# PFAS – Potential Impacts to the Sealing Industry

Jim Wasser
Brian Kalfrin
Denise Lee

john crane
a smiths company

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The information contained was deemed correct at that time

# Abstract

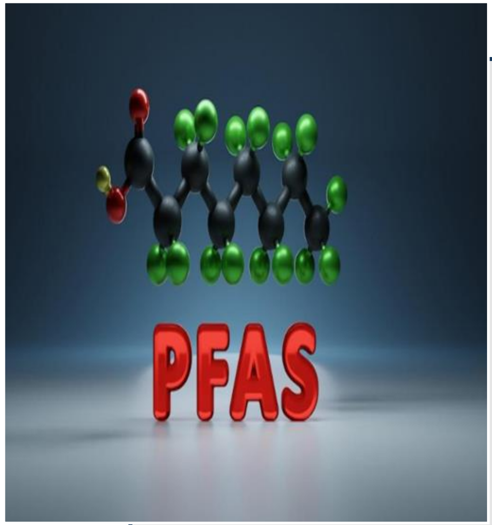
Per and polyfluoroalkyl substances, also known as PFAS, is a broad term that contains several categories and classes of durable substances. Fluoropolymers are one specific class of PFAS that are vital to the pump and sealing industry as part of the energy sector.

This tutorial overviews Per- and Polyfluoroalkyl Substances, providing the reader with everything they do not know or want to know about PFAS. Specifically, the tutorial will outline a science-based overview of PFAS, distinguishing hazardous from non-hazardous, and highlighting the potential impacts of proposed wholesale regulation of all PFAS materials. Additionally, the tutorial will highlight and discuss possible alternative approaches to avoid PFAS materials in mechanical seals and discuss the potential limitations in a broad design context to emissions and leakage management of such designs.

# Agenda

Everything You Didn't Know You Wanted To Know About PFAS!

- Overview
- What are PFAS?
- History of PFAS
- Where  Can PFAS Be Found?
- PFAS Applications Overlooked On The World Stage
- What Is The Impact On The Sealing Industry
- PFAS Materials Without The Surfactants (Processing Aids)
- Impact on Seal Design
- Realistic Impacts To Sealing Volatile & Hazardous Fluids




# Overview

# Overview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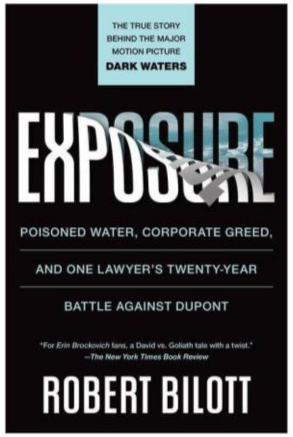
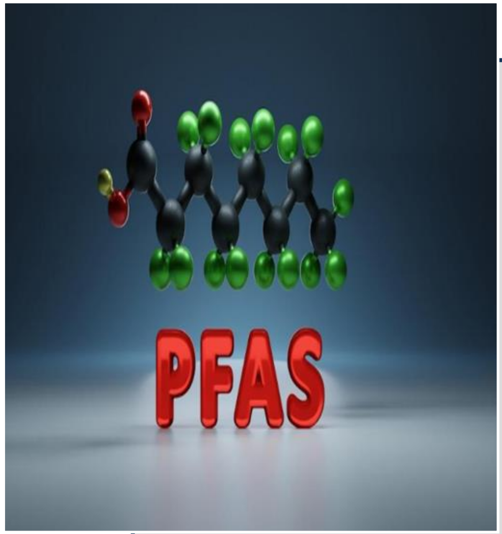



*The incredible true story of the lawyer who spent two decades building a case against DuPont for its use of the hazardous chemical PFOA, uncovering the worst case of environmental contamination in history - affecting virtually every person on the planet--and the conspiracy that kept it a secret for sixty years.*

*PFAS seems to be popping up everywhere as the public becomes more aware of these chemicals!*




# What Are PFAS?

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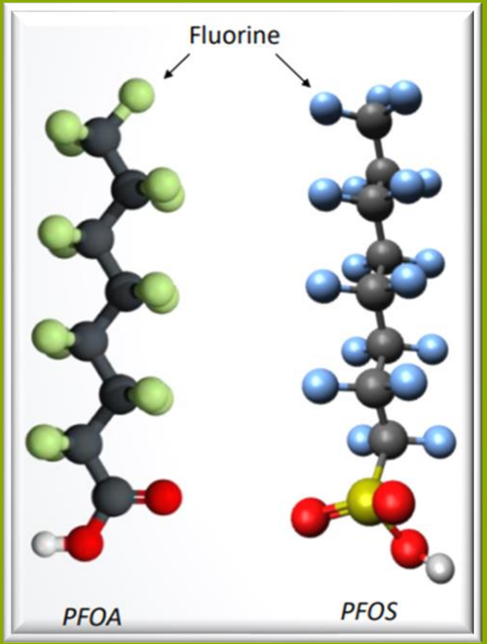
## PFAS




## "The Forever Chemicals"

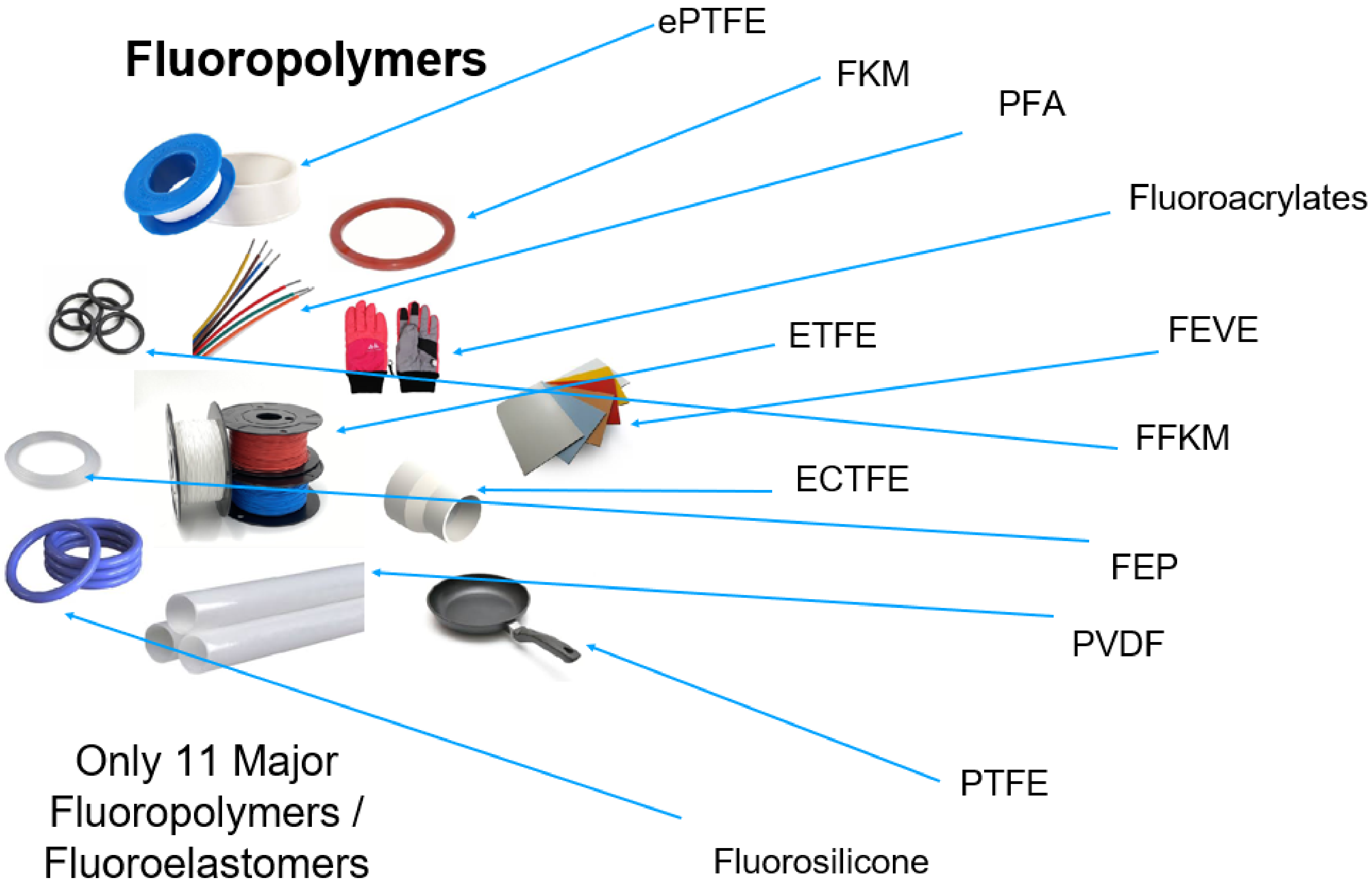
Manmade class of chemical compounds


The carbon-fluorine bond is the 4th strongest single bond

Stable in environment, unreactive, and resilient

# What Are PFAS?

**Fluoropolymers**



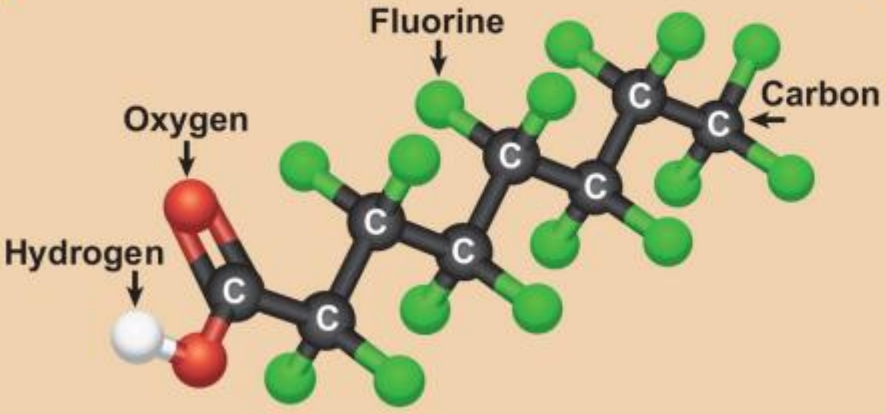

Only 11 Major Fluoropolymers / Fluoroelastomers

**PFAS = Per- and Poly- Fluoroalkyl Substances**

**Per-** or **Poly-** simply means **MANY**

**Fluoro** means they contain **Fluorine atoms**

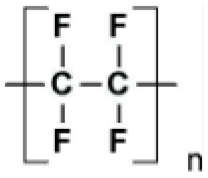
**Alkyl** means they have a **Carbon**



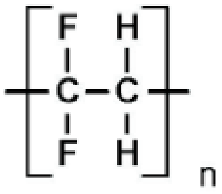
# What Are Polymer PFAS?

## Repeating chains

Fully Fluorinated Methylene

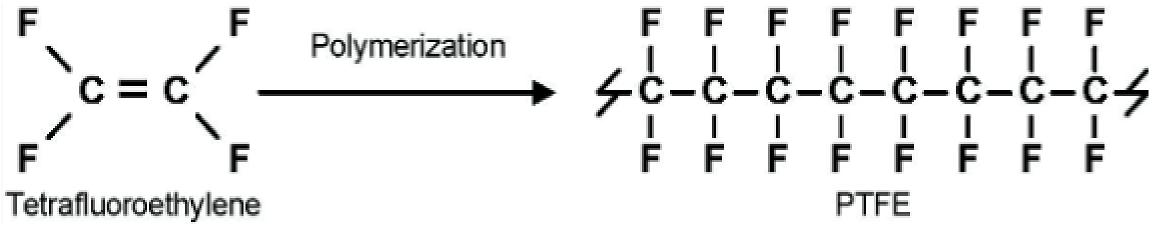


Fully Fluorinated Methyl

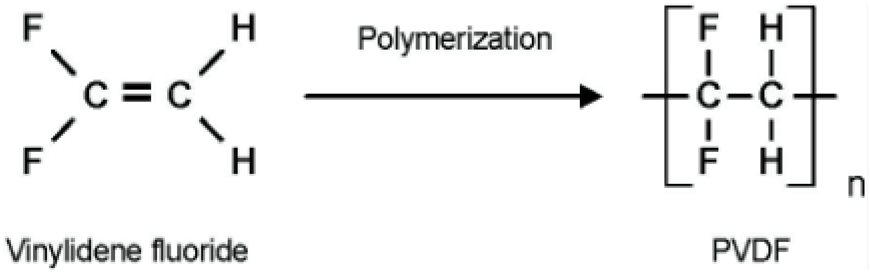


EXAMPLES:

PTFE (Polytetrafluoroethylene)



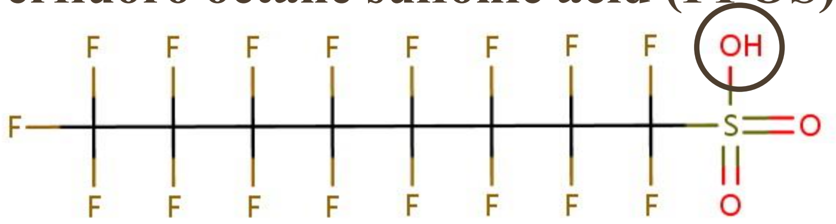

PVDF (Polyvinylidene fluoride)



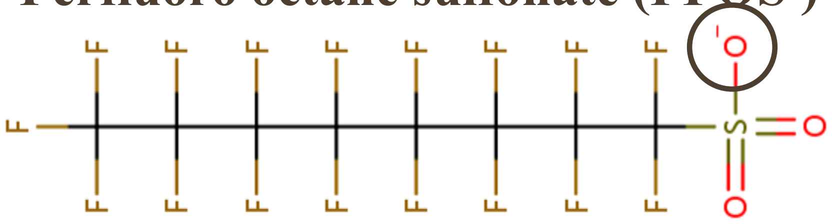
# What Are Non-Polymer PFAS?

## Sulfonic Acids & Sulfonates (PFSAs)

**Perfluoro octane sulfonic acid (PFOS)**

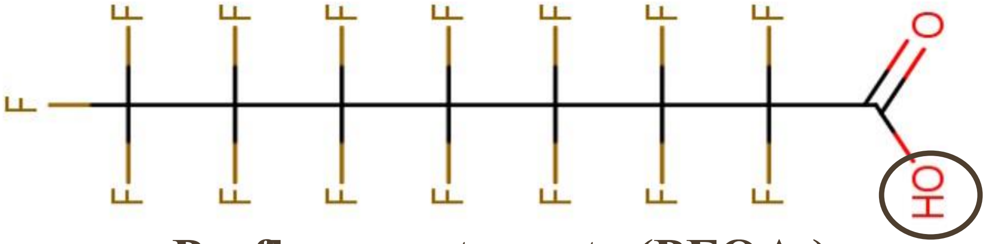


**Perfluoro octane sulfonate (PFOS$^-$)**

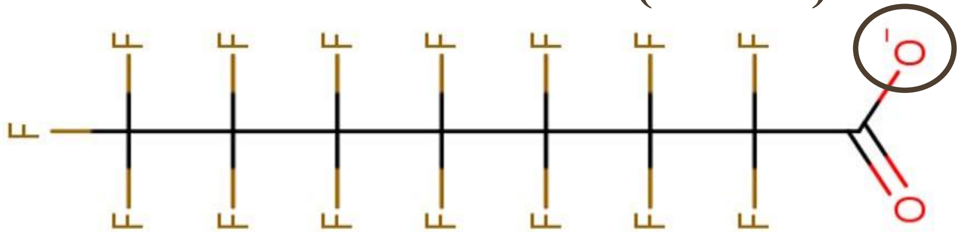


## Carboxylic Acids & Carboxylates (PFCAs)

**Perfluoro octanoic acid (PFOA)**

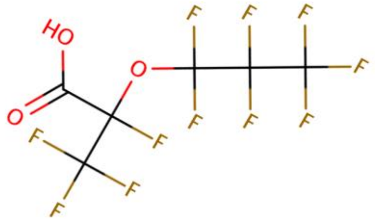


**Perfluoro octanoate (PFOA$^-$)**

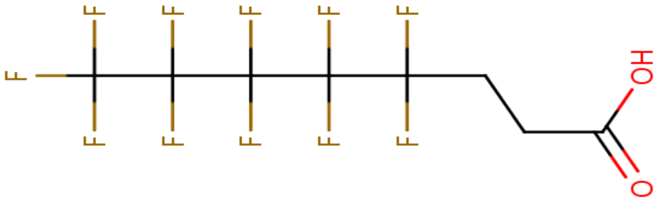


## Other

**HFPO-DA (GenX)**



**5:3 FTCA (alcohol)**



# PFAS Transformation Pathways

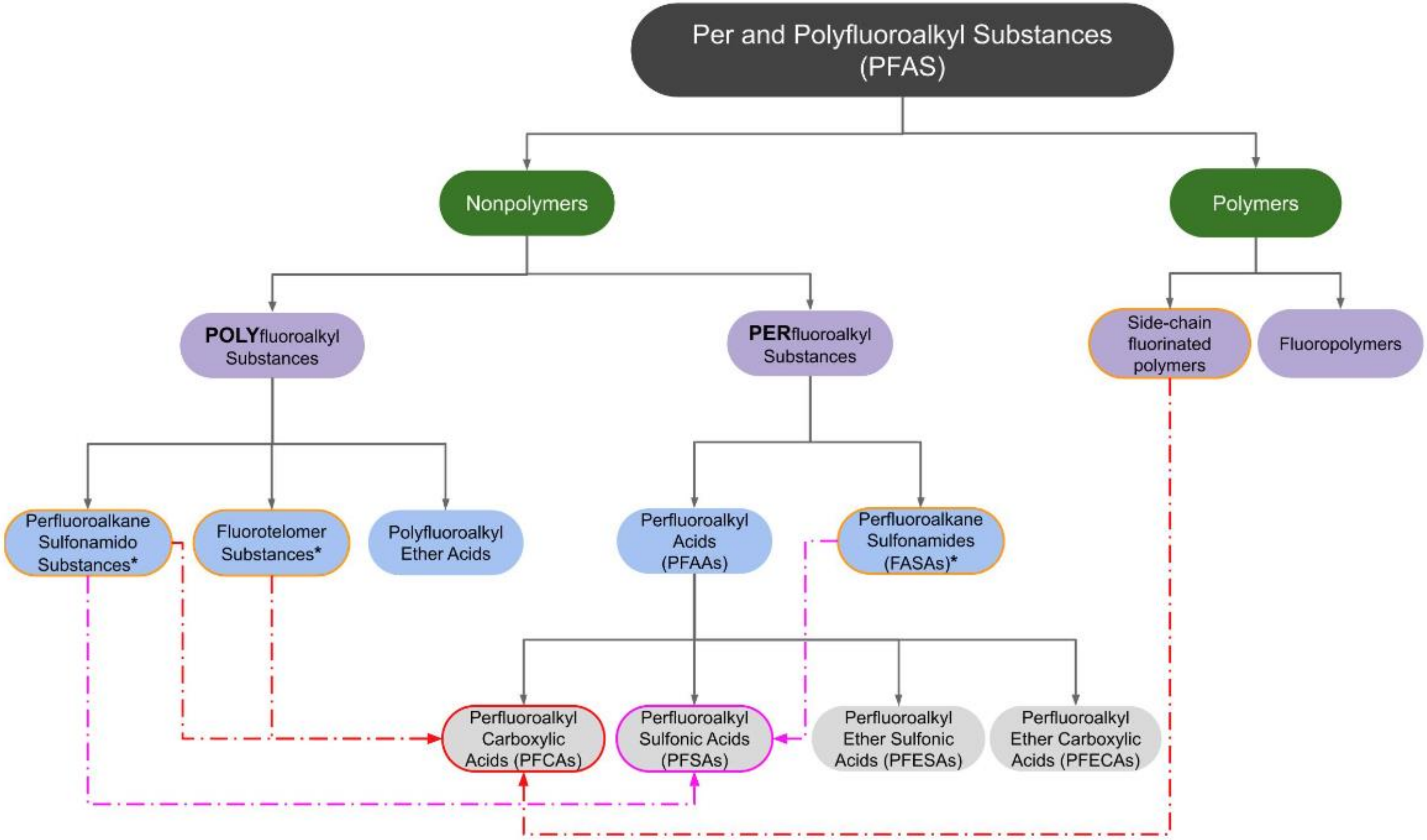
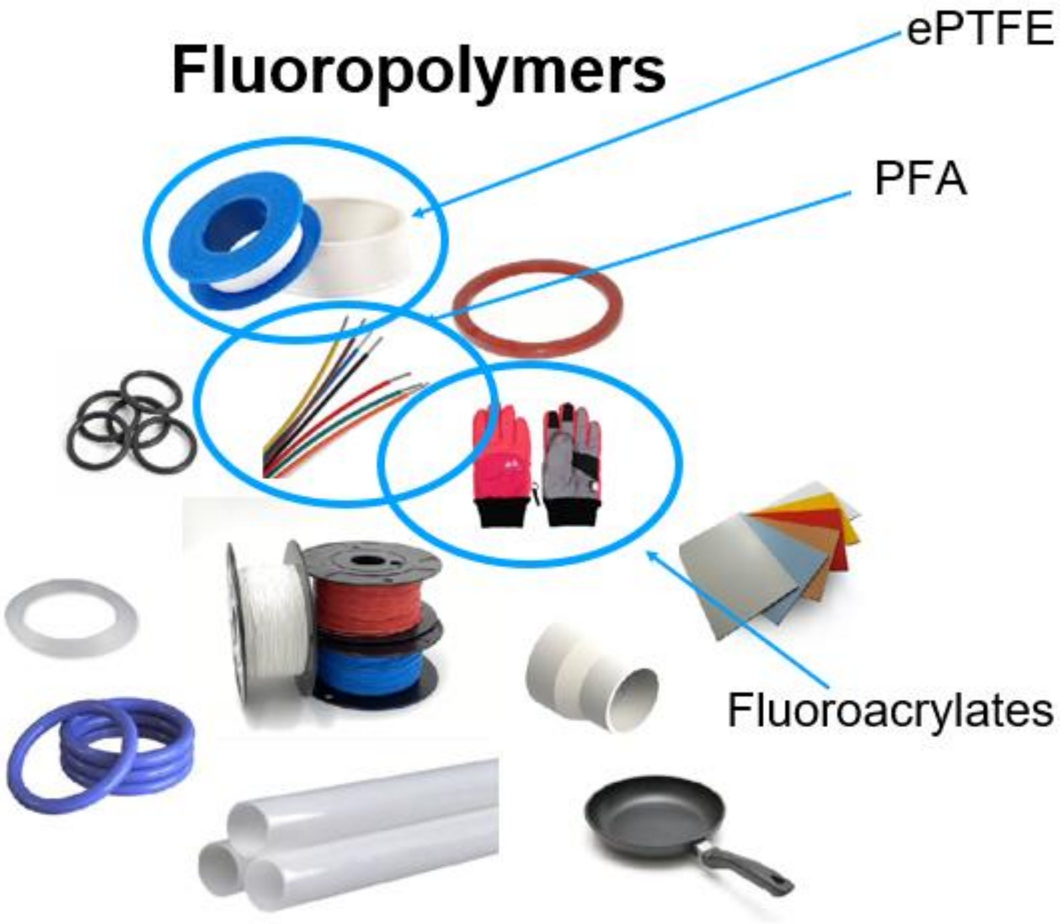


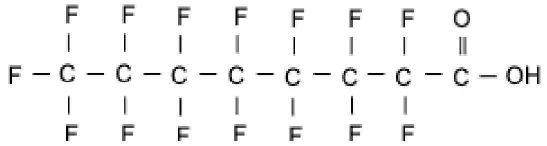

Image Credit: Interstate Technology & Regulatory Council (2022)

# Fluoropolymer Sources of PFAS Salts

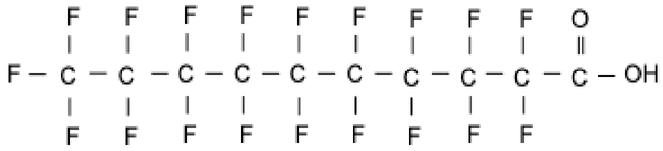



## Water Soluble PFAS Salts

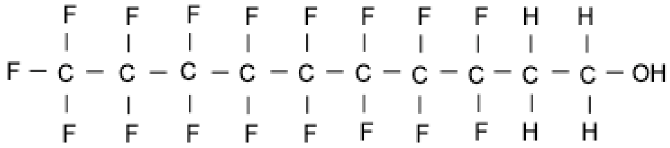
PFOA



PFDA

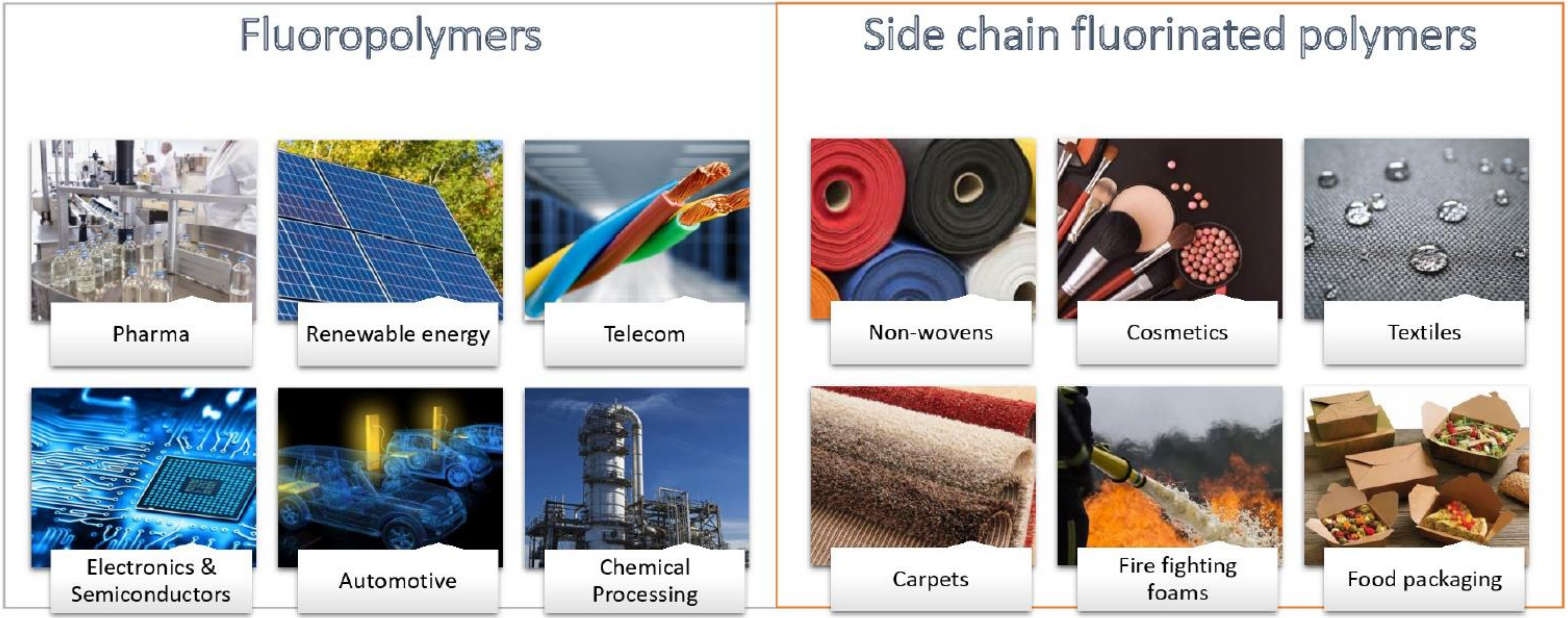


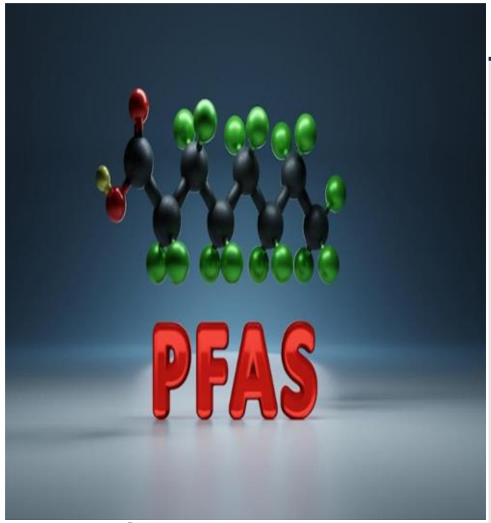
8:2 FTOH



There are ~20 fundamental PFAS salts

# PFAS Application: Industrial vs. Consumer






# History of PFAS

# History of PFAS

**1938**
- Polytetrafluoroethylene (PTFE) discovered by DuPont
- Roy Plunkett

**1949**
- PTFE used in products

**1956**
- Stain-resistant products (PFOS)

**1968**
- Navy developed AFFF

**1978**
- Detected in blood of manufacturing workers

**2002**
- PFOS manufacturing phased out

**2006**
- PFOA phased out
- EPA PFOA Stewardship Program

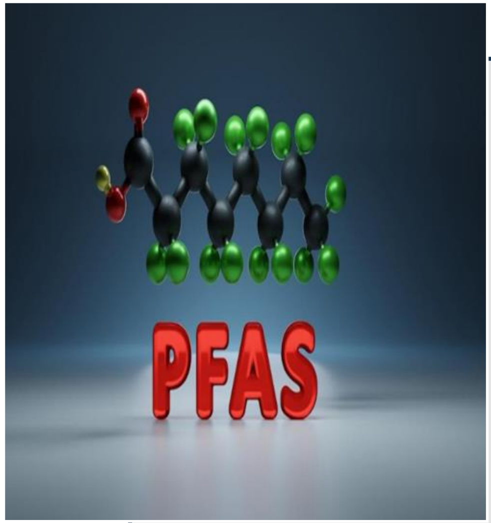
**2009**
- Stockholm Convention classifies PFOS as a persistent organic pollutant (POP)

**2015**
- PFOA phase-out complete
- Sampling of public drinking water wells for PFAS (EPA Unregulated Contaminant Monitoring Rule (UCMR3)

**2016**
- EPA Health Advisory announced for PFOA/PFOS (70 ppt, together and separately)

**and more ...**

6




# Where Can PFAS Be Found?

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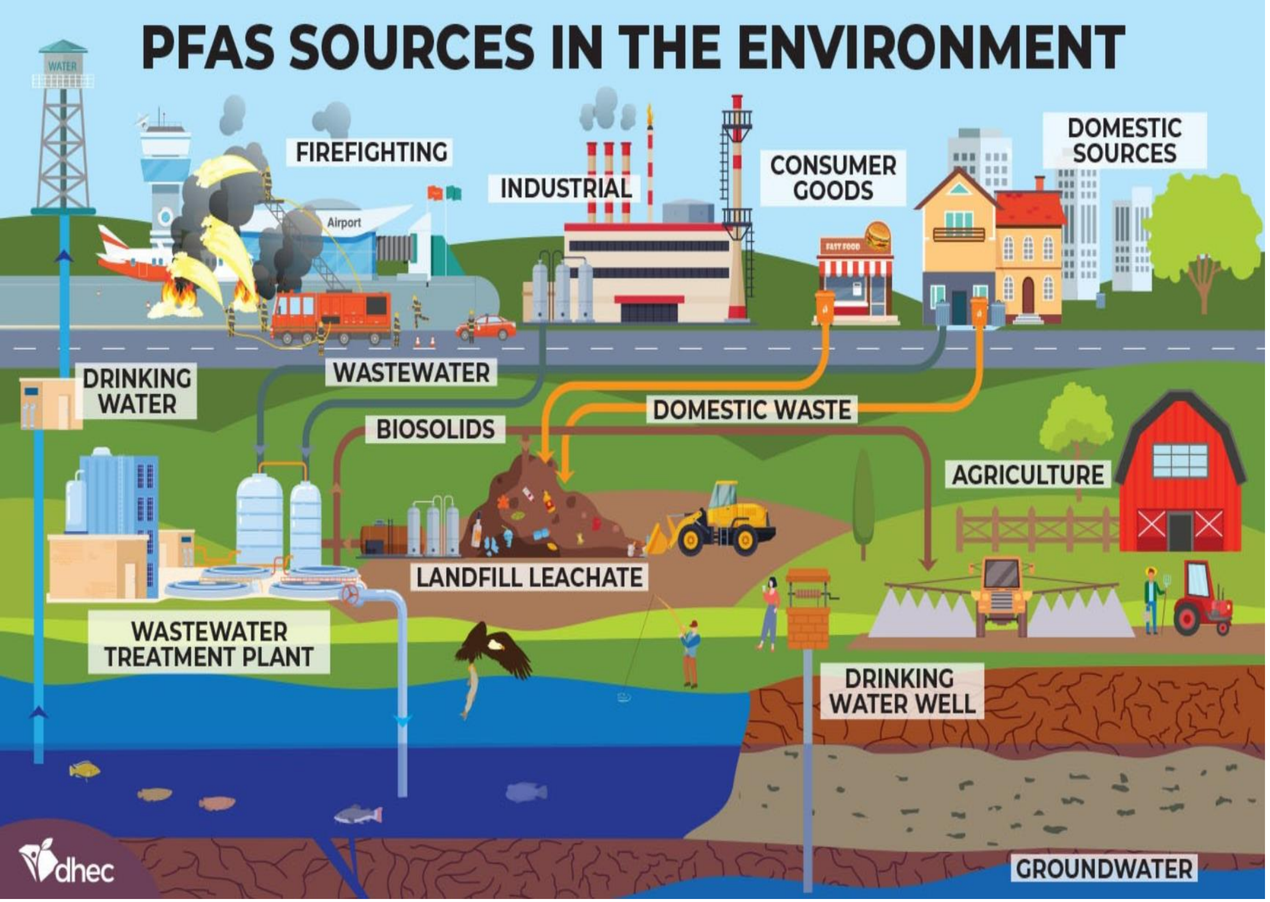
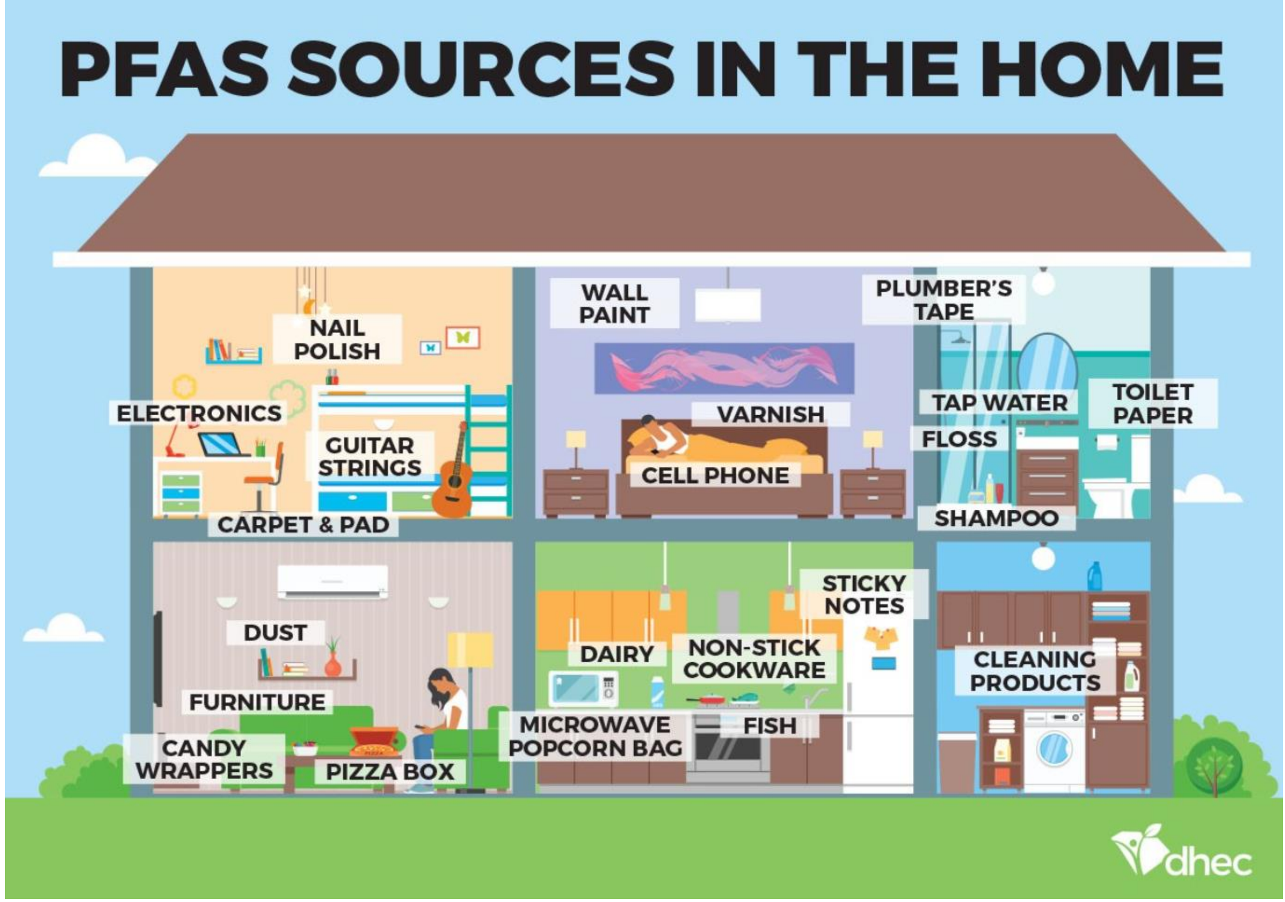



DHEC. (n.d.). *PFAS Sources in the Environment.* [Infographic]
https://scdhec.gov/environment/polyfluoroalkyl-substances-pfas

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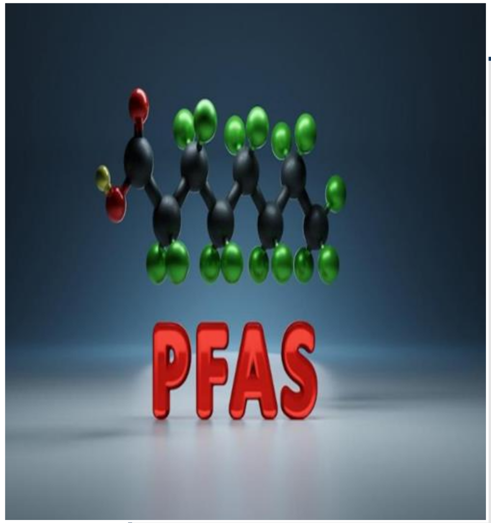



# PFAS Applications Overlooked On The World Stage

# PFAS Applications Overlooked On The World Stage

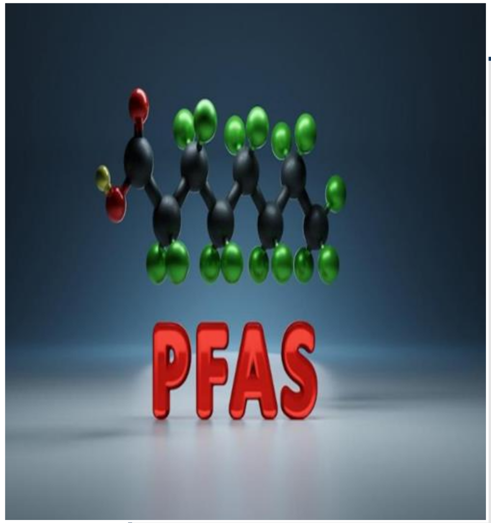
Mechanical seals are one application where PFAS containing materials have been commonly used. As the regulation of PFAS materials becomes more stringent, alternative approaches must be explored to avoid their use in mechanical seals.

One limitation is the compatibility of non-fluorinated materials with specific fluids or gases. PFAS containing materials have unique properties that allow them to resist degradation and remain effective in diverse chemical environments.

> Alternative materials must be carefully evaluated to ensure their compatibility and reliability, especially in demanding applications where chemical resistance and durability are critical. Additionally, the manufacturing and installation processes may need to be modified to accommodate these alternative materials efficiently.

Another consideration is the management of emissions and leakage in designs using alternative materials. PFAS containing materials have been valued for their ability to create effective seals in high-pressure or high-temperature settings.

> The replacement materials must demonstrate comparable performance to prevent leakage and maintain equipment integrity. Proper testing and evaluation protocols should be established to verify the effectiveness and longevity of alternative designs, ensuring they meet or exceed industry standards.




# What Impact on The Sealing Industry

# Regulation Impact on the Sealing Industry

PFAS containing materials are resistant to harsh chemicals, maintain the shape and ability to seal at high and low temperatures, are water and oil repellent, and have low friction coefficients.

These materials can handle the conditions found in refineries and chemical plants and are low cost compared to alternative materials.

PFAS elastomers can be molded into O-rings, gaskets, bellows, and can be used as a protective coating. They can seal against metals, plastics, ceramics, and itself if so desired.

When considering an O-ring, the elastomeric material must be able to be stretched (around a shaft/sleeve), must be resistant to chemical attack, have low swell due to heat and chemical, and must be able to be compressed (squeezed).

# Regulation Impact on the Sealing Industry

One spectrum grade of a FKM material (fluoroelastomer) or a FFKM material (perfluoroelastomer) can handle a large range of chemicals and temperature conditions without degrading or losing their shape. These materials have been successfully used in the sealing industry for decades. An example of an FKM material is Viton™ and an example of a FFKM material is Chemraz™.

Mechanical seals typically have several points of sealing; along the shaft, between the housing and gland plate, the sealing interface (seal faces), and at the secondary seals. Each component is designed based on the conditions and its purpose, but also with the materials of construction in mind.

It is critical to the seal performance and life of the seal that these components remain functioning in harsh conditions.

PTFE is a PFAS containing material. PTFE is commonly used as the gasket between the stationary equipment housing and the gland plate (housing) of the seal cartridge. PTFE is very inert to most chemicals; it is compressible up to 20-30% and is inexpensive. Among desirable properties, PTFE is easily molded into various shapes, and it does not cold flow if squeezed the proper amount. PTFE can be used with a binder, such as glass or carbon, to improve its strength and cold flow ability.

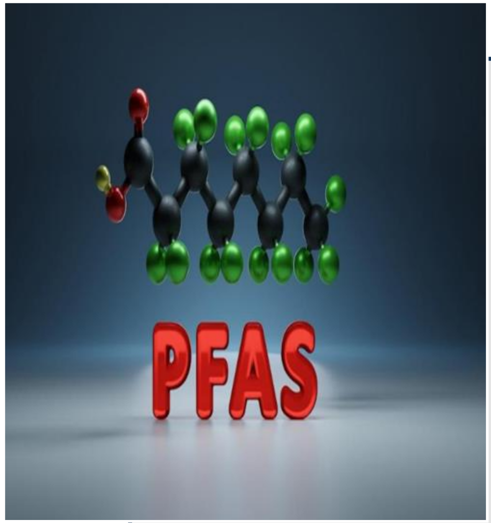
# Alternative Materials

| | POLYTETRAFLUOROETHYLENE (PTFE) | POLYAMIDE-IMIDE (PAI) | POLYBENZIMIDAZOLE (PBI) | POLYIMIDES (PI) | POLYETHERIMIDE (PEI) | POLYETHERSULFONE (PES OR PESU) | POLYSULFONE (PSU) | POLYPHENYLSULPHONE (PPSU) | POLYPHETHYLENE SULFIDE (PPS) | POLYPHTHALAMIDE (PPA) | LIQUID-CRYSTAL POLYMER (LCP) | POLYETHERETHERKETONE (PEEK) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| WORKING TEMPERATURE (°C) | 260 | 220 | 340 | 260 | 170 | 98 | 150 | 149 | 200 | 140 | 200 | 154 |
| TEMPORARY TEMPERATURE (°C) | 290 | 280 | 540 | 360 | 170 | 185 | 180 | 210 | 220 | 140 | 240 | 260 |
| YOUNG'S MODULUS (GPa) | 0.4-0.8 | 4.0-5.0 | 5.9 | 1.3-4.0 | 3.0 | 2.5-2.7 | 2.5-2.7 | 2.34 | 3.3-4.0 | 3.7 | 10.0-19.0 | 3.5-3.9 |
| ACID, DILUTED | + | + | ± | (±) | + | + | (+) | (+) | + | (+) | + | + |
| ACID, CONCENTRATED | + | + | - | (±) | + | + | ± | ± | + | (+) | (+) | (+) |
| BASES, DILUTED | + | ± | ± | - | + | + | + | + | + | + | + | + |
| BASES, CONCENTRATED | + | - | - | - | - | (+) | (+) | (+) | (+) | + | (+) | + |
| HYDROCARBONS, AROMATIC | + | + | + | + | - | + | - | (±) | + | + | + | + |
| HYDROCARBONS, ALIPHATIC | + | + | + | + | + | + | + | + | + | + | + | + |
| ESTERS & KETONES | + | + | + | + | (±) | - | - | - | + | (+) | + | + |
| ETHERS | + | + | + | + | + | + | ± | ± | + | (+) | + | + |
| SOLVENTS, CHLORIDE BASED | + | + | + | | (±) | ± | ± | - | ± | + | + | + |
| ALCOHOLS | + | + | + | ± | + | + | ± | ± | + | + | + | + |

KEY: + Resistant; (+) Partially Resistant; ± Conditionally Resistant; (±) Partially Not Resistant; - Not Resistant

# Alternative Materials

| Comparison | PTFE | PEEK | Silicone | Poly urethane | PFA | Irradiated PTFE | ePTFE | Fluoro acrylates | FKM | FFKM | PVDF | Nitrile Rubber | EPDM | Stainless steel | Fluoro silicone |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Low Friction | Excellent | Decent | Decent | Poor | Decent | Excellent | Excellent | Excellent | Poor | Poor | Decent | Poor | Poor | Poor | Excellent |
| Chemical Resistance | Excellent | Decent | Decent | Poor | Excellent | Excellent | Excellent | Excellent | Excellent | Excellent | Excellent | Decent | Decent | Poor | Decent |
| Water Resistance | Excellent | Excellent | Decent | Decent | Excellent | Excellent | Excellent | Excellent | Excellent | Excellent | Excellent | Excellent | Excellent | Excellent | Excellent |
| Oil Resistance | Excellent | Excellent | Poor | Excellent | Excellent | Excellent | Excellent | Excellent | Excellent | Excellent | Excellent | Excellent | Poor | Excellent | Excellent |
| Temperature Resistance | Excellent | Excellent | Excellent | Poor | Excellent | Excellent | Excellent | Excellent | Excellent | Excellent | Decent | Decent | Decent | Excellent | Excellent |
| Flexibility | Decent | Poor | Excellent | Excellent | Excellent | Excellent | Excellent | Excellent | Excellent | Excellent | Poor | Excellent | Excellent | Poor | Excellent |
| Forever Chemicals (initial) | Excellent | Excellent | Poor | Excellent | Decent | Decent | Decent | Decent | Decent | Decent | Excellent | Excellent | Excellent | Excellent | Poor |
| Forever Chemicals (over time) | Excellent | Excellent | Decent | Excellent | Decent | Excellent | Excellent | Decent | Excellent | Decent | Excellent | Excellent | Excellent | Excellent | Decent |
| Bio- compatibility | Excellent | Excellent | Decent | Decent | Excellent | Excellent | Excellent | Decent | Decent | Decent | Excellent | Decent | Decent | Excellent | Decent |
| Insulation | Excellent | Decent | Decent | Decent | Excellent | Excellent | Excellent | Excellent | Poor | Poor | Poor | Decent | Decent | Poor | Excellent |
| Radiation Resistance | Poor | Excellent | Poor | Decent | Poor | Poor | Poor | Poor | Poor | Poor | Decent | Poor | Decent | Excellent | Poor |




# PFAS Materials Without The Surfactants (Processing Aids)

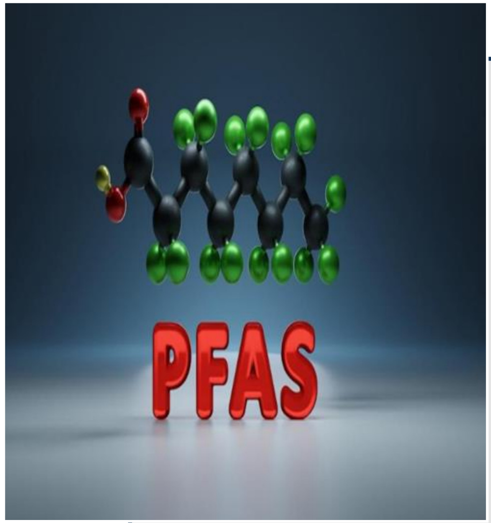
# PFAS Materials Without The Surfactants (Processing Aids)

Surfactants are used in PFAS materials production but are not found in the final material. The final process (emulsion reaction) in the material production is to recover the PFAS polymer, which also removes the surfactant.

Water is used as the fluid in the emulsion reaction. Historically, the surfactants were discharged with the water into waste stream by the major manufacturers. High levels of PFAS surfactants can be found near chemical processing plants and have found their way into rivers, streams, and farmland.

The top raw material suppliers are now moving away from the use of surfactants for FKM (fluoroelastomer) materials, but to date, there is no alternative for a surfactant free FFKM (perfluoroelastomer). How does this impact the sealing industry?

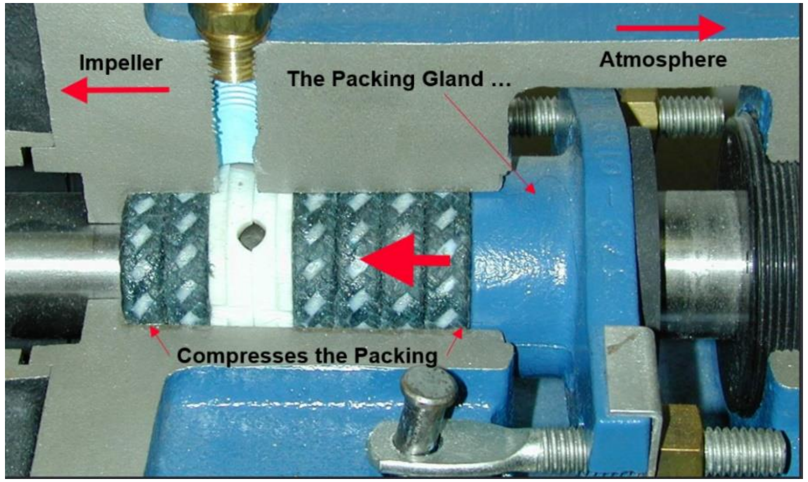
Mechanical seal designers need to test the surfactant free materials to determine if they retained their physical properties, especially those critical to seals' performance. Chemical compatibility is expected to be similar, but testing will be required to validate that statement. What will change is the cost to produce the raw material and the finished products. The demand for these new materials will be extreme and will only increase if the full PFAS ban is upheld.




# Impact on Seal Design

# Impact on Packing

The industry moved towards materials such as PTFE and non-HVOC treatments. Polytetrafluoroethylene (PTFE) and non-High Volatility Organic Compound (HVOC) are commonly used to improve the lubricating properties of the packing, while reducing the friction coefficient between the rotating shaft and the packing rings. Some packing materials incorporate PTFE within the yarn while others dip the rings post braiding. PTFE is considered a PFAS material and will need to be removed from the final process and product. Without a suitable alternative, the effectiveness of the seal packing materials will be negatively impacted.



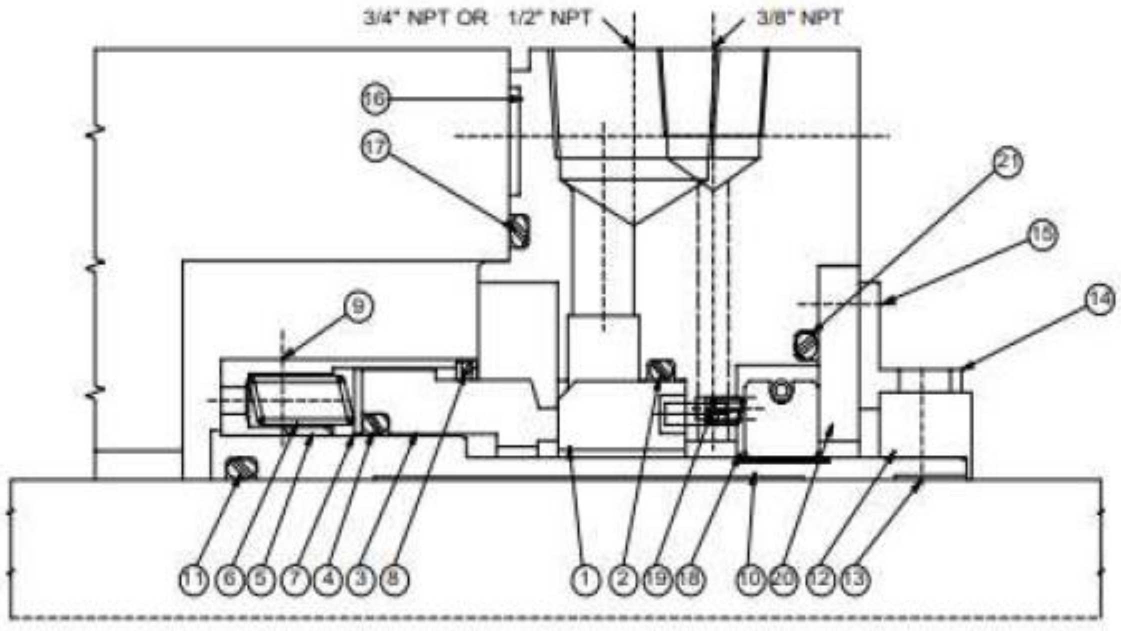

If an alternative material cannot provide similar properties to PTFE, end-users may counter the increase in friction (and the resulting added horsepower consumption), by reducing the squeeze (compression) on the rings. This may result in increased product leakage along the rotating shaft. This will result in an increase in emissions of the fluids being sealed.

# Impact on Seal Design

Secondary seal materials are an important part of the mechanical seal and special considerations need to be studied when considering alternative materials.

They can be either static or dynamic sealing devices. An example of a static seal is those sealing the equipment to the seal cartridge or those sealing the rotating shaft.

Dynamic secondary seals are those used to seal the sealing faces (primary ring and mating ring). It is important that dynamic seals remain flexible throughout the life of the seal. Elastomeric O-rings are one of the more common secondary seals used within a seal assembly.




**Part Name**

| | | | | | |
|---|---|---|---|---|---|
| 1 | Mating Ring | 8 | Snap Ring | 15 | Cap Screw |
| 2 | O-Ring | 9 | Set Screw | 16 | Gland Plate |
| 3 | Primary Ring | 10 | Sleeve | 17 | O-Ring |
| 4 | O-Ring | 11 | O-Ring | 18 | Bushing Assembly |
| 5 | Retainer | 12 | Collar | 19 | Spring |
| 6 | Spring | 13 | Set Screw | 20 | Auxiliary Gland |
| 7 | Disc | 14 | Spacer | 21 | O-Ring (optional) |

# O-Rings

The O-ring material and the amount of squeeze will greatly impact the performance of the seal

If the O-ring material is not properly selected, it will degrade, allowing leakage. The squeeze subjected onto the O-ring will influence the ability of the faces to track each other and allow the seal to tolerate minor vibration, shaft movement, and equipment misalignment

Squeeze is impacted by the thermal growth of the materials defining the bore, the amount of swell due to the material absorbing the sealed fluid and the effects of the temperature, and the amount of stretch of the O-ring when installed

Excessive squeeze results in the faces losing their flexibility which may result in higher wear, or low closing forces. Both will result in elevated leakage rates

When deciding on an elastomeric material, be sure to consider the temperature range of the conditions in which it will be installed and the hardness of the material within that range

Empirical data has shown that O-rings, particularly FKM material, leak considerably less than PTFE wedges, u-cups, and other pusher secondary sealing elements

*Source: Presented in a lecture from the proceeding of the Eleventh Pump Users Symposium (Kittleman 1994)*

# Static and Dynamic Secondary Seals

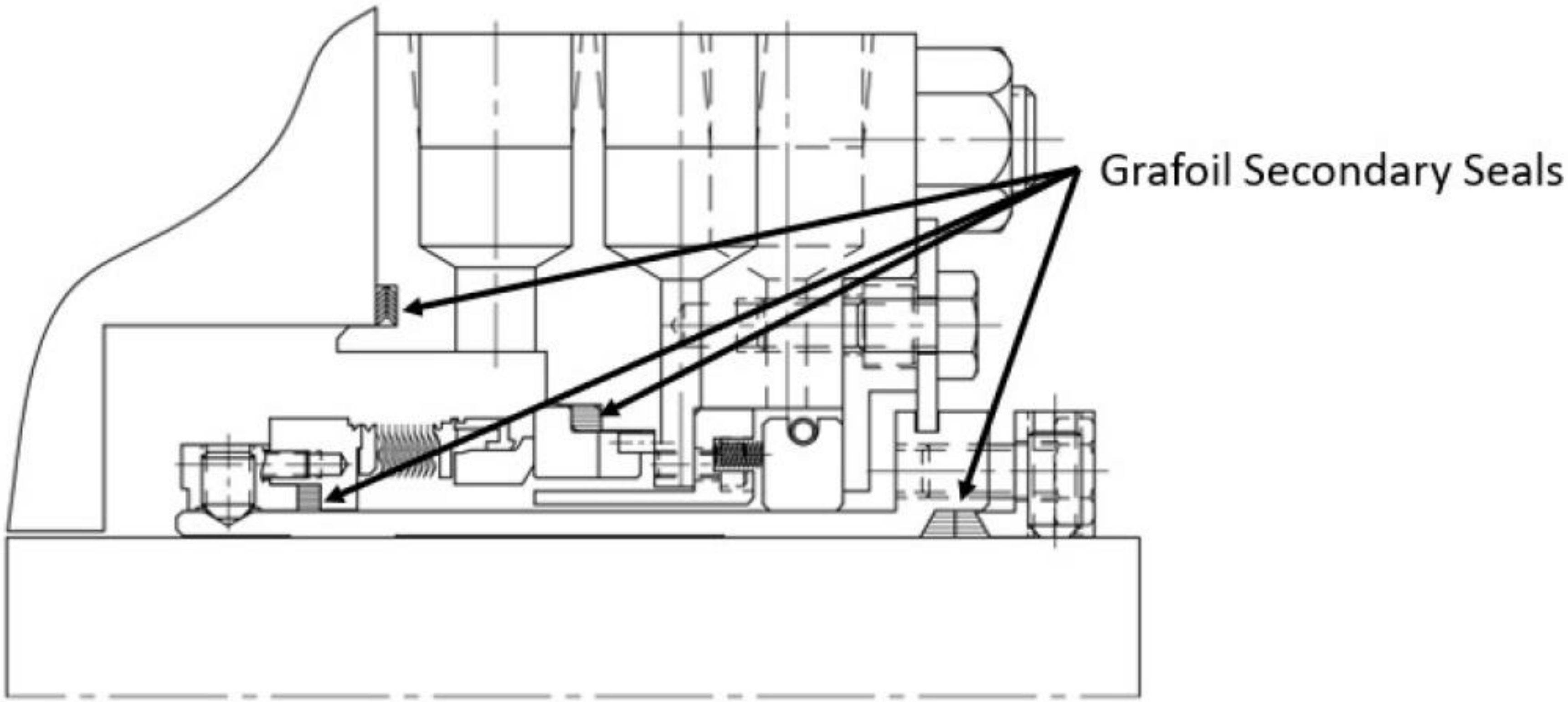
Flexible graphite rings are utilized in higher temperature applications

- These rings are wound thin sheets of graphite that vary in density.  When installed, the ring takes a set and the change in diameters due to temperature swings is far less than an elastomer
- They remain flexible and have good fluid compatibility
- They are more sensitive to shaft movement and thermal growth of the metals supporting the rings when used as a dynamic seal. Static seals made from flexible graphite are less sensitive to factors that negatively impact dynamic rings
- Grafoil is not considered an approved FCM (Food Contact Material)

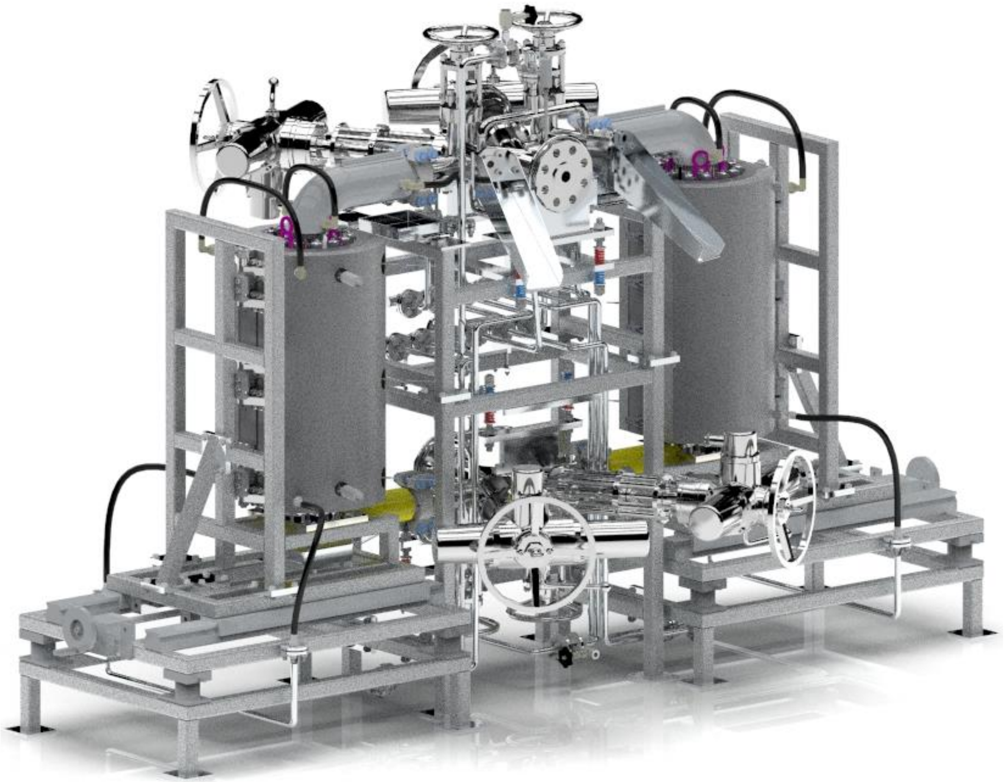
Another material not as commonly used for secondary seals is a composite material, such as PEEK

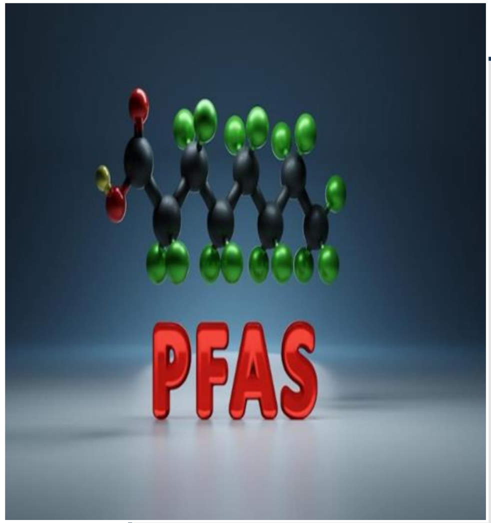
- These materials are chemically inert, but the thermal expansion of these materials is very high, and they can take a set.  Once these rings take a set, they tend to leak at equipment shutdown.  These materials are also very expensive, so they are not used as a standard material for most mechanical seals.

# Grafoil Secondary Seals



# Impact on Support Systems and Filtration






# Realistic Impacts To Sealing Volatile & Hazardous Fluids

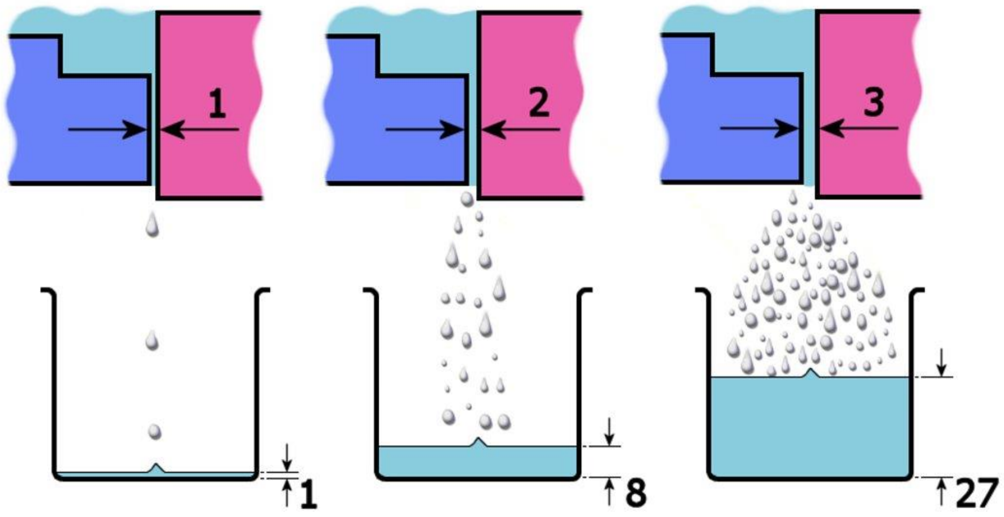
# Leakage of Mechanical Seals

The theoretical leakage rate of a liquid-lubricated mechanical seal can be calculated by the equation:

$$Q = \pi \cdot h^3 \cdot \Delta P / 6 \cdot \eta \cdot \ln(r_2/r_1)$$

Where:

- $Q$ = leakage rate in $m^3$/sec ($in^3$/sec)
- $r_1$ = inner face radius in mm (in)
- $r_2$ = outer face radius in mm (in)
- $h$ = gap height in µm (µin)
- $\Delta P$ = pressure differential in Pa (psi)
- $\eta$ = dynamic viscosity of the sealed fluid in Pa·s (lbf-sec/$in^2$) *at the seal face temperature*



# Impacts to Sealing Volatile and Hazardous Fluids

Wholesale regulation of PFAS would have significant environmental impact – emissions from mechanical seals would increase.

Processing of hydrocarbons as an example:

- Low molecular weight HC's have unique fluid properties.
- Ethane, Ethylene, and Propane are all gases at ambient temperature and pressure.
- Requirement is that these fluids need to be processed at either very high pressures or very low temperatures.

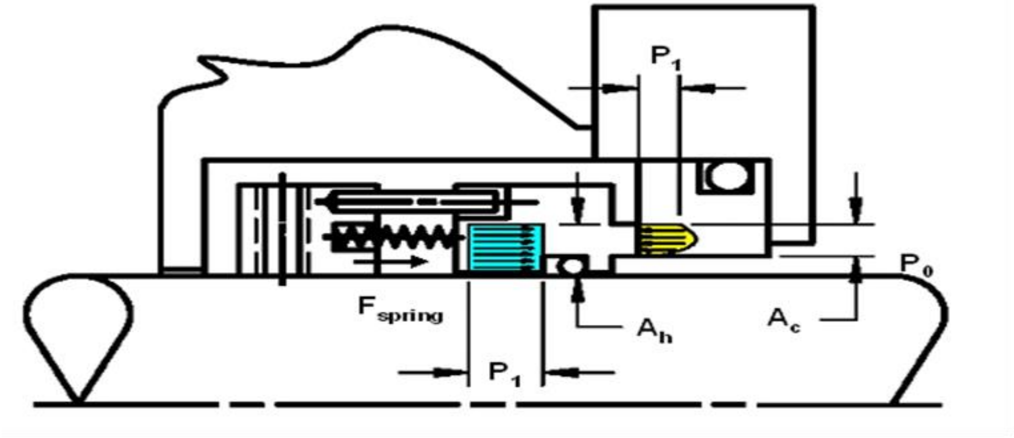
Processing requirements pose tremendous challenges to mechanical seals to minimize leakage and detectable emissions.

# Impacts to Sealing Volatile and Hazardous Fluids

Mechanical seals operating in the services described do so with very little hydrodynamic load support due to the low viscosities.

Face materials are likely to experience higher wear rates from increased temperature (rubbing friction).

Seal balance ratio, dimensionless value associated with closing and opening areas of the seal face geometry, must be optimized to minimize face generated heat.




$A_h$ = hydraulically loaded area

$A_c$ = contact area

$P_1$ = sealed pressure

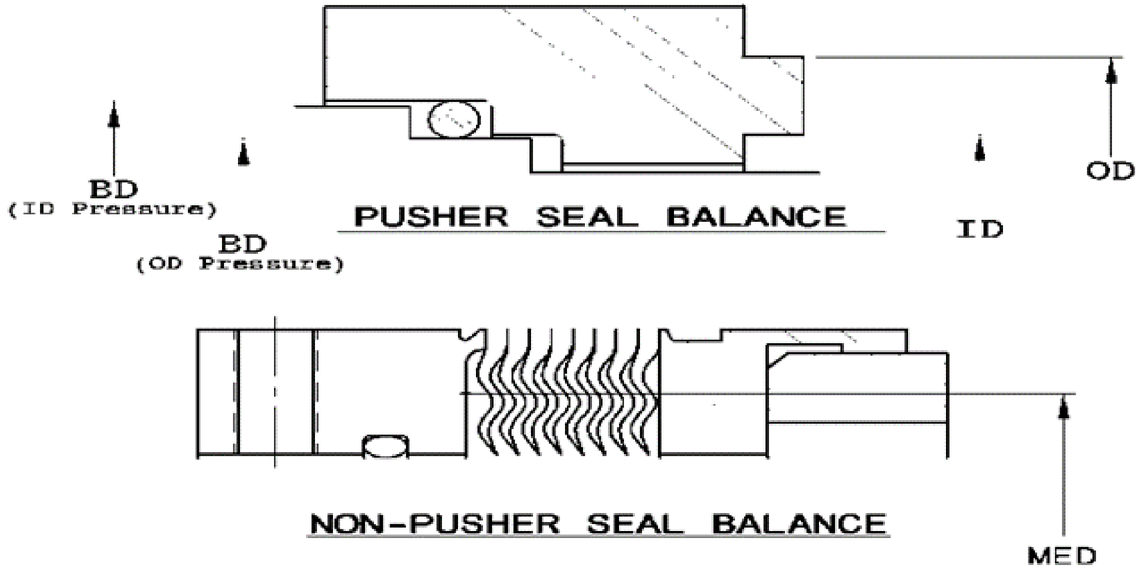
$P_0$ = pressure at the atmosphere side of the seal face

# Impacts to Sealing Volatile and Hazardous Fluids

For pusher mechanical seals, the balance diameter is the diameter of the sliding contact surface of the dynamic O-ring.

For non-pusher (bellows) seals, the balance diameter is the mean effective diameter of the bellows core.

As pressure increases, the balance diameter decreases, resulting in a net increase in face load and balance ratio.



# Impacts to Sealing Volatile and Hazardous Fluids

A natural inclination is to move towards a non-elastomer containing mechanical seal (Type C) as a wholesale alternative to Type A (pusher seals), which may contain PFAS elements.

Detectable emissions from a comparable Type C to a Type A seal in a light hydrocarbon application is typically 2 – 3 times higher.

Seal manufacturers and equipment owners have participated in numerous Leak Detection and Repair (LDAR) reduction programs over the last 30 years.
Implementation of best available sealing technology success is well documented, reducing emissions and improving equipment reliability.

Wholesale regulations including non-hazardous PFAS forms would undue successful emissions reductions.

# Impacts to Sealing Volatile and Hazardous Fluids

Beyond emissions reduction ramifications, there are potential safety concerns with hazardous fluids.

Hydrofluoric Acid, Ethylene Oxide, Propylene Oxide, and Hydrogen Sulfide are just a few aggressive chemicals that require PTFE and non-hazardous PFAS materials for O-rings / gaskets to prevent exposure.

Over-arching regulation increases environmental and personnel exposure, negating benefits.

# Questions