



## REVIEW

# Modified clays for barriers: a review

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**Abstract** The aim of this Specialized Lecture is to present the recent advances and issues, as well as original research, on Modified Clays for Barriers. Topics of interest include: (1) long-term hydraulic performance of modified clays for GCLs, (2) chemico-osmotic and diffusion efficiency of modified clays, (3) modeling coupled chemical-hydraulic-mechanical behavior of modified clays, (4) wet and dry ageing of modified clays, (5) use of novel bentonites for vertical barrier applications, and (6) organoclays for various barrier applications. In addition, the possible reuse of dredged sediments after polymer treatment will also be discussed. Environmental management and handling of dredged sediments are important worldwide because enormous amounts of dredged material emerge from maintenance, construction and remedial works within water systems. Usually these materials after temporary upland disposal in lagoons are disposed in landfills. The aim of this study is to analyse the possible reuse of these sediments as a low-cost alternative material for landfill covers. The mechanisms through which polymers can improve the efficiency of dredged sediments for waste containment low permeable barriers are discussed.

**Keywords** Hydraulic barriers · Modified clays · Polymer treated clays · Environmental Geotechnics

## Introduction

The aim of this Specialized Lecture is to present the recent advances and issues, as well as original research, on Modified Clays for Barriers. Topics of interest include:

1. Overview of recent advances on modified clays for barriers.
2. Long-term hydraulic performance of modified clays for GCLs.
3. Wet and dry ageing of modified clays.
4. Chemico-osmotic and diffusion efficiency of modified clays.
5. Use of novel bentonites for vertical barrier applications.
6. The possible reuse of dredged sediments after polymer treatment.

## Overview of modified clays for barriers

This section provides an overview of recent advancement in the field of modified clays for barriers. Hydraulic barriers containing clayey soils such as compacted clay liners (CCLs), geosynthetic clay liners (GCLs) and vertical barriers (cement-bentonite cut-off walls and soil-bentonite backfills) are widely used in geoenvironmental applications such as: (1) impermeable barriers for the confinement of waste disposals and of polluted sites, (2) sealing and protective layers under roads and railways, (3) containment for above-ground tank farms, (4) sealing under dams, canals,

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ponds, (5) for waterproofing of foundations and other similar geotechnical applications. Clayey barriers are largely used for the isolation of pollutants because of their low hydraulic conductivity to water. However, prolonged exposure of the clay to polluted liquids can drastically increase their hydraulic conductivity [65, 81], with consequent enormous damage to the environment and to the human health.

To overcome this problem, modified clays have been recently introduced in barrier applications to improve their chemical resistance to aggressive permeants. Some examples are: organoclays, multiswellable bentonites (MSB), trisoplast, HYPER clay, dense prehydrated (DPH) GCL, SW101, and bentonite polymer nanocomposite (BPN). In view of pollutant containment applications, it is of great interest to evaluate the potential benefits of these treated clays, by analyzing their transport parameters, investigating the mechanisms through which the polymers and organic molecules can improve the sealing capacity of a clay, to highlight the more suitable treatment techniques and to further investigate the weaknesses of the available products with the aim of future advancements and improvements.

### Organoclays

Organoclays are bentonite clays treated with organic molecules and have higher ion retention capacities than untreated clays. Extensive research has been conducted to characterize the sorption of organic compounds onto clay surfaces [1, 5, 46–49, 91]. Organobentonites are clays, typically amended by exchanging quaternary ammonium groups for the naturally occurring cations. This process renders the modified clay hydrophobic and highly organophilic. Organically modified clays have been found to be a promising alternative to resist pollutant transport. Organoclays have sorption capacities for organic compounds 4–5 times higher than untreated clays. However, the hydraulic conductivity of these clays may increase significantly upon modification with this type of organics.

### Multiswellable bentonite

Multiswellable bentonite (MSB), developed by [41], is a bentonite clay modified with propylene carbonate (PC). The propylene carbonate is an organic compound able to activate the osmotic swelling capacity of the clay. Propylene carbonate is placed in the interlayer of the smectite and attracts numerous water molecules. This results in an improved swelling ability even when the permeant contains polyvalent cations or a high concentration of monovalent cations. MSB showed high swelling capacity and low hydraulic conductivity values for monovalent and bivalent

solutions. Most values of the hydraulic conductivity of MSB are one to two orders of magnitude lower than those of the non treated clay for the same concentration levels [23, 38, 58, 70].

### Sand–clay–polymer mixtures

Trisoplast consists of a well-defined mixture of sand (lower than 89.1% by dry weight), bentonite (higher than 10.7% by dry weight) and a special polymer (higher than dry 0.2% by weight). The sealing and geotechnical properties of this sand–bentonite mixture can be ascribed to the amended polymeric additives used in the mixture [85]. The synthetic additive is a high molecular weight, hydrophilic and gel-forming polymer. All water transport processes in the mixture are strongly retarded by the polymer. In addition, it gives rise to some internal cohesion in the sand–bentonite mixture. This mixture showed a hydraulic conductivity one order of magnitude lower than conventional compacted clay liners [4, 85].

### Clays treated with cationic polymers

Cationic polymers dissolved in solution may easily be adsorbed onto clay surfaces [86]. Such adsorption can be irreversible and entropy-driven. Cationic polymers are able to protect the clay from cation exchange because a cationic polymer chain contains thousands of cations that would need to be exchanged simultaneously [3, 88]. However, the treatment with cationic polymers provides no decrease of the hydraulic conductivity of bentonites because the cationic polymer tends to aggregate clay particles, with a consequent compression of the diffuse double-layer thickness, which is not beneficial for the hydraulic performance of the clayey barrier.

### Dense prehydrated GCL

The Dense PreHydrated GCL (DPH GCL) is a manufactured patented geosynthetic clay liner densified by calendaring after the clay has been prehydrated with a polymeric solution containing Na-CMC (sodium carboxymethyl cellulose), sodium polyacrylate and methanol [15]. DPH GCL showed excellent performance in various aggressive solutions [23, 24, 38, 40, 55–57, 59, 80]. However, the polymer adsorption onto the clay may not last permanently. Mazzieri & Pasqualini [60] and Mazzieri and G. Pasqualini [54] studied the permeability of the DPH GCL subjected to dry/wet cycles using a 12.5 mM CaCl<sub>2</sub> solution and seawater as hydrating liquid. They observed that the additives were partially removed during the tests. In addition, long-term testing suggested that this type of amendment was not completely durable after prolonged permeation with water [23].

### Clay treated with anionic polymer and dehydration (HYPER clay)

Adsorption of anionic polymers onto clay surface is promoted by the presence of polyvalent cations which act as bridges between the anionic groups on the polymer and the negatively charged sites on the clay [67, 88, 89]. Qiu & Yu [74] modified a bentonite with CMC. X-Ray Diffraction (XRD) and Fourier Transform Infrared Spectroscopy (FTIR) analyses on a montmorillonite treated with CMC, showed that these polymer chains had intercalated into the clay sheets, and the strong chemical interaction between the ether bonds from the polymer and Si–O bonds from the clay was the driving force for intercalation. Treating the clay with CMC increases its water absorption and water retention ability. Given its high water retention capacity, Di Emidio [23] evaluated the pollutant containment ability of clays treated with such anionic polymer, Na-CMC. This clay, named HYPER clay, is mixed with a polymeric solution containing the polymer and then dehydrated in an oven at 105 °C to irreversibly adsorb the polymer to the clay surface. Dehydration at temperature higher than 60 °C has been proven to enhance the irreversible adsorption of the polymer on the clay surface [87]. After HYPER clay treatment, the anionic polymer intercalates in the interlayer region between clay platelets (as demonstrated by XRD analysis by [23]). The anionic polymer, negatively charged, maintained the interlayer between particles open probably due to the increased repulsion forces. This particular treatment method increased the water adsorption capacity of the clays (as demonstrated by liquid limit determination), reduced its hydraulic conductivity to electrolyte solutions (such as seawater and calcium chloride) that decreased with increasing polymer dosage. This treatment method also increased the ion adsorption capacity of the clay and, above all, it was able to maintain its performance in the long-term. For instance, clays treated with this technology showed a hydraulic conductivity to seawater one order of magnitude lower compared to untreated clays, and this behavior is still maintained after about 8 years of permeation. Ruehrwein and Ward [78] stated that the adsorption of anionic polymers onto clays occurs through ionic exchange. On the other hand, Michaels and Morelos [63] suggested that adsorption is mainly conditioned by hydrogen bonding. A third possibility would originate from the interaction between polyvalent cations acting as crosslinking agents between the clay negative surface and the anionic polymer [87]. In the presence of salts and cations naturally present at the clay surface, the negative charges of the clay and the anionic polymer are shielded from one another allowing the polymer to coil and collapse on the clay surface [14]. Stutzmann and Siffert [87] compared the quality of the adsorption of anionic polymers on

to montmorillonite surface for two scenarios: (a) drying the treated clay either at 60 °C and (b) drying under vacuum at 20 °C. They found that the adsorption of the polymer on the montmorillonite after drying at 60 °C can be considered as intense, irreversible fixation, corresponding to chemisorption. On the other hand, the adsorption observed with vacuum drying at lower temperatures corresponds rather to an unstable adsorption equilibrium, such as a reversible physisorptive adsorption.

The HYPER clay treatment technology was also able to improve the hydraulic performance of calcium bentonite clays compared to the untreated clay. The hydraulic conductivity of calcium clay treated with this technology was also compared to the same clay treated with standard sodium-activation treatment. The treated clay showed higher swelling and a lower hydraulic conductivity than those of the sodium-activated clay. It should be noted that the benefits of the sodium-activation could be lost in the long-term due to cation exchange as opposed to the polymer treatment that maintains the performance of the clay in the long-term. This technology has also been applied to low cost readily available clays such as low quality bentonites, kaolin clay and dredged sediments improving their quality due to the considerable decrease of their hydraulic conductivity [16].

### Salt-resistant bentonite, SW101

The SW101 (Wyo-Ben, Inc., Billings, MT) is a treated salt-resistant bentonite developed for drilling and cut-off wall applications where exposure to highly concentrated electrolyte solutions as seawater is expected. The treatment process used is unknown (proprietary). The mixture SW101 (salt-resistant bentonite) and lignosulfate thinner, was tested for a vertical soil–bentonite (SB) groundwater cut-off wall at a Superfund site in Colorado [71]. The test results showed that this mixture showed optimum performance, based on cost and low permeability, compared to a mixture of cement and bentonite. Malusis et al. [51] studied the viability of MSB and SW101 for SB vertical barriers. SB slurries containing MSB were compared against similar slurries and backfills containing natural bentonite (NB) and the salt-resistant SW101 bentonite. Test results illustrate that MSB slurry exhibited similar viscosity, density, and filtrate loss as NB slurry (values generally considered acceptable for slurry trench barriers), whereas the Marsh viscosity of the SW101 slurry was 200 s. To decrease these values to acceptable viscosity values, 0.3% of lignosulfate thinner was added to prepare the backfill samples. The three materials exhibited similar hydraulic conductivity to tap water, whereas MSB exhibited the better performance with a lower permeability to 50 mM CaCl<sub>2</sub> compared to NB or SW101.

## Bentonite–polymer nanocomposite

Bohnhoff & Shackelford [11], and Scalia et al. [79] studied a bentonite–polymer nanocomposite (BPN) which is a bentonite modified at the nanoscale level to maintain a low hydraulic conductivity under aggressive conditions. Nanoscale modification consisted of polymerizing acrylic acid within a bentonite slurry to form a stable interconnected structure. This modified material is then air-dried and ground to simulate the granule-size distribution of granular bentonite in geosynthetic clay liners. Index property tests indicate that BPN has different behavior than natural sodium bentonite. For example, free swell tests with natural Na-bentonite swelled to approximately 30 mL in deionized water, whereas BPN swelled to more than 70 mL in the same solution. GCLs were assembled and directly permeated with a range of calcium chloride ( $\text{CaCl}_2$ ) solutions known to cause large increases in the hydraulic conductivity ( $k$ ) of natural Na-bentonite. In contrast to natural Na-bentonite tested under the same conditions, BPN maintained low hydraulic conductivities for all solutions tested.

## Long-term hydraulic performance

Clays show a gradual decrease of their efficiency as hydraulic barrier after prolonged contact with aggressive solutions. This behavior is due to the collapse of the thickness of the diffuse double layer of the clay particle structure. This collapse causes an increase of the hydraulic conductivity and a decrease of the osmotic swelling. These two effects increase the flux of contaminants [66, 43, 83].

Research interest over the last years has especially focused on the study of clays treated with amendments to improve their chemical resistance [3–5, 10, 11, 17, 18, 22, 23, 38, 40, 58, 79, 91]. However, most of these enhancement methods show limitations related to the long-term hydraulic performance of the treated clays. This latter aspect is crucial. The experience in Europe [64] shows that the key aspects to demonstrate the good performance of alternative barrier materials may include, among others, the following requirements: low permeability of the material, long-term chemical and hydraulic stability, biological stability, mechanical stability, resistance to cyclic weather changes.

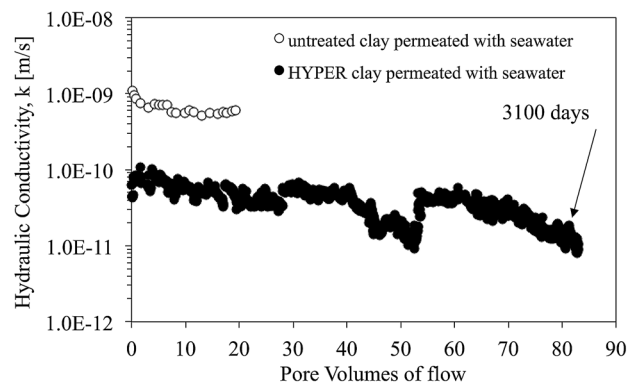
The HYPER clay technology significantly improved the hydraulic performance and membrane behavior of bentonite clays even after prolonged permeation with aggressive solutions, due to the irreversible adsorption of the anionic polymers onto the clay surface. Test results showed, in fact, that the addition of anionic polymers and dehydration have a positive impact on the long-term

sealing performance to high concentrated electrolytes solutions, such as seawater.

The low hydraulic conductivity of untreated bentonites is primarily due to adsorbed immobile water molecules and hydrated ions in the interlayer region of bentonite clays that restrict the pore space available for the flow and cause tortuous flow pathways. The thickness of the adsorbed layer is inversely related to the ions concentration and valence, therefore bentonites are particularly sensitive to changes in the composition of the pore fluid. In particular, electrolyte solutions with high ion concentration and valence, such as seawater, cause the thickness of the diffuse double layer to collapse and therefore the hydraulic conductivity to increase [36, 42]. In this Section the impact of polymer treatment on non-prehydrated samples is investigated by means of flexible wall permeameters, using an effective stress of  $\sigma' = 14$  kPa and an initial porosity  $n = 0.718$ . Hydraulic conductivity of HYPER clay and its base clay were tested here after direct permeation with natural seawater from the North Sea (near Oostende, Belgium).

The hydraulic conductivity of the untreated clay to seawater was higher than that to deionized water due to the high concentrated ions contained in the sea water that, entering the interlayer region between bentonite platelets, compress the double-layer thickness. The hydraulic conductivity to seawater was in fact  $k = 6.66 \times 10^{-10}$  m/s (after 19 PV of flow), about two orders of magnitude higher than that to deionized water ( $k = 6.42 \times 10^{-12}$  m/s).

The impact of HYPER clay treatment using 2% by dry weight of Na-CMC polymer addition on the hydraulic performance to seawater was investigated. Tests results showed that polymer addition decreases the hydraulic conductivity of the clay. Figure 1 compares the hydraulic conductivity to seawater of the untreated clay to that of the HYPER clay. As shown in the figure, the hydraulic conductivity of the HYPER clay to seawater



**Fig. 1** Hydraulic conductivity to seawater of the untreated clay and the HYPER clay

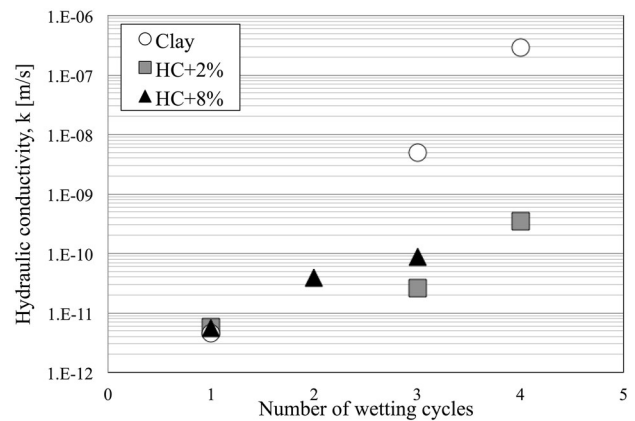
( $k = 1.1 \times 10^{-11}$  m/s) was between 1.5 and 2 orders of magnitude lower than that of the untreated clay ( $k = 6.66 \times 10^{-10}$  m/s). The long-term performance of the HYPER clay was demonstrated even after 80 PV of flow with a highly concentrated electrolyte solution, such as seawater, and after about 8 years of permeation. This test is still ongoing to further corroborate the long-term adsorption of the polymer and its long-term stability against biodegradation when HYPER clay technology is used.

### Wet and dry ageing with seawater

As these modified materials are relatively new, their durability and long-term performance needs to be evaluated also after wet and dry cycles in presence of aggressive ion concentrations. This ageing simulation may in fact induce degradation of conventional clay materials [8, 13, 25, 44, 77], but also on modified clays such MSB and DPH GCL [54].

In this regard, De Camillis et al. [25] simulated wet-dry ageing on HYPER clay using seawater as permeant liquid. Permeation was performed after each drying phase. The results showed that the benefit of the polymer amendment in reducing the hydraulic conductivity of bentonite to seawater was retained after four complete wet-and-dry cycles. The performance of the polymer-modified bentonite is due to the retention of the polymer within the bentonite matrix, due to irreversible adsorption of the polymer onto the clay upon thermal treatment of the clay-polymer mixture. In this study, the bentonite was treated with polymer dosage equal to 2 and 8% by dry weight of the clay. The swelling ability and hydraulic conductivity were evaluated. The specimens were subjected to six wet-dry cycles for the swell tests and to four cycles for the hydraulic conductivity tests (these cycles included 1 first reference cycle executed with deionized water).

One-dimensional swell tests results showed that HYPER clay 8% had swollen the most and that its thickness after the 6th wet-dry cycle was comparable to the maximum thickness of the untreated bentonite in deionized water. Unlike the untreated clay, both HYPER clays maintained low permeability to seawater throughout the wet-dry cycles. Figure 2 shows an overview of the hydraulic conductivities ( $k$ ) of sodium untreated bentonite (NaB), HYPER clay 2% (HC + 2%) and HYPER clay 8% (HC + 8%) after the first cycle in deionized water and 3 subsequent cycles in seawater. As shown in the figure, the greatest increase in  $k$  was observed for untreated sodium bentonite. NaB significantly increased its permeability up to  $2.93 \times 10^{-7}$  m/s during the fourth cycle. Overall, a difference of about five orders of magnitude was observed.



**Fig. 2** Hydraulic conductivities ( $k$ ) of sodium untreated bentonite (NaB), HYPER clay 2% (HC + 2%) and HYPER clay 8% (HC + 8%) after 4 wet and dry cycles [25]

Untreated bentonite forms aggregate structure once in contact with strong electrolyte solution due to the contraction of the DDL thickness.

As a consequence, self-healing and swelling capacity are weakened and the barrier performance of the bentonite is impaired. HYPER clays showed lower permeabilities compared to untreated clay. The hydraulic conductivity of HYPER clay 2% was lower than the regulatory threshold value of  $10^{-9}$  m/s until the fourth cycle ( $3.5 \times 10^{-10}$  m/s). At the end of the third cycle, the hydraulic conductivity of HYPER clay 8% was  $9.11 \times 10^{-11}$  m/s, around one order of magnitude higher compared to its initial value in DW but still considerably low compared to the typical regulatory limit of  $10^{-9}$  m/s.

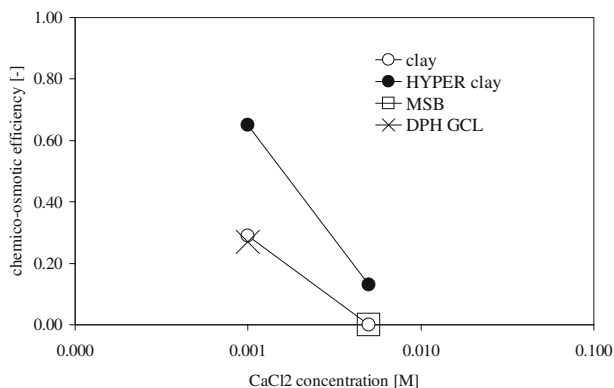
### Chemico-osmotic and diffusion efficiency of modified clays

Bentonite clay is widely used in clayey barriers because of its elevated sealing capacity in the presence of water and its ability to restrict the migration of solutes (chemico-osmotic efficiency or semi-permeable membrane behaviour). However, exposure to high concentrations of inorganic solutions can change the clay fabric increasing its hydraulic conductivity and destroying its membrane behavior [82]. The aim of this section is to show the chemico-osmotic performance of amended clays such as: HYPER clay, MSB, and DPH GCL. To demonstrate the potential benefits of polymer treatment chemico-osmotic tests were performed with  $\text{CaCl}_2$  solutions on treated and untreated clays, to evaluate the modified clays resistance to chemical attack. Unlike the untreated clay, HYPER clay treatment maintained low hydraulic conductivity of the clay to  $\text{CaCl}_2$  even in the long term (after chemico-osmotic test) and protected the clay against the destructive role of diffusion,

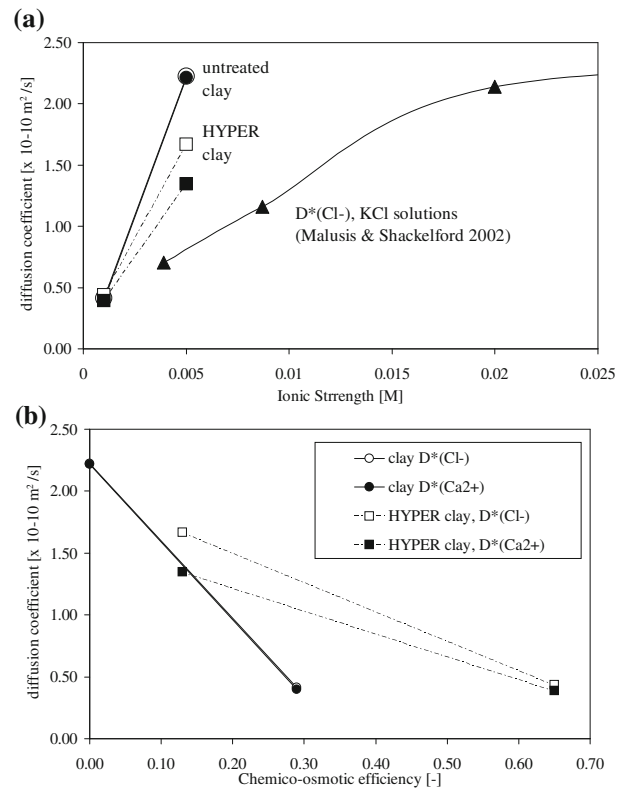
maintaining the initial osmotic efficiency. Chemico-osmotic test results were also compared with other amended clays MSB and DPH GCL. These two amended clay materials displayed a chemico-osmotic behaviour at the steady state similar to that observed on untreated clay. On the other hand, the preservation of the chemico-osmotic efficiency of the HYPER clay with time suggests that the carboxymethyl cellulose was not flushed out during the long period of permeation with deionised water.

Based on the improved hydraulic performance of MSB and DPH GCL, it was expected to also show an improved chemico-osmotic behaviour compared to the untreated clay. Conversely, Fig. 3 shows that these two amended clay materials displayed a chemico-osmotic behaviour at the steady state similar to that observed on the untreated clay, under the adopted experimental conditions (e.g. prolonged permeation to remove soluble salts). Different results may be obtained on amended clays by adopting different testing conditions (such as not prolonged flushing with deionized water to remove soluble salts from BPN samples, as in the paper of [9]). On the other hand, the preservation of the chemico-osmotic efficiency of the HYPER clay with time suggests that the polymer was not flushed out during the long period of permeation with deionised water. These results suggest that the use of the HYPER clay in containment application may be very promising.

Figure 4 shows that, as expected, for the untreated clay the diffusion coefficient ( $D^*$ ) increases with increasing the ionic strength and with decreasing the chemico-osmotic efficiency. In contrast, Fig. 4a shows that for the HYPER clay a lower increase of the diffusion coefficient was observed, suggesting that the increase of diffusion coefficient with the ionic strength was softened by the presence of the polymer. In fact, the higher solute concentrations in the pore space associated with an increase in the concentration of the source solution, causes contraction of the diffuse double layers that results in a decrease in chemico-



**Fig. 3** Chemico-osmotic efficiency overview on modified clays: HYPER clay, MSB, and DPH GCL



**Fig. 4** Effective solute diffusion coefficients plotted against: **a** ionic strength and **b** chemico-osmotic efficiency

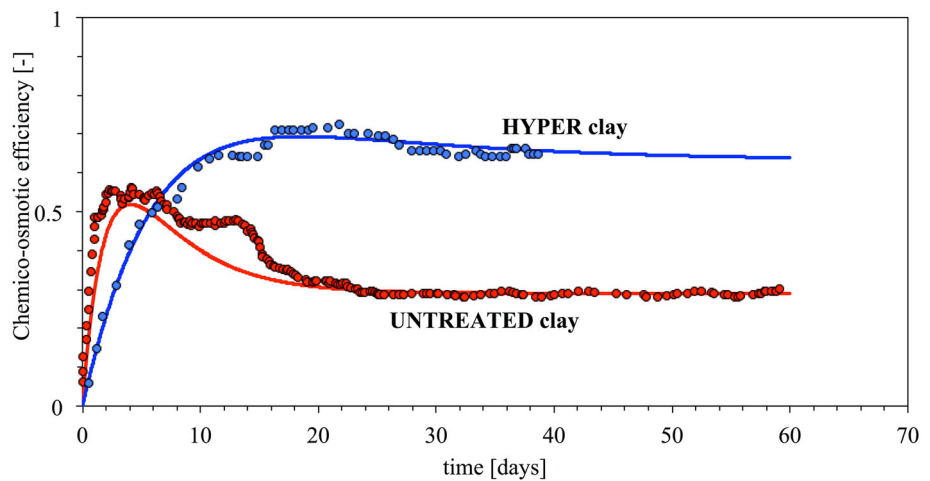
osmotic efficiency and a corresponding increase in  $D^*$  as more pores become available for solute transport. On the other hand, the polymer treatment, maintaining the DDL open, restricts the availability of pores for solute transport with a consequent decrease of  $D^*$ . In fact, the degree of solute restriction is greatest when the double layers of adjacent clay particles overlap in the pore space, leaving no free solution for solute transport [53].

### Modeling chemico-osmotic efficiency of amended clays

The studies conducted on amended clays show great variabilities in treated materials composition, especially concerning the type and amount of polymer, as well as in material preparation condition. General relationships between materials constitutive properties and their macroscopic engineering behaviour should be deduced. The experimental and theoretical analysis of amended chemical resistant clays (such as those treated with polymers) is nowadays at a preliminary stage.

An approach based on the Fixed Charge theory and Donnan equations [26], accounting for the effect of adsorbing anionic polymers in the nearfield of clay mineral surfaces, was described in Di Emidio [23]. For the analysis

**Fig. 5** Comparison of the theoretical modeling of the chemico-osmotic experiments on the HYPER clay and on the untreated clay: validation of the model with experiments



of the chemico- osmotic tests performed on HYPER clay and on the untreated base clay, transport equations for multi-ion systems were numerically solved in order to interpret the actual multi-ion scenario expected in situ. Specific boundary conditions were defined to model the chemico-osmotic properties of clays in a multi-ion system.

Figure 5 shows the comparison between the theoretical interpretation of the chemico-osmotic experiments on the HYPER clay and on the untreated base clay. As shown in the figure, the chemico-osmotic test results were well represented by the theoretical model. The important and new output of this simulation was that the fixed charge concentration,  $C_{X0}$ , of the HYPER clay was higher than that of the untreated clay, whereas, the number of platelets per aggregate ( $N$ ) was lower. This theoretical interpretation suggested that not only the anionic polymer maintains the interlayer open (low  $N$ ) but also it increases the negative charge concentration of the clay (high  $C_{X0}$ ).

## Novel bentonites for vertical barrier applications

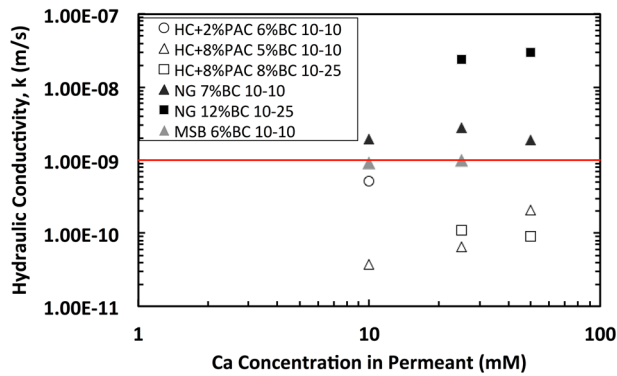
### Soil-bentonite backfills

The hydraulic conductivity,  $k$ , of model sand-bentonite backfills containing HYPER clay was investigated by Malusis and Di Emidio [50]. Flexible-wall tests were performed on backfill specimens composed of clean, fine sand and 2.7–5.6% HYPER clay containing either 2% (HC2) or 8% (HC8) of polymer by dry weight of the clay. The geometric mean  $k$  to water ( $k_w$ ) for HC8 specimens decreased by nearly two orders of magnitude (from  $\sim 3 \times 10^{-9}$  to  $\sim 3 \times 10^{-11}$  m/s) with increasing HC8 content from 2.7 to 5.6%. The geometric mean  $k_w$  of  $3 \times 10^{-11}$  m/s for the 5.6% HC8 backfill was nearly an order of magnitude lower than  $k_w$  reported previously for similar backfill specimens containing 5.7% Na bentonite

(Naturalgel® [NG]) or 5.6% multiswellable bentonite (MSB) due to the greater water absorption and swell capacity of HC8 relative to the NG and MSB. The 5.6% HC2 specimens exhibited slightly lower  $k_w$  relative to specimens containing 5.7% NG or 5.6% MSB. Also, whereas the NG and MSB specimens exhibited increases in  $k$  when the permeant liquid was changed to a 10 mM  $\text{CaCl}_2$  solution, no increases were observed for 5.6% HC2. The results illustrate the potential for HYPER clay to enhance the hydraulic performance of soil-bentonite vertical barriers.

More recently, a research cooperation with Bucknell University, USA, [69, 76] showed that the presence of multi-valent cations in the site water used in the preparation of bentonite slurry can result in a reduction in the quality of the slurry, directly affecting the viscosity and filtrate loss. This can result in an increase of the  $k$  of the backfills prepared with this slurry of 2–3 orders of magnitude [76] with consequent failure of the required hydraulic performance. The effects of electrolyte solutions on both slurry and backfill properties are important to consider in the trench construction and soil-bentonite backfill wall design.

The compatibility of HYPER clay was tested in the use of both bentonite slurries prepared with electrolyte solutions and sand-bentonite backfills permeated with electrolyte solutions. These tests represented the possible site preparation and pollutant conditions. Figure 6 shows that the hydraulic conductivity ( $k$ ) of soil-bentonite backfills containing HYPER clays (HC) is very low compared to untreated clays (NG) and even to MSB.  $k$  is plotted here vs. Ca concentration of the permeant solutions containing also 10 mM Na. The red line in the figure represents the limiting maximum  $k$  value. The legend shows, in the order, the polymer dosage of HC, the bentonite content (%BC) of the slurries, and the concentration in mM of NaCl and mM  $\text{CaCl}_2$  of the mixing contaminated water.



**Fig. 6** Hydraulic conductivity of soil-bentonite backfills containing HYPER clays (HC), untreated clays (NG) and MSB plotted here vs. Ca concentration of the permeant solutions containing also 10 mM Na [69, 76]

### Cement–bentonite cut-off walls

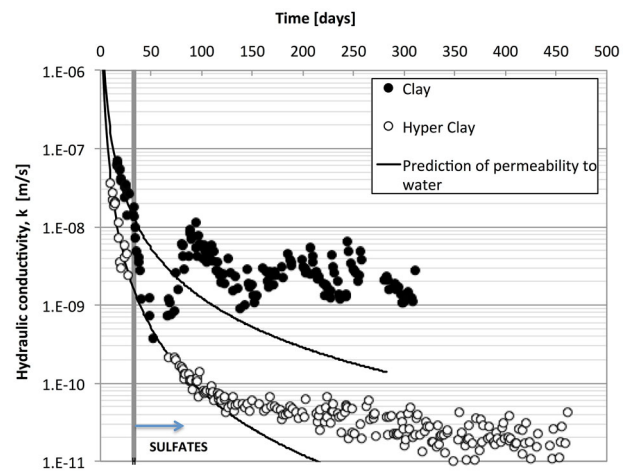
Cemented clays are regularly employed as cut-off walls to isolate polluted soils or in ground improvement technologies. The objective of this research was to evaluate the performance of a polymer-treated bentonite (HYPER clay) and its impact on hydraulic and mechanical properties of cement-bentonite (CB) mixtures in contact with sulfates. Tests results show that  $k$  of mixtures containing untreated bentonite increases due to contact with sulfates; conversely,  $k$  of mixtures containing HYPER clay remains unaffected. These observations suggest that the use of polymer-treated bentonites could improve the resistance of cement-bentonite mixtures to sulfate attack maintaining a low hydraulic conductivity.

Figure 7 shows that the hydraulic conductivity of CB containing untreated clay increased considerably after permeation with an aggressive solution containing sulfates (25 g/L  $\text{Na}_2\text{SO}_4$ ). Conversely, CB containing HYPER clay maintained a very low hydraulic conductivity showing its clear chemical resistance to sulfate attack.

### Reuse of dredged sediments

#### Introduction

Environmental management and handling of dredged sediments is important worldwide because enormous amounts of dredged material emerge from maintenance, construction and remedial works within water systems. Usually these materials after temporary upland disposal in lagoons have to be disposed in landfills. The aim of this section is to analyze the possible reuse of these sediments as a low-cost alternative material for landfill covers. The mechanisms through which polymers can improve the efficiency of



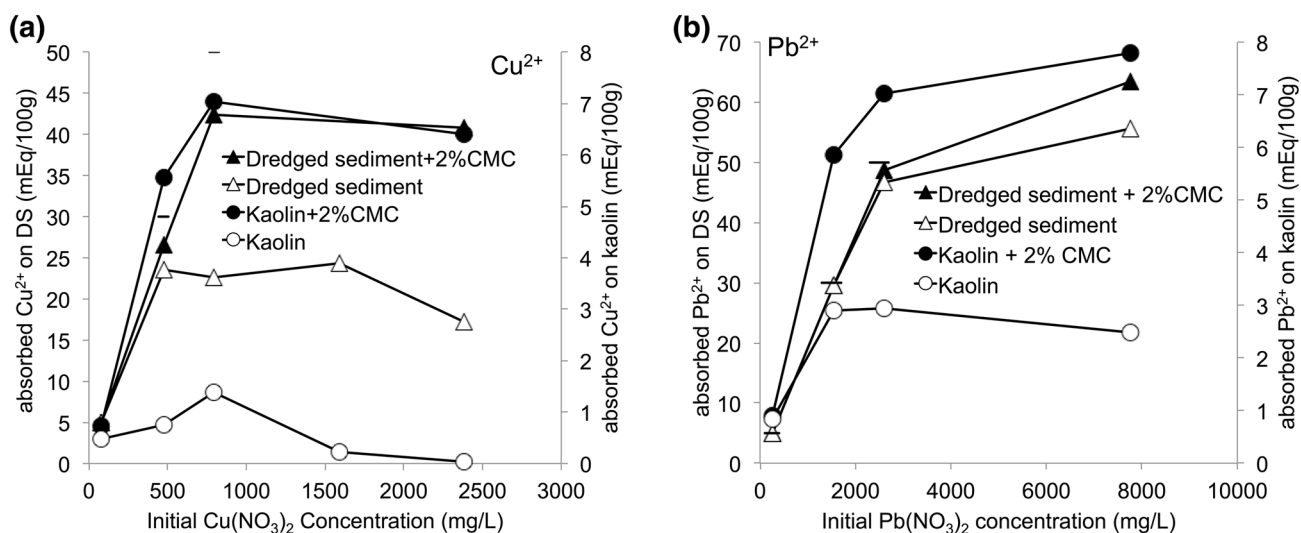
**Fig. 7** Hydraulic conductivity of CB containing untreated clay (Clay in the legend) increased considerably after permeation with an aggressive solution containing sulfates (25 g/L  $\text{Na}_2\text{SO}_4$ ). Conversely, CB containing HYPER clay (HYPER clay in the legend) maintained a very low hydraulic conductivity showing its clear chemical resistance to sulfate attack

dredged sediments for waste containment low permeable barriers are discussed.

Soil contamination by heavy metals has been a long-term and worldwide environmental problem. Heavy metals present in soils can find their way into human and animal populations through direct exposure or food chain/web, posing a serious risk to human health [29, 30, 45]. Heavy metals contamination may originate from chemical/industrial waste landfills if not properly designed. Alternative evapotranspirative barriers [39, 52, 92] or alternative barrier materials (such as, among others, paper sludge [33, 37, 75]) can be necessary when: high costs are associated with prescriptive materials and methods, prescribed materials are not readily available, and when alternative materials are available in large quantities [81]. In this regard, we have studied the suitability of dredged materials to be used as alternative cover liner material for landfills [19, 20].

Maintenance dredging is necessary to maintain the desired depth and the size of rivers, canals, docks and waterways that change in time due to natural processes. Dredging produces a vast amount of dredged sediments that needs to be disposed. Worldwide 1000 to 2000 million tons of sediment are dredged annually and about 30 to 50 million tons within the UK [12]. VITO (Flanders Institute for Technologic Research) estimated the total amount of dredged sediment in Flanders (Belgium) at 7 million tons of dry matter per year [68]. Sediments may be treated to reduce the concentration of pollutants [62, 63, 73], but this approach can be cumbersome, not environmentally friendly, and expensive [72, 84]. Most sediments are disposed in coastal and estuarine areas, which often form a





**Fig. 8** Sorption isotherms on kaolin and dredged sediment of **a**  $\text{Cu}^{2+}$  and **b**  $\text{Pb}^{2+}$

significant anthropogenic disturbance to the structure and functioning of the surrounding seabed, or on land sites [12]. Moreover, disposing sediments in aquatic environments increases the concentration of suspended particulate matter (SPM), which is one of the main pollutants identified by the Water Framework Directive (2000/60/EC) and the EU Marine Strategy Framework Directive (2008/56/EC) [28]. Lack of available space to dispose sediments implies alternative methods such as reuse.

Recent studies showed that treating kaolinite, bentonite or dredged sediments with anionic polymers and dehydrating them (following the HYPER clay technology) protects these materials against chemical attack maintaining a low hydraulic conductivity in the long term. Di Emidio et al. [21] studied the mechanisms through which polymers can improve the efficiency of dredged sediments reused as low permeable barriers for waste containment. An anionic polymer was adsorbed to the surface of kaolin and dredged sediments. Hydraulic conductivity and batch sorption tests were executed to study the barrier performance and the transport parameters of the treated soils. The polymer treatment maintained low hydraulic conductivity of the soil to electrolyte solutions. The polymer treatment also improved the adsorption capacity of the soil with regard to  $\text{Mg}^{2+}$  compared to the untreated soil ( $\text{Mg}^{2+}$  was used as first preliminary trial to simulate heavy metal cations). These results suggest the possible reuse of dredged sediments as alternative low permeable barrier materials.

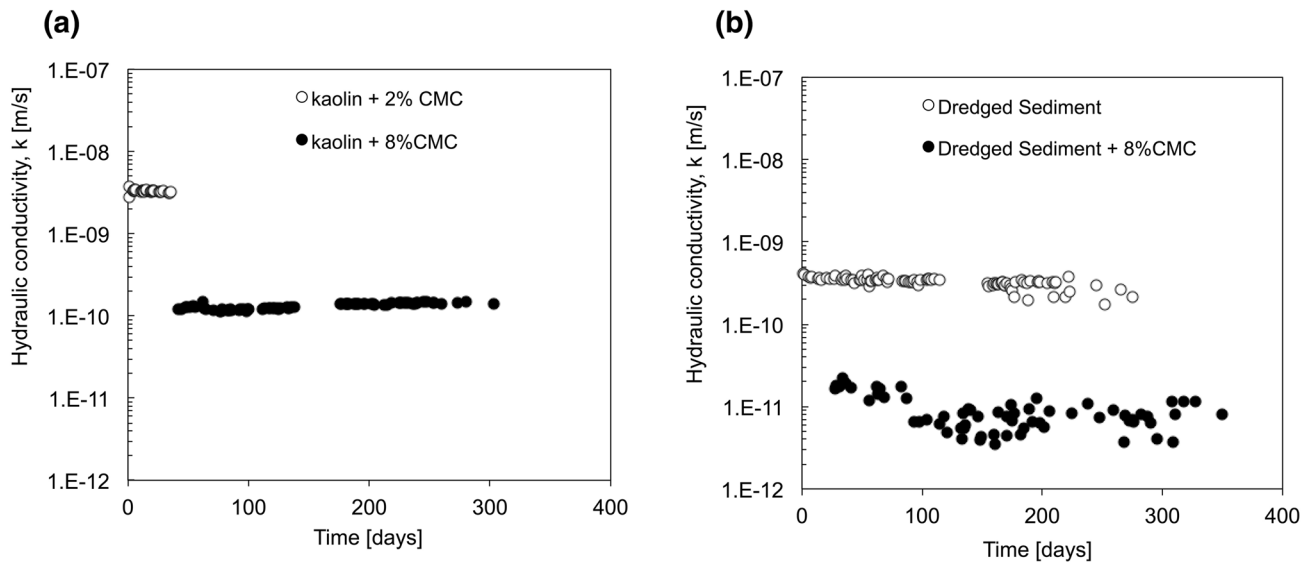
Further insights are required to better understand the mobility of heavy metals in polymer-treated clays and the ability of such clays to retain heavy metals. This paper shows the effects on both the hydraulic conductivity and the adsorption characteristics of HYPER clay treatment on

kaolin and dredged sediments. The adsorption on these polymer-treated clays of heavy metals such as  $\text{Cu}^{2+}$  and  $\text{Pb}^{2+}$  was evaluated.

**Batch sorption tests results**

The sorption isotherm shows the relationship between the mass of adsorbed ions and the equilibrium concentration of ions in the solution [74]. Figure 8 shows the sorption isotherms of the treated and untreated kaolin and of the treated and untreated dredged sediment. The adsorbed mass of ions is plotted here vs. the equilibrium concentration of the  $\text{Cu}(\text{NO}_3)_2$  and  $\text{Pb}(\text{NO}_3)_2$  solutions. Generally, the adsorption of lead is higher than that of copper due to its larger ionic radius and its consequent higher affinity to clays [27], such as montmorillonite (a type of smectite), illite (a type of mica) and kaolinite. As shown in Fig. 8, this behaviour was also noticed in the treated and untreated materials studied here. Figure 8 also shows that the adsorption of both  $\text{Pb}^{2+}$  and  $\text{Cu}^{2+}$  was higher for the sediments than for kaolinite, likely because the sediments contain phyllosilicate minerals in the clay fractions (such as mica, chlorite, and smectite) with a negative charged surface significantly larger compared to kaolin.

As shown in Fig. 8, batch sorption test results demonstrate that the sorbed mass of heavy metals was higher on the polymer-treated soil compared to the untreated soil due to the increased negative charge and the pH buffer behaviour provided by the anionic polymer Na-CMC addition. The sorption capacity of kaolin clay is pH dependent because its surface charge is more negative for pH values higher than its point of zero charge PZC [90]. Studies of Heidmann et al. [31, 32], Alkan et al. [2] and Jiang et al. [34, 35] confirmed that



**Fig. 9** Hydraulic conductivity test results of **a** kaolin clay 2% CMC and 8% CMC, and **b** dredged sediment and dredged sediment treated with 8% CMC, permeated with natural seawater

the adsorption of lead, copper, nickel and cadmium on kaolinite increases with increasing pH. Hence, the adsorption decrease noticed here at higher concentrations, which was most distinct for the adsorption of copper on the untreated kaolinite (Fig. 8a, open circles), is likely due to a decrease in pH noticed with increasing  $\text{Cu}(\text{NO}_3)_2$ . Precipitation observed at high concentrations could also have contributed to the low adsorption.

### Hydraulic conductivity tests results

Hydraulic conductivity tests were conducted on untreated and HYPER clays. The hydraulic conductivity of untreated clays increased by permeating the samples with electrolyte solutions. Conversely, HYPER clays maintained low hydraulic conductivity to seawater even after several days of permeation. Figure 9a shows the hydraulic conductivity ( $k$ ) to seawater of the kaolin treated with 2% Na-CMC ( $k = \times 10^{-9}$  m/s after 36 days and 189.3 pore volumes of flow, PVF) and 8% Na-CMC ( $k = 1.28 \times 10^{-10}$  m/s after 303 days and 89.6 PVF). As shown in the figure, the hydraulic conductivity to seawater of the kaolin treated with 8% CMC was lower compared to that of the kaolin treated with 2% CMC. This result demonstrates that increasing the dosage of the polymer, the hydraulic conductivity of the kaolin decreases. Figure 9b shows the hydraulic conductivity of the dredged sediment treated with 8% Na-CMC compared to the hydraulic conductivity of the untreated dredged sediment. As shown in the figure, the hydraulic conductivity of the treated dredged sediment ( $k = 8.54 \times 10^{-12}$  m/s after 350 days and 0.44 PVF) was lower compared to that of the untreated dredged sediment

( $k = 3.07 \times 10^{-10}$  m/s after 286.2 days and 2.1 PVF). These results demonstrate that the kaolin and the dredged sediment can be treated with the HYPER clay method to improve their hydraulic performance and this is maintained even after several days of permeation suggesting that the polymer remained adsorbed on the soil.

### Conclusions

Modified bentonites have been recently introduced in barrier applications to improve their chemical resistance to aggressive permeants. Among these treated soils, the clays treated with cationic polymers showed higher or slightly lower permeability compared to untreated clays. Organoclay treated with organic molecules showed higher retention capacities than untreated clays, but sometimes higher permeabilities. On the other hand, clays treated with propylene carbonate, polymerized acrylic acid or with anionic polymers showed high swelling capacity and low hydraulic conductivity values for monovalent and bivalent solutions. However, more research is needed to extend these conclusions to the long term. For this purpose, the impact of prolonged permeation on the amendments adsorption should be studied. Possible biodegradability of the organic compounds in the interlayer region of the clay should also be studied.

A destruction of membrane efficiency was observed in untreated clays due to diffusion. On the other hand, the polymer treatment of HYPER clay protected the clay against the destructive role of diffusion, maintaining the initial osmotic efficiency in the long term. Polymer

treatment modified the bentonite structure such that the double-layer thickness of the clay resisted collapse and the membrane efficiency was sustained. The diffusion coefficient of the HYPER clay was lower than that of the natural clay. This result suggests that the polymer protected the HYPER clay from cation exchange.

The preliminary interpretation of chemico-osmotic experimental data from laboratory tests provided a first validation of the proposed model. Nevertheless, further laboratory tests and theoretical considerations are necessary to obtain additional insights into the specific aspects that govern osmotic phenomena in modified clays.

Test results showed that the cement-HYPER clay mixtures were less permeable and less sensible to the microstructural changes caused by the interaction between cement hydration products and sulfates. Longer monitoring periods are necessary to evaluate the long-term behavior of CB samples.

The results of this study illustrate that HYPER clay may offer advantages over natural Na bentonite for soil-bentonite (SB) barrier applications, in terms of creating SB backfill with a lower hydraulic conductivity and improved compatibility with site groundwater containing multivalent cations.

The results of batch sorption test demonstrated that the sorbed mass of heavy metals was higher onto the HYPER clays compared to the untreated soils (dredged sediments and kaolin clay). These results are promising in view of heavy metals retention in polymer-treated dredged sediments. Hydraulic conductivity test results of treated and untreated soils were also shown. The hydraulic conductivity to seawater of the kaolin treated with 8% of polymer was lower compared to that of the kaolin treated with 2% of polymer. This result demonstrates that the hydraulic performance of a kaolin clay increases (the hydraulic conductivity decreases) with increasing polymer dosage. The hydraulic conductivity to seawater of the dredged sediment treated with 8% of polymer was significantly lower compared to that of the untreated dredged sediment. These results suggest the possible reuse of dredged sediments treated with HYPER clay technology, as alternative low cost impermeable barrier materials.

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