Wastewater Recycling at a Steel Plating Mill-

A Case Study in Membrane Technologies

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ABSTRACT

Steel manufacturing plants are large water consumers that use a tremendous amount of water in their production process. As a result of the increasing demand in resource sustainability, high quality process water and stringent discharge compliance, the U.S. steel industry has faced tough challenges in smart water management to survive today's global economic environment. The challenge is compounded by the complexity of the contamination of wastewater characterized by their high concentrations in dissolved solids, suspended particles, toxic metals, difficult-to-treat chemicals and complex organic compounds. Recent studies have revealed the significance of proper waste stream segregation, coupled with proper membrane filtration, to achieve maximum water quality and reuse at minimal capital and operating cost. This presentation shall identify the various wastewater sources of concern and assess the associated technical challenges that need to be recognized and overcome by the industry. The discussion will present exploration of the conceptual approaches and treatment alternatives via a pilot test program along with a full scale system case study. The case study will depict the design, engineering, and operations details of a Tubular Membrane/Reverse Osmosis (RO) wastewater recycle plant installed in a large mid-west US high speed steel plating mill as the replacement of a conventional system to meet the NPDES (National Pollutant Discharge Elimination System) permit requirements and the company's long-term water resource management objectives.

KEYWORDS: microfiltration, reverse osmosis, electroplating, steel mill, wastewater, recycling, membrane, metals removal, NPDES, discharge

INTRODUCTION

Steel manufacturing plants are large water consumers that use a tremendous amount of water in their production process. As a result of the increasing demand in resource sustainability, high quality process water and stringent discharge compliance, the U.S. steel industry has faced tough challenges in smart water management to survive today's global economic environment. The challenge is compounded by the complexity of the contamination of wastewater characterized by their high concentrations in dissolved solids, suspended particles, toxic metals, difficult-to-treat chemicals and complex organic compounds. This presentation shall identify the various wastewater sources of concern and assess the associated technical challenges that need to be recognized and overcome by the industry. The discussion will present exploration of the conceptual approaches and treatment alternatives via an extensive pilot test program along with a full scale system case study.

This mid-west steel plating mill was facing increasingly tighter discharge limits on its industrial wastewater NPDES permit. At the same time, their existing wastewater treatment system was nearing the end of its expected life. Maintenance costs were rising while reliability was declining. It was clear that a new system was in order and objectives were established. Several technologies were reviewed with regard to meeting the priorities and it was decided that the technology that best suited their wastewater stream and their objectives was tubular membrane microfiltration (MF) followed by reverse osmosis (RO). The other technical options considered were conventional lamella clarifier, polishing filtration and RO, ion exchange and evaporative technologies.

This plating mill has three high speed plating lines in operation, plating strip steel. The predominant metals plated are nickel, zinc, and occasionally cobalt. The nickel baths are mostly Watts nickel and the zinc is acid zinc. They also do acid pickling and alkaline cleaning. The spent acid pickle baths are sent to the wastewater treatment system. The spent aqueous alkaline cleaners are mainly hauled away.

New System Objectives

1. Replace the aging system with a more robust technology capable of meeting the tighter NPDES discharge limits.
2. Improve the quality of the sludge generated to reduce the disposal costs
3. Recycle as much water as is cost effective. This will at the same time reduce the consumption of city water as well as improve the quality of the water used.

Plant Survey

Prior to the commissioning of a pilot trial to confirm the efficacy of the chosen tubular microfiltration and reverse osmosis technology, a plant inspection was conducted to determine what, if any, streams might need to be segregated for pretreatment or treated outside the water recycling system. As is common in most plating operations aqueous cleaners are part of the process and their potential negative impact was discussed. Plans were already in place to segregate the cleaners and to haul the spent concentrates. If allowed to come to the treatment and recycling system, spent cleaners would foul the membranes with organic compounds and severely impede the operation.

MF Process

The chemically pre-treated wastewater is processed through the membrane microfiltration modules designed for separation of the precipitates from water. The wastewater is pumped at a velocity of 3.6 - 4.5 m/sec (12 – 15 ft/sec) through up to 18 membrane modules (Figure 1) connected in series (Figure 2). The turbulent flow, parallel to the membrane surface, produces a high-shear scrubbing action which minimizes deposition of solids on the membrane surface. During operation, filtrate permeates through the membrane, while the suspended solids retained in the re-circulation loop are periodically purged for further de-watering. An automatic back-pulse mechanism is an integral part of the operation design to provide physical surface cleaning by periodically reversing the filtrate flow direction.

Figure 1: 10-Tube Tubular Microfilter Module

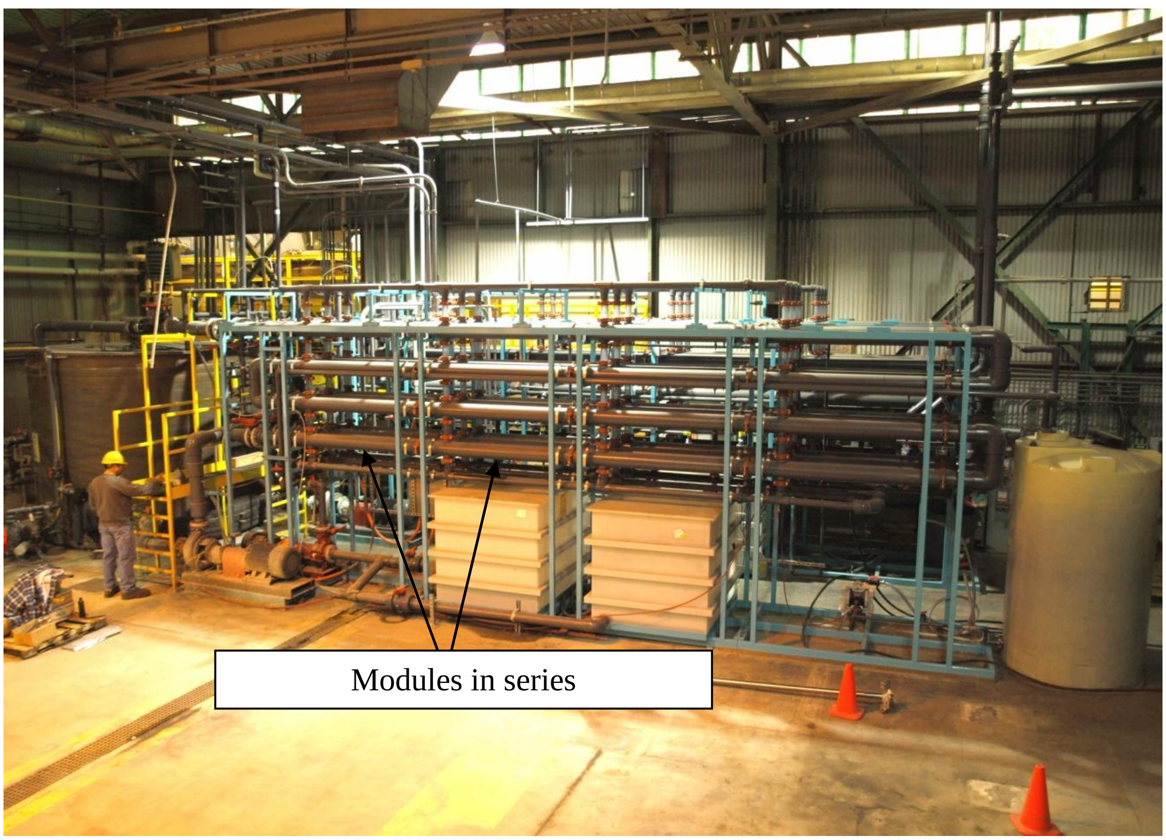

Figure 2: Microfilter skid with modules connected in series

RO Process

Reverse osmosis is a desalination process that has been employed in the metal finishing industry to purify raw water (e.g. city water) before use as rinse water, recover plating chemicals from rinse water, and polish wastewater treatment effluents (usually for reuse as rinse water). The effectiveness of the RO process is highly dependent on the ability of the pretreatment process to remove scale forming elements and other contaminants that foul RO membranes.

MF/RO Water Recycle Process Description

Tubular microfiltration has been used successfully for over 30 years for the compliant treatment of plating wastewater. It incorporates microfiltration membranes in a tubular configuration which use high turbulent flow to keep the membranes clean of suspended solids allowing continuous high filtration rates. The contaminants such as heavy metals are precipitated chemically and are separated in the microfilter. The microfilter filtrate is further treated by reverse osmosis for salt removal. The metals and foulants must be removed to low enough levels in the microfiltration filtrate to still be at compliant levels once re-concentrated in the RO brine which will be discharged. Figure 3 illustrates the wastewater treatment and water recycling concept.

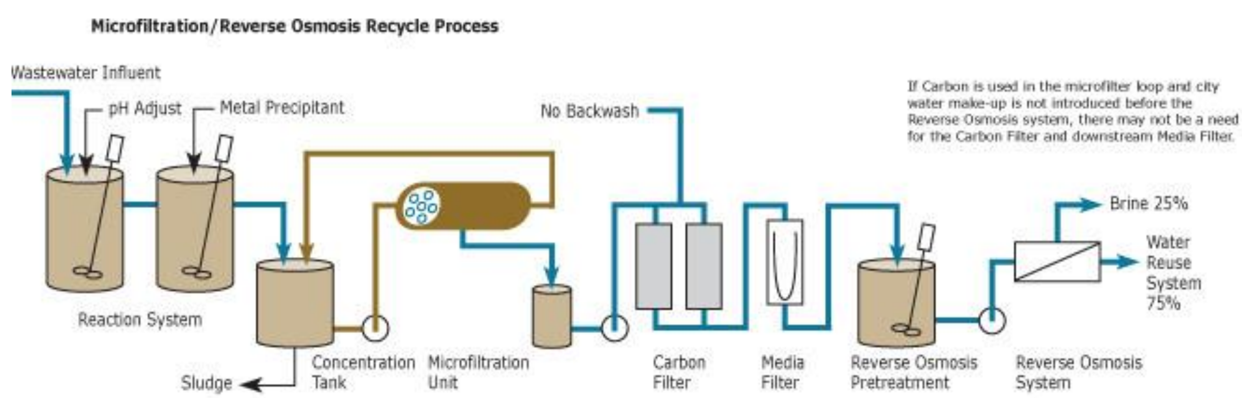

Figure 3: General Microfiltration / Reverse Osmosis Schematic

PILOT METHODOLOGY

MFRO Pilot System and Equipment

It was decided to do a "proof-of-concept" pilot trial on the site using actual steel mill plating wastewater. The pilot was run in March and April of 2010. Due to the short pilot duration it was decided to use a precipitant to help reduce the metals to the lowest possible levels from the beginning, essentially treating for the "worst case scenario". The contaminants that were tested were those for compliance consideration and those for optimizing the feed for the ROs. The duration of the pilot run was simply long enough to cover the operational fluctuations resulting from all three plating lines starting and stopping to change out tanks, products, and other maintenance procedures.

The pilot system equipment consisted of the following:

- Holding and Equalization tank 3,780 L (1000 gallons)
- Reaction tank one: 208 L (55 gal), mixer, pH control, NaOH feed, coagulant feed (NaALO2)
- Reaction tank two: 208 L (55 gal), mixer, precipitant: Sodium Dimethyldithiocarbamate (DTC)
- Microfiltration skid with concentration tank and a single 1-tube module. The membrane was 72 inches (1.8 m) long and 1 inch (2.5 cm) in diameter with 0.14 sq m (1.5 square ft) of membrane surface rated at 0.1 micron nominal porosity.
- Activated carbon was added to the concentration tank of the microfilter as a precaution to remove organics such as oil and grease but also to adsorb organics that can foul the downstream RO system;
- Reverse Osmosis system consisted of a high pressure pump feeding one 10.2 cm by 101.6 cm (4 inch by 40 inch) spiral wound TFC RO membrane with 7.2 sq m (78 square ft) of surface area.

MFRO Pilot Study Description

Raw wastewater was collected in the 3,780 L (1000 gallon) equalization and holding tank and then fed at a constant rate of 3.8 LPM (1.0 GPM) to the first reaction tank of the pilot system. Sodium Aluminate Coagulant was also fed volumetrically to this tank to maintain a dose of about 50 ppm per the manufacturer's recommendation. Sodium Hydroxide was added for pH control to maintain a pH of 9.3 S.U. The wastewater flowed by gravity to reaction tank 2 where DTC precipitant was added on ORP control to -20 mv to assure complete precipitation of metals. From reaction tank 2 the water flowed to the concentration tank of the microfilter that operated on level control. Powdered Activated Carbon was manually added to the concentration tank at a dose of about 350 grams per hour. Higher dosages resulted in higher microfilter flows and lower dosages resulted in lower microfilter flows. The filtrate from the microfilter was collected in a feed tank where the pH was reduced to 6.5 S.U. with sulfuric acid and from which it was pumped through two carbon columns and on to the reverse osmosis system.

MFRO Pilot Results

Table 1 below summarizes the analytical results for the raw sample, MF filtrate, RO permeate and RO brine generated from the test. Both the MF filtrate and RO permeate met the targeted removal efficiency.

The heavy metal reduction efficiency for CO, Cr, Cu, Ni, Pb and Zn are graphically presented in Figure 4.

Note: BDL= below detection limit 0.05 ppm for most metals, 20 ug/L for Hg

Analyte	Raw Wastewater mg/L (average)	Microfilter Filtrate mg/L	RO Permeate mg/L	RO Brine mg/L
Ammonia	80	0.26		0.8
BOD	20	15	4	40
Chromium total	1.0	0.025	BDL	BDL
COD	175	76	15	99
Conductivity	3,500 uS/cm	3,500	350	5,180
Copper	0.3	0.01	BDL	BDL
Hardness as CaCO3	100	43	1	60
Iron	70	0.05	BDL	BDL
Lead	0.6	BDL	BDL	BDL
Mercury	190 ug/L	4.3	BDL	BDL
Nickel	140	BDL	BDL	BDL
Oil and Grease	5	BDL	BDL	BDL
TDS	2,100	2,743	168	3,920
Zinc	70	BDL	BDL	BDL
TSS	291	2.6	BDL	46

Table 1 - Pilot Test Data

MFRO Metals Reductions

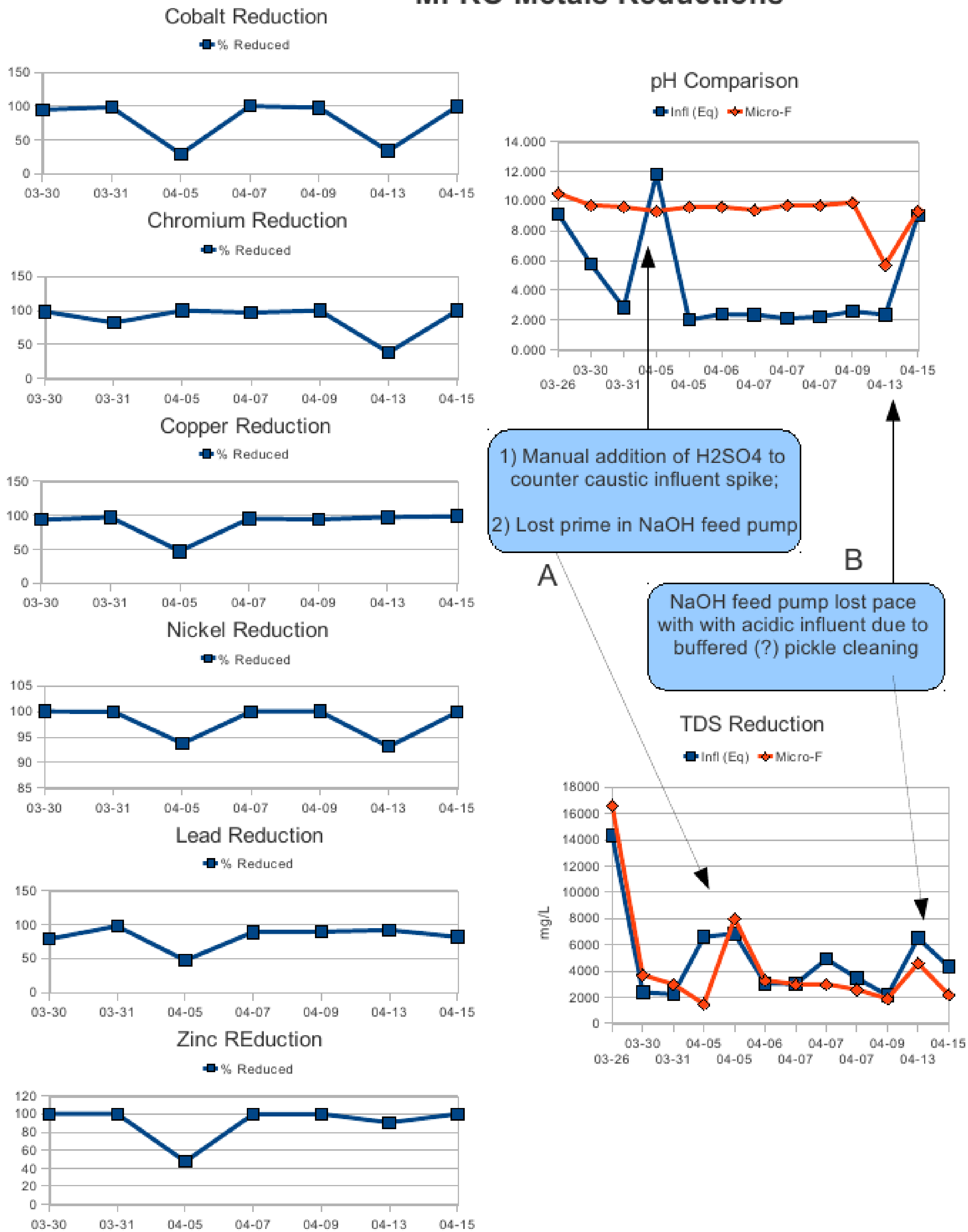

Figure 4: MFRO Metals Reductions- the Necessity of pH Control

MFRO Pilot Performance
The pilot ran for a total of 96 hours. During that time flows through the microfilter and the RO were stable and high. The microfilter flows ranged from a low of 36 dm/min to 72.7 dm/min (0.8 GPM to a high of 1.6 GPM). Conditions affecting flows were oil and grease concentration, carbon dosage and the accumulation of solids in the concentration tank. The average flux of the microfilter membranes was over 1000 GFD. The RO system was able to keep pace with the microfilter system (Question: What's the RO flux?). Metals were removed well below the level (Question: What is the targeted discharge limits?) that when re-concentrated by the RO they were still comfortably below the NPDES discharge limits. Neither the microfilter nor the RO were in need of cleaning by the end of the two week test period.

FULL SCALE SYSTEM IMPLEMENTATION
Based on the positive pilot results, it was decided to move forward with a full scale proposal for a 200 gallons per minute (GPM) system with a peak flow of up to 500 GPM. Between June and November of 2010 the engineering considerations were developed with regard to installing a new wastewater recycling system in the same space and while the existing system continues to operate non-stop. A three-stage plan was developed and the contracts were signed by January of 2011. Site preparation began in April and continued into September.

In stage one, site preparation was executed while the microfiltration skids were being built. Site preparation included vacating the space required for the microfiltration skids and installation of piping and electrical runs around existing operations. The existing filter press was moved to a new location with a new superstructure and the clarifier was re-plumbed to become the equalization and holding tank. Temporary diesel pumps were installed to pump the wastewater from the collection pits to the reactor tanks by-passing the clarifier in order to confirm performance of the microfilters and allow cleanout of the clarifier and switch-back to clarifier operation if necessary.

In stage two, the microfilters with module specifications and system configurations presented in Table 2 and Table 3, respectively, would be installed and commissioned. There would be a period of time that they would run proving performance and compliance with the NPDES discharge requirements. At this point, the system could still be switched back to the previous conventional clarifier and leaf filter mode of operation at any time. After proof of performance, the clarifier became the Equalization and Holding tank and the diesel pumps would be retired. Once confidence was established that the microfilters were working, decommissioning of the DE leaf filters would begin to make room for the carbon columns and the reverse osmosis systems.

In stage three, the ROs and carbon columns would be installed and started.

By September, Stage 1 was complete and the microfilters were installed. By late October, the microfilter was started up and operated according to the operating condition specified in Table 4. The microfilters continued to process all of the wastewater and discharged compliantly to the NPDES permitted discharge. The contaminants of concern for the raw wastewater, MF filtrate and RO permeate are summarized in Table 5. Between late October and December the process was fine-tuned, chemically optimized, and further management of the cleaners segregation plan were accomplished. By the end of 2011, stage three was begun. The ROs and carbon columns were installed and commissioned in February of 2012. As shown in Figure 5, each RO skid was designed as a 5 feeding 2 arrays, producing 200 GPM of permeate and recycles 30 GPM from the first array concentrate back to the raw water feed. The 30 GPM added to the 250 GPM feed from the microfilters adds up to a total first array feed of 280 GPM.

By the end of February the RO systems were fully operational and the entire system was recycling up to 80% of the wastewater treated.

MF Membrane Module Specifications	
Flow configuration	Cross-flow
No. of tubes per module	10
Dimensions	6" (15 cm) dia. x 72" (183 cm) long
Tube diameter	1" (2.5 cm)
Membrane area per module	15 ft^2 (1.40 M^2)
Shell construction	Schedule 40 PVC
Membrane material	PVDF
Nominal pore size	0.1 micron
Module weight	40 lbs (18.2 kg)

Table 2 - MF Membrane Specifications

MF Membrane System Configuration	
No. of MF modules (total)	96
No. of skids (total)	2
No. of DF modules / skid	48
No. of Trains / skid	3
No. of MF modules / Train	16
No. of skids in service mode	1
No. of skids in standby mode	1

Table 3 – Full-Scale MF Membrane Equipment Configuration

MF System Operating Data	
No. of modules per train	16
Max Operating inlet pressure	60 PSI (3.5 Kg/CM^2)
Operating temperature	<105°F (41^{0}C)
Operating TSS in Conc. Tank	2 to 3 % (wt.)
Feed flow velocity	15 Ft/Sec (4.5 M/Sec)
Feed flow per train	350 GPM (80 M^3/Hr)
Membrane flux (average)	>700 GFD (1,183 LMH)
Back-pulse frequency/duration	20 Min / 10 Sec
Back-pulse volume/module	1.5 – 3.0 GPH (6 – 12 LPH)
DF module cleaning frequency	3-4 days

Table 4 - MF System Operation Data

Contaminants	Influent (mg/L)	MF Filtrate (mg/L)	RO Permeate (mg/L)
Ni	50-200	0.05	<0.02
Cu	0.2-0.3	<0.1	BDL
Pb	0.3-0.8	0.01-0.02	<0.02
Zn	50-125	.01-.05	<0.01
Cr	0.9-1.4	0.02-0.03	----
COD	100-200	60-90	<5.0
TSS	250	2-3	ND
pH	2-11 S.U.	9.3 S.U.	6.5 S.U.
SDI	>Max. SDI Test Value	<3.0	----
NTU	Very High	<1.0	<0.5

Table 5- MF/RO System Influent/Effluent Analytical Data Summary

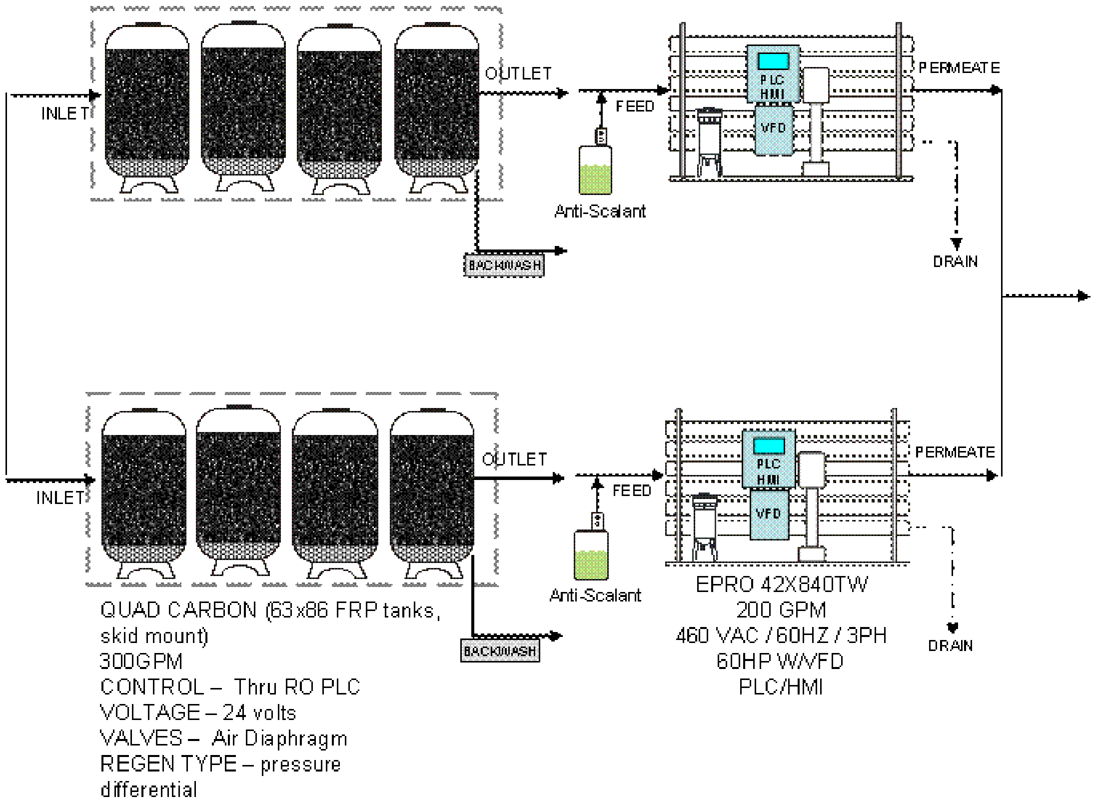

Figure 5: Carbon Column and RO System Configuration

Figure: 6 Carbon Columns and RO Skids Prior to Installation

SUMMARY

The initial company water management objectives were met, as well as the secondary objectives and more. The reuse of the RO recycled water (75+% of all wastewater influent) throughout the facility proved to be very effective. By providing a more pure source of process water, chemical demands were decreased at the plating operations, boiler house, and DI regeneration process areas resulting in significant annual savings. Metals reduction was stabilized at a higher efficiency achieving consistent effluent quality meeting the more stringent compliance standards. Sludge disposal costs have decreased and sludge quality is such that it is highly desired by the offsite smelter. Other added benefits included improved environmental and safety liabilities, electrical and control enhancements, waste minimization at plating lines, improved operator knowledge, better use of existing plant space, as well as upgraded water management practices to sustain long-term business growth. The RO brine is of such quality that the facility is now pursuing discharging to the city sewer and surrendering their river NPDES permit, improving the local surface water qualities and thus benefiting the local communities. The implemented water quality management practices resulting from the full scale installation has prepared the facility for upcoming regulatory compliance demands, streamlined wastewater treatment, and promoted green-technology water savings.

ACKNOWLEDGEMENTS

We would like to thank the host facility for giving us the opportunity to perform this pilot study and full scale installation, especially the management, operators, and process personnel. We would also like to thank J&T Technologies of Pottstown, Pennsylvania for execution of such a large scale installation wastewater project, Crane Environmental of Tampa Florida for their expertise in reverse osmosis, and also Water and Wastewater Laboratories for their dedicated analytical lab services.

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