HYDRAULIC PERFORMANCES OF NATURAL AND POLYMER TREATED BENTONITES IN SHORT AND LONG TERM LANDFILL CONDITIONS

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Summary

The paper presents experimental results relative to the hydraulic performances of a natural bentonite, used in a manufactured geosynthetic clay liner (GCL). Short and long term landfill conditions are considered in order to estimate the change in hydraulic conductivity of the GCL during the whole landfill life. In order to enhance the resistance of sodium natural bentonite to sodium-calcium exchange, that causes a compression of the diffuse double layer (DDL), different polymer-treated bentonites have been prepared. Preliminary hydraulic conductivity test results are reported in order to assess the potential benefits that can be obtained by these advanced materials.

1. Introduction

Geosynthetic clay liners (GCLs) are the most popular manufactured barriers used in landfill applications. GCLs generally contain a thin layer of sodium bentonite (dry thickness between 5 and 10 mm), sandwiched between two geotextiles or glued to a geomembrane, that ensures excellent containment performances in the short term regarding both advective and, if coupled with an attenuation layer, diffusive contaminant transport. The excellent hydraulic performances of GCLs, have to be attributed, in absence of a glued geomembrane, to bentonite characteristics (Shackelford et al., 2000).

Bentonite is a clay soil that usually contains at least 70% of the three layered (2:1) clay mineral montmorillonite. Isomorphic substitution in montmorillonite typically results in the replacement of a portion of the trivalent aluminum (Al^{3+}) in the crystalline structure with a divalent metal, such as magnesium (Mg^{2+}), and this causes a permanent negative surface charge. Montmorillonite crystals consist of parallel-aligned elementary alumino-silicate

lamellae, which are approximately 10 Å thick and 1000-2000 Å wide, and this crystalline structure determines a very high specific surface (≈ 760 m$^2 \cdot$g^{-1}).

Both the permanent negative charge and the very high specific surface determine the osmotic swelling ability of bentonite mineral during imbibition and, as a consequence, induce the very low hydraulic conductivity that characterized the saturated manufactured product. In fact, the mechanism of osmotic swelling takes place when (1) particles, due to their electric charge, interact with the ions contained in the pore solution and determine a change of the osmotic pressure with respect to the external equilibrium solution, and (2) bonds between lamellae are weak enough to allow water to penetrate.

The first condition is verified in most cases where pore solution is characterized by low electrolyte concentration and, in particular, by monovalent cations. As a consequence, the osmotic swelling ability of sodium bentonite results always higher than the swelling ability of calcium bentonite and this property results strictly influenced by the ion concentration in the pore solution, which depends on the chemical composition of the leachate and the soil surrounding the barrier.

The main problem concerning the use of bentonite as a sealing material is represented by the cation exchange of sodium with multivalent cations, such as calcium, dominant in the pore water of many soils, which causes the degradation of sodium bentonite into calcium bentonite and consequently a compression of the DDL that will turn in (1) a reduction of swelling ability, (2) expulsion of adsorbed water and (3) worsening of containment performances.

The landfill bottom barrier is required to ensure contaminant containment during the whole landfill active life (i.e. during waste storage phase), but also during decades in the post-closure period. During such a time, a barrier must guarantee performances in agreement with the requirements that are set by regulations. Many authors (Jo et al., 2001; Petrov et al., 1997; Shackelford et al., 2000) studied the behavior of natural sodium bentonite and GCLs in long term and reported results that highlight the strong degradation induced in hydraulic performance and swelling ability of the natural bentonite by the permeation with electrolyte solutions containing divalent cations.

To improve chemical resistance of bentonite to the cation exchange phenomenon, several innovative materials have been recently developed (Schroeder, 2001; Kolstad et al., 2004, Katsumi et at., 2008; Di Emidio, 2010; Scalia et al. 2011). The present trend, as reported in literature, is to prevent DDL compression and, accordingly, bentonite lamellae collapse, by adding large organic molecules, such polymers, that link to the montmorillonite surface and tend to maintain a wide interparticle distance even in the presence of strong electrolyte pore solutions. The organic molecules may also bond to the sodium ions in the interlayer space, minimizing exchange during permeation with solutions containing divalent or polyvalent cations (Trauger and Darlington, 2005).

In the study described in this Paper, the performances of a natural bentonite GCL, representative of short and long term landfill conditions, were evaluated in order to estimate the change in hydraulic conductivity of the GCL during the whole landfill life.

Moreover, some polymer-treated bentonites have been individualized. Polymer selection criteria were: (1) encourage maintenance of dispersed bentonite structure, even in the presence of calcium ions in the pore solution or aggressive organic solutions, (2) resistance to water washout, (3) resistance to biological degradation, (4) relatively low costs.

Preliminary hydraulic conductivity test results are also presented, concerning the improvement in hydraulic performances induced by the polymers added to the natural bentonite.

2. Materials and methods

2.1 Natural sodium bentonite

The GCL used in this study is reinforced (needle-pounched) and contains powdered sodium bentonite, encapsulated between a non-woven polypropylene geotextile and a woven polypropylene geotextile. The GCL is characterized by a thickness of 6 mm and a bentonite mass per unit area equal to 5000 kg/m^2 (at 12% average water content).

Powdered bentonite, which is contained inside the GCL, is characterized by a cation exchange capacity (CEC, measured using methylene blue adsorption method) equal to 105 meq/100g.

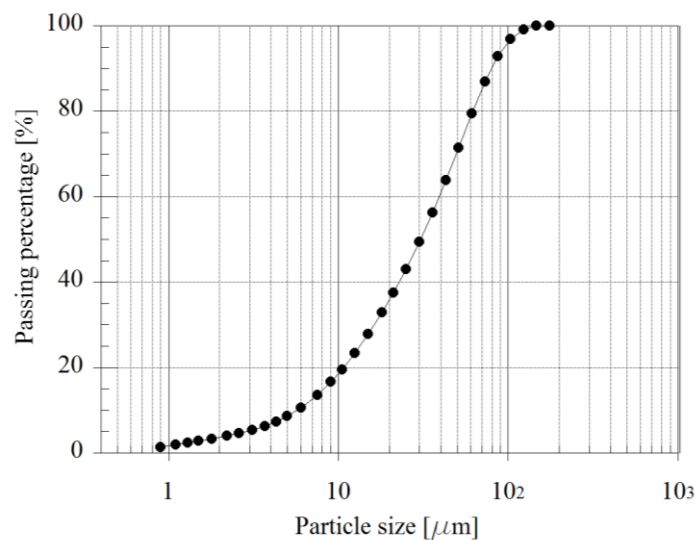In Figure 1 the sodium bentonite particle size distribution performed by Laviosa is reported.

Figure 1. Particle size distribution of the powdered NaB.

The mineralogical composition, evaluated through the x-ray diffraction analysis performed by Laviosa and shown in Figure 2, gives a bentonite mainly composed by smectite (> 98%) and calcite, quartz, mica and gypsum in trace.
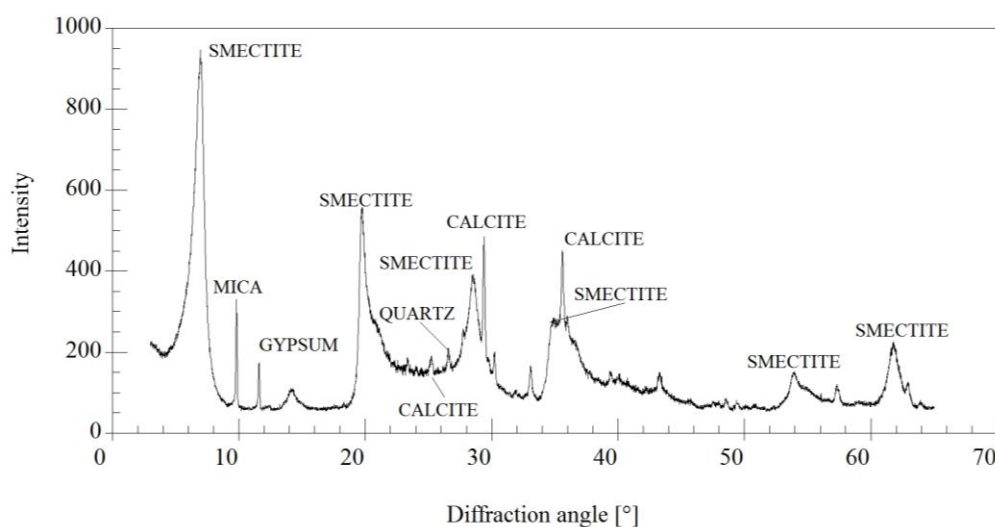

Figure 2. XRD mineralogical composition of powdered NaB contained in the studied GCL.

2.2 Modified bentonites

The polymer modified bentonites used in this study mainly consist of sodium montmorillonite manufactured by adding the following organic polymers: 10% of Nanosponge1, NS, and 10% of PEEK-WC solphonated, PS, (Trotta et al., 1998). In order to obtain modified bentonites, materials were separately dried at 60°C and then mixed at the dry state.

2.3 Permeant Liquids

Calcium solutions were prepared with calcium chloride dihydrate (ACS reagent, purity $\geq$ 99%) using de-ionized water (DW). Calcium solutions were used for simulating sodium bentonite degradation due to the cation exchange phenomenon. A 250 mM $CaCl_2$ was assumed to be a fair compromise between the need to accelerate the degradation process during the hydraulic conductivity tests and that to avoid the use of overly aggressive solutions.

2.4 Testing Methods and Equipments

Hydraulic conductivity test allows for the quantitative evaluation of barrier performances. The GCL and powdered modified bentonite were used for tests that were performed accordingly ASTM D 5887 and ASTM D 5084, using flexible wall permeameters and the "falling head method". Hydraulic conductivity test was performed on 10%PS specimen using the "constant volume-constant head method".

GCL specimens were prepared following the procedure described by ASTM D 5887, while powdered specimens were prepared using two different procedures:

- powdered mixtures were loosely deposited at dry state in a steel mold inside the permeameter. The bulk dry density was approximately equal to the gravimetric one (1 g/cm^3 for NS-bentonite mixture, 0.71 g/cm^3 for PS-bentonite mixture) in order to simulate the initial conditions of the bentonite in a GCL. Inside the mold the flexible membrane was adhered to the specimen, so that, after removing the mold, the permeameter could be completely assembled. The specimen was saturated for 48 h and then permeated.
- Powdered mixtures were saturated at a water content lower than the LL value and then statically compacted in a compaction mold, allowing excess water release. Also in this case bulk dry density was approximately equal to the gravimetric one. Compacted specimens were then accommodated inside the permeameter and after 48 h the permeation was started.

All specimens had 101.6 mm diameter and initial height equal to 6 mm and 10 mm for GCL and powdered specimens respectively. The only exception is 10%PS specimen, which had 5.0 mm diameter. Tests were performed using a maximum hydraulic gradient of 500 and following two consecutive stages: specimens were, firstly, permeated with DW, in order to evaluate their short term behavior, and, successively, with a 250 mM $CaCl_2$ solution, in order to evaluate the long term landfill conditions.

3. Results

A hydraulic conductivity test was carried out on the GCL in a flexible-wall permeameter under an initial effective confining stress of 27.5 kPa using DW initially and 250 mM $CaCl_2$ solution successively, in order to produce the sodium bentonite degradation induced by the cation exchange phenomenon. Lastly, effective stress was increased to 70 kPa with the aim of studying the effect of confining stress on hydraulic conductivity. The test was performed with

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[1] [F. Trotta, W. Tumiatti, R. Vallero. Italian Patent: MI2004A000614]

a maximum hydraulic gradient equal to 500.

Results are plotted in Figure 3 in terms of GCL hydraulic conductivity and void index as functions of pore volume of flow, which is a dimensionless parameter that represents the elapsed time of permeation, calculated as accumulated outflow divided by the pore volume of the specimen.

The hydraulic conductivity results obtained with de-ionized water (closed symbols) are compared with other three tests performed by Laviosa (open symbols). The mean value of these 4 tests was very low, $k \approx 9 \cdot 10^{-12}$ m/s, even if confining stress was low. However, subsequent permeation with the $CaCl_2$ solution, induced the cation exchange phenomenon and, consequently, increased the hydraulic conductivity value to $k \approx 6.9 \cdot 10^{-10}$ m/s. A further increase of the confining stress led to a slight recovery of hydraulic performance by inducing a decrease of conductivity value to $k \approx 3.4 \cdot 10^{-10}$ m/s.

With respect to the second part of Figure 3, the following comments can be made: GCL void index increases from 1.9 (dry state) to 2.8 during imbibition phase. Void index results stable during DW permeation and, subsequently, starts to decrease when the GCL is permeated with the $CaCl_2$ solution, due to the compression effect induced by the reduction of the swelling pressure. The void index values obtained with the $CaCl_2$ solution are equal to 2.5 (at 27.5 kPa confining stress) and 2.3 (at 70 kPa confining stress).

The GCL geotextiles and needle-punching is not expected to influence the hydraulic conductivity with respect to the values of bentonite alone. However new tests on bentonite specimens, prepared with different compaction procedures, are in program for the next future in order to evaluate the possible effect of the geotextile presence.
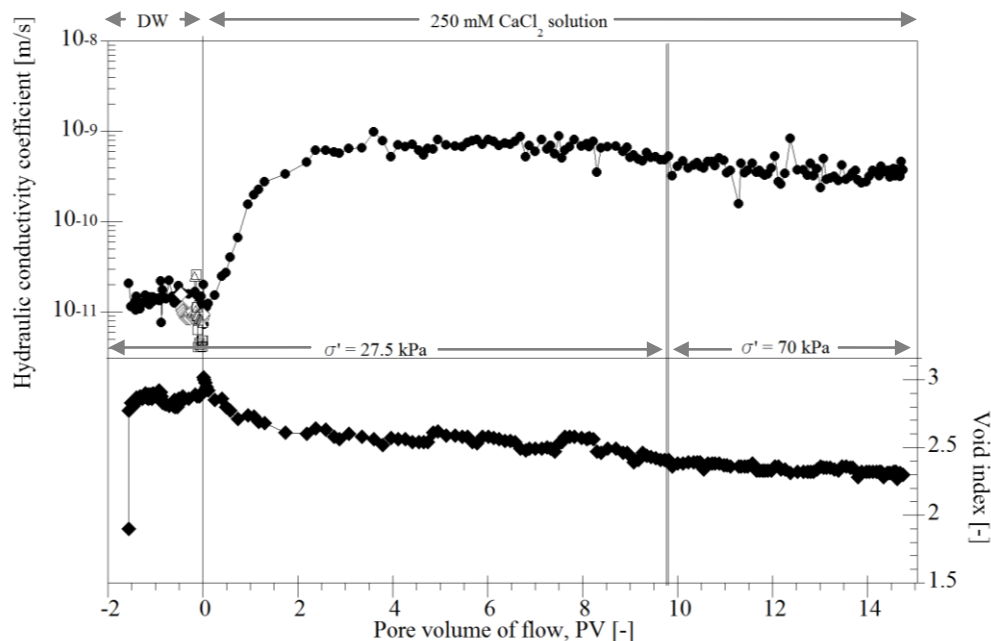

Figure 3. Change in hydraulic conductivity and void ratio of GCL permeated with DW and 250 mM CaCl2 solution.

With the aim of evaluating the improvement in hydraulic performances induced by the polymers mixed with the bentonite, hydraulic conductivity tests were conducted on 10%NS (prepared with the two different procedures exposed in the paragraph 2.3.3) and 10%PS (prepared using the second of the two procedures). Tests were conducted with powdered specimens in flexible-wall permeameters, under an effective confining stress equal to 70 kPa,

using DW initially and 250 mM CaCl2 solution successively. Tests were performed with a maximum hydraulic gradient equal to 500.

The obtained results are plotted in Figure 4. The horizontal line represents the hydraulic conductivity of the GCL permeated with the CaCl2 solution at 70 kPa confining stress.

Both the 10%NS specimens present similar hydraulic conductivity with respect to DW, $k \approx 2.0 \cdot 10^{-12}$ m/s, which is 5 times lower than the GCL hydraulic conductivity.
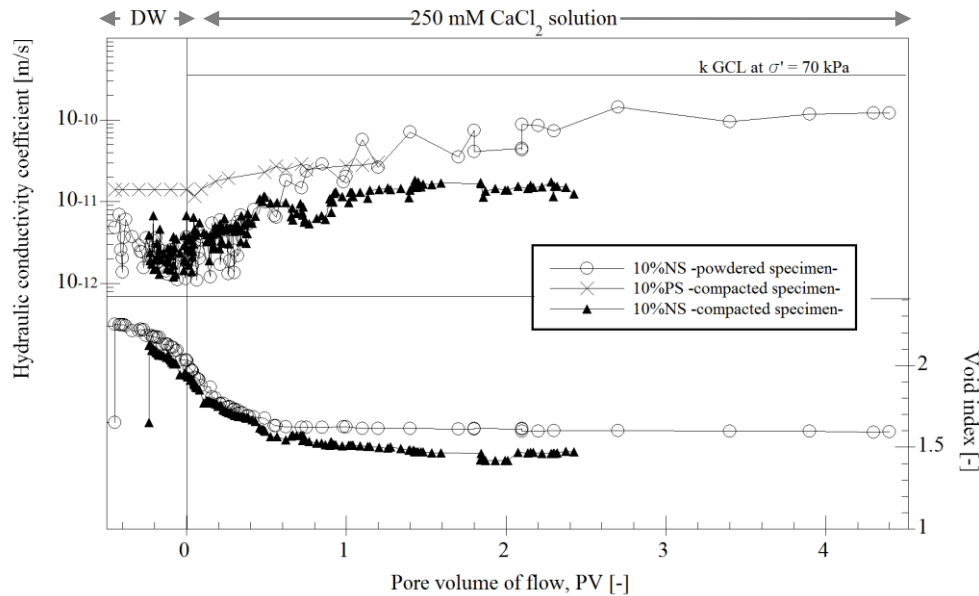

Figure 4. Change in hydraulic conductivity and void index of modified bentonites (10%NS, specimens prepared with both proposed procedure, 10%PS, specimen prepared with the second proposed procedure) permeated with DW and a 250 mM CaCl2 solution.

During permeation with calcium chloride solution, the two specimens show a different behavior: the 'powdered specimen', that has been prepared with the aim of simulating the bentonite contained in GCLs, presents a higher increase in the hydraulic conductivity, reaching an average value equal to $k \approx 1.0 \cdot 10^{-10}$ m/s (which is about 3 times lower than the GCL hydraulic conductivity) at steady state; the 'compacted specimen' appears to be more resistant to the degradation induced by the cation exchange phenomenon. This second test is still ongoing, although the value of hydraulic conductivity appears to be stable around the value $k \approx 1.5 \cdot 10^{-11}$ m/s.

In the second part of Figure 4, is reported the void index measured during the tests. The void index of both 10%NS specimens starts form 1.65 and increases during imbibition/swelling phase at 70 kPa confining stress. The compacted specimen swells less during this phase because it starts from a saturated state. The void index decreases during DW permeation. The value obtained with the CaCl$_2$ solution is equal to 1.6 for the powdered specimen and 1.5 for the compacted specimen.

Bentonite modified with NS is characterized by higher performances when permeated with both de-ionized water and the strong electrolyte solution. The specimen preparation procedure does not influence short term performance, while it seems to affect hydraulic conductivity in long term conditions.

10%PS specimen presents a hydraulic conductivity to DW equal to $k \approx 1.4 \cdot 10^{-11}$ m/s, higher than the average value measured for the GCL. As far as permeation with CaCl$_2$ is concerned the steady state hydraulic flux was reached for $k \approx 3.0 \cdot 10^{-11}$ m/s. These last results indicate

that PS does not appear to ensure a significant improvement to the natural bentonite: the low hydraulic conductivity value obtained against the strong electrolyte solution has probably to be attributed to the specimen preparation procedure.

4. Conclusions

The results obtained for a standard GCL show the strong degradation induced on the hydraulic performance of the natural bentonite contained in the GCL by the permeating electrolyte solutions. Hydraulic conductivity of GCL increases more than 70 times because of the cation exchange phenomenon. Such an increase in the hydraulic conductivity is partially recovered when the confining stress increases.

In contrast with the above results, bentonite modified using nanosponge macro-molecules presents higher hydraulic performance when permeated with de-ionized water (conductivity value results 5 times lower than that obtained for the GCL) and, moreover, shows greater resistance to the cation exchange phenomenon, especially when the specimen is saturated and statically compacted, at high confinement stress, before permeation. An higher hydraulic conductivity than that obtained for GCL was measured during permeation with DW also on the bentonite + PS mixture. With respect to the cation exchange phenomenon, the 10%PS specimen resistance could be attributed not only to the polymer, but also to the specimen preparation procedure.

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