

Laboratory procedures for the modification of soluble and exchangeable cations of geosynthetic clay liners

Original

Laboratory procedures for the modification of soluble and exchangeable cations of geosynthetic clay liners / Guarena, Nicolo; Mazzieri, Francesco; Dominijanni, Andrea; Fratolocchi, Evelina; Manassero, Mario. - In: E3S WEB OF CONFERENCES. - ISSN 2267-1242. - ELETTRONICO. - 644:(2025), pp. 1-9. (EUROGEO 8 - 8th European Conference on Geosynthetics Lille (Francia) 15-18 settembre 2025) [10.1051/e3sconf/202564402017].

Availability:

This version is available at: 11583/3007511 since: 2026-02-10T17:42:38Z

Publisher:

EDP Sciences

Published

DOI:10.1051/e3sconf/202564402017

Terms of use:

This article is made available under terms and conditions as specified in the corresponding bibliographic description in the repository

Publisher copyright

(Article begins on next page)

Laboratory procedures for the modification of soluble and exchangeable cations of geosynthetic clay liners

Nicolò Guarena^{1*}, Francesco Mazzieri², Andrea Dominijanni¹, Evelina Fratolocchi², and Mario Manassero¹

¹Polytechnic University of Turin, Department of Structural, Geotechnical and Building Engineering, 10129 Turin, Italy

²Polytechnic University of Marche, Department of Science and Engineering of Materials, Environment and Urban Planning, 60131 Ancona, Italy

Abstract. A novel dialysis procedure to modify the exchange complex composition of the bentonite component of geosynthetic clay liners, as well as to remove the excess soluble salts from the bentonite pores, has been developed in order to overcome the limitations associated with the currently used dialysis methods. Indeed, when the bentonite to be purified is characterized by an aggregated fabric, the presence of less accessible pores does not allow the interlayer exchangeable cations to be replaced by the cationic species contained in the dialysing solution, thus undermining the effectiveness of dialysis in homo-ionising the bentonite specimen. For such a reason, the novel dialysis procedure that is proposed in this study comprises a preliminary treatment phase, which comes before the homo-ionisation phase and is aimed to promote the break-up of the bentonite tactoids through dialysis cycles with deionised water. A natural powdered bentonite has been tested in the laboratory to evaluate the enhancement in the bentonite sodium homo-ionisation that is due to the adoption of the newly developed dialysis procedure, in substitution to the currently used one, showing that such substitution results in an increase in the exchangeable sodium percentage from 35% to 78% at the expense of a decrease in the exchangeable calcium percentage.

1 Introduction

The ability to control the composition of the exchange complex of bentonites, which are used as part of engineered clay barriers for pollutant containment applications (e.g., geosynthetic clay liners, slurry trench cutoff walls, and compacted bentonite buffers), is essential for the laboratory investigation of the influence of the type and relative abundance of bound (exchangeable) cations on the transport and mechanical properties of these barriers. For instance, dominance of the exchange complex by monovalent cations, such as sodium (Na^+) and potassium (K^+), over multivalent cations, such as calcium (Ca^{2+}) and magnesium (Mg^{2+}),

* Corresponding author: nicolo.guarena@polito.it

promotes the formation of a dispersed bentonite fabric, which in turn is responsible for a decrease in the hydraulic conductivity under fully saturated conditions [1-4] and an increase in the matric suction associated with a given bulk dry density and water content [5, 6]. Under the same molar salt concentration of the equilibrium bulk solution, occupation of the bentonite exchange sites by monovalent cations in place of multivalent cations further promotes the development of the diffuse double layers, which in turn is responsible for an increase in the ability to exhibit osmotic swelling [7-9] and an amplification of the semipermeable membrane behaviour [10-13]. Similar to the control of the composition of the exchange complex of bentonites, removal of the excess soluble salts, which are naturally present in the soil pores and differ from the bound cations insofar as they are not electrostatically held to the mineral surface, is beneficial to the laboratory characterisation of the fundamental mechanisms that govern the behaviour of bentonites.

Several laboratory procedures for the saturation of the exchange complex with a single cationic species, also referred to as homo-ionisation or clay purification, and for the reduction of the concentration of the soluble salts in the bentonite pores have been developed in the soil science and geotechnical engineering field over the past decades, including washing and centrifuging, e.g. [7, 8], and dialysis methods, e.g. [10, 14-16]. According to the dialysis procedure, the bentonite is placed inside a tube of selectively permeable membrane, sealed via clamps at each end of the tube, and immersed in the dialysis bath solution, which is referred to as the dialysate. It is essential to notice that the membrane tubing, typically made of regenerated cellulose or analogous materials with a molecular weight cut-off (MWCO) in the 1 to 10 kDa range, is permeable to the water and solute molecules, but not to the soil particles. On the basis of the type of dialysate, two distinct treatment phases can be identified, namely (1) dialysis with a concentrated salt solution (Fig. 1a) and (2) reverse dialysis with deionised water (Fig. 1b). Dialysis may comprise either the first treatment phase, if the purpose is only to modify the cations on the bentonite exchange complex, the second treatment phase, if the purpose is only to remove the excess soluble salts from the bentonite pores, or both the first and second treatment phases sequentially, if the bentonite needs to be simultaneously homo-ionised and rinsed of its natural soluble salts. For both the first and second treatment phases of the dialysis procedure, the bath solution is continuously stirred and replaced with fresh dialysate at regular time intervals to maintain a solute concentration difference between the bath and pore solutions, since diffusion is the mechanism that controls the transport rate of dissolved solutes through the membrane tubing.

Despite the importance of assessing the effectiveness of dialysis in achieving a sufficiently high degree of homo-ionisation (e.g., more than 95% of the exchange sites occupied by the desired cation) and a sufficiently low concentration of residual soluble salts after treatment, this latter issue has received limited attention so far. Sample-Lord and Shackelford [17] first evaluated for a GCL-grade granular bentonite the relation between the strength of the dialysate, which consisted of aqueous solutions of sodium chloride (NaCl) with concentrations in the 0.1 to 1.0 M range, and the extent of Na⁺ homo-ionisation, which was quantified in terms of the percentage of the bentonite exchange sites occupied by Na⁺ ions or exchangeable sodium percentage (ESP). The measured ESP values before and after dialysis with the strongest (1.0 M NaCl) bath solution were equal to 47% and 89%, respectively, thus demonstrating the potential of dialysis as a laboratory procedure to modify the exchange complex composition and the residual soluble salt concentration of chemically active clays.

This technical note aims to provide further insight into the effectiveness of dialysis, comprising the same treatment phases as those considered by Sample-Lord and Shackelford [17], and to suggest an alternative procedure to perform the bentonite purification via dialysis, so as to improve its effectiveness in the case of an aggregated bentonite fabric with Ca²⁺ ions as the dominant bound cations in the interlayer pores.

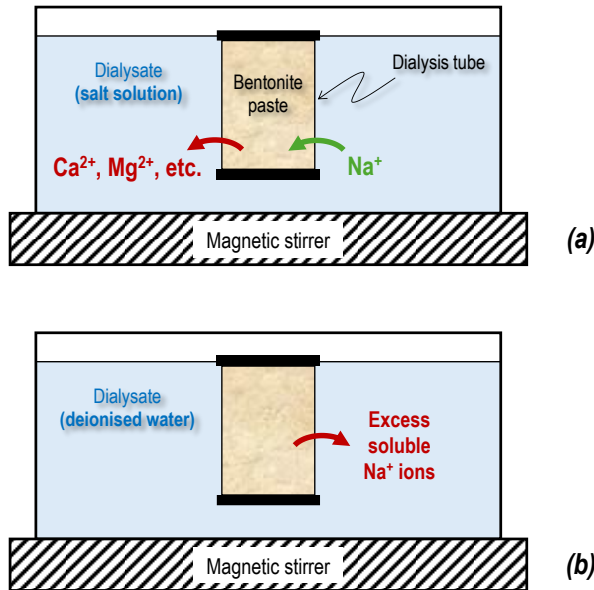


Fig. 1. Sequential treatment phases of the dialysis procedure: (a) dialysis with a concentrated salt solution for the purpose of modifying the cations on the exchange complex; (b) reverse dialysis with deionised water for the purpose of removing the excess soluble salts.

2 Materials and methods

2.1 Bentonite and chemical solutions

The natural powdered bentonite, which was treated via dialysis in this study, was supplied by Laviosa Chimica Mineraria (Livorno, Italy) and is used for the industrial production of a needle-punched geosynthetic clay liner. Further details about the physico-chemical properties of the tested material can be found in the studies by Dominijanni et al. [18, 19], Puma et al. [20], and Guarena et al. [21]. The cation exchange capacity (CEC) of the natural bentonite, as measured through the methylene blue titration method [22] to enhance the accessibility of the bentonite exchange sites as a consequence of the complete exfoliation (delamination) of the bentonite fabric [23], was equal to 98.9 meq/100g. The natural bentonite was also characterised through displacement with ammonium acetate [24] in terms of the concentrations of the bound Na^+ , Mg^{2+} , and Ca^{2+} ions, which were equal to 34.9, 7.0, and 13.5 meq/100g, respectively. The relative abundances of the bound Na^+ , Mg^{2+} , and Ca^{2+} ions on the exchange complex of the natural bentonite, as given by the ratio of the measured concentrations of the bound cations to the CEC and referred to as exchangeable cation percentages, thus resulted to be equal to 35.3%, 7.1%, and 13.6%, respectively.

The liquids used in this study included deionised water (DW) and an aqueous solution of sodium nitrate (NaNO_3) (ACS reagent, purity $\geq 99\%$, purchased from Merck KGaA, Darmstadt, Germany) with a concentration equal to 1.0 M.

2.2 Bentonite purification via dialysis

The natural powdered bentonite was subjected to a similar purification procedure to that evaluated by Sample-Lord and Shackelford [17], referred hereafter to as *Dialysis Type A*. The details of both the dialysis procedure evaluated by Sample-Lord and Shackelford [17]

and that implemented in this study can be found in Table 1. The 1.0 M NaNO₃ solution was used as the dialysate to homo-ionise the bentonite specimen with respect to sodium, and the concentration of NaNO₃ in the dialysate was selected so as to correspond to the upper bound of the salt concentration range investigated by Sample-Lord and Shackelford [17]. The salt concentration of the dialysate, as well as the duration of the homo-ionisation phase (seven ten-days-long dialysis cycles), were expected to be high enough to achieve a similar or greater effectiveness of *Dialysis Type A* compared to the purification procedure evaluated by Sample-Lord and Shackelford [17]. Also the reverse dialysis phase with DW, which comprised thirty-three one-day-long dialysis cycles, was run for a longer period of time compared to the Sample-Lord and Shackelford [17] study.

Table 1. Comparison between the treatment phases of the dialysis procedure evaluated by Sample-Lord and Shackelford [17] and the dialysis procedures implemented in this study (*Dialysis Type A* and *Dialysis Type B*).

			[17]	Dialysis Type A	Dialysis Type B
Phase (0) Breakup of tactoids	<i>Dialysate</i>				Deionised water
	<i>Total duration</i>	(day)			33
	<i>Frequency of dialysate replacement</i>	(day/cycle)			1
Phase (1) Na ⁺ homo-ionisation	<i>Dialysate</i>		NaCl (0.1 - 1 M)	NaNO ₃ (1 M)	NaNO ₃ (1 M)
	<i>Total duration</i>	(day)	7	70	70
	<i>Frequency of dialysate replacement</i>	(day/cycle)	1	10	10
Phase (2) Removal of soluble Na ⁺	<i>Dialysate</i>		Deionised water	Deionised water	Deionised water
	<i>Total duration</i>	(day)	13 - 14	33	33
	<i>Frequency of dialysate replacement</i>	(day/cycle)	1	1	1

The bentonite specimens were obtained by uniformly distributing a total amount of 60 g (oven-dried mass) of powdered bentonite inside four different dialysis bags (i.e., 15 g of bentonite per dialysis bag), which were made of regenerated cellulose (flat width = 76 mm, MWCO = 14 kDa, purchased from Merck KGaA, Darmstadt, Germany). For the preparation of the dialysis bags, four sections of the membrane tubing were cut with a length of 300 mm and soaked in DW for 24 hours, so as to remove the impurities. After soaking, one end of each dialysis bag was sealed with a plastic closure (width = 110 mm, purchased from Merck KGaA, Darmstadt, Germany), the powdered bentonite and the dialysate were sequentially poured through the open end until filling the dialysis bag for a length of approximately 150 mm, and the open end was finally sealed with another plastic closure. The four dialysis bags containing the untreated bentonite were then placed inside a glass jar, which was filled with

7 L of the dialysate and continuously stirred through a magnetic stirrer (max stirring capacity = 10 L, speed range = 100 - 2000 rpm, purchased from 2mag AG, München, Germany). In this study, the ratio of the dry mass of bentonite to the mass of dialysate was approximately equal to 1:117, which is of the same order of magnitude as the value reported by Sample-Lord and Shackelford [17] (1:280). At the end of the purification procedure, the bentonite paste was extracted from the dialysis bags, the water content was measured through oven-drying, and the dialysed bentonite was characterised through displacement with ammonium acetate [24] in terms of the concentrations of the bound Na^+ , Mg^{2+} , and Ca^{2+} ions. The determination of the bound cation concentrations was performed in two replicates.

In addition to *Dialysis Type A*, an alternative procedure for the bentonite purification via dialysis, referred hereafter to as *Dialysis Type B*, was developed and evaluated in this study to assess its potential for enhancing the ESP of the bentonite after treatment. As can be appreciated from Table 1, the latter dialysis procedure is identical to the former one regarding the homo-ionisation and soluble salt removal treatment phases, but differs because of the presence of an additional treatment phase, which comes before the homo-ionisation phase and comprises thirty-three one-day-long dialysis cycles with DW. Due to the sensitivity of the bentonite fabric to the chemical composition of the dialysate [15], delamination of the tactoids into their individual unit layers is expected to occur when the bentonite is equilibrated with DW, thereby favouring the substitution of the bound cations, initially segregated in the interlayer pore space of the tactoids, with the Na^+ ions contained in the dialysate during the subsequent Na^+ homo-ionisation phase.

3 Results and discussion

The bar chart in Fig. 2 reports the composition of the bentonite exchange complex, in terms of the percentages of exchangeable Na^+ , Mg^{2+} , and Ca^{2+} ions, before and after purification via dialysis. As far as *Dialysis Type A* is concerned, the percentages of exchangeable Na^+ (33.5%) and Mg^{2+} ions (11.9%) did not appreciably change from their initial values, which were equal to 35.3% and 7.1%, respectively, whereas the percentage of exchangeable Ca^{2+} ions increased from 13.6% to 43.9%. Such an evidence, which at first glance seems to be inconsistent with the results obtained by Sample-Lord and Shackelford [17], can be interpreted in the light of the bentonite fabric changes throughout the purification procedure and the different accessibility of the bentonite pore structures.

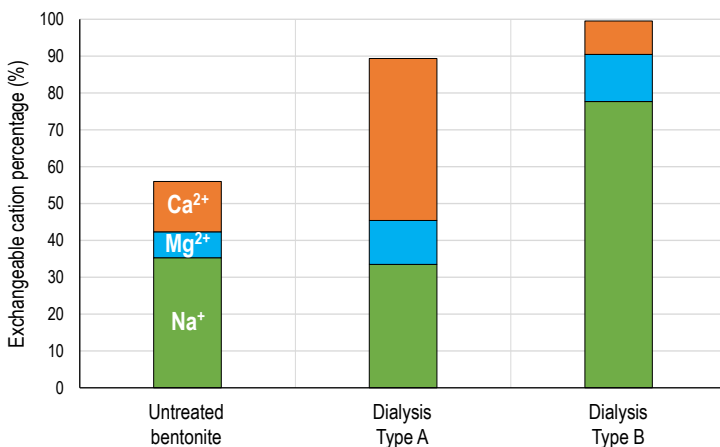


Fig. 2. Relative abundances of the bound Na^+ , Mg^{2+} , and Ca^{2+} ions on the bentonite exchange complex before and after purification via dialysis.

When the natural bentonite is initially characterised by an aggregated microstructure, multivalent cations tend to be segregated in the interlayer pore space (i.e., the void volume enclosed between adjacent montmorillonite unit layers comprising the tactoids), whereas monovalent cations are predominantly adsorbed on the external surface of the tactoids [25]. Under such conditions, the bound cations readily available for displacement with ammonium (NH_4^+) ions [24] are those located on the external surface of the tactoids, and only the latter ones contribute to the measured exchangeable cation percentage. According to the proposed interpretation, the failed characterisation of a portion (44.0%) of the exchange complex composition of the untreated bentonite should therefore be attributed to the presence of interlayer pores, which were not accessible for displacement with NH_4^+ ions.

As schematically illustrated in Fig. 3 for *Dialysis Type A*, dialysis of the bentonite specimens with the concentrated NaNO_3 solution only caused the multivalent cations bound to the external surface of the tactoids to be replaced by the Na^+ ions of the dialysate, whereas the multivalent cations bound to the internal surface of the tactoids were not significantly affected by dialysis. Besides removal of the excess soluble salts, during the subsequent reverse dialysis with DW a change in the bentonite fabric occurred, consisting in the delamination of the tactoids into their individual unit layers, and the composition of the bentonite exchange complex was no further modified. Under these latter conditions, the multivalent cations originally segregated in the interlayer pores were available for displacement with NH_4^+ ions, thus resulting, on the one hand, in the nearly complete characterisation (89.3%) of the exchange complex composition of the dialysed bentonite and, on the other hand, in the measured increase in the percentage of exchangeable Ca^{2+} ions.

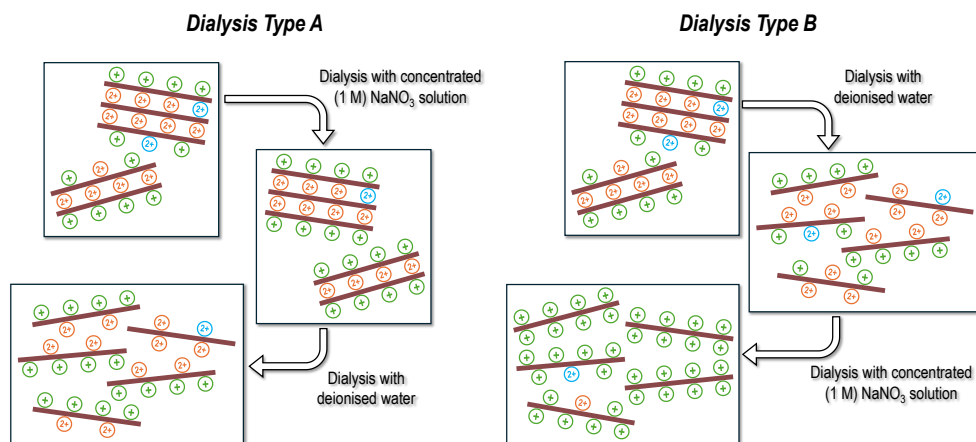


Fig. 3. Schematic representation of the changes in the bentonite fabric and the composition of the bentonite exchange complex, which were induced during the treatment phases of *Dialysis Type A* and *Dialysis Type B*.

On the basis of the bar chart in Fig. 2, it is possible to appreciate the different effectiveness of the Na^+ homo-ionisation phase, both without the preliminary treatment with DW (*Dialysis Type A*) and with the preliminary treatment with DW (*Dialysis Type B*). While the original dialysis procedure did not cause any appreciable change in the composition of the bentonite exchange complex, the newly developed dialysis procedure allowed the percentage of exchangeable Na^+ ions to increase from 33.5% to 77.7%, at the expense of a decrease in the percentage of exchangeable Ca^{2+} ions (from 43.9% to 9.1%). As shown in Fig. 3, a similar rationale to that proposed for *Dialysis Type A* provides a ground for an interpretation of the results pertaining to *Dialysis Type B*.

During the preliminary treatment phase with DW, dispersion of the bentonite fabric was induced without any alteration in the composition of the exchange complex from that of the untreated bentonite. Due to the formation of a dispersed bentonite fabric, the multivalent cations originally bound to both the external and internal surfaces of the tactoids were readily substituted by the Na^+ ions of the dialysate when the bentonite was dialysed with the concentrated NaNO_3 solution. In such a way, at end of all the treatment phases comprising *Dialysis Type B*, the exchange complex of the dialysed bentonite was largely saturated by Na^+ ions.

4 Conclusions

The development of purification procedures, with the goal to both saturate most of the exchange sites with a single cationic species and rinse the specimen of the excess soluble salts, is essential for a greater control over the testing conditions when chemically active clays (e.g., bentonites) are tested in the laboratory for assessing their physico-chemical, transport, and mechanical properties. For such a reason, the effectiveness of a dialysis procedure, which resembles that considered by Sample-Lord and Shackelford [17] and is referred to as *Dialysis Type A*, was evaluated in this study for the purification of a GCL-grade powdered bentonite. *Dialysis Type A* comprised a first treatment phase, aimed to saturate the bentonite exchange complex with Na^+ ions through dialysis with a concentrated NaNO_3 solution, and a second treatment phase, aimed to remove the excess soluble salts through dialysis with deionised water.

Due to the aggregated microstructure of the tested bentonite and the preferential segregation of multivalent cations in the interlayer pore space, the Na^+ homo-ionisation treatment phase of *Dialysis Type A* did not allow the exchangeable sodium percentage (ESP) of the dialysed bentonite to significantly increase compared to that of the untreated bentonite. An alternative procedure, referred to as *Dialysis Type B* and comprising a preliminary treatment phase for the breakup of the bentonite tactoids through dialysis with deionised water, was therefore developed with a view to improving the effectiveness of purification via dialysis. Addition of such a preliminary treatment phase to the dialysis procedure resulted in a notable increase in the ESP, which increased from 35% for the untreated bentonite to 78% for the bentonite that had been dialysed according to the newly developed *Dialysis Type B*.

References

1. T. Katsumi, H. Ishimori, A. Ogawa, K. Yoshikawa, K. Hanamoto, R. Fukagawa, Hydraulic conductivity of nonprehydrated geosynthetic clay liners permeated with inorganic solutions and waste leachates. *Soils and Foundations* **47**, 79-96 (2007). <https://doi.org/10.3208/sandf.47.79>
2. C.D. Shackelford, G.W. Sevick, G.R. Eykholt, Hydraulic conductivity of geosynthetic clay liners to tailings impoundment solutions. *Geotextiles and Geomembranes* **28**, 149-162 (2010). <https://doi.org/10.1016/j.geotextmem.2009.10.005>
3. M. Manassero, Second ISSMGE R. Kerry Rowe Lecture: On the intrinsic, state, and fabric parameters of active clays for contaminant control. *Canadian Geotechnical Journal* **57**, 311-336 (2020). <https://doi.org/10.1139/cgj-2019-0033>
4. N. Guarena, A. Dominijanni, M. Manassero, Pore-scale mechanisms underlying the behavior of enhanced bentonites exposed to aggressive inorganic solutions. *Applied Clay Science* **251**, 107318 (2024). <https://doi.org/10.1016/j.clay.2024.107318>

5. A. Seiphoori, A. Ferrari, L. Laloui, Water retention behaviour and microstructural evolution of MX-80 bentonite during wetting and drying cycles. *Géotechnique* **64**, 721-734 (2014). <https://doi.org/10.1680/geot.14.P.017>
6. G. Della Vecchia, G. Scelsi, G. Musso, Modelling the role of pore water salinity on the water retention behaviour of compacted active clays. *Rivista Italiana di Geotecnica* **53**, 16-29 (2019). <https://doi.org/10.19199/2019.3.0557-1405.016>
7. G. Mesri, R.E. Olson, Consolidation characteristics of montmorillonite. *Géotechnique* **21**, 341-352 (1971). <https://doi.org/10.1680/geot.1971.21.4.341>
8. C. Di Maio, Exposure of bentonite to salt solution: osmotic and mechanical effects. *Géotechnique* **46**, 695-707 (1996). <https://doi.org/10.1680/geot.1996.46.4.695>
9. G. Musso, R.M. Cosentini, A. Dominijanni, N. Guarena, M. Manassero, Laboratory characterization of the chemo-hydro-mechanical behaviour of chemically sensitive clays. *Rivista Italiana di Geotecnica* **51**, 22-47 (2017). <https://doi.org/10.19199/2017.3.0557-1405.022>
10. W.D. Kemper, J.B. Rollins, Osmotic efficiency coefficients across compacted clays. *Soil Science Society of America Journal* **30**, 529-534 (1966). <https://doi.org/10.2136/sssaj1966.03615995003000050005x>
11. C.D. Shackelford, J.M. Lee, The destructive role of diffusion on clay membrane behavior. *Clays and Clay Minerals* **51**, 186-196 (2003). <https://doi.org/10.1346/CCMN.2003.0510209>
12. F. Mazzieri, G. Di Emidio, P.O. Van Impe, Diffusion of calcium chloride in a modified bentonite: impact on osmotic efficiency and hydraulic conductivity. *Clays and Clay Minerals* **58**, 351-363 (2010). <https://doi.org/10.1346/CCMN.2010.0580306>
13. S. Tong, K.M. Sample-Lord, G.L. Bohnhoff, Diffusion through sodium and polymer enhanced bentonites exposed to dilute and aggressive solutions. *Canadian Geotechnical Journal* **58**, 603-618 (2021). <https://doi.org/10.1139/cgj-2019-0809>
14. D.E. Elrick, D.E. Smiles, N. Baumgartner, P.H. Groenevelt, Coupling phenomena in saturated homo-ionic montmorillonite: I. Experimental. *Soil Science Society of America Journal* **40**, 490-491 (1976). <https://doi.org/10.2136/sssaj1976.03615995004000040014x>
15. G.R. Armando, Luis de la Torre, L.A. García-Serrano, A. Aguilar-Elguézabal, Effect of dialysis treatment on the aggregation state of montmorillonite clay. *Journal of Colloid and Interface Science* **274**, 550-554 (2004). <https://doi.org/10.1016/j.jcis.2003.11.032>
16. M. Segad, S. Hanski, U. Olsson, J. Ruokolainen, T. Åkesson, B. Jönsson, Microstructural and swelling properties of Ca and Na montmorillonite: (in situ) observations with cryo-TEM and SAXS. *The Journal of Physical Chemistry C* **116**, 7596-7601 (2012). <https://doi.org/10.1021/jp300531y>
17. K.M. Sample-Lord, C.D. Shackelford, Dialysis method to control exchangeable sodium and remove excess salts from bentonite. *Geotechnical Testing Journal* **39**, 206-216 (2016). <https://doi.org/10.1520/GTJ20150065>
18. A. Dominijanni, M. Manassero, S. Puma, Coupled chemical-hydraulic-mechanical behaviour of bentonites. *Géotechnique* **63**, 191-205 (2013). <https://doi.org/10.1680/geot.SIP13.P.010>
19. A. Dominijanni, N. Guarena, M. Manassero, Laboratory assessment of semipermeable properties of a natural sodium bentonite. *Canadian Geotechnical Journal* **55**, 1611-1631 (2018). <https://doi.org/10.1139/cgj-2017-0599>

20. S. Puma, A. Dominijanni, M. Manassero, L. Zaninetta, The role of physical pretreatments on the hydraulic conductivity of natural sodium bentonites. *Geotextiles and Geomembranes* **43**, 263-271 (2015).
<https://doi.org/10.1016/j.geotextmem.2015.02.001>
21. N. Guarena, A. Dominijanni, M. Manassero, Reflection coefficient of a natural sodium bentonite in aqueous mixed electrolyte solutions: positive and negative anomalous osmosis. *Canadian Geotechnical Journal* (e-First). <https://doi.org/10.1139/cgj-2024-0119>
22. EUBA, Methodology for the determination of the methylene blue value of bentonite (European Bentonite Association, Brussels, 2002).
23. A. Dominijanni, E. Fratolocchi, N. Guarena, M. Manassero, F. Mazzieri, Critical issues in the determination of the bentonite cation exchange capacity. *Géotechnique Letters* **9**, 205-210 (2019). <https://doi.org/10.1680/jgele.18.00229>
24. ASTM D 7503-18, Standard test method for measuring the exchange complex and cation exchange capacity of inorganic fine-grained soils (American Society for Testing and Materials International, West Conshohocken, 2018).
<https://doi.org/10.1520/D7503-18>
25. D.A. Laird, Influence of layer charge on swelling of smectites. *Applied Clay Science* **34**, 74-87 (2006). <https://doi.org/10.1016/j.clay.2006.01.009>