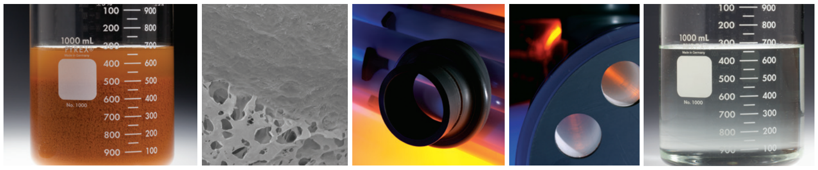


POREX® Tubular Membrane Filter (TMF™) Applied in a Plastic Plating Wastewater Reclaim System

Abstract Introduction

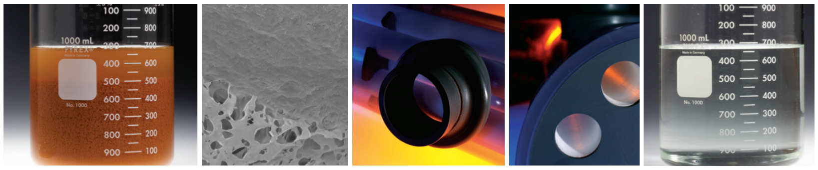
A large auto parts manufacturer located in the Zhejiang province of China was in need of a wastewater treatment system to address the complex wastewater produced by their plastic plating processes. Several streams of heavy metal contaminated wastewater are generated from their workshops that need to be thoroughly treated before discharge. In addition, the company is very environmental conscious and wanted to reduce their overall fresh water consumption by reusing the wastewater from the process. In 2012, a new system was built by a certified water treatment company to fulfill the client's expectation for a "treat and reuse" process.

There are four different streams of wastewater from the customer's workshop:

1. 312 m^3/day Acid/Alkaline and Copper wastewater
2. 144 m^3/day Nickel wastewater
3. 287 m^3/day Chromium wastewater
4. 274 m^3/day combined wastewater
   (including Electroless Nickel wastewater)

These 4 streams are treated separately with a reaction stage (alkali precipitation and coagulation, plus a reduction stage for Chromium wastewater), Porex Tubular Membrane Filter (TMF™) stage for solid/liquid separation, and single or double pass RO for desalination. The product water is then sent back to the workshop for reuse as process water.

System commissioning began in October 2012 and the performance has met the design standard. Conductivity of the treated water (for reuse) is less than 10µs/cm. The recovery rate of the inner reclaim system is 80%, with the recovery rate of the whole factory at 66%. Final discharge water (RO reject water, with further treatment process) has met the required limit values and in two months' time, 22,300m^3 of wastewater was reused. That equates directly to an equal amount of fresh water being saved. With this system, the Porex TMF benefits were demonstrated as a key process linking the wastewater treatment system to an RO desalination system.



Background

The customer had an existing wastewater treatment system built with a traditional process: chemical dosing/reaction stage and clarifier, with the supernatant of the clarifier passing through a multi-media filter. The remaining heavy metal was removed by an ion exchanger. This fed an RO unit for desalination to produce water for workshop reuse. The performance of this system was deemed not acceptable by the customer for the following reasons:

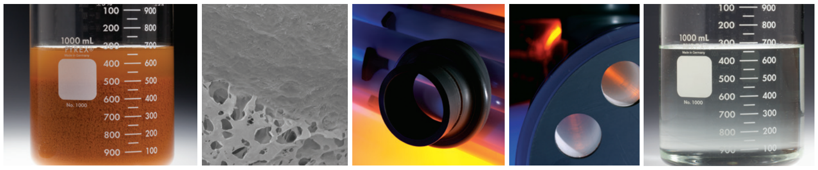
1. An inadequate chemical reaction stage: there were chelating agents in the wastewater such that simple alkaline precipitation was not enough to decrease heavy metal (Cu, Ni, Cr) concentrations to the required levels.

2. Frequent regeneration of the ion exchanger was needed, which consumed a large amount of acid and alkali, while at the same time a lot of wastewater was formed during regeneration. This resulted in a low system recovery rate and high running cost.

3. Variability of the supernatant from the clarifier resulted in unstable operation of the RO unit, requiring frequent chemical cleaning.

Based on the above reasons, the customer authorized a certified water treatment company to develop a customized total solution for the wastewater treatment system. New technology applied in this system includes electro-Fenton for oxidizing organics and breaking of chelating agents, and POREX TMF as a replacement for the conventional clarifier. The new system was designed to increase the water recovery rate, reduce operating cost, improve performance stability and increase the degree of automation.

As an effective solid/liquid separation method, the TMF system is a key unit of the overall process. By using TMF, less space is required, the treatment process is simplified and better and more stable filtrate is available as RO influent. TMF plays a major role in both increasing the recovery rate and making the final effluent meet regulated limit values. The whole system is now more stable and reliable.



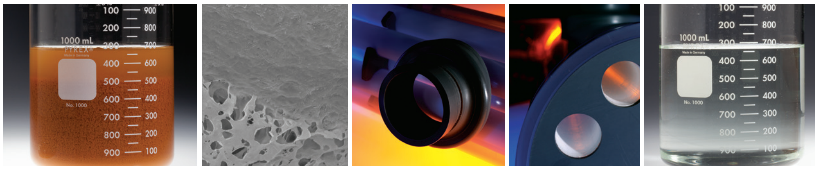
Wastewater Information

Four streams of wastewater, Cu WW, Ni WW, Cr WW and combined WW, are collected separately. The quantity and quality of each stream is listed in the table below. As a comparison, the corresponding TMF product water quality is also listed.

Item		Acid/Alkaline and Copper	Nickel	Chrome	Combined (including Electroless Nickel)
Quantity (m^3/day)		312	144	287	274
Flow rate (m^3/hr)		15.6	7.2	14.4	13.7
Quality (mg/l for all except pH and conductivity)	Influent	pH: 2.63 Cu: 36.6 Ni: 0.993 Cr: 0.464 Fe: 0.418 conductivity: 2590 μs/cm	pH: 8.34 Cu: 0.075 Ni: 87.1 Cr: not detected Fe: not detected conductivity: 454 μs/cm	pH: 2.99 Cu: 0.821 Ni: 0.18 Cr: 221.6 Fe: 1.054 conductivity: 846 μs/cm	pH: 3.16 Cu: 12.2 Ni: 81.5 Cr: 293.1 Fe: 0.692 conductivity: 2940 μs/cm
	TMF permeate	pH: 11.07 Cu: not detected Ni: not detected Cr: not detected Fe: not detected conductivity: 1303 μs/cm	pH: 9.12 Cu: not detected Ni: 0.107 Cr: not detected Fe: not detected conductivity: 512 μs/cm	pH: 11.78 Cu: 0.01 Ni: not detected Cr: not detected Fe: not detected conductivity: 2610 μs/cm	pH: 9.99 Cu: not detected Ni: 0.088 Cr: 0.211 Fe: not detected conductivity: 3770 μs/cm

NOTES:

1. Quantity means influent wastewater flow rate, not RO permeate flow rate.
2. The water quality values are from a third party inspection report, sample taken on December 7, 2012.
3. TMF permeate shows higher pH value due to alkaline precipitation reaction.
4. In above table, Cr means trivalent chromium, Fe means ferric in water.
5. The heavy metal levels in the TMF permeate are lower than the system design value.



Wastewater Information Continued

The treated water for reuse is designed to be product water for a two pass RO. The water quality index is listed below:

Item	pH	Conductivity (µs/cm)	Total Cu (mg/L)	Total Ni (mg/L)	Total Cr (mg/L)
Value	6-7	≤10	≤0.05	≤0.05	≤0.05
Item	Ca (mg/L)	Al (mg/L)	Fe (mg/L)	SiO_2	
Value	≤0.05	≤0.05	≤0.05	≤0.05	

NOTE:
According to a third party inspection report (also sampled on Dec. 7, 2012), the two pass RO product water pH was 6.64, conductivity was 4.84µs/cm, and all other above parameters were not detected. That means the system treated water met or exceeded the design value.

Reject from the RO skid, after appropriate further treatment, is the final effluent of the system. Quality is monitored according to Discharge Standard of Pollutants in Electroplating Wastewater (GB21900-2008) with related parameters listed below. This effluent has met or exceeded the standard.

Item	pH	Total Cr (mg/L)	Cr (6+) (mg/L)	Ni (mg/L)	Cu (mg/L)
Value	6-9	≤1	≤0.2	≤0.5	≤0.5

TMF Characteristics and Advantages

One of the applications for Porex TMF is as a replacement for a conventional solid/liquid separation process, i.e. clarifier. There are several advantages of Porex TMF compared with a traditional clarifier process including:

1. The Porex TMF filtrate water quality is much better than clarifier-treated water. Due to the presence of the filtration membrane, particles larger than the nominal pore size will be rejected. Treated water quality is equal to UF product water.

2. Due to the excellent filtrate water quality, the Porex TMF product water can be fed directly into an RO system without additional treatment. In comparison, water coming from a clarifier, typically requires a multi-media filter, activated carbon filter or ultrafiltration process prior to sending through RO.

TMF Characteristics and Advantages Continued

3. Use of coagulants (PAC, $FeCl_3$, $FeCl_2$, $FeSO_4$, etc.) is typically not necessary in a TMF system, or, if needed the dosage is greatly reduced. No flocculant (PAM) is required with a TMF system. Only caustic soda is required. Use of coagulants result in more sludge cake volume and higher treated water TDS. Use of a polymer will cause RO membranes to foul leading to performance recovery difficulties.

4. The unique design of the cross flow TMF system can easily handle a 2~5% suspended solids concentration. This produces less slurry and results in better filter press performance.

5. Ease of maintenance. The system can be designed for automatic operation and can be placed into service mode from standby mode at any time.

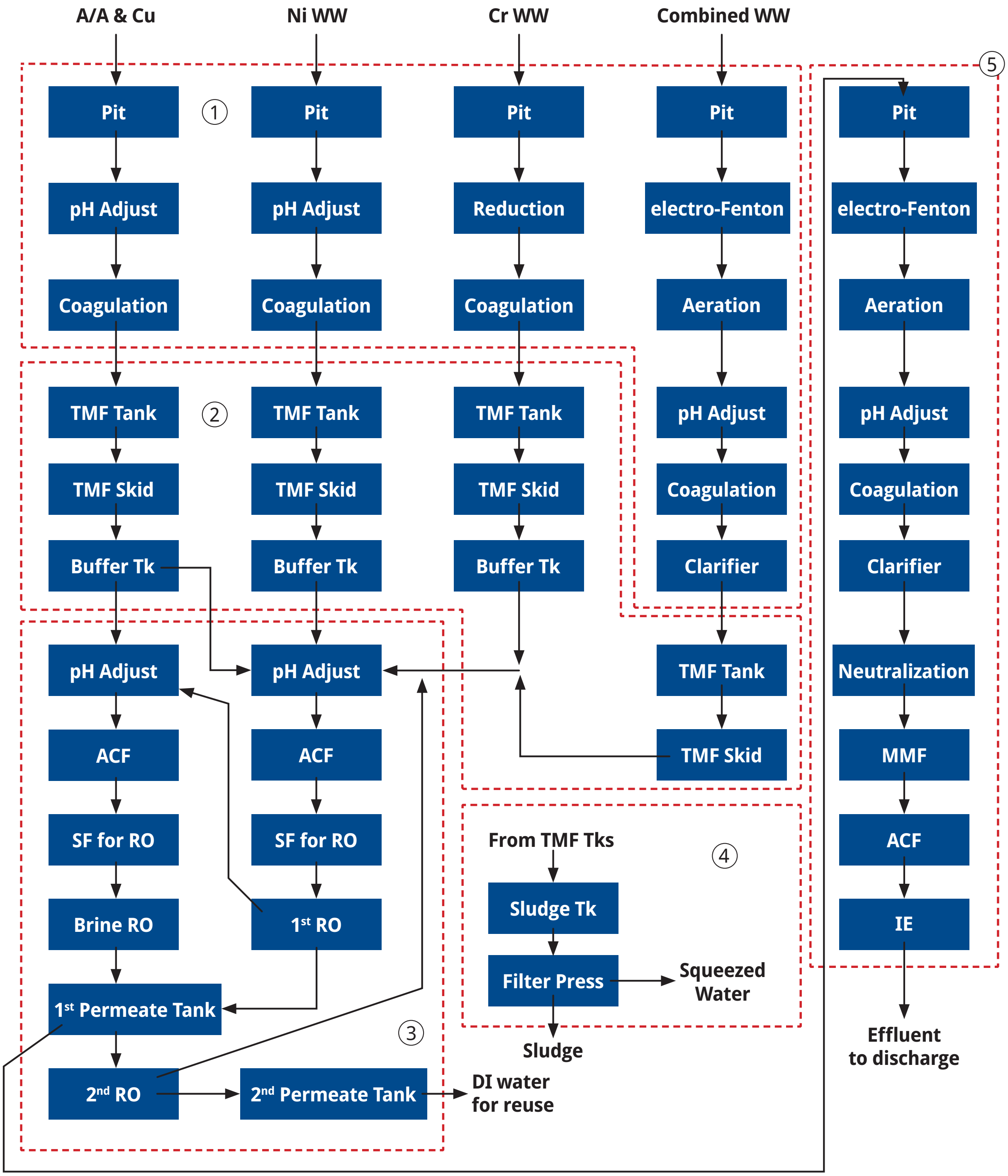
6. Compared with a traditional clarifier, the TMF skid frame requires less space. In addition, the TMF skid is available for expansion meaning that the water capacity can be enlarged by simply adding more skids or modules.

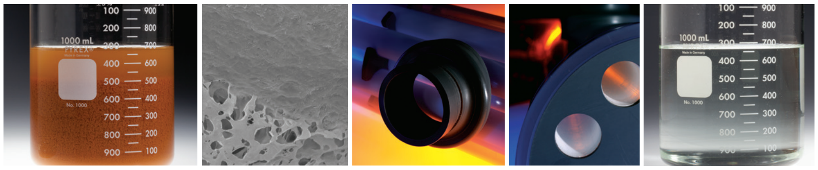
Porex TMF System Specification

The processes at this facility require a large and sophisticated wastewater treatment system for the whole factory. Separate TMF skids are installed for each water stream. In total there are 60 13-tube modules in this system. A chart of TMF specifications for each different wastewater stream is below.

Wastewater	Acid/Alkaline and Copper	Nickel	Chrome	Combined (including Electroless Nickel)	Spare skid
Capacity (m^3/hr)	15.6	7.2	14.4	13.7	
Modules/train	15	9	12	12	12
Trains/skid	1	1	1	1	1
Quantity of modules	15	9	12	12	12
Module specification	Model: MME3S01613VP, 0.1 μm pore size, 1 inch tube, 13 tubes in one module, 1.84 m^2 membrane area. PVC housing/PE substrate tube/PVDF membrane layer				

System Diagram





Process Description

The system is divided into several functional "blocks" as shown in the process schematic:

1. Pretreatment stages: wastewater collection, pH adjustment or oxidation. For Cr wastewater, an acidic reduction process is required before other units. And a first stage treatment composed of electro-Fenton reaction and air flotation is designed for combined wastewater streams (including Electroless Ni wastewater).

2. Solid/liquid separation is performed by the POREX TMF unit in each stream.

3. Reverse osmosis: 1st pass RO, 2nd pass RO and brine RO, including necessary pre-RO process steps of pH adjustment, activated carbon filter and guard filter.

4. Sludge treatment, which is designed for sludge dewatering. Each stream of concentrated liquid (sludge) is transferred from the TMF concentration tank to a separate holding tank before being sent to the filter press.

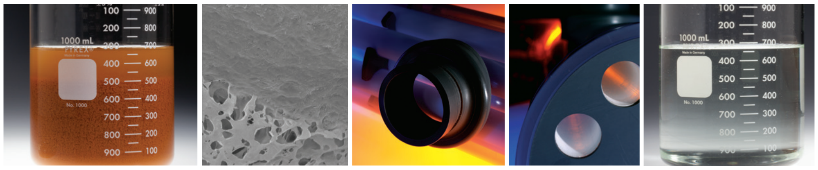
5. Brine RO reject treatment unit: a system consisting of chemical pretreatment, clarifier and final ion exchanger.

Four streams, totaling 1,070 m^3/day of wastewater, are collected separately into collection tanks. After treatment three paths are followed:

   a. Demineralized water is sent back to the workshop for reuse.
      Capacity: 800 m^3/hr (78.7% of total)
   b. Brine RO reject water is discharged to sewage water system after further treatment.
      Capacity: 217 m^3/hr (21.3%)
   c. A very small amount of water goes out with the sludge cake.

Wastewater stream #1 - Acid/Alkaline and Copper wastewater
Acid/Alkaline WW and Copper WW are equalized in a collection tank and then pumped into a pH adjusting tank. NaOH is dosed to increase the pH to the target value for alkaline precipitation reaction. H_2O_2 is dosed for the oxidation reaction and the water then overflows to a coagulation tank in which $FeSO_4$, lime and powder carbon are dosed for coagulation and organic adsorption. The precipitated mixed liquid overflows to the TMF concentration tank (or TMF circulation tank).

A circulation pump sends the mixture into a series of TMF modules for solid/liquid separation. In a cross flow process, most of the water returns to the concentration tank which causes the concentration to continually increase. The concentration is controlled to between 2 and 5% solids by drawing off concentrate and sending it to the filter press. Filtrate water is sent into another tank called the buffer tank. It then overflows to a pH re-adjusting tank, in which H_2SO_4 is added to reduce pH; also $NaHSO_3$ is dosed to reduce the remaining H_2O_2.



Process Description Continued

Part of the water in this buffer tank is sent to a bigger tank and mixed with other streams of POREX TMF permeate water before being sent to a common RO unit. The Cu buffer tank also collects reject water of this common 1st RO, these two streams, (Cu TMF filtrate and 1st RO reject water), are sent to post treatment units (brine RO).

Water in the pH re-adjusting tank is pumped to a carbon filter, a guard filter and then fed into the brine RO. Permeate water from this brine RO is collected before being sent to the 2nd RO unit where it is combined with other streams. The 2nd RO permeate water, (conductivity is less than 10 μs/cm), can be sent back to the workshop for reuse. Reject water of brine RO is sent to wastewater treatment units for further treatment before discharge.

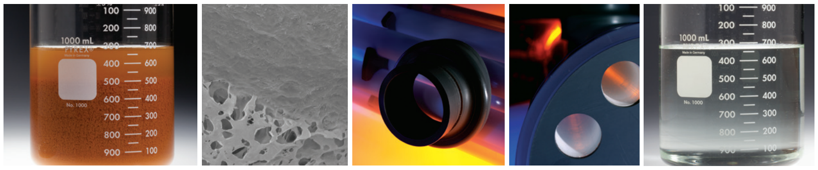
During system operation, suspended solids in the TMF concentration tank accumulate so that part of the concentrate water needs to be sent to the filter press for dewatering. Sludge cake, normally containing 70% water, is sent out for heavy metal recovery and squeezed water from the filter press is sent back to the collection tank.

Wastewater stream #2 - Nickel wastewater

Nickel WW is equalized in a collection tank and then pumped into a pH adjusting tank. NaOH is dosed to increase pH for alkaline precipitation. H_2O_2 is dosed for oxidation reaction. The water overflows to a coagulation tank in which $FeSO_4$, lime and powder carbon are dosed for coagulation and organic adsorption. Precipitated mixed liquid overflows to the Porex TMF concentration tank.

A circulation pump sends the mixture into a series of Porex TMF modules for solid/liquid separation. The concentration is controlled between 2 and 5% solids by drawing off concentrate and sending it to the filter press. Filtrate water is sent into another tank called the buffer tank. It overflows to a pH re-adjusting tank, in which H_2SO_4 is added to reduce pH, and $NaHSO_3$ is dosed to reduce remained H_2O_2.

This pH re-adjusting tank also adsorbs part of the POREX TMF filtrate of the Cu WW, and all of the Porex TMF filtrate of the Cr WW and combined WW. Water in this common pH re-adjusting tank is pumped to a carbon filter, a guard filter and then fed into the 1st RO. Permeate water from this RO is collected and sent to the 2nd RO unit, which is described above. Reject water of the 1st RO is sent to a pH re-adjusting tank of Cu WW before it is sent to brine RO.



Process Description Continued

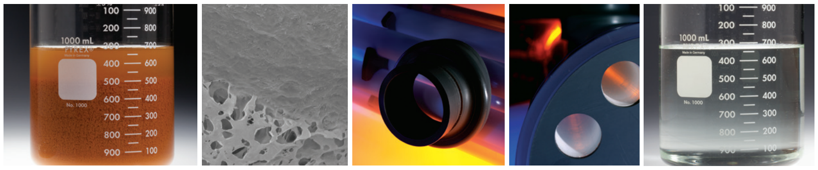
Wastewater stream #3 - Chrome wastewater and roughening wastewater
Chrome WW is equalized in a collection tank and then pumped into an Acidify reduction tank. H_2SO_4 is dosed to adjust pH, and $NaHSO_3$ is dosed to reduce hexavalent chromium to trivalent chromium. The water then overflows to a coagulation tank where $FeSO_4$, NaOH, lime and powder carbon are dosed for alkaline precipitation reaction, coagulation and organic adsorption.

The precipitated mixed liquid overflows to the Porex TMF concentration tank. A circulation pump sends the mixture into a series of TMF modules for solid/liquid separation. The filtrate water (amount equal to system capacity) is sent into another tank called the buffer tank. It then overflows to the common pH re-adjusting tank. The subsequent process has been described above.

Wastewater stream #4 - Combined wastewater (including Electroless Nickel wastewater)
Combined WW and Electroless Nickel WW are equalized in a collection tank and then pumped into an electro-Fenton process reaction tank. H_2SO_4 is dosed to adjust pH, and H_2O_2 is dosed for oxidation. The water then overflows to an aeration oxidation tank, and then to a pH adjusting tank where NaOH and lime are added for alkaline precipitation reaction and coagulation.

The precipitated mixed liquid overflows to a flocculation tank for PAM dosing and then it overflows to a clarifier. Part of the suspended solids load settles here while supernatant flows into the Porex TMF concentration tank. A circulation pump sends the mixture into a series of TMF modules for solid/liquid separation. The filtrate water is sent to the buffer tank. It then overflows to the common pH re-adjusting tank. The subsequent process has been described above.

Brine RO reject water treatment stage
Brine RO reject water is collected in a tank before being sent to the following treatment units: electro-Fenton process reaction tank, aeration oxidation tank, pH adjusting tank, coagulation tank, tube settler, buffer tank, multi-media filter, carbon filter and final ion exchanger. After completing the series of treatment units, the Brine RO reject water is discharged according to related limit concentration.



Operation Status

Construction of this system was completed in October, 2012. After two months' commissioning, the system performance met or exceeded the design standard, as explained below:

1. Combined with the pretreatment process, heavy metal concentration of the TMF filtrate is better than expected levels — less than 0.1 mg/l or undetectable. This performance is typically unattainable with a conventional clarifier.

2. Due to the well-designed pretreatment stage and effective solid/liquid separation performance, the RO units of this system are in excellent operating condition: recovery rate is equal to or better than the design value, with good permeate quality and longer intervals between CIP procedures.

3. Permeate water conductivity of the 2nd RO is steadily below 10 μs/cm. An analysis report from a third party showed heavy metals like Cu, Ni, Cr, and other multivalent cations like Ca, Al, Fe are not detected.

4. Effluent also meets discharge limit value, no excessive pollutants are discharged.

5. Recovery rate of the internal system is 80%, which means 80% of the influent has been treated and reused. This value has exceeded the primary demand (78.7%).

Summary

Porex Tubular Membrane Filters have been widely applied in wastewater treatment & reuse systems for plating workshops and related industry parks. This case study describes a large-scale system that involves the most common heavy metals like copper, nickel and chrome, and also involves several types of plating processes like electroplating and electroless plating. This is typical of a system for complex plating wastewater treatment.

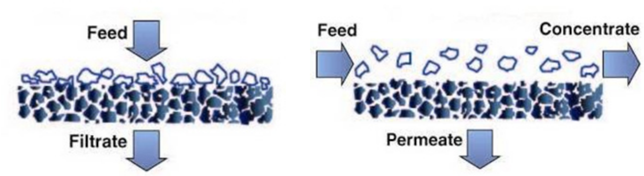
Porex TMF links the chemical reaction & coagulation stages with the RO desalination stages. The total treatment process has been shortened, system reliability has been enhanced, and compared with a conventional clarifier, the TMF filtrate contains significantly less heavy metal.

About Microfiltration

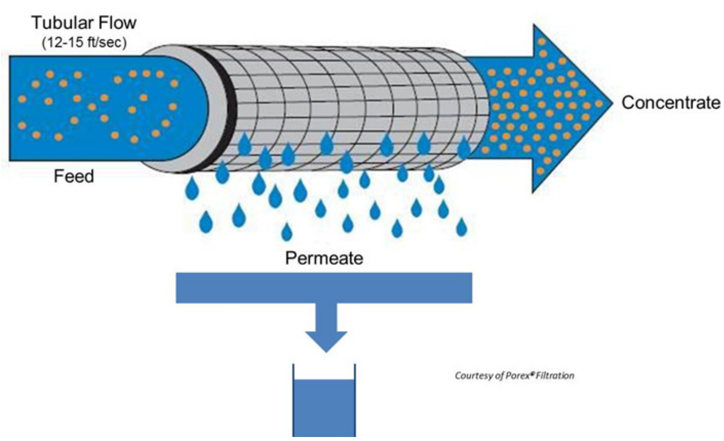
Microfiltration is a cross flow, pressure-driven membrane separation technology designed to remove submicron (and larger) suspended solids from water supplies. It differs from conventional ("dead-end") filtration in that in a conventional process the entire water supply passes through the filter medium, whereas in the crossflow process, a portion passes through the membrane, becoming "permeate," while the remainder exits the system as "concentrate," carrying away almost all of the suspended solids.

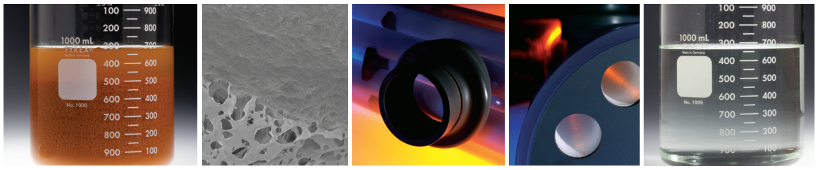
The following illustration compares these two processes.

Conventional Filtration **Crossflow Filtration**



The microfiltration membranes used in this application are POREX® TMF tubular membranes, depicted below.





About Microfiltration Continued

The tubes in this application are 1” I.D., with a polyethylene substrate supporting a PVDF (polyvinylidene fluoride) membrane with 0.1µm pores. The membrane module is illustrated below.

Each membrane module consists of thirteen 72” long tubes enclosed inside a PVC housing. Specifications on the modules and tubes are as follows:

Modules	
Housing Diameter	6”
Permeate Port (Qty 2)	2.875 x 1.89” L pipe stub
Concentrate Ports	6” pipe Anvile Gruvlok groove
Mounting Required	Horizontal; 2 point
Module Length	72”
Tubes	
Number of Tubes	13
Nominal ID	1”
Nominal OD	1.34”
Total Active Surface Area	19.8 ft^2 (1.82m^2)
Internal Liquid Volume	
Filtrate Volume	3.06 gallons
Concentrate Volume	3.18 gallons
Total Volume	6.25 gallons
Materials of Construction	
Potting	Solvent Cement
Internal Supports	Polypropylene
Gasket Material	None
Preservative (Shipping)	Propylene Glycol
Membrane	PVDF

The feed flow is down the center of the tube (lumen feed) with the permeate passing through the tubular wall and collected from the area around the outside of the tubes inside the housing. There are a total of 60 POREX TMF modules in this system.

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