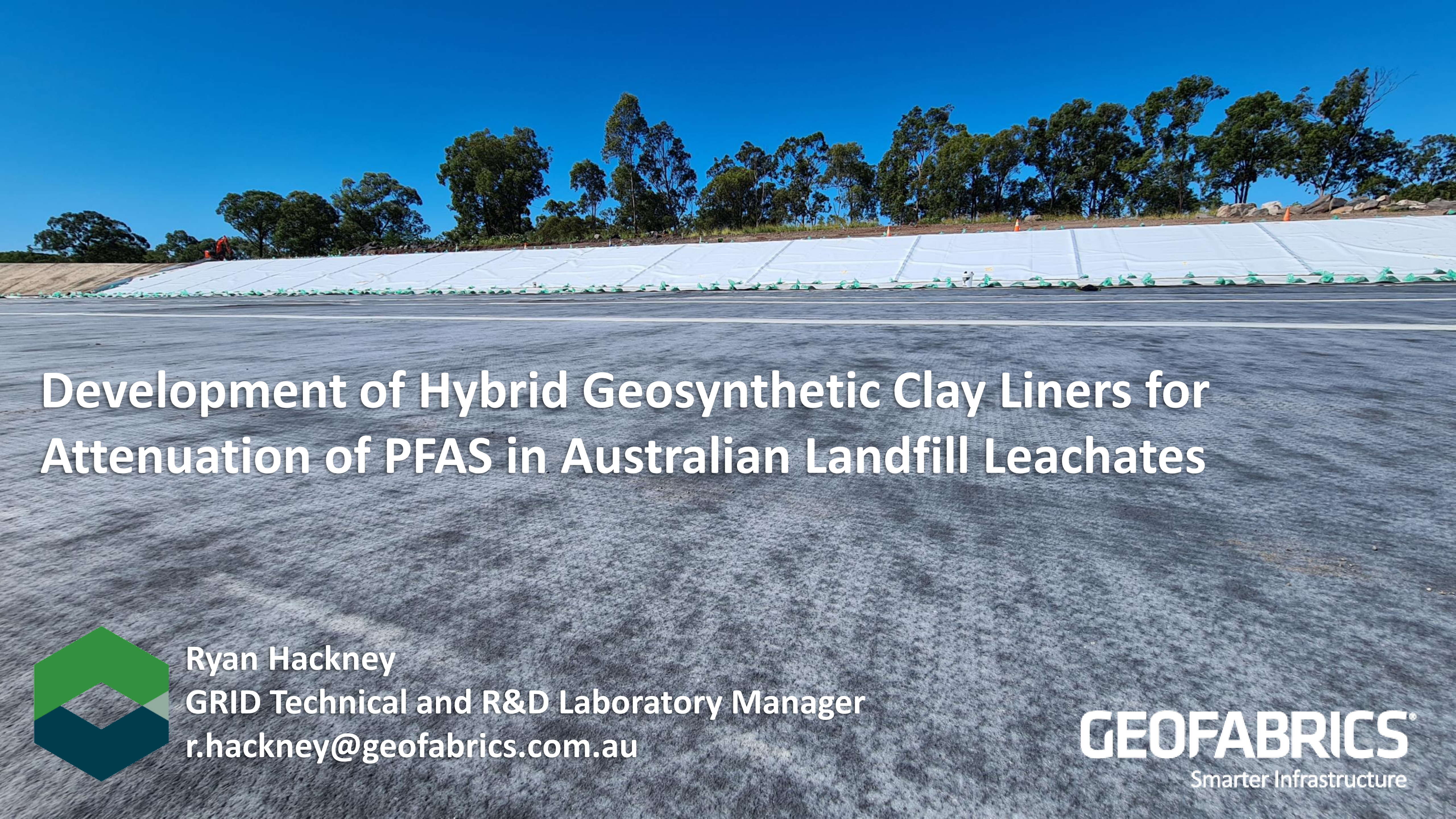

Development of Hybrid Geosynthetic Clay Liners for Attenuation of PFAS in Australian Landfill Leachates

Ryan Hackney
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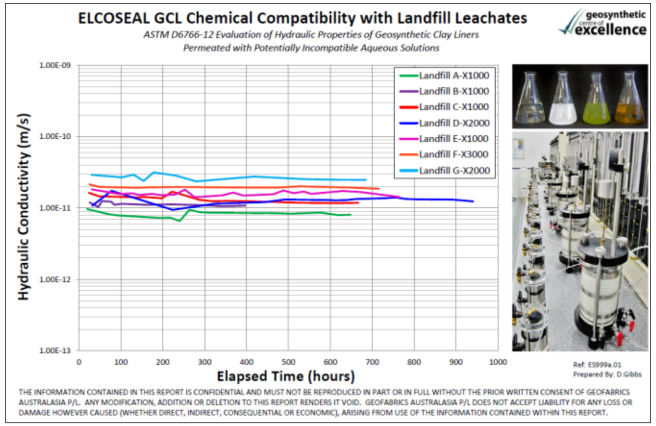
Geosynthetic R&D

GCL Chemical Compatibility

- The GRID have been undertaking chemical compatibility analysis on Geosynthetic Clay Liners (GCLs) & many bentonite sources with a large range of leachates, liquors and elutions for over 10 years
- This analysis quantifies the permeability of the GCL with the site specific leachates
- Each hydraulic assessment includes a chemical analysis of the hydrating and permeating liquid itself
- In addition to the hydraulic conductivity assessment, Swell Index and Fluid Loss are undertaken with the leachates
- A large database has been developed in order to link the hydraulic performance with
  - Clay mineralogy and chemistry
  - GCL configuration (mass per unit area, synthetic components, mechanical performance)
  - Leachate chemistry
  - Fluid Loss and Swell Index performance



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Geosynthetic Clay Liner Analysis

Hydraulic Conductivity Assessment

$$k_T = \frac{aL}{2At} \ln \left[\frac{\left(h_a, in - h_a, out + \frac{(V_{out} - V_{in})L_p}{V_p}\right)}{\left(h_a, in - h_a, out + \frac{(V_{out} - V_{in})L_p}{V_p}\right)} \right]$$

Definition: *hydraulic conductivity, k, n* — the rate of discharge of liquid under laminar flow conditions through a unit cross-sectional area of a GCL specimen under a unit hydraulic gradient and standard temperature conditions . . . . **ASTM D6766**

where:

k_T = hydraulic conductivity, m/s,

a = cross-sectional area of the reservoir containing the influent/effluent liquid, m²,

L = length of the specimen, m,

A = cross-sectional area of the specimen, m²,

t = elapsed time between determination of $h1$ and $h2$, s,

h_1 = head loss across the specimen at time $t1$, m, and

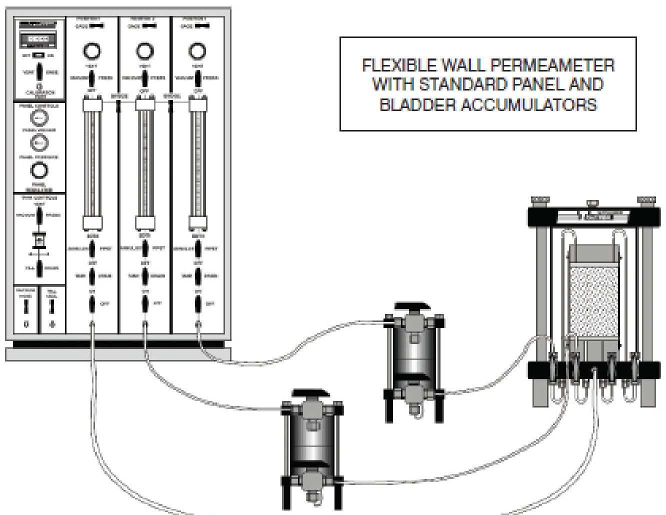
h_2 = head loss across the specimen at time $t2$, m.

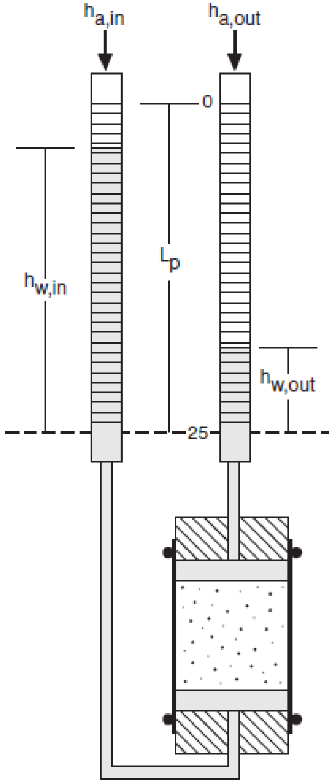
L_p = Length of pipette between 0 and 25mL mark, m

V / V_p = Volume / Total volume of pipette, m³

h_a = Air pressure expressed in m of H^2O

h_w = Distance between meniscus and 25mL mark on pipette, m





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Geosynthetic C

Hydraulic Conducti

$$k_T = \frac{aL}{2At} \ln \left[\frac{(h_a, in - h_a, o}{(h_a, in - h_a, o} \right.$$

D6766 – 20a

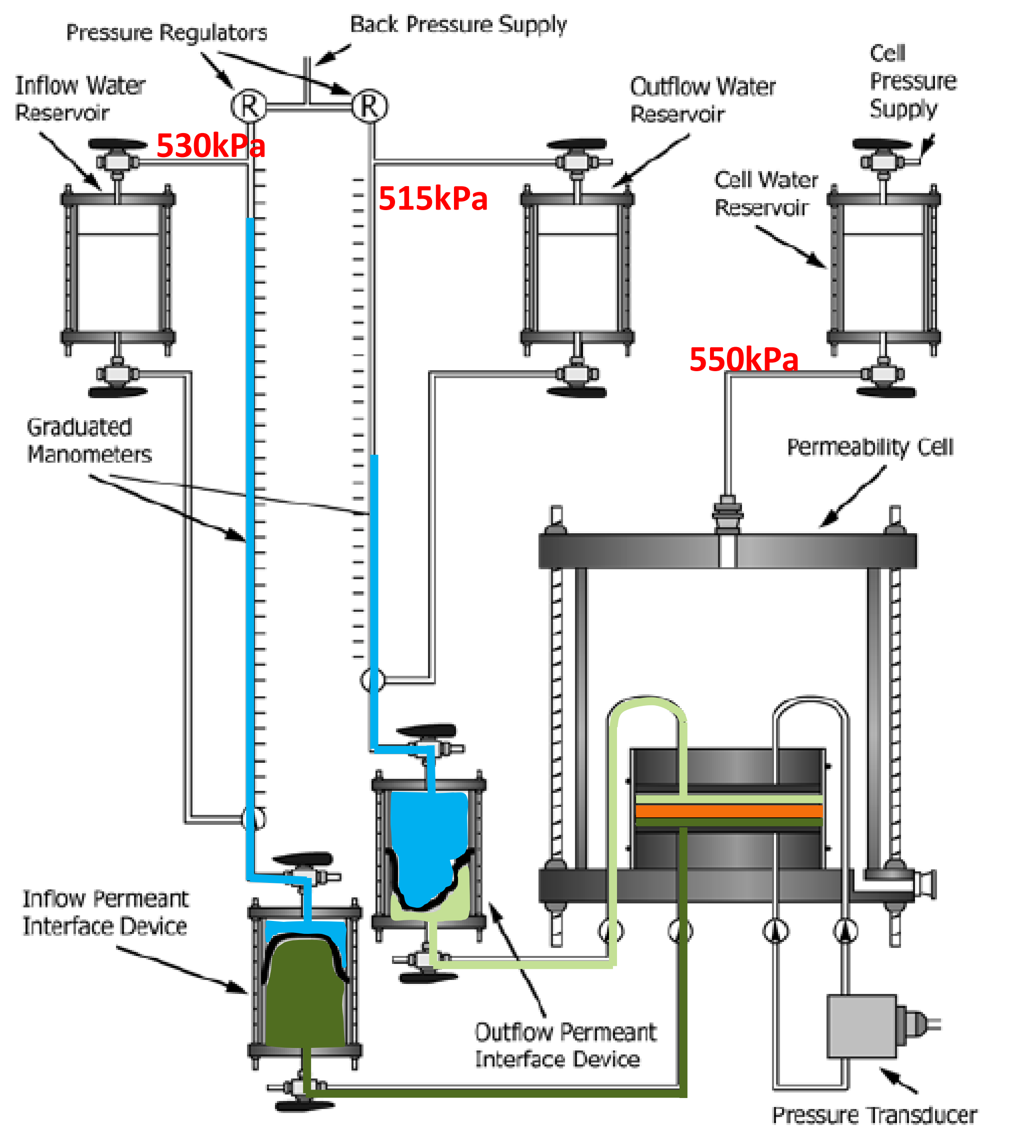
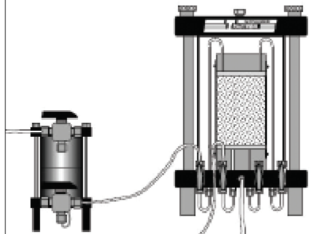
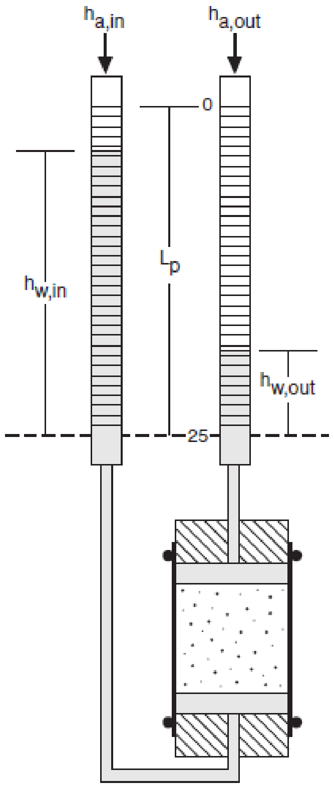


FIG. 3 Schematic Diagram of Test Setup

k, n — the rate of
ar flow conditions
a of a GCL specimen
ent and standard
M D6766

FLEXIBLE WALL PERMEAMETER WITH STANDARD PANEL AND BLADDER ACCUMULATORS





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Leachate Chemistry

PFAS in Landfill Leachates

- Over the past several years additional chemical analysis has been undertaken (externally) on the leachates received to quantify their PFAS concentrations
- Either direct injection or whole bottle extraction of the sample is taken according to the practical quantitation limit required
- Data is collected from an Extended PFAS Suite (28 Analytes) according to methods based on USEPA 537, ASTM D7968 and ISO 25101 using LC/MS-MS instruments

Page : 3 of 7
Work Order : EB1824616
Client : GEOFABRICS AUSTRALIA PTY LTD
Project : ES106

Analytical Results

Sub-Matrix: WATER (Matrix: WATER)

			Client sample ID	ES106DLcell10#10	ES106DLfastflow#1	ES077elution	----	----
			Client sampling date / time	09-Oct-2018 13:00	12-Aug-2018 15:00	09-Oct-2018 13:18	----	----
Compound	CAS Number	LOR	Unit	EB1824616-001	EB1824616-002	EB1824616-003	--------	--------
				Result	Result	Result	----	----
EP231A: Perfluoroalkyl Sulfonic Acids								
Perfluorobutane sulfonic acid (PFBS)	375-73-5	0.0005	µg/L	5.97	----	----	----	----
Perfluorobutane sulfonic acid (PFBS)	375-73-5	0.02	µg/L	----	21.8	<0.02	----	----
Perfluoropentane sulfonic acid (PFPeS)	2706-91-4	0.0005	µg/L	0.0780	----	----	----	----
Perfluoropentane sulfonic acid (PFPeS)	2706-91-4	0.02	µg/L	----	<0.10	<0.02	----	----
Perfluorohexane sulfonic acid (PFHxS)	355-46-4	0.0005	µg/L	1.03	----	----	----	----
Perfluorohexane sulfonic acid (PFHxS)	355-46-4	0.02	µg/L	----	0.93	<0.02	----	----
Perfluoroheptane sulfonic acid (PFHpS)	375-92-8	0.0005	µg/L	<0.0200	----	[illegible]	[illegible]	[illegible]
Perfluoroheptane sulfonic acid (PFHpS)	375-92-8	0.02	µg/L	----	<0.1	[illegible]	[illegible]	[illegible]
Perfluorooctane sulfonic acid (PFOS)	1763-23-1	0.0003	µg/L	0.100	----	[illegible]	[illegible]	[illegible]
Perfluorodecane sulfonic acid (PFDS)	335-77-3	0.0005	µg/L	<0.0200	----	[illegible]	[illegible]	[illegible]
Perfluorooctane sulfonic acid (PFOS)	1763-23-1	0.01	µg/L	----	0.20	[illegible]	[illegible]	[illegible]
Perfluorodecane sulfonic acid (PFDS)	335-77-3	0.02	µg/L	----	<0.1	[illegible]	[illegible]	[illegible]
EP231B: Perfluoroalkyl Carboxylic Acids								
Perfluorobutanoic acid (PFBA)	375-22-4	0.002	µg/L	<0.020	----	[illegible]	[illegible]	[illegible]
Perfluorobutanoic acid (PFBA)	375-22-4	0.1	µg/L	----	7.2	[illegible]	[illegible]	[illegible]
Perfluoropentanoic acid (PFPeA)	2706-90-3	0.0005	µg/L	<0.0200	----	[illegible]	[illegible]	[illegible]
Perfluoropentanoic acid (PFPeA)	2706-90-3	0.02	µg/L	----	1.36	[illegible]	[illegible]	[illegible]
Perfluorohexanoic acid (PFHxA)	307-24-4	0.0005	µg/L	0.794	----	[illegible]	[illegible]	[illegible]
Perfluorohexanoic acid (PFHxA)	307-24-4	0.02	µg/L	----	2.32	[illegible]	[illegible]	[illegible]
Perfluoroheptanoic acid (PFHpA)	375-85-9	0.0005	µg/L	0.390	----	[illegible]	[illegible]	[illegible]
Perfluoroheptanoic acid (PFHpA)	375-85-9	0.02	µg/L	----	0.34	[illegible]	[illegible]	[illegible]
Perfluorooctanoic acid (PFOA)	335-67-1	0.0005	µg/L	0.472	----	[illegible]	[illegible]	[illegible]
Perfluorooctanoic acid (PFOA)	335-67-1	0.01	µg/L	----	0.69	[illegible]	[illegible]	[illegible]
Perfluorononanoic acid (PFNA)	375-95-1	0.0005	µg/L	0.0300	----	[illegible]	[illegible]	[illegible]

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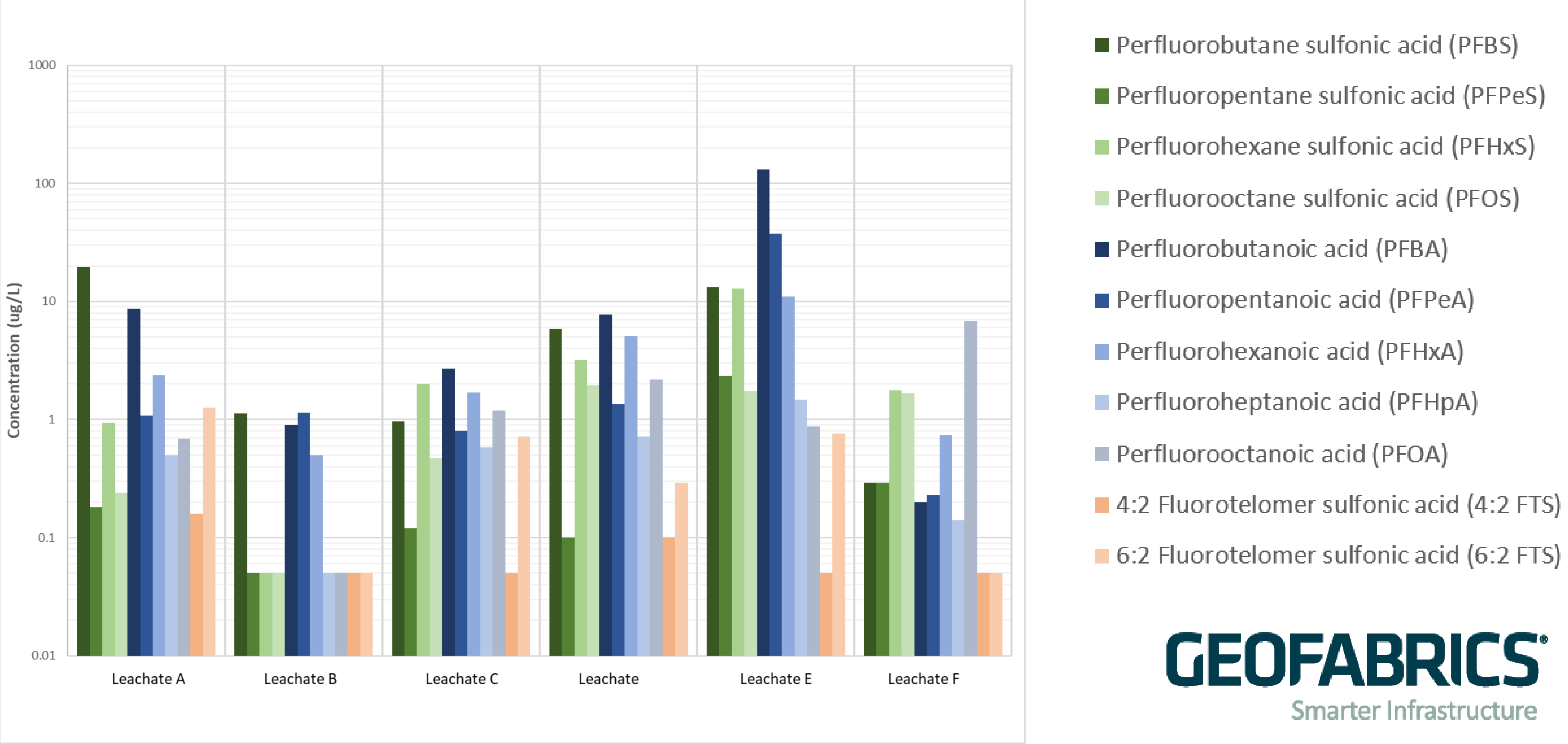
Leachate Chemistry

PFAS in Landfill Leachates



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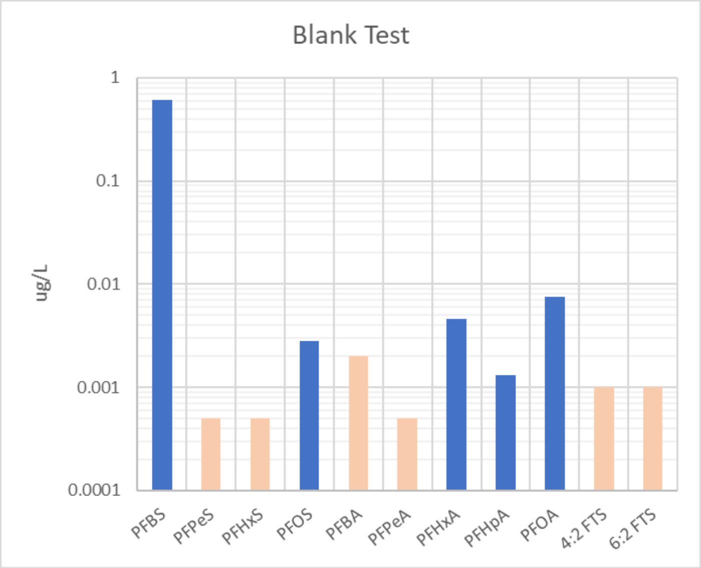
HC Equipment Compatibility

Equipment Verifications

Compound	Unit	Blank Test	DI Water
Perfluorobutane sulfonic acid (PFBS)	µg/L	0.606	<0.0005
Perfluoropentane sulfonic acid (PFPeS)	µg/L	<0.0005	<0.0005
Perfluorohexane sulfonic acid (PFHxS)	µg/L	<0.0005	<0.0005
Perfluorooctane sulfonic acid (PFOS)	µg/L	0.0028	<0.0002
Perfluorobutanoic acid (PFBA)	µg/L	<0.002	<0.0020
Perfluoropentanoic acid (PFPeA)	µg/L	<0.0005	<0.0005
Perfluorohexanoic acid (PFHxA)	µg/L	0.0046	<0.0005
Perfluoroheptanoic acid (PFHpA)	µg/L	0.0013	<0.0005
Perfluorooctanoic acid (PFOA)	µg/L	0.0075	<0.0005
4:2 Fluorotelomer sulfonic acid (4:2 FTS)	µg/L	<0.001	<0.001
6:2 Fluorotelomer sulfonic acid (6:2 FTS)	µg/L	<0.001	<0.001



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HC Equipment Compatibility

Equipment Components

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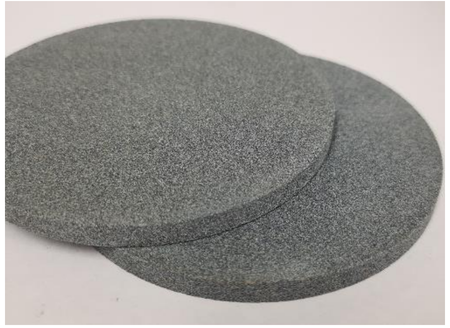
- Tubing
- Porous Plates
- 100mm Flexible Membrane
- Valves
- Flexible bladder
- Acrylic Base and Top Cap
- O'Rings
- Porous Plates
- Filter paper









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GCL PFAS Permeation

Standard Bentonite vs Polymer Modified Bentonite

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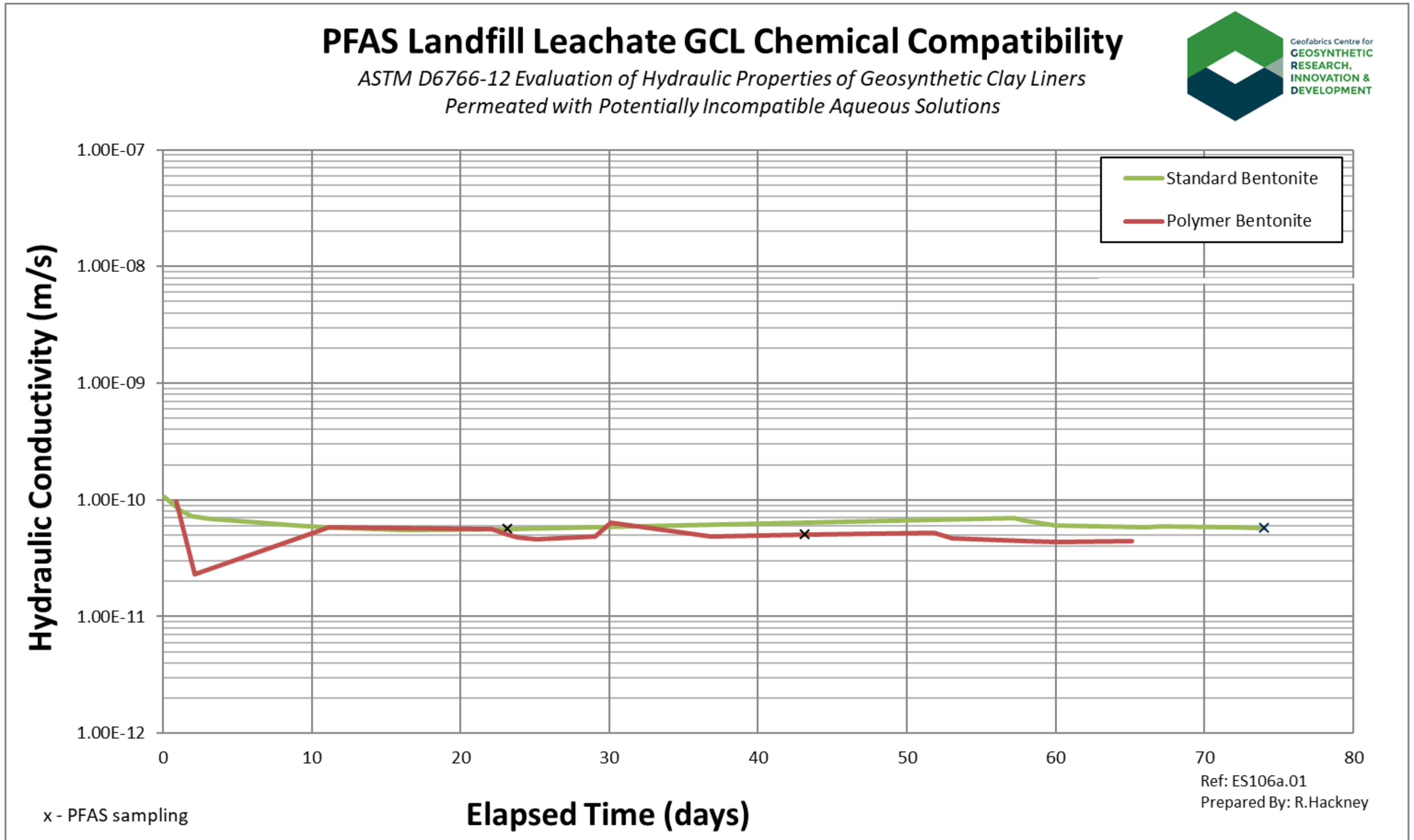

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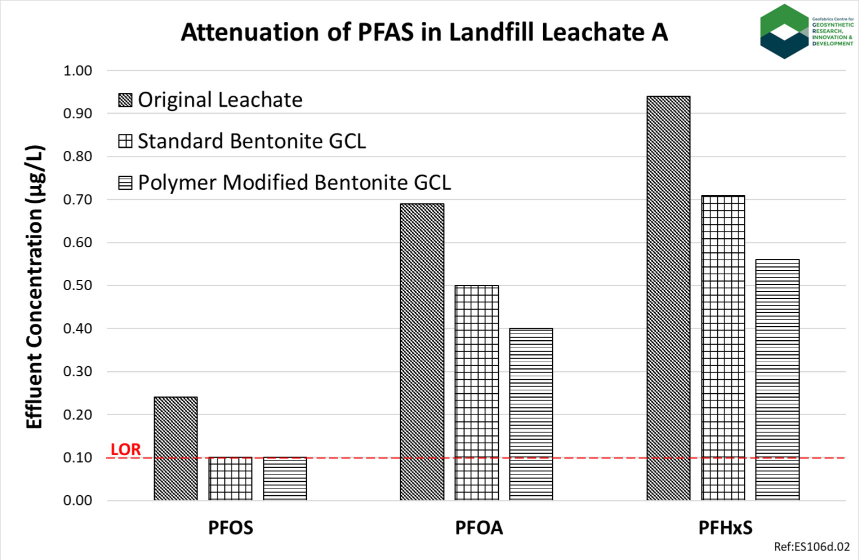

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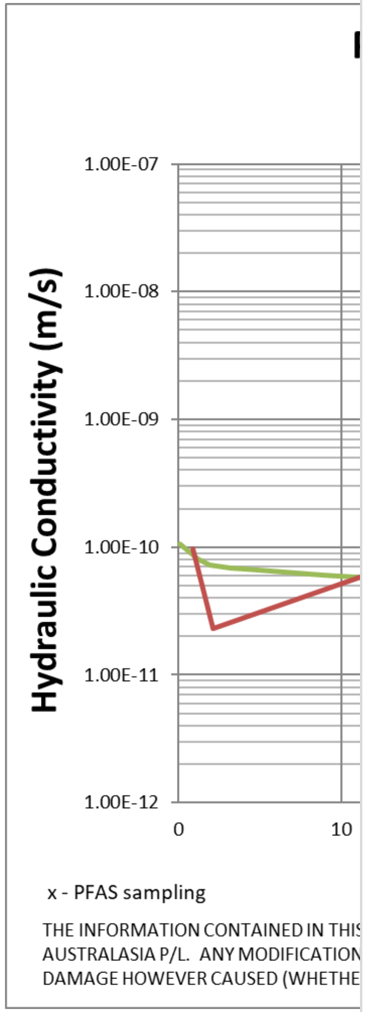
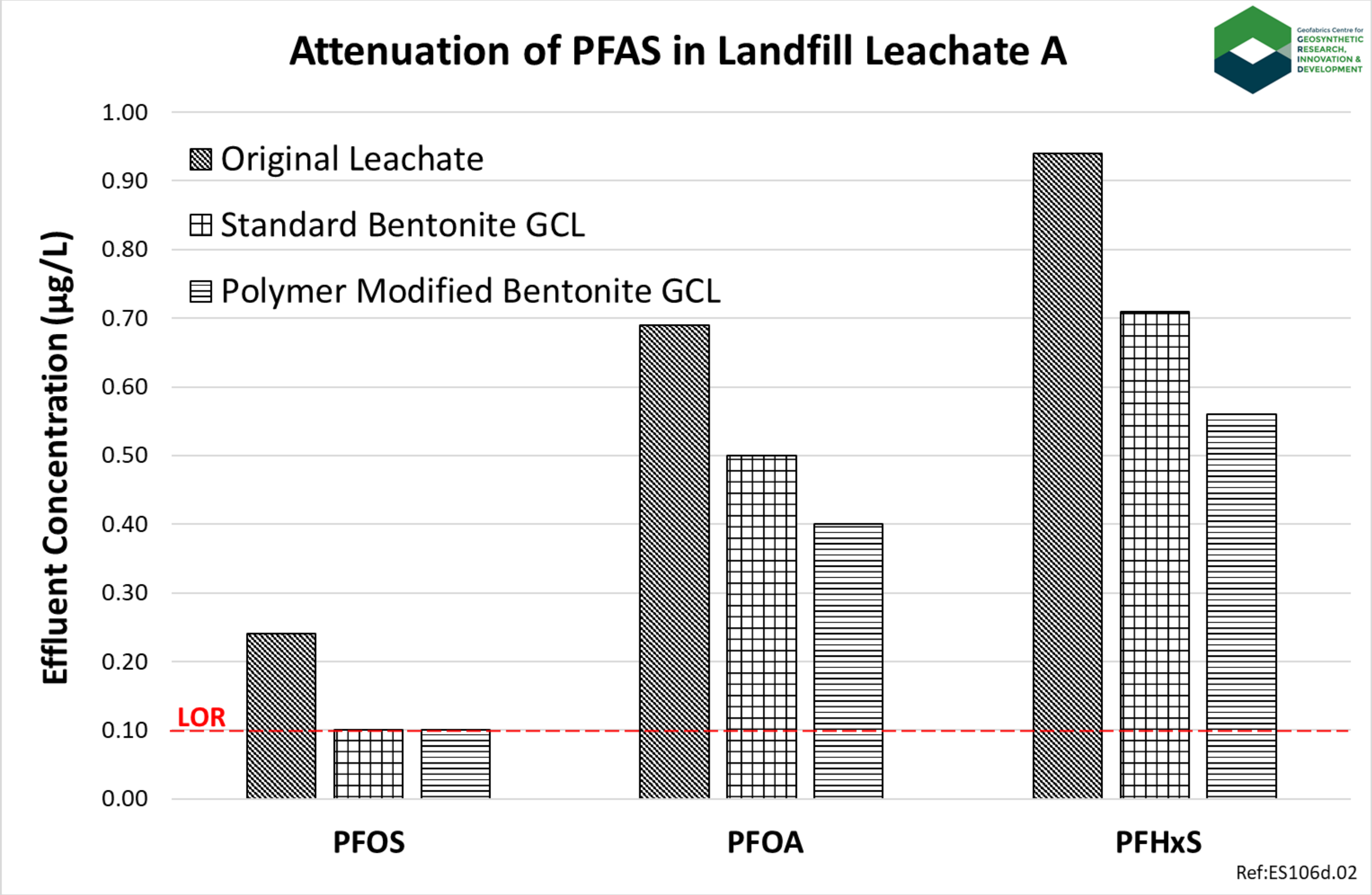
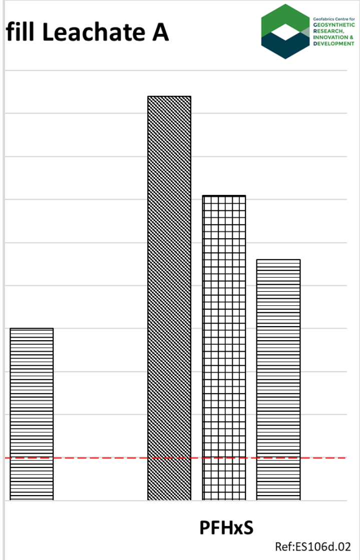
GCL PFAS Permeation

Standard Bentonite vs Polymer Modified Bentonite

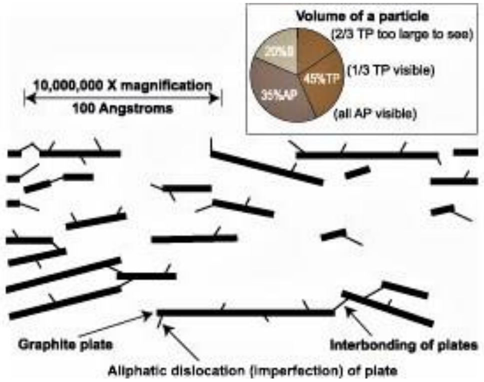


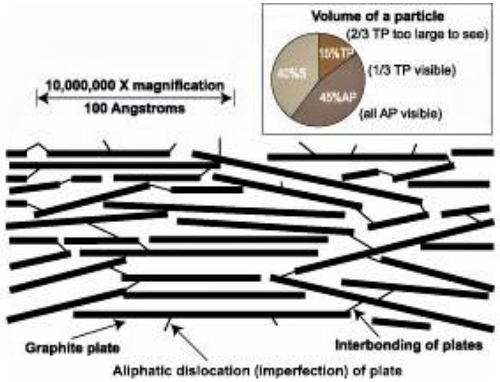


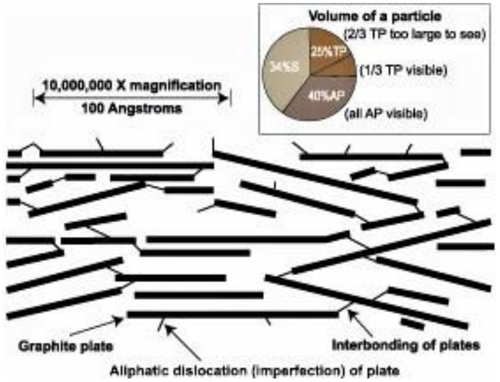


PFAS Attenuation
Activated Carbon

Activated Carbon can be manufactured from virtually any organic material; however, because of their high carbon contents, wood, coconut shells and coal are the most commonly used raw materials. There are three different coal types which are used; lignite, bituminous and anthracite with bituminous coal having the highest PFAS attenuation performance.







Source: Henry Nowicki, Wayne Schuliger, George Nowicki and Barbara Sherman. 2014. "*Evaluation of Activated Carbon Performance*".
http://wcponline.com/2014/06/17/evaluation-activated-carbon-performance/

PFAS Attenuation

Activated Carbon

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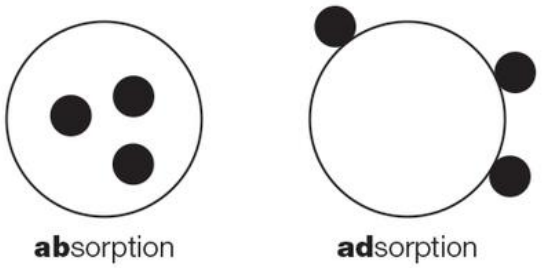
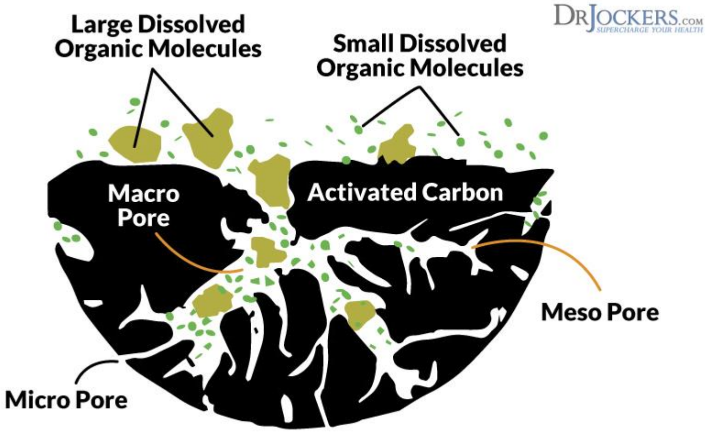
- Activated Carbon works by the process of adsorption. Adsorption is the attachment or adhesion of atoms, ions and molecules (adsorbates) from a gaseous, liquid or solution medium onto the surface of an adsorbent – activated carbon.
- The porosity of activated carbon offers a vast surface on which this adsorption can take place. Adsorption occurs in pores slightly larger than the molecules that are being adsorbed, which is why it is very important to match the molecule you are trying to adsorb with the pore size of the activated carbon. These molecules are then trapped within the carbon's internal pore structure.
- Activation may be carried out by chemical means or, more commonly, by high temperature steam activation in a controlled atmosphere.





Charcoal's powerful adsorbency capacity can soak up both large and small organic molecules into its pores

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Geosynthetic Clay Liner Modification

Modifying GCL with Activated Carbon

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- Various technologies related to the capture of PFAS were investigated for inclusion into a geocomposite including Knitted, Woven and Nonwoven Activated Carbon Fabrics, Activated Carbon Fibre (ACF), Powdered Activated Carbon (PAC) and Graphene Oxide (GO).

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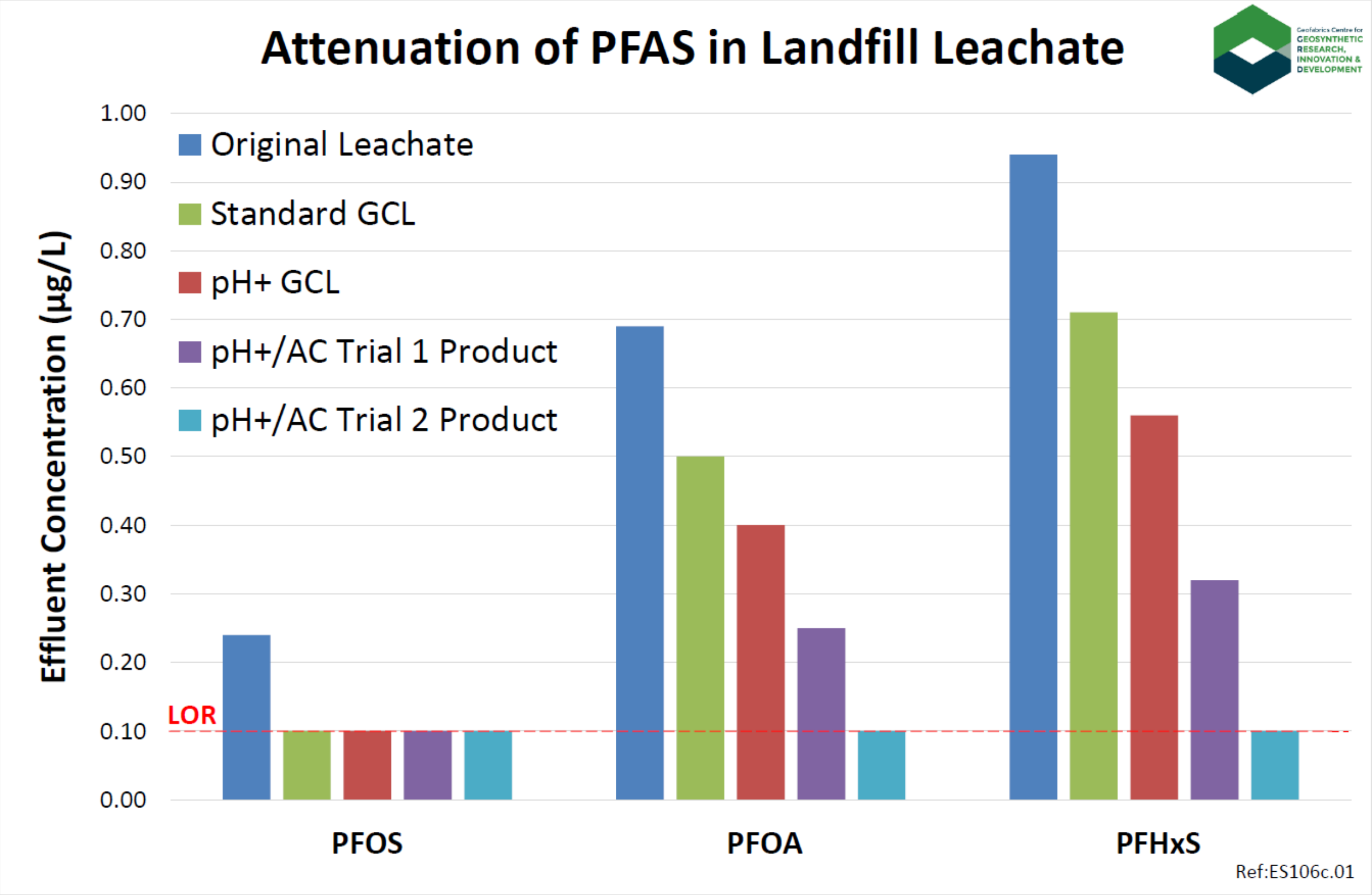
Geosynthetic Clay Liner Modification

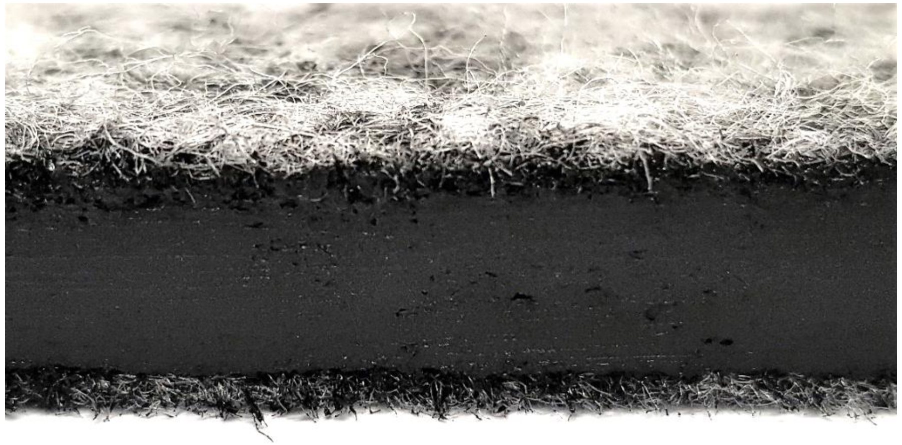
Modified GCL with Activated Carbon



- Multiple products initially assessed with respect to their ability to attenuate the 3 main PFASs listed in the NEMP
- The highest performing product contained a high surface area, powdered activated carbon
- Long-term analysis has allowed us to understand the behaviour of this product and determine PFAS saturation points

Hybrid Geosynthetic Clay Liner

Modified GCL – Activated Carbon Blend



- A powdered activated carbon hybrid geosynthetic clay liner (h-GCL) was developed to assist with the attenuation of PFAS while retaining a low level of permeability
- Based on the varying chemistries observed it was foreseen to have the capability to calibrate the blend within the hybrid GCL to suit specific project requirements
- By preserving the traditional GCL design, and by only adapting the powder blend, the product would still have the same mechanical performance of a GCL and could be designed with in the same manner

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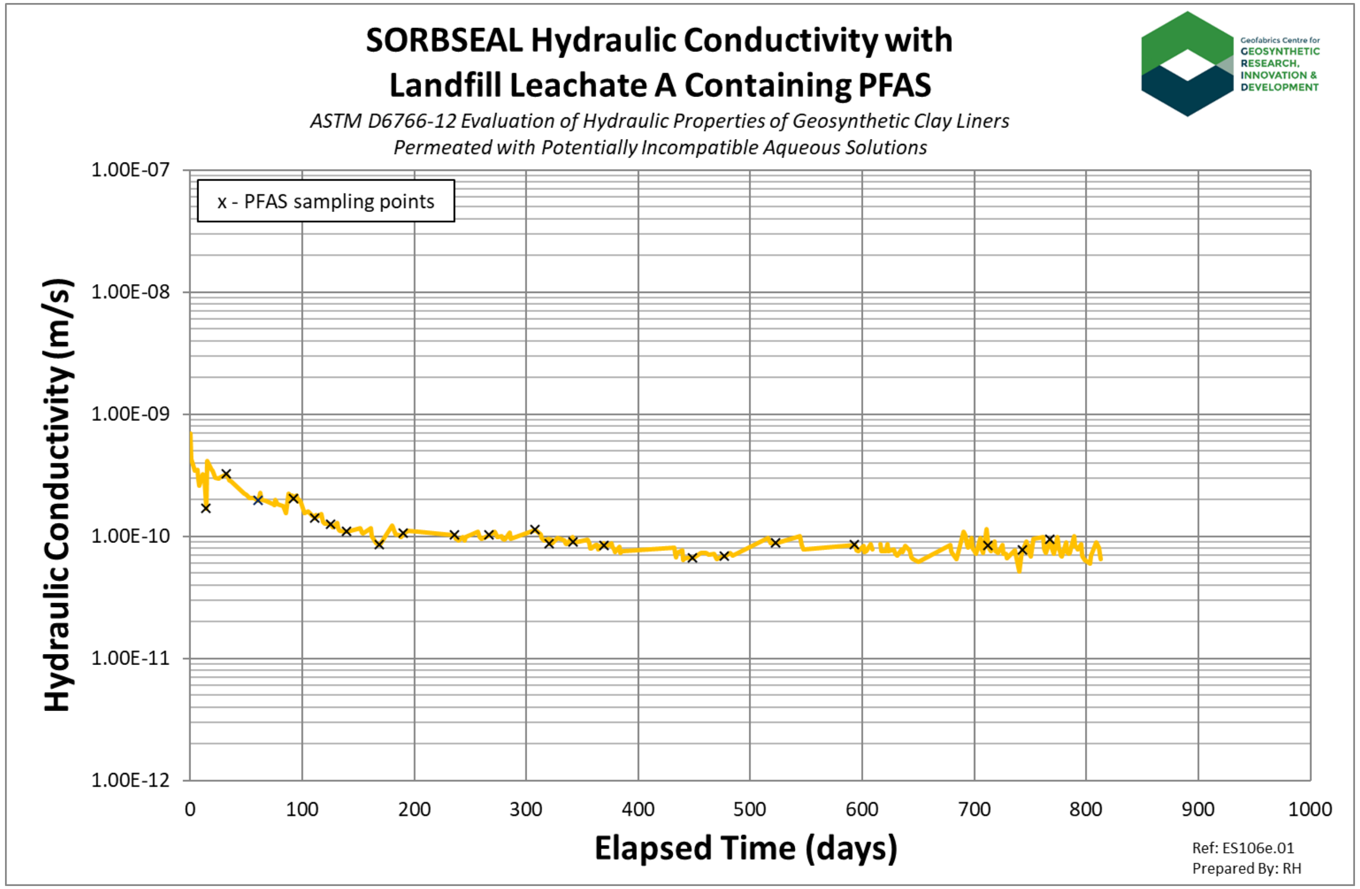
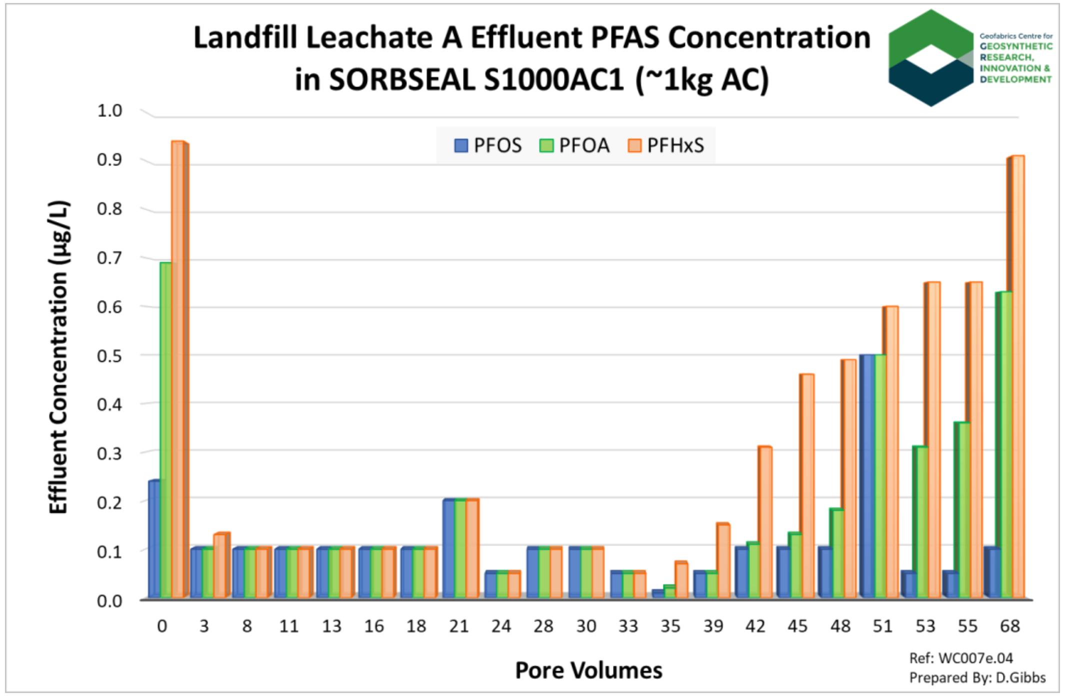
h-GCL Performance

Long Term Testing Leachate A





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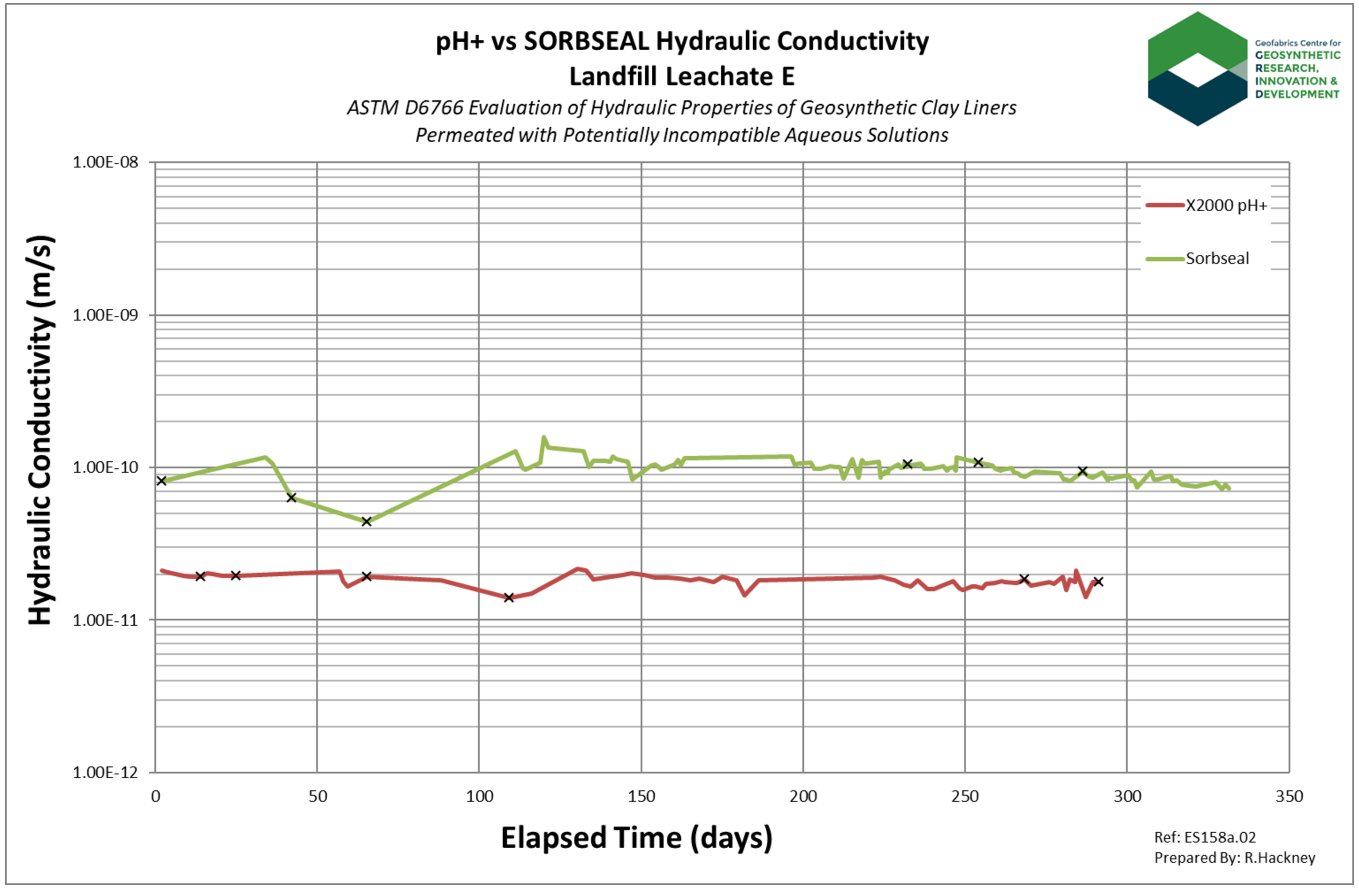
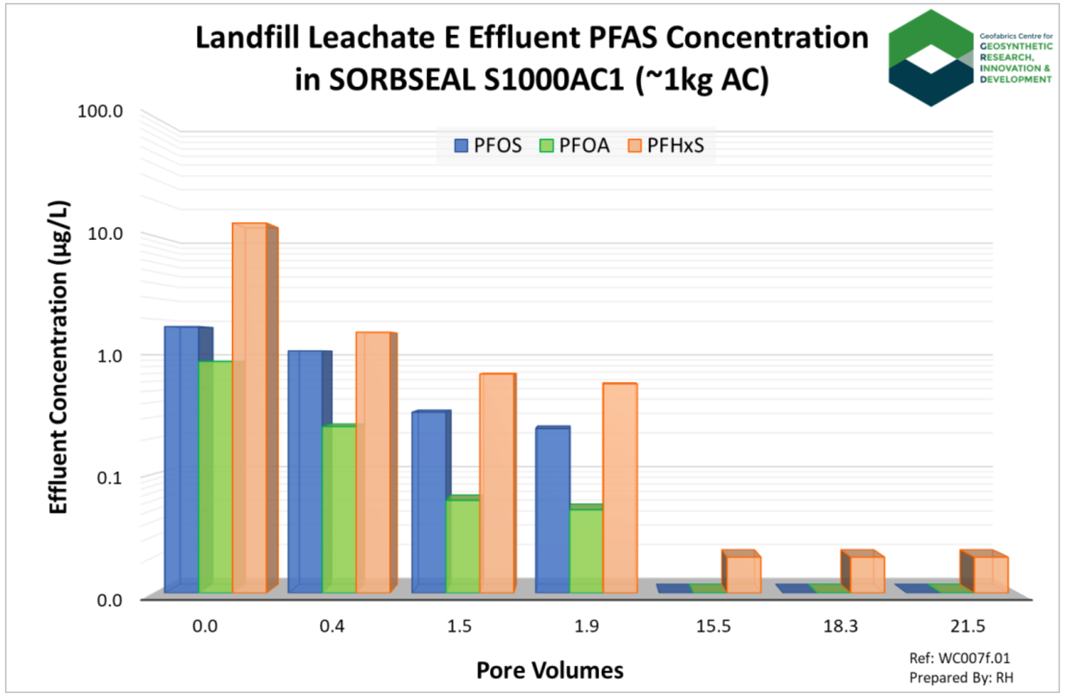
h-GCL Performance

Long Term Testing Leachate E





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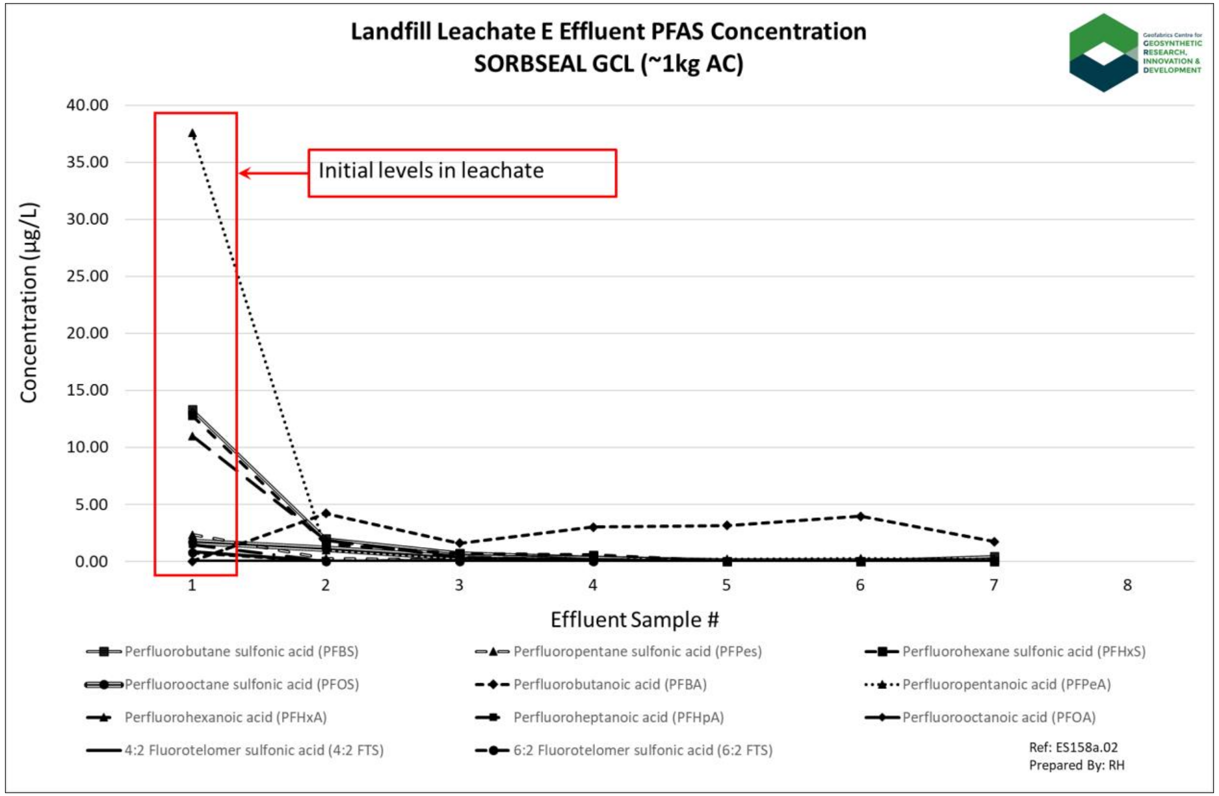
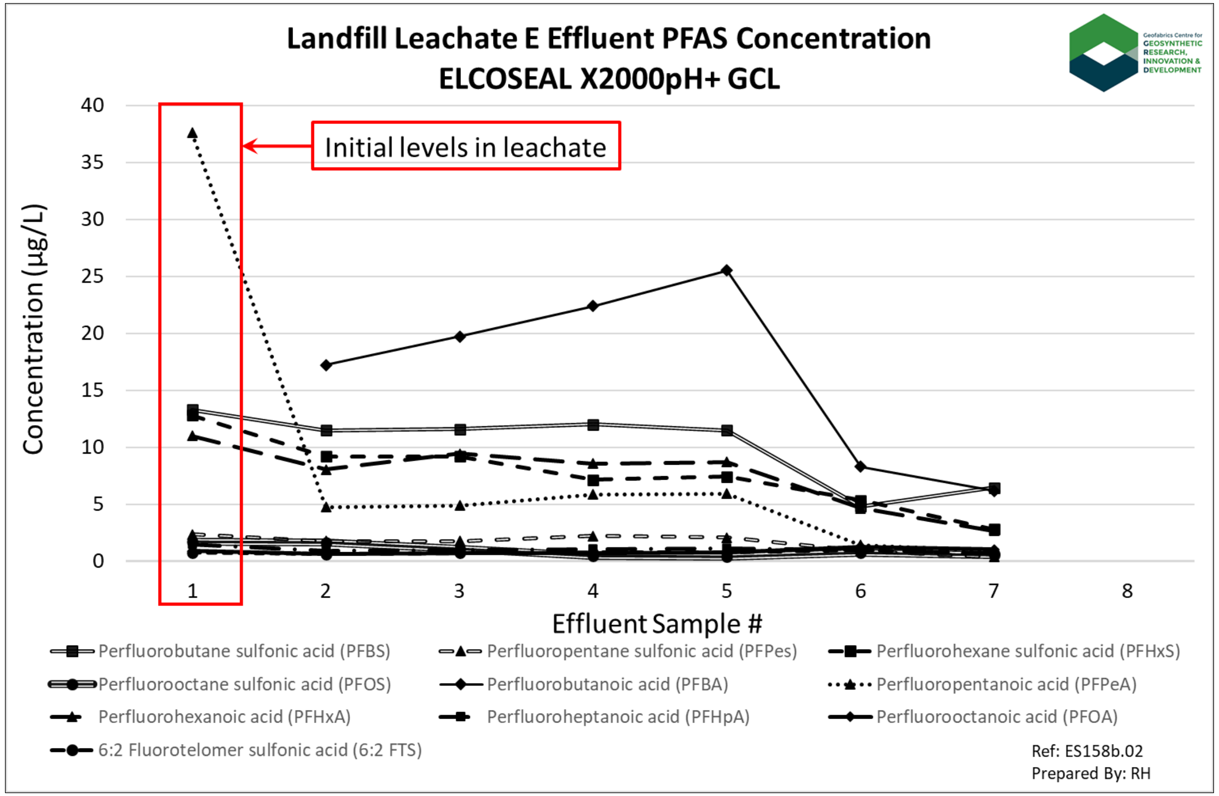
h-GCL Effluent Database

Long Term Testing Leachate E





h-GCL Development

Large Scale Production Trials

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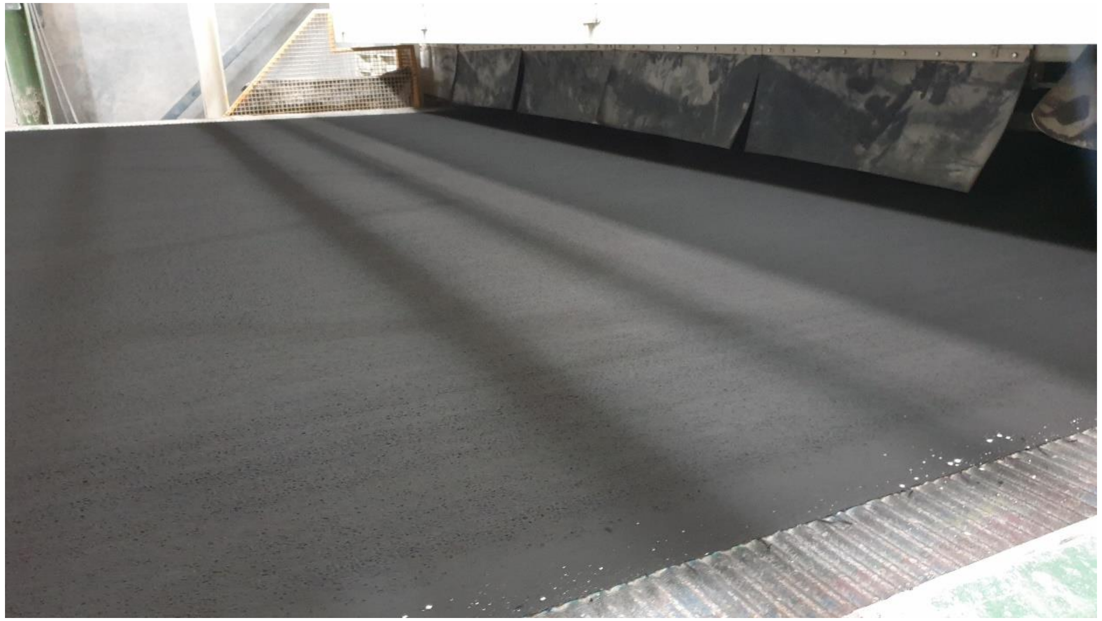

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h-GCL Development

Patent

- A provisional patent is covering this product at present, with the full patent filed and is pending public release

1

MINERAL-BASED GEOSYNTHETIC LINER

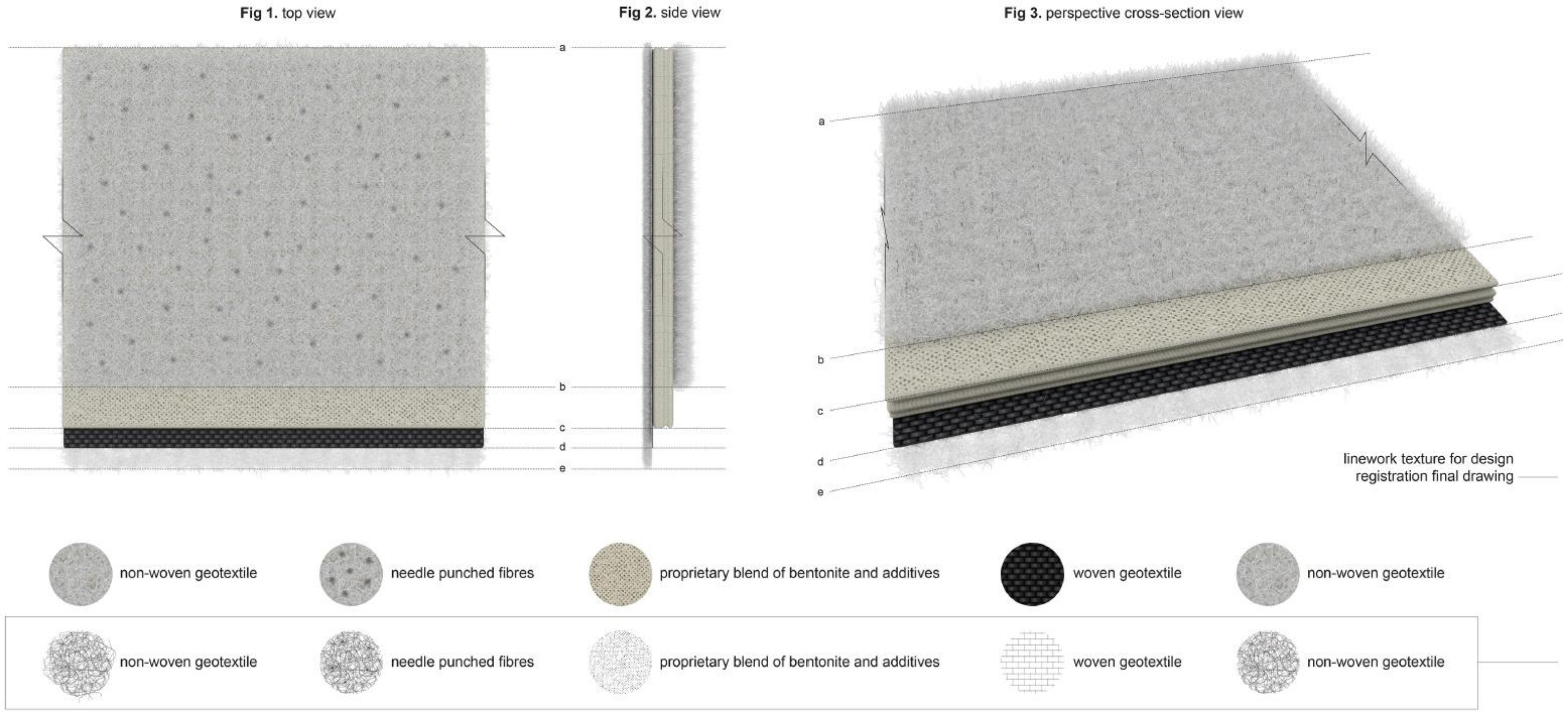
Technical Field

[0001] The present invention is broadly directed to a mineral-based powdered mixture for application in the attenuation of hazardous ground contaminants. The invention also generally relates to a geosynthetic liner and method of forming a geosynthetic liner having a mineral-based powdered layer including at least activated carbon being effective in attenuating hazardous ground contaminants.

Background

[0002] Conventional Geosynthetic Clay Liners (GCLs) are primarily used for containment of liquids. The bentonite core is typically comprised of a high-swelling, low permeability sodium bentonite (natural sodium or sodium-activated) which is sandwiched between two geotextiles. GCLs are used in a wide variety of engineering applications such as basal lining and capping of landfills and waste containment structures as well as in effluent ponds and tailings dams. They are also used in water storages such as dams and ponds as well as canals and irrigation channels. GCLs are used wherever it is desirable to restrict the passage of liquids into the subgrade.

[0003] GCLs have more specifically been used in an attempt to contain hazardous ground contaminants including polyfluoroalkyl substances (PFAS) and their precursors. PFAS are a group of man-made chemicals which have been used since the 1950's in household and industrial products that resist heat, oil, stains, grease and water, including non-stick cookware, food packaging and Aqueous Film Forming Foams (AFFF) used to fight liquid fuel fires. Due to their effectiveness in fighting fires, they were used extensively in Australia at Defence sites and airports up until around a decade ago. These chemicals, and their precursor chemicals are persistent, both in humans and the environment, have the potential to bio-accumulate and biomagnify through the food chain, have been suggested to have deleterious effects on human health over time, have a very high solubility in water and, as such, have a high transport potential in soil. Conventional GCLs do not provide an adequate low



h-GCL Production

Upgrading Manufacturing

- +$1.5M invested in upgrading the GCL production line
- 3 large internal hoppers
- 2 micro dosing units
- Blend line
- Automated sampling, core loading and rolling
- Can produce h-GCL with bespoke blends and standard GCL production rates

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h-GCL Development

Technical Data Sheet

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PROPERTY		TEST METHOD	MQC[1] FREQUENCY	VALUE TYPE	UNITS	SORBSEAL GRADE	
						S1000	S2000
Bentonite Properties							
Montmorillonite Content		XRD	100 tonnes	Minimum	%	≥70	
Carbonate Content		XRD	100 tonnes	Maximum	%	≤2	
Bentonite Form[2]		NH_4^+ Exchange	100 tonnes	N/A	-	Na^+	
Bentonite Particle Size (Dry Sieving)		AS 1289-3.6.1	100 tonnes	Minimum	% passing 75µm	≥65	
Cation Exchange Capacity		Methylene Blue	100 tonnes	Minimum	cmol/kg	≥80	
Activated Carbon Properties							
Iodine Number		ASTM D4607	Per batch	Minimum	mg/g	≥1000	
Ash Content		ASTM D2866	Per batch	Typical[3]	%	10	
Moisture Content		ASTM D2867	Per batch	Maximum	%	≤3	
Particle Size (d50)		EN 12902	Per batch	Typical	µm	10 – 30	
Apparent Density		ASTM D2854	Per batch	Typical	g/mL	0.3 – 0.4	
Ball Pan Hardness		ASTM D3802	Per batch	Typical	%	80 – 90	
Bentonite/Activated Carbon Blend Properties							
Free Swell Index		ASTM D5890	50 tonnes	Minimum	mL/2g	≥24	
Fluid Loss		ASTM D5891	50 tonnes	Maximum	mL	≤18	
Geotextile Properties							
Cover Nonwoven Geotextile Mass		AS 3706.1	10,000 m^2	Typical	g/m^2	250	250
Carrier Woven or Woven/Nonwoven Composite Mass		AS 3706.1	70,000 m^2	Typical	g/m^2	110	360
Component Durability (60°C forced air oven for 50 days)		ASTM D5721/D5035	Annual	Minimum	% strength retained	≥65	≥65
Geotextile Configuration (Carrier / Cover)						W / NW[4]	W+NW / NW
h-GCL Properties							
Mass Per Unit Area	Total *h*-GCL Mass @ 0% Moisture Content	ASTM D5993	2,500 m^2	MARV[5]	g/m^2	5,360	5,610
	Bentonite Mass @ 0% Moisture Content	ASTM D5993	2,500 m^2	MARV	g/m^2	4,000	4,000
	Bentonite Moisture Content	ASTM D5993	2,500 m^2	Maximum	%	≤15	≤15
	Activated Carbon Mass @ Typical Moisture Content	Online	Constant	Typical	g/m^2	1,000	1,000
Strength	Strip Tensile Strength MD[6]	ASTM D6768	10,000 m^2	MARV	kN/m	8	10
	Average Peel Strength	ASTM D6496	4,000 m^2	MARV	N/m	360	600
	Hydrated Peak Shear Strength[7] @ 10kPa	ASTM D6243	Periodic	MARV	kPa	30	35
	Hydrated Peak Shear Strength[7] @ 30kPa	ASTM D6243	Periodic	MARV	kPa	50	60
Hydraulic	Hydraulic Conductivity – DI Water	ASTM D5887	40,000 m^2	MaxARV[8]	m/s	5×10^{-11}	
	Hydraulic Conductivity – 0.05M $CaCl_2$	ASTM D6766	Annual	MaxARV	$(m^3/m^2)/s$	1×10^{-07}	
	Edge Sealing Performance	ASTM STP 1308 (Mod.)[9,10]	Periodic	MaxARV	m/s	5×10^{-11}	
Roll Parameters	Roll Mass (Standard Roll Length)	In-house scales	Per roll	Typical	kg	1315	1370
	Standard Roll Dimensions				m	4.7 x 45	4.7 x 45

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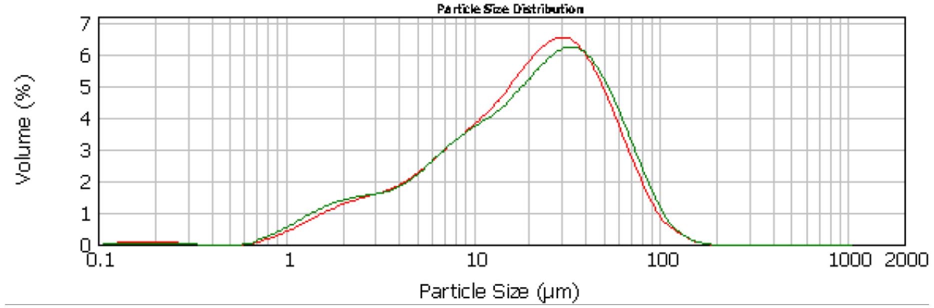
h-GCL Development

AC Technical Data

Activated Carbon Properties					
Iodine Number	ASTM D4607	Per batch	Minimum	mg/g	≥1000
Ash Content	ASTM D2866	Per batch	Typical[3]	%	10
Moisture Content	ASTM D2867	Per batch	Maximum	%	≤3
Particle Size (d50)	EN 12902	Per batch	Typical	µm	10 – 30
Apparent Density	ASTM D2854	Per batch	Typical	g/mL	0.3 – 0.4
Ball Pan Hardness	ASTM D3802	Per batch	Typical	%	80 – 90

- The carbon properties can assist in indicating the origin and quality of the activated carbon
- Density, ash content and hardness can indicate the source of the AC
- The iodine number and particle size relate to the surface area properties of the AC



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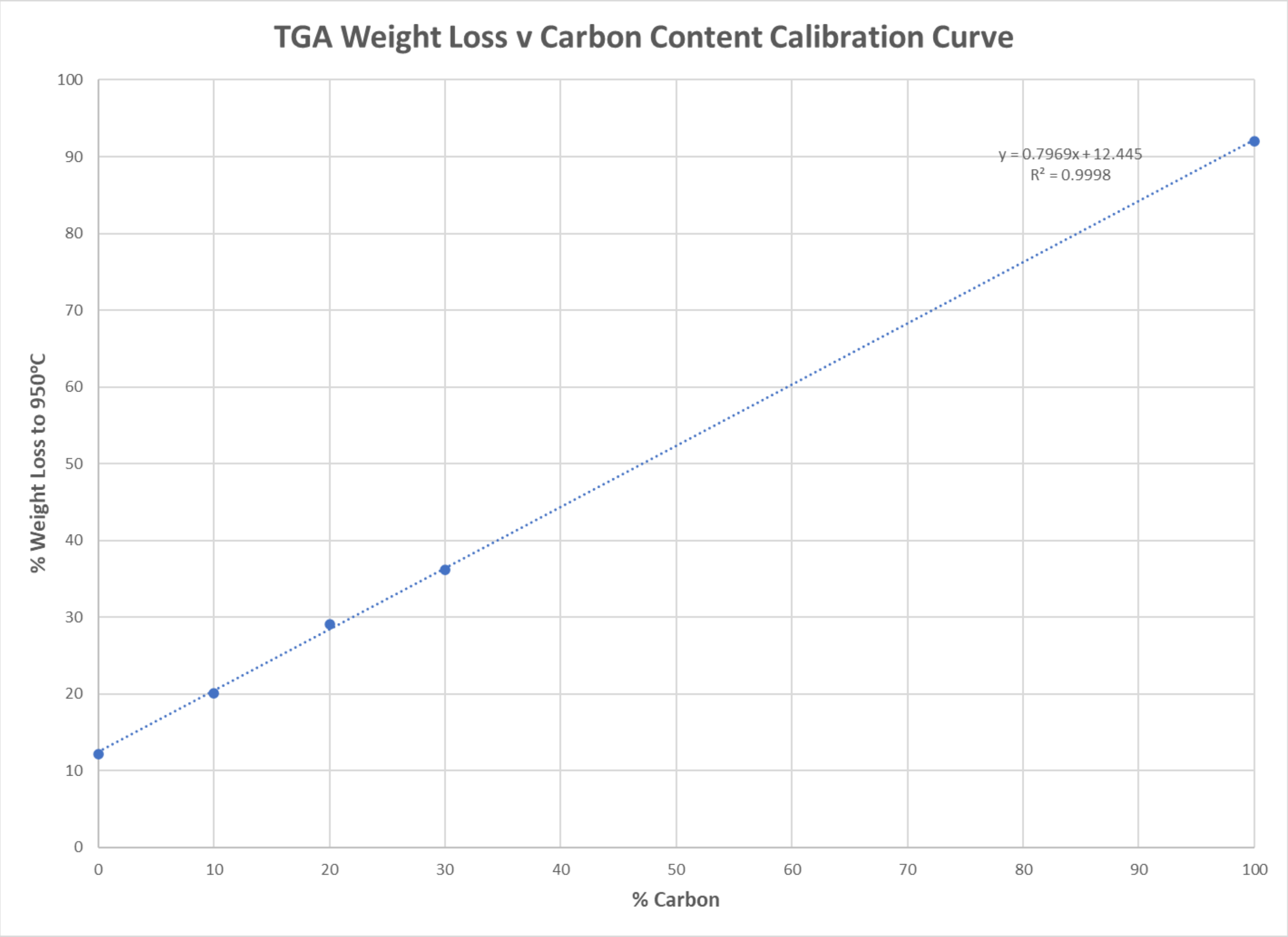
h-GCL Quality Assurance

QA/QC



- % Carbon content of the blend can be quantified by using traditional TGA or Muffle Furnace techniques
- Blends at 0, 10, 20, 30 and 100% carbon have been analysed giving a linear (R^2 = 0.9998) trend of weight loss at 950°C

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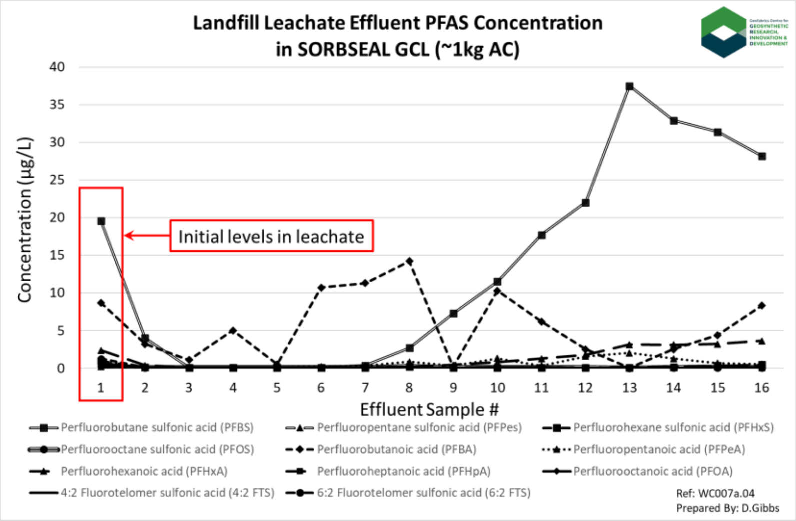
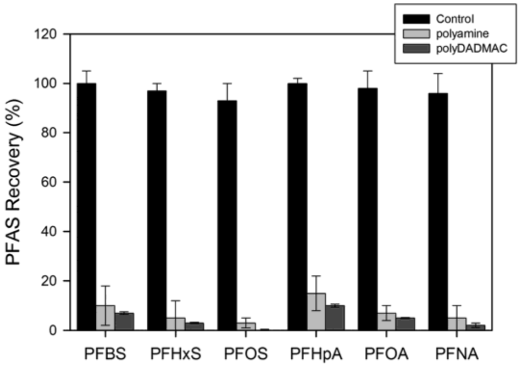
h-GCL Ongoing R&D

Continued Development

- The perfluoroalkyl sulfonates are considered short chain if they have five or fewer carbons, while the carboxylates are considered short chain if they have seven or fewer carbons
- Recent effluent analysis confirms a trend showing breakthrough of perfluorobutanoic acid (PFBA) and perfluorobutane sulfonic acid (PFBS), both of which are short-chain PFAS (C4)
- This led to further research into other options which may assist with removal of short-chain PFAS
  - Ion Exchange Resins
  - Cationic polymers
  - Other minerals
  - Other compounds





Ref: Yousof H. Aly et al. Enhanced adsorption of perfluoro alkyl substances for in situ remediation. Environmental Science: Water Research & Technology 2019, 5 (11) , 1867-1875.

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Summary

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- A hybrid GCL has been developed to assist in the attenuation of PFAS in landfill lining systems in order to protect the surrounding environment
- Each project is supported by laboratory analysis of the site specific leachate including it’s interaction and permeation with the hGCL
- Effluent data demonstrates the effectiveness of the hGCL with the leachate in question
- The hGCL has the same mechanical properties and structure as traditional GCLs
- Ongoing research is been undertaken to attenuate both long and short chain PFAS, but also understand the effectiveness of the ability to attenuate other emerging contaminants

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Thank you

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