# Important Characteristics of Membranes for Reliable Water and Wastewater Processes for Discharge and Re-use

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**Abstract** Treatment of raw water for operations and wastewater poses many challenges. Raw water often contains constituents such as particulates, organics and minerals that can make it unsuitable for potable, process re-use or discharge. Mine wastewater from operations and domestic applications can contain contaminants that require ever more stringent removal standards. A previous IMWA paper (Lilley, 2013) addressed ways operators can use membrane technology to economically treat wastewater for discharge or process re-use. This paper addresses low pressure membrane characteristics and how the various materials, manufacturing techniques and chemical compatibilities play a role in the performance, longevity, and ultimate selection.

**Key words** microfiltration, membrane, water treatment

## Introduction

The use of low pressure membranes has gained acceptance as an economical and robust method to treat raw and wastewater sources. The demand for higher quality incoming water and stricter discharge regulations are driving the trend toward membranes. This is true whether the low pressure membranes are used as pre or post treatment to other processes. Membranes provide excellent removal of coagulated or precipitated solids, as well as protecting high pressure, semi-permeable membranes such as Nano-Filtration (NF) or Reverse Osmosis (RO) products. The material and manufacturing process greatly affects the suitability of various membranes for these uses.

Low pressure hollow fiber membranes have been on the market for well over 25 years and improvements have been made in composition and manufacturing, resulting in increased durability, chemical compatibility and porosity. Knowledge of the various types of products on the market, their strengths and advantages, and their field experience is vital in applying membranes correctly.

## Membrane characteristics

Low Pressure (LP) membranes separate suspended particulate matter from water. High pressure membranes (NF, RO) separate dissolved solids from water (Lorch, 1981). LP membranes are usually configured as small, polymeric hollow fibers, potted together to form modules, which are assembled on racks to accommodate the required flows. They can be operated pressurized or as submerged under partial vacuum. Flow paths can be inside-out or outside-in. The choice of operating modes should be fully evaluated as several factors will affect the economics and effectiveness.

Hollow Fiber membranes are generally classified as Microfiltration (MF) or Ultrafiltration (UF). While the exact definitions of these terms are somewhat vague and the ranges overlap, MF for water treatment is usually in the 0.05 – 1.0 micron range while UF is typically measured in Molecular Weight Cut Off (MWCO) and the pores range from about 50 to 150 kilo Dalton (kD) when used in the water industry. Table 1 shows the approximate relationship between these numbers and ranges.

***Table 1*** *Comparative pore size measurements and membrane classification*

| Particle Size (Microns) | $10^{-4}$ | $10^{-3}$ | $10^{-2}$ | $10^{-1}$ | $10^{0}$ | $10^{1}$ | $10^{2}$ | $10^{3}$ |
|---|---|---|---|---|---|---|---|---|
| Approx. Molecular Wt. (Dalton) | 100 | 200 | 20,000 | 100,000 | 500,000 | ~ | ~ | ~ |
| Membrane Classification | | | UF | MF | | | | |

## Membrane materials

Hollow Fiber membranes can be manufactured from a number of materials, but most used to treat water are polymeric in nature; manufactured from a host of plastics but most commonly the following:

- Polyvinylidene Fluoride (PVDF)
- Polysulfone (PS)
- Polyacrlonitrile (PAN)
- Polyethersulfone (PES)
- Polyvinyl Chloride (PVC)
- Polypropylene (PP)

There are some ceramic based membranes on the market that can have niche applications and are being introduced to the general water treatment market, but the high initial cost has limited their desirability and acceptance.

One membrane in the market is constructed of polysulfone (PS), often used in the biopharmaceutical industry as they are tolerant of higher temperatures and can be heat sterilized. PS membranes are typically used for very fine particulate filtration, with some reaching the 6,000 MWCO range which can remove organics and long chain hydrocarbons. These membranes are typically not specified for wastewater applications due to durability limitations. PS membranes in the range of 6 – 30 kD are often intended for ultrapure water applications.

Membranes composed of polyethersulfone (PES) are more common in potable and wastewater applications, but a chlorine restriction of 200,000 ppm-hr may limit effectiveness on difficult feed sources where extensive cleaning is required.

PVDF polymeric membranes have become the material of choice in the US and other regions for drinking and waste water markets due to their high tolerance for cleaning chemicals and oxidizers used extensively in those applications. Mining is no exception as the use of a variety of coagulants, oxidants and cleaning chemicals are necessary for optimal operation. An installation in the tar sands in Alberta Canada recovered the condensate from stripping operations and the PVDF membranes had to be cleaned with a commercial degreaser. Despite this harsh use, the membranes had a useful life of more than 6 years. Figure 1 shows the molecular structure of PVDF. This fluorocarbon compound, if optimally processed into hollow fibers, makes a product especially resistant to high and low pH chemicals.

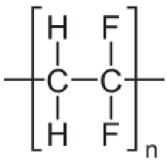


***Figure 1*** *Molecular Structure of Polyvinylidene Fluoride*

**Hollow Fiber membrane manufacturing**

Since PVDF is rapidly becoming the preferred membrane, it is important to understand the available manufacturing techniques. These can be responsible for major differences in membrane performance and life.

Most PVDF, UF membranes are produced by the Non-solvent Induced Phase Separation (NIPS) method. Here the PVDF-solvent solution, as it leaves the fiber producing equipment, is immersed in a non-solvent, usually water, where the solvent is exchanged for the non-solvent, leaving the water in the solidifying fiber and the solvent in the bath (Lloyd, 1990).

MF fibers can be produced by this process, but using a Thermally Induced Phase Separation (TIPS) method produces a membrane with higher porosity, strength, and chemical resistance. This is due to the high crystalline PVDF resulting from this method. In this process, semi-crystalline PVDF is solidified by removing the thermal energy from the solution. Table 2 compares these methods. Generally speaking, it is more common to produce MF membranes using the TIPS method.

***Table 2*** *Effects of Membrane Spinning Methods on the Physical and Chemical Strength of PVDF Membranes*

| Membrane Type | Pore Size | Spinning Method | Characteristics |
|---|---|---|---|
| Ultrafiltration Membrane | <0.01 – 0.01 micron | Non-solvent Induced Phase Separation (NIPS) | Generally, both physical and chemical strength is weak |
| Microfiltration Membrane | 0.05 – 1.0 micron | NIPS | Physical and chemical strength weak |
| Microfiltration Membrane | 0.05 – 1.0 micron | Thermally Induced Phase Separation (TIPS) | Physical and chemical strength is strong |

### Structure of PVDF membranes

The TIPS process results in a membrane that can be operated at a higher flow per unit area (flux), a very symmetrical structure, and superior chemical resistance. The bonds of the plastic structure are very solid, producing a long lasting membrane. Even on raw surface water the TIPS membranes have been proven to last up to 15 years in service, compared to an average life of 5-7 years for some NIPS fibers.

### Chemical Tolerance of PVDF membranes

Figure 2 shows the results of testing by Asahi of NIPS and TIPS fibers (Liu, 2007). A chemical compatibility soak was performed that showed the TIPS fibers could withstand a high pH solution proven to be very successful process cleaning product in remove organics from the fibers, including certain fats, oils and greases, often found in municipal and mining waste waters. The elongation retention is a measurement fiber ductility as compared to new.

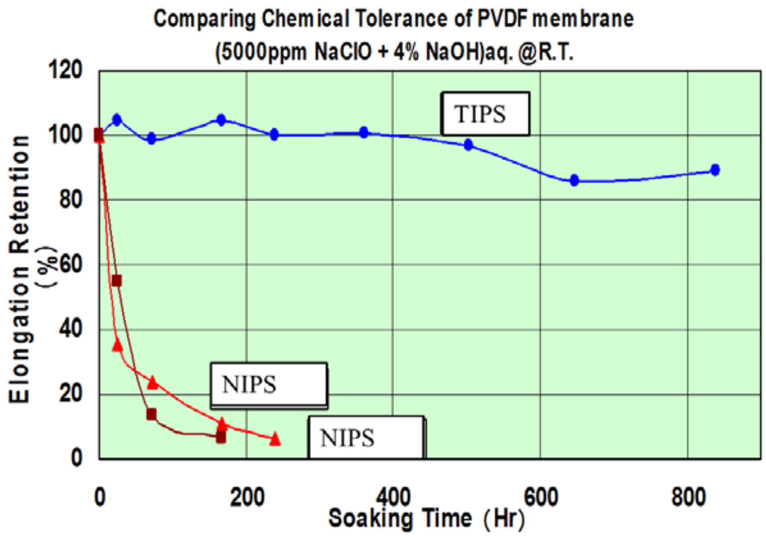



***Figure 2** Chemical tolerance of differing manufacturing methods of PVDF membranes*

### Ultra or Micro Filtration?

The differences in pore sizes for the two categories of Hollow Fiber filtration was presented in Table 1 above. The choice of UF or MF for mine process, drinking and waste water depends on many factors, including regulations (much of Europe for instance, require UF for drinking water treatment), particulate size of the contaminants to be removed and the need for aggressive cleaning of the membrane to remove particles and other foulants that are being removed from the stream.

Removal ratings however are very similar between the two membranes, so unless the elimination of virus or similar sized particles is necessary, a TIPS Microfiltration membrane is usually the better choice due to the robust nature product due to the material and manufacturing process. If coagulation is used before the MF, additional fine particles, including viruses can be removed. The coagulated solids can be settled out or removed directly by the membranes. A settleable floc is not necessary if membranes are employed. Table 3 shows the removal performance of MF and UF for drinking water pathogens and other solids.

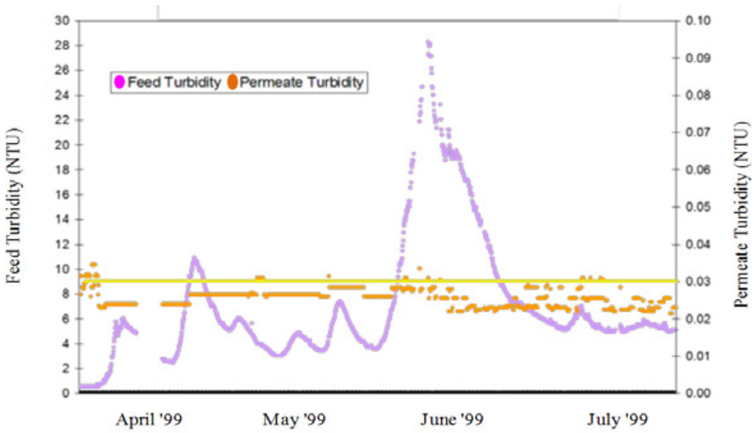
***Table 3** Contaminant Removal by MF and UF*

| Particle or Microbe | MF | UF |
|---|---|---|
| Giardia Cysts | 4.5-7 log | 5-7 log |
| Cryptosporidium | 4.5-7 log | 5-7 log |
| MS-2 Virus | 0.5-3.0 log | 4.5-6 log |
| Particle Counts | | |
| <2 micron | <10/ml | <10/ml |
| 2-5 micron | <10/ml | <10/ml |
| 5-15 micron | <1/ml | <1/ml |
| Filtrate Turbidity Average | 0.01-0.03 NTU | 0.01-0.03 NTU |

NTU – Nephelometric Turbidity Units

In comparison with conventional granular media or pressurized sand filtration, membranes provide a greater level of consistency and a much lower levels of turbidity in the filtrate. Due to the nature of the membrane pore distribution, this improved quality is independent of the level of particulates in the inlet water. Figure 3 shows an installation on surface water in the US State of Washington that had very "flashy" raw water turbidities, yet the filtrate turbidity was consistently less than 0.03 NTU

***Figure 3** Filtrate turbidity in relationship to Feed – MF*




## Hollow Fiber membrane applications

Most mining water applications are related to the treatment of waste generated by the mining operation or produced water that is a by-product of the excavation. Some treatment involves improving the water quality prior to high pressure water filtration for feed to boilers and other equipment. In either of these or other mine applications, the addition of chemicals to oxidize or precipitate metals, organics or particulates is often employed. It is worth repeating that the tolerance of the membrane to these chemicals, either completely reacted by the contaminant, or accidently overdosed is of vital importance to the success of the process and the life of the membrane. A typical "membrane solution" to a conventional coagulation system to remove metals, organics or fine particles is shown in Figure 4.

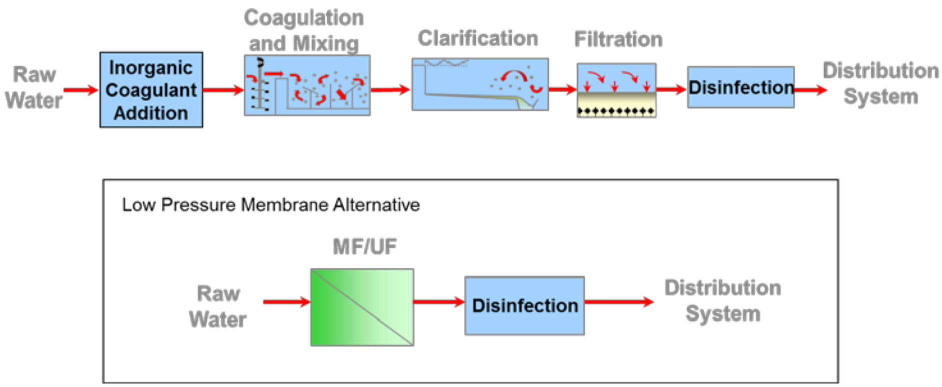



*Figure 4 Membrane versus conventional process treatment*

**Membrane systems advantages over convention treatment**

Figure 4 above illustrates one of the ways membranes can replace conventional treatment. The choice of membranes over conventional treatment provide the following additional benefits:

- Membranes provide a higher level of protection. Membranes provide an absolute barrier compared to conventional processes in water treatment do not. If the membrane integral, particles greater than the pore size are removed.
- Hollow fiber microfiltration produces a consistent effluent (typically 0.03-0.05 NTU) regardless of influent turbidity.
- Membranes have a higher recovery, up to 98% for MF. Less waste means less cost.
- Smaller footprint than conventional, often eliminating clarifiers. At least 10% to 20% savings
- Less sludge disposal issues if coagulation can be eliminated
- Can reduce chemical use.
- Integrity Testable
- Remote operation

**Conclusions**

Mine water operations can greatly benefit from employing low pressure membranes in their overall treatment scheme. Whether it is pre-filtration for Reverse Osmosis or coagulating and removing contaminants to achieve regulatory compliance, membranes provide an attractive option. But only if a full understanding of their characteristics, strengths and weakness is understood. A superior membrane allows the use of a wide range of chemical pre-treatments to allow the membrane to remove the substance of concern. Tolerance to a wide range of cleaning regimes is required to obtain the best value and longest life of the membranes.

PVDF, microfiltration membranes, manufactured by the TIPS method provide the best option on the market today. They are available in a number of configurations from very small packaged systems to mobile units that can be moved from site to site, to systems for very large volumes or flows.

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