

Alkaline-leachate induces pore-filling reactions in GCLs

W.P. Gates^{1*}, P. Hines²

¹Smectech Research Consulting, Moorabbin, Vic 3189 Australia and Monash University, Clayton, VIC
*gateswp@smectech.com.au; Presenting

²Australian Key Centre for Electron Microscopy and Microanalysis, University of Sydney, Sydney, NSW

Geosynthetic clay liners (GCLs) are increasingly important components of hydraulic barriers in waste containment systems (Gates et al., 2009). However, some leachates from the mining industry have been shown to alter barrier hydraulic performance of bentonites and GCLs. Often increases in saturated hydraulic conductivity result (e.g., Shackelford et al., 2010), but sometimes decreases are observed (e.g. Benson et al., 2008); the latter believed to be associated with pore-filling reactions.

The purpose of this study was to investigate further the reactions taking place within bentonite following exposure to mock solutions of high pH using scanning electron microscopy (SEM). We imaged the same samples as studied by Benson et al (2010) to determine whether pore-filling reactions occurred in GCLs permeated with solutions of 1.3 mM CsCl (GCLA) or 1M NaOH +1.3 mM CsCl (GCLB). CsCl was added as a tracer. Samples were prepared for SEM analysis following permeation studies by flash-freezing a section of 7-10 mm thick GCL in liquid nitrogen (LN₂) and cutting using a diamond rock saw (Streurs Acutum) into ~10x10mm squares to expose the GCL in cross section (parallel to permeant flow). Some cubes were then further cut to expose the longitudinal face (perpendicular to permeant flow) of the bentonite within the GCL. The face of each portion to be examined was sequentially polished on a series of plastic polishing papers of 100, 10 and 1 micron grits. Samples were kept frozen with LN₂ throughout the preparation process and placed overnight in a -80 °C freezer. Samples were analysed under vacuum using a computer controlled Philips XL 30 CP SEM with automated specimen stage, ultra-thin window EDS microanalysis and X-ray mapping.

SEM images reveal that in GCLA hydration induced swelling in 1.3 mM CsCl resulted in an open fabric consisting of large (>30 µm) areas (domains) of partially oriented smectites particles with a range of pore sizes (Figure 1). A ~5 µm thick, dense and low porosity interface of smectite particles having a highly orientated pore structure was observed between clay domains. These compression joints resulted from swell-induced compression of the edges of adjacent domains. Also observed in GCLA was evidence of clay flow and self healing (not shown). In contrast, hydration of GCLB in 1 M NaOH + 1.3 mM CsCl resulted in a largely featureless but strongly porous matrix with highly uniform pores covering large areas (>1 mm diameter) having few compression joints. Higher resolution images (Fig. 1) of areas where compression joints existed in GCLB revealed individual domains to be <30 µm in extent.

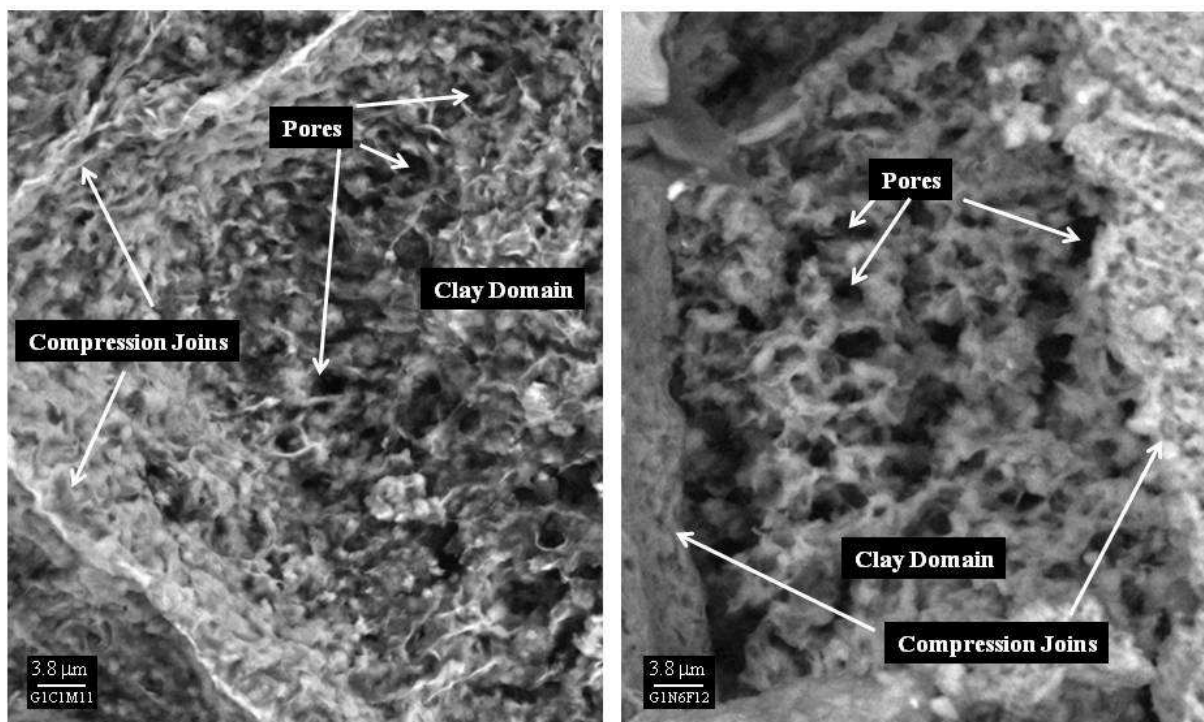


Fig. 1. Comparison of the pores within clay domains in GCLA (left) and GCLB (right).

Energy dispersive X-ray (EDX) mapping was conducted across a compression joint and into the domains on either side in GCLA (not shown). A large difference in Cs concentrations was observed between clay domains on either side of the compression joint, with one domain containing considerably less Cs than the other. Cs was largely concentrated near the compression zone, indicating that advective transport of CsCl may be along preferential flow paths between domains.

Benson et al. (2010) reported a slight increase in the permeability of GCLB to $\sim 4 \times 10^{-10}$ m/s from 9×10^{-10} m/s when eluted with 1 M NaOH + 1.3 mM CsCl, but after ~ 8 pore volumes of flow the permeability stabilised and decreased to $\sim 2 \times 10^{-10}$ m/s. Pore water chemistry pointed toward the possibility of pore-filling mineral precipitation reactions taking place during the reaction of 1 M NaOH with the bentonite and additive in GCLB. Mineralogical analysis (X-ray diffraction, infrared, thermal gravimetry and Al K-edge near edge X-ray absorption spectroscopy) identified the presence of various hydrous silicates and carbonates subsequent to the reaction of the same bentonite in batch solutions of 1 M NaOH that could be responsible for pore-filling reactions (Gates and Bouazza, 2010).

Figure 2 shows examples of direct evidence of precipitation of hydrous mineral phases. In Figure 2A a highly dispersed 'spider-web' phase with 4-5 micron diameter pores is observed in GCLB. EDX analysis indicated that the 'spider web' material in GCLB was a non-smectitic highly hydrous and siliceous phase (Benson et al., 2010). The image to the right of Figure 2B depicts a large ~ 60 μ m pore. The image on the left in Figure 2B is of a pore cast, formed during the pre-hydration phase of the experiment, from which the geotextile fibre broke and was subsequently pulled from the clay

matrix. Both pores are surrounded by densely flocculated clay and apparently served as preferential flow paths. The pores themselves are likely responsible for the higher overall permeability of GCLB to 1 M NaOH + 1.3 mM CsCl compared to GCLA to 1.3 mM CsCl. However, permeation with 1 M NaOH + 1.3 mM CsCl resulted in the deposition of material within both types of pores. The pore on the right in Figure 2B has been filled by a highly cross-linked siliceous material. Analysis of these pores indicates that average pore diameters has been reduced by 3 to 30 times, thus the advective flow path tortuosity increases significantly from such pore-filling reactions.

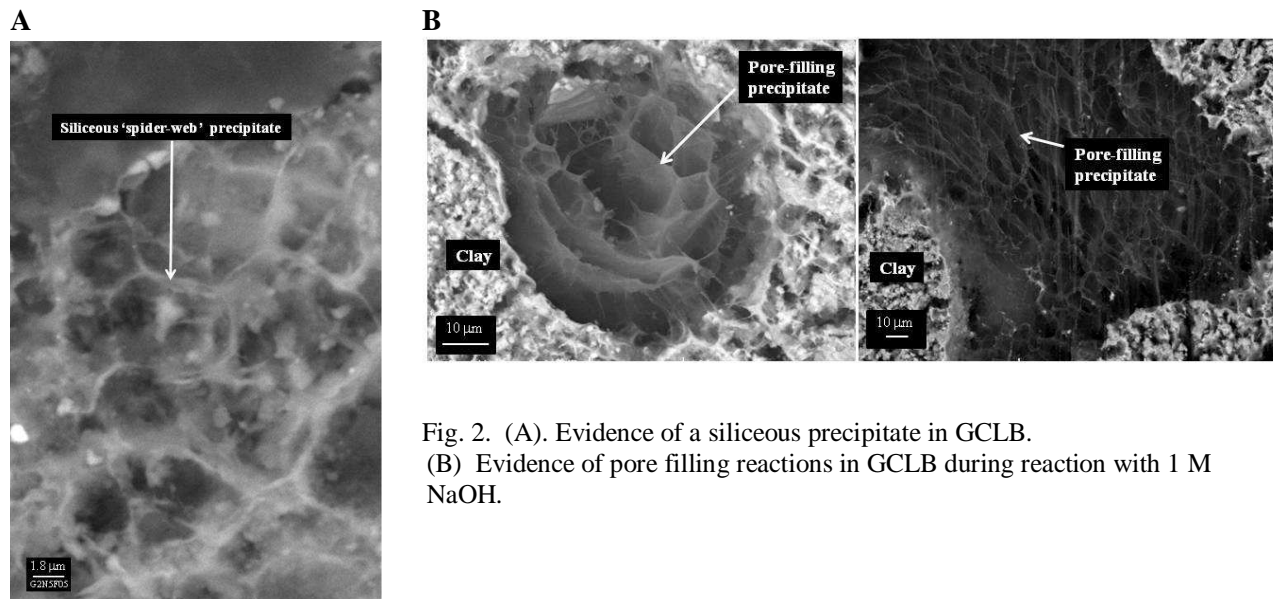


Fig. 2. (A). Evidence of a siliceous precipitate in GCLB. (B) Evidence of pore filling reactions in GCLB during reaction with 1 M NaOH.

Figure 3 shows the results of energy dispersive X-ray (EDX) analysis of the image in the left of Figure 2B. The matrix clearly has a smectite (aluminosilicate) composition, whereas the pore-filling material is significantly enriched in silica and carbon. As these analyses were conducted on the same GCL samples as tested by Benson et al. (2010), each of which retained saturated hydraulic conductivity values $< 4 \times 10^{-10}$ m/s at test completion, the SEM evidence presented here strongly suggests that these phases are responsible for the low permeability observed.

Pore-filling mineral precipitation reactions may therefore attenuate the adverse effects of smectites dissolution. Further studies are needed to understand the long-term stability of these reactions and their relationship to the performance of bentonites and GCLs as components in hydraulic barriers.

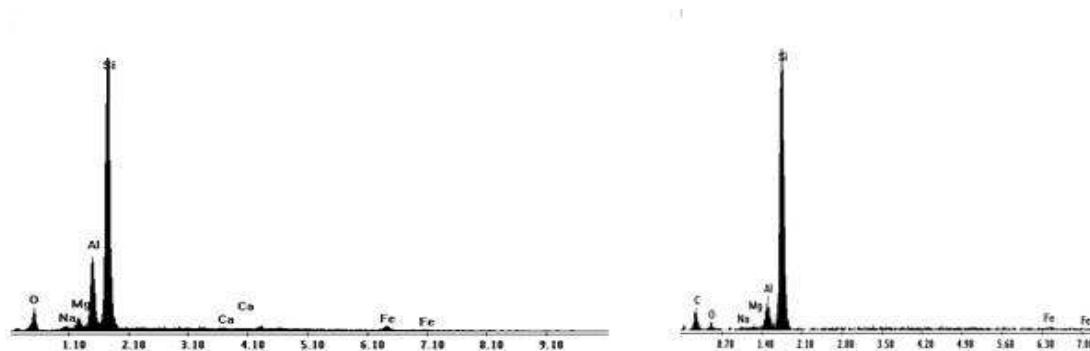


Fig. 3. Energy dispersive X-ray analyses of the pore shown in Figure 2B (left hand image). Left EDX is of the matrix smectites, Right EDX is of the pore filling material.

References

- Benson, C.H., Wang, X., Gassner, F., Foo, D. (2008) Hydraulic conductivity of two Geosynthetic clay liners permeated with an aluminium residue leachate. *GeoAmericas 2008*, International Geosynthetics Society. Proceedings Abstract.
- Benson, C.H., Ören, A.H., Gates W.P. (2010) Hydraulic conductivity of two geosynthetic clay liners permeated with a hyperalkaline solution. *Geotextiles and Geomembranes* 28: 206-218.
- Gates, W.P., Bouazza, A. (2010) Bentonite transformations in strongly alkaline solutions. *Geotextiles and Geomembranes* 28: 219-225.
- Gates, W.P., Bouazza, A., Churchman, G.J. (2009) Bentonite clay keeps pollutants at bay. *Elements* 5: 105-110.
- Shackelford, C.D., Sevick, G.W., Eykholt, G.R. (2010) Hydraulic conductivity of geosynthetic clay liners to tailings impoundment solutions. *Geotextiles and Geomembranes* 28:149-162.

Acknowledgements

The authors thank W. Hornsey of Geofabrics Australasia and S. Restall, formerly of ELCO Solutions and Monash University for support of this project.