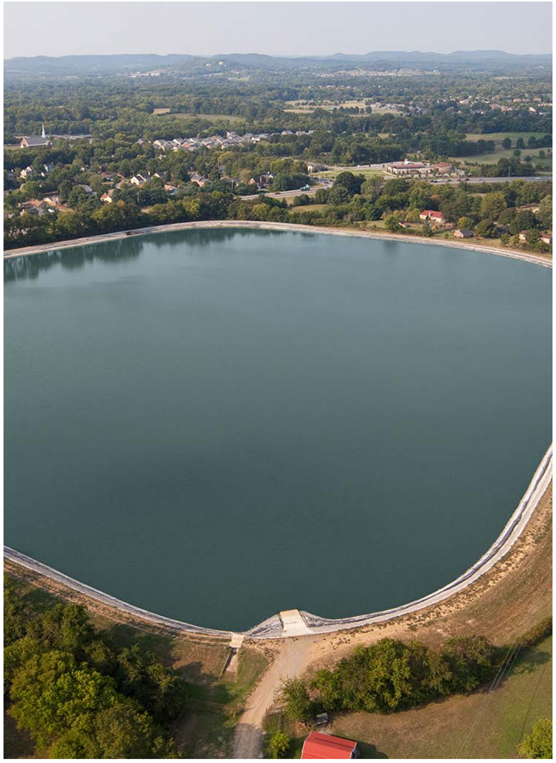
WHITEPAPER

PFAS: Geomembrane Use with Per- and Polyfluoroalky Substances

XR GEOMEMBRANES
By Seaman Corporation

INTRODUCTION

It is not difficult to find information about PFAS compounds. Per- and Polyfluoroalkyl Substances are toxic and now discovered to be widespread to the point they are termed “ubiquitous“, essentially meaning everywhere. Everywhere includes drinking water. PFAS are very stable, bioaccumulative, and toxic, resulting in an additional descriptor, “uPBT” (ubiquitous Persistent, Bioaccumulative and Toxic). In 2019, we published a document called “Application of Geomembranes in the Management of PFAS”, which was a state-of-the-art summary. With PFAS becoming more important as an environmental hazard, this whitepaper is an update, as much has changed in the industry since 2019.



In This Paper:

SOURCES OF PFAS

PFAS compounds have been used since 1940 in a variety of common applications. One of the notable uses was for firefighting foams, where the properties of PFAS along with surfactants functioned very efficiently as a two-part extinguisher, for Type B fires, which included jet fuel, gasoline and other hydrocarbon fuels. These foams were sprayed onto burning aircraft, aircraft mock-ups and other municipal and commercial-type firefighting activities, often without containment of any liquids. The result today is widespread ground and surface water contamination. Because PFAS are somewhat water soluble, they are easily transported, and not easily removed by conventional water and wastewater treatment processes. Having recognized these issues with PFAS compounds, the industry began phasing out their production in the early 2000s, although existing inventories of firefighting foams may still be in the process of being depleted. Additionally, a replacement for the PFAS-bearing firefighting foams (designated Aqueous Fire Fighting Foam, AFFF) was needed. Shorter chain, less toxic, PFAS were initially substituted but the ultimate goal was complete replacement with non-fluorine materials.

REGULATORY UPDATE

On March 14, 2023, the EPA announced the proposed National Drinking Water regulation of six PFAS, including those designed as PFOA and PFOS, generally thought to be the most common. The proposed Maximum Contaminant Level Goals (MCLGs) are zero with a proposed MCL (enforcement level) at 4.0 parts per trillion (ppt) or 4.0 nanograms per liter (ng/l). Four other PFAS are regulated via a hazard index. The rule is expected to be finalized by the end of 2023. These levels are the lowest of any substance regulated in drinking water and are down from the 70 ppt which EPA established as a Lifetime Health Advisory for PFOS + PFOA in May 2016. Several states preceded EPA in establishing MCLs for PFAS, none as stringent as 4.0 ppt, however.

DETECTION AND REMOVAL

An EPA document published April 10, 2023[1] listed facts about PFAS and PFAS management in two categories, with the following being excepts from that document

- **What EPA has learned so far**
  - PFAS are widespread; found in people, animals, water, air, and soil across the nation and globe.
  - They are long-lasting chemicals and break down very slowly.
  - Exposure may be linked to harmful effects in humans and animals.
  - The widespread nature of PFAS makes it challenging to study and assess the potential human health and environmental risks.
- **What EPA doesn't fully understand yet**
  - How to better detect and measure PFAS in air, water and soil.
  - How harmful PFAS are to people and the environment.
  - How to remove PFAS from drinking water.
  - How to manage and dispose of PFAS

While these statements seem a bit uncertain, the industry agrees that information regarding all aspects of PFAS and PFAS management is developing. As of early 2023, EPA has approved two methods of detection in water, EPA Methods 533 and 537.1, which combined detect a total of 29 unique per- and polyfluoroalkyl substances, including PFOA and PFAS. These tests are based on Liquid Chromatography/Tandem Mass Spectrometry (LC-MS).

Techniques for the removal of PFAS from water are also evolving. Most in the industry at this point agree Activated Carbon Adsorption or Ion Exchange have the most promise, with Reverse Osmosis and Ultrafiltration likely being the most effective. Regardless, all these methods are costly on a broad scale.

NEW PRODUCTS TO REPLACE PFAS

The use of AFFF is generally considered the primary source of water contamination. Some areas where the foams were used were lined securely with chemically compatible geomembranes, but many were not. The result is widespread PFAS-contaminated liquids seeping into groundwater, discharging to surface water and/or contaminating soil, air and any other contacted materials. Some geomembranes have been shown to contain AFFF as was outlined in the original 2018 edition of this white paper. From a chemical compatibility and permeation standpoint, most geomembranes function in the presence of the PFAS component of the AFFF. This is, as would be expected, due to the non-reactive, persistent nature of the material. The properties in addition to bioaccumulation and toxicity, are the problems with PFAS compounds and give them their designation as “forever chemicals”. PFAS are large compounds, making their permeability through other substances more unlikely and thus, more cumulative. However, many geomembranes are constructed from polymers that are not chemically resistance to the larger fraction of the AFFF, the surfactants and alcohols[2]. Those combined are as much as half of the AFFF in the concentrated form.

AFFF worked well as a fire suppressant in Type B fires in two ways:

1. The surfactants created a frothy mix of tiny bubbles light enough to sit atop burning fuel, but dense enough to begin to smother it. Surfactants are wetting agents, overcoming the tendency of water molecules to be attracted to each other due to being highly polar and stable. Wetting agents include surfactants, alcohols, soaps and other compounds.

2. The Fluorine in PFAS contains a small electrical charge (surface tension) that repels the fuel, creating a microscopic layer between the surfactant bubbles and the fuel surface. As the liquid drains from the bubbles, this layer is held at the fuel surface by the opposing electrical charge. The fuel is therefore covered, holding vapors and cooling the fuel somewhat.

Using surfactants alone results in the denser liquid (water and surfactants vs. fuel) sinking below the fuel and is less effective than with the Fluorine compound[3].

In the last decade, several PFAS-free firefighting foams (Fluorine Free Foam, F3), have been developed. It seems most have not been completely successful in replacing the firefighting properties of the AFFF as described in no. 2, above. It seems that only the extinguishing effects of the surfactants and alcohols have been retained, resulting in less effective materials with more variabilities, more quantity needed and slower response. The good news is the PFAS is (virtually) gone, while the bad news is the design of a containment system must still consider the chemical compatibility problems for some geomembranes, as discussed later in this paper.

EVOLVING STANDARDS AND SPECIFICATIONS FOR F3 PRODUCTS

To date, the only national standard for F3 concentrate is mil-prf-32725, designated "Fire Extinguishing Agent, Fluorine-Free Foam (F3) Liquid Concentrate, For Land-based Fresh Water Applications[4]. This document was issued as a performance specification by the Department of Defense (DOD) on January 12, 2023. DOD had in the past established an AFFF performance specification, mil- prf-24285.

Some of the highlights of this new F3 specification are as shown below.

- **Not for use with Polar Solvents**
- **3% concentrate, diluted to 100% with water (same as AFFF)**
- **Maximum PFAS content in concentrate of 1 ppb**
- **PFAS detection method is EPA 1633 (LC-MS/MS), not specific on PFAS content.**
- **Specified characteristics are Surface Tension, Interfacial Tension, pH, Viscosity, Foaming characteristics, Corrosion characteristics, BOD/COD ratio**
- **Fire performance (burn back)**

Note EPA Method 1633 applies to a variety of mediums including wastewater and soil, while EPA Methods 533 and 537.1 are specifically for drinking water.

The specification is stated as being an evolving standard as testing and the state of the industry improves. No other industry-wide specifications or standards exist as of Mid-2023, owing to the rapidly growing state of information regarding PFAS management.

DOD is a heavy user of firefighting foams and took the lead in establishing the first technical definition of F3, based on commercial products available at the time.

GEOMEMBRANES TO CONTAIN AFFF AND F3 AT THE POINT OF USE

While the extreme stability of PFAS makes them non-reactive with geomembranes, breaches due to incompatible carrier liquids (surfactants, alcohols), can result in a large amount of leakage. This is a situation analogous to that of PCBs in the late 20th century. PCBs added superior heat-resistant properties to hydrocarbon liquids and were thus carried with the hydrocarbons. While the halogenated compounds (PCBs, PFAS), are stable themselves, the carrier liquids were, and are, often incompatible with some geomembranes (PCB with oils, PFAS compounds with wetting agents). PFAS, however, are as much as 1000x more water soluble than PCBs, which makes positive containment by geomembranes very important.

Stress cracking of polyethylenes in the presence of surfactants is a documented problem that causes damage to the crystalline structure of these materials. Non crystalline geomembranes such as the XR-5 geomembranes have a proven history of contact with surfactants containing PFAS, confirmed by long-term laboratory testing as shown below.

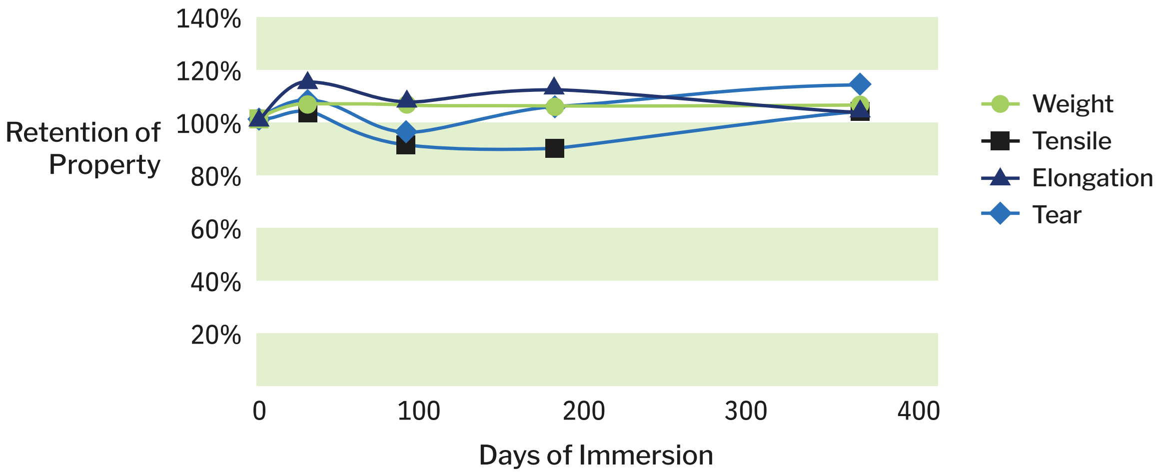


Figure 1 | Compatibility testing of XR-5 Geomembrane with AFFF Concentrate (up to 25% wetting agents)

Geomembranes are successfully used to line areas where foams are expected to be used such as firefighting training areas and other areas known or suspected to have foams applied.

Another consideration is the protection of water supplies from known water or subgrades contaminated with PFAS. Some owners are actively establishing clean water barriers made of surfactant/Alcohol/PFAS resistance geomembranes. An example is the Moose Creek Fuel facility which used the XR-5 Ethylene Copolymer geomembrane as both a fuel storage secondary containment barrier and as a barrier to prevent contaminated groundwater and soil from transmitting AFFF contaminants into the fuel containment area. The chosen geomembrane exhibited long-term chemical resistance and low permeation to wetting agents and jet fuel. The entire case history of the site can be viewed at *XRGeomembranes.com*.

Figure 2 | XR-5 Ethylene Copolymer Geomembrane Lined Jet Fuel Secondary Containment Alaska, USA *[photo source: Latitude 63]*

GEOMEMBRANES TO SUPPORT THE REMOVAL OF PFAS IN DRINKING WATER

On July 5, 2023, USGS released a study that concluded tap water in at least 45% of the homes in the U.S. could be contaminated with one or more PFAS compounds [5]. Coupled with this amount of widespread contamination and the EPA proposed drinking water to remove PFAS will be required very soon. PFAS and associated carrier products will possibly be present in source water and treatment processes up to the point of removal. As has been detailed in other documents[6,7], geomembranes are successfully used in exposed containment of raw water, process and clearwell tankage lining, floated finished water reservoir covers, and diversion baffles. The success of these lining applications is dependent on materials that are high strength with seam strength equal to sheet material strength, thermally stable and resistant to a variety of pollutants.

Figure 3 | Geomembrane Lined Raw Water Storage Impoundment
Tennessee, USA

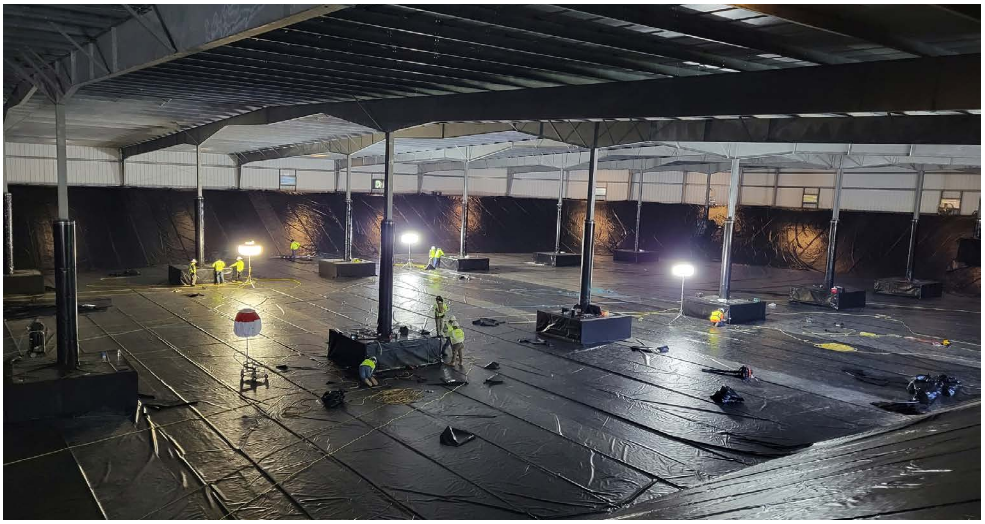


Figure 4 | XR-3 PW Geomembrane Lined Potable Water Storage Tank
North Carolina, USA

Hydraulic control in the drinking water management process will be important as Advanced Treatment becomes more widely used to remove PFAS. In various ways, containing and directing flow and storage is most efficiently done with membrane barriers designed for those operations.

The containment or separation of PFAS-contaminated wastewater or other groundwater has the same considerations for geomembrane containment as potable water.

WHAT NEXT?

A lot of information has been generated about PFAS management in the last several years. There will likely be even more developed, discovered and disseminated in the coming years. What is known is that wetting agents were, and are, a major part of firefighting foams, resulting in containment issues for some geomembranes. Future F3 products will likely continue to rely on those surfactants and alcohols as components. Some geomembranes should not be used in that environment, while the XR series of Potable Water geomembrane (tested by and approved by NSF to Standard 61) have proven to be compatible with PFAS, including the surfactants and alcohols, and has a long history of secure containment.

For an exposed environmental application that requires a long-term, high-performance geomembrane liner or cover, contact a technical expert at ***Seaman Corporation***.

Call ***(800) 927-8578*** for an in-depth consultation, or visit *www.XRGeomembranes.com*.

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