

Hydraulic performance of alginate-based bentonite

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ABSTRACT

Bentonite clay is widely used as a hydraulic barrier in geosynthetic clay liners and cut-off walls. The interaction of the clay with divalent electrolytic solutions such as Ca^{2+} or Mg^{2+} deteriorates its sealing properties. The treatment of bentonite with polymers has improved its hydraulic properties; however, sustainability concerns have led to the discovery of an alternate polymer. Sodium alginate was used to prepare a new, more sustainable polymerized bentonite clay. The alginate was selected due to its recent laboratory extraction from wastewater. This paper presents the performance of the alginate polymer-based bentonite clay in terms of swelling and hydraulic conductivity. Overall, the preliminary results were optimistic towards the use of alginate in polymerized clay. In short, the clay has the potential to be used as an effective hydraulic barrier in the construction industry, which would promote sustainable development.

INTRODUCTION

Sodium bentonite is well known for its low hydraulic conductivity or permeability to liquids and gases. The low hydraulic conductivity is attributed to the montmorillonite mineral that is primarily present in bentonite. The montmorillonite mineral, with a weak interlayer bond, swells significantly in the presence of monovalent cationic liquids. The swelling causes a considerable reduction in the inter-particle pore size to reduce the permeability (Aksu et al. 2015; Kolstad et al. 2004; Mitchell and Soga 2005). However, the interaction of the divalent cationic liquid with bentonite suppresses the swelling and hence increases the inter-particle pore size and hydraulic conductivity (Chen et al. 2019; Di Emidio et al. 2015).

In this situation, polymerized bentonite such as Bentonite polymer composites (BPCs) (Scalia IV et al. 2014), Sodium carboxymethyl cellulose (Na-CMC) based dense-prehydrated (DPH) geosynthetic clay liner (Katsumi et al. 2008; Mazzieri and Pasqualini 2008), and HYPER

clay (De Camillis et al. 2017; Di Emidio et al. 2010) can maintain low hydraulic conductivity in divalent cationic solutions. The interaction between polymer and bentonite defines the sealing mechanism of polymerized bentonite. Based upon the interaction ability, three types of composite structures are possible, i.e., phase-separated, intercalated, and exfoliated. BPCs are phase-separated, whereas DPH bentonite and HYPER clay are intercalated composites (Di Emidio 2010; Mazzieri and Emidio 2015). The sealing mechanism associated with all the composite structures is the tortuosity of flow paths. In the phase-separated composite structure, tortuous flow paths are attained by hydration of polymer, which creates hydrogel that fills the inter-particle pore space between bentonite granules (Tian et al. 2019). Whereas, in intercalated polymer bentonite composite structure, tortuosity of flow paths is achieved by an increase of basal spacing of interlayers (Di Emidio et al. 2017; Qiu and Yu 2008) that results in a decrease in the inter-particle pore size.

By mode of preparation, BPCs make use of in-situ polymerization, whereas DPH and HYPER clay are prepared by solution blending (Jlassi et al. 2017). BPCs are prepared by mixing the sodium bentonite with a monomer solution of acrylic acid along with neutralization of sodium hydroxide (Scalia IV et al. 2014). DPH is produced by mixing a polymeric solution containing Na-CMC, sodium polyacrylate, and methanol. HYPER clay is also prepared with Na-CMC solution (Di Emidio et al. 2017). The production of polymers used for the preparation of these polymerized bentonites are associated with environmental emissions (Foroughi et al. 2021; Petrescu et al. 2016). Along with these emissions, the cost of polymers is high. An alternate polymer would be optimal to reduce the environmental impact and decrease the production expenses of polymerized clay. The recent laboratory extraction of neo-alginate polymer from wastewater (TuDelft 2016) indicates its use for polymerized clay application. Therefore, in this study, the optimization of polymer amount is targeted by using commercial sodium alginate polymer, which would lead to the use of the neo-alginate in the production of polymerized clay to promote sustainable development. As the extracted form of the polymer could support its usage in both the DPH and the HYPER clay method. However, in this study, the HYPER clay method was used. The reason to select HYPER clay was the durable adsorption of the polymer onto the bentonite compared to DPH (Di Emidio 2010; Mazzieri and Pasqualini 2008).

This manuscript presents the use of commercial alginate as a polymer in the preparation of HYPER clay to optimize the polymer's quantity in the presence of electrolytic solution with the help of swell index, swell pressure, and hydraulic conductivity tests.

MATERIALS

The commercial sodium alginate (ALG), the sodium salt of alginic acid, was used in the pure form provided by Special Ingredients UK. Sodium alginate is an anionic polymer and a member of the hydrogel group, which makes it able to swell in water. The ability of water absorption arises from the presence of a hydrophilic functional group (OH^-). The molecular structure of Sodium alginate is shown in Figure 1. Sodium bentonite (CEB1) was used, which was treated according to the HYPER clay procedure proposed by Di Emidio (2010). The properties of CEB1 are shown in

Table 1. Three types of HYPER clays were produced, 4, 8, and 16% sodium alginate by weight of CEB1. The treatment consisted of mixing the CEB1 with ALG in deionized water for 30 minutes in a mechanical stirrer to make a slurry. The slurry was dried in the oven for 16 hours. After drying, the mixture was ground to powder form.

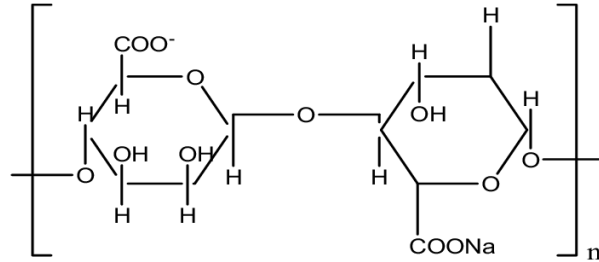


Figure 1. Molecular structure of sodium alginate (Homayouni et al. 2007)

Table 1. Physical and chemical properties of sodium bentonite (CEB1)

	Specific gravity	Liquid limit (%)	Plastic limit (%)	CEC (meq/100g)	EC* (Ca ²⁺)	EC* (K ⁺)	EC* (Mg ²⁺)	EC* (Na ⁺)
CEB1	2.66	649.7	48.3	70.17	43.25	1.52	15.56	40.28

*EC = Exchangeable cation

Three types of hydrating solutions were used, deionized water (DW), 10 mM CaCl₂, and seawater (SW). The properties of DW and SW are detailed in Table 2.

Table 2. Chemical properties of deionized water (DW), 10 mM CaCl₂, and seawater (SW)

	EC	pH	Na ⁺	K ⁺	Mg ²⁺	Ca ²⁺	Cl ⁻	SO ₄ ²⁻	HCO ₃ ⁻	CO ₃ ²⁻	NO ₃ ²⁻
	mS/cm		mg/L								
DW	0.002	6.57	-	-	-	-	-	-	-	-	-
10 mM CaCl ₂	1.634	6.65	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
SW	32.7	7.42	11518	469	1281	478	19897	2352	183	18	43

METHODS

Swell index tests were performed on CEB1 along with 4, 8, and 16% ALG HYPER clay samples in DW, 10 mM CaCl₂, and SW according to ASTM D5890 (2002). The swell pressure tests were performed on the same samples in DW. Besides, the CEB1, 4%, and 8% samples were also tested in 10 mM CaCl₂, and CEB1 and 8% in SW. The test setup used in the study is shown in Figure 2, which consists of a 7.1 cm diameter steel ring contained in a one-dimensional permeating cell and a load cell connected to a computer. The specimen was prepared by pouring a thin bentonite layer of fixed height (porosity of 0.718 and density of 0.45 g/cm²) between filter paper and porous

stones. After assembling the load cell and frame, the permeating cell was inundated with the respective solution and allowed to swell until the samples achieved a steady state. The swelling pressure at the steady state was measured with the help of the load cell by keeping the height of the specimen constant.

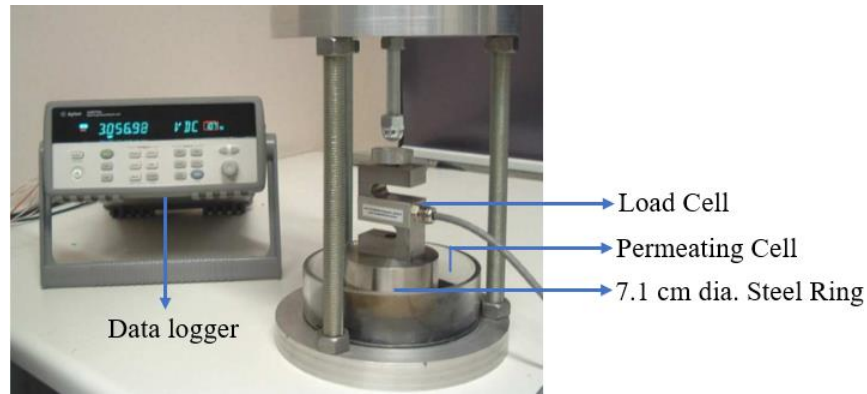


Figure 2. Swell Pressure test setup

Hydraulic conductivity tests were conducted on 4, 8, and 16% ALG HYPER clay samples in DW and subsequently in SW. The tests were carried out in a flexible wall permeameter using the falling head increasing tailwater method under the effective stress of 14 kPa according to ASTM 6766 (2002). The tests in DW achieved the hydraulic termination criteria, whereas the hydraulic conductivity tests in SW have not yet achieved chemical equilibrium according to the ASTM 6766 (2002); hence the tests are still ongoing.

RESULTS AND DISCUSSIONS

Swell Index. The swell index of CEB1, 4%, 8%, and 16% ALG in DW, 10 mM CaCl_2 , and SW is presented in Figure 3. The swell index in DW increases with an increase in alginate amount, and the value reached 61.5 ml/2g for 8% ALG mix, then decreases for 16% mix. The improvement with the rise in the amount of alginate is attributed to its intercalation within clay platelets, repulsion of charges on its chains, and release of sodium ions (Wang et al. 2014). The intercalation of the polymer in HYPER clay was observed by (Di Emidio 2010) based on the increase in basal spacing between clay platelets, which enhanced the swelling capacity. Besides, the repulsion of the local negative carboxylic group expands the chain. In the case of 16% ALG mix in 10 mM CaCl_2 , a 12% increase in the swell index was found, while in the case of 4% and 8%, the swell index was comparable to untreated bentonite. For SW, the swell index almost remained the same as that of CEB1. The trend of ALG HYPER clay was not conclusive on the swell index basis for sea water as the test did not indicate the increase in swelling.

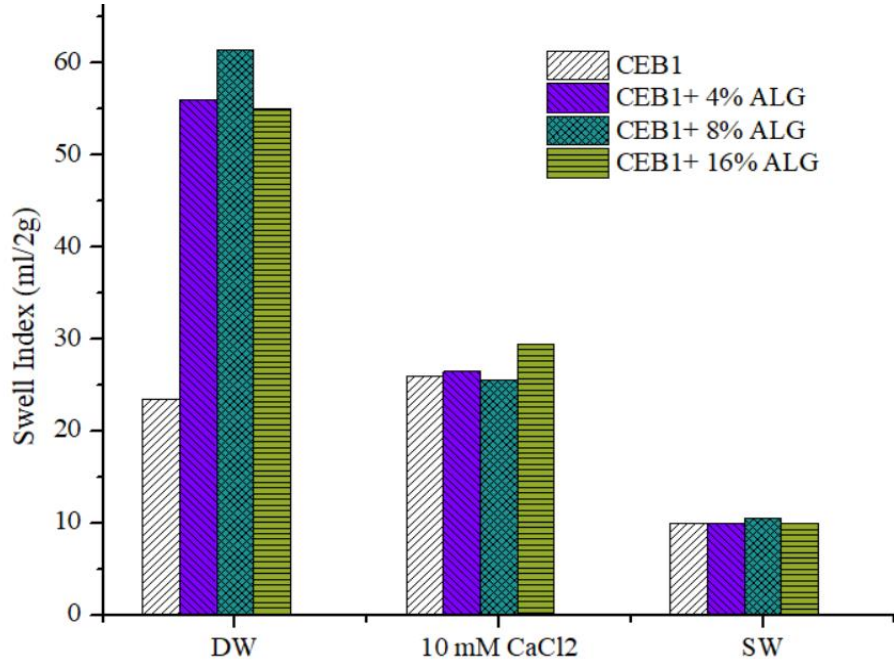


Figure 3. Swell Index of untreated bentonite (CEB1) and treated bentonite with 4, 8, and 16% alginate polymer in deionized water, 10mM CaCl₂, and seawater

Swell Pressure. The swelling clays under confined space exert pressure on its surrounding on hydration termed as swell pressure. The results of the swell pressure test are shown in Figure 4. The swell pressure increases with an increase in alginate content. Contrary to the swell index test, a considerable increase in swelling is depicted in the case of 10 mM CaCl₂ for ALG mixes with respect to CEB1. Besides, the swell pressure of the clays in 10 mM CaCl₂ was more than the swell pressure in DW. Furthermore, the swell pressure of 8% ALG HYPER clay in SW was more than CEB1 in DW. Literature shows that the swell index and swell pressure are directly linked with each other, in the case of sodium bentonite. However, in the current study, the swell index is not consistently related to swell pressure. The phenomenon seems to link with the difference of the condition under which swelling took place. In the swell index test, the bentonite was free to swell, whereas, in the swell pressure test, the clay was under confined condition. A similar phenomenon was observed in the case of BPC hydraulic conductivity, where the swell index is not consistently corresponded to hydraulic conductivity tested under 29 kPa effective stress (Gustitus and Benson 2021). The number of contradictions between the swell index and swell pressure test underlined the need to conduct the hydraulic conductivity test on all the ALG samples. Besides, it also indicates that the swelling cannot be regarded as an indication of hydraulic performance, which has also been shown in the literature (Li et al. 2021).

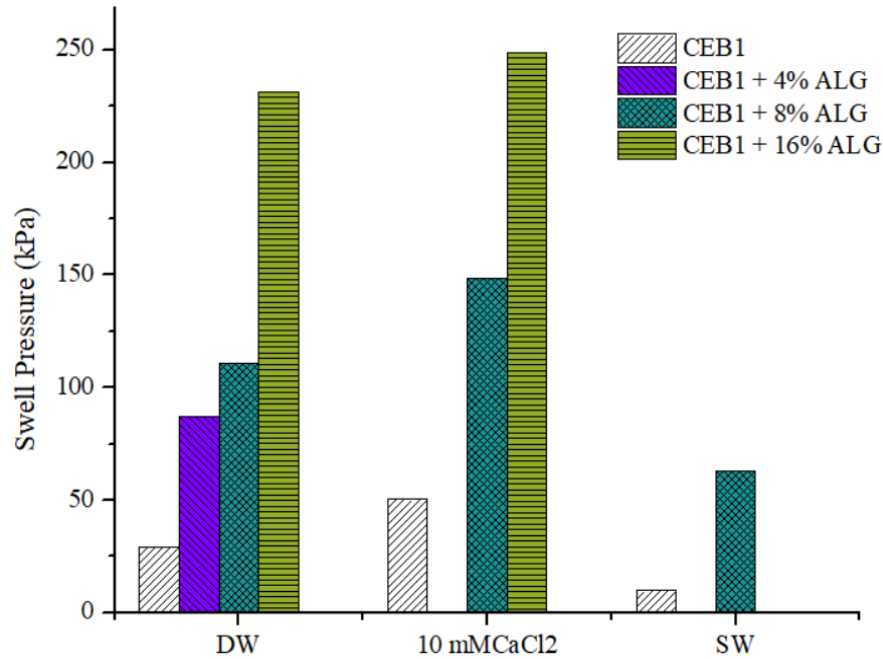
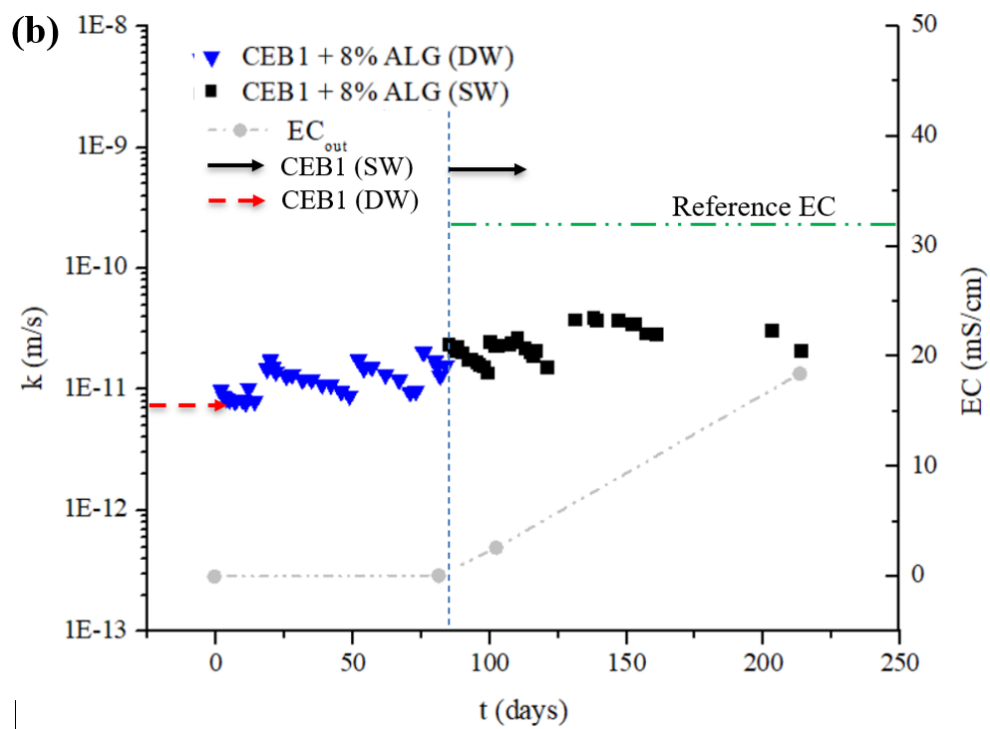
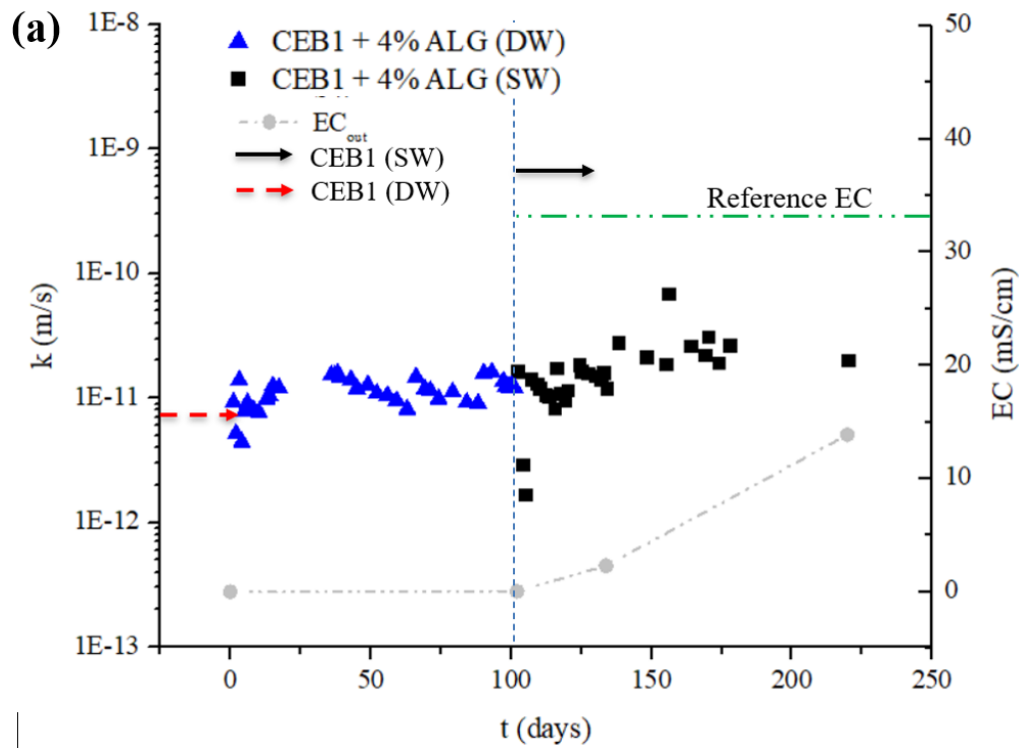


Figure 4. Swell Pressure of untreated bentonite (CEB1) and treated bentonite with 4, 8, and 16% alginate polymer

Hydraulic Conductivity. Figure 5 shows the results of the hydraulic conductivity test conducted on 4, 8, and 16% ALG samples in DW along with partial results in SW. Unlike the swell index and swell pressure test, the hydraulic conductivity of the CEB1, 4, 8, and 16% ALG polymerized clay samples in DW is almost equal; the arrows show the hydraulic conductivity of CEB1 (Di Emidio 2010). Whereas in the case of SW, the hydraulic conductivity of polymerized clays is 1 to 2-fold lower than untreated bentonite, although the tests have not reached the chemical equilibrium to make a conclusion between CEB1 and polymerized clays. Similarly, in the case of 8% ALG HYPER clay, the hydraulic conductivity has shown an increase of 0.2-fold with respect to the difference in hydraulic conductivities of CEB1 in DW and SW. Whereas the electric conductivity (EC) of the outflow in the case of 8% ALG HYPER clay has crossed half of the desired EC (labeled Reference), thus, depicting potentially improved sealing capacity of the HYPER clay. While comparing the polymerized clays, the hydraulic conductivity of 8% ALG HYPER clay is lower compared to 4% ALG samples.



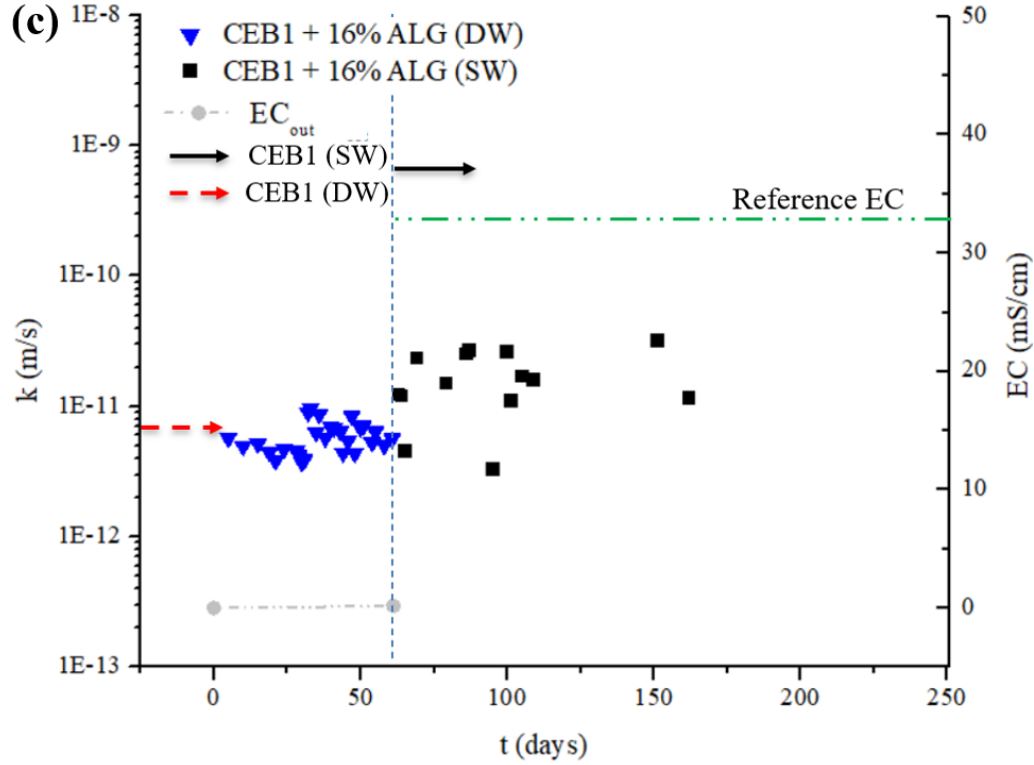


Figure 5. Variation in hydraulic conductivity (k) of (a) 4%, (b) 8%, and (c) 16% alginate polymer-based bentonite in deionized water and seawater with time along with final value (Arrows) of untreated bentonite

CONCLUSIONS

The swell index revealed higher swelling of alginate-based HYPER clay in DW and CaCl_2 but comparable swelling in seawater when compared to untreated bentonite. However, the swell pressure showed that the swelling of HYPER clays was higher compared to untreated clays. The hydraulic conductivity test has not yet achieved equilibrium, nonetheless, preliminary results show the hydraulic conductivity of HYPER clays 1 or 2 order of magnitude lower compared to that of untreated clays in CaCl_2 and seawater.

Overall, the results are promising towards the use of alginate in polymerized clay applications. After achieving the complete overview of the optimized quantity of polymer, further testing is planned on the neo-alginate extracted from the waste source. Based on the current scenario, alginate has the potential to be used in clay barrier application, which would be extracted from wastewater and would be used in the production of polymerized clay. Subsequently, it would reduce the environmental impact lead to sustainable development. More research is guaranteed to evaluate the economic impact of the polymer extraction from wastewater. However, in terms of reuse of waste products and due to the high costs of commercial polymers, it is expected also an economical advantage on using this type of recycled materials.

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