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1 PERMEABILITY AND SOLUTE RETENTION PROPERTIES OF 2 CONVENTIONAL AND POLYMER-TREATED PREHYDRATED GCLs

3 Francesco Mazzieri¹, Davide Bernardo² 4 5 ¹Department SIMAU, Marche Technical University, Via Brecce Bianche, 12, 6 Ancona 60131, Italy; e-mail: f.mazzieri@staff.univpm.it., corresponding author 7 ²Department SIMAU, Marche Technical University, Via Brecce Bianche, 12, 8 Ancona 60131, Italy; e-mail: d.bernardo@pm.univpm.it. 9 10 Keywords: Geosynthetic Clay Liners, hydraulic conductivity, heavy metals, 11 12 polymers 13 14 **ABSTRACT:** Polymer treatment is an increasingly adopted approach to mitigate the impact of aggressive liquids on GCLs' hydraulic performance. Dense PreHydrated 15 (DPH) GCLs are particular products that combine polymer treatment, prehydration 16 17 and densification to improve the overall containment performance. The paper investigated the saturated hydraulic conductivity, k, and heavy metals retention in a 18 19 conventional GCL and a DPH GCL. Both materials were permeated first with water and then with synthetic solution containing Zn, Cu, Pb, also with the purpose to 20 21 extend a previous study were a solution of the same solutes at higher concentrations had been used. The k of the conventional GCL increased by one order of magnitude 22 23 with respect to water upon permeation with the synthetic solution. The solutes were partly retained and the increase in k was associated with the breakthrough of solutes. 24 25 Upon permeation with the same solution, the k of the DPH GCL decreased by a factor 1.6 with respect to water. No significant breakthrough of metals was observed, 26 27 despite the considerably longer test duration. Under the adopted testing conditions, 28 owing to polymer amendment and densification the hydraulic performance and 29 solute retention properties of the DPH GCLs were superior to the conventional GCL. 30

32 **1. Introduction**

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Geosynthetic Clay Liners, (GCLs) consisting of a thin layer of bentonite clay incorporated between two geotextiles or glued to a geomembrane have been widely used as hydraulic and pollutant barriers (Bouazza, 2002). The content of sodium montmorillonite is the key factor for the characteristically low hydraulic conductivity of hydrated bentonite. GCLs are also employed in applications where metal-rich leachates and liquors must be contained (Bouazza, 2010, Liu et al., 2013).

40 Heavy metals such as Pb, Cu and Zn are commonly found in leachates of MSW 41 and HW landfills (Rowe et al., 2004) as well as in other containment applications such as mine water treatment systems (Lange et al., 2007; Lange et al., 2010). The 42 hydraulic conductivity performance and the retention capacity of GCLs in the 43 presence of metal-rich permeant liquids are thus of interest for these installations. 44 Lake et al. (2007) performed permeability and diffusion tests using a needle-punched 45 GCL and aluminum-rich solutions. The GCL was prehydrated with water and 46 maintained k lower than 5×10^{-11} m/s upon permeation with the aluminum solution. 47 Aluminum attenuation was observed, as a result of cation exchange and precipitation 48 49 of Al-minerals. Batch tests confirmed the high rate of aluminum uptake to the sodium bentonite, as well as nonlinear sorption behavior. Lange et al. (2007) 50 investigated the retention of metals in a needle-punched GCL permeated with two 51 synthetic mining leachates (ARD, acid rock drainage, and GMT, gold mine tailings). 52 The hydraulic conductivity remained of the same order of magnitude (from 53 1.6×10^{-11} m/s to 5×10^{-11} m/s) or increased to 1.3×10^{-10} m/s after 21 pore volumes of 54 permeation with the GMT and ARD solutions, respectively. The GCL tested showed 55 56 strong attenuation for a large number of metals and metalloids present in the synthetic leachates, which was ascribed to cation exchange, precipitation or co-57 58 precipitation.

Benson et al. (2008) conducted permeability tests on two needle-punched GCLs from different manufactures (GCL-A and GCL-B), using an alumina processing residue. Both prehydrated (with tap water) and nonprehydrated tests were performed. When permeated with leachate, GCL-A became more permeable than during permeation with water by a factor of 500, whereas the k dropped drastically for GCL-B, probably as a result of precipitation of aluminum salts. Nonprehydrated GCLs were 600-800 times more permeable than the prehydrated GCLs when permeated with the same leachate.

67 Shackelford et al. (2010) evaluated the hydraulic conductivity of two GCLs, a standard sodium bentonite GCL and a contaminant resistant GCL, considered as a 68 liner component for a mine tailings impoundment. The two GCLs were permeated 69 70 with groundwater and two electrolyte solutions, a process water (PW) and a simulated leachate (SL) with chemical compositions consistent with those expected 71 72 during operation. Test results showed that both PW and SL had a significant adverse impact on the hydraulic performance of both GCLs. The mean values of k based on 73 74 permeation with either PW or SL relative to the values of k based on permeation with ground water ranged from a factor of 200 to a factor of 7600. Unexpectedly, the 75 76 contaminant-resistant GCL performed worse than the standard GCL.

77 Naka et al. (2019) investigated the swell index, hydraulic conductivity and heavy metal attenuation of a GCL containing powdered Na-bentonite against six artificial 78 79 ARDs with an approximate pH of 3 and different metal concentrations (electrical conductivity, EC, ranging between 75 and 1000 mS/m; ionic strength ranging 80 between 8 and 400 mM). The hydraulic conductivity of the GCL permeated with 81 distilled water was 1.2×10^{-11} m/s, falling in the range of 7.9×10^{-12} to 1.1×10^{-10} m/s 82 when prehydrated with distilled water and permeated with ARDs. Ion exchange and 83 84 metal precipitation appeared to be the main mechanisms controlling the attenuation 85 on the bentonite. From the overall results, the tested GCL showed acceptably low hydraulic conductivity and the potential to attenuate heavy metals present in ARDs. 86

Gupt et al.(2020a; 2020b) evaluated by batch tests at controlled pH of 5 the adsorption capacity for Pb of bentonite (B) and bentonite amended with fly-ash (FA) for landfill liners applications. The adsorption of Pb to bentonite and FA admixtures was strongly nonlinear and well modelled by Langmuir and Freundlich isotherms. They reported that the hydraulic conductivity of B-FA mixtures is in the range $10^{-10} \div 10^{-12}$ m/s, showing the feasibility of B-FA mixtures as a replacement for conventional B-sand mixtures in landfill liner applications.

94 Bentonites amended with polymers (Ashmawy et al., 2002; Di Emidio 2010, Mazzieri et al., 2010; Bohnhoff and Shackelford, 2013; Malusis and McKeehan, 95 2013; Bonhoff et al., 2013; Scalia et al., 2014; Razakamantsoa et al., 2016; Scalia et 96 97 al., 2018; Tian et al., 2019; Chai et al., 2020; Lieske et al., 2020,) or organic molecules (Onikata et al., 1996, 1999; Lo et al., 1997; Fehervari et al., 2016;) have 98 99 been proposed with the purpose of maintaining low hydraulic conductivity when 100 permeated with aggressive liquids or solutions. Dense prehydrated (DPH) GCLs are 101 particular products obtained by a patented production process which combine prehydration, polymer amendment and densification by vacuum extrusion (Flynn and 102 103 Carter, 1998). DPH GCLs were shown to preserve low permeability against aggressive permeants (Shroeder et al., 2001, Kolstad et al, 2004; Katsumi et al., 104 105 2008; Mazzieri and Di Emidio, 2015) and to have higher chemico-osmotic efficiency coefficients than unamended bentonite (Malusis and Danyarov, 2016). Mazzieri et al. 106 107 (2013) investigated the permeability and solute retention properties of a conventional needle-punched (C GCL) and a DPH-GCL, which were permeated first with distilled 108 water (DW) and then with an acidic synthetic leachate containing metal cations. 109 After 21.5 pore volumes of permeation with the synthetic leachate, the k of both 110 GCLs increased by about one order of magnitude with respect to permeation with 111 DW, but remained relatively low $(3.3 \times 10^{-11} \text{ m/s})$ for the DPH GCL. All metals were 112 retained in both GCLs; however, the DPH GCL retained a larger amount of metals 113 114 than the C GCL. The retention of metals in the GCLs was ascribed to cation exchange, precipitation of metal solids, and, for the DPH CGLs, also to adsorption of 115 116 metals by the amending polymers (sodium carboxymethyl cellulose, Na -CMC and sodium polyacrylate, PAAC). 117

Di Emidio et al. (2017) performed batch sorption tests on kaolin and dredged sediments amended with 2% Na-CMC and found that polymer amendment increased the sorption capacity of the tested soils for Cu and Zn. Wang et al. (2020) prepared a polymer-calcium bentonite composite by pulping, drying and grinding the bentonite with Na (CMC) and sodium hexametaphosphate (SHMP). Characterization by XRD and FTIR showed that these CMC-SHMP-CB composites have a hybrid microstructure from the intercalation of polymer molecules in bentonite interlayers

and exfoliation action during preparation. Modification of CB with CMC and SHMP 125 significantly improved the hydraulic performance as, in the presence of Cd²⁺ and 126 Ni ²⁺ cations, the hydraulic conductivity of the composite was 3×10^{-11} m/s, which is 127 much lower than untreated CB. The adsorption capacity values of the composite for 128 Ni²⁺ and Cd²⁺ were 11.01 mg/g and 13.82 mg/g, respectively equal to 5.6 times and 129 130 7.2 times the values before modification. Therefore, the amendment significantly 131 improved the adsorption capacity of bentonite for heavy metals. The improvement was ascribed to the complexation of carboxylate (COO) groups in CMC with heavy 132 metal cations. 133

134 Most of the aforementioned studies have regarded the permeability and/or migration of solutes in GCLs containing conventional bentonite, whereas most 135 136 studies concerning polymer-amended bentonites have dealt with the hydraulic conductivity or investigated retention of solutes by batch-type experiments. Studies 137 that investigated the permeability and solute retention in polymer-modified 138 bentonites by means of column-type tests (Shackelford and Redmond, 1994) are 139 relatively rare, probably due to the long duration associated to this testing approach 140 in case of very low permeability. With reference to DPH GCLs, the author is not 141 aware of published results of column-type tests where effluent solute concentrations 142 143 were monitored, except those described in Mazzieri et al. (2013). In that study, relatively high solute concentrations were used, in order to reduce testing times by 144 145 enhancing the chemical interaction between solutes and bentonite; however, high solute concentrations often result in nonlinear soil-solute sorption behavior, which 146 147 makes the interpretation of column test results by conventional migration models considering linear equilibrium sorption difficult or inappropriate. In order to facilitate 148 149 the interpretation of the tests by linear models while allowing comparison with previous results, in the present study the same GCLs used in Mazzieri et al. (2013) 150 151 where permeated with a solution containing the same solutes (Pb, Zn,Cu), at 152 concentrations within the linear sorption range previously assessed by batch tests 153 (Mazzieri, 2012). Therefore, the purpose of the study was to assess the hydraulic conductivity of the two GCLs when permeated with the dilute leachate with respect 154 155 to the concentrated leachate. Moreover, the breakthrough of solutes through the

GCLs was monitored, with the purpose to obtain solute transport data to which transport models implementing linear sorption could be applied (transport modeling is however not reported in this paper). The interpretation of the test results was supported by pre-test and post-test X-Ray Diffraction (XRD) analyses and Scannig Electron Microscopy (SEM) observations of the GCLs microstructure.

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162 **2. Materials and Methods**

2.1 GCLs. The conventional GCL (C-CGL) used in this study is a commercial 163 needle-punched product. It consists of an nonwoven polypropylene cover geotextile 164 (300 g/m^2) and a carrier woven geoteotextile (200 g/m^2) , encapsulating a nominal 165 4200 g/m^2 of powdered natural sodium bentonite. The nowoven cover geotextile is 166 impregnated with additional powdered bentonite (800 g/m²). The bentonite has 167 cation exchange capacity CEC of 98 meq/100g, with sodium (77 meq/100 g) and 168 calcium (18 meq/100 g) as the main adsorbed cations. Further details on the C GCL 169 170 are given in Mazzieri et al. (2013).

171 Dense prehydrated Geosynthetic clay liners (DPH GCLs) are commercial products manufactured by mixing sodium bentonite with a proprietary hydrating 172 173 solution, which contains the water-soluble polymers Na-carboxymethyl cellulose (Na-CMC), Na-polyacrylate (Na-PAAC) and methanol. The additives are thought to 174 inhibit growth of bacteria and fungi (Schroeder et al., 2001), to increase the 175 workability of the mixture during production and to promote dispersion of bentonite 176 microstructure (Di Emidio, 2010; Wang et al., 2020). The hydrated bentonite mass is 177 then extruded under vacuum into a dense sheet (Flynn and Carter, 1998) and 178 subsequently coupled to geotextiles. The particular product used in this study has a 179 high strength woven polypropylene geotextile (100 g/m^2) and a perforated polyester 180 scrim geotextile (17 g/m^2) . 181

The dried bentonite from the DPH GCL was tested as per ASTM D-7503 for CEC, that was equal to 82.5 ± 2.5 meq/100 g with sodium (62.5 meq/100 g) and calcium (18.0 meq/100 g) as the main adsorbed cations. Further details on the DPH GCL are given in Mazzieri and Di Emidio (2015).

2.2 Permeant solution. GCLs specimens were first permeated with distilled water 187 (DW) and then with a synthetic solution containing metal cations $(Zn^{2+}, Cu^{2+}, Pb^{2+})$ 188 as nitrate salts. DW had average electrical conductivity (EC) equal to 0.014 mS/cm 189 190 and pH equal to 6.2. The synthetic permeant solution, indicated as DSL (Dilute Synthetic Leachate), aimed at representing dilution of a synthetic solution (SL) used 191 192 in previous studies concerning the same GCLs (Mazzieri, 2012; Mazzieri et al., 193 2013). The DSL had electrical conductivity EC = 2.10 mS/cm, pH=2.8 (average 194 values). The average measured solute concentrations in the permeant solution were $[Cu^{2+}]=1.39 \text{ mM}, [Zn^{2+}]=1.46 \text{ mM}, [Pb^{2+}]=3.42 \text{ mM}, [NO_3]=14.4 \text{ mM}.$ For the sake 195 of comparison, the SL solution used in Mazzieri et al. (2013) had (average values) 196 $EC=15.3 \text{ mS/cm}, \text{ pH}=1.9, [Cu^{2+}]=25.6 \text{ mM}, [Zn^{2+}]=24.6 \text{ mM}, [Pb^{2+}]=24.1 \text{ mM},$ 197 $[NO_{3}]=157 \text{ mM}.$ 198

199

2.3 Permeabily column tests. Permeability tests were carried out in 100 mm 200 201 diameter flexible-wall permeameter (FWP) as per ASTM D-6676. The GCL test specimens were cut by a sharp knife from the GCL roll. Care was taken to minimize 202 203 bentonite loss in specimen preparation. The test specimen was placed in the cell, 204 hydrated with DW without gradient for 7 days under an effective isotropic confining stress of 34.5 kPa and then permeated with DW to achieve saturation and determine 205 the reference hydraulic conductivity, $k_{\rm DW}$. Permeation was conducted by applying a 206 cell pressure of 103.4 kPa and pore pressures of 89.6 kPa and 68.9 kPa (back-207 pressure) at the inlet and outlet end, respectively. The effective stress level expected 208 209 in typical applications will in general be higher both in bottom liners of landfills (100-400 kPa) and in base liner of heap leach pads, where ore heights can reach up to 210 211 170 m (3200 kPa). In general, the effect of chemical interaction on bentonite performance is mitigated by increasing stress levels; therefore, the results obtained at 212 213 lower stress are to be considered as conservative with regard to actual stress levels 214 expected in applications (Thiel and Criley, 2005; Anastassopoulos et al., 2009).

Bladder accumulators where used both in the influent and effluent lines throughout the tests. The current height of the specimen, H, was calculated from the initial height (H_0) and the measurement of the vertical displacements by means of a rigid rod connected to a dial indicator. After permeation with DW (1^{st} stage), the permeant liquid was switched to the DSL solution (2^{nd} stage). The pH and EC of the inflow and outflow solutions were monitored during permeation. The outflow solutions were accumulated in the bladder and sampled over regular intervals. The chemical analyses of the influent and effluent solutions for dissolved metals and major ions were carried out by a Dionex ICS 1000 Ionic Cromatograph.

Termination criteria outlined in ASTM D-6676 (scenario 1) were pursued but not fully met for either test. The chemical equilibrium conditions in terms of inlet-tooutlet solute concentration ratio were more closely approached for the C GCL than the DPH GCL, despite the test duration were 340 days (0.93 ys) vs. 1934 days (5.3 ys) for the test C GCL and DPH GCL, respectively.

229 Due to the effort required and time consumption, no replicate tests were 230 performed. Although this approach does not allow assessing the variability of the test results, it is often adopted in case of time-consuming testing methods. Mazzieri 231 (2012 b) described the results of two column test replicates, similar to those 232 described herein, performed on the conventional C GCL using a multispecies metal 233 solution. After the same number of pore volumes with the metal solution (21.5), the 234 k of the two GCL specimens was 1.6×10^{-10} m/s and 7.5×10^{-11} m/s, respectively. The 235 curves of pH and EC of the effluent solutions vs. the pore volumes of flow were 236 practically coincident. Although the uncertainty of the measurement could not be 237 estimated quantitatively by two replicates only, the experimental method adopted 238 provided consistent and similar results between the two replicates. 239

241 2.4 Post-test bentonite analyses. At the end of the permeability tests, bentonite was sampled from the GCLs and examined by X-Ray diffraction. Pre-test and post-test 242 243 conditions were compared. The bentonite specimens were air dried and sieved through a 75µm aperture sieve before testing. Powdered randomly oriented samples 244 were X-ray analyzed by means of a Philips diffractometer constituted by a PW 1730 245 generator, a PW 1710 electronic unit, a PW 1050/70 goniometer equipped with 246 proportional counter. Cu k α (Ni filter) radiation ($\lambda = 1.54060$ Å) was used under the 247 following conditions: 40 kV, 30 mA, 1°-0.2°-1° slits, a continuous scanning rate of 248

1°/min, 0.020 step size (2 θ), time per step of 1 s and a range of 10⁴ c/s (photons per 249 Microstructural SEM observations were carried 250 second). out by а 251 FESEMSUPRA40–ZEISS, Germany (source: Schottky field output–FEG, detector Everhart-Thornley for secondary electrons, 4 sectors solid-state detector for 252 backscattered electrons, maximum voltage: 30 kV). After air drying, the bentonite 253 samples were gilded before the observations by means of an Emitech K550 sputter 254 255 coater.

- 256
- 257 **3 Results And Discussion**
- 258

3.1 Macroscopic effects of permeation: permeability and volume change. The hydraulic conductivity, k, is plotted versus the net number of pore volumes of flow (Shackelford and Redmond, 1995) *NPV*, in Fig.1a and Fig.1b for the C GCL and DPH GCL, respectively. The pore volume was calculated from the height of the specimen at the end of permeation with DW (H_{DW}).

The values of $k_{\rm DW}$ (Fig.1a) were in the range (1.0-2.5)×10⁻¹¹ m/s. During 264 permeation with the DSL, the k remained essentially constant or decreased slightly 265 up to NPV~10. Gas bubbles were observed in the drainage lines during this stage, 266 likely because of neutralization between HCO_3 anions present in the alkaline pore 267 water of the bentonite and H_3O^+ in the acidic permeant solutions, with consequent 268 release of gaseous CO₂. The k started to increase gradually until NPV \sim 55 and 269 remained practically constant until NPV~75 when the test was terminated (216 days 270 of permeation with the DSL solution). The final k was 2.0×10^{-10} m/s. 271

The results are consistent with those obtained in Mazzieri et al. (2013), where 272 273 the average k of the C GCL permeated with DW under the same effective stress state adopted in this study was 1.5×10^{-11} m/s. Upon permeation with the concentrated 274 synthetic leachate (SL), k increased gradually until NPV=5.0 and then remained 275 practically constant to $k \sim 1.8 \times 10^{-10}$ m/s until NPV=21.5 (94 d of permeation with 276 the SL). Therefore, permeation with SL also increased the k of the C GCL by one 277 278 order of magnitude. However, the increase in k was much faster and occurred for a 279 lower value of NPV, due to the higher metal loading. Despite the fact that chemical

equilibrium conditions specified in ASTM D -6676 were not fully met for the test described herein, further increase in k values were not expected had the test been continued, since the k value was very similar to that obtained on the same GCL permeated with a much more aggressive solution (SL).

The k_{DW} values of the DPH GCL (Fig, 1b) were in the range 284 7-10×10⁻¹² m/s. Upon permeation with the DSL, k remained essentially constant, 285 then started to decrease gradually until NPV ~9.0 and remained practically constant 286 thereafter at an average value 5.4×10^{-12} m/s. The test was terminated at NPV~ 32 287 (1565 days of permeation). The results indicate that the DPH GCL maintained a 288 lower permeability than the conventional GCL for a considerably longer time, in the 289 presence of the same permeant solution, confirming previous studies (Kolstad et al. 290 2004; Katsumi et al., 2008). However, unlike the C GCL, the k value observed in this 291 study may not be representative of longer permeation times allowing chemical 292 equilibrium conditions to be established. 293

Mazzieri et al. (2013) observed that the *k* of same DPH GCL to DW was 3.7×10⁻¹² m/s (the difference with the k_{DW} measured in this study is thought to be within the experimental scatter. Upon permeation of 21.5 pore volumes with the SL, *k* increased up to about 3.3×10⁻¹¹ m/s (by about one order of magnitude). The chemical equilibrium conditions were more closely approached than in the present study, owing to the higher solute concentrations.

The current height of the specimens during permeation, H; is shown in Fig. 1a and Fig.1b for the C GCL (initial height, H_{0} , equal to 5.5 mm) and the DPH GCL (H_{0} equal to 5.4 mm), respectively. During hydration and permeation with DW, the height of the GCLs increased to 6.75 mm (C GCL) and 10.0 mm (DPH GCL), due to swelling. Therefore, the swell of the DPH GCL was considerably larger than C GCL. Permeation with the DSL solution was associated, for both GLCs, with a decrease in H with respect to the stage of permeation with DW.

The increase in *k* and the reduction in volume relative to permeation stage with DW observed for the C GCL is consistent with the migration of divalent metal cations into the GCL. Divalent cations (Pb^{2+} , Zn^{2+} , Cu^{2+}) contained in the synthetic permeant solution substituted monovalent Na⁺ cations on bentonite surface exchange

sites., as confirmed by the measurement of Na⁺ concentration in the effluent solution 311 312 (data not shown). Bentonite retains less water when surface cations are multivalent (Jo et al. 2004), therefore exchange of monovalent cations (Na⁺) for divalent (e.g., 313 Pb²⁺) on the surface sites determines a volume reduction at macroscopic level, as 314 observed in this study. Protons can also replace Na⁺ on exchange sites, reduce the 315 316 swelling volume and increase the hydraulic conductivity of bentonite (Kolstad et al., 2004; Shackelford et al., 2010). However, the concentration of H_3O^+ was about 7.5 317 times lower than that of divalent cations, therefore the exchange for metals cations 318 likely was predominant. 319

320 Recent modeling approaches (Dominijanni and Manassero, 2018; Manassero, 2020) have related the bentonite fabric, intimately linked to its hydraulic 321 322 conductivity, to a single state parameter, N_{LAV}, the average number of 323 montmorillonite lamellae per tactoid (aggregate of bentonite platelets). The k of bentonite permeated with a given salt solution is determined by the state of 324 flocculation (represented by $N_{l,av}$), which determines the fraction of pore space 325 conductive to fluid flow (micro-void ratio). An increase in k upon permeation of a 326 bentonite or GCL with a salt solution is associated to an increase in N_{LAV}. At 327 macroscopic level, flocculation is associated with a volumetric contraction, as 328 observed in this study. 329

330 Despite the fact that permeation with DSL induced a volume contraction of the DPH GCL similarly to the C CGCL, the k did not increase, rather a significant 331 decrease (by a factor 1.8) with respect to k_{DW} was observed. This result could be 332 333 explained by the particularly dense and aligned arrangement of bentonite particles determined by calendering under vacuum of the bentonite sheet during production 334 335 (see section 3.4) and by the effect of the amending polymers which intercalate in the interlayers of montmorillonite lamellae and preserve dispersion of particles. Finally, 336 337 formation of metal precipitates in the pore spaces of the GCL cannot be excluded. This explanation is also consistent with the lack of breakthrough of metal cations in 338 339 the effluent solution.

340 341

Fig. 1 Hydraulic conductivity, k, (left axis) and specimen height, H (right axis)

343 versus NPV for the C GCL (a) and DPH GCL(b) during permeation with DW

344 (NPV<0) and with the DSL solution (NPV≥0)

345

346 3.2 Electrical conductivity and pH. The EC and pH in the outflow solutions are plotted versus NPV in Fig. 2 and in Fig. 3, respectively. The outflow EC during 347 348 permeation with DW reflects the dissolution of accessory salts from bentonite and/or 349 the presence of additives in the case of the DPH GCL. The outflow EC during 350 permeation with the DSL reflects both solute breakthrough and desorption of adsorbed cations from bentonite. For the C GCL, the EC continued to decrease in the 351 352 early stage of permeation with the DSL (0<NPV<8.2) then started to slowly increase. 353 This trend is likely a result of the dominance of residual soluble ions relative to 354 solutes in the DSL during the early stage of permeation. The subsequent increase in EC reflects the gradual breakthrough of solutes. The termination criterion in terms of 355 the outflow-to-inflow EC ratio (EC_{out}/EC_{in}= 1.0 ± 0.1) as per ASTM D-6676 was not 356 357 fully met when the test was terminated.

The effluent EC of the DPH GCL displayed a peak at NPV~ 5, a minimum at NPV~ 17.1 and then an increasing trend. The initial increase in EC mainly reflects the elution of adsorbed Na⁺ cations, due to replacement by metal cations, whereas the increase in EC after the minimum reflects also the breakthrough of nitrate from the DSL solution (see 3.3).

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Fig. 2. Electrical conductivity in the effluent solution (EC_{out}) of the C GCL and DPH GCL during permeation with DW and with the DSL ($EC_{in}=2.1$ mS/cm).

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For the C GCL, the pH was alkaline (7.3 <pH <8.4) during permeation with DW. Using the DSL (pH_{in}=2.8) as permeant, the outflow pH remained practically constant for 0<NPV<15, then gradually declined thereafter to about pH=4 when the test was terminated. Similarly to EC, the termination criteria in terms of the outflow-to-inflow pH ratio (pH_{out}/pH_{in}=1.0 \pm 0.1) were not fully met. However, the decrease in pH of the outflow solution is consistent with the partial breakthrough of protons after the initial buffering (neutralization and adsorption of protons by bentonite). The outflow pH of the DPH GCL during permeation with DW was slightly acidic to neutral (6.2 < pH < 7.2); no significant reduction was observed during permeation with DSL. Therefore, the buffering capacity of the DPH GCL was significantly higher than the GCL.

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Fig. 3. Effluent pH (pH_{out}) of the two GCLs during permeation with DW and with the DSL solution (pH_{in}=2.8)

381

3.3 Solute breakthrough. The breakthrough curves (C/C_0) , where C=outflow 382 383 concentration, C_0 =inflow concentration) of solute species in the permeant DSL solution are plotted in Fig. 4 and Fig. 5, for the CGL and the DPH GCL, respectively. 384 385 The delay in the breakthrough curve of nitrate in Fig. 4 suggests retardation that can partly be attributed to the dilution of the outflow solution by DW present in the 386 bladder from the first stage of permeation (Mazzieri et al., 2015). However, the 387 dilution effect alone cannot explain the observed delay. A specific test allowed to 388 389 verify that adsorption of nitrate and metal cations onto the latex membrane used to 390 wrap the specimen was negligible. Under the assumption that the delay was due to 391 adsorption by the bentonite, the mass balance indicated that the unit mass of nitrate 392 sorbed was of 10.4 mg/g of dry bentonite solids.

393 Some studies have reported no significant adsorption of nitrate to bentonite (e.g., 394 Xi et al., 2010) while others suggest removal capacity of bentonite from aqueous solutions ranging from 8.06 mg/g to 16.05 mg/g (Lazarotou et al., 2020). The 395 396 difference probably results from different experimental conditions (pH, temperature, 397 initial nitrate concentrations, etc.). A simple sorption experiment was performed to 398 support the interpretation of column test data by mixing and agitating for 48 hours 2 399 g of bentonite and 100 ml of the DSL (in duplicate). The mixture was then filtered 400 and the nitrate concentration in the filtrate measured. The mass of nitrate removed 401 from the aqueous phase was calculated from the difference between the initial and 402 final average concentrations; the calculated mass of nitrate adsorbed was 18.7 mg/g of dry soil. The test was repeated with 100 mL NaNO₃ solution having the same 403 nitrate concentration as in DSL, and no significant adsorption of nitrate was 404

observed, in accordance with Xi et al. (2010). The main differences between the two tests were the equilibrium pH (5.4 with DSL versus 9.4 with NaNO₃) and the presence of metal cations in the DSL. The lower pH may result in protonation of hydroxyl groups on the edge sites of montmorillonite particles, which may promote adsorption of NO_3^- anions (Sposito, 1984).

The attenuation order for metal cations inferred from the delay of breakthrough 410 curves in Fig. 4, is $Pb^{2+}>Cu^{2+}>Zn^{2+}$. Previous batch tests (Mazzeri, 2012) and test 411 results described in Mazzieri et al. (2013) using the higher concentration solution 412 (SL) showed the same order of retention of metal cations observed in this study. 413 414 However, owing to higher concentrations in the study by Mazzieri et al. (2013), all solutes (except H_3O^+) achieved complete breakthrough (i.e. C/C₀=1) after 21.5 pore 415 416 volumes permeated. This allowed to perform a mass balance between the inflow and 417 outflow solutions and determine the mass retained per unit mass of bentonite solids, S, $(Pb^{2+} = 60.7 \text{ mg/g}; Cu^{2+} = 11.6 \text{ mg/g}; Zn^{2+} = 10.3 \text{ mg/g})$. In the present study no 418 metals reached complete breakthrough, therefore only an approximate mass balance 419 was possible: the metals masses retained by the bentonite solids were estimated at the 420 test termination as $Pb^{2+} = 46.3 \text{ mg/g}$, $Cu^{2+} = 6.5 \text{ mg/g}$ and $Zn^{2+} = 4.6 \text{ mg/g}$. Gupt et al. 421 (2020) observed in batch sorption tests using a monospecies solution that Pb^{2+} was 422 adsorbed by unamended bentonite following a nonlinear Langmuir isotherm with 423 parameters q_{max} =43.3 mg/g and b=0.04 L/mg. Therefore, the maximum adsorption 424 capacity of Pb^{2+} by the unamended bentonite in a monospecies solution was close to 425 the adsorption capacity value observed in this study using a multispecies solutions. 426 427 Metals are retained by unamended bentonite via cation exchange, specific adsorption (complexation) and precipitation (Li, 1999; Gu et al., 2010). Desorption of Na⁺ and 428 Ca^{2+} in the effluent indicated that cation exchange was an active retention mechanism 429 for metals in the present study. Retention of metals in the solid matrix was 430 431 confirmed by EDS analyses performed on a small portion of bentonite at the end of the test (see section 3.4). 432

Fig.4. Solute (NO⁻₃, Zn²⁺, Cu²⁺, Pb²⁺) breakthrough curves determined during permeation of the C GCL with the DSL

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For the DPH GCL (Fig. 5), the breakthough of nitrate in the effluent solution clearly occurred at *NPV*=13.5. Therefore, the DPH GCL also displayed retardation of nitrate. A similar explanation as for retardation of nitrate in C GCL can be invoked, with the possible contribution of the much longer retention time of solutes within the DPH GCL, which may have favoured the adsorption phenomena.

All metals cations were retarded; Zn and Cu were detected in the effluent at 442 443 NPV=19.3, but no significant breakthrough was evident during the test. Desorption of sodium and calcium cations with respect to permeation with DW (Fig. 6) suggests 444 445 that metal cations were retained in the bentonite by cation exchange. Moreover, amendment of bentonite with the polymers Na -CMC (Wang et al., 2020) and Na-446 PAC (Chen et al., 2020), has been shown to significantly improve the adsorption 447 capacity of bentonite for heavy metals, owing to the complexation of metals to 448 carboxylate groups. Finally, the porewater of DPH GCL contains relatively high 449 concentrations of phosphate species, likely as a result of SHMP added to the 450 hydrating solution. Fig. 6 shows the concentration of total phosphate (PO_4^{3-}) in the 451 effluent of the DPH GCL during permeation. Precipitation of metal solids (see 452 section 3.4) is also possible as lead, copper and zinc phosphates are all practically 453 454 insoluble in water. Precipitation of metal solids clogging the pore space would be 455 consistent with the decrease in k observed in the early stage of permeation with the 456 DSL (Fig.1). Therefore, the combination of cation exchange, enhanced sorption by polymer treatment and metal precipitation is responsible of the metal attenuation 457 458 observed for the DPH GCL.

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Fig.5. Solute (NO⁻₃, Zn²⁺, Cu²⁺, Pb²⁺) breakthrough curves during permeation of the DPH GCL with the DSL

Fig.6. Desorption of major cations and anions during permeation of the DPH
GCL with DW and the DSL

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468 3.4 Post-test analyses. Pre-test and post-test powder XRD analyses and SEM observations were perfomed on bentonite extracted from the GCLs to investigate the 469 470 changes in mineralogical properties and microstructure. The pre-test and post-test 471 diffraction spectra of C GCL and DPH GCL bentonite are shown in Fig. 7a and 7b, 472 respectivey. The diffraction spectrum of pre-test C GCL (unamendend bentonite) shows the typical main reflection at $d_{001}=1.25$ nm of predominantly sodium bentonite 473 474 (Miles, 2001) and minor peaks attributed to accessory minerals (quarz, calcite, 475 feldspar, gypsum). The pos-test C GCL spectrum did not change significantly, except 476 for the disappearance of peaks relative to the more soluble minerals (calcite, 477 gypsum), presumably as a result of dissolution by the acidic permeant solution 478 (pH=2.8). In particular, the basal spacing remained practically unaltered, despite the replacement of sodium by heavy metal cations (see section 3.3). Nemeth (2008) 479 found that the basal spacing of Cu- and Pb- adsorbed montmorillonite is 1.3-1.4 nm 480 in case of low metal concentrations and high pH, while in case of high metal 481 concentration and low pH (as in the present study) the basal spacings tend to 1.25 nm 482 483 (one-layer water arrangement). Nemeth et al.(2005) noted that the characteristic basal reflection of Na-montmorillonite at 1.25 nm is progressively shifted to about 484 485 1.45 nm with increasing Zn concentration and decreasing pH. Thus, the basal spacing of post-test unamended bentonite (1.25 nm) is consistent with the predominant 486 487 occupancy of interlayers by Pb and Cu cations over Zn.

The diffraction spectrum of air-dried pre-test DPH GCL displays distinct 488 489 montmorillonite peaks, which suggests that the individual units of the clay preserve a well-defined layered structure (Tian et al., 2019). The basal reflection corresponds to 490 491 a basal distance $d_{001}=1.40$ nm (Fig. 7b). The increase in the basal distance with 492 respect to unamended Na-bentonite can be ascribed to the intercalation of polymer 493 molecules in the interlayer space of the clay (e.g., Qiu and Yu, 2008). The post-test 494 basal spacing of DPH GCL bentonite further increased to 1.54 nm, which could be 495 due to a partial replacement of Na by metal cations.

497 Fig.7. Comparison of pre-test and post test powder XRD spectra of C GCL (a) 498 and DPH GCL (b)

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SEM migrograph of the bentonites extracted from C GCL and DPH GCL are 500 501 shown in Fig.8a and 8b, respectively. The pre-test condition of C GCL (left) refers to 502 a water-permeated specimen, whereas the pre-test condition of the DPH GCL refers 503 to the as-received product. In general, C GCL bentonite microstructure presents large randomly oriented aggregates of flaky particles, but no significant differences 504 505 between pre-test (water permeation) and post test (DSL permeation) conditions are evident. The DPH GCL microstructure presents preferential orientation of particles 506 507 (Fig 8b -left) and a densely packed arrangement resulting from calendering and 508 vacuum extraction during manufacturing (Mazzieri and Di Emidio, 2015). This 509 microstructure is largely preserved in the post-test DPH GCL (Fig. 8b, right) which is consistent with the observation that the hydraulic conductivity did not increase but 510 rather decreased upon permeation with the DSL. No evidence of polymer strands or 511 webs (e.g., as in Tian et al., 2019) was visible in micrographs even at lower 512 513 magnification (not shown), reinforcing the hypothesis that polymer-clay interaction 514 occurs in this GCL product in the form of intercalation rather than phase-separated (intact clay particles or aggregates dispersed within a polymer). 515

516

517 Fig.8. Comparison of pre-test (left) and post test (right) SEM micrographs of 518 C GCL (a) and DPH GCL (b).

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EDS (Electron Dispersive Spectroscopy) spot-analyses were performed on the same specimens of the two GCLs materials used for SEM observations. The results are shown in Fig. 9. The EDS spectrum of the C GCL (Fig.9a) supports the retention of Pb and Cu, while Zn was not detected. The EDS spectrum of the DPH GCL allowed detecting Cu only. The absence of one or more elements in EDS spectrum may depend upon the limited EDS spot size and nonuniform distribution of retained elements within the specimen. A picture of the upstream surface of the bentonite of 527 the DPH GCL soon after disassembling the test is shown in Appendix (Figure 10). Since the cover geotextile has no bonding with the bentonite layer, the geotextile was 528 easily peeled off to expose the bentonite surface. Scattered whitish spots can be 529 530 observed on the bentonite surface, that can be ascribed to precipitated metal solids (lead phosphate, zinc phosphate,) all described as whitish in color in the relevant 531 532 literature. Further insight into the nature of this spots was not possible due to the 533 difficulty in selectively sampling the very small-sized spots. Similar visual observations were not possible on the C CGL, since peeling off the cover geotextiles 534 would have required cutting the dense network of needle-punched fibers and 535 536 probably destroying any such evidences.

537

538 Fig. 9. Post-test EDS results for C GCL(a) and DPH GCL(b).

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542 4 Conclusions.543

Polymer treatment of bentonite is an increasingly adopted approach to improve the 544 resistance of GCLs against chemical attack. The paper compares the hydraulic 545 546 conductivity, k, and solute retention properties of a conventional needle-punched GCL and a DPH GCL, a particular product where polymer treatment and 547 densification are combined to enhance the performance. The two CGLs were 548 permeated with a synthetic electrolyte solution containing Zn^{2+} , Cu^{2+} , Pb^{2+} and NO_{3} . 549 The k of the conventional GCL increased from 2.2×10^{-11} m/s (water) to 2.0×10^{-10} m/s 550 551 after 75 pore volumes of permeation with the synthetic solution (215 days). The 552 increase in k was associated with the replacement of bound Na^+ by metal cations and breakthrough of solute species. Conversely, the k of the DPH GCL decreased from 553 $k=8.9 \times 10^{-11}$ m/s (water) to 5.4 $\times 10^{-12}$ m/s after 32 pore volumes (1560 days of 554 permeation) with the synthetic solution. The permanence of low k likely was 555 favoured by polymer intercalation into the interlayers of montmorillonite and the 556 dense and oriented arrangement of clay particles induced by the manufacturing 557 procedure that was maintained after permeation, as confirmed by SEM imaging. No 558 559 significant solute breakthrough was observed, except for nitrate. Solute retention in

the GCLs was ascribed to cation exchange, metal solids precipitation and adsorption by polymeric additives in the DPH GCL. The results described in this paper confirmed previous studies showing that the permeability and the containment properties of DPH GCL proved significantly superior with respect to a conventional GCL under a given set of conditions. The contribution of polymer treatment to DPH GCL performance consists in the improvement of workability during manufacturing as well as in the increase in water and solute retention during service life.

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569 **5.References**

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Fig.1. Hydraulic conductivity , k, (left axis) and specimen height, H (right axis) versus NPV for the (a)C GCL and (b)DPH GCL during permeation with DW (NPV<0) and with the DSL solution (NPV \geq 0).

Fig.2. Effluent Electrical Conductivity (EC_{out}) of the C GCL and DPH GCL during permeation with DW and with the DSL ($EC_{in}=2.1 \text{ mS/cm}$).

Fig.3. Effluent pH (pH_{out}) of the of the C GCL and DPH GCL during permeation with DW and with the DSL solution $(pH_{in}=2.8)$.

Fig.4. Solute (NO⁻³, Zn^{2+} , Cu^{2+} , Pb^{2+}) breakthrough curves determined during permeation of the C GCL with the DSL.

Fig .5. Solute $(NO^{-3}, Zn^{2+}, Cu^{2+}, Pb^{2+})$ breakthrough curves during permeation of the DPH GCL with the DSL.

Fig.6. Desorption of major cations and anions during permeation of the DPH GCL with DW and the DSL.

Fig.7. Comparison of pre-test and post-test powder XRD spectra of (a) C GCL and (b) DPH GCL.

Fig.8. Comparison of pre-test (left) and post-test (right) SEM micrographs of (a) C GCL and (b) DPH GCL.

Fig.9. Post-test EDS results for the (a) C GCL and (b) DPH GCL.

Fig.10 (in APPENDIX). Whitish spots on the upstream surface of the DPH GCL

at the end of the test (presumably lead and copper phosphate solids)



Fig.1. Hydraulic conductivity , k, (left axis) and specimen height, H (right axis) versus NPV for the (a) C GCL and (b) DPH GCL during permeation with DW (NPV<0) and with the DSL solution (NPV ≥ 0).



Fig.2. Electrical conductivity in the effluent solution (EC_{out}) of the C GCL and DPH GCL during permeation with DW and with the DSL (EC_{in}=2.1 mS/cm).



Fig.3. Effluent pH (pH_{out}) of the two GCLs during permeation with DW and with the DSL solution $(pH_{in}{=}2.8)$



Fig.4. Solute (NO⁻₃, Zn²⁺, Cu²⁺, Pb²⁺) breakthrough curves determined during permeation of the C GCL with the DSL



Fig.5. Solute (NO⁻₃, Zn²⁺, Cu²⁺, Pb²⁺) breakthrough curves during permeation of the DPH GCL with the DSL



Fig.6. Desorption of major cations and anions during permeation of the DPH GCL with DW and the DSL



Fig.7. Comparison of pre-test and post-test powder XRD spectra of (a) C GCL (b) and DPH GCL.



Fig. 8. Comparison of pre-test (left) and post-test (right) SEM micrographs of (a) C GCL and (b) DPH GCL.



Fig.9. Post-test EDS results for (a) C GCLand (b) DPH GCL.

APPENDIX



Fig. 10. Whitish spots on the upstream surface of the DPH GCL at the end of the test (presumably lead and copper phosphate solids)