Process engineers are faced with the decision of choosing the correct valve material for corrosive applications. Decision criteria are sometimes based on cost, availability, reliability, durability, and performance history. Fluoropolymers are often times the preferred choice for valves in corrosive services due to their relative cost position compared to high alloy valves and due to their availability. Many times the proof test to determine if a fluoropolymer lined valve will work or not is if the process temperature is below 400°F. If the temperature remains below 400°F it is assumed that the fluoropolymer lined valve will work as expected. One pitfall of this approach is that fluoropolymer lined valves can be specified in certain applications resulting in unexpected performance due to other process conditions such as permeation, steam, and abrasive media.

Without a proper knowledge of fluoropolymer materials they are often times over specified. Fluoropolymers are used extensively in the construction of valves for the Chemical Process Industry. From their use as seats, packing, seals, diaphragms, and liners it is important to have a good understanding of these materials in order to properly specify the correct materials for your application. The best place to start in order to understand fluoropolymers is to start with a definition.

**Fluoropolymers**

What is a fluoropolymer? A fluoropolymer is an organic compound consisting of fluorine and carbon atoms but can also contain oxygen or hydrogen. The atoms are held together by bonds to form monomers such as tetrafluorethylene (TFE). When the monomer is polymerized they form into long chains to which TFE becomes polytetrafluoroethylene (PTFE). Fluoropolymers can be either fully fluorinated or partially fluorinated. Fully fluorinated simply means that fluorine atoms completely surround the carbon atoms while partially fluorinated means that fluorine atoms partially surround some of the carbon atoms. The strong chemical resistance of fluoropolymers is directly linked to the strong bond between the carbon and fluorine atom within the polymer. Therefore, fully fluorinated fluoropolymers are typically more resistant to more chemicals and have higher temperature resistance than partially fluorinated fluoropolymers.

Following are some examples of fully fluorinated polymers along with select physical data, manufacturing processes and common valve applications.

**Polytetrafluoroethylene (PTFE)**

As you can see by the picture above all the carbon atoms are surrounded by fluorine atoms. Again, the strong carbon-fluorine bond leads to the high chemical resistance of this material. The picture above represents one monomer of TFE which when polymerize becomes PTFE.

PTFE is probably one of the most widely used fluoropolymers within the valve industry for components. It uses include seats, packing material, and diaphragms. The reason it is used for these components is due to its high molecular weight leading to its high strength compared to other fluoropolymers and its resistance to wear from cycling applications. PTFE provides excellent chemical resistance and also excellent mechanical strength. Fabrication of PTFE is accomplished by a press and sintering process. PTFE cannot be melt processed, also known as injection molded or rotomolded. Therefore its application is limited mostly to valve components. Occasionally, PTFE is used to line valve bodies but it is mostly found in large diameter components or components with large volumes. It differs in appearance to PFA (described later) in that it is more of a solid white color as compared to the translucent white of PFA.
Modified PTFE is simply PTFE with the addition of less than 1-% perfluoropropylvinylether (PPVE). This is represented above by the chain coming off the third fluorine atom. The addition of PPVE has no effect on the chemical compatibility or temperature capabilities of the PTFE but does change the mechanical properties of the base PTFE. Modified PTFE is a stronger and more durable material than PTFE. Benefits in valve applications are less deformation under load and less permeability providing for longer service life in cycling applications and better creep resistance. Modified PTFE is still limited to fabrication by sintering and therefore we see seats, packing material, and diaphragms being the most common valve components from these materials.

Perfluoroalkoxy (PFA)

Perfluoroalkoxy, or PFA, is probably the most commonly applied valve liner. PFA is very similar to modified PTFE in that is has an additive of PPVE except the amount is increased from 1% to 4%. Chemical compatibility and temperature capabilities are unchanged but mechanical properties are changed. The most significant change results in this material now being able to be melt-processed. This change enables the use of molding technologies such as injection molding and transfer molding. Injection and transfer molding allow for intricate parts to be completely lined in PFA. Past include valve bodies, bonnets, balls and stems.

Polyvinylidenefluoride (PVDF)

Polyvinylidenefluoride, or PVDF is a partially fluorinated fluoropolymer. Meaning that not all of the carbon atoms are surrounded by fluorine atoms resulting in a lower chemical resistance than the fully fluorinated fluoropolymers. Hydrogen atoms have replaced some of the fluorine atoms, which have a weaker bond and are more subject to chemical attack. Ketones, esters and organic amines can attack PVDF. The benefit of PVDF to valve users is in its high mechanical strength at its permeation resistance. PVDF has good cold flow resistance and high impact strength resulting in great abrasion resistance. PVDF can be melt processed and therefore is found more commonly as a valve liner. PVDF is also used to line large parts such as vessels due to its ability to resist stress cracking when cooling.

Perfluoroethylene-propylene (FEP)

Perfluoroethylene-propylene, or FEP, is another commonly applied valve liner. FEP is made from tetrafluoroethylene and approximately 15 - 20 % hexafluoropropylene. Its chemical resistance is nearly the same as PTFE, Modified PTFE and PFA, however it’s thermal resistance is less than PTFE.

TFM or PFA. Typically you can see a reduction in valve temperature capabilities of 120°F. The decision to use FEP instead of PFA as a valve liner is primarily driven by cost. FEP is a lower cost resin material than PFA. However, one should use caution when giving up temperature capabilities for a slightly lower cost and truly weigh out the two factors against each other. In fact the amount of FEP used in smaller valve sizes can sometimes be so small that there is practically no price difference between a FEP and PFA lined valve. For this reason FEP is more commonly specified on large diameter vessels where the cost of the material has more of an effect on the overall price. FEP can be melt processed in a similar manner as PFA and also is a translucent white color. There is no apparent visual difference when comparing the two materials.
More than 15 years ago Ethylene-tetrafluoroethylene (ETFE) and Ethylene-chlorotrifluoroethylene (ECTFE) were widely used as valve liner materials. At the time they provided the best in chemical and temperature resistance that the industry had to offer. Today these materials are being replaced with PFA which provides higher chemical and temperature capabilities. ETFE is still used today but more commonly found as a liner in diaphragm valves and to a lesser extent some niche ball valve applications. ETFE provides a lower cost alternative to PFA while providing better abrasion resistance. Fillers materials such as glass are occasionally added to ETFE to enhance the abrasion resistance. Chemical and temperature resistance are limited as compared to the fully fluorinated fluoropolymers.

Lastly, there is polypropylene (PP). As evident in the picture above polypropylene is neither partially or full fluorinated resulting in a material that has less chemical and temperature resistance than all the fluorinated polymers. Its typical application range is up to 200°F and is found most commonly used in mildly corrosive services. It is probably best known for its use as a liner for diaphragm valves used in demineralizers.

**Application Decisions**

So with all the available lining and component materials how is an engineer to choose the correct material for their corrosive application? Fortunately many valve manufacturers have already chosen the material combinations that best fit most applications. Also, valve manufacturers are able to provide you with guidance and direction as to proper selection of materials to limit the factors influencing valve performance. More times than not, PFA as a valve liner and PTFE or Modified PTFE as seats and packing, will work for your corrosive applications. Below are the factors that might effect performance and possibly cause you to look for other alternatives. Or at least plan on a shorter life expectancy.

**Abrasive and Corrosive Media**

Solids or particulate have a negative effect on fluoropolymer lined valves. Especially, when a valve element such as a ball, plug or disk are being turned into the body/seat. The presence of abrasive material can drastically effect the life of a fluoropolymer lined valve causing them to leak past the seat prematurely. To counter this effect one can specify a ceramic ball or metal plug to eliminate the wear point of this plastic component. However, the turning motion of the element is still present and will continue to have a negative effect on the life of the PTFE seat. Other alternatives would be to use a stronger material such as PVDF or reinforced ETFE. Or, one could use a valve that does not have a turning element such as a diaphragm valve.

**Permeating media**

Fluoropolymer lined valves provide for excellent chemical resistance to aggressive media. However, one of the downfalls of these materials is that certain chemicals can permeate the fluoropolymer and reach the base metal components causing valve failure. Media to be concerned with are those that contain chlorine, fluorine, or bromine. These could be hydrochloric acid, hydrofluoric acid or hydrobromic acid. Factors effective permeation are concentration of the media, temperature of the media, time of exposure and liner thickness.

Effects of process parameters on permeation

Permeation is something that is best left to experience and direct consultation with valve engineers, as all of the factors listed above need to be taken into consideration when selecting the correct material. For example PFA can be the correct choice for applications that are at ambient temperature while PFA with the same chemical at 350°F may not be the correct choice. Fillers are another common solution to permeation but some fillers may be aggressively attacked by certain chemicals or not acceptable due to FDA requirements. Again, the best place to start is with a consultation with a valve engineer.

**Steam**

Lastly, steam cleaning of process piping is a common procedure in some industries. Steam can also have a negative effect on the life of fluoropolymer lined valves. Unfortunately there are not a great deal of alternatives other than to carefully monitor the pressure and length of time for steam cleaning. The common recommendation is 30-psi steam for no longer than 60 minutes a day. The failure mode for fluoropolymer lined valves that have failed from steam cleaning is deformation of the fluoropolymer or delamination from the base metal. Steam is a
small molecule and can permeate the surface of the fluoropolymer similar to chlorine, fluorine, or bromine. When a valve is cooled the steam can then condense in the liner. When the valve is steamed again the condensed liquid will vaporize causing the liner to deform or delaminate from the base metal.

**Summary**
The correct decision on what fluoropolymer material to use for your corrosive application begins with truly understanding all the parameters of your application. Next, it involves an understanding of the capabilities of the materials you are considering. Lastly, it is always good to consult with valve engineers, as chances are that your application is not unique and they may be able to provide the most appropriate solution.

**Biography**
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**References**
- Dyneon PFA Product Summary 98-0504-1046-7
- Dyneon Injection Molding Guide 98-0504-0988-1
- Dyneon TF1620 Product Information 98-0504-1222-4
- Dupont Product Information Brochure E-89758-3
- Dupont Product Information Brochure H-65000-3
- Atofina Kynar Performance Characteristics & Data ADV 010108 7.5M C&Q 9/01

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