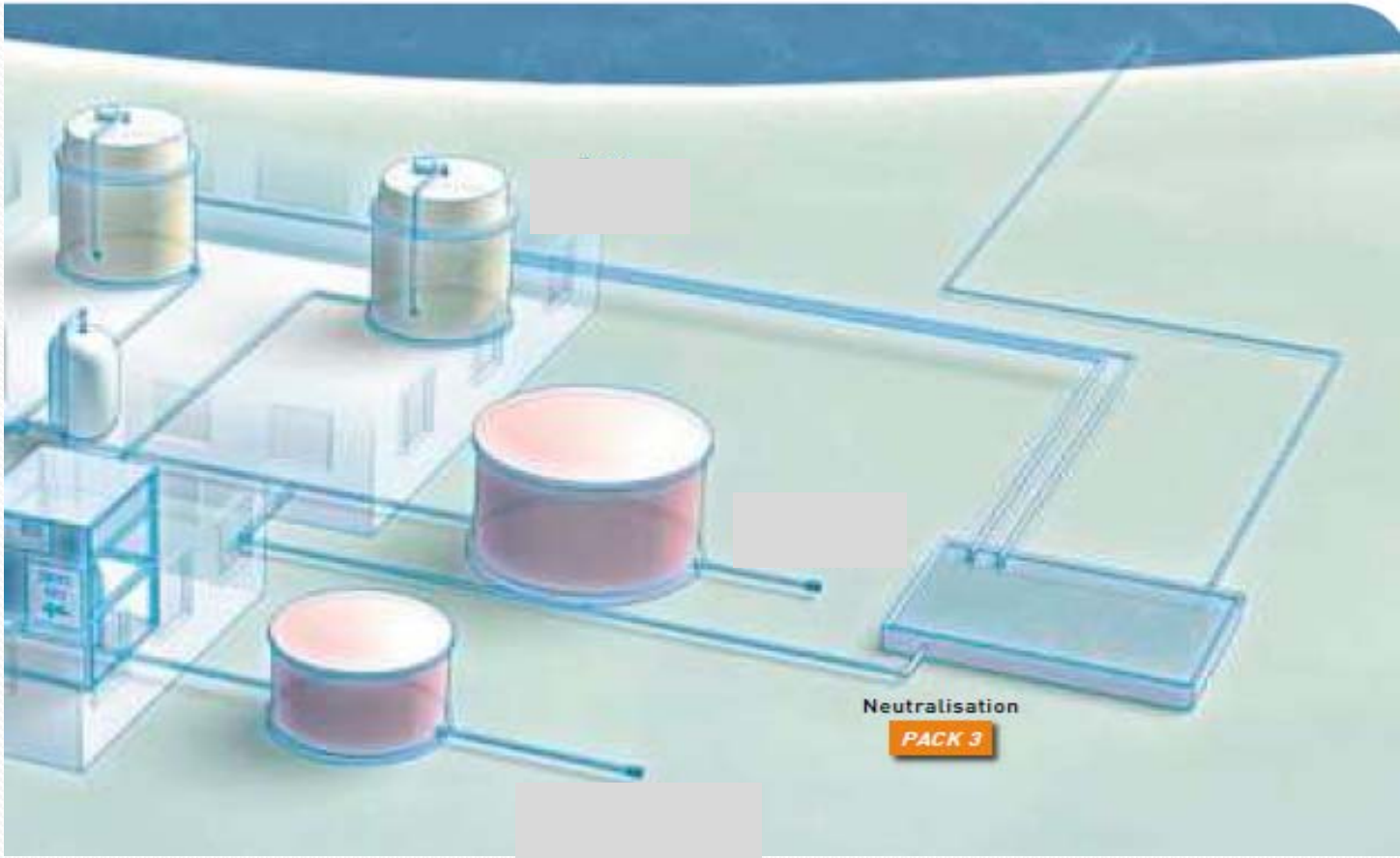
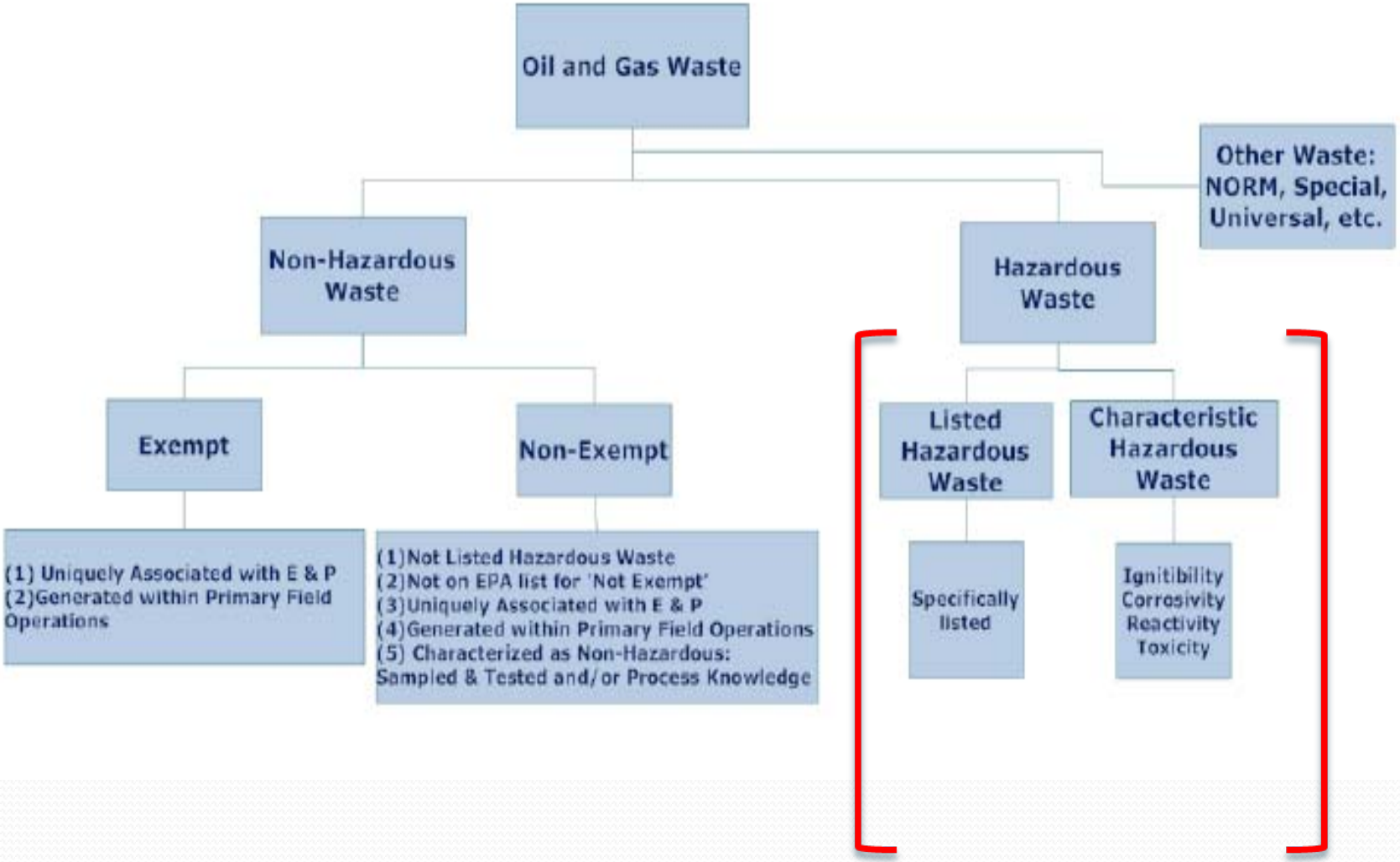
# PVDF & ECTFE ANTI CORROSION THERMOPLASTICS MATERIAL FOR HAZARDOUS WASTE in OIL and GAS sector



# Oil and Gas Waste Hierarchy



## Oil and Gas Waste Are Broadly Defined to Include

- Drilling, operation, and plugging of wells associated with the exploration, development, or production of oil and gas, including oil and gas wells, fluid injection wells used in enhanced recovery projects, and disposal wells;
- Separation and treatment of produced fluids in the field or at natural gas processing plants;
- Storage of crude oil before it enters a refinery;
- Underground storage of hydrocarbons and natural gas;
- Transportation of crude oil or natural gas by pipeline;
- Solution mining of brine; and
- Storage, hauling, disposal, or reclamation of wastes generated by these activities.

'Oil and Gas Waste' includes both hazardous and non-hazardous wastes arising from generally recognized oil and gas operations. These wastes may be in any liquid, semi-liquid or solid form.

## Characteristic Hazardous Waste

**IGNITABILITY (flash point > 60 C)**
**CORROSIVITY (pH < 2 or pH > 12.5)**
**REACTIVITY (unstable under normal condition)**
**TOXICITY (harmful or fatal when ingested or absorbed)**

# Characteristic Hazardous Waste

**IGNITABILITY**

- Liquids with a flash point less than 140° F ( 60°C )
- Ignitable compressed gas
- Materials other than liquids that at standard conditions are capable of causing fire by spontaneous chemical changes, by absorption of moisture or through friction.

Examples : -cleaning solvents (may also be listed hazardous waste); -degreasers; -paint waste

**CORROSIVITY**

- Aqueous materials with a pH < 2.0 to pH > 12.5
- Liquid materials that corrode steel (SAE 1020) at a rate greater than 0,25 inch/year at temp. 50°C

Examples : -acid or caustic cleaning wastes, -unused well acidizing fluids (that have not been down the borehole), -rust removers

**REACTIVITY**

- Any waste that reacts violently with water, forms explosive mixtures with water, or generates any toxic fumes with water
- Any waste that is explosive at standard conditions or if heated
- Any waste that contains cyanide or sulfide at concentration that will emit toxic cyanide or sulfide gases when exposed to pH of 2.0 to 12,5

Examples : -certain waste oxidizers

**TOXICITY**

Potential to contaminate ground water by leaching as determined in a laboratory using the toxicity characteristic leaching procedure (TCLP) test.

# Listed Hazardous Oil and Gas Waste

| TYPE OF WASTE | EXAMPLES OF OIL AND GAS WASTES THAT MIGHT BE FOUND ON EPA LISTS * |
|---|---|
| Hazardous wastes from non-specific sources | Spent solvents (trichloroethylene, methylene chloride, tetrachloroethylene, xylene, acetone, benzene, ethyl benzene, methyl ethyl ketone, nbutyl alcohol, methanol, toluene, and solvent mixtures/blends that contain more than 10% of these solvents |
| Hazardous wastes from specific sources | None identified |
| Acute hazardous wastes (Commercial chemical products that become acute hazardous waste when disposed of) | Acrolein, beryllium, carbon disulfide, parathion, vanadium pentoxide |
| Toxic hazardous wastes (Commercial chemical products that become toxic hazardous wastes when disposed of) | Acetone, benzene, carbon tetrachloride, chloroform, chrysene, formaldehyde, formic acid, hydrogen fluoride, hydrogen sulfide, lindane, mercury, methanol, methyl ethyl ketone, methyl isolbutyl ketone, methylene chloride, naphthalene, toluene, xylene |

LISTED RCRA HAZARDOUS OIL AND GAS WASTES

Hazardous waste from the oil sector are mostly chemical in nature (Hydrocarbon sludge, contaminated soils, drilling fluids and waste oil) adding to that radioactive waste and gases.

**Waste prevention = Minimizing volume**

**Recycle and compost as much waste as possible**
**Reuse as many things as possible.**
**Chemically or biologically treat or incinerate waste that can't be reduced, reused, recycled, or composted.**

# Waste Treatment Process

**HAZARDOUS WASTE LANDFILL**

Stable hazardous wastes are deposited directly into the onsite hazardous waste landfill. The methods and materials used in the construction of the landfill assure its integrity. Water (called leachate) that drips through the waste and is trapped by the impermeable layers of HDPE liner and then collected and treated onsite. Skilled personnel operate the landfill to international standards. Redundant environmental monitoring systems provide proof of the system integrity.

**STABILIZATION**

Stabilization process for waste delivered in a non-stable form. Hazardous Waste cannot be landfilled until it is certain the wastes are physically and chemically stable. The stabilization process involves various forms of chemical pre-treatment followed by a mixing process involving portland cement, absorbent clay, water and other reagents in varying proportions to create a stable, substance. Once stabilized, the end product is deposited safely into the secure landfill.

**THERMAL DESTRUCTION**

Thermal destruction technology using a modern cement kiln for complete incineration and treatment of the waste. The high temperature (1,200 – 1,400 °C) and long retention time inside the cement kiln ensure that the mixture is completely destroyed.

**OIL SLUDGE TREATMENT FROM EXPLORATION, PRODUCTION, AND REFINERY ACTIVITIES**

Oil Sludge Treatment System separates and recovers oil from oil sludge. The technology incorporates various processes including centrifuge, purification systems and stabilization. The remaining solid can be disposed of secure landfill or destroyed thermally. The waste water can also be treated to meet the discharge standards.

**BIO REMEDIATION**

By utilizing active bacteria, natural biological systems and industry know how, bio-remediation technology is able to treat various types of waste matrices such as oily sludge, tars and contaminated soil. Bio-remediation technology can also be used to treat groundwater that has been contaminated with phenols, poly aromatic hydrocarbons, organic solvents and other volatile hydrocarbons.

## Main air pollutans emitted by waste treatments and their main sources

| Main air emissions | Waste treatment operation |
|---|---|
| Acids (HCl) | Incineration<br>Physico-chemical treatments |
| Ammonia | Biological treatments<br>Physico-chemical treatments |
| Carbon oxides | Energy systems<br>Thermal treatments<br>Biological treatments |
| Microbiological pollution | Biological treatments<br>Biofilters |
| Nitrogen oxides ($N_2O$, NO, $NO_2$) | Energy systems<br>Thermal treatments<br>Biological treatments |
| Sulphur oxides | Energy systems<br>Thermal treatments |
| Particulates (including metals) | Energy systems<br>Storage and handling of solids<br>Thermal treatments |
| Volatile organic compounds (VOC) | Biological treatments<br>Waste oil treatments<br>Waste solvent treatments<br>Hydrocarbons/water separation systems<br>Storage and handling of organic substances |
| Note: Refer to Chapter 3 for specific emissions to different waste treatment operations. | |

## Main water pollutants (parameters) emitted by waste treatments

| Main water emissions | Waste treatment operations |
|---|---|
| Chlorinated compounds (e.g. AOX) | Waste solvents treatments |
| Metals (e.g. As, Cd, Cu, Hg, Ni, Sn, Zn) | Biological treatments<br>Common storage and handling of waste<br>Physico-chemical treatments of metal extraction, finishing waste, fine chemicals and organic manufacture.<br>Waste oil treatments |
| Organic chemicals (e.g. BOD, COD, TOC, hydrocarbons, phenols, BTEX) | Waste oil treatments<br>Waste solvent treatments<br>Energy systems |
| Total nitrogen | Physico-chemical treatments<br>Biological treatments |
| Total phosphorus | Physico-chemical treatments<br>Biological treatments |
| Note: Refer to Chapter 3 for specific emissions to different waste treatment operations. | |

# The following equipment is typically available for reactors in order to control reactions :

- **storage vessels** for separate storage, depending on the type of treatment
- **reaction containers** with adjustable agitators and temperature indicators
- **sedimentation containers**
- **metering equipment**
- receiver and **storage tanks for** chemicals
- storage tanks and **reservoirs for the waste** to be treated
- **dosing equipment**
- material resistant to acids and alkalis
- control of pH value for the chemicals
- containers for setting and mixing ancillary agents
- measurement and automatic controls
- ventilation and filtering of the reaction tanks with facilities for cleaning the exhaust air.

**Dosing Equipment**

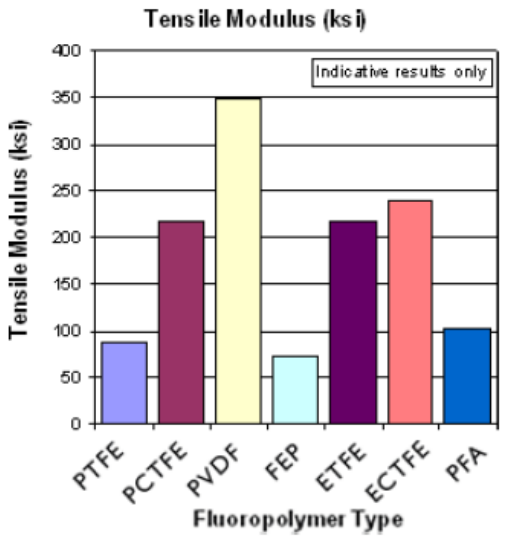
**The oil and gas industry offers challenging applications for most polimeric materials and demands high temperature performance, chemical resistance, excellent electrical insulation, chemical permeation resistance, toughness and flexibility, and long term reliability**

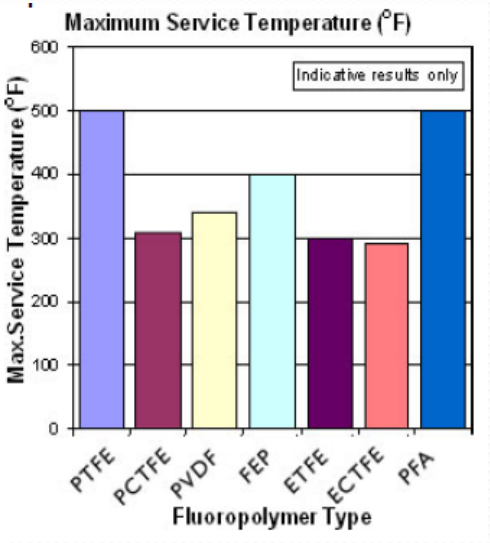
## Nonmetallic Materials The Possible alternative

**Fluorocarbons ___ these are the most versatile and important group of plastics for the process industries, maximum chemical resistance and heat stability** are provided by this class of materials **as pipe liners, tank linings, impellers, mixers, spargers, tower packing, lined, valves,** etc.

The original polytetrafluoroethylene (PTFE) provides adequate heat stability to 260°C for many applications, and resistance to essentially all chemicals. Fabrication of PTFE is very difficult, as it cannot be welded nor can it be applied adhesively except by special pretreatment, precluding its use as a liner. Note that the term "teflon" no longer applies and should not be used without further designation.

Modifications of the original PTFE developed rapidly. **The modified variants have somewhat lower heat stability limits and slightly reduced chemical resistance, but are much more amenable to fabrication by welding, hot forming, cold working, and adhesion. Substansially impermeable linings or coatings, which cannot be made with PTFE. Among these modifications are PVDF and ECTFE**




**ASTM D648**

| | 66 psi | 264 psi | Melt Point |
|---|---|---|---|
| PTFE | 250°F | 132°F | 620°F |
| PVC | 135°F | 140°F | <285°F |
| LDPE | - | 104°F | 221°F |
| UHMW PE | 155°F | 110°F | 265°F |
| PP | 225°F | 120°F | 330°F |
| PFA | 164°F | 118°F | 590°F |
| FEP | 158°F | 124°F | 554•F |
| PVDF | 298°F | 235°F | 352°F |
| ECTFE | 240°F | 170°F | 464°F |
| CTFE | 258°F | 167°F | 424°F |
| ETFE | 220°F | 165°F | 518°F |

**Heat Deflection Temperature**

# Corrosion in oil and gas

**The principle factors controlling corrosion are :**

- the $CO_2$ partial pressure
- the $H_2S$ partial pressure
- the fluid temperature
- the water salinity
- the water cut
- the flue dynamic
- the pH

**Additional factors influencing corrosion rates in petroleum refineries and petrochemical plants including offsite facilities and pollution control facilities are** :

- Organic acids (naphtenic acids)
- Hydrogen (atomic)
- Amine solution
- Sulfur
- Sodium hydroxide
- Ammonia
- Hydrofluric acid
- Glycol
- Cyanide
- Sulfuric acid
- Galvanic couple
- Chloride
- Bacteria
- Concentration of corrosives
- Aeration
- Heat flux
- Welding defects
- High temperature oxidation and corrosion

# Advantages of PVDF

- wide temperature range
- high heat deflection temperature
- excellent chemical resistance, even at high temperatures
- good resistance against uv and y-radiations – high ageing resistance
- excellent abrasion resistance (low friction coefficient)
- very good anti-friction properties
- good mechanical properties
- excellent insulating characteristics in connection with very good electrical values
- flame retardant
- physiologically non toxic
- good and easy processing
- PVDF is a halogen and offers excellent fire protection without flame retardant additives, during combustion of PVDF only a slight amount of smoke development arises
- PVDF is distinguished in comparison with PTFE (Polytetrafluoroethylene) by its high mechanical strength and good chemical resistance even at high temperatures.

**The polymer material polyvinylidene fluoride (PVDF) has been around commercially since 1964. installed annually in pulp and paper, nuclear, chemical plant, offshore oil platform, underground fuel containment, high-purity semiconductor, biotech system, plenum-rated waste pipe, metal preparation, food- and beverage-handling, potable water, mining reclamation and wastewater treatment applications.**

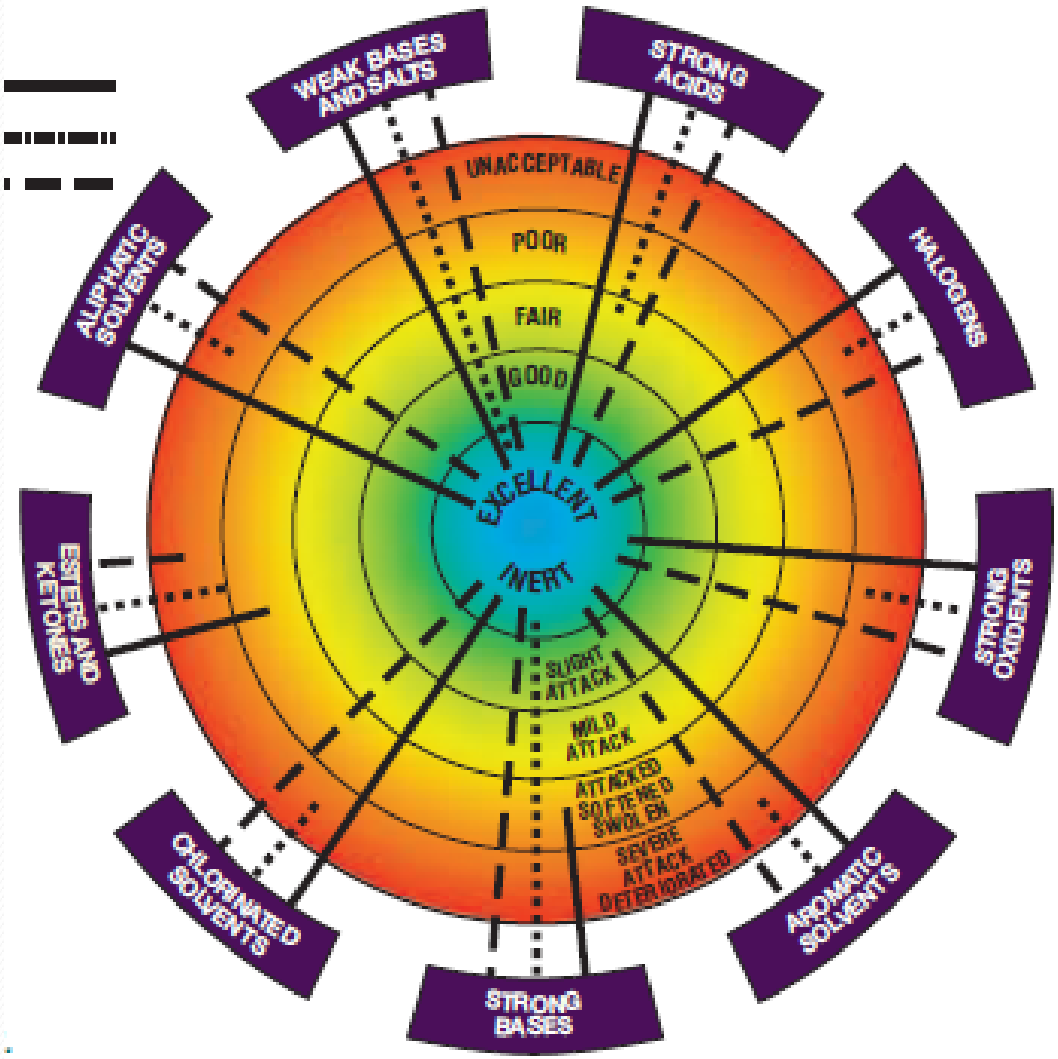
## PVDF and ECTFE Chemical Resistance

It seems that the most common chemical applications for PVDF piping and lining systems are those involving:

- Halogens (bromine, chlorine and iodine).
- Strong acids (chromic, hydrobromic, hydrochloric, hydrofluoric, methane,sulfonic, nitric, phosphoric and sulfuric).
- Chlorinated compounds (chlorobenzene, methyl chloride, sodium hypochlorite, sodium chlorate and chlorine dioxide).
- Water (mixed waste, salt, brine, deionized
- Fuels (gasoline, diesel, biodiesel and gasohol).
- Ozone sterilization.
- Pressure steam cleaning.

# Chemical Resistance PVDF in comparison with other plastics

PVDF
PP
ECTFE

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