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# Innovative EVOH Geomembranes with VOC and GHG Barrier

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## ABSTRACT

Although Polyolefin geomembranes provide excellent chemical resistance and hydraulic resistivity, they do not offer good diffusive barrier to volatile organic compounds found in municipal solid waste leachate. Typical compounds found in leachate include BTEX, chlorinated solvents and PFAS all of which are considered environmental pollutants and carcinogenic health hazards. As the industry approaches zero leachate leakage rates, the diffusion component of the total mass transport through the geomembrane becomes more significant. Incorporating a thin layer of EVOH into a geomembrane can significantly reduce the diffusion of VOCs through the geomembrane while not adversely affecting the key mechanical properties of the membrane and allowing for the use of traditional deployment and installation techniques. Containment of greenhouse gases is another benefit of EVOH geomembranes when used as landfill covers. Relative to PE, EVOH offers significantly better barrier to methane and carbon dioxide as the main components of landfill gas. Hydrogen sulfide which is emitted from landfills at trace levels causes bad odors that are sensitive to the human nose at ppm levels. California is looking at hydrogen sulfide as a health risk driver for future regulations. EVOH offers substantially better barrier to hydrogen sulfide than HDPE and can provide immediate relief to landfill owners from odor complaints from encroaching neighbors and related lawsuits. The paper will highlight a case study to illustrate how EVOH geomembranes are quickly becoming the best odor management tool for landfills in the U.S.

*Keywords: EVOH geomembrane, VOC barrier, greenhouse gas containment, odor management*

## 1. INTRODUCTION

The waste management industry has over its history been proactive and resourceful in finding ways to contain environmental pollutants resulting from the landfilling of municipal solid waste (MSW). At the bottom of the landfill, geomembranes with electric leak detection, geocomposite clay liners, and compacted clay liners have played major roles in reducing the leakage rate of contaminants in the liquid phase into the surrounding soil and water table. At the top of the landfill, gas extraction systems combined with the use of geomembranes and soil covers help owners manage greenhouse gas emissions.

Traditional geomembranes are made of polyvinyl chloride (PVC), ethylene interpolymer alloys (EIA), flexible polypropylene (fPP), chloro-sulfonated polyethylene (CSPE), linear low density polyethylene (LLDPE) or high density polyethylene (HDPE). These polymers provide excellent mechanical properties, hydraulic barrier, and chemical resistance to MSW leachate. Incorporating a thin layer of ethylene vinyl alcohol (EVOH) into a polyolefin geomembrane can significantly reduce the diffusion of volatile organic compounds (VOCs) through the geomembrane while using traditional deployment and installation techniques. In addition to benzene, toluene, ethylbenzene, and xylene (BTEX), EVOH offers barrier to other contaminants typically found in MSW leachate such as 1,2-dichloroethane (DCE) and trichloroethylene (TCE).

New emerging compounds referred to as per- and poly-fluoroalkyl substances (PFAS) are wreaking havoc with contamination of the environment. PFAS can spread readily in surface and ground water and have maximum concentration values that pose health concerns to human beings in the parts per trillion range. PFAS originates from the manufacturing of non-stick pan coatings, water-repellent fabric coatings, fire-fighting foams, and other man-made goods. Although manufacturers in the U.S. have agreed to phase out the production of PFAS compounds, the recalcitrant and persistent nature of PFAS (forever chemical), their mobility in the environment and the associated human health concerns at environmental levels will pose challenges to environmental engineers for decades to come.

Within the U.S. regulatory framework, prior to 2018, state legislators such as Michigan Department of Environmental Quality (DEQ) took the initiative to establish surface water and underground water action thresholds at 13 parts per trillion (ppt) and 70 ppt respectively. In the summer of 2018, the U.S. Environmental Protection Agency (EPA) awarded several grants to various research institutes to develop methods to mitigate PFAS contamination in the environment. In December 2021, EPA finalized the fifth unregulated containment monitoring rule. In November 2022, EPA released a report documenting the Agency's first year of progress under the PFAS Strategic Roadmap to research exposure, restrict further contamination of the environment, and remediate contaminated sites. The report also proposed designation of two PFAS as CERCLA hazardous substances, actions taken which will expand PFAS testing nationwide by requiring monitoring for 29 different PFAS in drinking water.
As of October 2022, Northeastern University's public PFAS tracker documents 1,784 contaminated sites in the U.S. The database shows that the average PFAS contamination level of the sites is 131,500 ppt. All 50 states are affected, and PFAS contamination ranges from the ppt level to as high as 3.3%. Of the total number of documented sites, 547 (31%) of them are landfills. Globally, Australia, New Zealand, Germany, Italy, and The Netherlands have reported numerous cases of concern that far exceed the health limits.

Neighborhood encroachment of MSW landfills in urban areas leads to neighborhood complaints from drifting bad odors. Hydrogen sulfide ($H_2S$) is a particularly noxious gas that has a very low threshold to the human nose and is often the dominant contributor to the odor issues. Odor issues are more prevalent during the warmer spring/summer months. An accepted indicator of elevated landfill temperature is the inversion of themethane to carbon dioxide ratio from a typical 1.0~1.2 to a ratio that is less than 1.0. In several cases the odor issues lead to neighbor complaints that can escalate to class action lawsuits between a municipality or a state and the landfill owner.

## 2. DESIGN OF AN EVOH GEOMEMBRANE

EVOH geomembranes may be manufactured by direct coextrusion via a multilayer blown (annular die) film or cast (flat die) film. The multilayer die technology combined with the excellent thermal and viscosity stability of polyolefins and EVOH allow the manufacturing of multifunctional composites in a single coextrusion step. A typical coextrusion line for EVOH has at least five layers where the core layer is EVOH, the EVOH layer is encapsulated by two adhesive or "tie" layers that are chemically compatible with EVOH and physically compatible with two skin polyolefin layers. The geomembrane may alternatively have seven or more layers where the additional layers add design flexibility to further optimize the overall properties of the multilayer composite.

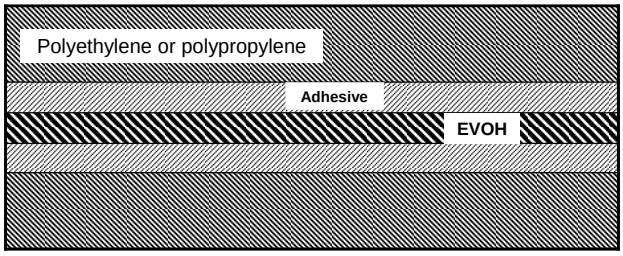



***Figure 1.*** *Model of an EVOH Geomembrane*

The manufacturing process and raw materials used to make EVOH geomembranes are more sophisticated than those that are used to make traditional polyolefin geomembranes. The new equipment and material innovation results in a higher manufacturing cost to the geomembrane manufacturer that must be offset by a higher selling price. In the final version of this paper, this section will detail how the price premium of EVOH geomembranes can quickly be offset by the reduction in neighbor complaints that have been reported by owners that have adopted EVOH geomembrane technology early.

Alternatively, EVOH geomembranes may also be fabricated by laminating a barrier geofilm to a traditional geomembrane without EVOH. Furthermore, Chow and Koerner (2014) show that EVOH geomembranes may be seamed using conventional techniques including solid wedge, dual track, and extrusion welding.

## 3. PHYSICAL PROPERTIES OF AN EVOH GEOMEMBRANE

The physical properties of a geomembrane are a critical performance requirement so the effect of EVOH inclusion on properties of the model geomembranes is of significant interest. Armstrong and Chow (2012) fabricated prototypes and studied the key physical properties of monolayer HDPE and coextruded model HDPE/tie/EVOH/tie/HDPE geomembranes. The model coex geomembranes had a target structure outlined in Table 1. The reference monolayer sample was produced using Marlex K306 at a target thickness of 1.5 mm. The testing of the physical properties was conducted by Chevron Phillips Chemical Co. LP.

***Table 1.*** Model coextruded geomembrane structure

| Layer | Polymer | Resin | Thickness (μm) |
|---|---|---|---|
| 1 | HDPE | Marlex K306[a] | 687 |
| 2 | Adhesive Tie | Admer GT6E[b] | 50 |
| 3 | EVOH | EVAL F171B[c] | 50 |
| 4 | Adhesive Tie | Admer GT6E | 50 |
| 5 | HDPE | Marlex K306 | 687 |
| Total | | | 1524 |

[a] 0.937g/cc, 12g/10min HLMI (190ºC/21.6kg) PE, [b] 0.92g/cc, 1.0g/10min MAh-LLDPE, [c] 1.19 g/cc, 1.8g/10min, 32mol% et. EVOH

The coextruded EVOH geomembrane had higher stiffness and puncture energy than the monolayer HDPE geomembrane, while a reduction in elongation at yield and break was observed. The inclusion of EVOH did not significantly reduce or influence either the standard oxidative induction time (OIT) or the high pressure oxidative induction time (HP-OIT) – a summary of key results is presented in Table 2.

***Table 2.*** Physical properties of HDPE monolayer vs. coex model geomembrane

| Properties | Methods | Units | HDPE | HDPE/EVOH/HDPE |
|---|---|---|---|---|
| Tensile Stress at Yield MD | ASTM D6693 (500mm/min) | MPa | 18.9 | 20.4 |
| Tensile Stress at Break MD | ASTM D6693 (500mm/min) | MPa | 34.3 | 24.5 |
| Tensile Elongation at Yield MD | ASTM D6693 (500mm/min) | % | 12 | 9.2 |
| Tensile Elongation at Break MD | ASTM D6693 (500mm/min) | % | 657 | 556 |
| Tensile Modulus | ASTM D6693 | MPa | 651.0 | 827.9 |
| Total Energy for Puncture | ASTM D3763 | N | 667 | 730 |
| Std OIT | | Minutes | 212 | 195 |
| HP OIT | | Minutes | 2374 | 2232 |

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## 4. GAS BARRIER PROPERTIES OF EVOH

As a copolymer of ethylene and vinyl alcohol, different grades of EVOH are produced by varying the amount of ethylene units in the polymer backbone. EVOH is polymerized in a range of 24 to 48 mole percent ethylene or the m units of Equation 1, where m represents the molar content of ethylene and n represents the molar content of vinyl alcohol in the EVOH:

$$– [(CH_2 – CH_2)_m – (CH_2 – CH\text{-}OH)_n] – \quad (1)$$

The lower the ethylene content of EVOH, the higher its barrier properties to gases and organic solvents. The permeability of a select gases through a 32 mol% ethylene EVOH and HDPE is provided in Table 3 normalized to a thickness of 20μm of material per meter square when the permeant gas has a partial pressure of 100% on the source side of the dual cell test apparatus. The permeability of these select gases through 32mol% et. EVOH is three or more orders of magnitude lower than through HDPE.

***Table 3.*** *Gas Permeability of EVOH and HDPE to various gases (ASTM D1434)*

| Gas | 32 mol% et. EVOH | HDPE |
|---|---|---|
| | $cm^3.20\mu m/m^2.day.atm$ (23ºC, 0% relative humidity) | |
| **Nitrogen** | 0.02 | 190 |
| **Oxygen** | 0.25 | 2300 |
| **Sulfur dioxide** | 0.30 | 21840 |

## 5. VOLATILE ORGANIC COMPOUND BARRIER OF EVOH

The effectiveness of a geomembrane against VOCs depends firstly on its hydraulic barrier to liquids particularly when the lining systems are installed with a minimal number of holes. As the geosynthetic industry continues to reduce leakage rate of installed geomembranes, the diffusion of contaminants through the geomembrane becomes more and more significant.

The derivation of the relationship between the mass flux due to diffusive migration and the solubility of the solvent in the polymer is defined by the permeation coefficient. The relationship between the mass flux *f*, the solubility, diffusion, and permeation coefficients ($S_{gf}$, $D_g$ and $P_g$) is given by Equation 2 where $c_f$ is the solution concentration and *z* is the position through the membrane.

$$f = -S_{gf} D_g \frac{d_{c_f}}{d_z} = -P_g \frac{d_{c_f}}{d_z} \qquad (2)$$

McWatters and Rowe (2010) studied the permeation coefficients of benzene, toluene, ethylbenzene, and xylene (BTEX) through thin monolayer EVOH films using double compartment cells for aqueous phase diffusion tests. The source cell was filled with a dilute aqueous BTEX solution where the initial source concentration was approximately 40 mg/l (parts per million; ppm) for *m&p*-xylenes and 20 ppm for the other compounds. The receptor cell was filled with deionized water. Both cells were agitated to maintain a homogeneous concentration. The source and receptor were sampled and measured using gas chromatography until equilibrium was reached. The permeation coefficients of BTEX through low and high ethylene content EVOH (Table 4) were found to be in the order of $10^{-14}$ $m^2/s$.

***Table 4.*** *Partitioning ($S_{gf}$), diffusion ($D_g$) and permeation ($P_g$) coefficients for BTEX through EVOH films*

| Contaminant | 15µm 32mol% et. EVOH | | | 15µm 44mol% et. EVOH | | |
|---|---|---|---|---|---|---|
| | $S_{gf}$ (—) | $D_g$ (x$10^{-15}$ $m^2s^{-1}$) | $P_g$ (x$10^{-14}$ $m^2s^{-1}$) | $S_{gf}$ (—) | $D_g$ (x$10^{-15}$ $m^2s^{-1}$) | $P_g$ (x$10^{-14}$ $m^2s^{-1}$) |
| **Benzene** | 12 | 15 | 25 | 15 | 2.5 | 3.0 |
| **Toluene** | 20 | 10 | 15 | 25 | 1.5 | 3.6 |
| **Ethylbenzene** | 30 | 5 | 38 | 30 | 1.3 | 4.4 |
| **m&p-Xylenes** | 50 | 3 | 63 | 40 | 1.0 | 5.3 |
| **o-Xylene** | 50 | 3 | 58 | 50 | 1.1 | 5.3 |

Chlorinated solvents are also common contaminants found in landfill leachate, near chemical refineries, laundry dry cleaners and in brownfield sites where the quality of the soil has been most likely compromised by to the lack of an adequate chemical barrier. Table 5 compares the permeation of BTEX, trichloroethylene (TCE) and 1,2-dichloroethane (DCE) through a 44 mol% et. EVOH and HDPE. Results show that the permeation coefficient of the chlorinated compounds through EVOH is two to three orders of magnitude lower than the through HDPE (McWatters, 2011).

***Table 5.*** *Permeation coefficients ($P_g$) of Organic Solvents through EVOH and HDPE*

| Contaminant | 44 mol% EVOH | HDPE |
|---|---|---|
| | x $10^{-14}$ $m^2s^{-1}$ | |
| **Benzene** | 3.0 | 1000 |
| **Toluene** | 3.6 | 3000 |
| **Ethylbenzene** | 4.4 | 5000 |
| **m&p-Xylenes** | 5.3 | 6000 |
| **Trichloroethylene** | 6.6 | 3400 |
| **1,2-dichloroethane** | 2.3 | 480 |

Advancements in coextrusion technologies give geomembrane manufacturers the capability to combine the vapor diffusion barrier properties of EVOH with the hydraulic barrier properties of polyolefins. For example, a blown film line equipped with a 5-layer coextrusion die head is used to manufacture a

structure that is represented in Figure 2. The core layer of EVOH is encapsulated by two tie layers that are physically compatible with LLDPE and chemically compatible with EVOH.

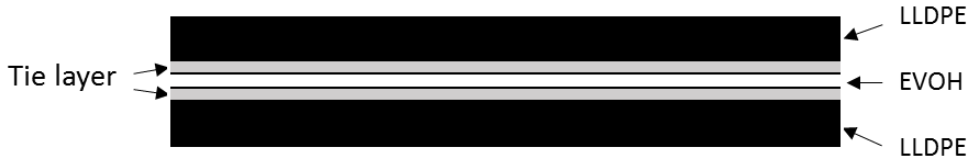



***Figure 2.*** *Schematic of EVOH geomembrane with LLDPE outer layers*

McWatters and Rowe (2010) show that a 0.53mm (20mil) LLDPE/tie/EVOH/tie/LLDPE geomembrane with 4% EVOH has a lower mass transport coefficient of benzene (39x), toluene (37x), ethylbenzene (14x), m&p-Xylenes (19x) and o-Xylenes (20x) versus an LLDPE geomembrane of equivalent thickness tested under the same conditions. Even when compared to a 1.5 mm (60mils) HDPE conventional geomembrane, the 0.53mm (20mils) LLDPE/tie/EVOH/tie/LLDPE geomembrane exhibited lower mass transport of benzene (5.7x), toluene (10x), ethylbenzene (8.9x), m&p-Xylenes (13x) and o-Xylene (9.8x) solvents. The results are summarized in Table 6.

***Table 6.*** *Permeation coefficient ($P_g$) for BTEX for EVOH and Various Geomembranes*

| **Contaminant** | **32mol% EVOH (**15µm**)** | **44mol% EVOH (**15µm**)** | **38mol% EVOH (**21µm**)** | **LLDPE/ EVOH[a]/LLDPE (**0.53mm**)** | **LLDPE (**0.53mm**)** | **HDPE (**1.5mm**)** |
|---|---|---|---|---|---|---|
| | | | $x10^{-14}$ $m^2s^{-1}$ | | | |
| **Benzene** | 25 | 3.0 | 0.90 | 180 | 7000 | 1000 |
| **Toluene** | 15 | 3.6 | 0.85 | 300 | 11000 | 3000 |
| **Ethylbenzene** | 38 | 4.4 | 0.80 | 560 | 8000 | 5000 |
| **m&p-Xylenes** | 63 | 5.3 | 0.80 | 480 | 9000 | 6000 |
| **o-Xylene** | 58 | 5.3 | 0.75 | 410 | 8000 | 4000 |

[a] 38 mol% et. EVOH film removed from the 0.53 mm LLDPE with EVOH GM

In an evaluation of traditional geomembranes, Chow (2016) shows that a 1.0mm PVC geomembrane has the highest BTEX permeation followed by the group of the 0.76mm CSPE, 1.14mm EIA and 0.76mm LLDPE geomembranes. On the other hand, the 1mm HDPE geomembrane demonstrated the best barrier performance of all the polyolefin geomembrane tested. For the sake of comparison, the performance of a thinner (0.53mm) EVOH geomembrane is added for comparison to Table 7. Taking o-Xylene as an example, we note that the permeation coefficient of o-Xylene through the 0.53mm EVOH geomembrane is 156 times lower than the permeation coefficient of o-Xylene through the 1.0mm PVC geomembrane.

***Table 7.*** *Permeation coefficients ($P_g$) of BTEX through traditional geomembranes*

| **Geomembrane Type (mm)** | Coex[a] (0.53) | HDPE (1.0) | LLDPE (0.76) | PVC (1.0) | CSPE[b] (0.76) | EIA1[c] (1.14) | EIA2[d] (0.91) |
|---|---|---|---|---|---|---|---|
| | | | | $x10^{-10}$ $m^2s^{-1}$ | | | |
| **Benzene** | 0.018 | 0.23 | 0.34 | 1.20 | 0.38 | 0.46 | 0.44 |
| **Toluene** | 0.030 | 0.39 | 0.59 | 2.76 | 1.00 | 1.09 | 1.07 |
| **Ethylbenzene** | 0.056 | 0.70 | 1.43 | 5.73 | 1.82 | 1.80 | 2.34 |
| **m&p-Xylenes** | 0.048 | 1.04 | 1.71 | 7.04 | 2.45 | 2.18 | 2.65 |
| **o-Xylene** | 0.041 | 0.72 | 1.62 | 6.41 | 1.97 | 1.91 | 2.55 |

[a] Coex = LLDPE/EVOH/LLDPE with 4% layer of 38mol% et. EVOH, [b] CSPE = Hypalon, [c] EIA1 = XR5, [d] EIA2 = Petrogard VI

Commercial installations have shown EVOH geomembranes offer the excellent durability that we have come to expect from their HPDE only counterparts. McWatters, et.al. (2014) used an HDPE/EVOH/HDPE geomembrane in a research biopile to assess its effectiveness to remediate contaminated soil from a fuel spill at Casey Station, Antartica. After a decade since its installation and exposure to cold temperatures and harsh solar radiation, the EVOH geomembrane is holding well providing the expected superior hydrocarbon barrier versus three other types of geomembranes.

## 6. PERMEATION OF PERFLOUROALKYL SUBSTANCES THROUGH EVOH

Over the past decade EVOH has been used in mulching films to effectively contain fumigants used to control soil-borne pathogens for the cultivation of fruits and vegetables (Chow, 2010). The chemistry of the common fumigants used involves high vapor pressure brominated, sulfonated, and chlorinated

compounds intended to diffuse readily through the soil. In this application a mere 1~2µm layer of EVOH in a 25~30µm PE/tie/EVOH/tie/PE film has allowed growers to reduce fumigant emission dose without sacrificing crop yield and quality. Relative to the performance of prior generation barrier films, EVOH mulch film has been coined as TIF or "Totally Impermeable [Fumigation or Mulching] Films". Extensive lab testing and monitored field trials to measure fumigant emissions and fumigant efficacy led to development of performance-based regulations. The U.S. Environmental Protection Agency (EPA) grant growers that choose TIF the highest buffer zone credits to maximize arable land for farms adjacent to populated buildings. The fumigant barrier performance of EVOH in TIF films led to interest in understanding the permeation PFAS through EVOH.

Two of the most studied PFAS surrogates, perfluorooctanoic acid (PFOA) and perfluoro-octane sulfonate (PFOS) were chosen for the testing. After more than three years of testing by Di Battista et. al (2020), preliminary best estimate $P_g$ values are consistently lower for the coextruded LLDPE/EVOH/LLDPE compared to its LLDPE counterpart. Coupled with high diffusive resistance of EVOH to hydrocarbons, the increase time to detection and lower best estimate $P_g$ values indicate that PE/EVOH/PE geomembranes are superior in reducing the diffusive flux for common landfill contaminants compared to PE alone.

***Table 8.*** *Permeation coefficients (Pg) of PFAS through PE and Coextruded EVOH*

| **Geomembrane** | | **PFOA** | | | **PFOS** | | |
|---|---|---|---|---|---|---|---|
| | Temp. (ºC) | $D_g$[a] ($x10^{-16}$ $m^2s^{-1}$) | $S_g$ (-) | $P_g$ ($x10^{-16}$ $m^2s^{-1}$) | $D_g$[b] ($x10^{-16}$ $m^2s^{-1}$) | $S_g$ (-) | $P_g$ ($x10^{-16}$ $m^2s^{-1}$) |
| 0.1 mm LLDPE | 23 | ≤ 0.09 | 0.9~1.4 | ≤ 0.1 | ≤ 0.06 | 2.8~5.3 | ≤ 0.33 |
| 0.75 mm LLDPE | 23 | ≤ 4.12 | 0.9~1.4 | ≤ 4.53 | ≤ 2.44 | 2.8~5.3 | ≤ 12.9 |
| 0.75 mm LLDPE | 35 | ≤ 4.48 | 0.9~1.4 | ≤ 4.92 | ≤ 3.17 | 2.8~5.3 | ≤ 16.8 |
| 0.75 mm LLDPE | 50 | ≤ 3.50 | 0.9~1.4 | ≤ 3.85 | ≤ 2.61 | 2.8~5.3 | ≤ 13.8 |
| 0.1 mm COEX [c] | 23 | ≤ 0.11 | 1 | ≤ 0.11 | ≤ 0.13 | 1 | ≤ 0.13 |
| 0.75 mm COEX [c] | 23 | ≤ 3.31 | 1 | ≤ 3.31 | ≤ 3.28 | 1 | ≤ 3.28 |
| 0.75 mm COEX [c] | 35 | ≤ 3.55 | 1 | ≤ 3.55 | ≤ 3.5 | 1 | ≤ 3.5 |
| 0.75 mm COEX [c] | 50 | ≤ 3.71 | 1 | ≤ 3.71 | ≤ 3.5 | 1 | ≤ 3.5 |

[a] Based on Sgf = 1.1; [b] Based on Sgf = 5.3, [c] Based on Sgf = 1

## 7. GEOMEMBRANES AS LANDFILL COVER

Landfill gas is 45~50% methane, 45~50% carbon dioxide and small concentration of $H_2S$ hydrogen sulfide, aromatic solvents, chlorinated compounds, mercaptans and other VOCs. The landfill industry manages landfill gas emissions by containing, collecting, and controlling emissions. Cover soil and/or a synthetic geomembrane is used to contain gases. The implementation of gas extraction wells in the 1990s made a significant reduction in the emissions of greenhouse gas emissions from MSW landfills. Finally, emissions may be controlled by flaring or preferably by using the gas for electrical power, compressed natural gas or even pipeline quality gas.

Methane emissions from landfills are a significant source of greenhouse gas emissions in the United States and emission controls that capture landfill $CH_4$ are an effective reduction strategy. Hence, the U.S. EPA recently proposed that new, modified, exiting landfills would begin collecting and controlling landfill gas (LFG) at emission levels nearly one-third lower than current requirements. The proposal is also a part of the U.S. "Climate Action Plan-Strategy to Reduce Methane Emissions." Therefore, methodology to directly control $CH_4$ emissions is warrant for landfill areas that have reached interim or final grades and have not received a final cover. Interim landfill covers help control odor, vermin infiltration, and landfill gas emissions (19-40 Tg/yr) (Bogner and Matthews 2003). One of the methods for interim covers is to incorporate a geomembrane within the interim cover layer (Aitchison 1993; Boeckx et al. 1996).

## 8. METHANE BARRIER OF EVOH GEOMEMBRANES

Eun (2014) found that $CH_4$ diffusion coefficient through an EVOH geomembrane is 170~290 times smaller than through conventional geomembranes.

***Table 9.*** *Diffusion coefficients of $CH_4$ through PVC, LLDPE and EVOH geomembranes*

| **Geomembrane (mils)** | **$m^2/s \times 10^{-11}$** |
|---|---|
| **PVC (30)** | 2.61 |

| | |
|---|---|
| **LLDPE (30)** | 2.35 |
| **LLDPE/EVOH/LLDPE (30)** | 0.012 |

U.S. EPA estimates that greenhouse gas emissions in 2020 were 5981 MMT (million metric tons) of $CO_2e$ ($CO_2$ equivalents).

- By type of gas: $CO_2$ (79%), $CH_4$ (11%), $N_2O$ (7%), fluorinated gases (3%)
- By economic sector: transportation (27%), electricity generation (25%), industry (24%), agriculture (11%), commercial (7%), and residential (6%)
- By industry: natural gas systems (32%), enteric fermentation (27%), landfills (17%), manure management (9%), coal mining (6%), other (9%)

The 2020 GHG emissions by the waste sector are 155.6 MMT CO2e or 2.6% of total U.S. GHG emissions. Emissions by waste operation from landfills (**109.3 MMT**), WWT plants (18.3 MMT), composting (2.3 MMT), biogas facilities (<0.5 MMT). Considering total emission of landfill gas per year, relative to a LLDPE intermediate cover, an EVOH intermediate cover would reduce methane emissions by as much as 15,749MT

***Table 10.*** *Estimated reduction of $CH_4$ emissions with EVOH geomembranes as a landfill cover*

| Geomembrane (mils) | $m^2/s \times 10^{-11}$ | Estimated $CH_4$ Emissions (MT/yr)[a] |
|---|---|---|
| **LLDPE (30)** | 2.35 | 15830 |
| **LLDPE/EVOH/LLDPE (30)** | 0.012 | 81 |
| **Difference** | | -15749 |

[a] Assumptions: 47.5% $CH_4$ LFG concentration, 3000 landfills in the U.S. with an average surface area of 600 acres

## 9. VALUE JUDGEMENT ON NEIGHBOR COMPLAINTS

Hydrogen sulfide is a noxious gas that is known for its characteristic rotten egg odor smell and although it can be found at trace concentrations in landfill gas, it has a very low odor threshold level for the human nose. Furthermore, $H_2S$ is highly toxic, and some states including California are considering $H_2S$ as a human health risk driver for future landfill regulations.

Aside from the distractions from managing landfill operations, landfill owners numerous work hours spent, and expenses incur by owners dealing with odor complaints from encroaching neighbors, operators incur significant expenses related to odiferous gas. Modified sump pump systems, covers on leachate tanks and solidification pits, upgraded gas collection systems, deodorants, synthetic daily covers, thicker intermediate covers, improved monitoring, and in some cases legal fees all can contribute to the bottom line of landfill operators as they manage odors.

Eun (2014) found that $H_2S$ diffusion coefficient through EVOH geomembrane was more than 80~100 times smaller than through conventional geomembranes.

***Table 11.*** *Diffusion coefficients of $H_2S$ through PVC, LLDPE and EVOH geomembranes*

| Geomembrane (mils) | $m^2/s \times 10^{-10}$ |
|---|---|
| **PVC (30)** | 1.06 |
| **LLDPE (30)** | 0.87 |
| **LLDPE/EVOH/LLDPE (30)** | 0.011 |

## 10. CASE STUDY – RUMPKE SANITARY LANDFILL

Rumpke is a family-owned municipal waste landfill that serves a 40-mile radius area that includes Cincinnati and Dayton OH in the U.S. Rumpke has been in business since the 1930s and has approximately 330 acres of built landfill with some other 300 acres available for expansion. In 2020, Rumpke landfill direct hauled and transferred 217,057MT and 291,616MT of MSW respectively.

Following numerous complaints after a subsurface heating event in 2009 in the north end (Phase 5) of the facility, Rumpke installed an Odor Control Blanket (OBC) in 2011. The OBC was a 60mil EVOH geomembrane on 51 acres of the affected phase. A site visit was made in 2017 to get an update on the performance of the geomembrane. Mr. John Butler, Site Engineer, reported that the implementation of the EVOH geomembrane as an intermediate cover had moved them from a constant fire-fighting mode to a maintenance mode.

Mr. Butler explained that “We really don’t have a significant section with HDPE anymore as we used to have many issues with odor breakthrough before we installed the EVOH geomembranes. Since the installation of the EVOH geomembrane, we have not replaced the cover except for some tears due to settlement in the order of 50 feet in hot spots.” He added that “odor complains have gone down from approximately 400 per month to a handful a month (from very particular neighbors).” The description of the smell of the bulk of the remaining complains are consistent with the characteristic smell of the field applied deodorant that has traditionally been used to mask the odiferous gases. The performance improvement was validated in their 2018 Odor Report.

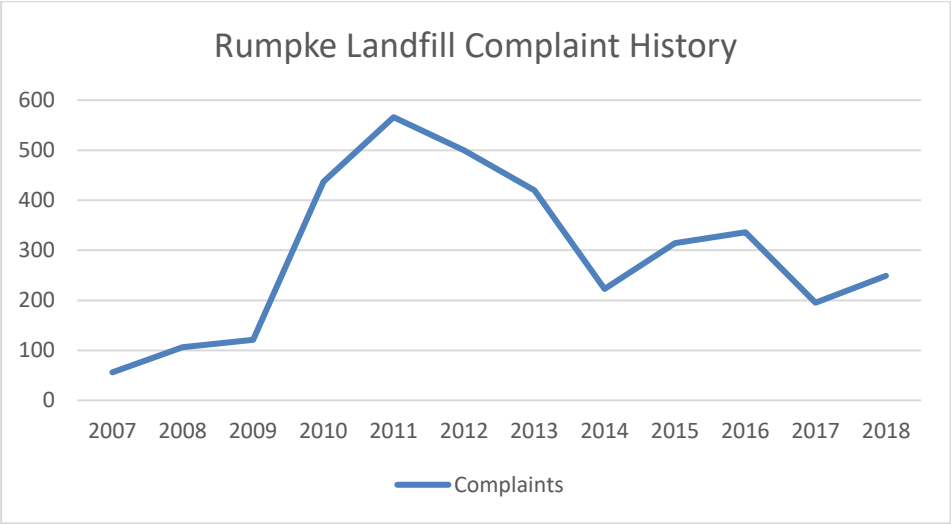



***Figure 3.*** *Odor Complaint History at Rumpke Sanitary Landfill*

Furthermore, Mr. Aaron Abdon, Assistant Operations Manager at Rumpke, stated that the barrier cover makes it easy to locate any incidental tears that might occur from waste settlement.
The visit concluded with Mr. Butler of Rumpke and Mr. Russell Brown of the Ohio EPA being open to conducting field flux measurements on the existing installation and future cover and liner demonstrations that could be done under an R&D exemption existing in the legislation.



***Figure 4.*** *Stakeholders atop the landfill cell with EVOH at the Rumpke Sanitary Landfill*
4(left) Robert Armstrong (Kuraray), Michelle Ackenhausen (Ohio EPA), Russell Brown (Ohio EPA)
4(center) Dr. Jim Tinjum (UW-Madison), John Butler (Rumpke Site Engineer), Gary Kolbasuk (Raven)
4(right) Aaron Abdon (Rumpke), Dr. Craig Benson (UV-Arlington), Edgard Chow (Kuraray)

## 11. EFFECT OF TEMPERATURE ON THE BARRIER OF VOCs AND PHENOL THROUGH EVOH

Like other polymers, elevated temperatures will influence the properties of EVOH. To understand the degree of influence of elevated temperatures on the diffusive barrier to volatile organic compounds through EVOH, sorption and dual cell diffusion studies were compared at 23ºC, 38ºC and 75ºC.

***Table 12.*** *Effect of Temperature on Partitioning and Diffusion Coefficients of Common VOCs Through a Coextruded EVOH Geomembrane*

| | | Partitioning Coefficient (L/kg) | | | Diffusion Coefficient ($cm^2/s \times 10^{-11}$) | | |
|---|---|---|---|---|---|---|---|
| | | **23ºC** | **38ºC** | **75ºC** | **23ºC** | **38ºC** | **75ºC** |
| | Methylene chloride | 7.825 | 10.91 | 15.8 | 0.31 | 0.446 | 0.750 |
| **0.5-mm** | Trichloroethylene | 5.61 | 8.61 | 10.97 | 0.12 | 0.221 | 0.418 |
| **Coex** | Toluene | 5.52 | 7.58 | 9.59 | 0.084 | 0.162 | 0.231 |
| | Phenol | 15.64 | 18.22 | 22.50 | 0.384 | 0.788 | 1.29 |
| | Methylene chloride | 3.38 | 4.32 | 5.24 | 1.01 | 1.30 | 1.66 |
| **1.5-mm** | Trichloroethylene | 69.02 | 74.51 | 84.31 | 0.517 | 0.601 | 0.774 |
| **HDPE** | Toluene | 88.56 | 97.21 | 112.19 | 0.406 | 0.501 | 0.621 |
| | Phenol | 4.951 | 6.25 | 8.94 | 0.699 | 0.840 | 1.02 |

The partitioning coefficients for EVOH increased by 36% as temperature increased from 23 to 35°C and by 82% as temperature increased from 23 to 75°C. The diffusion coefficients increased by 82% and 200% over the same temperature ranges.

The net effect of temperature increase on permeation of the chemical compounds through the HDPE and EVOH geomembrane is summarized on Table 13.

***Table 13.*** *Effect of Temperature on Permeation Coefficients of Common VOCs Through a Coextruded EVOH Geomembrane*

| | | Permeation Coefficient ($cm^2/s \times 10^{-11}$) | | |
|---|---|---|---|---|
| | | **23ºC** | **38ºC** | **75ºC** |
| | Methylene chloride | 2.43 | 4.87 | 11.9 |
| **0.5-mm** | Trichloroethylene | 0.0673 | 1.90 | 4.59 |
| **Coex** | Toluene | 0.0464 | 1.23 | 2.22 |
| | Phenol | 6.01 | 14.4 | 29.0 |
| | Methylene chloride | 3414 | 5616 | 8698 |
| **1.5-mm** | Trichloroethylene | 35680 | 44780 | 65260 |
| **HDPE** | Toluene | 35960 | 48700 | 69670 |
| | Phenol | 3461 | 5250 | 9119 |

The affinity of the hydroxyl group for EVOH results in higher permeation coefficients for phenol. For non-polar compounds HDPE is more sensitive to temperature increases than EVOH. Even at the most severe test condition, the thinner EVOH geomembrane offers two orders of magnitude better barrier to phenol and as much as five orders of magnitude better barrier to VOCs. Overall, the transport of VOCs occurs more rapidly through both EVOH and HDPE when the membrane temperatures are higher.

## 12. CONCLUSION

As a landfill liner EVOH geomembranes offer barrier to VOCs found as typical constituents of MSW landfill leachate including aromatic and chlorinated organic solvents. To demonstrate barrier performance, even when compared to a 1.5mm HDPE conventional geomembrane, a 0.53mm LLDPE/EVOH/LLDPE geomembrane offers six to 13 times better barrier to organic solvents. Furthermore, permeation testing conducted over the last three years indicates that EVOH geomembranes offer remarkable barrier to PFAS compounds. After more than three years of testing, preliminary best estimate permeation coefficients of PFAS are consistently lower for the coextruded LLDPE/EVOH/LLDPE compared to its LLDPE counterpart. Coupled with the high diffusive resistance of EVOH to non-polar and chlorinated compounds, the increased time to detection and the lower best estimate permeation coefficients of PFAS, coextruded PE/EVOH/PE geomembranes offer a more robust environmental protection alternative than PE geomembranes alone.

Complementary to required gas extractions systems, when used as intermediate or final covers, EVOH geomembranes offer substantially better barrier to methane versus Polyethylene only covers. The methane diffusion coefficient through an EVOH geomembrane is 170~290 times smaller than through conventional geomembranes of the same total thickness. As demonstrated by various projects in the U.S. and documented in the Rumpke Sanitary Landfill case, EVOH geomembranes, when used as temporary covers, and possibly as daily covers, provide a cost-effective solution to manage odor complaints from encroaching neighbors for landfills operating in urban areas. Fifty percent reduction of odor complaint incidents translates to a reduction in operating expenses and increase in waste management time that is of tremendous value to the operator.

Coextrusion technology and polymeric material innovations have led to the commercialization of novel geomembranes that combine the hydraulic barrier of polyolefins with the diffusive barrier of EVOH. Coextruded EVOH geomembranes give geotechnical engineers a mitigation tool to deal with regulatory drivers and liability risks associated with emissions of greenhouse gases and the containment of traditional and emerging contaminants found in municipal solid waste landfill leachate.

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