

Effectiveness of a geocomposite liner to diffusion of aromatic hydrocarbons at low temperature

Mukunoki, T.

Kumamoto University

Rowe, R.K.

GeoEngineering Centre Queen's University – RMC, Queen's University

Keywords: GCL, geomembrane, diffusion, hydrocarbons, temperature effect

ABSTRACT: A geocomposite liner composed of a fluorinated high density polyethylene (f-HDPE) geomembrane and a geosynthetic clay liner (GCL) was used to control migration of a hydrocarbon spill from fuel tanks in the Canadian arctic. This paper evaluates the performance of the geocomposite liner materials with respect to the diffusion and sorption of several hydrocarbons. Parameters deduced from diffusion and sorption/immersion tests are then used to predict contaminant migration through the barrier in the field and to comment on its potential effectiveness as a contaminant barrier in this environment.

1 INTRODUCTION

Bathurst *et al.* (2006) reported the use of a composite liner (a fluorinated high density polyethylene geomembrane: f-HDPE GM and a geosynthetic clay liner: GCL) to contain a hydrocarbon spill (Jet A1) at a former Distant Early Warning radar site (BAF-3) located in the Canadian arctic. This barrier, which was constructed in August 2000, is intended to provide temporary containment while a more permanent cleanup is conducted in this remote and hard to access site. The GeoEngineering Center at Queen's University – Royal Military College of Canada evaluated the performance of geocomposite barrier materials both in the laboratory and field for the five years since construction (Rowe *et al.* 2005a).

Since there is permafrost at a depth of 2-3 m, the hydrocarbons are restricted to the shallow active zone which is subzero in the winter and gets to 5–7°C in the summer months. The hydraulic head at the site is very low and since both the geomembrane and the GCL each provide an excellent advective barrier to hydrocarbons at low gradients, the migration of hydrocarbons can be expected to be dominated by diffusion. This is particularly likely to be true for the light and more mobile components such as aromatic hydrocarbons.

This paper uses a 1-dimensional numerical model to evaluate the effectiveness of the geocomposite barrier with respect to diffusion and sorption of benzene, toluene, ethylbenzene, and xylenes (BTEX). A particular focus of this paper is the potential effectiveness of the composite liner as a contaminant

barrier in a cold environment. Details with regard to laboratory testing used to obtain parameters are given by Rowe *et al.* (2005a).

2 MODEL OF BAF-3

2.1 Geocomposite liner

Figure 1 illustrates a design of geocomposite barrier (Bathurst *et al.*, 2006). Construction involved first excavating a trench to permafrost and then placing each liner component on the slope as shown in Fig. 1. The geocomposite barrier was comprised of (from top down) (a) a geotextile (GT) to protect the GM surface from scratching; (b) a fluorinated, f-HDPE, GM, and (c) a needle-punched, thermally treated, GCL with granular sodium bentonite. The contaminated area was covered with a geomembrane ((d) in Figure 1) to minimize infiltration into the contaminated area. Consequently, geocomposite liner was subject to very low hydraulic head.

2.2 Interfacial tension of Jet A1 and water

Jet A1 is categorized as a light non-aqueous phase liquid (LNAPL) and its solubility limit is about 10 mg/L at 20°C. To evaluate the permeability of the GCL with respect to Jet A1, Rowe *et al.* (2005b) performed a series of flexible wall permeameter tests. Figure 2 shows a cumulative inflow volume with a pressure difference of 7 kPa across a GCL specimen for one of these tests. After introduction of Jet A1 and permeation of the water ahead of the hydrocarbon,

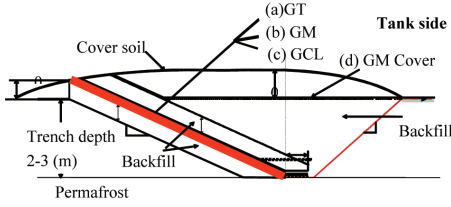


Figure 1. Schematic of geocomposite liner installed at BAF-3 (modified from Bathurst *et al.*, 2006).

the inflow dropped to zero. This arose because the interfacial tension between Jet A1 and pore water exceeded the applied pressure and hence Jet A1 can not permeate into a GCL specimen unless the applied pressure difference exceeds the entry pressure. Given the field conditions, Rowe *et al.* (2005a) concluded that it was unlikely that Jet A1 would permeate through a GCL even if there were no geomembrane and hence the transport of the constituent hydrocarbons would be controlled by diffusion.

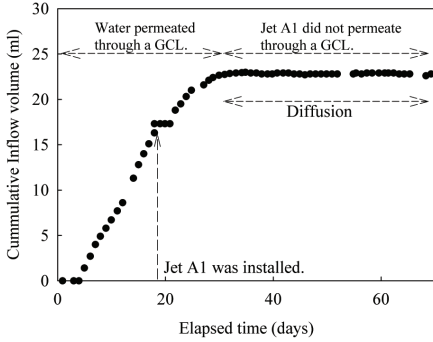


Figure 2. Cumulative inflow volume of Jet A1 into a GCL specimen.

2.3 Mass transport model

As for mass transport in a geocomposite liner, one-dimensional contaminant transport of a single reactive solute through a homogeneous, saturated porous media, with linear reversible sorption and instantaneous equilibrium is described by:

$$n \frac{\partial c_f}{\partial t} = nD \frac{\partial^2 c_f}{\partial z^2} - v_a \frac{\partial c_f}{\partial z} - \rho_d K_d \frac{\partial c_f}{\partial t} \quad (1)$$

where

$$D = D_e + D_{md} \quad (2)$$

c_f is the concentration at depth z and time t [ML^{-3}]; n is the effective porosity [-]; D is the coefficient of hydrodynamic dispersion [L^2T^{-1}]; v_a is Darcy's velocity [LT^{-1}], D_e is the effective diffusion coefficient, D_{md} is the coefficient of mechanical dispersion, ρ_d is dry density [ML^{-3}]; and K_d is the partitioning

coefficient [L^3M^{-1}]. The migration through a geocomposite liner should be dominated by diffusion because v_a , and hence D_{md} , are both zero.

In the transient state, diffusion through a geomembrane is governed by Fick's second law:

$$\frac{\partial c_g}{\partial t} = D_g \frac{\partial^2 c_g}{\partial z^2} \quad (3)$$

where c_g is the concentration in geomembrane and D_g is a diffusion coefficient in geomembrane. According to Henry's Law, there will be partitioning between the hydrocarbon in solution (c_f) and the geomembrane (c_g) described by the partitioning coefficient (S_{gf}):

$$c_g = S_{gf} c_f' \quad (4)$$

Combining Fick's and Henry's laws, diffusion in a geomembrane can be described by:

$$f = -D_g \frac{dc_g}{dz} = -S_{gf} D_g \frac{dc_f'}{dz} \quad (5)$$

where f is the mass flux (Rowe *et al.* 2005a and Sangam and Rowe 2001). The computer program POLLUTE v7 (Rowe and Booker 2004a), was used to solve the governing equations.

2.4 Boundary conditions in BAF-3

Figure 3 illustrates a model based on actual condition as show in Fig. 1. A cover is installed around the fuel tanks (Fig. 1) to prevent infiltration. This combined with the geocomposite barrier will prevent advection through the liner. While there may be a very thin film of neat hydrocarbon on the groundwater surface, the worst case condition for contaminant transport is to assume that the concentration hydrocarbon in the groundwater adjacent to the barrier is at the solubility limit over the entire saturated thickness and remains at this level due to the availability of neat jet fuel. This corresponds to a constant concentration boundary condition at the geomembrane surface. Once Jet A1 diffuses through the geocomposite liner (GM and GCL), precipitation would combine with contaminated pore water accelerating its horizontal movement but also providing dilution.

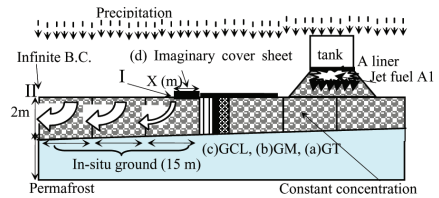


Figure 3. Schematic of problem considered.

Due to the fact that the barrier was on a slope but modeling assumes it is vertical, there was some cut-

off of precipitation over the width of the wall. To take account of this effect, a zone of length X downgradient of the wall (Fig. 3) was assumed to have no precipitation.

Table 1 summarizes the three cases modeled (i.e. no barrier, a barrier with full precipitation adjacent to the barrier ($X = 0$), a barrier but no precipitation for a distance $X = 0.6$ m downgradient of the barrier.

Table 1. Model cases.

Case	Barrier	X (m)
Case 1	No	–
Case 2	Yes	0.0
Case 3	Yes	0.6

2.5 Parameters

An annual infiltration of 0.05 m/a was examined. Dispersion downgradient of the barrier was modeled as indicated in Table 2. The distance between geocomposite liner and the beach is variable, ranging from 15-30 m (Bathurst *et al.*, 2006). To be conservative it was assumed to be 15 m and hence contaminant impact was calculated at two points: Point I was at 0.6 m and Point II at 15 m from the barrier. Table 2 summarizes the other parameters used in this study.

Table 2. Parameters for numerical modeling.

Source concentration	10 mg/L
Thickness of GM	1.5 mm
Thickness of GCL	10 mm
Dispersivity*	$D_{md} = \alpha V_a/n$

* D_{md} = coefficient of mechanical dispersion (D_{md}) in in-situ ground α = Dispersivity: $L^2/100$, $L \leq 100$, L = a length of in-situ ground layer, V_a = the Darcy's velocity [LT^{-1}] and n = effective porosity [–] (Rowe *et al.* 2004b).

3 RESULTS AND DISCUSSION

3.1 Temperature effect of diffusion and sorption

Most published values for diffusion and sorption are for room temperature. However at the field site the summer temperature in the active groundwater zone is only about 5°C. Thus to realistically model transport one needs to estimate parameters for the diffusion of Jet A1 through the composite liner at 5°C. This can be achieved by examining the available data for diffusions and sorption of BTEX compounds at different temperatures and using this relationship together with measured parameters for Jet A1 at room temperature to estimate values for Jet A1 at 5°C. Table 3 shows partitioning coefficients (S_{gf}) of BTEX compounds for an f-HDPE geomembrane at 22 and

Table 3. Partitioning coefficient (S_{gf}) of BTEX for a f-HDPE geomembrane.

Chemical	22°C	5°C
Benzene	33	21
Toluene	114	87
Ethylbenzene	308	214
mp-xylene	339	247
o-xylene	265	184

5°C obtained from sorption tests. S_{gf} at 5°C is 26–44% less than that at 22°C. Rowe *et al.* (2005a) evaluated the effect of temperature on diffusion (D_e) and sorption (K_d) of aromatic hydrocarbons (i.e. benzene, toluene, ethylbenzene and xylenes) for a GCL. In this case the value of K_d for the geotextiles in the GCL at 5°C was 22–44% less than that at 22°C (depending on the contaminant). Likewise, there was a decrease in diffusion coefficient with temperature. Thus the effect of lower temperature is to reduce both the diffusion and partitioning coefficients. These have an opposite effect on mass transfer. Lower diffusion results in reduced mass transport while lower sorption results in more mass transport (other things being equal). However the net effect of a reduction in temperature is a decrease in mass transport though the geocomposite liner (Rowe *et al.* 2005a), demonstrating that the decrease in diffusion coefficient dominates over the effect of the change in partitioning coefficient. Based on the results described above, the diffusion and partitioning coefficients of Jet A1 to a geomembrane at 5°C were inferred to be 40% less than those obtained from the laboratory tests at 22°C (Table 4) and are given in Table 5.

Table 4. Diffusion and partitioning coefficients obtained for Jet A1 from laboratory tests on GM and GCL at 22°C.

	Diffusion coefficient (m^2/s)	Partitioning Coefficient
GM	4.0×10^{-13}	400 (–)
GCL	3.5×10^{-10}	4.4 (mL/g)
In-situ soil	7.0×10^{-10}	0.0 (mL/g)

Table 5. Diffusion and partitioning coefficients deduced for Jet A1 at 5°C.

	Diffusion coefficient (m^2/s)	Partitioning Coefficient
GM	2.4×10^{-13}	240 (–)
GCL	2.2×10^{-10}	2.2 (mL/g)
In-situ soil	4.2×10^{-10}	0.0 (mL/g)

3.2 Effect of the geocomposite liner

Figures 4 and 5 show the calculated variation in the concentration of Jet A1 at two points (I and II; Figure 3) down gradient of the wall. If there is no precipitation, transport by diffusion is very slow and Jet A1 does not reach Point II for at least 100 years. However

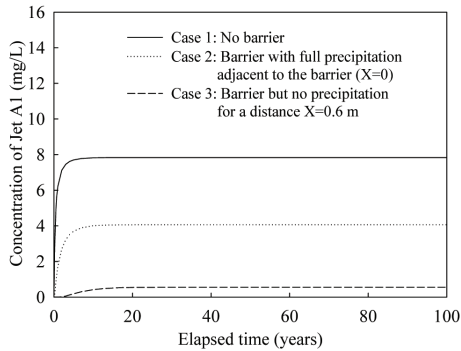


Figure 4. Variation in Jet A1 concentration with time.

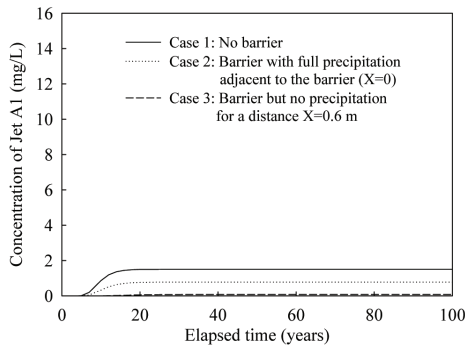


Figure 5. Variation in Jet A1 concentration with time.

there will be some precipitation which will accelerate contaminant transport but also provide some dilution. The concentration at Point I increased to 7.8 mg/L after 10 years for Case 1 (No barrier). Case 2, with the barrier, gave a 48% reduction in the concentration of dissolved Jet A1 compared to the no wall case (Case 1). For Case 3 the reduction (compared to Case 1) was 93% at steady state. At Point II the concentration increased to 86 µg/L after 10 years and 1.5 mg/L after 20 years (Figure 5) for Case 1 (No barrier). For Case 3 the maximum concentration was only 80 µg/L after 100 years.

4 CONCLUSIONS

Numerical modeling of potential contaminant migration through the barrier wall installed at BAF-3 for the anticipated scenario (Case 3) indicate that the concentration of Jet A1 in the groundwater at point I (immediately downgradient of geocomposite barrier) is below 1 mg/L indefinitely. The modeling suggests that the concentration at Point II (15 m from the barrier) only reached 80 µg/L after 100 years. This is considered to be a worst case scenario for the assumed infiltration since much of the year the ground will be at a temperature below 5°C (further slowing diffusion through the barrier). In addition, there is likely to be some biodegradation of hydrocarbons in the soil. This demonstrates that so long as the integrity of the barrier and cover is maintained, the barrier system can be expected to be very effective at controlling the migration of Jet A1 for decades. This is consistent with the observed excellent performance of the barrier system over the past 5 years.

ACKNOWLEDGEMENT

The study was financially supported by the Canadian Department of National Defence.

REFERENCES

- Bathurst, J.R., Rowe, R.K., Zeeb, B. and Reimer, K. (2006) "A Geocomposite barrier for hydrocarbons containment in the arctic", International Journal of Geoenvironment Case Histories 1(1): 18-34.
- Rowe, R.K. and Booker, J.R. (2004a). "Pollute v7", GAEA Technologies Ltd., 87 Garden St, Whitby, Ontario, www.gaea.ca.
- Rowe, R.K., Quigley, R.M., Brachman R.W.I and Booker, J.R. (2004b) "Barrier systems for waste disposal facilities", Taylor & Francis Books Ltd (E & FN Spon) London, 587 p.
- Rowe, R.K., Mukunoki, T. and Sangam, P.H. (2005a) "BTEX diffusion and sorption for a geosynthetic clay liner at two temperatures", ASCE J. Geotech. Geoenviron. Engng 131 (1): 1211-1221.
- Rowe, R.K., Mukunoki, T., Bathurst, R.J., Rimal, S., Hurst, P. and Hansen, S. (2005b) "The Performance of a Composite Liner for Retaining Hydrocarbons under Extreme Environmental Conditions", Geo-Frontiers 2005, Austin, (CD-R).
- Sangam, H.P. and Rowe, R.K. (2001). "Migration of Dilute Aqueous Organic Pollutants Through HDPE Geomembranes", Geotextiles and Geomembranes, Vol. 19, pp. 329-357.