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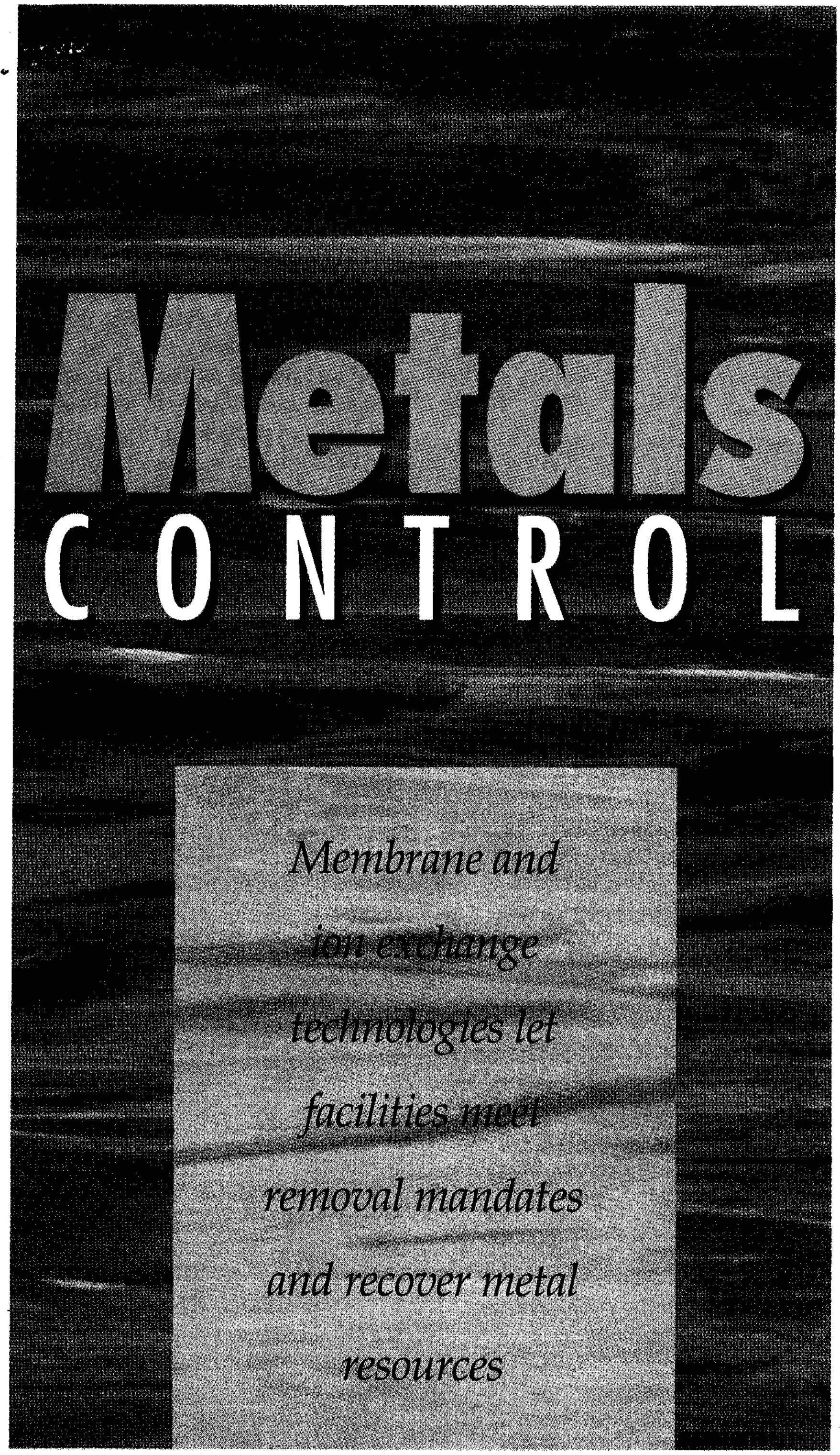


Metals CONTROL

Membrane and ion exchange technologies let facilities meet removal mandates and recover metal resources

By Robert S. Capaccio

Increasingly stringent regulations are forcing operators and engineers to review their manufacturing processes and wastewater treatment systems to determine the best means of attaining today's toxicity-driven limits. In considering various in-process and end-of-pipe options, design engineers must first determine the physical state of the metals causing the problem. Are they dissolved or particulate? If dissolved, are they "free" or "complexed"? If particulate, can they be settled or filtered out? The answers to these questions often dictate which technique is most appropriate (see Figure 1 on next page).

Dissolved Metals

Dissolved metals that are "simple" — non-complexed and non-chelated — can be removed with conventional hydroxide-based chemical precipitation techniques. Dissolved metal ions that are complexed or chelated often require a carbamate, iron-based or other "advanced" chemical precipitation technique capable of breaking the metal-complexed bond before precipitation.

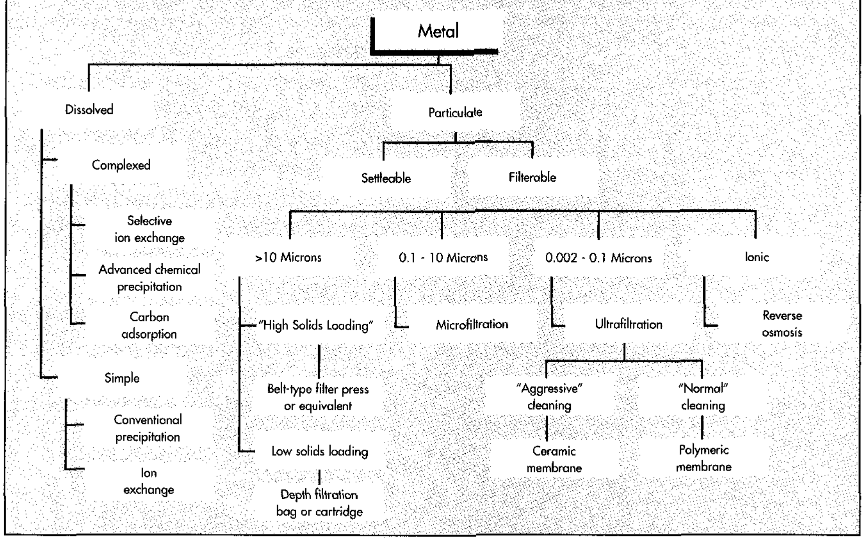
In either case, metal ions are converted from the soluble, dissolved form to a "solid" metal particulate that can be removed via clarification or filtration. Dissolved metals also can be removed directly via activated carbon adsorption for organics, reverse osmosis for ionic species or, the most prevalent mechanism, ion exchange resins.

EPA considers chemical precipitation to be the best practicable control technology for the metal-finishing industry and, as such, it has been widely implemented. It is advantageous for batch-treating low-volume wastestreams containing high concentrations (20 ppm to 30 ppm) of more than one regulated metal because operators can change chemistries or dosage rates to maintain effluent quality under changing influent conditions.

High-volume, low-concentration wastestreams, meanwhile, typically require continuous-flow systems. When a wastestream is fairly constant, such systems can include chemical precipitation in combination with clarification, advanced filtration particulate removal, or both. Advanced chemical precipitation generally is easy to add to an existing end-of-pipe system, but it has some disadvantages. It generates up to twice as much sludge as conventional precipitation techniques because metal ions, such as iron from the iron-based chemistry, will also precipitate. It also has difficulty achieving lower limits without filtration, and additional treatment usually is required before wastewater can be reused.

FIGURE 1

Choosing a Removal Technique



For these reasons, some facilities with high-volume, low-concentration wastestreams opt for an ion exchange process. These processes use a resin of positively or negatively charged ionic species (cationic or anionic) attached to an inert polymer to remove metals.

The typical ion exchange treatment operation consists of four cycles: service, backwash, regeneration and rinsing. During the service cycle, the wastestream passes through the resin (usually in a resin bed or column), where ions in the wastestream with greater affinity for the resin are "exchanged" for similarly charged ions "attached" to the resin bed. After most of the exchange sites have been used, the resin is considered to be *spent*, or *exhausted*, and is either discarded and replaced or, more typically, regenerated and reused.

Before regeneration, spent resin is backwashed to remove particulates and re-suspend the bed. A regenerant solution is then passed through the resin bed to remove the now-concentrated metal ions and "re-attach" the original ionic species. Spent regenerant may require further treatment, such as batch treatment or electrolytic metals recovery, before recycling and reuse or disposal. In the rinse cycle, water is used to remove residual regenerant solution from the bed.

Ion exchange resins typically are used to concentrate heavy metals from a dilute rinsewater wastestream, which reduces the volume of waste and enhances the opportunities for metals recovery.

Ion exchange techniques typically require minimal space and operator attention, can easily be added in-process, readily meet lower metals limits and allow for some wastewater reuse. Spent resin can be regenerated offsite at a licensed facility, thus eliminating the need for onsite treatment of spent regenerant, although onsite treatment can be beneficial when the resin is used to remove a particular metal that is recovered for reuse. Disadvantages associated with this technique include the cost of the resin and the potential for resin fouling.

Particulate Metals

Particulate metals can be redissolved to take advantage of ion exchange techniques, but, more commonly, they are removed via filtration. Filters commonly used for metals removal fall into two categories:

- depth filters, which include cartridge or bag filters, belt-type filter presses and plate-and-frame filter presses, and
- cross-flow filters, which include macrofilters (0.05 to 2 microns), ultrafilters (0.0015 to 0.1 microns) and nanofilters (300 to 1,000 molecular weight).

With depth filters, the wastestream flows down through the medium, causing particles to collect on its face. As the depth of the particles on the medium increases, pressure across the medium face builds until the filtration rate decreases or filtration stops. At that point, the medium is replaced or scraped clean and reused. Several precoat materials are available to increase the depth of particles a filter can retain before it reaches the critical pressure differential. Pore size ratings of 50 microns or higher are used most often by industry for wastewater treatment.

Cross-flow filters, meanwhile, use a high-velocity flow path across the medium. This tangential flow "scrubs" the filter surface clean of solids, which means the solution being filtered sees a relatively clean filter face. They continue to operate as long as the solids concentration does not cause a significant drop in the rated flux rate (gallons per square foot of filter media per day). A drop in the flux rate is considered significant if it causes the permeate, or filtrate, flowrate to drop below acceptable treatment requirements (minimum design flow). When that occurs, recirculated solids are dewatered in a pressure filter and disposed, and the cross-flow filter membrane surface must be cleaned for reuse.

Cross-flow filters come in various pore sizes — from those that allow only ions to pass through them to those that allow particles to pass through. Metal hydroxide solids usually are removed by microfilters, while ultrafilters are reserved for smaller metal particles, and nanofilters are used for still smaller organometallic dyes.

Cartridge and bag filters have the lowest capital cost of the commonly used depth filters, but they have the highest operating cost of all filtration methods because spent media must be disposed. However, because of their low capital cost, these depth filters can be cost-effective for end-of-pipe polishing systems that handle light metal loadings. Case studies indicate that relatively low effluent limits can be reached when effluent from a conventional clarifier is "polished" with either a cartridge or bag filter. A polishing filter also can remove hard-to-settle pin-floc generated by advanced chemistries, such as carbamate chemistry.

More advanced depth filters, such as belt filter presses, rotary vacuum filters and plate-and-frame filter presses, also can remove filterable metals after appropriate pretreatment, such as conventional or advanced precipitation, coagulants, polymers or other filter aids. These reusable filters lower disposal costs and offset capital costs when metal concentrations or solids loadings are high. Here too, filtration life can be extended through the use of precoat filter aids, such as activated carbon, diatomaceous earth or various proprietary agents. (A rice hull-based mixture has been reported to successfully remove metals from high-solids wastestreams.)

Microfilters typically are used as an alternative to clarifiers. The advantages of this type of cross-flow filter are consistent metal solids removal and the ability to attain lower effluent limits than most clarification processes. Pretreating metal wastestreams to ensure that dissolved metals are in a filterable, insoluble form is critical to the success of the microfilter.

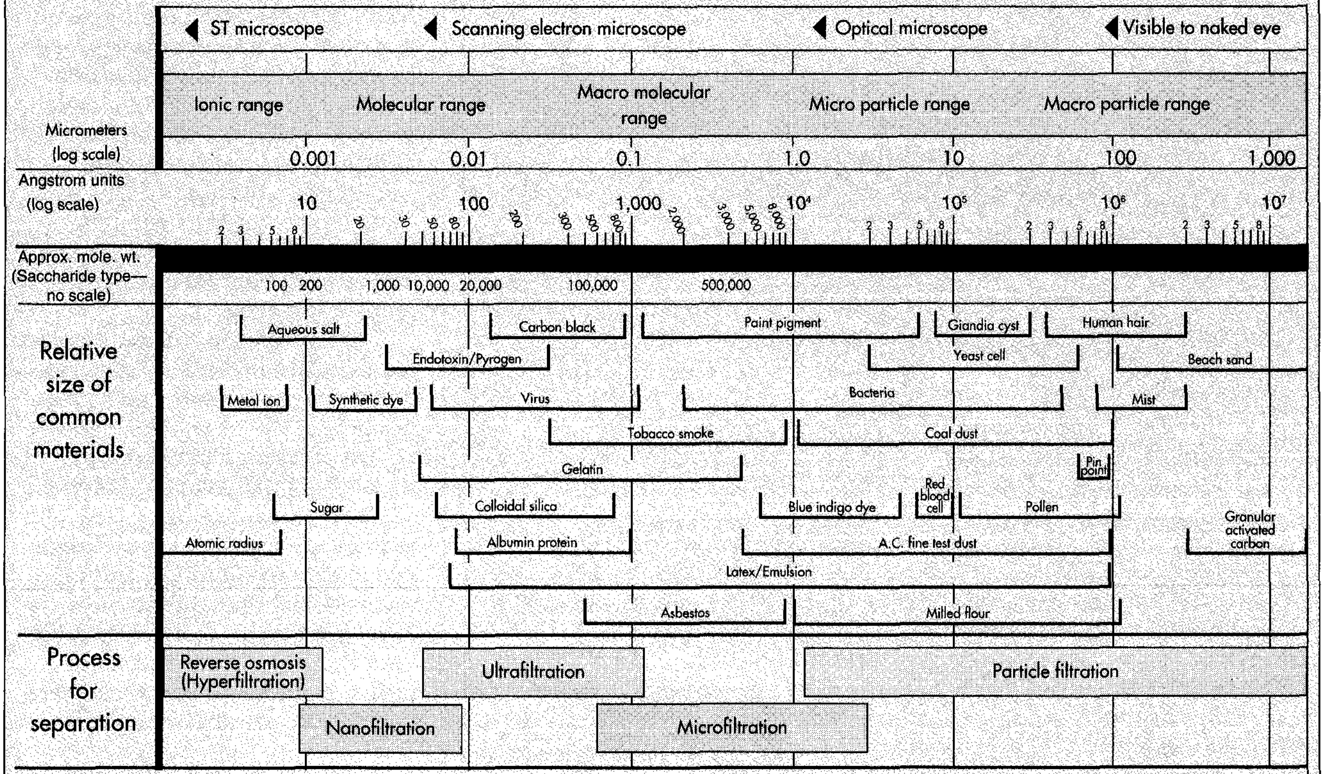
Particle sizing tests show that most microfilters remove metal hydroxide solids efficiently but have difficulty with metal fines smaller than 0.1 micron. Lab- or pilot-scale tests can help determine the appropriate chemistry for the filter and ensure a high flux rate, good rejection of metal solids, membrane compatibility, membrane cleaning efficacy and extended filter membrane life. Microfilters have been used extensively in recent years to convert clarification-based systems to filter-based systems that can meet today's tighter effluent limits.

Ultrafilters have a smaller pore size than microfilters, which enables them to handle relatively small particles and larger molecules. Ultrafilters are widely used in wastewater treatment applications to remove emulsified oil. They also are widely used in process applications, such as the recycling of aqueous cleaners and powder coating solutions, where they must be able to handle variations in temperature, pH and chemistries (see Figure 2).

Developments in membrane technology now allow design engineers to use membranes in more aggressive chemical metal removal scenarios. In one case where high levels of organics had to be removed before regulated metals could be removed, the engineer tried carbon adsorption, ion exchange, chemical precipitation and depth filtration to no avail. Eventually, he solved the problem by using a ceramic-based ultrafiltration membrane to remove the organics, followed by advanced chemical precipitation to remove metals. The new ceramic-based membrane was successful because it could withstand the aggressive chemical clean-

FIGURE 2

The Filtration Spectrum



Note: 1 micron (1 x 10^{-6} meters) = 4 x 10^{-5} inches (0.00004 inches).
1 angstrom unit = 10^{-10} meters = 10^{-4} micrometers (microns).

Courtesy of Osmonics Inc. (Minnatonka, Minn.)

ing made necessary by the organics to restore flux rates at the membrane surface.

Pilot tests are recommended in any situation involving the use of ultrafilters for wastewater treatment applications, because membrane fouling can take a few weeks or several months to appear. Pilot testing also lets engineers and membrane manufacturers more accurately determine long-term flux rates and ensure (and in the manufacturer's case, warranty) suitable membrane life. Clients can ill-afford to install a membrane that becomes irreversibly fouled in a short time.

Nanofilters are useful when dealing with molecular-sized metals, such as organometallic-based dyes. Because they reject compounds in the 300-plus molecular weight size, these filters are useful in situations that require further effluent polishing. One facility, for example, uses ultrafiltration followed by nanofiltration to remove metals to below regulatory limits. Key to the system's success is the protection of the nanofilter membrane by the initial, more rugged and "cleanable" ultrafilter membrane.

Reverse osmosis (RO) is classified as a filtration technique because the membrane's minute pores physically block the passage of metal ions. Unlike chemical precipitation, ion exchange or adsorption, which rely on electrochemical reactions, RO removes dissolved ionic metals from solution via filtration. More specifically, RO systems reject ions by reversing the natural osmotic pressure that exists at a selective membrane between concentrated and dilute solutions. Nature usually drives the metal ions from the concentrated solution to the more dilute solution, but, by using a pump to apply pressure, the dilute solution can be forced to give up even the small amount of metal ion it holds to become nearly "metal free."

Reverse osmosis is used most commonly in the water treatment field to produce electronic-grade water from city water and to desalinate salt water. In-process applications also can be cost-effective, depending on the value of the metal ion being removed. This technology probably will become more popular as the need to recycle water becomes more critical, although, because it is susceptible to fouling, a significant investment of time and money must be made in extensive pilot-scale testing.

The time of conventional systems has passed. New toxicity-based effluent standards require advanced technology. Metals removal technology has advanced from conventional precipitation to state-of-the-art use of advanced chemistries and technologies, such as ion exchange and membrane filtration, and the progress continues. Researchers are developing resins with increased selectivity for particular metals, as well as membranes that are more resistant to irreversible fouling. ■

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