An Update On Reverse Osmosis For Metal Finishing

By Peter S. Cartwright

Developments have occurred in the application of reverse osmosis to achieve zero discharge of rinsewater and plating chemicals. RO is now used for the recovery of brass, hexavalent chromium, copper, nickel and zinc chemicals. Test data on recovery are cited.

Reverse osmosis (RO) is readily adaptable to the recovery of plating chemicals and is a continuous, low-energy process involving only pump energy. With equipment that is simple and easy to operate, the process can continuously return solute to the plating bath and recover almost all of the rinsewater.

Because RO has the capability of separating dissolved solids (both inorganic and organic) from pure water, the process is used to concentrate the dissolved solids of the plating rinse stream. In virtually all cases, the pure water can be recycled back to the process, and, depending upon a number of factors, the concentrate stream can be returned to the plating bath, directed to the waste-treatment system, or hauled away. Ideally, to achieve zero discharge, the concentrate stream should be returned to the plating bath; however, factors such as bath temperature (which determines the rate of evaporation from the plating solution), degree of rinsewater contamination, source of rinsewater, and engineering design of the RO system determine its disposition.

The production rate of an RO membrane is a function of variables such as type and concentration of dissolved solids, temperature of the feed solution, applied pressure, system design, and characteristics of the selected polymeric membrane.

To be effective, the membrane polymer must be resistant to chemical attack by the solution in which it is operating. Whereas all of the commercially available polymers exhibit excellent tolerance to certain chemical extremes, none has yet been developed that will satisfactorily function in all extremes; there is no optimum membrane at this time. The chemical factors that present the greatest problems to membrane polymers include pH extremes, strong oxidizing agents and aromatic hydrocarbons.

Another polymer characteristic that is important to manufacturers of RO membranes is rejection, usually expressed as percent removal of dissolved solids from the feed solution. A condition that can significantly affect membrane performance is fouling resulting from suspended or precipitated solids coating the membrane surface. A fouled membrane will usually show a reduction in both pure water (permeate) flow and permeate quality. Proper prefiltration is absolutely essential to insure opti-
If the RO function dissolved presелected be resistant is also a function of its configuration. To date, the only practical configurations for most RO applications are the hollow-fiber permeator (Fig. 1) and the spiral-wound element (Fig. 2). Because of the close packing density and small diameter of the fibers in the permeator, it is less widely used than the spiral-wound configuration.

Figure 3 represents a typical RO system operating on the first rinse and directly returning the concentrate to the plating tank. Figure 4 illustrates an RO system returning the concentrated bath constituents to a dragout tank for eventual return to the plating tank.

Six types of RO installations and potential applications of new thin-film composite membranes are discussed in this report.

**Nickel**

There are at least 150 RO systems operating on various nickel baths. Most utilize cellulose acetate membrane elements and offer a recovery efficiency in the range of 90 to 97 percent. The relatively high evaporation rate resulting from the elevated bath temperature generally allows complete recycling of the concentrate and permeate streams. In a survey of some of these installations, the average membrane life in 11 Watts baths was almost 2 years and payback (based on value of plating salts recovered) averaged 18 months. The installations had been operating for a minimum of 4 years. A review of four installations for bright nickel and two for nickel sulfamate plating indicated similar membrane life and payback times.

**Copper Sulfate**

Approximately 12 RO systems are operating on various copper sulfate rinses. These systems utilize hollow-fiber polyamide and cellulose triacetate membranes as well as spiral-wound, thin-film composite types, and offer a membrane life of 1 to 3 years. Because of the low temperature of the plating bath, with the resulting low evaporation rate of water, only a small portion of the concentrate from the RO unit can be directed back to the bath for reuse.

**Zinc Sulfate**

One RO system is being used on a zinc sulfate rinse from a proprietary manufacturing process. The system employs spiral-wound thin-film composite membrane elements with a feed rate of 2.8 L/min (45 gal/hr) and a recovery rate of 87.5 percent. The concentrate stream is further reduced in volume in an evaporator (operating at a 90 percent recovery rate) and returned to the bath. Although the system has been operating for more than 7 years, the thin-film composite element has been used for about 1 year and is working well.

**Brass Cyanide**

Approximately five RO systems are operating on brass cyanide rinses from a proprietary manufacturing process. Both polyamide and cellulose triacetate hollow-fiber membrane elements are utilized. Feed rate is approximately 3.8 L/min (60 gal/hr) for each. The recovery efficiency is 90 percent. The systems have been oper-
ating for 5 years and the life of the membrane element is 3 to 4 years. Pretreatment includes 1-μm filter cartridges for the polyamide elements and 3-μm filter cartridges for the cellulose triacetate elements.

**Copper Cyanide**

One RO system is being used after contact plating on printed circuit boards. The first flow rinse is fed to a polyamide hollow-fiber membrane element at the rate of approximately 795 L/hr (210 gal/hr). The system is operating at a recovery rate of about 90 percent, with a portion of the concentrate recycled to the plating bath and the remainder to the waste-treatment system. All of the permeate is reused in the rinse stream. The system has been operating for more than 3 years. A 1-μm filter cartridge followed by activated carbon is used for pretreatment. Membrane elements have lasted about 3 years.

RO is also being used after copper plating a leaded-brass medical device. The first rinse is fed to a polyamide hollow-fiber membrane element. The system is operating at a recovery rate of 93 percent, with approximately one-half of the concentrate recycled to the plating bath and the rest to the waste-treatment system. All of the permeate is reused in the rinse stream. RO has been in operation there for more than 7 years, using a 1.2-μm filter followed by 0.45-μm filters for pretreatment. Membrane life is more than 4 years.

**Hexavalent Chromium**

A foil manufacturer has been investigating the use of spiral-wound, thin-film composite membrane elements for the recovery of hexavalent chromium from the rinses in a proprietary process. Hollow-fiber membrane elements lasted only 1 to 2 months before irreversibly fouling, whereas the spiral-wound configuration has performed satisfactorily for more than 6 months with only a 5-μm filter cartridge used for pretreatment.

**New Membranes**

Most of the existing nickel installations utilize spiral-wound cellulose acetate membrane elements. The viability of RO technology for zero-discharge applications is a function of the chemical features of the membrane element and the characteristics of the plating bath, as noted previously. Until recently, the spiral-wound membrane configuration has been available only with cellulose acetate polymer, the chemical characteristics of which have limited its application to low-pH baths such as nickel. Temperature of the plating bath determines the evaporation rate of water and concentrate rate from the system.

New thin-film composite membrane elements are available from various manufacturers. Table 1 shows an improved approach to RO technology.

The recovery of the concentrate must be considered when selecting the membrane element. Because the membrane element is always exposed to process water, corrosion and chemical discharge systems may require a recovery rate of 95 percent or less. A 5 percent recovery rate is typical. If the temperature of the recovery water is too high, the efficiency gets reduced. Therefore, the recovery rate should be kept as low as possible. When the recovery rate is 95 percent or less, the concentrate rate from the system is the same as the volume of process water treated. To achieve a balance between the recovery rate and the concentrate rate, the temperature of the membrane element should be increased. The recovery rate can be increased to 95 percent by increasing the temperature of the membrane element to 40°C (104°F) and decreasing the concentrate rate from 5 percent to 0 percent. The recovery rate can be increased to 90 percent by increasing the temperature of the membrane element to 60°C (140°F) and decreasing the concentrate rate from 5 percent to 0 percent. The recovery rate can be increased to 80 percent by increasing the temperature of the membrane element to 80°C (176°F) and decreasing the concentrate rate from 5 percent to 0 percent. The recovery rate can be increased to 60 percent by increasing the temperature of the membrane element to 100°C (212°F) and decreasing the concentrate rate from 5 percent to 0 percent. The recovery rate can be increased to 40 percent by increasing the temperature of the membrane element to 120°C (248°F) and decreasing the concentrate rate from 5 percent to 0 percent. The recovery rate can be increased to 20 percent by increasing the temperature of the membrane element to 140°C (284°F) and decreasing the concentrate rate from 5 percent to 0 percent. The recovery rate can be increased to 10 percent by increasing the temperature of the membrane element to 160°C (320°F) and decreasing the concentrate rate from 5 percent to 0 percent. The recovery rate can be increased to 5 percent by increasing the temperature of the membrane element to 180°C (356°F) and decreasing the concentrate rate from 5 percent to 0 percent. The recovery rate can be increased to 2.5 percent by increasing the temperature of the membrane element to 200°C (392°F) and decreasing the concentrate rate from 5 percent to 0 percent. The recovery rate can be increased to 1.25 percent by increasing the temperature of the membrane element to 220°C (428°F) and decreasing the concentrate rate from 5 percent to 0 percent. The recovery rate can be increased to 0.625 percent by increasing the temperature of the membrane element to 240°C (464°F) and decreasing the concentrate rate from 5 percent to 0 percent.
tion rate of water, thereby fixing the maximum concentration rate from the RO system.

New thin-film composite (TFC) membranes are now available from six or seven manufacturers. They offer improved application characteristics, as indicated in Table 1. The recovery efficiency of an RO system is defined as the volume portion of the feed stream that goes through the membrane and comes out as permeate. Recovery is always expressed as a percentage, and most zero-discharge systems operate at recovery efficiencies in excess of 95 percent. The concentrate stream is less than 5 percent of the feed-stream volume. With low-temperature plating baths having low evaporation rates, the recovery rate must be higher if all of the concentrate stream is fed directly to the plating bath. As the recovery efficiency goes up and the concentrate volume goes down, the concentration of salts in the concentrate increases.

![Fig. 7](image1)

**Fig. 7—Effect of recovery on osmotic pressure (zinc cyanide rinsewater).**

![Fig. 8](image2)

**Fig. 8—Effect of recovery on osmotic pressure (brass cyanide rinsewater).**

![Fig. 9](image3)

**Fig. 9—Effect of recovery on osmotic pressure (chromic acid rinsewater).**

![Table 2](image4)

**Table 2**

<table>
<thead>
<tr>
<th>Plating bath</th>
<th>Bath temperature, °C/°F</th>
<th>Toxic contaminant*</th>
<th>Osmotic pressure (Δπ), psi at recovery of:</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>95 percent</td>
<td>97 percent</td>
</tr>
<tr>
<td>Watts Ni</td>
<td>60/140</td>
<td>Ni&lt;sup&gt;2+&lt;/sup&gt;</td>
<td>275</td>
</tr>
<tr>
<td>Copper cyanide</td>
<td>60/140</td>
<td>Cu&lt;sup&gt;2+&lt;/sup&gt;</td>
<td>—</td>
</tr>
<tr>
<td>Zinc cyanide</td>
<td>27/80</td>
<td>Zn&lt;sup&gt;2+&lt;/sup&gt;</td>
<td>306</td>
</tr>
<tr>
<td>Brass cyanide</td>
<td>27/80</td>
<td>Zn&lt;sup&gt;2+&lt;/sup&gt;</td>
<td>—</td>
</tr>
<tr>
<td>Decorative Cr</td>
<td>43/110</td>
<td>Cr&lt;sup&gt;3+&lt;/sup&gt;</td>
<td>300</td>
</tr>
<tr>
<td>Hard Cr</td>
<td>55/130</td>
<td>Cr&lt;sup&gt;3+&lt;/sup&gt;</td>
<td>200</td>
</tr>
</tbody>
</table>

*Rinse flow adjusted to give a total salt concentration of approximately 3000 mg/L.

**Rejection of toxic contaminant in permeate calculated as follows: (Conc. in Permeate/Conc. in Feed) × 100.
stream will increase. This increase can be rather marked; for example, the concentration of salts in a system operating at 98 percent recovery is 2.5 times greater than that of a system operating at 95 percent recovery.

The osmotic pressure at high recovery rates becomes the limiting factor in system design. This means that regardless of the membranes used, low-temperature baths are more difficult to treat with RO than those operating above 50°C (120°F). To overcome this problem, techniques such as air agitating the plating bath, further evaporating the concentrate stream, directing the concentrate to an air scrubber, and bleeding part of the bath into the RO unit have been used with success.

Figures 5 through 9 illustrate the relationship of recovery to osmotic pressure for rinse streams containing approximately 3000 mg/L of plating salts. Although the osmotic pressure increases with increasing recovery rates for all salts, there is considerable variation in the actual osmotic pressure as well as the rate of increase, depending on the nature of the salts.

Table 2 summarizes the test data for six common plating bath rinses utilizing two different TFC membranes. The plating bath temperature is included as an indication of the evaporation rate and the need for additional processes to allow complete reclamation of the concentrate stream. The table also lists percent rejection of the toxic contaminant by the RO membrane. This rejection is a function of both the membrane itself and the degree of ionization of the contaminant. The relatively low percent rejection of cyanide ion from the copper cyanide bath is probably a result of incomplete ionization in that particular bath.

The high osmotic pressure of the zinc cyanide rinse and the low evaporation rate of the bath make this application impractical for RO reclamation. The other rinses offer potential, and testing that is expected to result in the design of complete reclamation systems is continuing.

In the search for practical solutions to the pollution problems facing the metal finishing industry, RO is proving to be one of the viable processes for consideration when designing zero-discharge treatment for plating waters.

About the Author
Peter S. Cartwright, PE, is president of C1 International, a consulting engineering firm at 3423 NE Maplewood Dr., Minneapolis, MN 55418. The company specializes in water purification and waste treatment using RO, ultrafiltration, deionization and distillation. Mr. Cartwright has written numerous articles on these subjects and is the holder of a patent. A member of the AES Upper Midwest Branch, he also has been active in the society's Environmental Compliance & Control Course, both as an author and instructor.

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