Public consultation input provided by DuPont de Nemours, Inc to the Annex XV proposed restriction on per- and polyfluoroalkyl substances (PFAS) related to the use of PVDF in water and wastewater treatment membranes

Executive Summary

Water insecurity has been and will likely become an even larger challenge globally as climate continues to negatively impact humanity and our environment. As a result, water security is appropriately identified as one of the 17 UN Sustainable Development Goals. Although UN SDG 6 – clean water and sanitation - is critical, at least seven of the other sixteen UN SDGs cannot be realized without water security.

Water security and human health improve tremendously when water and wastewater treatment use is enabled by polymeric membranes for the removal of bacteria, pathogens, viruses, and suspended molecules/particles. Water and wastewater treatment membranes made from polyvinylidene fluoride (PVDF, [-$C_2H_2F_2$-] CAS # 24937-79-9) enable domestic, agricultural, and industrial water users to fulfill their progress to practice more sustainable water and wastewater management. The use of fluoropolymers (e.g., PVDF) in water and wastewater treatment was not addressed in Table 9 of Annex XV Restriction Report. Due to the global criticalness of water and the societal benefits of PVDF in water and wastewater treatment, ensuring evidence is submitted and considered for the use of PVDF in water and wastewater treatment is considered high priority. Putting unnecessary technology constraints on the ability to purify water and wastewater should be avoided to insure a more water secure future for generations to come.

Many others are advocating for removal of fluoropolymers such as PVDF from the scope of the restriction proposal. We endorse this approach because it aligns with our understanding of the socioeconomic benefits of the use of PVDF in water and wastewater treatment applications, as well as PVDF being a low-risk substance that is non-toxic and non-bioaccumulating. Moreover, it can be fully mineralized by incineration. Our consultation submission is not intended to detract from such arguments. Instead, **in the event that the evidence submitted to justify removal of fluoropolymers from the scope of the restriction proposal altogether is insufficient, we respectfully request your consideration for adding a 13.5 year derogation to Annex XV for PVDF membranes used in highly regulated industrial water and wastewater treatment use** for new and existing plants producing drinking water, industrial process water, industrial wastewater and urban wastewater. This time is necessary to discover and develop water and wastewater treatment products using an alternative material with minimized inferior performance impacts.

Water and wastewater treatment is highly regulated in Europe with respect to both the water quality produced and the safety of materials/components used in the process (described herein: ***EU water policy strategy and regulations***). PVDF is used to manufacture microfiltration (MF) and ultrafiltration (UF) membranes which, in the last 30 years, have become widely adopted in drinking water production and wastewater treatment all over the world. The proven ability of these technologies to remove a broad range of contaminants - including harmful pathogens resistant to other forms of disinfection - reliably and safely is one of the important features responsible for its adoption in addition to affordability, size, and operational efficiency (see herein: ***Attributes of polymeric PVDF membranes; Technical feasibility of non-PVDF alternatives in water and wastewater treatment***).

If no derogation is given to PVDF water and wastewater membranes, actions that Europe is taking to improve water security in the region will be negatively impacted. For example, many municipal and industrial wastewater treatment plant owners will need to expand their assets' capacity in landlocked, urban environments or improve the quality of the treated water for discharge to meet the 2022 revised nitrogen and phosphorus discharge levels outlined in the *Urban Wastewater Treatment Directive – Council Directive 91/271/EEC.* These plants won't have access to the best proven technology - which in many cases will be a PVDF based membrane bioreactor technology. Additionally, the adoption of circular water under the *Circular Economy Action Plan (CEAP)*[1] to convert municipal and industrial wastewater to fresh water for agricultural irrigation, cooling tower waters or other many uses will also be inhibited without available and proven PVDF membrane technology to use for filtration and disinfection. Moreover, alternatives are not currently available for like-for-like replacement without regrettable impacts. (see herein: ***Technical feasibility of non-PVDF alternatives in water and wastewater treatment***)

PVDF has been studied alongside other polymer types like polysulfone (PS) and polyether sulfone (PES) to make membranes, but due to the combined mechanical robustness, chemical tolerance, and excellent separation properties, after nearly 30 years of research and optimization, 77% of the MF/UF membranes used globally in water and wastewater treatment systems are PVDF based. When considering time for new polymer discovery, product development and scaling to commercial level, will likely take more than 15 years to develop effective alternatives to PVDF and avoid inferior substitution which could result in higher energy demand, larger treatment systems unable to fit into small urban spaces, and/or more water wastage due to fouling and cleaning inefficiencies. (see herein: ***Technical feasibility of non-PVDF alternatives in water and wastewater treatment)***

It is estimated that in 2021, 1029 tonnes of PVDF were introduced to Europe as new water or wastewater treatment products. It is also estimated that 967 tonnes of PVDF membranes reached end of life in 2021. The long lifetime performance of PVDF membranes in service (7-20 years) alone provides reduced impacts of the membrane's end of life; however, through the combination of landfill, incineration, and material recycling efforts currently being explored, these impacts can be reduced further.

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[1] Document 52020DC0098 "Communication from the commission to the European parliament, the council, the European economic and social committee and the committee of the regions: a new Circular Economy Action Plan for a cleaner and more competitive Europe", Mar 11, 2020.

Landfill and incineration studies of PVDF each indicate no degradation or full mineralization, respectively. Additionally, studies show that PVDF fulfills the widely accepted polymer hazard assessment criteria to be a polymer of low concern. Together - the low annual volume, low concern hazard assessment, and end of life solutions that do not create secondary hazards – the stewardship of PVDF water and wastewater treatment products can be well managed. Further more, studies are in progress to evaluate the feasibility to recycle PVDF from hollow fiber ultrafiltration membranes and provide option to increase the time produced PVDF is used before being landfilled or incinerated. (See evidence herein: ***Emissions over the lifecycle of PVDF MF/UF membranes in Europe***)

Society Impact of PVDF MF/UF Membranes

Water is necessary to sustain life. PVDF microfiltration (MF) and ultrafiltration (UF) membranes enable circular water adoption and can ensure water security despite natural occurring clean water supply declining. For some, water is used without thought but for others, the thought of water consumes their day – conserving and rationing to ensure their families' necessities are met. With climate change, regions once rich in water are beginning to experience water insecurity.

To improve water security, circular water adoption, where wastewater is recycled and reused, is not currently commonly practiced in Europe. The European commission reports[2] that at least 11% of Europeans are affected by water scarcity (~82 million people), only 1 billion m^3 of treated urban wastewater is reused annually, but six times more treated water could be reused than current levels. The urgency to recycling and reusing more wastewater is present and will continue to increase in Europe and globally.

The summer of 2022, 47% of Europe was in drought warning conditions and the region experienced a 500 year drought.[3] The Rhine River could not support shipping vessels – slowing the movement of supplies in the region.[4] Italy's Po River – which provides fresh water for irrigating crops – was becoming salty due to ocean water moving up stream making it unsuitable for irrigation and exasperating the food insecurity issue started by the war in Ukraine.[5] In France, in the midst of an energy crisis, low river water levels caused some nuclear power plants to reduce output to ensure enough cooling capacity.[6] The economic impact of the 2022 drought is still being tallied. Nature climate change[7] reported in 2021 that annual drought losses in the

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[2] https://environment.ec.europa.eu/topics/water/water-reuse_en

[3] Drought in Europe, Aug 2022 https://edo.jrc.ec.europa.eu/documents/news/GDO-EDODroughtNews202208_Europe.pdf.

[4] Nov 25, 2022, https://www.weforum.org/agenda/2022/11/drought-trade-rivers-supply-chain/#:~:text=Summer%202022%20brought%20low%20water,worst%20drought%20in%20500%20years

[5] https://www.forbes.com/sites/arielcohen/2022/08/24/hot-cities-and-cold-turbines-energy-in-a-time-of-drought/?sh=13e3fd6e13d3

[6] https://www.theguardian.com/business/2022/aug/03/edf-to-reduce-nuclear-power-output-as-french-river-temperatures-rise; https://www.wired.com/story/nuclear-power-plants-struggling-to-stay-cool/; https://www.weforum.org/agenda/2022/08/drought-impacts-europe-unexpected/

[7] Naumann, G.; Cammalleri, C.; Mantaschi, L.; Feyen, L. "Increase economic drought impact in Europe with anthropogenic warming" *Nature Climate Change* **2021**, 11, 485-491

European Union and UK combined are €9 billion and projected to rise annually with global warming effects; therefore, the impact from the 2022 are expected to be more than €9 billion.

The 2022-2023 winter snow did not provide the needed relief. France experienced the driest winter since 1959 and Italian Alps snow fall was down by 53%.[8] The regions are bracing for another dry growing season. The impact to food availability, industrial processing and supply chains, energy availability, etc. are likely to continue.

Spain has been experiencing repeated droughts for years and has been taking measures to become more water resilient by turning to unconventional water sources to quench the thirst of their people, crops and industries. More and more, Spain is treating seawater and wastewater to provide safe freshwater sources. These treatment processes are usually multi-step and rely on membrane technology to provide reliable, affordable, separation performance to remove pathogens, virus, trace contaminants and salts. PVDF MF/UF membranes provide a key function in the treatment process to remove suspended solids, viruses and pathogens and to enable biologically treated wastewater to be used for agricultural irrigation or industrial cooling.

Without access to the proven, safe performance of PVDF MF/UF membrane technology, improving Europe's water resiliency in an environment of progressing climate change will be delayed affecting generations

Socioeconomic Analysis

Water is a core element of the planet and human existence and PVDF water and wastewater treatment membranes are a critical component to ensure water security. Many socioeconomic analyses related to water and wastewater treatment around the world have been published.[9,10,11,12,13,14] The most notable and recent was published by the United Nations Environment Programme in March 2023.[15] These reports emphasis that no society is immune to water's impact. Shortages of safe water and wastewater management can disrupt homes, schools, industry, agriculture, and even public health and safety.

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[8] BBC, February 2023.

[9] Gomez, M.; Perdiguero, J.; Sanz, A. "Socioeconomic factors affecting water access in rural areas of low and middle income countries" *Water* **2019**, *11*(2), 202

[10] Kong, Y.-L.; Anis-Syakira, J.; Fun, W.H.; Balqis-Ali, N.Z.; Shakirah, M.S.; Sararaks, S. "Socio-economic factors related to drinking water source and sanitation in Malaysia" *Int. J. Environ Res. Public Health* **2020,** *17,* 1799

[11] Dolan, F.; Lamontagne, J.; Link, R.; Hejazi, M.; Reed, P.; Edmonds, J. "Evaluating the economic impact of water scarcity in a changing world" *Nature Comm.* **2021**, *12,* 1915

[12] https://www.twdb.texas.gov/waterplanning/data/analysis/doc/2016/FINAL-2016%20Socioeconomic%20Impact%20-%20Region%20K.pdf

[13] Water Pollution Economic Effects: https://www.thebalancemoney.com/water-pollution-effects-causes-and-solutions-4775830#:~:text=of%20this%20pollution.-
,The%20Bottom%20Line,waste%20discharges%2C%20and%20uncontrolled%20runoff.

[14] https://www.worldbank.org/en/news/press-release/2019/08/20/worsening-water-quality-reducing-economic-growth-by-a-third-in-some-countries

[15] 2023 UN environment programme "Measuring Progress: Water-related ecosystems and the SDGs"

According to the World Bank,[16] EEA countries withdrew 186.2 billion cubic meters of water in 2019 – 23.5% for Domestic use, 30.4% for Agricultural use, and 46.0% for Industrial use. As shown in Table 1, each country in EEA, however, has a unique water demand profile depending on its economic structure. As such, each country is impacted differently when challenged with water scarcity. As an added complexity to water management, many EEA country's water sources are transboundary. As water becomes more stressed, the potential for disputes pertaining water rights become more likely.

Table 1. EEA Freshwater withdrawal and use (World Bank).

EEA Country	**Annual fresh water withdrawal (billion m^3)**	**% Domestic**	**% Agriculture**	**% industrial**	**Annual fresh water withdrawal-Domestic (billion m^3)**	**Annual fresh water withdrawal-Agriculture (billion m^3)**	**Annual fresh water withdrawal-Industrial (billion m^3)**
Austria	3.5	21	2	77	0.74	0.07	2.70
Belgium	4.4	17	1	81	0.75	0.04	3.56
Bulgaria	5.4	16	15	69	0.86	0.81	3.73
Croatia	0.7	63	11	26	0.44	0.08	0.18
Republic of Cyprus	0.2	40	60	6	0.08	0.12	0.01
Czech Republic	2	43	3	54	0.86	0.06	1.08
Denmark	0.9	41	54	5	0.37	0.49	0.05
Estonia	1	8	0	92	0.08	0.00	0.92
Finland	3	17	14	69	0.51	0.42	2.07
France	26.9	20	11	69	5.38	2.96	18.56
Germany	24.4	37	1	62	9.03	0.24	15.13
Greece	10.1	17	80	3	1.72	8.08	0.30
Hungary	4.5	15	11	74	0.68	0.50	3.33
Ireland	1.4	59	5	36	0.83	0.07	0.50
Italy	34	28	50	23	9.52	17.00	7.82
Latvia	0.2	51	32	17	0.10	0.06	0.03
Lithuania	0.3	54	22	24	0.16	0.07	0.07
Luxemberg	0	90	1	9	0.00	0.00	0.00
Malta	0	62	37	2	0.00	0.00	0.00
Netherlands	8.4	23	3	74	1.93	0.25	6.22
Poland	9	22	14	64	1.98	1.26	5.76
Portugal	6.1	14	56	30	0.85	3.42	1.83
Romania	6.4	17	22	61	1.09	1.41	3.90
Slovakia	0.6	48	13	39	0.29	0.08	0.23
Slovania	0.9	18	0	82	0.16	0.00	0.74
Spain	29.5	15	65	19	4.43	19.18	5.61
Sweden	2.4	40	3	57	0.96	0.07	1.37
Total	**186.2**				**43.79**	**56.73**	**85.70**

The UN notes that 3 out of 4 jobs that make up the global workforce are either heavily or moderately dependent on water.[17] In 2022, 193,458,000 people aged 20-64 years were

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[16] https://data.worldbank.org/indicator/ER.H2O.FWTL.ZS

[17] UN Environment Programme, World Water Day Geneva, 22 March 2016. (https://www.unep.org/news-and-stories/press-release/three-four-jobs-global-workforce-depend-water-says-un-world-water)

employed in Europe[18], thus using the 3 out of 4 ratio, it is estimated that 145 million people's jobs are dependent on water.

The World Bank reports that nine out of ten natural disasters are water-related and the impact cascades through food, energy, urban and environmental systems.[19] Temperatures in Europe have increased at more than twice the global average over the past 30 years with an increase rate of 0.5°C per decade between 1991 and 2021. The World Economic Forum[20] reported that climate change has cost the EU €145 billion in a decade. In 2022, approximately one third of the losses was due to hydrological events. Further, it is estimated that if no action is taken to mitigate the impacts of climate change and water events, Europe could lose around 11% of its GDP by 2050.

Water shortages impact the price of water, the cost of energy, as well as supply chain to ship materials. Each are closely tied to industrial growth. As such, to stay cost competitive in a global market and enable continued business growth, industrial investment aligns closely to availability and cost of water. The migration of industries towards water availability (or away from water scarcity) impact local communities that rely on jobs and tax revenues to support their people, schools, and government. Building water resiliency through circular water approaches serves to protect economic growth in regions.

Water shortages also impact agriculture yields. Droughts forcing communities to rely on far reaching supply chains to feed the local populations which increases food prices. In this scenario, low- income families are impacted the most. Take for example olive oil. The price of olive oils in March 2023 is 46.3 percent more than the same time in 2022.[21] Heat and drought in the Mediterranean caused production yield to be only 50% of typical harvest.[22] Building water resiliency through circular water approaches ensures communities are fed in a fair and equitable way.

EU water policy strategy and regulations

The European Union is taking measures to drive change for improved water access and quality. Drinking water quality standards are being strengthened with the *Drinking Water Directive [EU 2020/2184]*, *Industrial Emission Directive [2010/75/EU], and Microplastics Restriction Proposal.* To control pollution of freshwater streams, the *Urban Wastewater Treatment Directive [Council Directive 91/271/EEC]* has been updated with more stringent limits for endocrine disruptors, and nitrogen and phosphorous levels being discharged to the environment. Additionally, under the

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[18] Eurostat, Employment – annual statistics

[19] "Water" https://www.worldbank.org/en/topic/water/overview

[20] Dec 2, 2022 "Climate change has cost the EU €145 billion in a decade"
https://www.weforum.org/agenda/2022/12/climate-europe-gdp-emissions/

[21] Paolo DeAndreis, April 22, 2023, *Olive Oil Times* "Olive oil prices rising faster than inflation in Italy"

[22] Clarisa Diaz, May 9, 2023, *Quartz* "The global price of olive oil hit a 26-year high"

Circular Economy Action Plan (CEAP)[23], barriers for practicing water reuse for agricultural irrigation have been lowered by establishing *Regulations on minimum requirements for water reuse [EU 2020/741]*.

In addition, countries in Europe have established certification processes to ensure materials used in drinking water applications are safe, including UK [DWI regulation 31 Certification], Germany [KTW-BWGL Attestation of Conformity], France [Attestation de Conformité Sanitaire], the Netherlands [Dutch Drinking Water Certification], and National Sanitary Foundation [NSF/ANSI/CAN 61]. These standards review the materials used to make the product and that remain as residuals. The migration of the residual materials during use is evaluated and the resulting concentration compared versus established substance safe migratory concentration limits. Products are not certified if the substance migration exceeds these limits.

Water Resiliency using PVDF MF/UF membranes

Water and wastewater purification technologies are available through advances in polymeric membrane technology. Using membranes, water can be managed to meet the increasing world demand. Polymeric membrane technology balances the economics of treatment with assurance of contaminant removal. For example, the benefits of low pressure micro- and ultrafiltration membrane technology (MF/UF) emerged in response to a cryptosporidium outbreak in Milwaukee, Wisconsin USA in 1993 that led to widespread hospitalizations. The city was sourcing their water from Lake Michigan which was contaminated by Cryptosporidium which is thought to come from overflowing sewers or sewage treatment plants due to heavy rains. Cryptosporidium is a microscopic protozoan parasite that can be present in water, is resistant to conventional disinfection with chlorine and causes diarrhea in humans. Cryptosporidium is effectively removed from water using microporous filtration membranes. From this event, MF and UF membrane filtration emerged to be a well-recognized reliable method for producing safe drinking water[24] and since then, PVDF has become the material of choice for this.

Water resiliency requires the transformation of impaired waters into renewed, safe freshwater sources for use. Traditionally, municipal or industrial wastewater is treated in large tanks/ponds using microorganisms to lower the organic content of the water to a safe level before it is discharged into the environment after clarification (this is commonly known as the biological treatment). In water scarce conditions, this discharged water can be transformed into a valuable source of freshwater after being filtered through the micropore structure of PVDF MF/UF membranes to remove residual bacteria, pathogens, and sediment. The filtered water is then safe for reuse as agricultural irrigation or industrial cooling tower water or to be further treated by reverse osmosis process. The European Commission has incentivized reuse by introducing EU

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[23] Document 52020DC0098 "Communication from the commission to the European parliament, the council, the European economic and social committee and the committee of the regions: a new Circular Economy Action Plan for a cleaner and more competitive Europe", Mar 11, 2020.

[24] Davis, R., 2010. Ten Years of Low-Pressure Membrane Plant Operations in Kenosha. Water and Wastes Digest, 14 October 2010.

2020/741 which provides minimum requirements for water reuse as well as guidance of the type of treatment needed to achieve the requirement. For example, when treating wastewater for used as irrigation water for food crops consumed raw, the guidance prescribes secondary biological treatment, filtration and disinfection to achieve a minimum water quality of E. Coli <10/100ml, BOD_5 <10 ppm, TSS <10 ppm, and Turbidity <5 NTU. PVDF MF/UF membranes are proven technologies that provide both the filtration and disinfection properties to meet the requirements for this process.

In the above treatment description secondary biological treatment, filtration and disinfection are stated as if they would exist as three separate treatment steps. Membrane Bioreactors (MBR) provide a space saving solution where the biological treatment and filtration take place in a single process step. Membrane bioreactors use a tank for promoting biological digestion of organics but also submerge PVDF UF/MF membranes directly into the biologically activate water to filter clean water from the digestion cocktail. Not only are there footprint benefits from a single step process, but when using the high pathogen barrier properties of PVDF UF/MF membranes, the inventory of micro-organisms in the biological system can be maintained at a much higher level than conventional systems. This allows the same amount of carbon to be consumed in a much smaller tank (or more carbon to be consumed in the same size tank). The single step MBR process increases the treatment capacity of existing conventional treatment systems and allows a higher degree of carbon, nitrogen and phosphorous removal without needing to add larger tanks. In addition, to meeting the requirement for water reuse, such features will be drawing more attention by municipalities in Europe to comply with the *Urban Wastewater Treatment Directive-Council Directive 91/271/EEC* which was changed in 2022 to lessen the allowed Nitrogen and Phosphorus levels to be discharged.

Market size of MF/UF membranes

The global market for Ultrafiltration membranes has recently been reviewed in a February 2022 BCC market research report.[25] Table 2 summarizes the Global and European market share of ceramic and polymeric technologies. Polymeric membranes are used 10 times more than ceramic and is aligned to the difference in attributes between the two types of material that is described in more detail in the following two sections. Of the polymeric membranes it is estimated that 77% are PVDF.[26]

The amount of PVDF membranes sold in Europe in 2021 for potable water, wastewater, food and beverage and industrial processing (7,912,000 m2, Table 3) is estimated to be enough treat the volume of water equivalent to that consumed by nearly 123 million European households.[27] The market growth rate of polymeric membranes ranges between 5-6.5%. Typically, MF/UF membranes last more than 7 years before needing to be replaced, thus of membranes sold in

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[25] BCC Publishing "Ultrafiltration membranes: Technologies and Global Markets", Feb 2022, Report Code: MST044F

[26] Pearce, G., 2019. Microfiltration and Ultrafiltration Market Report, s.l.: Membrane Consultancy.

[27] Assumes 77% of polymeric membranes sold are PVDF. Assumes 65 Liters per square meter per hour. Assumes the average EU household uses 100L of water per day.

2021 if one assumes that the 6% growth rate is related to new systems and the remaining are for replacement membranes, the estimate number of membranes currently installed in Europe in 2021 is 10.2 million m^2 of membrane. This is enough to treat 21.3 million m^3/day of water which is enough to supply 159 million households.

Table 2. Summary of the UF/MF membrane active area sold in 2021 (excluding hemodialysis).

	Total	Ceramic	Polymeric
Global (1000 m^2)	62,442	5,421	57,055
Europe (1000 m^2)	11,220	1,002	10,275

Table 3. Estimated 2021 PVDF UF/MF membrane volume (excluding hemodialysis).

	PVDF UF/MF (1000 m^2)[i]	PVDF UF/MF (tonnes)[ii]	Est. amt of water treated (m^3/h)[iii]	Est. # of European households (millions)[iv]
Global	43,932	5,711	2,855,580	-
Europe	7,912	1,029	514,280	123

Assumptions: [i] 77% of polymeric MF/UF provided in Table 2 is PVDF;[28] [ii] hollow fiber membrane conversion of area to weight of 0.13 kg/m^2; [iii] a flux of 65 Liters per square meter per hour; [iv] 100 Liters of water per day per household.

Attributes of polymeric PVDF membranes

PVDF MF/UF polymeric membranes are used in the water and wastewater treatment process to remove of bacteria, pathogens, viruses, and suspended molecules/particles. Identifying high performing polymer types to use for MF/UF membranes has been and continues to be the subject research and development for more than 30 years.[29,30,31] PVDF has risen to be the most preferred polymer for MF/UF membranes used in water and wastewater treatment applications and is used in approximately 77% of the world's MF/UF membrane systems.[32]

PVDF is uniquely positioned to meet the challenges of the water sector because of several key features.

a) PVDF is a water insoluble, high molecular weight porous membrane forming material
b) PVDF is a high purity polymer that is a homopolymer produced from a gaseous monomer that does therefore not remain in the polymer as a non-polymeric PFAS impurity

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[28] Pearce, G., 2019. Microfiltration and Ultrafiltration Market Report, s.l.: Membrane Consultancy.

[29] Aani, S.A.; Mustafa, T.N.; Hilal, N. "Ultrafiltration membranes for wastewater and water process engineering: A comprehensive statistical review over the last decade", *J. of Water Process Eng.* **2020**, 35, p 101241

[30] Kammakakam, I.; Lai, Z. "Next-generation ultrafiltration membranes: a review of material design, properties, recent progress, and challenges" *Chemosphere* **2023,** 316, 137669

[31] Awad, E.S.; Sabirova, T.M.; Tretyakova, N.A.; Alsalhy, Q.F.; Figoli, A.; Salih, I.K. "A mini-review of enhancing ultrafiltration membranes (UF) for wastewater treatment: Performance and stability" *ChemEngineering* **2021**, 5(3), 34.

[32] Pearce, G., 2019. Microfiltration and Ultrafiltration Market Report, s.l.: Membrane Consultancy

c) PVDF can be made without the use of PFAS processing aids, so the concern for using, needing or containing residual processing aid, is not a concern,
d) The unique way PVDF is synthesized and that fact that is such high purity, it uniquely meets stringent regulatory requirements for products used in drinking water production [e.g., NSF61; DWI – BS EN 15768:2015]
e) PVDF has resistance to a broad range of chemicals either present in the wastewater feed streams or used as cleaners to maintain filtration performance over long (more than 7 years) useful lifetimes
f) PVDF has exemplary bacteria log removal separation performance defined by NSF/ANSI 419
g) PVDF membranes can be readily scaled to meet EU's growing water filtration demands and can create societal benefit as a preferred choice (cost to operate, reduced infrastructure footprint and capital costs) when compared to alternatives.
h) For PVDF each square meter of membrane area will treat 5.7 million liters of water in a 7 year lifetime (assumes an operating flux of 65 liters/m2/hour).

Technical feasibility of non-PVDF alternatives in water and wastewater treatment

In municipal water and wastewater treatment, approximately 77 percent of the total installed capacity of MF/UF use PVDF and its use has been growing.[33] For membrane bioreactors used to treat municipal wastewater, nearly 100 percent of the membranes are PVDF due to especially challenging treatment environment where aggressive measures are used to control fouling (e.g., air pulses and cleaning chemicals). The use of MF/UF for water and wastewater treatment requires materials of construction that possess a balance of:

- membrane and film forming properties– for fabrication, design flexibility and high surface area need to achieve space saving, low capital treatment processes
- fouling resistance and high permeability
- chemical resistance – for compatibility with water treatment chemicals (i.e., acids, bases, disinfection, and oxidizing agents)
- long lifetimes with uncompromised performance
- mechanical strength – to withstand trans-membrane pressures and air scouring forces
- materials of construction that satisfy leachable limits and other health regulations – safe for use in drinking water applications.
- cost effectiveness – for economic feasibility for use in large scale operations commonly required by publicly/government managed municipalities

The field of MF/UF membranes is well studied with many literature references and reviews.[34] PVDF is the preferred material in MF/UF water treatment. Alternative materials that have been

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[33] Pearce, G., 2019. Microfiltration and Ultrafiltration Market Report, s.l.: Membrane Consultancy
[34] Marshall, J.E., et. al. "On the Solubility and Stability of Polyvinylidene Fluoride" *Polymers (Basel)*, **2021**, 13(9), 1354. Liu, Fu, et. al. "Progress in the production and modification of PVDF Membranes, *J. Membrane Sci.,* **2011**,

used to make MF/UF include polyether sulfone (PES), polysulfone (PS), Chlorinated polyethylene (Cl-PE) and ceramics. These non-PFAS alternatives do not offer a comparable combination of physicochemical properties as PVDF in difficult to treat waters such as wastewater (Table 4).

Table 4. PVDF membrane attributes compared to alternative materials

	PES	PS	Cl-PE	ceramic
Hollow fiber membrane forming properties	=	=	-	-
Chemical Resistance	-	-	-	+
pH Resistance	=	=	-	-
Mechanical Resistance	-	-	-	-
Material cost/ m^2 membrane	+	+	+	--

= equivalent to PVDF, + better than PVDF, - worse than PVDF

Although the alternative polymeric material costs are less than PVDF and despite decade of research, PVDF has still risen to be the preferred material for MF/UF hollow fiber membranes. PES and PS can be made into hollow fiber membranes, whereas Cl-PE and ceramic membranes are in the flatsheet or tubular form where footprint of the systems tend to be larger. In the case of PES, and PS, it has been documented that these materials have limited compatibility with the disinfectants and chemical cleaning agents used in water and wastewater treatment system maintenance, and the polymer undergoes significant degradation; particularly in response to disinfectants.[35] The chemical compatibility of Cl-PE[36] is noted to be unsatisfactory with halogenated solvents, ferric chloride – a common flocculant used in wastewater treatment, sodium hypochlorite, and common cleaning acids such as citric acid and hydrochloric acid.

Polyether sulfone (PES) membranes are the second most popular ultrafiltration membrane behind PVDF. To achieve the strength needed, multi-bore hollow fiber technology (see Figure 1) has been adopted when using PES and the membranes are used in an inside-out configuration where the impaired water enters the inside of the hollow fiber and the clean water permeates through the outer membrane area. As a comparison PVDF hollow fibers are designed to work in an outside-in configuration where the impaired water permeates through the outer surface of the fiber and the clean water is channelled out of the fiber through the inner core.

375, 1-27. Siagian, Utjok W. R., et. al. "High-performance ultrafiltration membrane: Recent Progress and Its Application for Wastewater Treatment", *Current Pollution Report* **2021**, 7, 448-462. Kammakakam, Irshad and Lai, Zhiping "Next-generation ultrafiltration membranes: A review of material design, properties, recent progress and challenges" *Chemosphere,* **2023**, 316, 137669

[35] Malczewska, B. & Zak, A., 2019. Structural Changes and Operational Deterioration of the UF Polyethersulfone (Pes) Membrane Due to Chemical Cleaning. Scientific Reports, 9(422).

[36] Technical Handbook “Chemical Resistance Table”, Parker https://www.parker.com/literature/Fluid%20Transfer%20Hose%20-%20Europe/Chemical%20Table.pdf

Figure 1. Muli-bore PES hollow fiber UF membrane (left), PVDF hollow fiber UF membrane (right)

The inside-out multi-bore configuration is proven to be suitable for easier to treat waters with lower levels of contamination. However, using the inside-out configuration when high levels of contamination is present can clog the membrane and make it difficult to clean. PES is also more sensitive to some cleaning chemicals than PVDF which may shorten the lifetime of the membrane. Li *et.al.*[37] compare the effects of 5000 mg/L hypochlorite exposure on PES and PVDF membrane strength at different pH over a 100 hour exposure period. The tensile strength of PVDF is retained regardless of the pH; however, at pH ranging from 3-11, the tensile strength of PES decreases by 14 to 33% after exposure with the worse effect measured at pH 7 and 9. Reduced membrane strength leads to shorter useful lifetimes and more frequent membrane replacement rates. In addition, it is reported that PES is brittle and suffers from poor durability in long term operation.[38] W. Fu and W. Zhang reported[39] changes in surface porosity, surface roughness, tensile strength, and elongation due to exposure of PES membranes to sodium hypochlorite. Such properties indicate a weakening of the membrane but can also negatively impact the separation performance.

Ceramics have demonstrated good filtration performance and chemical resistance in a number of MF/UF applications. In general, the footprint per square meter of ceramic membrane active area is larger than polymeric membranes. To compensate for this, ceramic membranes are operated at approximately 2-3 times the typical flux used for polymeric membranes. When treating challenging waters with high suspended solids, high flux operation leads to thicker cake layers on the membrane surface that create resistance to water flow. To manage water permeability, more frequent backwashes are used which can lead to lower water recovery. Additionally, to further save footprint, multiple ceramic cartridges have been assembled into a single pressure vessel while using o-rings as a barrier preventing contact of contaminated feed

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[37] Li, K. et al., 2021. Aging of PVDF and PES ultrafiltration membranes by sodium hypochlorite: Effect of solution pH. Journal of Environmental Sciences, Volume 104, pp. 444-455.

[38] Park, H.-D., Chang, I. & Lee, K.-J., 2015. Principles of Membrane Bioreactors for Wastewater Treatment. Boca Raton: CRC Press.

[39] Fu, W.; Zhang, W. “Chemical aging and impacts on hydrophilic and hydrophobic polyether sulfone (PES) membrane filtration performance” *Polymer Degradation and Stability* **2019**, 168, 108960.

water with the clean permeate water. The use of o-rings can present failure points and put the integrity of the clean water at risk.

Ceramics are rigid materials and are reported to be vulnerable to mechanical and thermal shock/shattering and undergo wear and abrasion in difficult feedwater applications.[40] The greatest hurdle for ceramic membranes, though, is economics.[41] Ceramics use inorganic materials comprising one or a combination of the following: alumina, silica, titanium, or zirconium. The manufacturing process is a multi-step process of coating multiple symmetric layers with uniform pore size throughout each layer. Each layer is produced by pumping a slurry of oxide particles and solvents into a membrane channel. The slurry coats the inside of the channel, and the element is then sintered (fired in a kiln) at high temperatures to form the membrane. The particle size used in the process determines the pore size and the last layer will determine the pore size of the membrane element. With this type of process, the cost of the ceramic will increase as the pore sized requirement decreases. Thus, MF based ceramics will be less expensive than UF ceramics. Additionally, the inorganic ceramic materials are significantly more expensive than organic polymeric materials. They are sourced from mines with few global sources – China is the largest producer of alumina[42] and silicon[43] with Russia also as a major producer of each. Additionally, these inorganic materials are not biodegradable and can accumulate in landfills.

The difficult manufacturing scalability and the cost of ceramic membranes have resulted in their limited application to mainly specialty applications (e.g., oil and gas produced water). PVDF membranes, on the other hand, provide a balance of manufacturing scalability and the necessary robustness and space (i.e. footprint) efficiency in the application to be the material of choice for large scale in MF/UF applications, especially for membrane bioreactor applications treating wastewater.[44]

Process to develop alternatives

It is estimated that it will take more than 15 years to develop an effective alternative for PVDF MF/UF hollow fiber membranes used in water and wastewater treatment that would provide the same confidence in water quality and operational reliability without the negative consequences of increased energy consumption, frequent replacement rates or need for a large system footprint. The membranes used in municipal water and wastewater treatment must meet the balance of technical requirements, economic considerations, scalability and health and

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[40] American Membrane Technology Association, 2018. Ceramic Membranes, Stuart: American Membrane Technology.

[41] BlueTech Research Insight Report “Ceramic Membranes for Water and Wastewater Treatment”, March 2023.

[42] “Aluminum Facts”, 2021. https://natural-resources.canada.ca/our-natural-resources/minerals-mining/minerals-metals-facts/aluminum-facts/20510

[43] Statista 2023, Published by M. Garside, Feb, 22, 2023

[44] Judd, S., 2017. The material question − choosing MBR membrane materials.
Available at: https://www.thembrsite.com/blog/the-material-question-choosing-mbr-membrane-materials/

environmental regulatory requirements. To date, despite decades of research, a material to replace PVDF wholly in MF/UF hollow fiber membranes has not been found.

The first step to defining an alternative to PVDF membranes is to identify and develop an alternative polymer that is chemically resistant, mechanically robust and can be scaled in a continuous hollow fiber membrane forming process to create a porous membrane with effective rejection properties without compromising flow. The polymer and materials used in the membrane forming process must meet the requirements to be drinking water certified (e.g., KTW-BWGL, DVGW W 270:2007; NSF/Ansi/CAN 61). This will be an iterative process including bench scale research as well as process scale up research with no guarantee of success. Due to the complex nature of the research and the number of critical performance criteria to meet, it could take 5-10 years to find alternative polymeric candidates.

The second step is to develop technology to pot the fibers as bundles into the same or similar housing as current PVDF water and wastewater treatment products with comparable membrane active area. Effectiveness of the potting material must be examined for integrity after exposure to conditions commonly encountered during a water or wastewater treatment process – such as cleaning chemicals. This work may take 1-2 yrs to complete.

The third step is to pilot test the membranes in water treatment systems after they are assembled into the different product types including pressurized UF, submerged UF, and membrane bioreactors. Testing will include flux and rejection performance measurement, as well as fouling and cleaning evaluation. Accelerated testing under aggressive operating conditions will also be used to help simulate exposure over longer operating periods and to understand the potential performance impact. This phase of testing will take approximately ~3 years. In parallel with the third step, the products with the new materials can be submit for drinking water certifications in the relevant countries. This process can take 12-18 months or possibly longer given the volume of products that will need to be certified and the limited capacity of existing 3rd party testing and review resources in Europe.

And finally, assuming that the alternative product will be developed to be like-for-like replacement of existing PVDF products, certified, commercial systems treating different water types will be chosen to serve as reference sites. Ideally, users of water treatment technology desire references in specific water types that show operating performance over the entire lifetime of a product. This helps them understand seasonal impact on the performance as well as changes in performance due to long term exposure to cleaning chemicals and other water contaminants. At minimum 2 years operating time to demonstrate proof of performance over the seasonal (spring, summer, fall, winter) cycles is needed.

PVDF MF/UF membrane products have performance lifetimes of 7-20 years (lifetime is highly dependent on operating discipline practiced over the lifetime of the product, which can vary greatly by end user site), so once alternative polymer products are developed and commercialized, it will take an additional 7+ years to replace and phase out the use of installed PVDF products.

Barriers to transition to non-PFAS alternatives

There are several barriers to replace PVDF MF/UF membranes including: a large installed base in the market, lack of interchangeability, drinking water certifications, and costs.

Estimated installed base of membranes.

Typically, MF/UF membranes have useful lifetimes of 7-20 years before needing to be replaced. It is estimated that of 7,912,000 m^2 of membranes sold in 2021, approximately 94% are for replacing existing membranes and 6% are for new systems.[45] From this it is estimated that 10.2 million m^2 of MF/UF membrane area is currently in use in Europe. That's enough membrane to generate nearly 15.9 million cubic meters per day of treated water which is enough for approximately 159 million households[46] but is water distributed between industrial, drinking and wastewater treatment purposes. This large installed base of membrane would present a disruption to the operation of Europe if PVDF MF/UF membranes were ban and water supply or wastewater treatment was disrupted.

Lack of interchangeability

The MF/UF market does not have standardized products that can be easily interchanged between different suppliers regardless of the membrane material type. This includes variation in physical module size, the amount of active membrane area per module, as well as different designs used to manage water flow. Some attempts have been made to develop adapters to accommodate the system design difference challenge, but these will generally require more space that may or may not be available in the existing plants. Additionally, it is likely that alternative polymers may require thicker membranes than current PVDF membranes to achieve the required mechanical strength needed for challenging water treatment applications. These thicker membranes will create hollow fibers with a larger outer diameter which will reduce the amount of membrane area that can be packed into the same size housing. As such more space will be needed to add the additional modules in existing systems to ensure the needed operating flux is maintained. This extra space may or may not be available. The lack of like for like replacements risks a reduction in treatment capacity until suitable replacement can be developed or extra space is secured for housing larger sized systems.

Drinking water certifications

New materials brought into the drinking water market will face an entry barrier of getting numerous approvals and certifications. Products using PVDF membrane have repeatedly demonstrated compliance to the rigorous evaluation completed for achieving drinking water certifications including an evaluation of migration materials. In Europe, the UK (DWI regulation 31 Certification), Germany (KTW-BWGL Attestation of Conformity), France (Attestation de Conformité Sanitaire), and the Netherlands (Dutch Drinking Water Certification) each have their

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[45] This assumes the 6% CAGR reported in the BBC Publishing Feb 2022 market report is from new projects.

[46] Assumes 65 Liters of clean water produced per sq. meter of membrane per hour. Also assumes 1EU household consumes 100 L of water per day.

own approval systems which is a pre-requisite for supply. Each approval takes approximately 12-18 months and costs can reach €50-100k per product approval. Given the volume of product which will need new certifications due to this change, additional delays may be expected due to a limit number for qualified testing facilities to do the certification.

Re-certifications are also conducted to maintain continued approval for use. The re-certification process creates a barrier for changing component supplier in the future, thus care will need to be taken to choose a supplier and products with a strong business model and proven performance.

Membrane replacement costs

Alternative materials provide total solutions that are less economical options to PVDF especially when used in membrane products treating challenging waters. By comparison, the capital and material costs for manufacturing polyethersulfone (PES), polysulfone and chlorinated polyethylene (Cl-PE) membrane elements would be similar to PVDF.[39] However, in applications with difficult feedwaters containing high concentrations of solids and organic matter – such as municipal wastewater, tertiary wastewater treatment, industrial wastewater treatment, and membrane bioreactors – and/or in applications that rely heavily on the use of disinfectants and oxidizing cleaning chemicals, the technical limitations of PES and PS membranes would lead to significantly higher costs due to the need for more chemical use (coagulation and flocculation chemicals), more frequent membrane replacement and other operational inefficiencies (e.g., energy and water recovery).

Compared to a typical PVDF membrane plant, the cost of ceramics has been estimated at 500% higher on a filtration area basis, and 218% higher on a filtered volume basis.[37] Ceramic membranes use minerals such as aluminum, silicon, titanium or zirconium which are sourced from limited mined reserves. Hence, economically ceramics are not a viable alternative to replace PVDF[38] which explains the very small market share held by this technology.

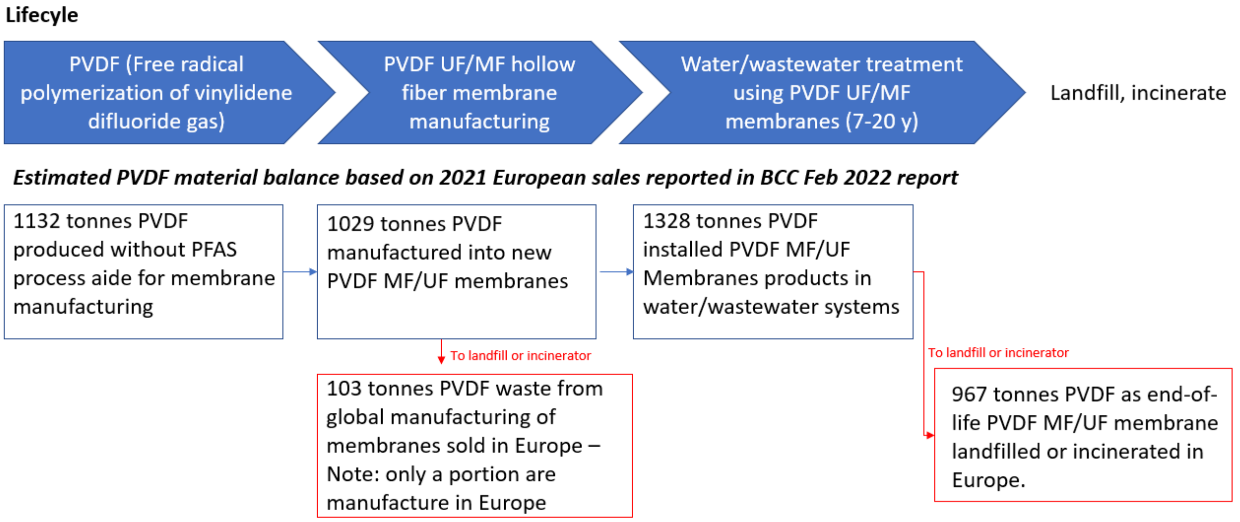
Emissions over the lifecycle of PVDF MF/UF membranes in Europe

The lifecycle of PVDF membranes used in water and wastewater treatment membranes is summarized in Figure 2. The process starts by sourcing PVDF polymer from producers that do not use PFAS processing aides. Care is taken in material selection since membranes used in water applications are required to meet stringent material migration limits to be certified for use.

The PVDF is manufactured into porous MF/UF hollow fiber membranes where more than 90% of the PVDF is made into a suitable water treatment membrane and assembled into a product. The PVDF water and wastewater treatment products are assembled into treatment systems and used continuously for a lifetime ranging between 7-20 years.

End of life PVDF MF/UF products are replaced with new PVDF MF/UF products and the water or wastewater treatment system continues to serve its 20-30 year purpose. The end of life product is currently either landfilled or incinerated depending on the availability of waste handling serves in the region that the product is used. PVDF suppliers, membrane manufactures, and others in the water industry value chain are currently investigating the potential to recover the PVDF hollow fiber of MF/UF membranes and recycle the material for other purposes. A recycle solution is attractive means to extend the lifetime benefit of the durable polymeric properties of PVDF.

Figure 2. Lifecycle of PVDF MF/UF hollow fiber water and wastewater treatment membranes



The 2021 BCC Publishing[47] market report estimates 10.2 million square meters of polymeric UF membranes were sold in Europe for potable water, wastewater, food and beverage, and industrial processing in 2021. Assuming 77 percent[48] of the membranes are made from PVDF and the weight of a PVDF hollow fiber membrane is 0.13 kilograms per square meter,[49] the estimated PVDF introduced to Europe through the marketing, and sale of membranes was 1029 tonnes in 2021 (7.9 million m2 of membrane). The published compound annual growth rate (CAGR) of sales ranged between 5-6.5%, thus one can assume that approximately 6% of the 2021 sales is for new systems and the remaining is for replacement membranes at the end of their 7-20 yr life span.

Using the above information, in 2021, it is estimated that 1029 tonnes of new PVDF was introduced to Europe in the form of water and wastewater treatment membranes. It is also estimated that 1328 tonnes (10.2 million m^2) of PVDF are installed and operating in water and wastewater treatment systems. Finally, it is estimated that approximately 967 tonnes (7.4 million m^2) of PVDF water and wastewater treatment membranes were landfilled or incinerated (Figure 1). If the highly unlikely hypothetical worse case were considered where the 967 tonnes of used PVDF membranes converted to PFAS emissions, it would constitute only 1.2% of the overall

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[47] "Ultrafiltration Membranes: Technologies and Global Markets", BCC Publishing, Feb 2022, Report code: MST044F

[48] Pearce, G., 2019. Microfiltration and Ultrafiltration Market Report, s.l.: Membrane Consultancy.

[49] Standard weight of a PVDF hollow fiber produced by DuPont is 0.13 kg/m2

75000 tonnes PFAS emissions reported by ECHA in 2020. The evidence in the below section "End of life of PVDF membranes" indicates that PVDF is not known to decompose in landfills and is highly likely to achieve high degrees, if not 100% mineralization, when incinerated. Thus, the emissions will be extremely low or negligible.

Sustainable sourcing of PVDF

PVDF belongs to the class of high molecular weight fluoropolymers. Fluoropolymers are distinct from non-polymeric PFAS substances with different physicochemical, toxicological, and environmental profiles.[50,51] Some reports indicate fluoropolymers are not "really of low concern" mainly due to the use of PFAS processing aides.[52] **For assurance for obtaining drinking water certifications, PVDF used in producing membranes are grades which do not use PFAS processing aides.** The high molecular weight polymer, PVDF, meets the OECD definition of a polymer of low concern and is non-toxic, biocompatible, non-soluble and immobile molecules and are found to have insignificant environmental and human health impacts.[53,54]

The PVDF used for membranes is a high molecular weight homopolymer (>100,000Da) produced from either suspension or emulsion polymerization of gaseous vinylidene fluoride in water. The weight fraction of the polymer below 1000Da is generally below 0.5% +/- 0.3% and residual monomer is detected to be less than 50 ppb according to supplemental information provided in ref. 51. **The polymerization can be conducted in the absence of a PFAS processing aid, and suppliers of PVDF used for water treatment membrane provide letters verifying that PFAS processing aids are not used.** The certificate of analysis of the polymers confirms a white color appearance, low volatile (water) content, a melt flow index consistent of a thermoplastic, and a melting point greater than 170 ^{o}C.

Manufacturing of PVDF membranes

The manufacture of porous hollow fiber membranes balances demands of material science and engineer to create a high yielding, high performing, high volume membrane which can be

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[50] PlasticsEurope, 2021. Fluoropolymers: Irreplacable Applications. Available at: https://fluoropolymers.plasticseurope.org/irreplaceable-uses

[51] Henry, B. J.; Carlin, J.P.; Hammerschmidt, J.A.; Buck, R.C.; Buxton, L.W.; Fiedler, H.; Seed, J.; Hernandez, O "A critical Review of the application of polymer of low concern and regulatory criteria to fluoropolymers" *Integrated Env. Assess. And Management* **2018,** 14(3) 316-334,

[52] Lohmann, R.; Cousins, I.T.; DeWitt, J.C.; Gluge, J.; Goldenman, G.; Herzke, D.; Lindstrom, A.B.; Miller, M.F.; Ng, C.A.; Patton, S.; Scheringer, M.; Trier, X.; Wang, Z. "Are Fluoropolymers really of low concern for human and environmental Health and separate from other PFAS?" *Environ. Sci. Technol.* **2020**, 54(20), 12820-12828.

[53] GSI Environmental Inc, Jan 31, 2023 "Draft Report of Human and Ecological Toxicity Profiles for 21 PFAS", GSI Job No.: 6299.

[54] Korzeniowski, S.H.; Buck, R.C.; Newkold, R.M.; El Kassmi, A.; Laganis, E.; Matsuoka, Y.; Dinelli, B.; Beauche, S.; Adamsky, F.; Weilandt, K.; Soni, V.K.; Kapoor, D.; Gunasekar, P., Malvasi, M.; Brinati, G.; Musio, S. "A critical review of the application of polymer of low concern regulatory criterial to fluoropolymers II: Fluoroplastics and fluoroelastomers" **2022**, 19(2), 329-354. (see also published supplemental data)

assembled into fiber bundles to produce water and wastewater treatment products for assembly into system. The manufacturing processes producing product for Europe are located in various locations around the globe and prepare products that are distributed globally. Each manufacturing plant is obligate operate under the local regulatory requirements.

PVDF porous membranes are produced by either a thermally induced phase separation (TIPS) or non-solvent induced phase separation (NIPS) process.[55] In a TIPS process, the polymer is heated to a molten state with a solvent/non-solvent mixture. The solvent/non-solvent mixture is selected so that the polymer is dissolved above a certain temperature and is not soluble at lower temperatures. The hot solution is extruded through a spinneret to form a hollow-fiber and passed through an air gap and further cooled in quench bath or on a cooled roll. As the solution cools, polymer rich phases and solvent rich phases form. The polymer rich phases solidify and the solvent rich phased are eventually rinsed out and become pores.

In place of a temperature change, a NIPS process relies on diffusion of a non-solvent into the dissolved PVDF to achieve a phase change. A solution of PVDF is cast through a spinneret to form a hollow fiber which is immersed into a non-solvent bath. The non-solvent diffuses into the hollow fiber and induces phase separation to polymer-rich and solvent rich domains. The polymer-rich domains become the membrane and the solvent rich domains become the pores.

PVDF hollow fiber spinning by either a TIPS or NIPS process is easily scaled with parallel operating spinnerets to yield large volumes of PVDF membrane active area. The final membrane is comprised of nearly 100% PVDF with pore sizes ranging from 0.02-0.05 microns for UF membranes and 0.1-10 microns for MF membranes. Similar processes have been developed and commercialized for producing hollow fibers made from other polymer types (e.g., polyethersulfone, polysulfone).

Membrane producers have optimized the membrane hollow fiber making process to minimize PVDF waste through in-process recovery mechanisms and yield optimizations. Loss of PVDF during manufacturing is generally less than 10% and the resulting waste is treated by the permitted waste management process of the producer in compliance with the region in which they operate. Landfill or incineration are generally available options.

The PVDF hollow fiber membranes are assembled into bundles for use in pressurized ultrafiltration modules, submerged UF/MF systems, or membrane bioreactors. The product

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[55] Jung, J.T.; Kim, J.F.; Wang, H.H.; di Nicolo, E.; Drioli, E; Lee, Y.M. “Understanding the non-solvent induced phase separation (NIPS) effect during fabrication of microporous PVDF membranes via thermally induced phase separation (TIPS). Garcia, J.U.; Iwama, T.; Chan, E.Y.; Tree, D.R.; Delaney, K.T.; Fredrickson, G.H. “Mechanism of asymmetric membrane formation in non-solvent induced phase separation” *ACS Macro Lett.* **2020**, 9(11), 1617-1624.

datasheet for UF/MF products discloses to the customer what polymer is used to make the fibers installed in the product. Thus, choosing PVDF type membranes is transparent to the customer.

The PVDF UF/MF membrane containing products are installed into water or wastewater treatment systems for 24/7 operation. With routine maintenance using common cleaning detergents such as bleach or caustic, the membranes can last between 7-20 years in service. On average the membranes will produce 65 liters of water per square meter of membrane active area per hour, thus each square meter of membrane area will treat 5.7 million liters of water in a 7 year lifetime.

End of life of PVDF membranes

As part of a standard water and wastewater treatment maintenance process, membranes showing reduced performance will need to be replaced. When treating dirty waters (those containing high levels of suspended solids like bacteria or silt and/or contain high levels of organic matter) , MF/UF membranes will become fouled which leads to more energy (i.e., pressure) required to drive water through the membrane. To regain performance, the membranes are cleaned with chemicals such as base, acid, bleach, peroxide, etc. Because irreversible fouling (i.e., foulants that don't clean off the membrane) is the main reason for membrane replacement, research is often focused on understanding the fouling mechanism in various applications to both optimize the operating conditions and identify effective cleaning regimens.[56,57,58] The tolerance of PVDF to a wide range of cleaning chemicals offers the most options for finding an effective cleaning process. Ultrafiltration membranes made with PES have a more restrictive tolerance to cleaning chemicals leading to more frequent replacement.[59,60]

Due to the chemical resilience of PVDF to cleaning chemicals, PVDF membranes are the longest lasting polymeric UF membranes commercially available and commonly last more than 7 years before needing to be replaced. This long lifetime serves to reduce the volume of UF membranes discarded each year. When the membranes have reached the end of their lifetime, three material management options exist – landfill, incinerate, and/or recycle.

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[56] Chen, M.; Ding, W.; Zhou, M.; Zhang, H.; Ge, C.; Cui, Z.; Xing, W. "Fouling mechanism of PVDF ultrafiltration membrane for secondary effluent treatment from paper mills" *Chem. Eng. Res. and Design,* **2021**, *167*, 37-45

[57] Ding, W.; Chen, M.; Zhou, M; Zhong, Z.; Cui, Z.; Xing, W. *"*Fouling behavior of poly(vinylidene fluoride) (PVDF) ultratiltration membrane by polyvinyl alcohol (PVA) and chemical cleaning method*" Chinese J. of Chem. Eng.* **2020**, 28(12), 3018-3026

[58] Ahmad, M.A.; Zainal, B.S.; Jamadon, N.H.; Yaw, T.C.S.; Abdullah, L.C. "Filtration analysis and fouling mechanism of PVDF membrane for POME treatment" *J. of Water Reuse and Desalination* **2020**, 10(3), 187-199

[59] Li, K.; Su, Q.; Li, S.; Wen, G.; Huang, T. "Aging of PVDF and PES ultrafiltration membranes by sodium hypochlorite: effect of solution pH" *J. Environ. Sci (China)* **2021**, 104, 444-455.

[60] Malczewska, B.; Zak, A. "Structural changes and operational deterioration of the UF polyethersulfone (PES) membrane due to chemical cleaning" *Scientific Reports* **2019**, 9, 422 doi:10.1038/s41598-018-36697-2

Landfill

PVDF is chemically, thermally, and biologically stable and is not known to transform to dispersive non-polymeric PFAS when disposed in a landfill. The results of simulated landfill exposure of PVDF has been published and reported.[61] Two test methods considered to be state of the art environmental studies were used: OECD 301F – aerobic biodegradability (28 days duration) and ASTM D5511 – Anaerobic biodegradability[62] (90 days duration – equivalent to 6.25 years in a landfill). No biodegradation was observed in either study. In addition, no presence of by-products in the environment were detected. As such, the hazards of the material in a landfill will be the same as the hazards of the PVDF material - a substance of low concern.

Incineration

The largest share of fluoropolymer waste in Europe is reported to be thermally treated through waste to energy plants.[63] Hazardous waste combustion technologies are considered the most promising destruction approaches to achieve high PVDF destruction efficiency; however, published data ensuring complete mineralization is achieved is still limited.[64]

Gujarat Fluorochemicals Limited,[65] a producer of PVDF, provided key stakeholders an unpublished summary of the preliminary results of an incineration study executed by the Karlsruhe Institute of Technology in cooperation with Societe Generale de Surveillance. In this study, incineration under standard operating conditions for municipal and industrial waste incineration (850 ^{o}C – 1100 ^{o}C for two seconds respectively) was evaluated under the consultancy of German Federal Environment Agency (Umweltbundesamt). They found that PVDF was converted to inorganic fluorides (HF and silicon tetrafluoride) and carbon dioxide. Total organic fluorides were non-detectable down to a reporting limit of 0.08 ppm and trifluoroacetic acid was non-detectable down to a reporting limit of 0.04 ppm. Gujarat Fluorochemicals Limited will be submitting results in a separate ECHA consultation entry. It is expected that the methodology and results will be detailed in their report.

A literature survey found additional evidence indicating effective incineration conditions are available. In 2020 study, when PVDF homopolymer was incinerated at 950^{o}C, the main pyrolysis reactions occurred between 400 ^{o}C and 500 ^{o}C. At 900 ^{o}C a complete devolatilization was achieved and the mass was conserved. A negligible difference between theoretical fluorine

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[61] Henry, B. J.; Carlin, J.P.; Hammerschmidt, J.A.; Buck, R.C.; Buxton, L.W.; Fiedler, H.; Seed, J.; Hernandez, O "A critical Review of the application of polymer of low concern and regulatory criteria to fluoropolymers" *Integrated Env. Assess. And Management* **2018,** 14(3) 316-334,

[62] https://www.astm.org/d5511-18.html

[63] Conversio Report: Post-consumer fluoropolymer waste in Europe, 2019

[64] EPA's interim guidance on destruction and disposal, 2020. https://www.epa.gov/pfas/interim-guidance-destroying-and-disposing-certain-pfas-and-pfas-containing-materials-are-not

[65] Incineration Study On Fluoropolymers at their end-of-life by GFL

content (59.4 wt%) and measured fluorine content when incinerated to 950ºC in a two-stage system (59.7 wt%) or measured from oxygen bomb combustion (57.6%) was measured.[66]

In another published study, pyrolysis of PVDF up to 455ºC was conducted and demonstrated mineralization to HF, complex mixtures of other volatile products and char.[67] They note that temperatures higher than 455 ºC are needed for complete mineralization.

The temperature needed to mineralize PVDF has been shown to be lowered by the addition of an oxidizing agent.[68] The addition of aqueous potassium permanganate to PVDF is found to enable mineralization at only 250 ºC. This approach may offer a more energy efficient approach to mineralization than classic incineration.

To provide additional evidence of incineration conditions to achieve complete mineralization, The American Chemical Council is also conducting a study with details of the study and inital conclusions expect as early as Sept 2023. The first phase of the study is to review existing literature and peer reviewed studies characterizing normal municipal solid waste-to-energy plan incinerator conditions. The second phase involves conducting bench-scale studies to characterize the fate of the fluoropolymers under conditions of municipal incinerators. A full-scale phase study is planned for fourth quarter of 2024 to confirm the bench scale results. Polyvinylidenefluoride PVDF) is included in this study.

Other mineralization processes leading to second life value

A recent study by J. Hamaura, *et al.*[69] evaluated the potential mineralization of PVDF to generate fluoride ions for capture and reuse. The generated fluoride ions are allowed to react with calcium hydroxide ($Ca(OH)_2$) to produce a synthetic form of calcium fluoride, CaF_2 – a raw material in high demand for the production of aqueous hydrofluoric acid.[70] Mined Fluorspar (CaF_2) supplies the current demand, but these mines are limited to a few countries.[71] Mineralization of used PVDF could provide a new source of CaF_2 which is independent of nature reserves and accessible to more countries. Additionally, it also provides an environmental benefit by avoiding mining

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[66] https://www.ncbi.nlm.nih.gov/pmc/articles/PMC6789843/#B19-toxics-07-00047

[67] Staper, J.T.; Barnes, W.J.; Yelland, W.E.C. "Thermal degradation of polyvinylidene fluoride and polyvinyl fluoride by oven pyrolysis" US Army Natick Laboratories, 1968.

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[70] Fluorspar Data Sheet - Mineral Commodity Summaries 2020 (usgs.gov)

[71] Mineral Commodity Summaries 2021, U.S. Geological Survey, Reston, 2021, pp. 60–61. https://pubs.usgs.gov/periodicals/mcs2021/mcs2021.pdf

operations for CaF_2 while also avoiding the landfill of a persistent polymeric material, PVDF. Moreover, the laboratory studies indicate that complete defluorination of PVDF can be achieved by superheated water at 250 ^{o}C in the presence of either a low concentration of potassium or sodium hydroxide. These temperatures are substantially lower than that needed for mineralization in incineration process and will be more energy efficient. The economics and environmental impact of this approach can be weighed vs. direct incineration with energy recovery.

Recycling

The stable nature of PVDF makes it a good candidate for primary recycling.[72] Hollow fiber PVDF MF/UF membranes are especially attractive candidates since most producers do not produce them as composite materials. The hollow fibers membranes are bundled and potted at each end to help direct water flow in a housing. Approximately, 80% of the hollow fibers is free not confounded by the potting material and is available to be recycled. Research is in progress between DuPont and Solvay, a producer of PVDF, to evaluate the ability to recycle PVDF from used, “End of Life” MF/UF membranes.

The first phase of this project is in progress. Bundles of hollow fiber PVDF membrane taken from a large Municipal Drinking Water Treatment Plant were provided to Solvay for analytical characterization and comparison to virgin PVDF. The Municipal Drinking Water plant was treating surface water to create potable drinking water. In the process, water from a nearby reservoir undergoes screening, direct coagulation dosing (1-2 ppm aluminum chlorohydrate, ACH), and PVDF Ultrafiltration followed by chlorine addition before being distributed to households and businesses. The plant serves over 100,000 people in the nearby community. The PVDF ultrafiltration membranes provides an absolute barrier against pathogens such as Cryptosporidium and Giardia. Such a plant represents one of hundreds of similar municipal water plants that rely on PVDF membrane technology to supply safe drinking water to local communities.

The used PVDF hollow fiber membrane samples were in operation for approximately 5 years. During operation foulant cake layers build on the membrane surface. Frequent backwashing is used to release the foulant, and a routine chemical cleaning discipline is also adopted. In the case of these membranes the exposure to standard chemical cleaning conditions was as follows.

- every 30 days chemical cleaning (CIP) was conducted – two steps (1) sulphuric acid (pH=2), followed by (2) 1000ppm hypochlorite (pH~10-10.5), and
- short daily maintenance wash (MW) with (1) 200ppm hypochlorite (pH~9.5)

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[72] Veiga, A.G.; de A. Dias, F.G.; do N. Batista, L.; M. Rocco, M.L.; Costa, M.F. “Reprocessed poly(vinylidenefluoride): A comparative approach for mechanical recycle purposes” *Materials Today Comm.* **2020**, 25, 101269.

The total chlorine exposure of these membranes will have been approximately 200,000 ppm.hrs. The likely contaminants on the membranes are expected to be largely comprised of the residual ACH as well as some mineral clays (e.g. alumino silicates).

To test the feasibility for PVDF to be recycled, the properties of PVDF from the used membranes ("End of Life") and virgin PVDF were compared to show that the exposure to the cleaning chemicals did not degrade the material. A summary of the collection of this data is provided in the Appendix. The conclusions so far indicate that the "End of Life" PVDF membrane material has a similar if not the same material characterization as the virgin material. No signs of degradation were observed. The next step in the process is to develop a PVDF purification process to separate the PVDF from the residual foulants that were on the membrane. Subsequent submissions to the consultation will be made as additional information is made available before the close of the consultation period.

End of Life options summary

For the most sustainable End of life option a balance should be considered 1. Energy footprint, 2. The potential for creating secondary hazards from material degradation, 3. The environmental accumulation and 4. Potential for valorizing in a second life application. A summary of the relative impact of the four disposal options describe above are provided in Table 5 where red represents a negative impact and green a favorable one. With the continued use of PVDF for water and wastewater treatment applications, a combination of these methods can be developed and implemented to provide a reduced overall environmental impact of the polymer's persistent nature.

Table 5. PVDF end of life options and relative impact

	Net Energy	Secondary hazards from material degradation	Environmental Persistence	Valuable material to sell
Landfill	🟩	No degradation observed	🟥	🟥
Incineration	Gujarat study shows ~1000^{o} C is needed	Gujarat study complete and preparing to publish; ACC study in progress	🟩	🟥
Incineration + CaF_2 generation	Lab Data shows only ~250 ^{o}C is needed for mineralization	lab data shows full mineralization possible	🟩	🟩
PVDF recycle	🟩	🟩	🟩	🟩

Summary

Polyvinylidene fluoride (PVDF, [-$C_2H_2F_2$-] CAS # 24937-79-9) water and wastewater treatment membranes are safely working to provide a water secure future across the globe under regulatory guidance for both materials used in drinking water systems as well as quality of the water produced. Yet the Annex XV PFAS restriction proposal does not provide a derogation for PVDF water and wastewater treatment membranes. Given the already well-studied MF/UF polymeric membrane field, developing an alternative to PVDF that provides the performance criteria needed to avoid regrettable substitution including meeting regulatory requirements for use in water and wastewater treatment applications, **it will take more than 15 years to develop a replacement to PVDF MF/UF hollow fiber water and wastewater treatment membranes**. Current known materials used in challenging contaminated water and wastewater treatments environments will suffer with higher energy demand, larger treatment systems unable to fit into small urban spaces, more water wastage due to fouling and cleaning in efficiencies, and more frequent replacement.

New regulations that compromise the availability of proven and effective water and wastewater treatment technology used under existing water and wastewater regulatory requirements can disrupt homes, schools, industry, agriculture and even public health and safety.

The evidence provided herein ***supports a recommendation to add a 13.5 year derogation to Annex XV for the use of PVDF to produce membranes used in the highly regulated industrial water and wastewater treatment applications including new plant construction and maintaining existing plants producing drinking water, industrial process water, industrial wastewater and urban wastewater.***

APPENDIX A.

“End of life” PVDF from Water Filtration application – analysis and summary provided by Solvay.

“End of life” membranes hollow fibers of PVDF Solef® 6020 were characterized in terms of Thermal analysis, Calorimetric analysis, Spectroscopy (Nuclear Magnetic Resonance), Solubility, Recyclability.

“End of life” hollow fibers PVDF Solef® 6020 are disassembled, by separating the cage with the hollow fibers from the module structure. “End of life” PVDF Solef 6020 fibers contain on average 1%wt/wt of impurities, mostly metals.

TGA was performed in air, according to ASTM E 1131/ISO 11358 and shows that “end of life” PVDF Solef® 6020 has the same thermal stability as virgin PVDF Solef® 6020, based on T(°C) 50% wt/wt decomposition (see Table 1).

DSC was performed according to ASTM D 4591/ISO 11357 and the results confirm that “end of life” PVDF Solef® 6020 has the same crystalline structure as virgin PVDF Solef® 6020, based on T second fusion and enthalpy second fusion (ΔH, J/g) (see Table below).

Table 1 - Thermal and Calorimetric Analysis

PVDF Sample	Residue (%wt/wt) T>750°C	[T50]±10(°C) (%wt/wt)	T crystallization ±5(°C)	ΔH crystallization±3(J/g)	T 2nd fusion ±1(°C)	ΔH 2nd fusion ±3(J/g)
Virgin Solef® 6020	0	495	134	60	169	57
“End of life” Solef® 6020 fiber	0	489	138	59	170	57

Note: [T50] is the Temperature at which PVDF lost 50% initial weight

Characterization of “end of life” Solef® PVDF 6020 demonstrated the equivalence to virgin Solef® 6020 as thermal and crystalline behavior confirming the PVDF stability and absence of degradation in application.

Solubility testing

Solubility test method was performed by weighting 85.0g of solvent in a glass bottle and subsequently, under magnetic stirring, 15.0g of PVDF were added. The bottle was warmed at 65.0°C under magnetic stirring on a heater plate for 30 minutes. After that period, stirring and heating were stopped and the content of the bottle was visually inspected and the observations recorded.

The solubility tests were performed by using as solvent Dimethylsulfoxide (DMSO), dissolving either virgin PVDF Solef® 6020 or “end of life” PVDF Solef® 6020 respectively, and, as a further cross-check, by using N-Methyl-Pyrrolidone (NMP) as solvent, dissolving either virgin PVDF Solef® 6020 or “end of life” PVDF Solef® 6020, respectively.

Solubility results for all tests demonstrate that the “end of life” PVDF Solef® 6020 is equivalent to virgin PVDF Solef® 6020, in terms of solubilization, solution flowability, at same concentration, time, temperature of dissolution. The only observed difference is related to slight yellowing and slight turbidity of “end of life”PVDF Solef® 6020 solution.

Spectroscopic results

NMR Characterization

Sample preparation procedure: 0.6 ml of DMSO d6 were added to 40 mg of sample in a 5 mm NMR tube. The tube was heated at 70°C for some hours until complete dissolution of the sample and then 1 H and 19 F spectra were collected using a 500 MHz NMR.

PVDF Solef® 6020 stability and absence of degradation is confirmed by NMR spectroscopic investigation: the 19F-NMR spectra recorded respectively for virgin PVDF Solef® 6020 and for "end of life" PVDF Solef® 6020 show no difference.

Recyclability: "end of life" PVDF Solef® 6020 fibers have been recycled by physical (green solvent based) recycling to produce recycled PVDF Solef® 6020. PVDF Solef® 6020 stability and absence of degradation enable recycling of "end of life" PVDF. The cage containing the hollow fibers is insoluble in the solvents for PVDF and this feature allows the recyclability of fibers.