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# Chemico-osmotic behaviour of modified “Multiswellable” bentonite

## Comportement à membrane d’une bentonite modifiée à gonflement amélioré

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### ABSTRACT

The potential for membrane behaviour of a chemically modified bentonite (MSB) is evaluated. Test results showed that MSB exhibited initial membrane behaviour. However, the membrane behaviour was gradually destroyed in the presence of a 0.005 M CaCl<sub>2</sub> solution. Conversely, the impact of the 0.005 M CaCl<sub>2</sub> solution on the hydraulic conductivity of MSB is shown to be mild.

### RÉSUMÉ

Le potentiel comportement à membrane d’une bentonite modifiée à gonflement amélioré (MSB) est examiné. Les résultats montrent que la MSB peut manifester ce comportement. Toutefois, le contact avec une solutions 0.005 M CaCl<sub>2</sub> a détruit le comportement à membrane. Au contraire, l’ effet sur la perméabilité a été modéré.

### 1 INTRODUCTION

Low permeability clayey soils (e.g., bentonites) have been shown to behave as semipermeable membrane, i.e., restrict the movement of solutes while allowing the flow of water in direction opposed to the chemical gradient (chemical osmosis). Chemico-osmotic behaviour of clayey soils typically used in engineered barriers for pollutants containment (e.g. soil-bentonite mixtures, GCLs) is being regarded with great interest in view of the beneficial impact of membrane behaviour on containment capability, since a barrier exhibiting chemical osmosis will generally perform better in terms of solute containment than a barrier where chemical osmosis is absent (Kejzer et al., 1999, Malusis and Shackelford 2002). Soil volume changes induced by chemico-mechanical coupling may also affect the barrier’s behaviour and must be taken into account for a reliable prediction of its performance (Van Impe et al., 2003).

In the case of charged solutes, membrane behaviour is generally attributed to electrostatic repulsion of the ions by electric fields generated by the overlapping diffuse double layers of closely spaced clay particles (Fritz, 1986). However, clay soils usually behave as “leaky” semipermeable membranes, restricting only partially the movement of solutes. Therefore, the osmotic behaviour may be altered by the migration of solutes that cause double layer compression, e.g., multivalent ions and/or high electrolyte concentrations (Mazzieri et al., 2003; Shackelford and Lee, 2003). Typically, multivalent ions also increase the permeability of clayey soils (Jo et al., 2001).

Several types of chemically-resistant bentonites have been recently developed to improve the chemical compatibility to potentially aggressive permeants (Lo et al. 1997, Onikata et al. 2000). The proposed paper deals with the behaviour of a modified “Multiswellable” bentonite (MSB, Hojun Corp., Japan), obtained by treating natural sodium bentonite with an organic polymer (propylene carbonate). It has been proven that MSB exhibits higher swelling capacity and hydraulic conductivity values of one to two orders of magnitude lower than untreated bentonite in various electrolyte solutions (Katsumi et al., 2001). Therefore, in view of pollutant containment applications, it is of interest to evaluate the potential for chemico-osmotic behaviour of MSB.

The authors are not aware of published experimental data on chemico-osmotic behaviour of modified bentonites. The primary objective of the paper is to present the first results a test-

ing program aimed at evaluating the behaviour of MSB in terms of pollutant containment. In particular, the paper focuses on the results of chemico-osmotic testing of MSB performed in the presence of a CaCl<sub>2</sub> solution.

### 2 MATERIALS AND METHODS

#### 2.1 Multiswellable bentonite (MSB)

Onikata et al. (2000) showed that propylene carbonate (PC) forms complexes with montmorillonite by intercalation, and that the PC-montmorillonite complexes exhibit osmotic swelling even in concentrated aqueous electrolyte solutions. MSB is composed by 80 % Na-bentonite and 20% PC on dry weight basis. Table 1 summarizes the main physical and chemical properties of MSB.

Table 1. Physical and chemical properties of MSB

Property	Source	Value
Trade name	Product information	MULTIGEL
Principal mineral	Product information	Montmorill.
Water content(w)	ASTM D4959	21 %
Specific gravity (G <sub>s</sub> )	Product information	2.1 ±2.2 (-)
Liquid Limit (LL)	JIS A 1205	500 %(*)
pH	Product information	7.0-8.0
EC (1:50 extract)	-	188 µS/cm
CEC	-	52.6 meq/100g
Exchangeable cations		
Na <sup>+</sup>	-	41.0 meq/100g
Ca <sup>2+</sup>	-	16.9 meq/100g
Mg <sup>2+</sup>	-	6.8 meq/100g
K <sup>+</sup>	-	0.8 meq/100g
Soluble ions :		
Na <sup>+</sup>	-	13.5 meq/100g
Ca <sup>2+</sup>	-	1.7 meq/100g
Mg <sup>2+</sup>	-	0.8 meq/100g
K <sup>+</sup>	-	0.6 meq/100g
Cl <sup>-</sup>	-	1.4 meq/100g
HCO <sub>3</sub> <sup>-</sup>	-	8.6 meq/100g
SO <sub>4</sub> <sup>2-</sup>	-	3.9 meq/100g

\*Katsumi et al. (2001); - =direct measurement performed in the study

## 2.2 Testing apparatus and procedures

The chemico-osmotic test was carried out by means of the testing apparatus described in Mazzieri et al. (2003). The complete set-up consists essentially of two main parts: the pumping system and the testing cell (Figure 1).

The pumping system is used to circulate solutions of different concentrations of an electrolyte at either end of the soil specimen in order to induce a chemical gradient across the soil. The cell consists of a mould containing the soil specimen and a pressure chamber separated by a rigid piston. The soil specimen is housed in the lower mould and is confined between two porous stones. Swelling of the soil during the test is prevented by blocking the top piston.

The solutions are infused and withdrawn at the same rate through the porous plates. At the top boundary the solution is infused into the porous plate at concentration  $c_{ti}$  and is withdrawn at concentration  $c_{to} < c_{ti}$  as a result of diffusion of solutes into the soil. At the base boundary the infused solution has concentration  $c_{bi} = 0$  (distilled water, DW) and is withdrawn at concentration  $c_{bo} > c_{bi}$  as a result of solute diffusion from the soil. If the circulation rate is high enough, diffusion has a negligible effect on the concentrations, such that  $c_{to} \approx c_{ti}$  and  $c_{bo} \approx c_{bi} = 0$  (perfect flushing). As no water can leave or enter the soil, no fluid flow occurs across the soil. In the presence of osmotic behaviour, a differential pressure (the osmotic pressure difference) arises across the soil sample. The differential pressure can be measured by means of the differential pressure transducer (Figure 1). The steady-state osmotic efficiency coefficient  $\omega$  can be calculated as follows:

$$\omega = \frac{\Delta(P)}{\Delta(\Pi)} \quad (1)$$

where  $\Delta(P)$  is the measured differential pressure and  $\Delta(\Pi)$  is the osmotic pressure difference according to the van 't Hoff's equation, which can be calculated by measuring the steady-state concentration gradient.

A 0.005 M CaCl<sub>2</sub> solution (pH= 5,72 ; EC=1,14 mS/cm) was selected as the electrolyte solution to be infused at the top of the specimen ( $c_{ti}$ ) during the chemico-osmotic stage. The solution's composition and concentration were selected in order to allow comparison with published data concerning a similar test on untreated bentonite (Shackelford and Lee, 2003). Free swell tests (ASTM D 5890) were preliminarily conducted in DW and 0.005 M CaCl<sub>2</sub> to observe the impact of the electrolyte on the swelling behaviour of MSB.

The MSB specimen was prepared by spreading a thin layer of dry MSB (0.45 g dry solids/cm<sup>2</sup>) into the lower mould. The mould was then inundated with DW and the MSB specimen allowed to saturate and swell freely to a height of about 10 mm.

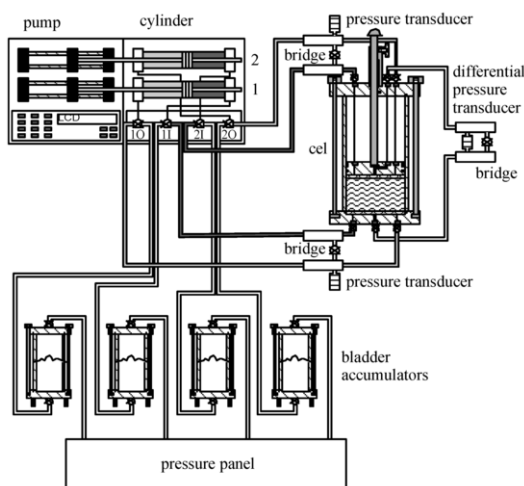


Figure 1 Chemico- osmotic test set-up

The swollen MSB was then consolidated to the desired height of 7.4 mm (corresponding to a porosity of 0.717) by pressurizing the chamber above the top piston. Due to the considerable salt content of MSB the specimen was first permeated with DW to remove soluble salts, improve the saturation and measure the reference hydraulic conductivity.

After permeation, DW was first circulated for 1 day at either ends of the specimen to establish a reference differential pressure and remove residual salts from the porous plates. The electrolyte solution was then circulated at the top end of the specimen until the steady state. Permeation with 0.005 M CaCl<sub>2</sub> finally carried out in order to assess the impact of the electrolyte solution on the hydraulic conductivity of MSB.

## 3 RESULTS AND DISCUSSION

### 3.1 Free swell

Free swell tests (ASTM D5890) provide an index of the swelling behaviour of bentonite in DW or in a certain liquid. In the attempt to simulate the sequence of the chemico-osmotic test, the same MSB was used to for the free swell test in DW and in 0.005 M CaCl<sub>2</sub>. After completion of the test in DW, bentonite was recovered, air dried and reused for the test with 0.005 M CaCl<sub>2</sub>. The swelling power of MSB in DW was of 23 mL/2g whereas in 0.005 M CaCl<sub>2</sub> the swelling power was 50 mL/2g. Onikata et al. (2000) attributed the swelling of MSB in electrolyte solutions to the formation of thick electrical double layers consisting of PC and water that coordinate to the interlayer cations between the silicate layers (osmotic swelling).

Katsumi et al. (2001) report results of free swell tests on MSB in deionized water (DI) and in CaCl<sub>2</sub> solutions of concentrations ranging from 0.1 M to 0.5 M. They found that the swelling power of MSB in CaCl<sub>2</sub> solutions was always lower than in DI. However, they report no data for concentrations lower than 0.1 M, therefore the results obtained in this study are not necessarily in contrast with previous findings. In any case, Katsumi et al. (2001) found that free swell results do not always correlate well with the performance of MSB. For example, they found that the swelling power of MBS increased from 28 mL/2g in DI to 40 mL/2g in 0.5 M NaCl, but the Liquid Limit decreased from 500% in DI to 320 % in 0.5 M NaCl. The hydraulic conductivity remained substantially unaltered, varying from 2.5·10<sup>-11</sup> m/s in DI to 1.0·10<sup>-11</sup> m/s in 0.5 M NaCl. As a consequence, a considerable increase of the swelling power of MSB in a given liquid does not necessarily produce a significant improvement of the material performance as hydraulic barrier.

### 3.2 Chemico-osmotic efficiency

The results of the chemico-osmotic test are illustrated in Figure 2. Figure 2a shows the differential pressure measured across the MSB specimen over time. During circulation of DW a small differential pressure  $\Delta(P)_0 \approx 1.2$  kPa was measured, probably as a result of slightly different hydraulic conductivities of the porous plates (Malusis et al., 2001) and/or different residual salt content. Replacement of DW with the 0.005 M CaCl<sub>2</sub> solution caused an immediate increase of the differential pressure to a peak value of 7.3 kPa. The peak value occurred within about 16 h. Thereafter, the differential pressure gradually dropped to a steady state value close to  $\Delta(P)_0$ . Considering the scatter of the measurements, the steady state was essentially achieved after 22 days of circulation of the electrolyte solution.

The osmotic efficiency can be calculated using Eq.(1) at steady state (ss). Being  $\Delta(P)_{ss} = 0$ , (where deduction has been made for  $\Delta(P)_0$ ),  $\omega_{ss} = 0$ . An estimate of the osmotic efficiency  $\omega_{max}$  in correspondence of the peak value can be obtained by inserting in Eq.(1) the peak value  $\Delta(P)_{max} = 7.3$  kPa and  $\Delta(\Pi) = 36.6$  kPa, that is the maximum theoretical osmotic pressure difference for a concentration difference of 0.005 M

CaCl<sub>2</sub> across the soil in accordance with the van 't Hoff equation, which yields  $\omega_{max} = 0.20$ . Therefore, MSB initially exhibited membrane behaviour, that was gradually destroyed during the test.

The results obtained qualitatively resemble previous findings by Shackelford and Lee (2003). They also observed a variable osmotic efficiency, with a peak value followed by a gradual decrease to zero. They observed that the time required to destroy the membrane behaviour correlated well with the time required to reach steady-state diffusive transport of Ca<sup>2+</sup> ions through the GCL specimen. They attributed the destruction of chemico-osmotic behaviour to the compression of double layers surrounding hydrated clay particles caused by increasing concentrations of bivalent Ca<sup>2+</sup> in the pore fluid.

The impact of solute diffusion in the present study can be assessed by the analysis of concentrations of Ca<sup>2+</sup> and Cl<sup>-</sup> in the outlet solutions over time (Figure 2b). Concentrations are expressed in meq/L to visualize the balance of positive and negative charges. The breakthrough of Cl<sup>-</sup> at base occurs much earlier than Ca<sup>2+</sup>. Hence, the transport of Ca<sup>2+</sup> is retarded compared with Cl<sup>-</sup>, which is consistent with adsorption of Ca<sup>2+</sup> ions onto the MSB surface of as a result of cation exchange.

Table 1 shows that Na<sup>+</sup> is the major exchangeable cation of MSB. Na<sup>+</sup> concentrations in the outlet solutions were measured at selected times. The dashed lines in Figure 2.b) represent the sum of Na<sup>+</sup> and Ca<sup>2+</sup> equivalents in the outlet solutions. The lines tend to approach those representing Cl<sup>-</sup>, in accordance to the requirement for electroneutrality of the solutions.

During the transient phase of the test, both Na<sup>+</sup> ions and Ca<sup>2+</sup> ions diffused downwards along with Cl<sup>-</sup> in order to satisfy the electrical balance. It is interesting to observe that exchanged Na<sup>+</sup> diffused also upwards into the top solution. Release of Na<sup>+</sup> into the soil pore fluid as a result of exchange with Ca<sup>2+</sup> created a local Na<sup>+</sup> concentration gradient between the soil close to the top end and the fresh 0.005 M CaCl<sub>2</sub> solution

(which is free from Na<sup>+</sup>) so that counter-diffusion of Na<sup>+</sup> occurred in direction opposed to that of the main chemical gradient (Jugnicket et al. 2004). At steady-state, the contribution of the released ion vanished, therefore electroneutrality is satisfied only by Ca<sup>2+</sup> and Cl<sup>-</sup>.

The solute transport parameters  $D^*$  (effective diffusion coefficient) and  $R_d$  (retardation factor, with the hypothesis of linear equilibrium adsorption reactions) can be estimated by application of the time-lag method to the diffusive mass fluxes data (Malusis et al., 2001), for a measured porosity of 0.717 and specimen height of 7.4 mm. The results of the analysis are reported in Table 2.

Table 2. Diffusive transport parameters

Solute	Time lag* (days)	Steady-state* (days)	$R_d$ (-)	$D^* \cdot 10^{10}$ (m <sup>2</sup> /s)
Cl <sup>-</sup>	2.8	11.5	4.6	1.79
Ca <sup>2+</sup>	13.8	30.0	17.5	1.60

\*1 day circulation of DW has been deducted.

As apparent in Figure 2, the steady state diffusion occurs much earlier for Cl<sup>-</sup> (11.5 days) than for Ca<sup>2+</sup> (30 days). This is also consistent with the calculated  $R_d$  values, since the retardation factor for Cl<sup>-</sup> is lower than for Ca<sup>2+</sup>. The retardation factor  $R_d > 1$  for Ca<sup>2+</sup> is consistent with adsorption of Ca<sup>2+</sup> onto MSB as a result of cation exchange. The calculated  $R_d > 1$  for Cl<sup>-</sup> warrants some discussion.

Cl<sup>-</sup> is usually considered a conservative tracer in soil diffusion studies since it tends to be repelled from negatively charged surfaces. Theoretically, a conservative tracer should yield  $R_d = 1$ . Firstly, the calculated  $R_d$  value may depend upon inappropriate interpretation of the transient phase of the test. The time-lag method explicitly assumes that the boundary concentrations are maintained constant throughout the test (perfect flushing), whereas Figure 2b demonstrates that the boundary concentrations vary during the test as a result of diffusion. Moreover, the time-lag method does not take into account electrostatic interactions between ions in the transient phase. For example, the apparent retardation of Cl<sup>-</sup> could be partly explained by the counter-diffusion of Na<sup>+</sup> into the top solution, that may delay the diffusion of Cl<sup>-</sup>. Secondly, it cannot be excluded that treatment with PC might have conferred MSB some anion adsorption capacity. No direct measurement of anion adsorption capacity of MSB was carried out during this study.

The steady-state diffusion coefficients of Cl<sup>-</sup> and Ca<sup>2+</sup> are very close, in accordance with the electroneutrality constraint. The values of diffusion coefficients compare well with published data regarding the diffusion coefficients of Ca<sup>2+</sup> and Cl<sup>-</sup> in bentonite at similar porosities (Malusis et al., 2001; Shackelford and Lee 2003). The estimated time required to reach steady-state diffusion of Ca<sup>2+</sup> is 30.0 days. As mentioned earlier, the estimated time required for destruction of chemico-osmotic behaviour is 22 days.

Shackelford and Lee (2003) found almost exact correlation between the time required for destruction of chemico-osmotic behaviour and the time required to achieve steady-state diffusion of Ca<sup>2+</sup>. The correlation is less evident in the present study. However, it must be emphasized that the scatter of the differential pressure measurements (probably due to temperature fluctuations) might have precluded the exact evaluation of the time required to essentially destroy chemico-osmotic behaviour. Moreover, although the time-lag analysis predicts that steady-state diffusion of Ca<sup>2+</sup> was achieved after 30 d of circulation of the electrolyte solution, a slight increase of Ca<sup>2+</sup> concentration at the base boundary is still noticeable after 30 d, suggesting that the steady state might have been approached but not necessarily reached.

Despite the poorer correlation between the steady states of differential pressure and solute diffusion, the authors propose an explanation similar to that provided by Shackelford and Lee

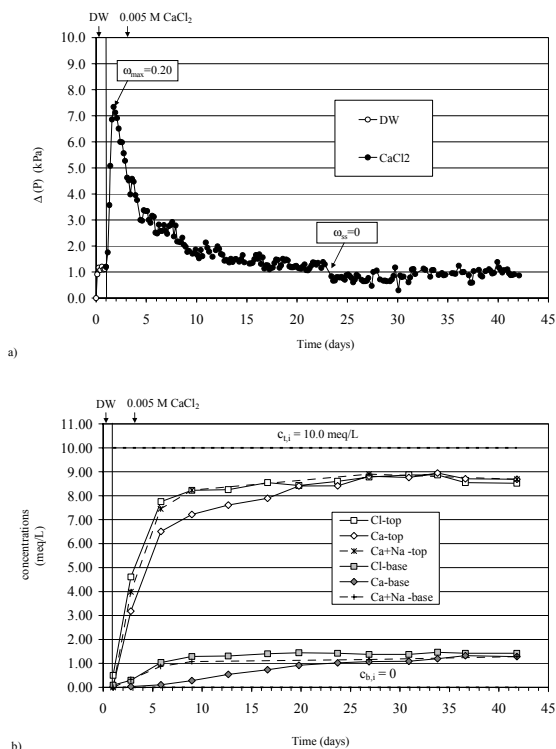


Figure 2 Chemico-osmotic test results: a) differential pressure; b) measured outlet concentrations

(2003) to their results. The authors exclude that destruction of membrane behaviour may depend on short circuiting of the specimen caused by preferential flow along the cell walls during permeation. In particular, sidewall leakage would have probably resulted in even faster decrease of the osmotic efficiency. The results suggest that migration of  $\text{Ca}^{2+}$  into the MSB caused compression of the double layers as a result of increased pore water concentration and cation valence. Replacement of monovalent  $\text{Na}^+$  with bivalent  $\text{Ca}^{2+}$  during the test has been clearly demonstrated.

The results obtained on MSB are qualitatively very similar to those obtained on untreated Na-bentonite. In particular, the results suggest that treatment with PC does not confer MSB the ability to sustain membrane behaviour in the presence of  $\text{CaCl}_2$ . Onikata et al. (2000) observed that PC is gradually hydrolysed to propylene glycol (PG) by reaction with water in the interlayer space of MSB. Since MSB was permeated with DW for about 3 months to remove soluble salts, PC might well have been hydrolysed to PG. However, Onikata et al. (2000) also showed that PG-bentonite mixtures have swelling properties similar to PC-bentonite mixtures. In any case, a more appropriate evaluation of the effect of the additive requires to repeat the chemico-osmotic test on the same untreated bentonite utilized to produce MSB.

### 3.3 Permeability

Hydraulic conductivity of the MSB was measured with DW during the flushing phase and with 0.005 M  $\text{CaCl}_2$  after the chemico-osmotic phase. The hydraulic conductivity  $k$  of MSB in DW was  $1.0 \cdot 10^{-11}$  m/s, whereas in 0.005 M  $\text{CaCl}_2$ ,  $k$  increased to about  $6.9 \cdot 10^{-11}$  m/s.

As for the chemico-osmotic stage, the occurrence of sidewall leakage during permeation with 0.005 M  $\text{CaCl}_2$  appears unlikely, since the applied hydraulic gradient was much lower than during permeation with DW, and side-wall leakage would have probably resulted in much higher permeability.

The increase in hydraulic conductivity tends to support the interpretation of chemico-osmotic test proposed above, since at constant porosity, compression of the double layers caused by diffusion of  $\text{Ca}^{2+}$  into the soil results in increase of the pore space available to ions and water transport. Hence, the increase of permeability is consistent with the observed decrease of chemico-osmotic efficiency.

Katsumi et al. (2001) performed permeability tests on MSB and with DI and  $\text{CaCl}_2$  solutions ranging from 0.1 M to 0.5 M. The MSB was of slightly different composition from the type used in this study (25% PC vs. 20% PC) and the specimens contained 0.79 g of dry solid / $\text{cm}^2$ . They found  $k = 1.5 \cdot 10^{-11}$  m/s with DI, that is very similar to value  $k = 1.0 \cdot 10^{-11}$  m/s obtained in this study with DW. However, they obtained  $k = 2 \cdot 10^{-11}$  m/s with 0.1 M  $\text{CaCl}_2$  and  $k = 7 \cdot 10^{-11}$  m/s with 0.3 M  $\text{CaCl}_2$ . Therefore, they measured the same  $k$  value obtained in this study with a  $\text{CaCl}_2$  concentrations 60 times higher. The reasons for the difference might be several:

- the slightly different composition of MSB;
- the different mass of solids per unit area used to prepare the specimens (0.79 g/ $\text{cm}^2$  vs. 0.45 g/ $\text{cm}^2$  used in this study);
- the use of flexible wall permeameters as opposed to the rigid wall testing cell used in this study;
- the hydration sequence (direct hydration with the  $\text{CaCl}_2$  solutions versus pre-hydration and permeation with DW used in this study);
- the final porosities of the specimens.

Unfortunately Katsumi et al. (2001) did not report the final porosities of MSB specimens. In any case, comparisons of the results obtained in this study and the previous findings suggest that very different performances of MSB can be obtained as a function of the testing conditions and of slightly different changes in composition.

## 4 CONCLUSIONS

The purpose of the work described in the paper was to evaluate the potential for membrane behaviour of MSB. Test results showed that MSB exhibited initial membrane behaviour. Although preliminary, the results are encouraging as far as the potential for membrane behaviour of MSB is concerned. However, the membrane behaviour was gradually destroyed as a result of salt migration into the MSB. An electrolyte solution 0.005 M  $\text{CaCl}_2$  was sufficient to destroy the membrane behaviour. In analogy with untreated bentonite, MSB appears unable to sustain membrane behaviour in the presence of  $\text{Ca}^{2+}$  ions. Nonetheless, more research is warranted to extend this conclusion to different solutes and to different porosities of MSB. It is noteworthy to mention that the hydraulic conductivity, that represents the major concern in pollutant containment problems, increased only slightly in the presence of  $\text{CaCl}_2$ . Therefore, the use of MSB in containment application remains very promising.

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