivapullaiah, P.V., Sridharan, A. and Stalin, V.K. (2000), "Hydraulic conductivity of bentonite-sand mixtures", *Can. Geotech. J.*, **37**(3), 406-413.
- van Olphen, H. (1977), *An Introduction to Clay Colloid Chemistry*, John Wiley & Sons, New York, USA.
- Villar, M.V., Martín, P.L., Bárcena, I., García-Siñeriz, J.L., Gómez-Espina, R. and Lloret, A. (2012), "Long-term experimental evidences of saturation of compacted bentonite under repository conditions", *Eng. Geol.*, **149-150**, 57-69.
- Yong, R.N. (2001), *Geoenvironmental Engineering, Contaminated Soils, Pollutant Fate and Mitigation*, CRC, New York, USA.
- Yong, R.N. and Sethi, A.J. (1977), "Turbidity and zeta potential measurements of clay dispersibility", *ASTM, STP*, **623**, 419-431.
- Yong, R.N., Ouhadi, V.R. and Goodarzi, A.R. (2009), "Effect of Cu²⁺ ions and buffering capacity on smectite microstructure and performance", *Geotech. Geoenvir. Eng.*, **135**(12), 1981-1985.

- Yukselen-Aksoy, Y., Kaya, A. and Ören, A.H. (2008), "Seawater effect on consistency limits and compressibility characteristics of clays", *Eng. Geol.*, **102**(1-2), 54-61.
- Zhu, C.M., Ye, W.M., Chen, Y.G., Chen, B. and Cui, Y.J. (2013), "Influence of salt solutions on the swelling pressure and hydraulic conductivity of compacted GMZ01 bentonite", *Eng. Geol.*, **166**, 74-80.

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