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Date: January 8, 2020 Title: Containment of PFAS type materials with geosynthetics

Introduction:

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. Global standards for these barrier materials have a great deal of commonality. Most waste is stored above a geosynthetic composite liner, comprised of 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. HDPE geomembranes are unaffected by pH extremes, acids, bases, oxidizing and reducing agents, and most common chemicals. However, there is a small family of a particular type of chemical that does interact with HDPE geomembranes: low molecular weight halogenated materials. These types of materials, characterized by ethylene dichloride, dichloromethane and other chemicals, will penetrate the HDPE geomembranes at a higher rate than other types of chemicals. Exposing an HDPE geomembrane to low molecular weight halogenated materials will cause the geomembrane to swell in volume and physical properties and barrier performance will change.

With this background we now consider the containment of family of chemicals generally identified under the names PFAS (per and polyfluoroalkyl substances), PFOS (perfluorooctane sulphonate) and aqueous film-forming foam (AFFF).

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.

PFAS/PFOS and AFFF contaminated sites are being closed and remediated. 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. While there is some data available on the permeation rates of chemicals similar in structure to PFAS/PFOS/AFFF, there is no published data on the permeation of these materials through geomembranes or geosynthetic composite liners. Given the chemical structure and biological behavior (or lack thereof) of PFAS/PFOS/AFFF materials there is a reasonable need to determine how they will interact with geomembranes and geosynthetic composite barriers. Further, there are other geomembrane materials which are commercially available today and used in the fumigation and agricultural arena that may provide a better, less permeable geomembrane barrier.

Ongoing research:

The missing information 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). To that end, a series of permeation tests for PFAS and geomembranes are underway at Queen's University, Kingston, Ontario, Canada in the laboratories of Dr. Kerry Rowe. His colleague, doctoral candidate Ms. Vanessa DiBattistas is conducting the work.

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.

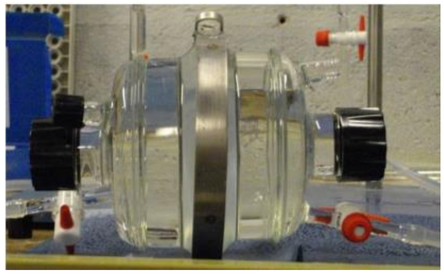

Figure 1: dual cell permeameter (overview)

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 (LLDPE) material, the other a multi-layer geomembrane utilizing an ethylene vinyl alcohol polymer as a barrier layer. There is a need to reach a compromise between the response time of the test and the use of commercial thickness materials. The tests are also being 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 typical 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 are initial results and observations. It should be noted that these results are not yet complete and testing is ongoing. Dr. Rowe and his associates will publish the results in a peer-reviewed professional journal when they are complete or sufficient data exists to support publication in this fashion. The testing was initiated over a year ago.

At this writing, some of the samples have begun to exhibit “breakthrough”, that is the presence in the receptor cell of levels of previously absent contaminates at measurable levels. This has occurred first in the thinner (LLDPE) material samples being evaluated at elevated temperature. Breakthrough has not yet occurred for the geomembranes utilizing ethylene vinyl alcohol polymer as a barrier layer.

Initial estimates of the permeation coefficients of the LLDPE geomembrane materials are in the range of 10^{-15} to 10^{-17} meters^2 /sec. As breakthrough has not yet occurred for the geomembranes utilizing ethylene vinyl alcohol polymer as a barrier layer estimated permeation coefficients are not available. These values can be compared to an established permeation value of 10^{-11} meters^2 /sec for benzene through LLDPE materials. 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.

Additional Activities and Conclusions:

This testing is currently ongoing; however, the conclusion of these tests is likely sometime in the relatively distant future. Lacking historical data, it is a reasonable decision to attempt to store PFAS/PFOS/AFFF contaminated materials in geotechnically engineered and geosynthetic lined landfills. This is clearly the best option to follow at this time, and consistent with the available information. However, it is important to complete this testing and establish “complete” permeation coefficients for PFAS/PFOS/AFFF type chemicals through polyethylene geomembranes. The information presented here, while incomplete, does at least offer insight on real data that can support engineering hypothesis and guide disposal decisions. Further, this testing has, initially, and will continue to supply information that can be used to estimate the effectiveness of containment and confirm the performance of the type of geomembrane that can supply the best practice barrier performance for the future containment efforts.

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.

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