

CHEMICAL ENGINEERING

May
2007

www.che.com

SPECIAL
SECTION:
Gulf Coast Refining
PAGE 76



INDUSTRIAL ELECTROCHEMISTRY: A Look at the Plus Side

PAGE 50

**Coal-fired Power Plants
As Chemical Makers**

**Using Spreadsheets
As Curve Fitting Tools**

**Good Times
for Refiners**

**Wastewater Treatment
For the CPI**

**Minimizing
Flame Impingements**

 Access
Intelligence

MICROFILTRATION For CPI Wastewater

Consider this method for high-purity water needs, including that for steam generation and biofuels processing

Brad Buecker

Kansas City Power & Light Co.

Pure water is an essential ingredient in the manufacture of a vast amount of products in the U.S. and, of course, throughout the world. In the industry for which I work, electricity generation, high-purity water is an absolute must for feeding high-pressure steam generators. But of course, steam generation is also important in the petroleum-refining and petrochemical industries, pharmaceutical plants, the steel and non-ferrous metals industries, and so on. Furthermore, high-purity water for other processes — computer-processor and circuit-board manufacturing come quickly to mind — is also an absolute necessity. And, let's not forget the blossoming biofuels industry.

As has been reported in this magazine and elsewhere, the techniques of microfiltration (MF) and ultrafiltration (UF) are gaining popularity as pretreatment methods for industrial makeup-water production. This article outlines fundamental principles of these technologies, and why they are replacing previous technologies. It also discusses lessons I have learned from direct experience with a microfiltration system.

Filtration issues

As a precursor to microfiltration review, consider filtration from both sides (particle-size wise) of MF. (See *Chem. Eng.*, January 2007, pp. 40–44, for an excellent article on cartridge

filtration [1].) Direct filters operate on the simple principle of particulate capture, where the solids latch onto or lodge between filter fibers. As the article outlines, direct filtration can remove particles down to 0.5 microns in size — excellent indeed! The major drawback to direct filtration is that the filters foul irreversibly, and thus must be replaced on a regular basis. Excessive particulate loading will minimize the advantages of direct filtration.

At the ultimate end of the filtration spectrum is reverse osmosis (RO), which has found wide acceptance in many industries for its ability to remove dissolved ions. People often think of RO membranes as having discrete pores, but this is a misconception. A more accurate description is a membrane with torturous paths whose effective diameters are only angstroms in size. RO does not remove impurities by direct filtration, but rather via an electromechanical process whereby water forms a boundary layer along the membrane surface and “pore” walls. The extremely small pore size and water boundary layer prevent the passage of most dissolved ions, particularly larger ions such as calcium, magnesium, bicarbonate, chloride, and sulfate. The inability for the large ions to pass through the membranes greatly reduces the ability of small ions — Na⁺ is the primary example — to pass, as the solution must maintain ionic neutrality.

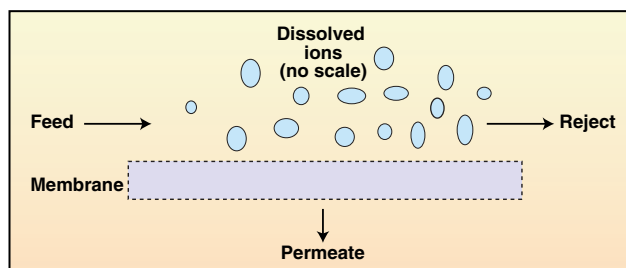


FIGURE 1. In crossflow filtration, a portion of the water is forced through the membrane while the dissolved solids flow with the remainder to the waste stream outlet

Via the technique of crossflow filtration, where the pressurized feed to the RO passes tangentially to the membrane surface, a portion of the water is forced through the membrane while the dissolved solids flow with the remainder to the waste stream outlet (Figure 1). Placement of membranes in series allows water recovery values typically around 75% with solids rejection of 99% or better with modern membranes. RO has become important, especially in the power industry, as an ionic load-reducing mechanism ahead of ion-exchange polishers.

Microfiltration's role

So, how does microfiltration fit into the water treatment scheme? The point to remember is that industrial makeup originates from a primary water source such as a lake, river, underground aquifer, or perhaps even the ocean. All surface supplies contain suspended solids in varying degrees. We have already noted that direct filters, such as the cartridge devices that protect RO membranes, will quickly foul when overloaded, which would be the case if they served as the primary filter of surface supplies.

The upside of this issue is that effective upstream pretreatment is required ahead of the final polishing devices. For many years, the pretreatment technology of choice was clarification followed by media filtration. Certainly, this technique is very

Feature Report

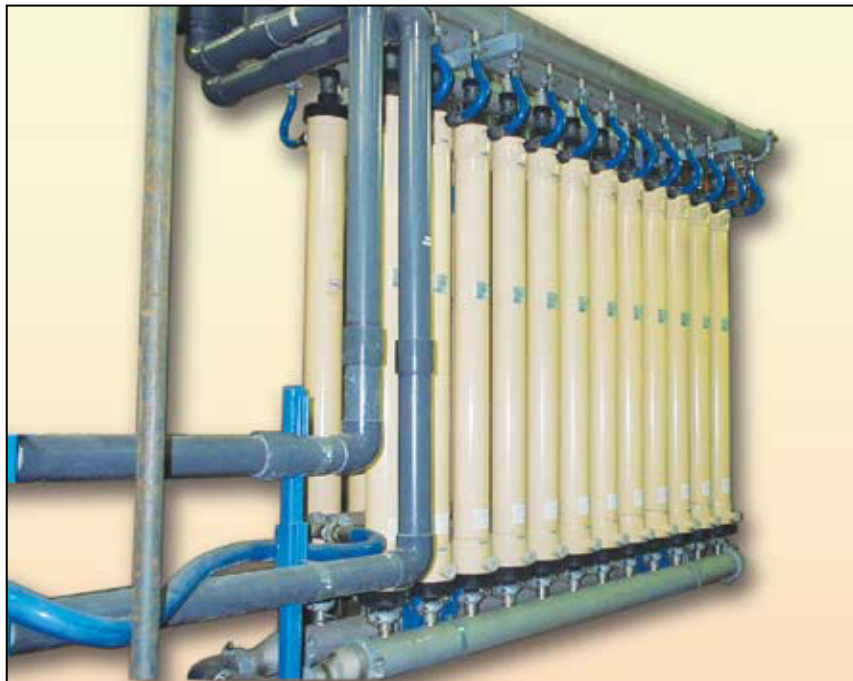


FIGURE 2. Most membrane housings use hollow-fiber membranes that are spaghetti-sized in diameter

viable, and the technology has improved over time just like everything else. However, even the most modern clarifiers require feed of a coagulating chemical followed by feed of a flocculating chemical. Operator attention is necessary to ensure that the clarifier beds do not overflow due to improper chemical feed or changes in the inlet water quality, a common issue with surface-water supplies. Not infrequently, operators may find a depleted or vanished bed due to malfunction of a sludge, blowdown valve.

MF and UF are becoming popular because the processes utilize crossflow filtration, similar to RO but with a different type of membrane, to continuously filter makeup water. Particulate material 0.1 micron in size and even smaller is removed by the membranes, with minimal operator attention required [2].

Membrane configuration

The most popular systems utilize hollow-fiber membranes, which are spaghetti-sized in diameter. This author's direct experience is with the unit shown in Figure 2.

Each of the pressure vessels contains approximately 6,000 hollow-fiber membranes. Raw water enters the vessels from the bottom and is col-

lected in headers at the top of the skid for downstream distribution.

The fibers are all manufactured of polyvinylidene fluoride (PVDF). PVDF is quite tough and corrosion resistant, and is an excellent material for this application, in large part because pore sizes can be larger (and operating pressures much lower) than for RO. PVDF is not suitable for RO membranes, because the material cannot be fabricated to establish the extremely small pore size.

Like RO, MF and UF units are also designed for crossflow filtration, in which the water flows along the membrane surfaces and the filtered water passes through the walls. The typical configuration is raw water flow along the outside of the membrane, with permeate flow into the hollow area of the fibers. An outside-in flow-path configuration is preferred by many, as the particles can be more easily flushed from the membranes during cleaning than with the opposite flow pattern. The common process is to produce filtered water for a set period of time, followed by a regular but relatively short backwashing step. In the system shown above, the operators normally set the process flow timer within a 10- to 20-min range, interrupted by a one-minute scrub with filtered water via

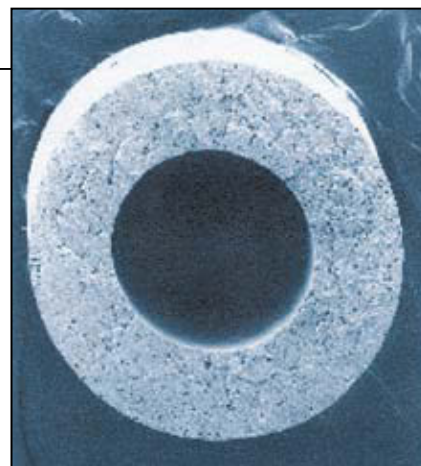


FIGURE 3. Magnified view of a hollow fiber membrane

an inside-out flow path. The backwash cycle also includes an air scrub, on the external membrane surfaces, to scour particles.

Lessons learned

Even with regular backwash cycles, MF membranes will accumulate solids over time. Periodically, a unit shutdown and off-line cleaning is required. Cleaning may be performed on a regular basis, say once a quarter, or may be set up on an as-needed basis by monitoring the differential pressure across the membranes.

A common method involves a step-wise circulating wash (perhaps two hours or so) with a warm (100°F), dilute sodium hydroxide (1%) and sodium hypochlorite (500 parts per million [ppm]) solution, a rinse with filtered water, a two-hour cleaning with a warm citric acid solution (0.5%), and then another rinse. We have found that cleaning every two to three months is good for maintaining membrane cleanliness. The unit takes water from a lake, where the maximum turbidity may reach 15 nephelometric turbidity units (NTU). This value is low compared to other sources, such as a river, where heavy rains upstream may produce temporary turbidity readings in the hundreds of NTU.

For these more-challenging applications, systems are available with a supplemental semi-automatic cleaning system that will shut the unit down and clean the membranes with acid and caustic on a timed interval or based on membrane differential pressure. I say semi-automatic because the plant chemists or technicians are still responsible for ensuring the proper chemical mixes in the cleaning feed tanks.

We also discovered that continuous

feed of a residual oxidizing biocide, (0.2–0.5-ppm concentration) was excellent for controlling microbiological growth in the membranes. PVDF is quite resistant to common biocides. We feed a compound that produces bromine due to the fact that the inlet raw water typically has a pH in the range of 8.0 to 8.5. Simple bleach is not particularly effective at alkaline pH.

This particular system replaced an aging clarifier and sand filters, where annual chemical, operating, and maintenance costs were \$80,000 or more per year. Calculated costs for the microfilter are \$20,000 per year, mostly for power consumption by the feed pump and the regeneration pump. This calculates to \$0.15 per 1,000 gal of water produced. Except for repair of a few mechanical couplings on interconnecting lines, maintenance requirements have been minor.

Future issues

The need for pure water continues to grow. As was mentioned in the introduction to this article, the biofuels industry is one such area of expanded growth. *Chemical Engineering* and other important publications have provided steady reports on the issues related to the biofuels industry [2–5] and the fact that if cellulose-based fuel can be produced efficiently, the market will really expand. Of course, water is a vital ingredient in biofuel manufacturing. However, there is a twist to this issue, and it applies to other industries as well. The twist is

that fresh water supplies are becoming more scarce, with the result that water conservation is taking on increased importance. This issue was brought out quite clearly at a biorenewables conference held at Iowa State University in November 2006 [6].

Of course, excitement ran through the crowd as scientists discussed new advances with regard to biomass-to-fuel developments. However, the seminar included many pragmatic papers and roundtable discussions on auxiliary issues. Topics included the logistics of collecting biomass, effects of biomass collection on subsequent soil quality, transport of finished products, and the effects of high water usage on groundwater sources and other supplies in and near the physical locations of biorefineries and biofuels plants. Recycling of waste streams almost certainly will become very important, and this is where microfiltration coupled with downstream treatment can be of great benefit. Wastewater typically picks up many suspended solids, and if these can be economically removed, subsequent polishing by RO and/or ion exchange returns the fluid to top quality.

Recycling will not be confined to the biorenewables industry. I regularly see or hear reports of other facilities that are considering the use of “gray” water for plant makeup. Gray water is often only thought of as the effluent from a sanitary wastewater plant, although it can be waste from other sources. The key point is that these waters fre-

quently contain suspended solids of several-hundred ppm concentration. Steady-state removal of the particulates, as is offered by microfiltration, opens a window to recycling. ■

Edited by Rebekkah Marshall

References

1. Hampton, J., Cartridge Filtration Principles For the CPI; *Chem. Eng.*, pp. 40–44, January 2007.
2. Buecker, B., Microfiltration: An Up and Coming Approach to Pre-Treatment for the Power Industry; presented at the 26th Annual Electric Utility Chemistry Workshop, May 9–11, 2006, Champaign, Ill.
3. Farrell, A., et. al., Ethanol Can Contribute to Energy and Environmental Goals; *Science*, January 2006.
4. Ondrey, G. The Path to Biorefineries; *Chem. Eng.*, pp. 27–30, April 2006.
5. Buecker, B., Hitting the Gas: The development of energy from crops and other vegetation is gaining momentum; *Environmental Protection*, pp. 32–37, July/August 2006.
6. A Call to Action Summit, November 28, 2006, Iowa State University, Ames, Iowa.

Author



Brad Buecker (Email: beakertoo@aol.com) is the air quality control specialist at a large, Midwestern power plant. He has previous experience as a chemical cleaning services engineer, a water and wastewater system supervisor, and a consulting chemist for an engineering firm. He also served as a results engineer, flue gas desulfurization (FGD) engineer, and analytical chemist for City Water, Light & Power, Springfield, Ill. Buecker has written more than 70 articles on steam generation, water treatment, and FGD chemistry, and he is the author of three books on steam generation chemistry and steam generator fundamentals published by PennWell Publishing, Tulsa, Okla. Buecker has an A.A. in pre-engineering from Springfield College in Illinois and a B.S. in chemistry from Iowa State University. He is a member of ACS, AIChE, ASME, and NACE.



Pall Power Generation
25 Harbor Park Drive
Port Washington, NY 11050

Tel: (516) 484-3600
Fax: (516) 484-0364
www.pall.com

Filtration. Separation. Solution.SM