Integration of Ceramic Micro Filtration & Reverse Osmosis For Recycle of Metal Finishing Wastewater

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A patented system for removal of heavy metals from wastewater streams based upon ceramic membrane technology has been developed. Most metal finishing wastewaters also contain high levels of dissolved solids, making direct wastewater reuse problematic. By processing the ceramic microfilter effluent with reverse osmosis technology, TDS levels were reduced from 6,000 mg/L to below 350 mg/L (>94% salt rejection). This process is suitable for all purposes within a conventional metal finishing facility, including DI feed water. This approach, combined with water quality segregation, has reduced city water usage by 67%.

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Introduction

The Strategic Goals Program (SGP) is a cooperative effort between the U.S. Environmental protection Agency (EPA) and various metal finisher associations and societies that is promoting the investigation and testing of innovative technologies and ideas that will improve management of process fluids and generated wastewaters within metal finishing facilities. One of the main goals of this cooperative is to investigate the feasibility of approaching zero discharge (AZD), more specifically, zero wastewater discharge[1].

The difficulty in developing and implementing AZD solutions is that site-specific (facility specific) requirements and constraints define the final AZD solution. It is beyond the scope of this paper to discuss these requirements and constraints in detail, however, some practical considerations include costs, plant configuration (i.e. waste stream segregation or combination), applicability of recovery technologies, and the ability to improve overall process conditions. Although an optimal AZD solution can be complex and expensive to implement, current technologies are available that can make a significant impact on overall plant performance and water use at marginal additional cost.

Currently, there are various treatment methods available for the removal of heavy metals from waste streams produced from rinse tanks and process baths within a metal finishing facility. From a simplistic viewpoint, there are five main processes that purify wastewater or process bath solutions in an effort to move closer to AZD goals. These processes include: 1) microfiltration; 2) electrodyalisis; 3) diffusion dialysis; 4) ion exchange; 5) and electrowinning technologies[1]. In addition, promising new technologies that will aid in AZD include reverse osmosis, vacuum evaporation, crystallization, and adsorption filtration. Although there has been considerable effort using these processes to reduce contaminant solution discharges from metal finishing facilities, there remains considerable investigative effort to combine these processes to effectively, and economically achieve reduced wastewater discharge levels.

This paper discusses the use of ceramic microfiltration coupled with reverse osmosis (CMF/RO) to reduce overall wastewater discharge from metal finishing facilities.

CMF/RO Integration

Ceramic microfiltration is an effective wastewater treatment technique that replaces clarifiers in conventional chemical precipitation treatment schemes. One major benefit of microfiltration is that the process produces a more reliable effluent quality compared to conventional gravity clarifiers. In addition, microfiltration effluents only have particles less-than the nominal pore size of the membrane, typically below 0.2 um. This is an important fact considering that RO membranes are very sensitive to particulates and colloidal materials. In most cases the silt density index (SDI-15min.) for spiral-wound RO membranes must be less-than 3 to5[2]. Therein, ceramic microfiltration can produce effluent that is suitable for continued treatment by RO.

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Figure 1 illustrates a conceptual wastewater management scheme in which a portion of the microfilter treated waste water is used for non-critical rinses and the remaining effluent is processed by an RO system that can produce rinse water of high quality that can be used in critical rinse operations.

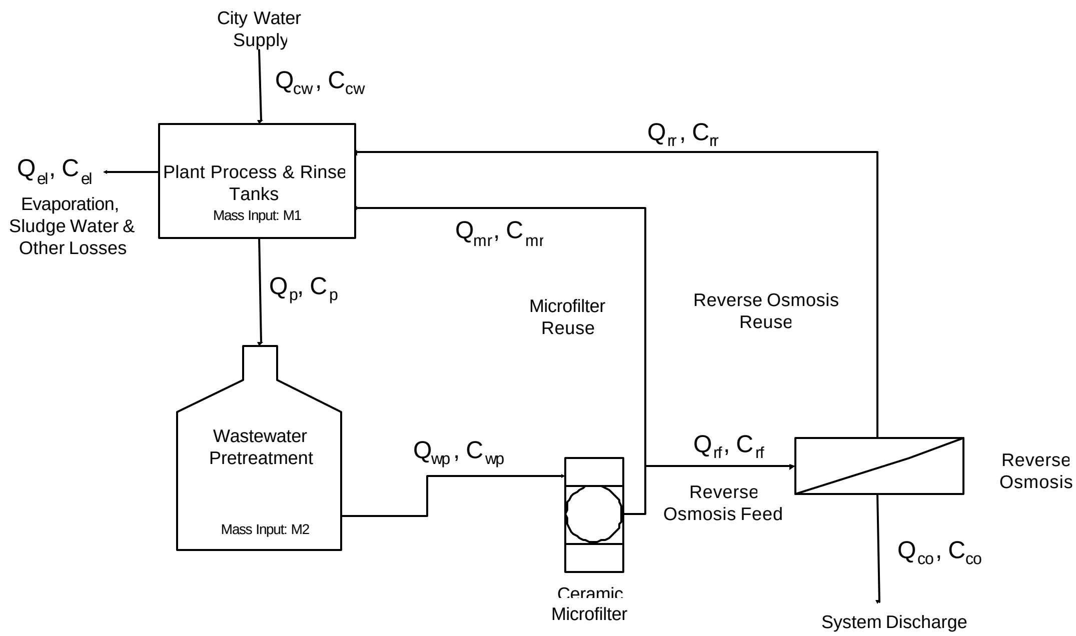

Figure 1. Wastewater material balance for a CMF process coupled with RO treatment.

The advantages of using the wastewater management scheme presented in Figure 1 are based upon the recovery rate of the RO system and the amount CMF effluent directly reused for non-critical rinses. Even if a relatively low RO recovery rate of 50% can be maintained and 15% of the microfilter effluent can be utilized for non-critical rinses, the system could theoretically cut overall water usage by 55%. Possibly a more important result is that the implementation of this type of wastewater management scheme could increase rinse water flow rate through the metal finishing facility thereby increasing product quality while maintaining the same city water usage. As is the case for any water recovery treatment scheme, water recovery allows for plant expansion without increasing city water usage or increased wastewater discharge.

Practical Considerations of CMF/RO Integration

The major constraint in integrating a reverse osmosis process into an existing facility is the impact of influent water quality on the subsequent short-term and long-term operation of the system. More specifically, influent water constituents including sulfates, carbonates, various heavy metals, organics, and silica contribute to membrane fouling by the formation of scale. Various anti-scaling additive or physical technologies can be employed to reduce scale formation.

Thus, understanding influent water characteristics and scale formation potential is critical to proper integration of reverse osmosis systems into existing or new facilities.

Although individual wastewater streams from metal finishing facilities vary in chemical composition, the composition of waste streams after primary wastewater treatment using chemical precipitation is similar depending on the specific chemical utilized during treatment. For example, after primary treatment utilizing hydroxide precipitation followed by microfiltration, the main contaminants of concern are typically carbonates (bicarbonate and carbonate), calcium if softening is not used at the facility, and silica[3]. In special instances, aluminum can also be a concern if the facility has anodizing processes.

Scale formation can be managed by using chemical anti-scaling products or by simply using the correct pH in the RO feed water. The predominant scale formed on RO membranes after primary metals removal is carbonate based[3]. Therefore, depending on the solution chemistry, lower pH values can minimize carbonate scale formation. However, there are limits to pH adjustment depending on the concentration of soluble aluminum present and the pH tolerance of the RO membranes. Most wastewater treatment systems utilizing hydroxide precipitation as the primary mechanism for heavy metal precipitation operate in a pH range of 9 to 10.5 depending on the type of metals present in the waste stream[4]. At these pH ranges most metals, except trivalent aluminum, will be removed to very low concentration levels. Therefore, if significant amounts of aluminum are present in the influent waste stream, significant amounts of soluble aluminum will be present in the influent to the RO system. Due to the amphoteric nature of aluminum, a decrease in pH from 10.5 to 9 will produce an aluminum hydroxide precipitate that may physically clog a RO membrane although the decrease would theoretically decrease carbonate scale formation. Although this type of problem appears to be formidable, innovative membrane designs and operation can handle many types of integration issues.

Case Study: CMF Followed by RO Treatment

Testing Equipment

A small 5-gpm reverse osmosis system was tested downstream of a full-scale, operational ceramic microfiltration (CMF) system (30-gpm)*. A slipstream of microfilter effluent was discharged into a RO pretreatment holding tank. This tank served as the feed source for the RO system. Figure 2 provides a simplified process diagram of the system.

The feed tank received water directly from the microfilter permeate discharge line. A city water line was added later to control influent TDS levels. A metering pump was used to pump concentrated sulfuric acid into the feed water tank to adjust the influent pH of the water. Typically, the microfilter permeate water entering the RO system had a pH between 9.5 to 10.5 and was adjusted to pH 9.0. using a pH controller that added sulfuric acid to maintain the set-point pH within a narrow pH range. Antiscalant* was added into the RO feed stream just prior to the RO membrane housings using a proportional-metering pump. The dosage of antiscalant varied depending on the testing phase. Influent flow rate to the RO membranes was adjusted by using a throttling valve located after the main system pump. Backpressure on the RO membranes was

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* BASX Systems, Fort Collins, CO
* SpectraGuard™, Professional Water Technologies, Inc., Escondido, CA

adjusted by using a valve located on the reject discharge line. These two valves were used to adjust influent, reject, and permeate flow rates.

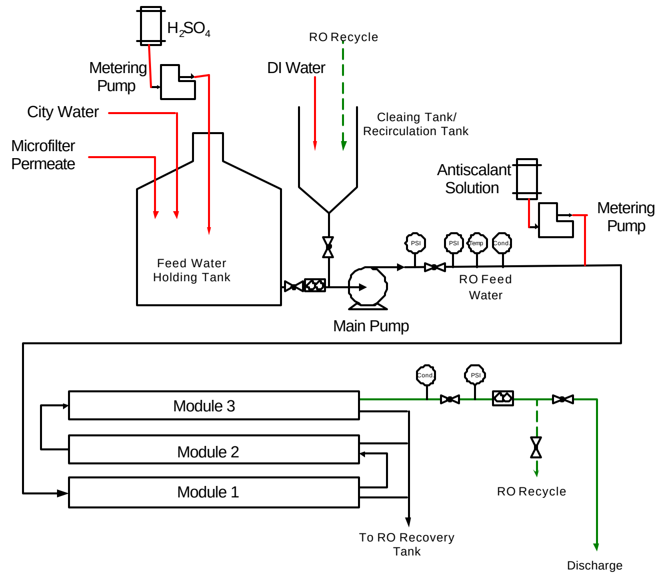

Figure 2. RO system testing equipment installed after CMF system.

During the last phase of the RO pilot study, a recirculation loop was added to the RO system. This system recirculated a portion of the reject water back into the cleaning tank. This reject water was then re-pumped through the RO membranes.

System Operation
Membrane performance and overall operability were determined by gathering operational data and analyzing the results. Operational results included:

- Feed and reject flow rates
- Feed and reject pressures
- Conductivity of feed, reject and permeate water
- Total flow processed
- Temperature
- pH

The data gathered was analyzed and normalized according to standard RO evaluation equations. Percent recovery was varied during pilot testing because recovery rate significantly impacts overall water and cost savings.

Membrane Flux
The flow of water through a semipermeable membrane is dependent on many factors including the type of membrane material, membrane thickness, solute type and concentration, temperature, and pH. The basic behavior of water flux through a semipermeable membrane indicates that the flux of water is proportional to the pressure gradient (Hagen-Poiseville type flow)[5].

Not surprising, water flux depends on applied pressure. An increase in feed water pressure will increase the flux through the membrane. A practical limit exists for this relationship because as the flux of water through the membrane increases, the concentration of solutes increases, therein increasing the osmotic pressure and subsequently decreasing the net driving pressure (NDP) of the system. Typical average system flux rates for most RO applications with high influent TDS are 8 to 12 gal/ft^2.day (gfd)[2]. As flux rates increase, the loading rate of potential foulants to the membrane surface increases. In a staged array configuration, the flux rate decreases from the beginning to the end of system because feed TDS and subsequently osmotic pressure increases in the trailing membrane modules. The flux rates of the various stages can be balanced to extend the intervals between cleanings. Flux balancing can be achieved by permeate backpressuring the first stages or by interstage feed pressure.

Figure 3 illustrates the effect of pH and TDS on RO performance.

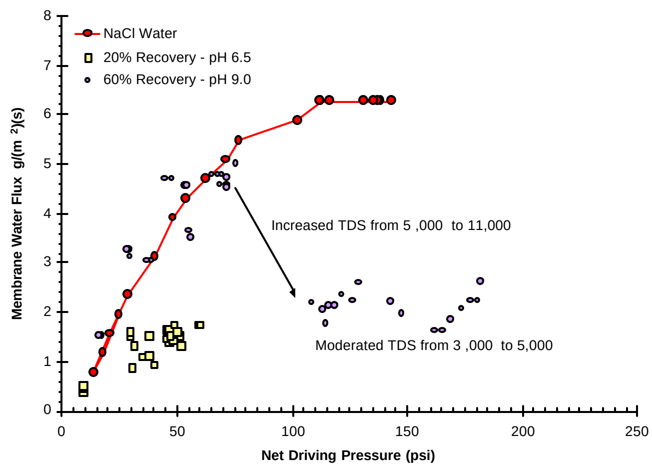

Figure 3. Membrane water flux versus Net Driving Pressure (NDP): effect of pH and TDS on RO membrane fouling.

The data illustrated in Figure 3 shows the relationship between flux and NDP for a NaCl solution (red line) at 5,000 mg/L TDS; water flux increases with increasing NDP. The non-linearity of this line is due to hydraulic limitation within the hardware of the system. The NaCl baseline indicates the maximum average water flux of the membrane system of 6.3 g/m^2-sec (≈ 13.3 gal/ft^2/day), consistent with manufacturers specifications*.

At a pH of 6.5, the formation of aluminum hydroxide floc occurred because of the high concentration of aluminum in the RO feed solution (>18 ppm). This aluminum hydroxide floc caused high turbidity and suspended solids in the RO feed water, severely fouling the membrane in a short period of time. When the solution pH was maintained at pH 9, the formation of aluminum hydroxide was limited and resulted in minimum fouling of the membrane as witnessed by the similar result obtained when a NaCl test solution was tested. However, the membranes fouled at pH 9 when the feed water TDS was raised to 11,000 mg/L TDS from 5,000 mg/L TDS. This fouling event was caused by over saturation of carbonates in the reject water stream. After

* 4820 HR TFC, Koch Membrane Systems Inc., Chicago, IL

influent TDS levels were adjusted back down to 5,000 mg/L, fouling of the RO membranes was not observed.

The tendency to form $CaCO_3$ scale is typically determined by calculating the Langelier Saturation Index (LSI) of the concentrate stream.

$$LSI = pH_{\text{concentrate stream}} - pH_{\text{solution}}$$

Positive LSI values indicate potential for calcium carbonate precipitation while negative LSI values indicate corrosive tendencies. The LSI at a TDS of 5,000 mg/L was slightly negative while the LSI at a TDS of 11,000 was positive.

For a constant RO feed water TDS concentration, increasing the recovery rate increases the concentration of solutes (salts) on the reject side of the membrane. If the influent TDS is high enough for a specific solute, the resulting concentration in the reject stream may exceed the ion product (IP) of a specific insoluble precipitate. The effect of reject stream TDS on membrane performance is further illustrated in Figure 4, which shows the effect of recovery rate on RO membrane performance and fouling characteristics.

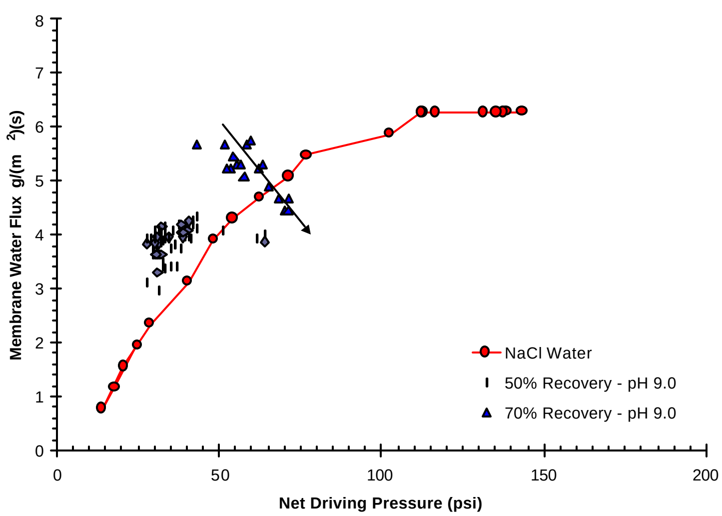

Figure 4. Membrane water flux versus Net Driving Pressure (NDP): effect of recovery rate on RO membrane fouling.

Figure 4 indicates that as the recovery rate increased from 50% to 70%, the membrane water flux decreased versus NDP at 70%, whereas at 50% the membrane water flux was relatively constant. Although this graph does not show the rate of membrane fouling, it does indicate that the higher recovery rate did impact the potential for membrane fouling. At a 50% array recovery, the membranes showed no decrease in water flux between a NDP of 30 to 70 psi.

Simple relationships can be derived that incorporate equations used to calculate the transmembrane pressure differential (P_{tm}) and the transmembrane osmotic pressure differential (π_{tm}). These equations can be used to calculate the relationship between water flux and the NDP. This relationship is represented by the water permeability coefficient (ω). This coefficient is constant for a given set of operating conditions and will account for changes in TDS due to overall changes in the NDP. Therefore, changes in the water permeability coefficient represents a change in the permeability of the membrane given that operating set-points of the RO system do not change. This is a useful method in ascertaining optimal operating conditions for the RO system.

Data analysis indicated that at 50% recovery, the water permeability coefficient remained relatively constant at 0.11 (± 0.017) g/m^2-sec-psi. At 70% recovery, the water permeability coefficient decreased rapidly due to fouling of the membranes.

Membrane Recovery
Product water recovery is simply the permeate (or filtrate) flow rate divided by the feed water flow rate. The product recovery rate was varied throughout the test phase. Therefore, the water flux varied across the membrane because it is proportional to the recovery rate (flux is related to osmotic pressure). Figure 5 illustrates this relationship.

Although the relationship between product recovery and water flux appears simple and straightforward (i.e. increasing water flux corresponds to an increase in product recovery), the situation is more complex in reality because applied pressure, antiscalant dose, and temperature vary during normal operation. A more meaningful and operationally effective method of analyzing data is
to evaluate the relationship between product recovery, water flux, antiscalant dose, and influent TDS on fouling rates and potentials. The influent TDS is very important when considering overall recovery rates because the concentration of solutes in the reject stream of an RO system increases as recovery rates increase. This is a critical point to consider when designing a RO system.

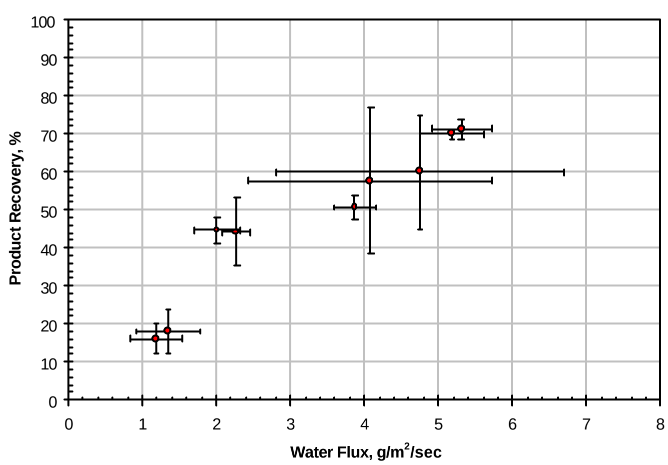

Figure 5. RO Product Recovery versus Water Flux. (error bars correspond to one standard deviation from the average value - red dots).

Membrane Salt Rejection
Salt (solute) rejection is influenced by the particular membrane used, the recovery rate, feed water solute concentration, and chemical valance of the ions in the solute. For example: some ions with a valance of +3 are rejected to a lesser extent than at a +5 valance state. Simply stated, salt

rejection is the fraction of solute in the membrane feed water that remains in the reject stream and does not enter the product stream.

Salt rejection for all the experiments ranged between 94 to 97%, corresponding to decreases in TDS from 6,000 mg/L to below 350 mg/L. Figure 6 illustrates the average salt rejection for each major experimental group. Statistical analysis indicated that the average salt rejections were the same
for each experimental condition. This is to be expected because, in general, solute flux is not dependent on applied pressure.

It is possible to calculate the flux of solute through the membrane. However, since the solute rejection rates were statistically similar (Figure 6), the flux of solute would also be similar for each experiment. The fact that most RO influent waters will have a complex combination of various ions and the concentration of individual ion species will change over time, it is difficult to ascertain the effect of recovery on solute rejection. Typically, this effect is minimal so the relationship between permeate solute concentration and recovery rate may be neglected. However, since solute flow through the membrane is directly related to individual constituent concentration in the feed-concentrate, permeate quality decreases as recovery increases. In a complex system with many solutes, this fact can be difficult to establish from data because changes in TDS do not necessarily correspond to a proportional change in concentration of a specific solute. More specifically, a change in TDS may be due to one or more ions each with their respective solute rejection rates.

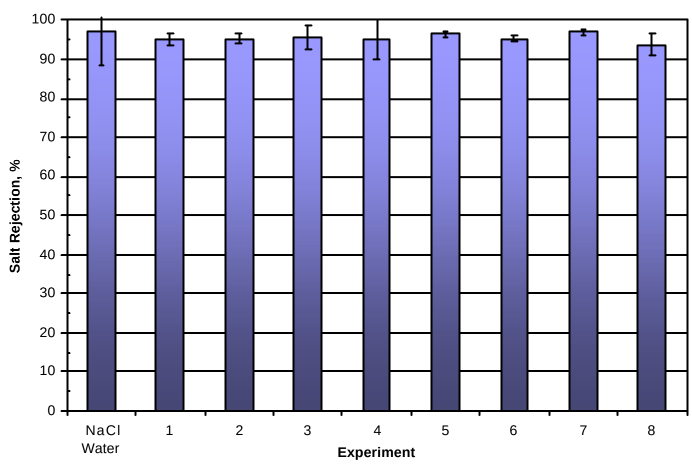

Figure 6. Average salt (solute) rejection from the RO system for all testing conditions.

Conclusions

- Direct microfilter reuse and RO treatment can be an effective water management scheme that can increase water reuse rates, by as much as 60 to 70% depending on facility configuration.

- TDS must be maintained at levels below 6,000 mg/L for optimal RO performance.

- Recovery rates of approximately 50% were witnessed during onsite testing.
- Solute (salt) rejection was relatively constant at 94 to 97% rejection efficiency.
- The control of scaling, by either pH adjustment or antiscalant addition, must be addressed when integrating an RO system into a water recovery strategy.
- Conventional RO configurations are not effective in treating pretreated wastewater from metal finishing facilities. Substantial modifications are required to integrate RO treatment into an overall water management scheme at metal finishing facilities.

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