Integrity of HDPE Pond Liner Systems during and after PFAS Flocculation and Stabilization

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ABSTRACT

The class of emerging per- and polyfluoroalkyl substances (PFAS) is a challenge for environmental remediation. In lined ponds with PFAS contaminated water there are several options for treatment, including in situ treatment within the pond. In the case of a lined pond, in situ treatment of the PFAS was proposed via flocculation and subsequent stabilization of dissolved and particle associated PFAS with chemical flocculants. This pond has a high-density polyethylene liner system that could be vulnerable to damage or distress from treatment activities. To evaluate the integrity of the liner system during and after treatment, an integrity testing program was undertaken. After aging in solution, coupons were visually inspected and then mechanically tested for tensile capacity. Both visual inspection and mechanical tensile testing showed that none of the flocculants or other chemical treatment alternatives resulted in significant deterioration of the liner, although high concentrations of one polymer flocculant showed low levels of attack on the liner material.

INTRODUCTION

Per- and polyfluoroalkyl substances (PFAS), a group of thousands of compounds, are emerging contaminants of concern globally. Specifically, two (2) PFAS, perfluorooctane sulfonate (PFOS), and perfluorooctanoic acid (PFOA) are a current focus of the United States (US) Environmental Protection Agency (EPA), which issued a Health Advisory Level (HAL) for drinking water of 70 nanograms per liter (ng/L; either individually or the summation of the two) in 2016. In this paper we assess how HDPE liners react to various treatment options for removing PFAS. This work contributes to a broader case study intended to demonstrate the viability of an innovative technique to remove and treat PFAS from surface water collection ponds. In brief, this approach is to treat contaminated water with a chemical additive, which will subsequently bind PFAS and form floc. The floc will then be removed and treated with stabilizing agents for long term storage or destruction on or off site. Our objective is to ensure that remediation strategies do not harm the pond liner during the treatment process. This is an innovative treatment process, and no other similar treatments were found in the literature.

A pond in Western South Dakota is the focus of this case study. Details have been kept from this paper due to certain confidentiality restrictions on the project for which this study was done, certain parties participating in the research, and the location of the pond. For lack of any additional description details, this pond is simply referred to as “The Pond” in the rest of this paper. The Pond is a surface water retention pond designed to facilitate treatment of contaminated surface water runoff. All flow into The Pond is through a flow structure on the east side of the pond. While The Pond primarily receives stormwater, inflow to the pond is observed during extended dry periods. A V-shaped weir is located approximately 50 meters downstream of pond outlet culverts; however, a stream gage has not been set up to continuously measure gage height, and it does not have a developed rating curve to estimate stream flow. Flow rates and intervals into and out of The Pond is unknown. Water quality has been evaluated in the past, but current contaminant concentrations may be different than previously reported. The Pond is roughly round in shape and increases in depth near the outflow structure (weir). Topography / bathymetry and sediment load for the pond have been evaluated.

The Pond was relined recently with 60-mil High Density Polyethylene (HDPE) geomembranes. These geomembrane sheets were laid along the compacted clay bottoms and side walls of the pond excavation. The sheets were secured to the rim bulwark of the pond with galvanized steel bolts. Seams between sheets were site-welded together using proprietary equipment used by the vendor/installer of the lining. The 60-mil HDPE is designed to be robust against typical pond contaminants and leachates and is used in a variety of geo-environmental applications at other sites such as lining ponds at mineral extract facilities and mines, lining the bottoms of landfill cells, and in containment ponds for fracking. HDPE liners are industry standard due to their good performance against common solvents, fuels, and acids encountered in typical geo-environmental problems. The typical 60-mil HDPE liner will have tensile strength of approximately 16 to 24 MPa, depending on manufacturer, grade of polymer, and aging. Aging of HDPE liners occurs through fatigue loading, thermal cycling, antioxidant depletion, thermooxidative degradation, exposure to ultraviolet light, and exposure to freeze-thaw cycles. The deaggregation of HDPE and chemical aging are described in excellent detail by Rowe (2020). Despite its good performance in typical applications, HDPE is known to be sensitive to exotic organic acids and aggressive solvents. Examples include aromatic hydrocarbons such as toluene or xylene, aromatic ketones, halogenated hydrocarbons, and chlorinated solvents such as trichloroethane or trichlorobenzene. These sensitivities are generally time and temperature dependent, with exposures over 7-days often needed for noticeable damage at temperatures exceeding 20°C (See Rowe et al. 2013 and Hsuan and Koerner 1998). At higher concentrations of chemicals and higher temperature combinations, immediate damage may occur. At lower concentrations and temperatures, damage may occur after 30 days of exposure.

WATER QUALITY

While water quality is not the focus of this paper, it is presented here because we used water from The Pond for liner stability tests, and the various chemicals/compounds/contaminants present in The Pond may affect liner stability with or without treatment for PFAS compounds. To establish baseline contaminant concentrations in The Pond, water samples were assessed for a suite of parameters including: per- and polyfluoroalkyl substances (PFAS), purgeable aromatic compounds, general chemistry parameters, and metals. Twenty-four (24) PFAS compounds were evaluated Pre TOP with EPA 537M QSM5.3, and nineteen (19) PFAS compounds were evaluated Post TOP with Method MLA-111 (Table 1). Secondary reactions creating organic acids may be considered as those organic acids could have an effect on the HDPE liners.

Table 1. Mean PFAS concentration for each sample event. Values shown represent the mean ± standard error for each sample event (Initial Char., Prior to Mixing Event, and During Mixing Event) separated by analytical method (Pre TOP, and Post TIP).

PFAS abbreviation	Pre TOP (E537M_QSM5.3) n = 10		Post TOP (MLA-111) n=15		
	Initial Characterization	During Mixing Event	Initial Characterization	Prior to Mixing Event	During Mixing Event
PFBA	70.7 ± 9.731	84.4 ± 1.009	146.2 ± 15.256	129.4 ± 2.088	113.8 ± 2.396
PFDA	**60.5 ± 10.27 a**	**94.7 ± 0.556 b**	**67.1 ± 12.577 a**	**129.8 ± 4.769 c**	**99.3 ± 4.606 b**
PFDoA	**4.2 ± 0.354 a**	**7.3 ± 0.15 b**	3.2 ± 0.004 U	2.6 ± 0.004 U	4.9 ± 0.964
PFHpA	69.8 ± 10.483	58.6 ± 0.291	92.1 ± 12.734	93.2 ± 1.484	78.9 ± 0.997
PFHxA	197.2 ± 31.018	187.8 ± 1.02	349 ± 46.882	379.2 ± 7.857	308.6 ± 3.172
PFNA	19.4 ± 3.338	22.3 ± 0.284	28.4 ± 3.78	37.4 ± 2.308	29.2 ± 1.478
PFOA	137.6 ± 21.608	131 ± 0.707	159.6 ± 24.521	183.4 ± 4.885	147 ± 3.795
PFPeA	266 ± 45.085	201.8 ± 1.319	375.8 ± 57.288	323.4 ± 9.558	262 ± 3.376
PFTeA	1 ± 0 U	1 ± 0 U	3.2 ± 0.004 U	2.6 ± 0.004 U	2.6 ± 0.007 U
PFTrDA	1 ± 0 U	3.3 ± 1.455	3.2 ± 0.004 U	2.6 ± 0.004 U	2.6 ± 0.007 U
PFUdA	**3.9 ± 0.57 a**	**6.4 ± 0.37 b**	**7.1 ± 1.035 a**	**3.9 ± 0.76 b**	**4.7 ± 0.842 b**
PFBS	17.8 ± 2.366	24.9 ± 0.163	**20.3 ± 2.306 a**	**35.7 ± 1.791 c**	**23.1 ± 1.158 b**
PFDS	1 ± 0 U	1 ± 0 U	8 ± 0.019 U	3.3 ± 0.005 U	3.3 ± 0.008 U
PFHpS	5.7 ± 0.697	6.5 ± 0.093	4 ± 0.006 U	3.3 ± 0.005 U	3.3 ± 0.008 U
PFHxS	97.3 ± 7.448	104.8 ± 0.8	**112.2 ± 11.793 a**	**140.6 ± 1.435 c**	**104.9 ± 3.994 b**
PFNS	1 ± 0 U	1.3 ± 0.39	4 ± 0.006 U	3.3 ± 0.005 U	3.3 ± 0.008 U
PFOS	**357.2 ± 43.227 a**	**494 ± 4.087 b**	**322 ± 35.323 a**	**408.2 ± 11.741 b**	**361.2 ± 16.696 a**
PFPeS	15.7 ± 1.825	19.3 ± 0.255	**18.6 ± 1.862 a**	**30.1 ± 1.459 b**	**20.2 ± 1.448 a**
PFOSA	**11.3 ± 1.728 a**	**17.3 ± 0.136 b**	-	-	-
N-MeFOSAA	3.8 ± 0 U	3.8 ± 0 U	-	-	-
N-EtFOSAA	3.8 ± 0 U	3.8 ± 0 U	-	-	-
4:2 FTS	1.9 ± 0 U	1.9 ± 0 U	-	-	-
6:2 FTS	**12.1 ± 0.703 a**	**18.8 ± 0.312 b**	-	-	-
8:2 FTS	**5.6 ± 0.409 a**	**11.2 ± 0.213 b**	-	-	-
sum PFAS	1352.1 ± 163.523	1494.4 ± 11.038	1697.8 ± 198.96	1892.6 ± 36.335	1555.7 ± 24.671

Significant differences between sample events for each analytical method are indicated in Table 1 with bold and a letter and are valid for the indicated PFAS only within the specified method. Values followed by a U (grey text), indicate that PFAS was undetected in all 5 samples for the particular PFAS compound, sample event, and method.

Co-contaminants include those shown in the Appendix. As The Pond is in an active chemical environment, the chemical profile of the pond water is in constant flux. Sampling at any given day may result in a different profile than if sampled immediately prior to rainfall and runoff into

The Pond, or immediately after said rainfall or runoff event. Thus, water quality and the chemical profile of contaminants were measured at different times. Complicating matters is that The Pond, like most water bodies, contains sediments. These sediments potentially entrap PFAS and co-contaminants, so that the true chemical profile of The Pond would only be known from a treatment perspective, in the case that The Pond was in a mixed state, with sediment suspended. Suspension of sediments would also be essential for treatment, and so a fully mixed water quality state was desired.

To characterize water quality parameters, water samples were collected during three sampling events, Initial Characterization, Prior to Mixing, and During Mixing. The first sampling event occurred in February 2020 and is categorized as Initial Characterization. The second and third sampling events occurred in June 2020 concurrent with an assessment of hydrologic conditions within The Pond. The second sampling event occurred before mixing of the pond and is categorized as Prior to Mixing. The third sampling event occurred while The Pond was being mixed and is categorized as During Mixing. For Initial Characterization, water samples were collected from The Pond, with three samples, and one duplicate collected on February 26, 2020, and two samples one field blank and one equipment blank collected on February 27, 2020. For Prior to Mixing, five water samples were collected on June 2, 2020. For During Mixing, five water samples were collected on June 4, 2020. HDPE membrane testing utilized bulk water collected During Mixing. PFAS data from the Mixing Event and Initial Concentrations are presented in Figure 1, showing that EPA thresholds are in violation and that The Pond indeed needed treatment to remove PFAS.

FLOCCULANTS FOR WATER TREATMENT

Seventeen organic and inorganic chemical additives were evaluated for effectiveness at removing suspended solids and PFAS from pond water with sediment. Full details are not presented here, as the subject of the paper is the HDPE liners. This assessment included 4 phases: Clarification, PFAS removal (PFAS Phase 1), sensitivity analysis for PFAS removal (PFAS Phase 2), and confirmation and optimization for PFAS removal (PFAS Phase 3).

Chemical additives were selected for further evaluation in subsequent phases based on observed floc formation, measured absorbance after 15 minutes of settling, and settling rates. The combination of visible floc formation with faster settling rates and low absorbance (high solid removal) was considered better. In contrast, no floc formation, slow settling rates, and high absorbance (low solid removal) was considered worse.

Chemical additives with the fastest settling rates and the highest solid removal rates were selected for the next stage of testing, PFAS removal. Additives were chosen that were commercially available, designated as generally regarded as safe for human and environmental applications, and have been shown to be effective in solids removal within wastewater and industrial processing.

Ten different cation agents were tested, consisting of iron and aluminum salts, poly (acrylamides), and amine-polymer blends. Along with these, 6 different anionic agents were tested, including low, moderate, and high molecular weight poly (acids). In addition, different combinations of iron-oxyhydroxides were prepared and tested within the process because PFAS may be associated with iron-oxyhydroxide (Li et al. 2018, Anderson et al. 2019, Lyu et al. 2020).

The four (4) chemical additives with the most promising solids removal and thus implied ability to remove PFAS were selected to evaluate their ability to remove PFAS (see Table 2 for the list of additives used in the experimental program). These chemical additives become the crux of this study. Will these additives cause, through primary or secondary chemical reactions, damage to the liner of The Pond? If so, the additives cannot be used for PFAS treatment, no matter how effective in removing PFAS from The Pond. Thus, an experimental program was designed to study the impacts to liner integrity from PFAS removal treatments from these chemical additives. The water-sediment mixture used for this assessment was water collected from The Pond, while pond sediment was entrained during the June 2020 mixing event.

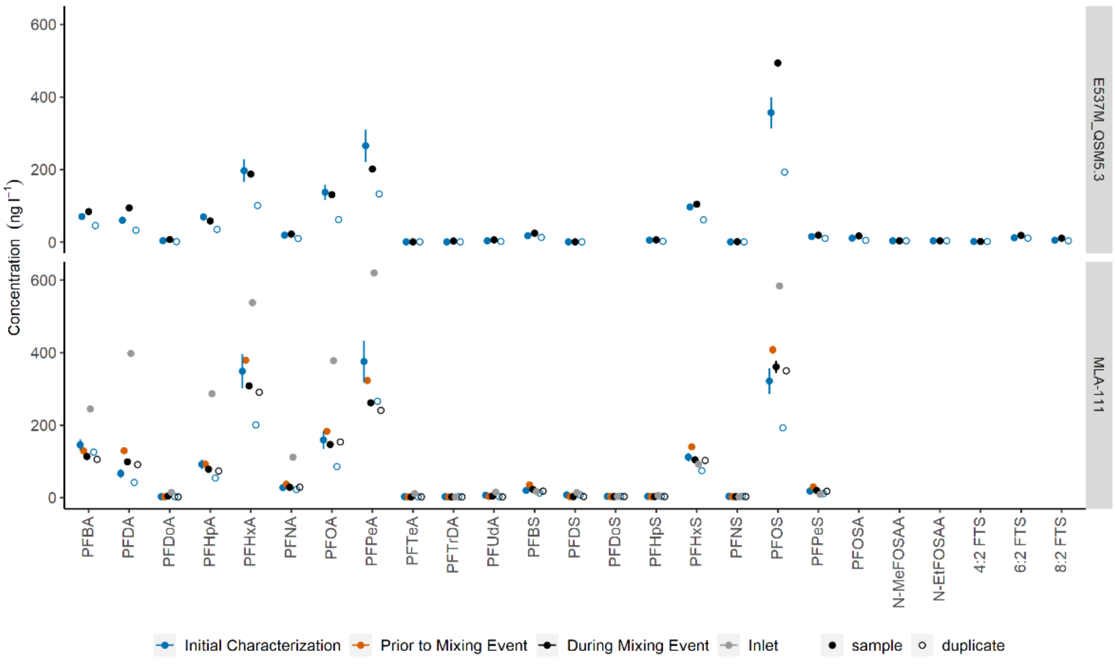

Figure 1. Concentration of PFAS compounds measured in The Pond during Initial Characterization, and During Mixing Event. Panel labels indicate analytical method Post TOP MLA-111 (bottom) and Total PFAS EPA 537 (top). Color indicates sampling event: Initial Characterization (blue), Prior to Mixing (orange), and During Mixing (black) Dots represent the mean of 5 samples, with lines indicating standard error. Open circles indicate results for a duplicate sample collected during the sampling event.

For these experiments the coagulant/flocculant was added with mixing and then solids were allowed to settle for 30 minutes. Chemical additives were prepared as suggested by the manufactures specifications. The additives were mixed at 120 RPM for 1 minute, and then at 40 RPM for 2 minutes. Sedimentation was monitored through ASTM hydrometers as well as several optical and chemical means described in other papers. Sedimentation cylinders for ASTM hydrometers are shown in Figure 2, which shows the relative clarification of the water from different flocculants at different time intervals compared to baselines. No artificial solids removal was used (e.g., filtration). Dosages were chosen based upon the amount of additive that was needed for efficient solids removal; there was no pre-knowledge to understand if higher or lower concentrations of flocculant would help remove PFAS. The dosage rate ranged from 5 - 25 ppm in 500mL water samples. PFAS removal rates and effectiveness are discussed separately. In this paper, the effects of the flocculants on the HDPE liner are our focus.

Table 2. Flocculants evaluated in HDPE membrane liner integrity tests.

Product Name
CAT-FLOC 71264
FERRALYTE 8130
ULTRION 8176
Proprietary Flocculant

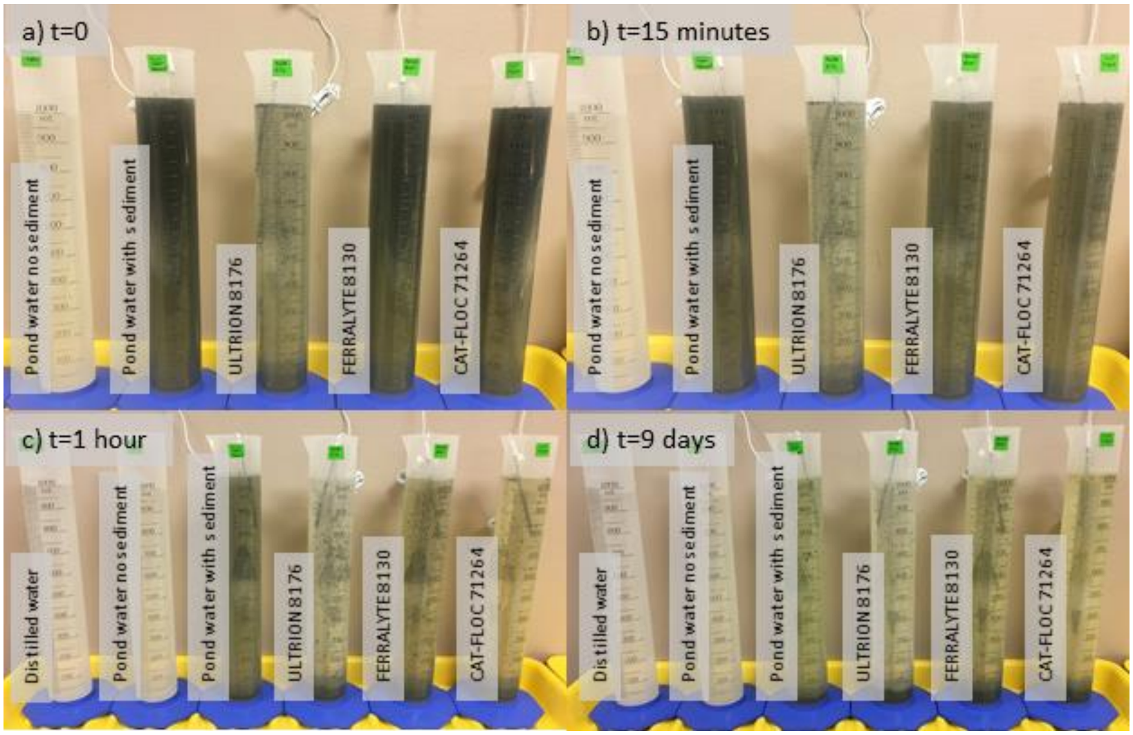

Figure 2. Comparison of flocculants for clarification of sediment-water for 150 mg/L concentrations. a) t = 0, b) t = 15 min, c) t = 1 hour, d) t = 9 days. From the left the cylinders contain distilled water, pond water with no sediment, sediment-water, and flocculants 8176, 8130, and 71264. Note that at 9 days, the waters are becoming green due to vigorous organism growth. Iron hydroxide and proprietary flocculants not shown.

HDPE GEOMEMBRANE INTEGRITY TESTING METHODOLOGY

As the objective of the paper is to study possible loss of integrity in the HDPE liner from PFAS and PFAS treatment chemical additives, it is essential to have a quantifiable metric for loss of integrity. This is difficult, as there are a variety of different pathways for loss of integrity. In this study it was decided for convenience to use geomembrane tensile strength as a proxy for stability, integrity, and survival of the geomembrane liner to any inadvertent chemical attack from either the flocculant and co-contaminants or development of exotic organic acids associated with any flocculant-co-contaminant interactions. This approach to use mechanical tensile strength as the proxy for integrity is consistent with testing of HDPE membranes for MSW or hazardous waste landfill leachates (see Rowe 2020). The secondary proxy chosen in this study for potential loss of liner integrity used was visual assessment of material degradation. As material texture and tensile strengths degrade, these infer that the liner's stability and integrity are degrading and that liner survival during dredging is decreasing. Visual assessment is the first measurement made on the geomembrane coupons, as this must occur prior to mechanical tensile testing, as mechanical tensile testing changes the physical appearance of the HDPE. Visual assessment is to observe the percentage of the area of the coupon with any change in color, texture, blistering, warping, fracturing, spotting, or other observation that differs from typical aging in distilled water. This is documented by photograph (both sides of the coupon) before and after soaking.

In this work the controls for the material degradation are 1) Geomembrane coupons tested for tensile strength in a dry condition, after being held in distilled water, and 2) a separate set tested after being held in pond water with no chemical additive. The controls (HDPE soaked in distilled water and HDPE soaked in pond water with no flocculants) allow for any other environmental factors to be assessed, and only the effects of flocculants to be included. The use of two controls are needed in case the contaminants of the Pond itself are impacting HPDE liner stability. Geosynthetic strength changes were determined using the ASTM standards D4595 or D6693. Specimens were removed from a bath of pond water plus flocculant and were tested for mechanical strength at the following time intervals: 3 days, 7 days, 14 days, 28 days, 45 days and 60 days. A seventh hold-sample is tested at 180 days for long-term exposure risk quantification.

Geomembrane coupons were trimmed to 50-mm by 200-mm rectangles from material provided by the same vendor as provided the material for The Pond. The same HDPE liner material, grade, and vendor were used to be consistent with the conditions in the pond. Liner coupons were aged in the sunlight for 14 days, so that some UV exposure occurred. The HDPE liner in The Pond received low dosages of UV light each day through the water, and 14 days was judged as an adequate attempt to achieve some minor aging of the liner from UV light. Coupons were then placed in baths of pond water in HDPE vessels with volumes of 2 liters. The vessels were labeled by chemical additive type and concentration. Three coupons were aged for each time increment. The containers were held in secondary containment in a constant temperature and humidity room with conventional florescent lights. Rather than accelerate aging with higher temperatures and pressures, the conditions were held at typical since there were concerns that differing temperatures and pressures would alter the water chemistry.

At the end of the time increment, the three coupons were removed from the solution, air dried, decontaminated twice, dried again, and then taken to the Advanced Polymer Engineering Laboratory on the campus of the South Dakota School of Mines and Technology for mechanical tensile testing along with coupons that had not been placed in water at all. Decontamination was performed using Alqinox detergent, following best practices for PFAS decontamination from the USACE and EPA. A detergent was chosen over methanol for these experiments. Wastewater from all activities and decontamination water were disposed of as hazardous waste. Prior to testing, each coupon was inspected for obvious signs of degradation. Each specimen was trimmed to a dog-bone shape with a router table and jig in the Polymer Laboratory to comply with ASTM tensile testing requirements. These dog bone shaped specimens were then pulled into extension until failure occurred.

RESULTS AND DISCUSSION

No visual degradation of any coupon occurred in any solution. No blistering, warping, change in color or texture or other physical difference between before and after soaking were observed visually. Although no physical degradation was observed to the HDPE coupons themselves, physical degradation was observed in the tracking media affixed to each coupon. We placed conventional office steel staples in the corners of each coupon for tracking purposes. These steel coupons degraded quickly and dramatically. Though the liners did not have any reductions in strength or stiffness, the steel staples corroded greatly in all instances in which a chemical additive was included in the solution (Figure 3). Steel staples only had minor discoloration in Distilled Water. In pond water without chemical additives, the staples corroded, but at lesser rates. Rates of corrosion were not measured quantitatively. Only qualitative observations were made as to steel corrosion. Figure 3 shows a set of HDPE geomembrane coupons in a container with pond water, sediment, and chemical additive. The chemical additive has flocculated the sediments and the floc has settled to the bottom of the container. In the field treatment condition, the sediments and floc would be in physical contact with the coupons, while in the experiments, the contact was limited.

Figure 3. HDPE coupons in a combination of contaminated pond water with one of the flocculants at one week in the bath. Water has clarified by this time. Note floc at the bottom of the liquid from the applied chemical flocculant treatment. Also note the corrosion on the steel staples.

The mechanical tensile testing results are shown in Figure 5. Figure 5 results consists of triplicate identical specimens for each water and treatment combination. Triplicate specimens were used for statistical reliability and to judge the repeatability of the testing program. The baseline condition of HDPE coupons not placed in any water, but aged 14-days in UV light, are shown on the left edge of the plot. Results observed in Figure 5 indicate that although each solution produced more scatter at 45-days, no solution resulted in overall loss in tensile strength at 60-days. The scatter in Figure 4 represents test-to-test variability, which was maximized at 45-days, while lessening at 60-days. In all cases, the variability within the three specimens exceeded 2 MPa, consistent with the testing that was performed on 14-day UV light aged HDPE coupons held as controls (see the left of Figure 5 for control range of the UV aged specimens). The HDPE material varies in strength from 17 to 20 MPa after UV aging (nominal strength of the material is 19 MPa +/- 1 MPa). Nominal strengths were confirmed via three specimens that were completely unaged specimens. The reason for more scatter in the results at 45-days is unknown. At 60-days, the HDPE specimens still fell in that same range. Curiously, the treatment that had the lowest overall strength at 45 days, saw some of the highest strengths at 60 days.

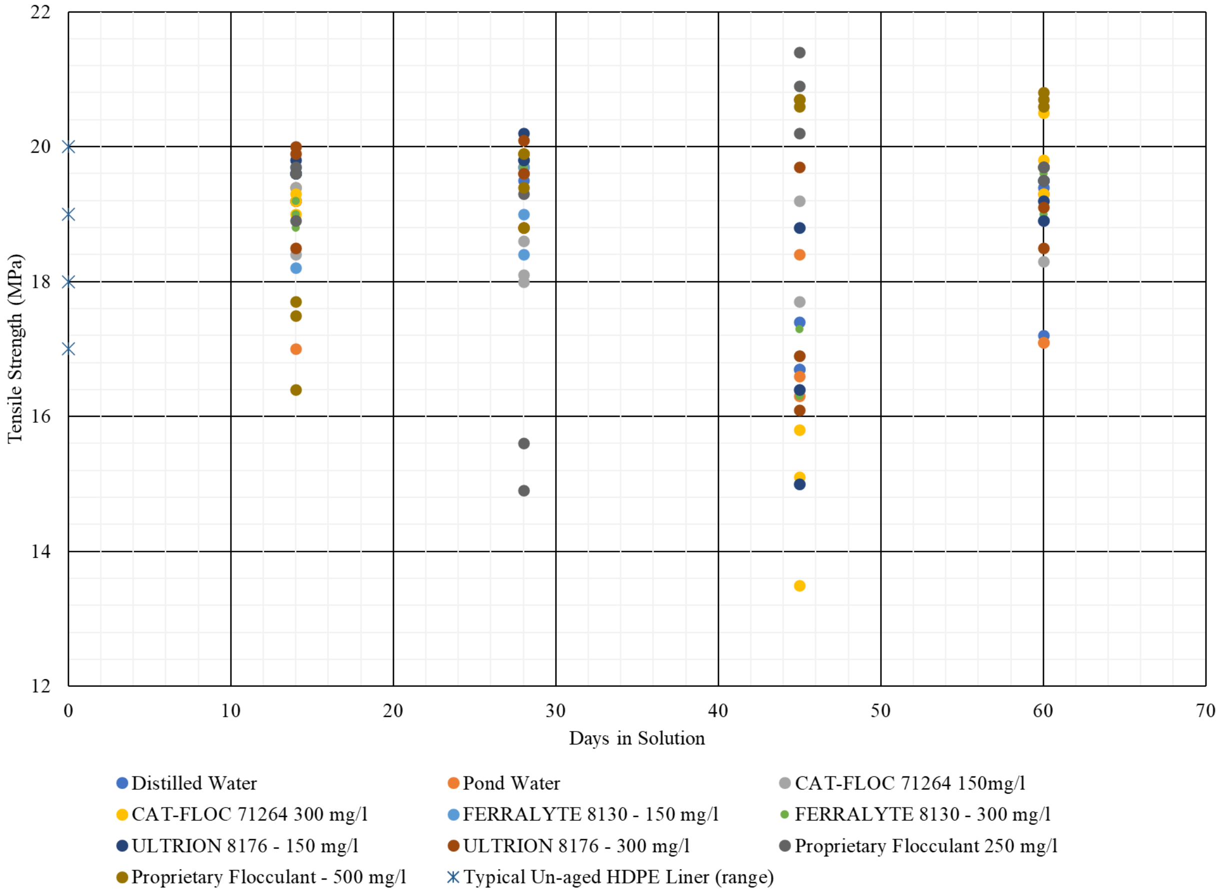

Figure 4. Summary of HDPE geomembrane liner tensile integrity testing by solution

Sample to sample variability is concerning from these results, not as a function of the different flocculants, which appeared to have no strong impact on HDPE performance, but on the HDPE material's inherent variability itself. All specimens were sampled at random from a single sheet of HDPE. Specimens were trimmed with a razor blade and were then routed into the dog-bone shape in a consistent manner. No visual distress, weakness, cracks, or defects was visible in any specimen, yet high sample to sample variability persisted.

CONCLUSIONS

After 60 days of soaking in various iterations of the water from a heavily contaminated surface water containment pond, with and without chemical additives for flocculation, no drop in HDPE material strength was measured although significant variability was exhibited by the HDPE material. No visual degradation of the HDPE liner material was observed, even at concentrations double or triple those proposed for treatment of heavily contaminated pond water. However, steel staples corroded at greatly accelerated rates with all chemical additives.

Therefore, no matter the treatment chosen for The Pond, and metal fittings or equipment used in treatment should be carefully evaluated and use of stainless steel or have other corrosion protecting coatings may be warranted. HDPE geomembranes appear to be resilient to both PFAS and PFAS contaminated water chemical additive treatments and should be considered for further use by the industry.

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