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(Article begins on next page)

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

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10
11 **Keywords:** Geosynthetic Clay Liners, hydraulic conductivity, heavy metals,
12 polymers

13
14 **ABSTRACT:** Polymer treatment is an increasingly adopted approach to mitigate the
15 impact of aggressive liquids on GCLs' hydraulic performance. Dense PreHydrated
16 (DPH) GCLs are particular products that combine polymer treatment, prehydration
17 and densification to improve the overall containment performance. The paper
18 investigated the saturated hydraulic conductivity, k , and heavy metals retention in a
19 conventional GCL and a DPH GCL. Both materials were permeated first with water
20 and then with synthetic solution containing Zn, Cu, Pb, also with the purpose to
21 extend a previous study where a solution of the same solutes at higher concentrations
22 had been used. The k of the conventional GCL increased by one order of magnitude
23 with respect to water upon permeation with the synthetic solution. The solutes were
24 partly retained and the increase in k was associated with the breakthrough of solutes.
25 Upon permeation with the same solution, the k of the DPH GCL decreased by a
26 factor 1.6 with respect to water. No significant breakthrough of metals was observed,
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
31

32 1. Introduction

33

34 Geosynthetic Clay Liners, (GCLs) consisting of a thin layer of bentonite clay
35 incorporated between two geotextiles or glued to a geomembrane have been widely
36 used as hydraulic and pollutant barriers (Bouazza, 2002). The content of sodium
37 montmorillonite is the key factor for the characteristically low hydraulic conductivity
38 of hydrated bentonite. GCLs are also employed in applications where metal-rich
39 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
42 such as mine water treatment systems (Lange et al., 2007; Lange et al., 2010). The
43 hydraulic conductivity performance and the retention capacity of GCLs in the
44 presence of metal-rich permeant liquids are thus of interest for these installations.
45 Lake et al. (2007) performed permeability and diffusion tests using a needle-punched
46 GCL and aluminum-rich solutions. The GCL was prehydrated with water and
47 maintained k lower than 5×10^{-11} m/s upon permeation with the aluminum solution.
48 Aluminum attenuation was observed, as a result of cation exchange and precipitation
49 of Al-minerals. Batch tests confirmed the high rate of aluminum uptake to the
50 sodium bentonite, as well as nonlinear sorption behavior. Lange et al. (2007)
51 investigated the retention of metals in a needle-punched GCL permeated with two
52 synthetic mining leachates (ARD, acid rock drainage, and GMT, gold mine tailings).
53 The hydraulic conductivity remained of the same order of magnitude (from
54 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
55 permeation with the GMT and ARD solutions, respectively. The GCL tested showed
56 strong attenuation for a large number of metals and metalloids present in the
57 synthetic leachates, which was ascribed to cation exchange, precipitation or co-
58 precipitation.

59 Benson et al. (2008) conducted permeability tests on two needle-punched
60 GCLs from different manufactures (GCL-A and GCL-B), using an alumina
61 processing residue. Both prehydrated (with tap water) and nonprehydrated tests were
62 performed. When permeated with leachate, GCL-A became more permeable than

63 during permeation with water by a factor of 500, whereas the k dropped drastically
64 for GCL-B, probably as a result of precipitation of aluminum salts. Nonprehydrated
65 GCLs were 600-800 times more permeable than the prehydrated GCLs when
66 permeated with the same leachate.

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

77 Naka et al. (2019) investigated the swell index, hydraulic conductivity and heavy
78 metal attenuation of a GCL containing powdered Na-bentonite against six artificial
79 ARDs with an approximate pH of 3 and different metal concentrations (electrical
80 conductivity, EC, ranging between 75 and 1000 mS/m; ionic strength ranging
81 between 8 and 400 mM). The hydraulic conductivity of the GCL permeated with
82 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
83 when prehydrated with distilled water and permeated with ARDs. Ion exchange and
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
86 hydraulic conductivity and the potential to attenuate heavy metals present in ARDs.

87 Gupt et al.(2020a; 2020b) evaluated by batch tests at controlled pH of 5 the
88 adsorption capacity for Pb of bentonite (B) and bentonite amended with fly-ash (FA)
89 for landfill liners applications. The adsorption of Pb to bentonite and FA admixtures
90 was strongly nonlinear and well modelled by Langmuir and Freundlich isotherms.
91 They reported that the hydraulic conductivity of B-FA mixtures is in the range
92 10^{-10} ÷ 10^{-12} m/s, showing the feasibility of B-FA mixtures as a replacement for
93 conventional B-sand mixtures in landfill liner applications.

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

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

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

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

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

161

162 **2. Materials and Methods**

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

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

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

186

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

199

200 **2.3 Permeability column tests.** Permeability tests were carried out in 100 mm
201 diameter flexible-wall permeameter (FWP) as per ASTM D-6676. The GCL test
202 specimens were cut by a sharp knife from the GCL roll. Care was taken to minimize
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
205 stress of 34.5 kPa and then permeated with DW to achieve saturation and determine
206 the reference hydraulic conductivity, k_{DW} . Permeation was conducted by applying a
207 cell pressure of 103.4 kPa and pore pressures of 89.6 kPa and 68.9 kPa (back-
208 pressure) at the inlet and outlet end, respectively. The effective stress level expected
209 in typical applications will in general be higher both in bottom liners of landfills
210 (100-400 kPa) and in base liner of heap leach pads, where ore heights can reach up to
211 170 m (3200 kPa). In general, the effect of chemical interaction on bentonite
212 performance is mitigated by increasing stress levels; therefore, the results obtained at
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).

215 Bladder accumulators were used both in the influent and effluent lines
216 throughout the tests. The current height of the specimen, H , was calculated from the
217 initial height (H_0) and the measurement of the vertical displacements by means of a

218 rigid rod connected to a dial indicator. After permeation with DW (1st stage), the
219 permeant liquid was switched to the DSL solution (2nd stage). The pH and EC of the
220 inflow and outflow solutions were monitored during permeation. The outflow
221 solutions were accumulated in the bladder and sampled over regular intervals. The
222 chemical analyses of the influent and effluent solutions for dissolved metals and
223 major ions were carried out by a Dionex ICS 1000 Ionic Chromatograph.

224 Termination criteria outlined in ASTM D-6676 (scenario 1) were pursued but
225 not fully met for either test. The chemical equilibrium conditions in terms of inlet-to-
226 outlet solute concentration ratio were more closely approached for the C GCL than
227 the DPH GCL, despite the test duration were 340 days (0.93 ys) vs. 1934 days
228 (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
231 results, it is often adopted in case of time-consuming testing methods. Mazzieri
232 (2012 b) described the results of two column test replicates, similar to those
233 described herein, performed on the conventional C GCL using a multispecies metal
234 solution. After the same number of pore volumes with the metal solution (21.5), the
235 k of the two GCL specimens was 1.6×10^{-10} m/s and 7.5×10^{-11} m/s, respectively. The
236 curves of pH and EC of the effluent solutions vs. the pore volumes of flow were
237 practically coincident. Although the uncertainty of the measurement could not be
238 estimated quantitatively by two replicates only, the experimental method adopted
239 provided consistent and similar results between the two replicates.

240

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

249 1°/min, 0.020 step size (2θ), time per step of 1 s and a range of 10^4 c/s (photons per
250 second). Microstructural SEM observations were carried out by a
251 FESEMSUPRA40–ZEISS, Germany (source: Schottky field output–FEG, detector
252 Everhart–Thornley for secondary electrons, 4 sectors solid-state detector for
253 backscattered electrons, maximum voltage: 30 kV). After air drying, the bentonite
254 samples were gilded before the observations by means of an Emitech K550 sputter
255 coater.

256

257 **3 Results And Discussion**

258

259 **3.1 Macroscopic effects of permeation: permeability and volume change.** The
260 hydraulic conductivity, k , is plotted versus the net number of pore volumes of flow
261 (Shackelford and Redmond, 1995) NPV , in Fig.1a and Fig.1b for the C GCL and
262 DPH GCL, respectively. The pore volume was calculated from the height of the
263 specimen at the end of permeation with DW (H_{DW}).

264 The values of k_{DW} (Fig.1a) were in the range $(1.0-2.5)\times 10^{-11}$ m/s. During
265 permeation with the DSL, the k remained essentially constant or decreased slightly
266 up to $NPV\sim 10$. Gas bubbles were observed in the drainage lines during this stage,
267 likely because of neutralization between HCO_3^- anions present in the alkaline pore
268 water of the bentonite and H_3O^+ in the acidic permeant solutions, with consequent
269 release of gaseous CO_2 . The k started to increase gradually until $NPV\sim 55$ and
270 remained practically constant until $NPV\sim 75$ when the test was terminated (216 days
271 of permeation with the DSL solution). The final k was 2.0×10^{-10} m/s.

272 The results are consistent with those obtained in Mazzieri et al. (2013), where
273 the average k of the C GCL permeated with DW under the same effective stress state
274 adopted in this study was 1.5×10^{-11} m/s. Upon permeation with the concentrated
275 synthetic leachate (SL), k increased gradually until $NPV=5.0$ and then remained
276 practically constant to $k\sim 1.8\times 10^{-10}$ m/s until $NPV=21.5$ (94 d of permeation with
277 the SL). Therefore, permeation with SL also increased the k of the C GCL by one
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

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

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

294 Mazziari et al. (2013) observed that the k of same DPH GCL to DW was
295 3.7×10^{-12} m/s (the difference with the k_{DW} measured in this study is thought to be
296 within the experimental scatter. Upon permeation of 21.5 pore volumes with the SL,
297 k increased up to about 3.3×10^{-11} m/s (by about one order of magnitude). The
298 chemical equilibrium conditions were more closely approached than in the present
299 study, owing to the higher solute concentrations.

300 The current height of the specimens during permeation, H ; is shown in Fig. 1a
301 and Fig.1b for the C GCL (initial height, H_0 , equal to 5.5 mm) and the DPH GCL (H_0
302 equal to 5.4 mm), respectively. During hydration and permeation with DW, the
303 height of the GCLs increased to 6.75 mm (C GCL) and 10.0 mm (DPH GCL), due to
304 swelling. Therefore, the swell of the DPH GCL was considerably larger than C GCL.
305 Permeation with the DSL solution was associated, for both GCLs, with a decrease in
306 H with respect to the stage of permeation with DW.

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

311 sites., as confirmed by the measurement of Na^+ concentration in the effluent solution
312 (data not shown). Bentonite retains less water when surface cations are multivalent
313 (Jo et al. 2004), therefore exchange of monovalent cations (Na^+) for divalent (e.g.,
314 Pb^{2+}) on the surface sites determines a volume reduction at macroscopic level, as
315 observed in this study. Protons can also replace Na^+ on exchange sites, reduce the
316 swelling volume and increase the hydraulic conductivity of bentonite (Kolstad et al.,
317 2004; Shackelford et al., 2010). However, the concentration of H_3O^+ was about 7.5
318 times lower than that of divalent cations, therefore the exchange for metals cations
319 likely was predominant.

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

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

340
341

342 **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
347 plotted versus *NPV* in Fig. 2 and in Fig. 3, respectively. The outflow EC during
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
351 adsorbed cations from bentonite. For the C GCL, the EC continued to decrease in the
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
355 EC reflects the gradual breakthrough of solutes. The termination criterion in terms of
356 the outflow-to-inflow EC ratio ($EC_{out}/EC_{in}=1.0 \pm 0.1$) as per ASTM D-6676 was not
357 fully met when the test was terminated.

358 The effluent EC of the DPH GCL displayed a peak at $NPV \sim 5$, a minimum at
359 $NPV \sim 17.1$ and then an increasing trend. The initial increase in EC mainly reflects
360 the elution of adsorbed Na^+ cations, due to replacement by metal cations, whereas the
361 increase in EC after the minimum reflects also the breakthrough of nitrate from the
362 DSL solution (see 3.3).

363

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

366

367 For the C GCL, the pH was alkaline ($7.3 < pH < 8.4$) during permeation with DW.
368 Using the DSL ($pH_{in}=2.8$) as permeant, the outflow pH remained practically constant
369 for $0 < NPV < 15$, then gradually declined thereafter to about $pH=4$ when the test was
370 terminated. Similarly to EC, the termination criteria in terms of the outflow-to-inflow
371 pH ratio ($pH_{out}/pH_{in}=1.0 \pm 0.1$) were not fully met. However, the decrease in pH of
372 the outflow solution is consistent with the partial breakthrough of protons after the
373 initial buffering (neutralization and adsorption of protons by bentonite).

374 The outflow pH of the DPH GCL during permeation with DW was slightly acidic
375 to neutral ($6.2 < \text{pH} < 7.2$); no significant reduction was observed during permeation
376 with DSL. Therefore, the buffering capacity of the DPH GCL was significantly
377 higher than the GCL.

378

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

381

382 **3.3 Solute breakthrough.** The breakthrough curves (C/C_0 , where C =outflow
383 concentration, C_0 =inflow concentration) of solute species in the permeant DSL
384 solution are plotted in Fig. 4 and Fig. 5, for the CGL and the DPH GCL, respectively.
385 The delay in the breakthrough curve of nitrate in Fig. 4 suggests retardation that can
386 partly be attributed to the dilution of the outflow solution by DW present in the
387 bladder from the first stage of permeation (Mazzieri et al., 2015). However, the
388 dilution effect alone cannot explain the observed delay. A specific test allowed to
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
395 solutions ranging from 8.06 mg/g to 16.05 mg/g (Lazarotou et al., 2020). The
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
403 of dry soil. The test was repeated with 100 mL NaNO_3 solution having the same
404 nitrate concentration as in DSL, and no significant adsorption of nitrate was

405 observed, in accordance with Xi et al. (2010). The main differences between the two
406 tests were the equilibrium pH (5.4 with DSL versus 9.4 with NaNO₃) and the
407 presence of metal cations in the DSL. The lower pH may result in protonation of
408 hydroxyl groups on the edge sites of montmorillonite particles, which may promote
409 adsorption of NO₃⁻ anions (Sposito, 1984).

410 The attenuation order for metal cations inferred from the delay of breakthrough
411 curves in Fig. 4, is Pb²⁺>Cu²⁺>Zn²⁺. Previous batch tests (Mazzeri, 2012) and test
412 results described in Mazzieri et al. (2013) using the higher concentration solution
413 (SL) showed the same order of retention of metal cations observed in this study.
414 However, owing to higher concentrations in the study by Mazzieri et al. (2013), all
415 solutes (except H₃O⁺) achieved complete breakthrough (i.e. C/C₀=1) after 21.5 pore
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,
418 S , (Pb²⁺ =60.7 mg/g; Cu²⁺ =11.6 mg/g; Zn²⁺=10.3 mg/g). In the present study no
419 metals reached complete breakthrough, therefore only an approximate mass balance
420 was possible: the metals masses retained by the bentonite solids were estimated at the
421 test termination as Pb²⁺ =46.3 mg/g, Cu²⁺ =6.5 mg/g and Zn²⁺=4.6 mg/g. Gupt et al.
422 (2020) observed in batch sorption tests using a monospecies solution that Pb²⁺ was
423 adsorbed by unamended bentonite following a nonlinear Langmuir isotherm with
424 parameters q_{\max} =43.3 mg/g and b =0.04 L/mg. Therefore, the maximum adsorption
425 capacity of Pb²⁺ by the unamended bentonite in a monospecies solution was close to
426 the adsorption capacity value observed in this study using a multispecies solutions.
427 Metals are retained by unamended bentonite via cation exchange, specific adsorption
428 (complexation) and precipitation (Li, 1999; Gu et al., 2010). Desorption of Na⁺ and
429 Ca²⁺ in the effluent indicated that cation exchange was an active retention mechanism
430 for metals in the present study. Retention of metals in the solid matrix was
431 confirmed by EDS analyses performed on a small portion of bentonite at the end of
432 the test (see section 3.4).

433

434 **Fig.4. Solute (NO_3^- , Zn^{2+} , Cu^{2+} , Pb^{2+}) breakthrough curves determined during**
435 **permeation of the C GCL with the DSL**

436

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

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

459

460

461 **Fig.5. Solute (NO_3^- , Zn^{2+} , Cu^{2+} , Pb^{2+}) breakthrough curves during permeation of**
462 **the DPH GCL with the DSL**

463

464

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

467

468 **3.4 Post-test analyses.** Pre-test and post-test powder XRD analyses and SEM
469 observations were performed on bentonite extracted from the GCLs to investigate the
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 respectively. The diffraction spectrum of pre-test C GCL (unamended bentonite)
473 shows the typical main reflection at $d_{001}=1.25$ nm of predominantly sodium bentonite
474 (Miles, 2001) and minor peaks attributed to accessory minerals (quartz, calcite,
475 feldspar, gypsum). The post-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
479 replacement of sodium by heavy metal cations (see section 3.3). Nemeth (2008)
480 found that the basal spacing of Cu- and Pb- adsorbed montmorillonite is 1.3–1.4 nm
481 in case of low metal concentrations and high pH, while in case of high metal
482 concentration and low pH (as in the present study) the basal spacings tend to 1.25 nm
483 (one-layer water arrangement). Nemeth et al.(2005) noted that the characteristic
484 basal reflection of Na-montmorillonite at 1.25 nm is progressively shifted to about
485 1.45 nm with increasing Zn concentration and decreasing pH. Thus, the basal spacing
486 of post-test unamended bentonite (1.25 nm) is consistent with the predominant
487 occupancy of interlayers by Pb and Cu cations over Zn.

488 The diffraction spectrum of air-dried pre-test DPH GCL displays distinct
489 montmorillonite peaks, which suggests that the individual units of the clay preserve a
490 well-defined layered structure (Tian et al., 2019). The basal reflection corresponds to
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.

496

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

499

500 SEM micrograph of the bentonites extracted from C GCL and DPH GCL are
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
504 randomly oriented aggregates of flaky particles, but no significant differences
505 between pre-test (water permeation) and post test (DSL permeation) conditions are
506 evident. The DPH GCL microstructure presents preferential orientation of particles
507 (Fig 8b –left) and a densely packed arrangement resulting from calendaring 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
510 is consistent with the observation that the hydraulic conductivity did not increase but
511 rather decreased upon permeation with the DSL. No evidence of polymer strands or
512 webs (e.g., as in Tian et al., 2019) was visible in micrographs even at lower
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
515 (intact clay particles or aggregates dispersed within a polymer).

516

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

519

520 EDS (Electron Dispersive Spectroscopy) spot-analyses were performed on the same
521 specimens of the two GCLs materials used for SEM observations. The results are
522 shown in Fig. 9. The EDS spectrum of the C GCL (Fig.9a) supports the retention of
523 Pb and Cu, while Zn was not detected. The EDS spectrum of the DPH GCL allowed
524 detecting Cu only. The absence of one or more elements in EDS spectrum may
525 depend upon the limited EDS spot size and nonuniform distribution of retained
526 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).
528 Since the cover geotextile has no bonding with the bentonite layer, the geotextile was
529 easily peeled off to expose the bentonite surface. Scattered whitish spots can be
530 observed on the bentonite surface, that can be ascribed to precipitated metal solids
531 (lead phosphate, zinc phosphate,) all described as whitish in color in the relevant
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
534 observations were not possible on the C CGL, since peeling off the cover geotextiles
535 would have required cutting the dense network of needle-punched fibers and
536 probably destroying any such evidences.

537

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

539

540

541

542 **4 Conclusions.**

543

544 Polymer treatment of bentonite is an increasingly adopted approach to improve the
545 resistance of GCLs against chemical attack. The paper compares the hydraulic
546 conductivity, k , and solute retention properties of a conventional needle-punched
547 GCL and a DPH GCL, a particular product where polymer treatment and
548 densification are combined to enhance the performance. The two CGLs were
549 permeated with a synthetic electrolyte solution containing Zn^{2+} , Cu^{2+} , Pb^{2+} and NO_3^- .
550 The k of the conventional GCL increased from 2.2×10^{-11} m/s (water) to 2.0×10^{-10} m/s
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
553 breakthrough of solute species. Conversely, the k of the DPH GCL decreased from
554 $k=8.9 \times 10^{-11}$ m/s (water) to 5.4×10^{-12} m/s after 32 pore volumes (1560 days of
555 permeation) with the synthetic solution. The permanence of low k likely was
556 favoured by polymer intercalation into the interlayers of montmorillonite and the
557 dense and oriented arrangement of clay particles induced by the manufacturing
558 procedure that was maintained after permeation, as confirmed by SEM imaging. No
559 significant solute breakthrough was observed, except for nitrate. Solute retention in

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

567

568

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732

LIST OF FIGURE CAPTIONS

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. Effluent Electrical Conductivity (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 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)

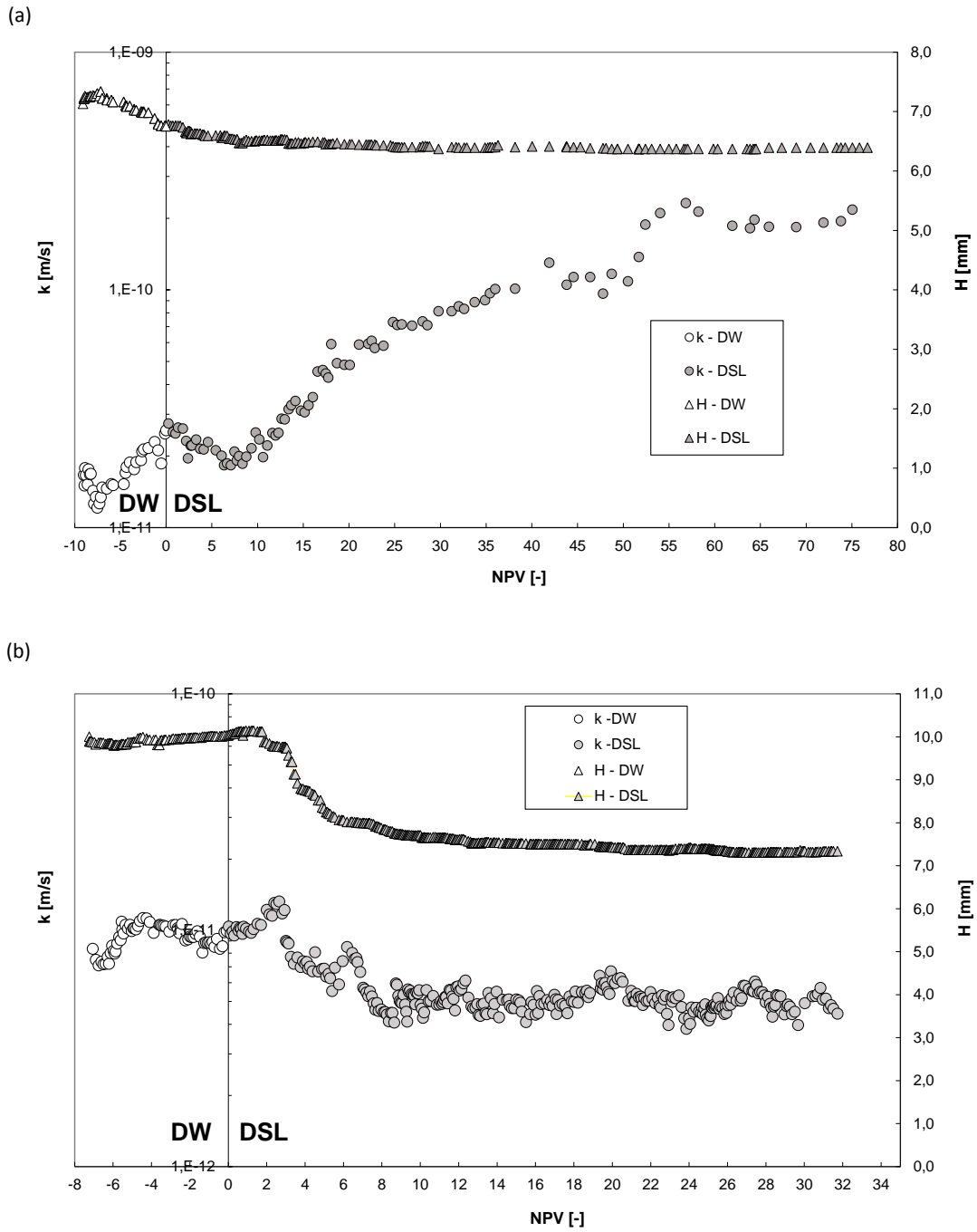


Fig.1. Hydraulic conductivity , k , (left axis) and specimen height, H (right axis) versus NPV for the (a) C GCL and (b) DPH GCL during permeation with DW (NPV<0) and with the DSL solution (NPV≥0) .

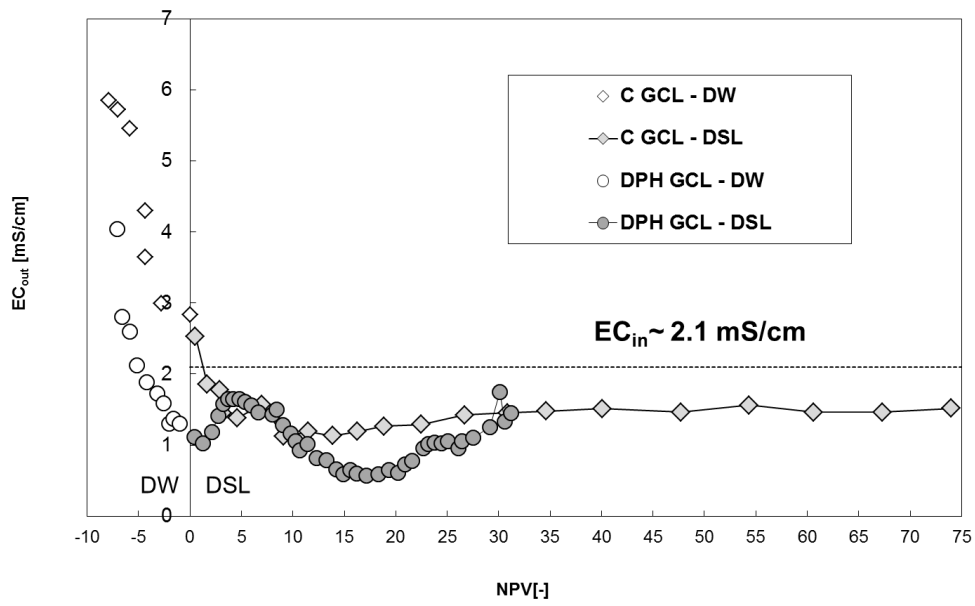


Fig.2. Electrical conductivity in the effluent solution (EC_{out}) of the C GCL and DPH GCL during permeation with DW and with the DSL ($EC_{in}=2.1$ mS/cm).

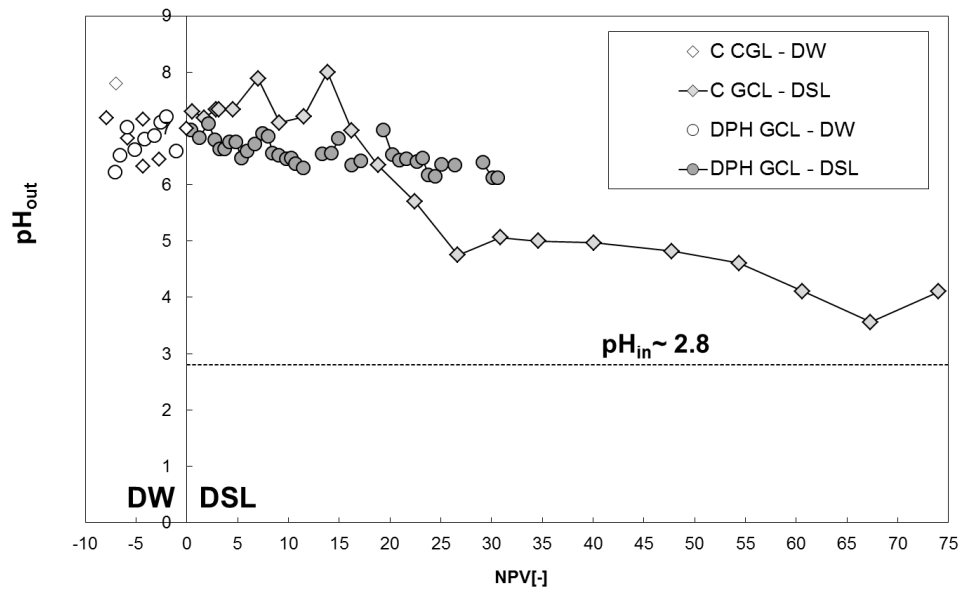


Fig.3. Effluent pH (pH_{out}) of the two GCLs during permeation with DW and with the DSL solution ($pH_{in}=2.8$)

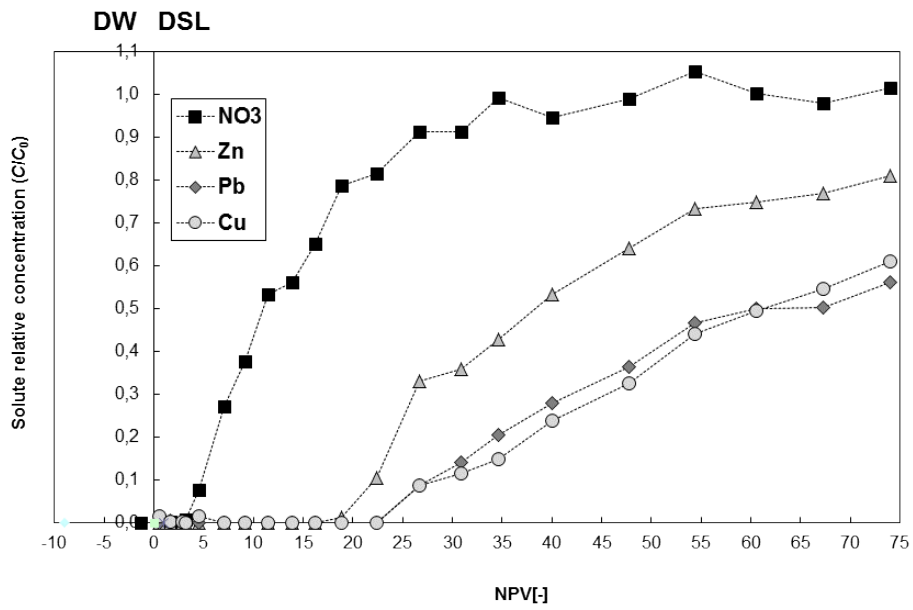


Fig.4. Solute (NO_3^- , Zn^{2+} , Cu^{2+} , Pb^{2+}) breakthrough curves determined during permeation of the C GCL with the DSL

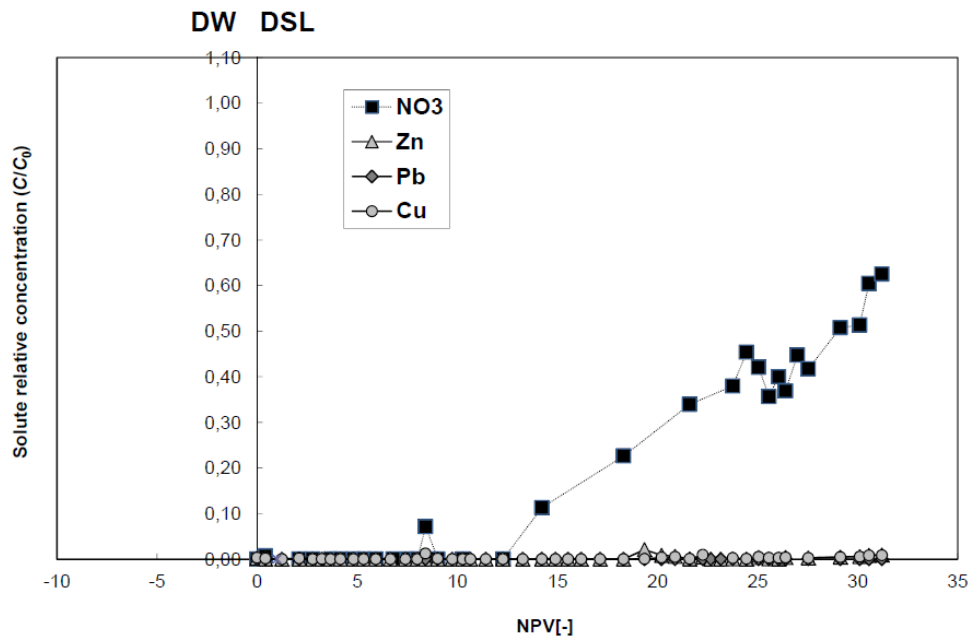


Fig.5. Solute (NO_3^- , Zn^{2+} , Cu^{2+} , Pb^{2+}) breakthrough curves during permeation of the DPH GCL with the DSL

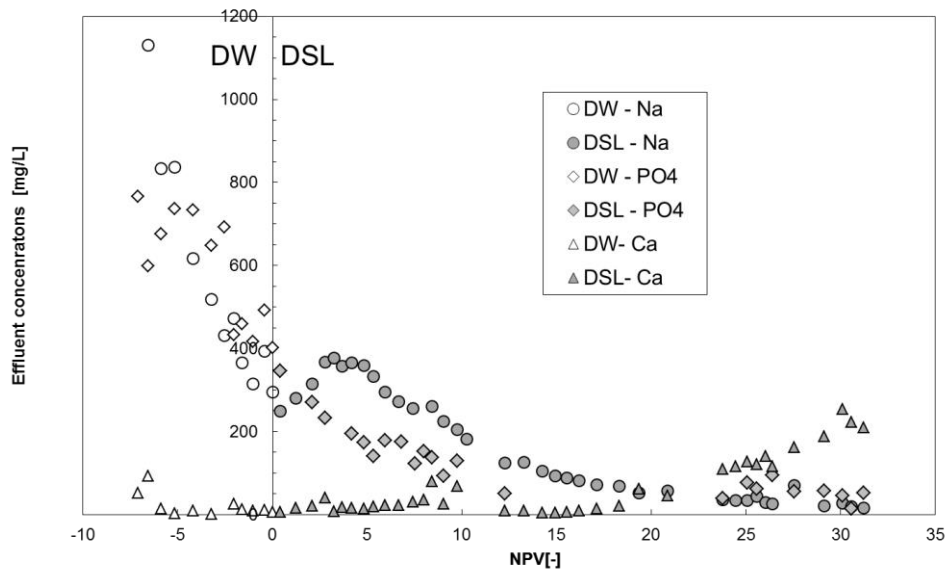


Fig.6. Desorption of major cations and anions during permeation of the DPH GCL with DW and the DSL

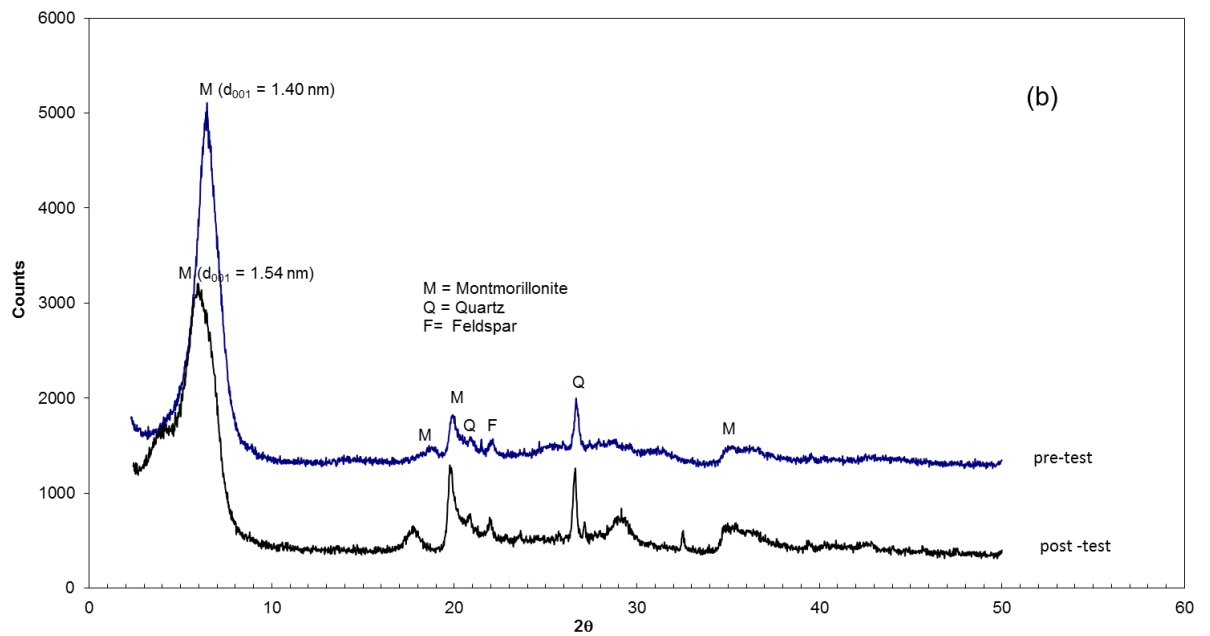
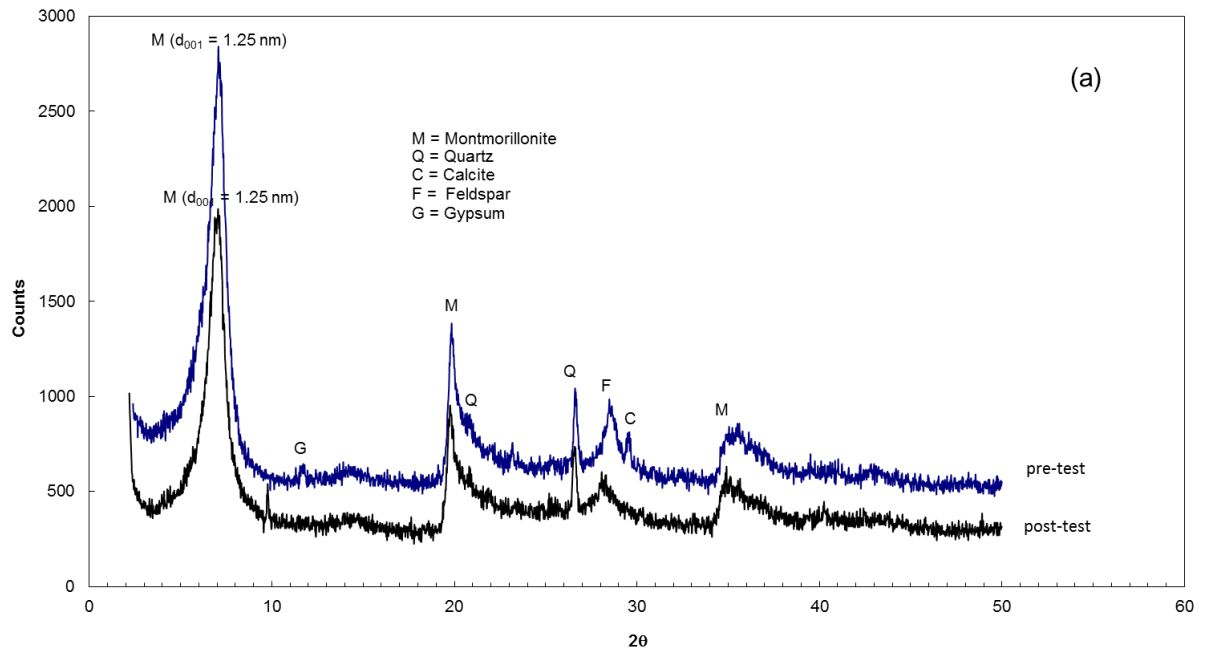


Fig.7. Comparison of pre-test and post-test powder XRD spectra of (a) C GCL (b) and DPH GCL.

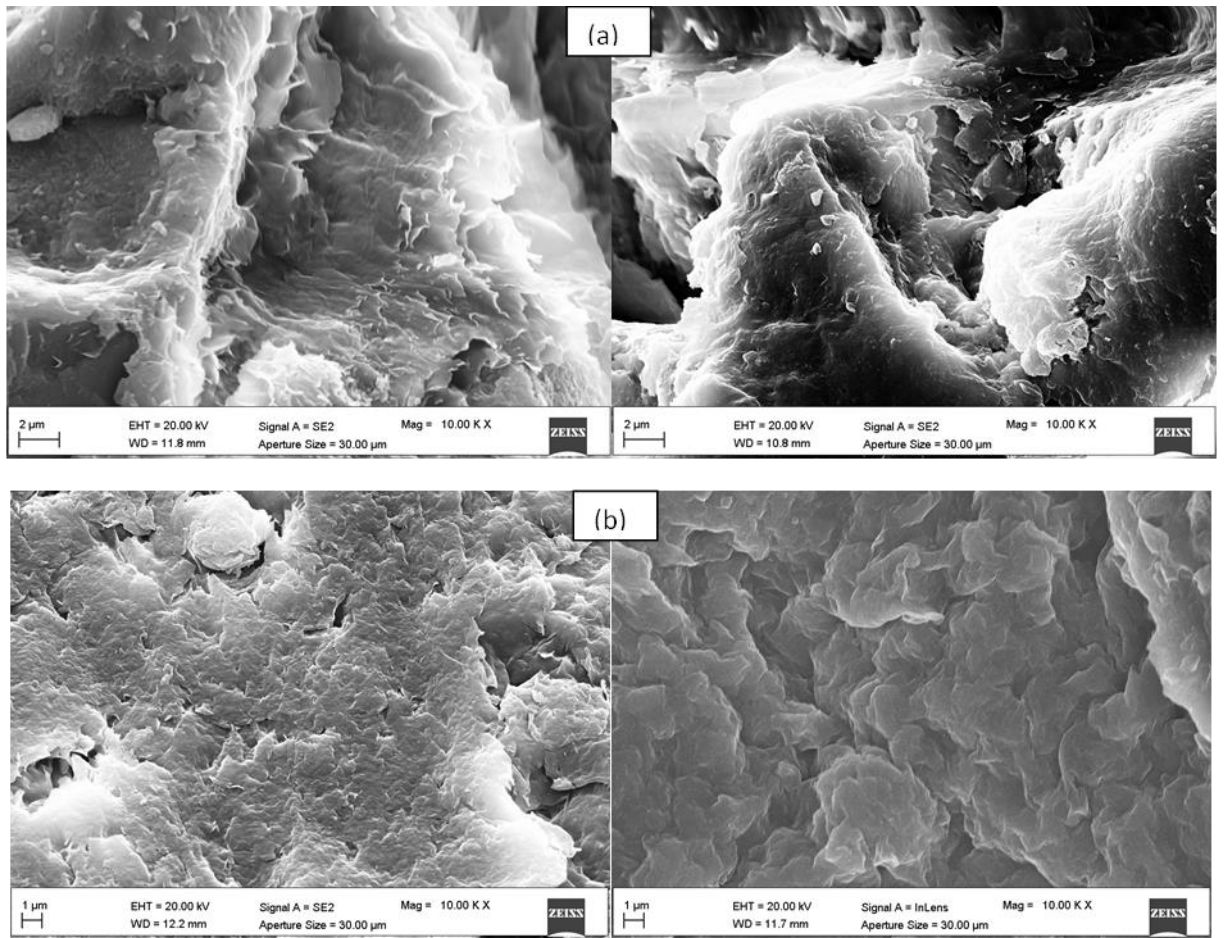


Fig. 8. Comparison of pre-test (left) and post-test (right) SEM micrographs of (a) C GCL and (b) DPH GCL.

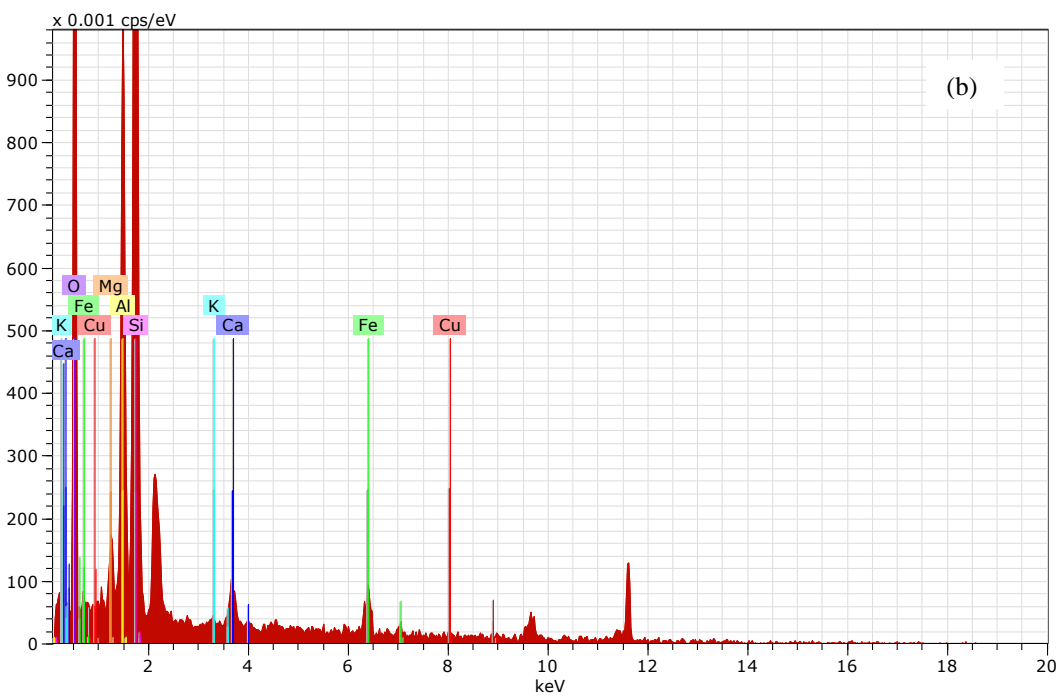
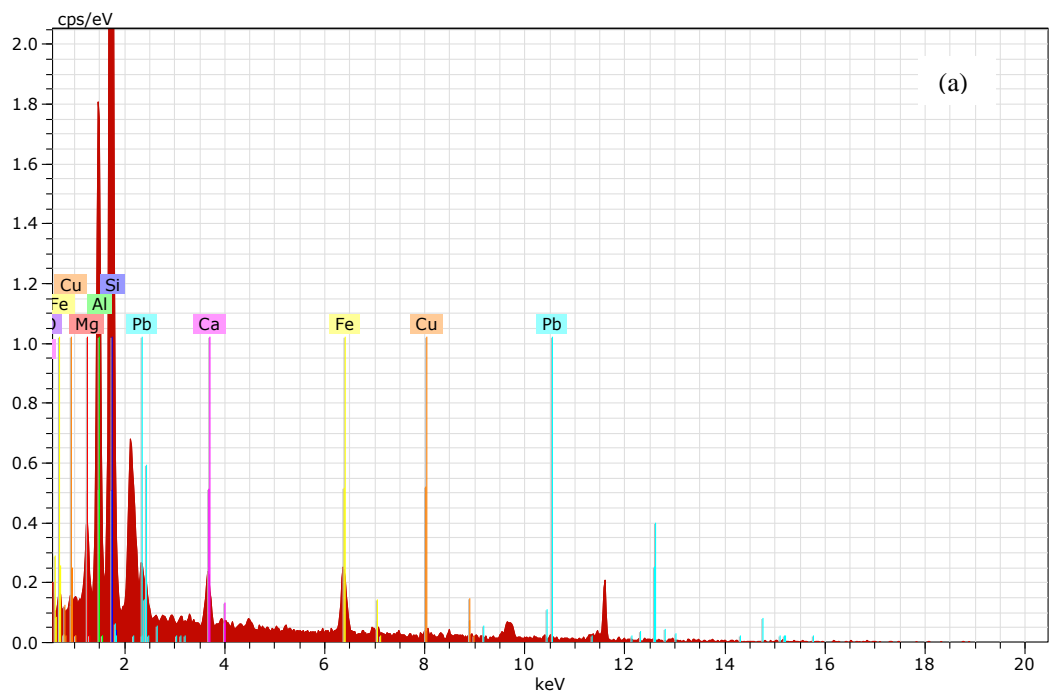


Fig.9. Post-test EDS results for (a) C GCLand (b) DPH GCL.

APPENDIX

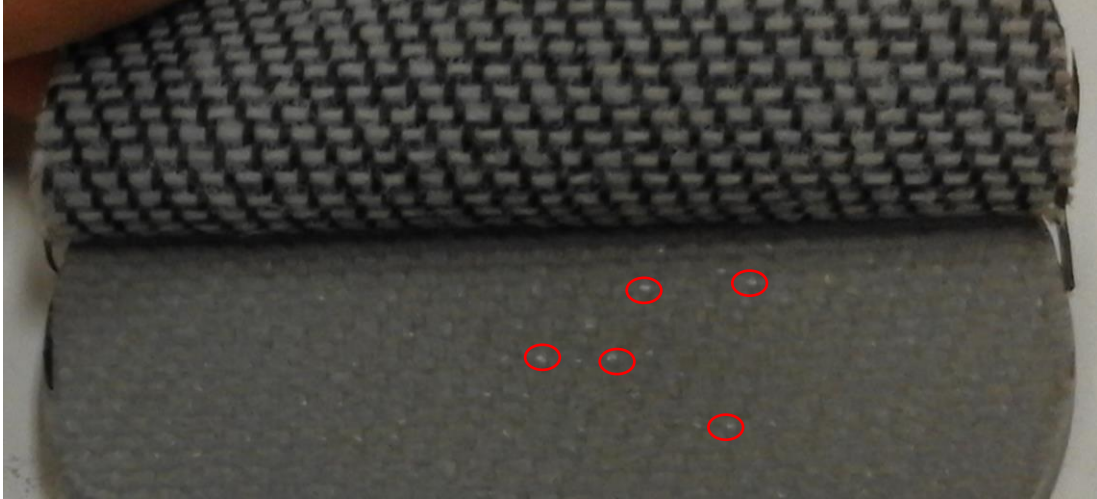


Fig. 10. Whitish spots on the upstream surface of the DPH GCL at the end of the test (presumably lead and copper phosphate solids)