

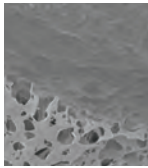
## POREX® Tubular Membrane Filter (TMF™) Applied in Copper/Nickel Wastewater Treatment System for an Electroplating Industry Park



### Abstract Introduction

Plating is a widely used process across many industries and is also one of the most fragmented of industries. Due to its historic development, the electroplating industry in China has several common characteristics: small in scale, low degree of specialization, inefficient production lines, and marginal economic return. In addition, many of these facilities are often located close to residential areas. This can create significant environmental problems as electroplating can produce toxic solid and liquid waste and air pollution in the proximity of the plant.

Most of the electroplating factories in China are small in scale, and for some manufacturing facilities, plating is just an auxiliary workshop attached to a large factory. These characteristics often cause many disadvantages for these businesses such as: high monetary investment, large amount of wastewater effluent, difficult wastewater collection, repeated cycles in a Waste Water Treatment Plant (WWTP), plus high construction and operating cost for the WWTP. In recent years many local governments in China have actively promoted an 'industry park' policy for electroplating factories, concentrating plating workshops in one location. This is beneficial for pollution control. The wastewater can be separately collected and sent to targeted treatment facilities designed, built and operated by professional environmental protection engineering companies.



## Abstract Introduction Continued

This allows the plating facilities in the park to leverage the central treatment infrastructure and only pay for the quality and quantity of wastewater generated from their specific workshop. This policy reduces the plating factories' investment for both construction cost and ongoing operating cost. It also makes it easier to ensure that effluent quality meets the local discharge limits. More and more successful experiences support the industry park concept as a significant improvement for development of the electroplating industry in China.

This paper introduces a successful Copper/Nickel wastewater treatment system located in the Houjing Plating Industry Park, Wenzhou city, Zhejiang province. With the application of POREX® Tubular Membrane Filter (TMF™) modules for solid/liquid separation the effluent quality is much better, (at or below required standards), as compared to a conventional clarifier system or air flotation tank.

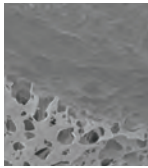
## Background

Covering an area of 200,000 square meters, Houjing Plating Industry Park was built in 2006 and currently comprises 58 standard factory buildings and 95 plating companies. The park has one centralized WWTP and one heating facility. The WWTP was also built in 2006 with 12,000 m<sup>3</sup>/day capacity. In May of 2009, this WWTP passed the periodic check and acceptance of the local environmental protection agency.

Since this was one of the earliest plating industry parks constructed, they required some modifications to meet the requirements of the current regulations. To complete pollution abatement, Chrome and Nickel wastewater needed to be collected and treated separately. As a challenge, there was no additional space to add a large emergency tank, (2,500 m<sup>3</sup>); therefore, a POREX TMF system was designed as a key unit to reduce the space required and shorten the total processes to produce reliable effluent water quality.

## Wastewater Information

Copper and Nickel wastewater is first collected from all factories in the industry park. Capacity is designed as 1,000 m<sup>3</sup>/day, or 65 m<sup>3</sup>/hr. influent wastewater containing 100 mg/l Cu<sup>2+</sup> and 300 mg/l Ni<sup>2+</sup>, with pH ranges from 2.5 to 4.0. Because the wastewater collection system is not perfect, Cyanogen and Chrome (including Cr<sup>6+</sup> and Cr<sup>3+</sup>) wastewater also flow into this stream, which creates difficulty for the pretreatment chemical reaction stage design.



**Wastewater Information Continued**

The table below shows actual wastewater quality analyzed during the commissioning period.

Item	pH	Total Cu (mg/L)	Total Ni (mg/L)	Total CN (mg/L)	Total Cr (mg/L)	Hexavalent Chromium (mg/L)
Value	2-3	25-40	238-300	1-25	100-150	30-140

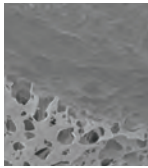
Effluent is required to meet the following limit values, based on Emission Standard of Pollutants for Electroplating (GB21900–2008).

Item	pH	Total Cu (mg/L)	Total Ni (mg/L)	Total CN (mg/L)	Total Cr (mg/L)	Hexavalent Chromium (mg/L)
Value	6-9	0.5	0.5	0.3	1.0	0.2

**TMF Characteristics and Advantages**

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

1. Better water quality. The POREX TMF filtrate water is better quality than clarifier-treated water. Due to the presence of the filtration membrane, all particles larger than the nominal pore size will be rejected. Treated water quality is equal to UF product water.
2. No additional filter treatment. Due to the improved filtrate water quality, the POREX TMF product water can be fed directly into a RO system without any other treatment. In comparison, when the water comes from a clarifier, a multi-media filter, activated carbon filter or ultrafiltration process is typically needed prior to sending through RO.
3. Reduced or no use of coagulants. Use of coagulants e.g. PAC, FeCl<sub>3</sub>, FeCl<sub>2</sub>, FeSO<sub>4</sub>, etc., is typically not necessary in a POREX TMF system or if needed the dosage is greatly reduced. No flocculent, e.g. PAM, is required with a POREX TMF system. Only caustic soda is needed. The use of coagulants in other systems results in more sludge cake volume and higher treated water TDS. The use of a polymer, often necessary in other systems, will cause RO membranes to foul which can be problematic, leading to performance recovery difficulties.
4. Better filter press performance. The unique design of the cross-flow POREX TMF system can easily handle a 2~5% suspended solids concentration. This produces less slurry and results in better filter press performance.



### TMF Characteristics and Advantages Continued

- 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. Ease of operation. Often upsets in the clarifier process can result in less than satisfactory treatment and water quality. POREX TMF modules eliminate the possibility of clarifier upsets and requires less operator intervention.
- 7. Smaller footprint. Compared with a traditional clarifier, the POREX TMF skid frame requires less space. In addition, the POREX TMF skid is available for expansion, meaning the water capacity can be enlarged by simply adding more skids or modules.

### System Information

Water capacity:	65 m <sup>3</sup> /hr
Module Specification:	Porex TMF modules (module model #MME2S01637VP)
Tubes per Module:	37
Housing specification:	6" Sch40 PVC
Tube diameter:	½ inch
Membrane pore size:	0.1 micron
Filtration area:	2.58 m <sup>2</sup> per module
Array:	2 skids, 3 trains per skid, 10 modules per train, total of 60 modules.



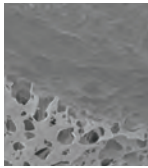
TMF Pumps



TMF Skid



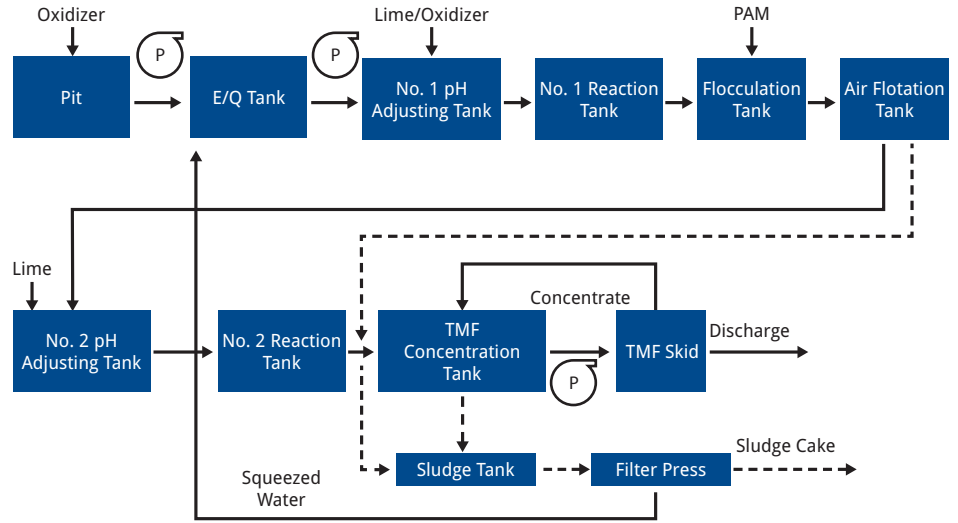
CIP Unit



# POREX FILTRATION

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### System Schematic



No. 1 pH Adjusting Tank

No. 1 Reaction Tank

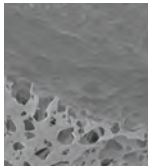
Flocculation Tank



Air Flotation Tank



No. 2 pH Adjusting Tank/  
Reaction Tank



## Process Description

Copper and Nickel wastewater are collected in a sump into which a small amount of oxidizer is dosed. This water is then pumped to an equalization tank. Chelating agents are oxidized and reduced to an acid condition. Then the water is pumped to a 1<sup>st</sup> stage treatment facility. The purpose of the 1<sup>st</sup> stage is for partial removal of Cyanogen and Chrome.

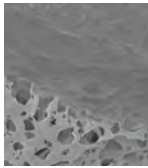
In this stage the wastewater pH is raised through lime dosing to 7–8 in the 1<sup>st</sup> pH adjusting tank and more oxidizer is added for Cyanogen breakdown. The water then overflows to a reaction tank and then a flocculation tank. In the flocculation tank PAM is dosed and then the water flows to an air flotation tank for solid/liquid separation. Sludge is sent to a separate holding tank with a subsequent dewatering system. Product water of the flotation tank is then sent to the 2<sup>nd</sup> stage treatment system.

Wastewater from 1<sup>st</sup> stage treatment enters the 2<sup>nd</sup> pH adjusting tank in which more lime is dosed to raise the pH to 11–12. It then overflows to a 2<sup>nd</sup> reaction tank. Ferrous sulfate is added to reduce residual chlorine and reduce  $\text{Cr}^{6+}$  to  $\text{Cr}^{3+}$ . The  $\text{Cr}^{3+}$  forms precipitate to  $\text{Cr}(\text{OH})_3$ . At the same time, other heavy metal ions like Copper and Nickel also form their respective hydroxide precipitants.

The pretreated solid/liquid mixture overflows to a POREX TMF concentration tank. A circulation pump sends the mixture into a series of POREX TMF modules for solid/liquid separation. In a cross-flow process, most of the liquid returns to the concentration tank where the suspended solids concentration increases. Part of the concentrate water is sent into a filter press for dewatering. The removed concentrate maintains the solids in the concentration tank at 2 to 5%. Sludge cake, normally containing 60–70% water, is sent out for heavy metal recovery. The filtrate water from the filter press is sent back to the equalization tank.

The filtered water from the POREX TMF system, (the amount equal to the system capacity), is sent into a pH re-adjusting tank before discharge to the sewage system.

Due to design safety considerations, there are two treatment stages in this system. In the 1<sup>st</sup> stage a conventional solid/liquid separation method uses air flotation. The POREX TMF is applied in the 2<sup>nd</sup> stage. It is generally recognized that Cyanogen and Chrome require a more complex treatment than other metal salts. Cyanogen needs to be broken down through oxidation before undergoing alkaline precipitation. Hexavalent Chromium needs to be reduced to trivalent Chromium before alkaline precipitation. The optimum pH range for precipitation of trivalent Chromium is different than that of Copper and Nickel. So the system has to remove Chromium first and then remove Copper and Nickel.

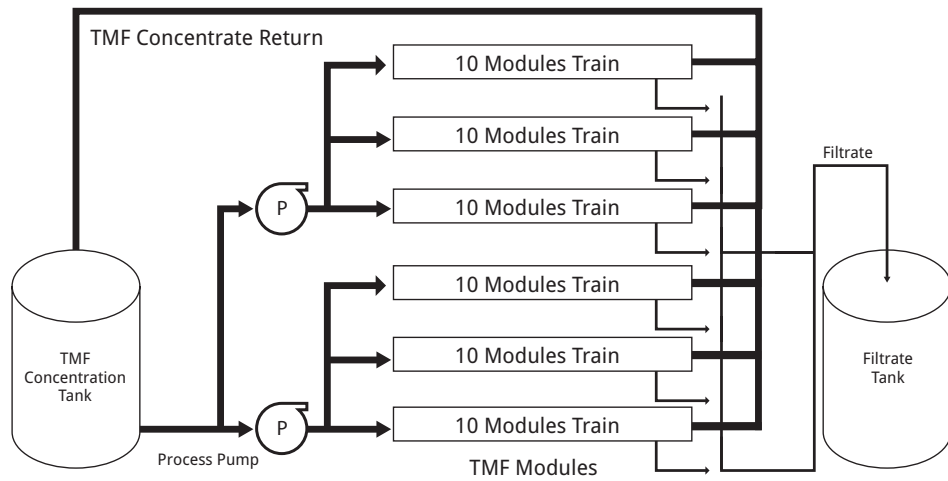


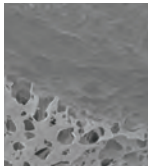
## POREX FILTRATION

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#### System Specifications

There are 6 total trains in this system, installed in 2 skids of 3 trains each. Each train contains 10 modules connected in series. There is one common process pump for three trains, with each train containing separate filtrate flow meters, back pulse units and a set of isolation valves. A common CIP unit, (including 2 tanks and 1 air diaphragm pump), is set for the whole system. The system is designed to ensure that each train is back pulsed individually. The operator also can perform CIP for each train separately.





### Operation Status

Construction of this system was finished in Oct. 2012 and system performance has met or exceeded the design standard, as explained below:

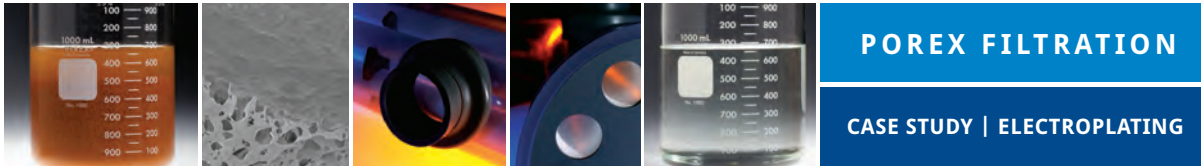
1. Each skid contributes 65 m<sup>3</sup>/hr filtrate flow, which is about twice the design value. This is due in part to very low fouling agents, (free of oil and organic compounds), existing in the wastewater and a very complete and effective pretreatment reaction system.
2. Module train inlet pressure is approximately 3.0 bar. There is no back pressure at the concentrate side due to sufficient filtrate flow rate.

Effluent sample analysis report is collected in the table below:

Date	Time	pH	T-CN	Cr <sup>6+</sup>	T-Cr	T-Cu	T-Ni
12.10	9:30	11.2	0.042	0.659	0.941	0.126	0.01
	11:00	10.2	<0.016	0.094	0.076	0.1	0.01
	13:30	10.5	0.249	<0.01	0.838	<0.01	0.077
	15:00	10.3	0.019	0.36	0.941	0.046	0.069
12.11	9:30	10.8	0.025	0.914	1.401	0.014	0.044
	11:00	10.4	<0.016	0.507	0.623	0.09	0.099
	13:30	9.2	0.017	0.94	1.31	0.148	0.123
	15:00	9.5	<0.016	0.998	1.131	0.052	0.134

According to the analysis report, Copper and Nickel were always below the discharge limit value when the target pH was set to higher than 9.0. There was a little fluctuation on the Chromium level, perhaps due to the existence of both Cyanogen and Chromium. It was challenging to pick the best target pH value and chemical type/dosage. Reaction conditions for these two types of contaminants are quite different, which explains why a favorable removal effect was not possible in only one system.



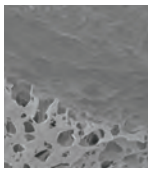


## Summary:

This is the first large scale application of POREX TMF modules in an electroplating industry park.

A well-designed wastewater collection process is the key factor to achieving targets such as reducing operating cost and getting more stable and better quality effluent. In this system, there is no complex chemical reaction mechanism for precipitation of Copper and Nickel. After eliminating the effects of chelating agents, pH is adjusted to a target value for the alkaline precipitation reaction to occur. Following that, a well-developed solid/liquid separation measure (POREX TMF modules), provides excellent filtrate water quality. Cyanogen and Chromium can be challenging to this system. Even so, the POREX TMF modules still deliver excellent permeate water quality far beyond what can be generated from a conventional clarifier or air flotation tank. In this case, the POREX TMF modules presented several advantages:

1. Smaller footprint. Space requirement was reduced since a large clarifier was not required and a huge emergency tank was not needed due to the stable POREX TMF filtrate quality.
2. Improved filtrate quality. Copper and Chromium levels in the effluent are far below required discharge limits and effluent quality is more stable and reliable. Unlike a clarifier or air flotation tank, the POREX TMF performance is not affected by temperature changes, mechanical design, water flow and flocculation condition, etc.
3. Good performance. With the challenge of the existence of both Cyanogen and Chromium the POREX TMF system still demonstrates good treatment performance on these two contaminants.

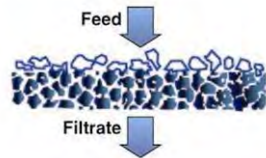


## About Microfiltration

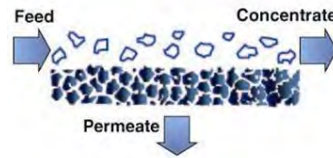
Microfiltration is a cross-flow, pressure-driven membrane separation technology designed to remove submicron and larger suspended solids from water supplies. It differs from conventional “dead-end” filtration in that in a conventional process the entire water supply passes through the filter medium, whereas in the cross-flow 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.

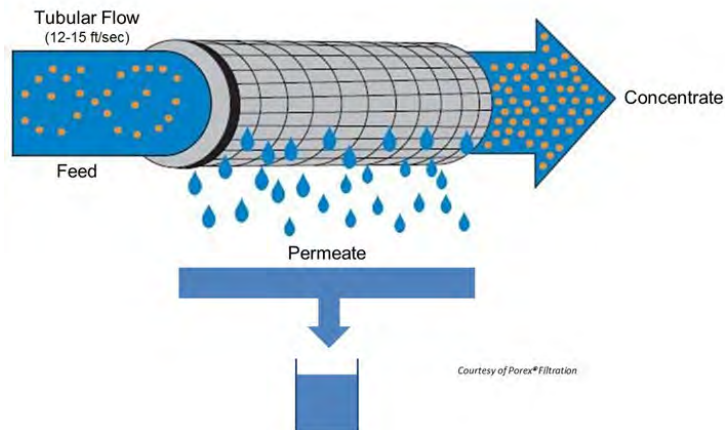
### Conventional Filtration

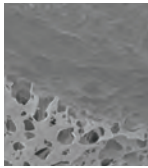


### Cross-flow Filtration



The microfiltration membranes used in this application are POREX Tubular Membranes, depicted below.





## POREX FILTRATION

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## About Microfiltration Continued



The membrane module tubes (pictured) in this application are ½" I.D., with a polyethylene substrate supporting a PVDF (polyvinylidene fluoride) membrane with 0.1 µm pores.

Each module consists of 37 tubes 72" long enclosed in PVC housing. Specifications of 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	37
Nominal ID	½"
Nominal OD	0.79"
Total Active Surface Area	27.75 ft <sup>2</sup> (2.58m <sup>2</sup> )
Internal Liquid Volume	
Filtrate Volume	3.07 gallons
Concentrate Volume	2.26 gallons
Total Volume	5.33 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.