Membrane Filtration of Oil- in Water Emulsions

Water is a by-product of virtually all oil and gas exploration. When oil and gas is brought to the surface, it is accompanied by varying quantities of so-called produced water, which tends to increase with the age of the well. The quantity of produced water in the United States is, for instance, eight times larger than the quantity of oil produced. In the beginning of the life cycle of a well, the produced water presents a disposal problem and is often reinjected into disposal wells at a distance from the producing well at significant cost. This disposal method places no specific requirements on the quality and composition of the produced water, except that its components should not plug the pores in the formation into which it is injected. Later in the life cycle of a well, it is common to use enhanced recovery techniques, which involves injecting water or steam under the remaining oil in the reservoir, often with the injected water finding a path through a porous formation to have the desired yield enhancing effect. In this case, the composition of the injected water is more crucial. The ideal situation calls for this water to have approximately the same composition as the naturally occurring water, but without any constituent which may cause plugging of the pores in the formation. These harmful constituents are mainly minerals causing precipitation, such as sulphates and carbonates, and, in some cases, also oil and oily constituents, when produced water is used for water or steam flood. The idea of using produced water in connection with enhanced recovery techniques is obvious, but it is not without problems, since the produced water must essentially be oil free and softened.

When enhanced recovery techniques have to be applied to a well, the quantity of produced water is often larger than the quantity required for injection, and part of the produced water becomes a disposal problem. Injections into disposal wells are particularly expensive and troublesome in offshore situations, and the ideal situation is to be able to dispose of the produced water directly to the ocean, in which case the environmental regulations must be observed. This means that the content of oil, heavy metals, etc. must conform to the locally determined disposal limits, which again means that the produced water must be treated to meet these limits. Water is becoming an increasingly scarce commodity in many parts of the world. Produced water can be viewed as a natural resource instead of an environmental or a disposal problem, and there are several possibilities for putting it to good use. The main obstacle is the cost and complexity of treating it to an appropriate quality and composition to allow the water to be safely used. Many technologies help to accomplish one of the steps necessary to purify produced water, but it takes a number of technologies to achieve the desired result. Economic purification of produced water for a given application can only involve one or a very few technologies.

Membrane Filtration

In the spectrum of filtration and separation technologies membrane filtration is a relative newcomer. The first reliable and useful membrane was a reverse osmosis (RO) membrane made of cellulose acetate, which became commercially available toward the end of the 1960's. It was intended for desalination of seawater, a criteria that it never quite met, but it was fully capable of purifying brackish water and thus producing drinking water by rejecting even very small molecules like sodium chloride. In the process of making RO membranes, additional membranes were developed that allowed sodium chloride to pass, but which rejected larger molecules like protein. Protein rejection is far from desalination and this membrane filtration area was dubbed ultrafiltration (UF). Membranes allowing even larger molecules to pass, but which rejected virus, bacteria, etc., were already known as microfiltration (MF) membranes. With the advancement of polymer technology several new UF and MF membranes were made between 1965 and 1975, but it was not until 1978 that the dream of making drinking water from seawater was realized with the thin-film polyamide RO membrane.

With this monumental step forward, membrane technology took on a life of its own. Several new materials and membrane concepts developed rapidly. Membranes were applied for production of drinking water in arid areas and membranes were also applied in numerous industrial processes. The gap between RO and UF was filled around 1990 with a new technology, which was named nanofiltration (NF). Sodium chloride will typically pass through a nanofiltration membrane, but larger molecules, for instance contributors to hardness in the water, are rejected. (See Figure 1: Genesis of Membrane Technology)

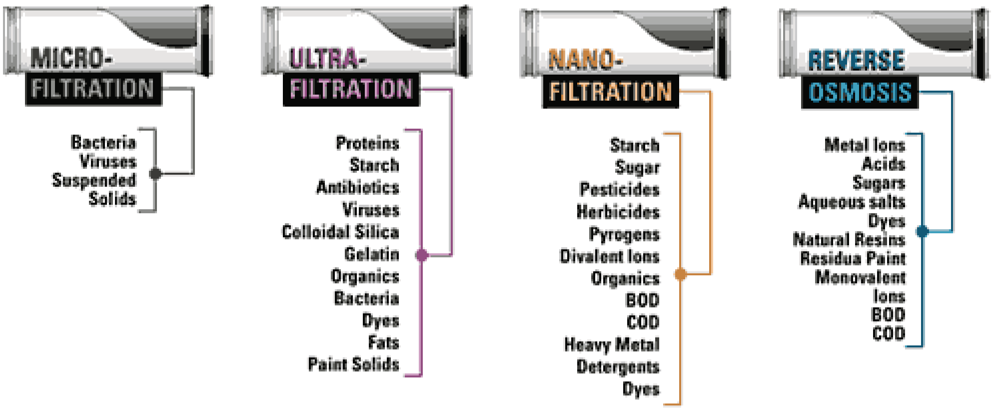


Figure 1.

The now classical example of membrane technology turning a pollution problem into profitable business is the dairy industry. Making one pound of cheese requires ten pounds of milk. The difference is cheese whey, which is a liquid containing 0.7% valuable protein, 0.9% minerals, 4.5% milk sugar (lactose) and it also contains approximately 50,000 mg/l BOD5. UF concentrates and isolates the valuable protein, which is used to enhance numerous food products. NF isolates and concentrates lactose, which is used as a substrate for many industrial fermentation processes. RO purifies the remaining liquid and returns high quality water, for instance for steam production. It is not uncommon for a large cheese plant to derive one third of its revenues from the cheese whey, which formerly presented a pollution and disposal problem to the dairy industry.

Because membranes separate very small molecules and mostly operate with a crossflow intended to clean the membrane surface during operation, the feed stream must be carefully pre-treated to prevent surface fouling. The most common sources of fouling are (1) sparsely soluble species, which are concentrated in the process (silica, calcium sulphate, barium sulphate, calcium carbonate and others), (2) small particles, which are transported to the membrane surface faster than the they are removed by the crossflow, and (3) oil, grease and fat. The latter feed constituents rendered membrane technology problematic or impossible to apply to oil and gas field produced water for a long time. Fortunately, material science is a fast developing scientific discipline and a break-through discovery changed this in the 1990's.

The AWATEC O-Series Membrane

The post-treatment renders to the membrane so hydrophilic that oil, grease and fat are actually repelled by the membrane and will not blind or foul it. (See Figure 2: How Membranes Work).

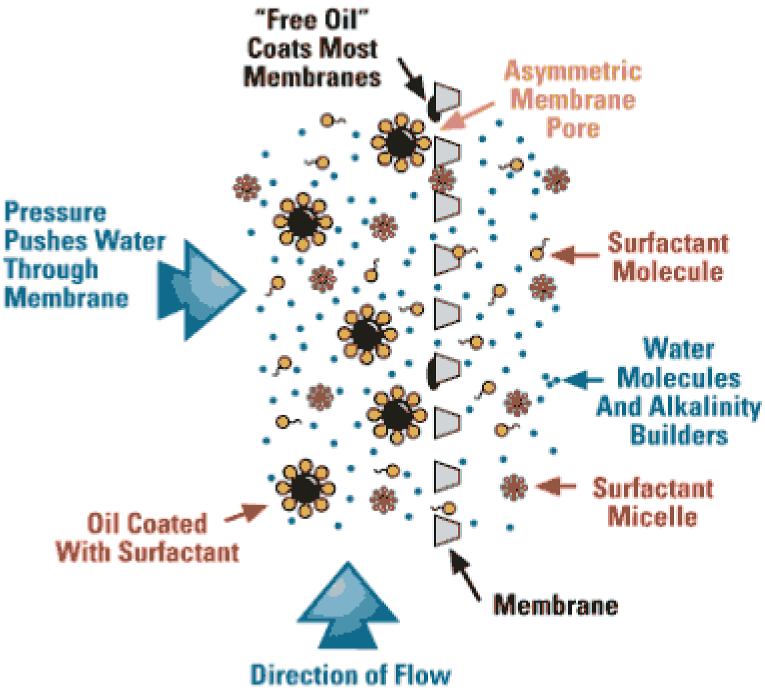


Figure 2.

At the time, the surface finishing industry was under pressure to change from solvent based cleaners to water based cleaners. Alkaline aqueous cleaners were developed and applied with good results. They were fairly expensive, which prompted several schemes for reusing them. The most successful solution was a spinning disc membrane device realized the potential for this membrane in other applications, most prominently for oil field produced water, and acquired the company in 1998. The challenge was to develop the membrane for use in spiral wound membrane elements, which offers the highest packing density of the commonly used membrane filtration devices. (See Figure 3: Spiral Element Construction).

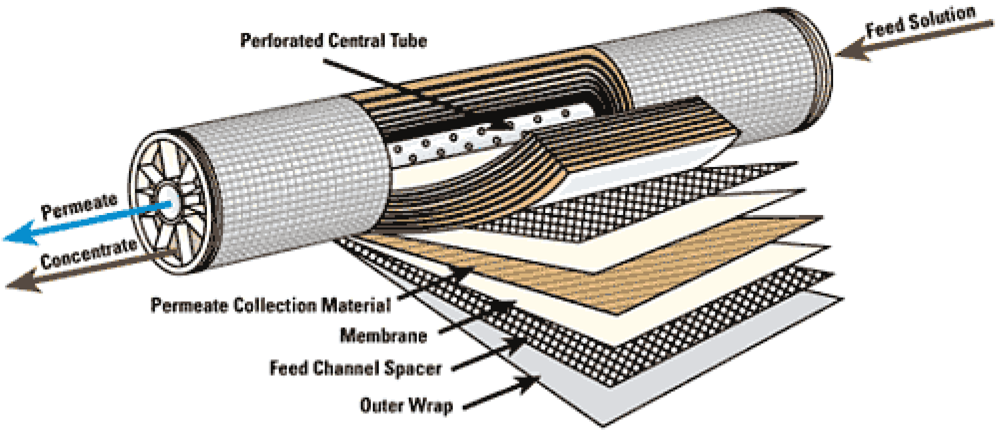
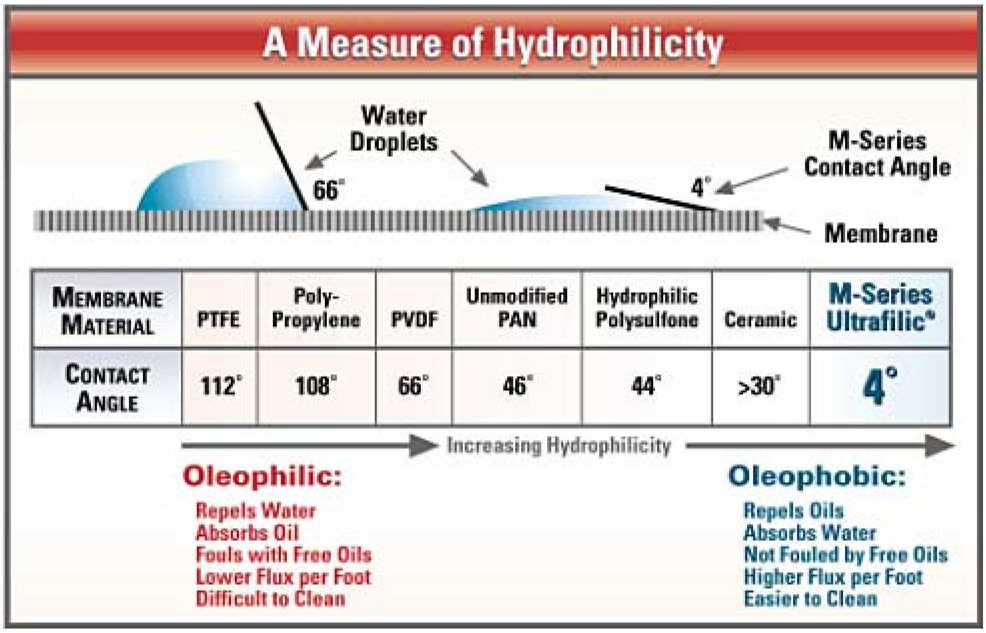


Figure 3.

The distinguishing feature of the membrane is its extremely hydrophilic surface, which will allow water to pass through and reject oil, grease and fat. Hydrophilicity is measured by placing a drop of water on the surface of a material and then measuring the contact angle. The contact angle of the membrane is only 4, which compares to 30 for ceramic membranes and 44 to 112 for other polymeric membrane materials. (Figure 4: Measure of Hydrophilicity).



MEMBRANE MATERIAL	PTFE	Poly-Propylene	PVDF	Unmodified PAN	Hydrophilic Polysulfone	Ceramic	M-Series Ultrafilic®
CONTACT ANGLE	112°	108°	66°	46°	44°	>30°	4°

Oleophilic:

- Repels Water
- Absorbs Oil
- Fouls with Free Oils
- Lower Flux per Foot
- Difficult to Clean

Oleophobic:

- Repels Oils
- Absorbs Water
- Not Fouled by Free Oils
- Higher Flux per Foot
- Easier to Clean

Figure 4.

It is evident that the membrane is totally unique in the spectrum of membranes, and it performs separation of oil from water at a hitherto unknown efficiency. Free and emulsified oil is rejected with equal efficiency.