Boyd Ramsey Consulting LLC
9490 FM1960 Bypass West
Suite 200-320
Humble, TX 77338 USA
Phone: +1 281 797 6183
Email: boydramsey@me.com
Web: www.boydramsey.com

Date: July 25, 2020 Title: Containment of PFAS type materials with geomembranes

Introduction:

This paper contains new data and references to additional testing on the permeation of PFAS through geomembrane materials. This testing was (and is) occurring at Queen's University, Kingston, Ontario Canada. The newly reported results are attached and the data and information are summarized here.

Proper storage of waste materials is a landmark of civilized human society. While reduction of waste and increased recycling are clearly essential for continued human life, in the current time and near-term future, humankind needs places to store waste that will not negatively impact sub-surface and ground and surface water quality and the general environment. Traditionally, and generally successfully, this has meant storing waste in engineered and technically designed landfills that are constructed with materials specifically installed to contain the waste and provide a barrier between the waste and the environment. This is generally accomplished with a geomembrane barrier (most commonly polyethylene due to broad based chemical resistance) used in combination with a compacted clay or geosynthetic clay liner.

Polyethylene (generally HDPE, or High-Density PolyEthylene) is used for multiple reasons, but key to the selection and successful performance is the chemical resistance of HDPE geomembranes. However, until recently there has been no direct testing or available data for geomembranes in the containment of PFAS type materials. That changes with the publication of the attached paper: "PFOA and PFOS Diffusion through LLDPE and LLDPE Coextruded with EVOH at 22℃, 1 35℃, and 50℃" authored by V. Di Battista et.al and accepted for publication in *Waste Management*.

Current situation:

PFAS, PFOS and AFFF chemical compounds are nearly ubiquitous in today's world. They have been manufactured for decades and are components in items from firefighting foam for aviation and critical electronic installations to coatings on kitchenware, carpeting and fabrics. While these material types offer useful functionality and utility, in recent years these materials have come under increasing scrutiny, investigation, regulation and concern. The materials have demonstrated extreme environmental durability and are very long-lasting within the earth's ecosystem. The products have been shown to bioaccumulate and several investigations are underway to determine an acceptable level of human exposure and how these types of materials may affect human health and safety.

Known PFAS/PFOS and AFFF contaminated sites are being closed and remediated, however, additional sites of contamination are being found on a recurring basis and need to be managed. The optimum methodology for capture and remediation/elimination of these materials is being investigated. Current best practices include adsorption with activated carbon, possible incineration (following increases in concentration) and other methods of gathering these materials in higher concentration levels. However, even when these types of efforts are successful, what does one do with the now contaminated adsorbents?

“Nature” reported in February 2019, *“…there is the question of what to do with the foam, or carbon filters, that have become concentrated with PFASs. Currently, much of that ends up in landfills. But that just moves the problem, says Knappe. PFASs can migrate out of the filters and seep into the ground with rain and other liquids in unlined landfills, threatening groundwater. Indeed, the multinational manufacturing firm 3M was sued in Minnesota for having “deliberately disregarded the high probability of injury to Minnesota’s natural resources” by landfilling PFAS-contaminated waste, which then leaked into groundwater. The lawsuit was settled for $850 million in February 2018 and did not attribute any legal responsibility to 3M for contamination or injury*.”

This concern extends to lined (geotechnically engineered) landfills as well. It was necessary to establish and publish data on the permeation of these materials through geomembranes and accordingly, through geosynthetic composite liners.

Results and continuing research:

The new information supplied in the Di Battista paper that is commonly used by design engineers is the permeation rate or hydraulic conductivity of geomembranes relative to PFAS. These values are understood and published for water vapor and other chemicals (methyl chloride, halogenated aromatics and others). Over the last two years, a series of permeation tests for PFAS and geomembranes were undertaken at Queen’s University in the laboratories of Dr. Kerry Rowe. His colleague, doctoral candidate Ms. Vanessa Di Battista has conducting the work and a summary is included here as well as the complete publication.

The testing is modelled after ASTM F739 - Standard Test Method for Permeation of Liquids and Gases through Protective Clothing Materials under Conditions of Continuous Contact and is (generically) pictured below.

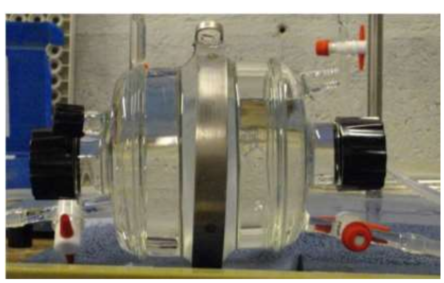

Figure 1: dual cell permeameter (overview) Photo courtesy INRAE

Two cells are separated by a barrier, in this case, the geomembranes that are being evaluated. A contaminate/permeant of interest is placed in one cell and the opposite cell is utilized as a receptor and monitored on regular intervals for the presence and concentration of the contaminate.

Not discussed here, but certainly considered were several test apparatus variables that could possibly introduce unintentional presence of halogenated substances within the testing apparatus.

Multiple geomembrane samples were, and are being evaluated using different thicknesses and temperatures. The geomembranes are of two varieties: one is a Linear Low-Density Polyethylene (identified as LLDPE) material, the other a multi-layer geomembrane utilizing an ethylene vinyl alcohol polymer as a barrier layer (identified as CoEx). The tests are run at a variety of temperatures (22, 35 and 50^{o} C). It is a common practice, as is being done here, to evaluate permeability on thinner samples and use slightly elevated temperatures and extrapolate to real world performance. Two varieties of permeant/contaminate are being evaluated: Perfluorohexane Sulfonic Acid - CAS Number 355-46-4 and Perfluorooctanoic acid - CAS Number: 335-67-1, these are thought to be representative of real world contaminates and can be accurately measured for presence and concentration levels. The concentration levels used for contaminate/permeant introduction are low – 20-30 ppm for several sets of samples and approximately 60 ppb for other additional sets. Quantification is being done using liquid chromatography mass spectrometry measurements with duplicate samples being run to assure accurate and repeatable measures of content.

The following results are taken from the paper. It should be noted that these results will be supplemented as testing is still ongoing.

"For PFOA, CoEx 14 had $P_{g\text{CoEx}} < 0.26\text{x}10^{-16}$ m^2/s at 23^{o}C, $< 11\text{x}10^{-16}$ m^2/s (35°C), and $< 10\text{x}10^{-16}$ m^2/s (50°C) while LLDPE had $P_{g\text{LLDPE}} < 3.1\text{x}10^{-16}$ m^2/s (23˚C), $<13\text{x}10^{-16}$ m^2/s (35°C), and $< 19\text{x}10^{-16}$ m^2/s (50°C). For PFOS, CoEx and LLDPE had $P_{g\text{CoEx}} <0.55\text{x}10^{-16}$ m2/s and $P_{g\text{LLDPE}} < 3.2\text{x}10^{-16}$ m2/s (23˚C), 17 $P_{g\text{CoEx}} <8.3\text{x}10^{-16}$ m^2/s and $P_{g\text{LLDPE}} <40\text{x}10^{-16}$ m^2/s (35°C), and $P_{g\text{CoEx}} < 8.2\text{x}10^{-16}$ m^2/s and $P_{g\text{LLDPE}}$ 18 $<52\text{x}10^{-16}$ m^2/s (50°C)."

These results compared two types of materials LLDPE and CoEx with the CoEx materials demonstrating an improved performance (containment of contaminates) of approximately two orders of magnitude at normal temperatures.

In general, both chemical resistance and permeability are improved (less effect of contaminate chemicals and increased resistance to permeation) with increasing polyethylene density. This is relevant as most technically designed and existing landfills are lined with a HDPE geomembrane barrier contrasted with the LLDPE materials that were tested. LLDPE is commonly used for capping and installations with a lower expected lifespan such as contaminated soil containment.

Summary and Conclusions:

Testing has been completed, identifying permeation coefficients for two geomembrane types against two types of PFAS chemicals. These values can be used by engineers to calculate permeation rates and evaluate effective containment of geomembrane barriers in field installations. This is the first such data to be made available for specific PFOA/PFOS compounds.

The testing clearly indicates that the standard of practice for PFAS type containment is the use of multilayer (Ethylene vinyl alcohol) containing geomembranes, offering a two order of magnitude improvement in barrier properties.

Finally, it should be noted that a potential strategy that may be most appropriate at this time is one of mitigation rather than remediation. Covering contaminated areas, even those with footprints of 20 or more hectares is often a reasonable and best-practice plan for eliminating additional water intrusion and minimizing or halting the spread of some contaminates/sites. This option merits consideration.

References:

Buck, R.C., (2001), "Perfluoroalkyl and Polyfluoroalkyl Substances in the Environment: Terminology, Classification, and Origins", Integrated Environmental Assessment and Management — Volume 7, Number 4—pp. 513–541.

Chao, K.P., et.al. (2006). "Estimation of Diffusion Coefficients and Solubilities for Organic Solvents Permeation through High-Density Polyethylene Geomembrane". Journal of Environmental Engineering 132(5) DOI: 10.1061/(ASCE)0733-9372(2006)132:5(519).

DiBattista, V., Rowe. R.K., Patch, D. and Weber, K. (2020) PFOA and PFOS Diffusion through Geomembranes at Multiple Temperatures, Waste Management (as accepted on 15/7/20).

Haukåsa, M. et.al, (2007), "Bioaccumulation of per-and polyfluorinated alkyl substances (PFAS) in selected species from the Barents Sea food web", Environmental Pollution, Volume 148, Issue 1, July 2007, Pages 360-371.

McWatters, R. S. and Rowe, R. K. (2009), "Transport of volatile organic compounds through PVC and LLDPE geomembranes from both aqueous and vapour phases". Geosynthetics International, 16, No. 6, 468–481. [doi: 10.1680/gein.2009.16.6.468]

Rowe, R.K., et.al., (1995), "Diffusion of Chloride and Dichloromethane Through an HDPE Geomembrane", Geosynthetics International, Vol. 2, No. 3, pp. 507-536.

Tainted water: the scientists tracing thousands of fluorinated chemicals in our environment. (2019, February 6). Nature. Retrieved from https://www.nature.com/articles/d41586-019-00441-1, on November 13, 2019.

Touze-Foltz, N., et.al. (2016). Diffusion of phenolic compounds through two high-density polyethylene geomembranes after 17 years under different exposure conditions. Geosynthetics International, 23, No. 5, 381–393. [http://dx.doi.org/ 10.1680/jgein.16.00004]