IMPROVING GCL CHEMICAL RESISTANCE

The purpose of this technical reference is to discuss chemical compatibility of standard GCLs, and to evaluate the hydraulic performance of two new GCLs, Resistex and Continuum, in contaminated chemical environments.

Background

Sodium bentonite is an effective barrier primarily because it can absorb water (i.e., hydrate and swell), producing a dense, uniform layer with extremely low hydraulic conductivity, on the order of 10^{-9} cm/sec. Water absorption occurs because of the unique physical structure of bentonite and the complementary presence of sodium ions in the interlayer region between the bentonite platelets. Sodium bentonite's exceptional hydraulic properties allow GCLs to be used in place of much thicker soil layers in composite liner systems.

Sodium bentonite which is hydrated and permeated with relatively "clean" water will perform as an effective barrier indefinitely. Past testing and experience have shown that sodium bentonite is chemically compatible with many common waste streams, including Subtitle D municipal solid waste landfill leachate (TR-101 and TR-254), some petroleum hydrocarbons (TR-103), deicing fluids (TR-109), livestock waste (TR-107), dilute sodium cyanide mine wastes (TR-105), and selected coal combustion residuals (TR-347).

Evaluating Chemical Compatibility of Standard GCLs

In calcium- or magnesium-rich chemical environments, the interlayer sodium ions in bentonite can be replaced with cations dissolved in the water that comes in contact with the GCL, a process known as ion exchange. This type of ion exchange reaction can reduce the amount of water that can be held in the interlayer, resulting in decreased swell. The loss of swell usually causes increased porosity and increased GCL hydraulic conductivity. Experience and research have shown that calcium and magnesium are the most common source of compatibility issues for GCLs (Jo et al, 2001, Shackelford et al, 2000, Meer and Benson, 2004, Kolstad et al, 2004/2006). Additionally, brines and seawater can also pose compatibility issues; even though these highly concentrated solutions do not necessarily contain high levels of calcium, their high ionic strength can reduce the amount of bentonite swelling, resulting in increased GCL hydraulic conductivity.

TR-345 discusses CETCO's tiered approach to evaluating GCL chemical compatibility and the associated laboratory test methods. The current industry practice, taken from Kolstad et al (2004/2006), is to use information about the leachate chemistry to predict a GCL's long-term hydraulic conductivity in contact with that leachate. This method uses two chemical properties of the leachate: ionic strength (I) and the ratio of monovalent-to-divalent ions (*RMD*). Ionic strength is an indicator of the total concentration of soluble ions. RMD is an indicator of whether the leachate is calcium-rich or sodium-rich, where lower RMD values indicate higher relative calcium contents. These terms are defined below in equations 1 and 2.

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$$I = \frac{1}{2}\sum_i^n c_i \times z_i^2 \qquad (1)$$

$$RMD = \frac{[Na]+[K]}{\sqrt{[Ca^{2+}]+[Mg^{2+}]}} \qquad (2)$$

If a leachate's *RMD* and *I* are known, they can be plotted on Figure 1, from Kolstad et al, to obtain a prediction of a GCL's expected hydraulic conductivity. In general, increasing the ionic strength of a leachate increases the hydraulic conductivity of the GCL. For a given ionic strength, decreasing the RMD of the leachate results in a higher GCL hydraulic conductivity.

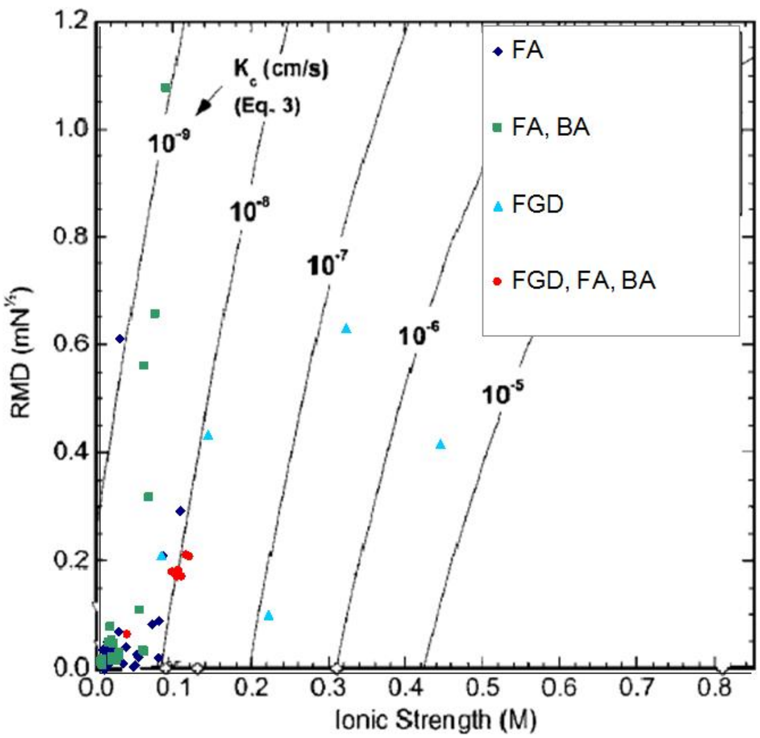

Figure 1. Isoperm chart with anticipated hydraulic conductivities for various CCR leachates (from TR-347)

It is important to note that the Kolstad method outlined above is based on laboratory testing where the GCL was directly hydrated with the salt solutions (i.e., no freshwater prehydration) and testing was performed at a confining pressure of 2.9 psi (representing less than 5 feet of waste). These testing conditions may be overly conservative for certain sites. For example, in situations where the GCL will be deployed on a subgrade soil that is compacted wet of optimum, the GCL will very likely hydrate from the relatively clean moisture in the subgrade (TR-222), long before it comes in contact with the potentially aggressive site leachate. Lee and Shackelford (2005) showed that a GCL which is pre-hydrated with clean water (before being exposed to a harsh solution) is expected to exhibit a lower hydraulic conductivity than one hydrated directly with the solution.

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Another site-specific consideration is confining pressure. Certain applications, such as landfill bottom liners and mine heap leach pads, involve up to several hundred feet of waste, resulting in high compressive loads on the liner systems. Petrov et al (1997) showed that higher confining pressures will decrease bentonite porosity, and tend to decrease GCL permeability. TR-321 shows that higher confining pressures will improve hydraulic conductivity even in contact with aggressive calcium solutions.

Plotted in Figure 1 are the expected hydraulic performances of standard GCLs in contact with various coal combustion residual (CCR) leachates, including fly ash (FA), bottom ash (BA), flue gas desulfurization (FGD) wastes, taken from TR-347. It is apparent that the fly ash and bottom ash chemistries have low RMD values (ranging from 0.01 to 1.1 $M^{1/2}$), but the ionic strength of these leachates is also very low (ranging from 0.01 to 0.1 M). The low ionic strength for the FA and BA wastes would allow for the use of traditional GCL liners since the anticipated hydraulic conductivites are < 10^{-8} cm/sec. Also apparent from Figure 1 is the aggressiveness of wastes that incorporate the FGD waste. The FGD systems were shown to have ionic strengths ranging from 0.08 to 0.45 M and RMD values ranging from 0.05 to 0.6 $M^{1/2}$. The anticipated hydraulic conductivities from these systems ranged from 10^{-8} to 10^{-5} cm/sec, indicating that some FGD leachates, specifically those where sluice water is recirculated to produce highly concentrated solutions, may pose GCL compatibility issues. In these situations, improved clay technologies are needed in order to maintain a low GCL hydraulic conductivity.

The followings sections discuss the new technologies available for improving GCL compatibility in moderately to highly aggressive chemical environments.

Resistex GCL (Dry Blend of Polymers and Bentonite)

The traditional method for improving GCL chemical compatibility is to amend the bentonite with different polymers. Resistex GCL is such a product, where a suite of polymers are dry blended with the sodium bentonite. In this scenario, the polymers help to reduce the effects of cation exchange and elevated ionic strength by swelling, filling the open pore space, and partly offsetting the reduced bentonite swell. The polymer addition allows a low hydraulic conductivity to be maintained in moderately aggressive leachate environments that would normally cause an increase in standard GCL's hydraulic conductivity. Examples of the benefit of Resistex over standard GCLs are presented in Table 1 for various leachate types. The test results in Table 1 were all obtained in the laboratory in flexible wall permeameters per ASTM D6766.

Table 1 shows that amending the bentonite with dry polymer can significantly improve the GCL's hydraulic performance in moderately contaminated chemical environments. However, it should also be noted there is a limit to this benefit, and that in exceptionally contaminated waters, such as the high-ionic strength CCR leachate in Table 1, the polymer-treated bentonite does not provide an improvement over standard bentonite. In these types of situations that exceed the limits of Resistex, an alternate technology is needed.

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Table 1. Hydraulic conductivity comparison between standard GCL and Resistex GCL for various leachate types

Leachate Type	Chemical Data	Prehydration	Standard GCL K (cm/s)	Resistex GCL K (cm/s)
Gypsum Slurry	I = 0.25 M RMD = 0.05 $M^{1/2}$	None	2E-07	2E-09
Diluted Seawater	I = 0.2 M RMD = 1.1 $M^{1/2}$	None	6E-09	1E-09
low-pH uranium mill tailings	pH = 1.9 I = 1.0 M RMD = 1.2 $M^{1/2}$	Prehydrated	> 1E-07	1E-08
Hydrometallurgical mine waste	I = 0.55 M RMD = 0.05 $M^{1/2}$	None	> 1E-07	2E-09
CCR Leachate	I = 1.04 M RMD = 1.67 $M^{1/2}$	None	2E-06	2E-06

Continuum GCL (Bentonite-Polymer Alloy)

The latest GCL technology incorporates a bentonite-polymer alloy (BPA) into the GCL for improved chemical compatibility. BPA is a departure from the traditional dry polymer blends. It is a unique polymer-clay alloy that is created through a proprietary process whereby a water-soluble monomer is polymerized in a hydrated bentonite slurry. Polymerizing the clay and monomer together results in a large distribution of polymer sizes within the clay matrix. On exposure to aggressive leachates the polymer chains are quickly activated since they are less entangled due to their distribution in the clay. The polymers within the clay matrix can quickly interact with bentonite clay particles and each other to provide a tortuous path, which reduces the hydraulic conductivity of the system. Addition information about BPA, and ongoing research at the University of Wisconsin-Madison, is available in Scalia et al (2011).

CETCO's Continuum GCL incorporates the BPA technology. Samples of the Continuum GCL have been tested against several aggressive leachate systems at CETCO's R&D laboratory. Testing is being performed in flexible wall permeameters using ASTM D6766. Tests were performed at low effective stress (5 psi) and with the samples in direct contact with the leachate (i.e., no benefit of freshwater prehydration), simulating the most conservative field conditions. The leachate chemical compositions are shown in Tables 2 and 3. Table 2 shows the chemistry for a high ionic strength/high RMD solution, representative of a concentrated CCR leachate. Table 3 shows the chemistry for a high ionic strength/low RMD solution, representative of a calcium-rich FGD leachate.

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Figure 2 shows the hydraulic conductivities for the CETCO Continuum GCL versus a standard bentonite-based GCL in these two aggressive leachates. For the high ionic strength / high RMD solution, Continuum exhibited a permeability of 1×10^{-9} cm/sec. For the high ionic strength/ low RMD solution, Continuum exhibited a permeability of 5.6×10^{-9} cm/sec. These results represent an improvement of over four orders of magnitude (10,000x) over a standard GCL. Testing continues, and this technical reference will be updated as further data becomes available.

Table 2. Water chemistries for the high ionic strength / high RMD solution.

Chemical	Chemical Formula	Conc (mg/L)	MW (g/mol)	Conc (mol/L)
Calcium Chloride	CaCl2	4,373	111.0	0.039
Sodium Chloride	NaCl	15,887	58.4	0.272
Sodium Sulfate	Na2SO4	19,307	142.0	0.136
Magnesium Chloride Hexahydrate	MgCl2-6H2O	14,719	203.3	0.072
Potassium Sulfate	K2SO4	1,270	174.3	0.007
		Conc (mol/L)	z	cz^2
	Na^+	0.54	1	0.54
	K^+	0.01	1	0.01
	Ca^{2+}	0.04	2	0.16
	Mg^{2+}	0.07	2	0.29
	Cl^-	0.50	1	0.50
	$SO4^{2-}$	0.14	2	0.57
	RMD =	1.67	[I] =	1.04

Table 3. Water chemistries for the high ionic strength / low RMD solution.

Chemical	Chemical Formula	Conc (mg/L)	MW (g/mol)	Conc (mol/L)
Calcium Chloride	CaCl2	55,493	111.0	0.500
		Conc (mol/L)	z	cz^2
	Ca^{2+}	0.50	2	2.00
	Cl^-	1.00	1	1.00
	RMD =	0.00	[I] =	1.50

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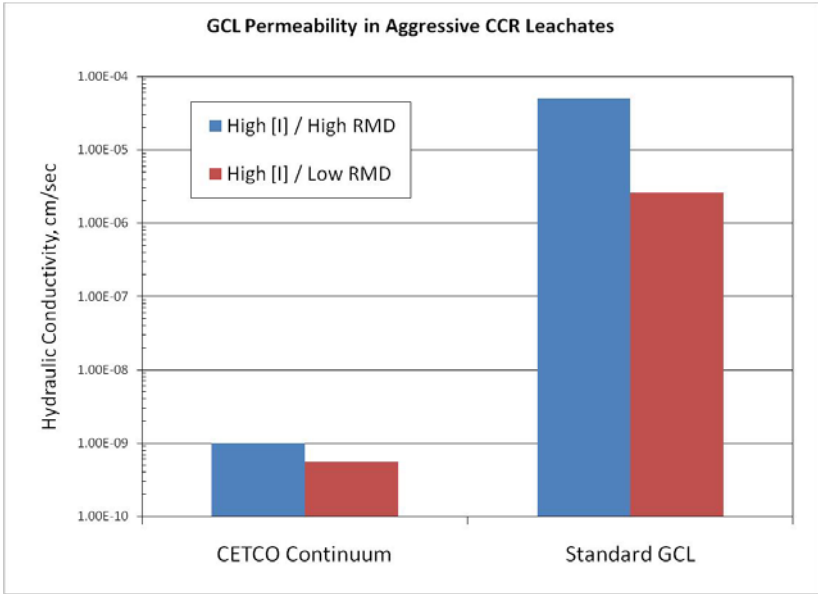

Figure 3. Hydraulic conductivities for CETCO Continuum and standard GCLs in CCR leachates.

Summary
The purpose of this technical reference is to discuss chemical compatibility of standard GCLs, and to evaluate the hydraulic performance of two new GCLs, Resistex and Continuum, in contaminated chemical environments.

Past testing and experience have shown that standard GCLs are chemically compatible with many common waste streams, including Subtitle D municipal solid waste landfill leachate (TR-101 and TR-254), some petroleum hydrocarbons (TR-103), deicing fluids (TR-109), livestock waste (TR-107), dilute sodium cyanide mine wastes (TR-105), and selected coal combustion residuals (TR-347). To address higher strength leachates, such as high ionic strength FGD wastes, CETCO has developed two new engineered clay technologies:

- **Resistex GCL** is produced using dry blends of polymers and sodium bentonite. The polymers help to reduce the effects of cation exchange and elevated ionic strength by interacting with the clay platelets, thereby filling the open pore space, and partly offsetting the reduced bentonite swell. The polymer addition allows a low hydraulic conductivity to be maintained in moderately aggressive leachate environments that would normally cause an increase in standard GCL's hydraulic conductivity. However, there are limits to this benefit – in exceptionally contaminated waters, the dry blends of bentonite and polymer in Resistex may not provide an improvement over standard bentonite.

- For exceptionally contaminated waters, **Continuum GCL**, made with a bentonite-polymer alloy (BPA), can offer improved performance. Polymerizing the clay and monomer together results in a large distribution of polymer sizes within the BPA that readily activate, even in aggressive chemical environments. Laboratory testing of the Continuum GCL in contact with high ionic strength CCR leachates (both low- and high-

RMD) show improvements in hydraulic conductivity of over four orders of magnitude (10,000x) compared to a standard GCL.

For projects where there are questions about GCL chemical compatibility, compatibility testing is recommended. CETCO follows a tiered approach for chemical compatibility testing outlined in TR-345. If a particular site leachate is found to pose compatibility problems with standard bentonite, CETCO can identify possible polymer (Resistex) or BPA (Continuum) technologies to provide solutions targeted to your site-specific leachate. Please contact CETCO Technical Services for additional information.

References

1. ASTM D 6141, Standard Guide for Screening Clay Portion of Geosynthetic Clay Liner for Chemical Compatibility to Liquids.
2. ASTM D 6766, Standard Test Method for Evaluation of Hydraulic Properties of Geosynthetic Clay Liners Permeated with Potentially Incompatible Liquids.
3. Some Aspects of the Properties and Degradation of Polyacrylamides
4. Caulfield, M.J., Qiao, G.G., and Solomon, D.H., (2002), "Some Aspects of the Properties and Degradation of Polyacrylamides" Chem. Rev., 2002, 102 (9), 3067-3084.
5. CETCO TR-101, "The Effects of Leachate on the Hydraulic Conductivity of Bentomat".
6. CETCO TR-103, "Compatibility Testing of Bentomat (Gasoline, Diesel and Jet Fuel)".
7. CETCO TR-105, "Bentomat Compatibility Testing with Dilute Sodium Cyanide".
8. CETCO TR-107, "GCL Compatibility with Livestock Waste".
9. CETCO TR-109, "GCL Compatibility with Airport De-Icing Fluid".
10. CETCO TR-222, "Hydration of GCLs Adjacent to Soil Layers".
11. CETCO TR-254, "Hydraulic Conductivity and Swell of Nonprehydrated GCLs Permeated with Multispecies Inorganic Solutions".
12. CETCO TR-321, "GCL Performance in a Concentrated Calcium Solution; Permeability vs. Confining Stress".
13. CETCO TR-341, "Addressing Ion Exchange in GCLs".
14. CETCO TR-345, "Evaluating GCL Chemical Compatibility".
15. CETCO TR-347, "Chemical Compatibility of GCLs with CCRs".
16. Jo, H., Katsumi, T., Benson, C., and Edil, T. (2001) "Hydraulic Conductivity and Swelling of Nonprehydrated GCLs with Single-Species Salt Solutions", *Journal of Geotechnical and Geoenvironmental Engineering,* ASCE, Vol. 127, No. 7, pp. 557-567.
17. Jo, H., Benson, C., Shackelford, C., Lee, J., and Edil, T. (2005) "Long-Term Hydraulic Conductivity of a GCL Permeated with Inorganic Salt Solutions", *Journal of Geotechnical and Geoenvironmental Engineering,* ASCE, Vol. 131, No. 4, pp. 405-417.
18. Kolstad, D., Benson, C. and Edil, T., (2004) "Hydraulic Conductivity and Swell of Nonprehydrated GCLs Permeated with Multispecies Inorganic Solutions", *Journal of*

Geotechnical and Geoenvironmental Engineering, ASCE, Vol. 130, No. 12, December 2004, pp.1236-1249.

19. Kolstad, D., Benson, C. and Edil, T., (2006) Errata for "Hydraulic Conductivity and Swell of Nonprehydrated GCLs Permeated with Multispecies Inorganic Solutions".
20. Lee, J. and Shackelford, C., (2005) "Concentration Dependency of the Prehydration Effect for a GCL", *Soils and Foundations,* Japanese Geotechnical Society, Vol. 45, No. 4.
21. Meer, S. and Benson, C., (2004) "In-Service Hydraulic Conductivity of GCLs Used in Landfill Covers – Laboratory and Field Studies", Geo Engineering Report No. 04-17, University of Wisconsin at Madison.
22. Petrov, R., Rowe, R.K., and Quigley, R., (1997) "Selected Factors Influencing GCL Hydraulic Conductivity", *Journal of Geotechnical and Geoenvironmental Engineering,* ASCE, Vol. 123, No. 8, pp. 683-695.
23. Scalia, J., Benson, C.H., Edil, T.B., Bohnhoff, G.L., and C.D. Shackelford, C.D., (2011) "Geosynthetic Clay Liners Containing Bentonite Polymer Nanocomposite", Presented at ASCE Geo-Frontiers 2011, Dallas, Texas.
24. Shackelford, C., Benson, C., Katsumi, T., Edit, T., and Lin, L. (2000) "Evaluating the Hydraulic Conductivity of GCLs Permeated with Non-Standard Liquids." *Geotextiles and Geomembranes*, Vol. 18, pp. 133-162.

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