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## Challenges of Recycling Cooling Tower Blow Down in a Power Plant

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## Abstract

This paper provides a review of the challenges faced with the application of membrane processes in zero liquid discharge (ZLD) water recycle systems for cooling tower blow down (CTBD) recovery and recycle. The most important factor in water recycling and reuse with Reverse Osmosis (RO) is the pretreatment that protects the RO membrane against fouling, scaling or degradation. The recent trend to the widespread application of low-pressure cross-flow membrane Microfiltration (MF) / Ultrafiltration (UF) prior to Reverse Osmosis is not without challenges. Like RO, MF/UF is subject to fouling by various organic, mineral, and chemicals that are unique to the specific membrane property. Pre-treatment chemistry is demonstrated as a critical part of the membrane based water recycle process in maintaining the operation efficiency by removing the unwanted or incompatible contaminants or converting them into MF/UF membrane-compatible species. Advancement made in membrane fouling minimization technique results in substantial reduction in both the capital (CAPEX) and operating (OPEX) cost of MF or UF systems used for protection of RO desalinization systems.

This paper provides a review of field operating data for pretreatment chemistries applied in ZLD water recycle systems to achieve membrane fouling reduction and flux rate enhancement for the MF pretreatment process. The case study is presented for pretreatment chemistries developed for cooling water blow-down recycle from a power plant.

## Introduction

Recycling water from a cooling tower in a power plant requires a complete understanding of the cooling tower chemistry and operation. Large volumes of water are supplied to the power plant from various sources such as, lakes or reservoirs, rivers, subsurface aquifers, or municipal suppliers. The composition of the feed water from these sources can vary from season to season based upon source availability and composition. The components of the water that are of importance to the cooling tower operation are pH, Total Suspended Solids (TSS), Total Dissolved Solids (TDS), Alkalinity (ALK), Total Hardness (TH), Heavy Metals (HM) Chemical Oxygen Demand (COD), Phosphate ($PO_4$) and Silica ($SiO_2$).

Incoming water is normally pH adjusted, and TSS is coagulated and separated in a high rate clarifier and sand-filter combination. This water is used for non-contact cooling in the power generation process and the hot water is sent to the cooling tower. Feed water flow rates to the tower can vary from 1,000 gallons per minute (GPM) to several thousands of GPM. The water is cooled by evaporation and the components in the incoming water are concentrated by a factor of 5 times or more depending on the water chemical composition and the operating conditions and material of construction of the towers.

Complex and proprietary chemicals, such as: anti-scaling compounds, biocides, corrosion inhibiters, detergents and emulsifying agents , are added to these towers to prevent corrosion, precipitation, scaling, and biological growth, which are all processes that reduce the efficiency of the tooling tower operation. As the concentrations of these components reach the threshold levels, the operator will bleed off a concentrate stream of cooling tower water at a specified rate for treatment and recycling or disposal. The by-product water stream is called the cooling tower blow down (CTBD). This flow rate can be as large as 10 to 20 % of the total incoming water flow (100 to 1000 gpm) to the power plant.

If the CTBD is to be recycled, many of the components must be removed or reduced to the acceptable levels prior to reuse in the power plant. These components include: TSS, TH, ALK, COD, SiO2, HM, and biological growth. Reverse Osmosis (RO) has demonstrated its capability in the separation of most, if not all, of these chemical species. To prevent pre-mature fouling and/or degradation of the delicate RO membranes, tubular cross-flow membrane filtration is being used as a part of the pre-conditioning process to remove the incompatible or harmful elements detrimental to the RO performance. The choice to go to a ZLD system further reduces the allowable levels of the components in the feed to the RO system.

## ZLD Concept

Use of reverse osmosis (RO) membrane filtration for wastewater recycling and reuse is no longer a new idea. This concept has been improved and integrated as a key part of today's zero liquid discharge (ZLD) technology. ZLD is a combination of multiple technologies to achieve elimination of discharge of wastewater. The equipment needed to achieve ZLD varies depending on the characteristics of the wastewater as well as the wastewater volume. Management of the entire water cycle for industrial applications is driving efficiency and innovation towards ZLD.

A typical cooling tower blow down ZLD starts with a pre-treatment process followed by RO for dissolved solid (TDS) separation. The RO system will be designed to purify 90 to 95% of the water. Operating the RO at maximum pure water recovery is done in order to minimize the expense of the brine treatment process. Concentrated RO brine solution (reject) at 5 to 10% of the influent flow is sent to an evaporator/crystallizer system for further water recovery. In many cases, falling film evaporation is used to further concentrate the RO brine to the point of crystallization. The crystal laden brine is dewatered essentially converting all the TDS into insoluble solids for proper off-site disposal. The RO permeate and evaporator condensate generated from the treatment process can be used as cooling tower/boiler makeup and water source for plant maintenance, eliminating the discharge of liquids. The overall ZLD concept is presented in Figure 1.

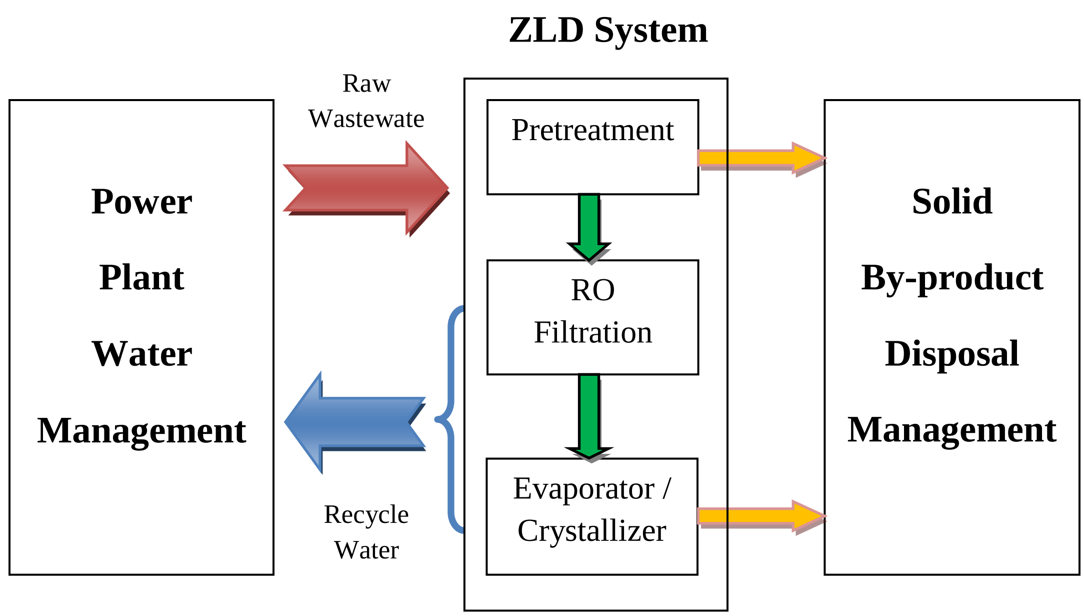



Figure 1 – Typical ZLD Process Concept

The ZLD concept has been proven in the field as a technically viable approach. However, the economic value of the ZLD technology has yet to reach a generally acceptable level in cooling tower blow down application. To justify the CAPEX and OPEX of the ZLD design, the recovery efficiency, performance reliability and life-cycle cost of the RO operation must be optimized and predictable. To accomplish this goal, the RO pretreatment process must be understood based upon the water chemistry and operation of each facility. If the RO pretreatment process is properly engineered, a smaller RO reject volume will be produced, reducing the size and operating cost of the more capital- and energy-intensive evaporator/crystallizer systems. Consequently, minimizing the RO membrane fouling is necessary to lower the life-cycle cost in favor of the investment in the ZLD system.

## RECYCLING COOLING TOWER BLOW DOWN (CTBD)

Reverse Osmosis are the core technology of most ZLD systems. RO Systems are designed for removal of dissolved solids with high efficiency, but the RO membranes could be adversely affected or fouled by suspended solids, colloidal material or scale. Common examples of such foulants are calcium precipitates, metal oxides, colloidal silica and various organics. CTBD water typically contains most, if not all, of these fouling substances. Once fouled, RO membranes are limited by their membrane material properties, only mild cleaning chemicals such as citric acid and detergent can be used to restore the flux. Stronger or more effective cleaning chemicals, such as sulfuric acid, hydrochloric acid, bleach, and peroxide cannot be applied as they will cause irreversible damages to the RO membranes. In CTBD applications, RO can rarely function independently without any protection from the fouling materials. Appropriate pretreatment processes must be provided to achieve stable performance of RO membranes.

**RO PRETREATMENT**

Pre-treatment plays a key role in RO membrane-based treatment or recycle. Properly designed and controlled pre-treatment mitigates the effects of the fouling components on RO membranes because it removes these foulants from the feed to the RO system. The RO pre-treatment process consists of two main steps: Chemical Reaction and Membrane Microfiltration.

*Chemical Reaction* - The principle pre-treatment chemistries for different contaminants are presented in Table 1.

Table 1 – Pre-treatment Chemistry Examples

| Contaminants | Pre-treatment Chemistry |
|---|---|
| Hardness (Ca & Mg) | • Chemical softening - Lime & soda ash |
| Heavy Metals | • Hydroxide precipitation – Caustic/lime<br>• Sulfide precipitation – Sodium sulfide |
| Sulfate | • Sulfate precipitation - lime and aluminum salt. |
| Silica | • Chemical adsorption – Magnesium salt |
| Oil & Grease | • Adsorption – Lime / activated carbon<br>• Acid Cracking – Sulfuric acid |
| Organic | • Adsorption – Lime / activated carbon<br>• Coagulation – Aluminum/iron salts<br>• Oxidation destruction – Bleach / Peroxide |

After the contaminants and foulants are converted into or adsorbed onto insoluble particles using these chemistries, they must be separated from the water flow and yield a water quality with a Silt Density Index of less than 3.0 as suggested by the RO membrane manufacturers (SDI is a measurement of RO fouling characteristics of water.). In the past, a large number of industrial plants have employed the flocculation / clarification / sand filtration process to perform this separation. However, this conventional process has experienced a great difficulty to achieve this low fouling water quality. MF and UF membranes are being tested and have demonstrated on a commercial scale as a technically and economically viable separation devises to assure the necessary removal of these fouling materials.

*Membrane Microfiltration (MF)* – Certain MF products have demonstrated the ability to handle concentrated wastewater and significantly reduce membrane fouling to provide stable, predictable RO performance. The success of MF for this application can be attributed to the following key reasons:

- MF membrane is designed to remove suspended solids and colloidal particles (RO foulants). Some of the MF products, such as the one with tubular configuration, can handle very high TSS of >5,000 mg/L in the influent.
- MF membrane can be made of a variety of polymeric materials, including PVDF, which exhibit strong resistance to concentrated chemicals. As a result, the membrane can be cleaned with mineral acids, oxidizers (bleach, peroxide), caustic and selected organic solvents for removal of different persistent fouling elements, both inorganic and organic, which are difficult to be removed with weak cleaning chemicals.
- MF filtration produces a quality product water stream with NTU (<1.0) and SDI (<3.0) values in full compliance with the feed water criteria specified by all RO manufacturers.
- The chemical or physical characteristic of the foulants in the wastewater can be modified or manipulated with a large degree of flexibility to compatible forms suitable for removal by MF filtration.

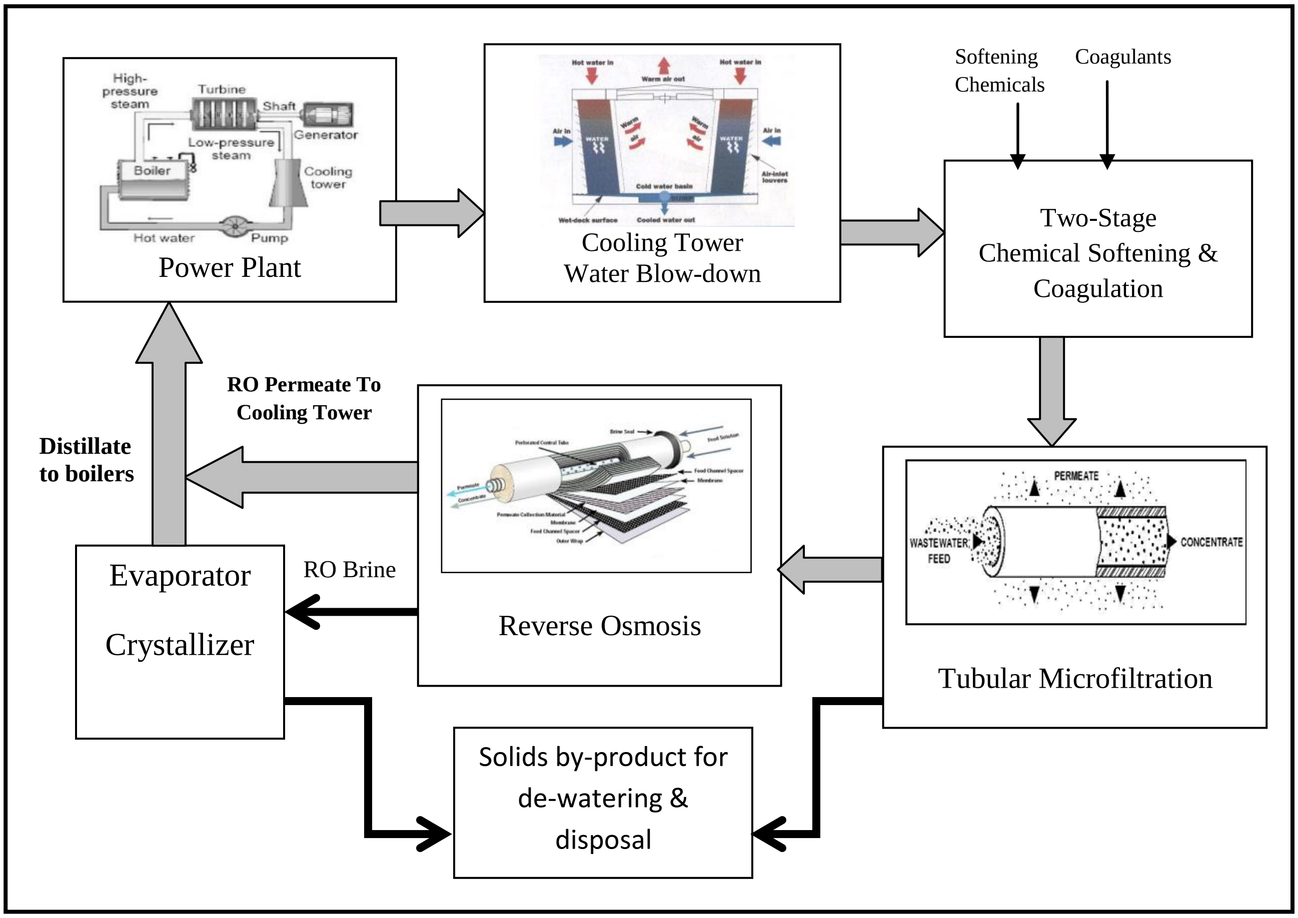
The MF membranes are manufactured in a tubular configuration designed to handle high solid concentration. The membranes, made of PVDF, are cast on the surface of porous polymeric tubes to produce a nominal pore size of 0.1 micron. Figure 2 illustrates one of the 10-tube MF membrane modules installed in the system. Bleach (5% concentration) and hydrochloric acid (10% concentration) are typically used for membrane cleaning in the CTBD application.

Figure 2 – MF Membrane Module

Figure 3 – MF System Assembly

The chemically pre-treated wastewater is processed through the MF membrane modules designed for separation of the precipitates from water. The wastewater is pumped at a velocity of 12 – 15 ft/sec through the membrane modules connected in series as shown in Figure 3. 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. The MF has been operated with an average flux of 300-500 GFD. The entire treatment process is depicted in Figure 4.

Figure 4 – Simplified CT Blow-down Recycling Process Flow Diagram




## Case Study – Power Plant ZLD

***Project Data***

Plant Type/Location: Gas-Fired Power Plant in California

Project Objective: 100% recycle of cooling tower blowdown (CTB)

Years of Operation: 8 Years

Average CTB Flow: 300 GPM

Treatment Concept: The process starts with chemical softening and microfiltration followed by RO. The RO permeate is returned to the cooling tower, and the reject stream is fed to a two-stage thermal system that evaporates the RO reject into crystalline solids. The solids are disposed of as landfills, the distillate is used as makeup water for the heat recovery steam generators (HRSG), and the balance is returned to the cooling tower with an evaporation rate of over 3,000 GPM.

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Major RO Foulants: Hardness (Calcium and Magnesium), Silica, Organic (Anti-scalant & Dispersants) and total suspended solids (TSS)

***Fouling Mitigation Process***

| | | | |
|---|---|---|---|
| Chemical Softening: | Reaction I – | Ferric salt | (Organic coagulation) |
| | | $Na_2CO_3$ to pH 8.5 | (pH adjustment) |
| | | NaOCl | (Bio-growth control) |
| | | Magnesium salt | (Silica adsorption) |
| | Reaction II - | $Na_2CO_3$ & Lime to pH 10.5 | (Hardness precipitation) |

Microfiltration: The MF membranes are manufactured in a tubular configuration designed to handle high solid concentration. The membranes, made of PVDF, are cast on the surface of porous polymeric tubes to produce a nominal pore size of 0.1 micron. Microfiltration modules Model DF-415 are manufactured by Duraflow. The key MF operating data is summarized in Table 2 below.

Table 2 – Key MF System Operating Data

| Parameters | Operating Condition |
|---|---|
| No. of modules per train | Up to 12 |
| Operating inlet pressure | 50 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) | 300 GFD (510 LMH) |
| Back-pulse frequency/duration | 20 Min / 10 Sec |
| MF module cleaning frequency | 1 – 1.5 Weeks |
| Recovery Rate | 98% |
| MF modules replacement | 5 - 6 Years |

Reverse Osmosis: Given the above chemical and MF pre-treatment, the RO system was documented to yield the following operating results.

1. Flux – 15 GFD (26 LMH)
2. Recovery Rate – 90%
3. Cleaning Frequency – Every 6 months
4. Membrane Replacement Frequency – 4 to 5 years

***Process Performance Data***

The fouling component removal efficiency for the MF and RO process is presented in Table 3.

Table 3 – MF & RO Filtration Quality Summary

| **RO Membrane Foulants** | **Influent (CTB) (mg/L as ion)** | **MF Filtrate (mg/L as ion)** | **RO Permeate (mg/L as ion)** |
|---|---|---|---|
| Ca | 260 | <25.0 | <1.0 |
| Mg | 130 | <10.0 | <0.5 |
| $SiO_2$ | 120 | <10.0 | <1.0 |
| COD | 400 | <150 | <5.0 |
| TSS | 250 | <1.0 | ND |
| SDI | >Max. SDI Test Value | <3.0 | ---- |

**The chemical pretreatment is critical for producing the very high quality in the microfiltration filtrate. This is the key to (1) high flux rates for both MF and RO membranes, (2) high water recovery rates, (3) minimal membrane cleaning and (4) long membrane service life. These four key benefits of the chemical pre-treatment process are the source of the major reductions in the CAPEX and OPEX of these ZDL systems**

## Conclusion

Recycle and reuse of cooling tower blow down is becoming a standard water conservation practice in most of today's power plants on a global basis. The CTBD stream is known to consist of a broad range of complex organic and inorganic chemical constituents. Most of them are obvious and defined, but many are hidden as proprietary chemicals unknown to the design engineers. To make a membrane based ZLD system feasible, chemical pre-treatment plays a key role to provide the needed flexibility to transform the wastewater into a membrane-friendly form. Equally important to the design is the incorporation of a high-solid tolerant membrane for effective separation of the resulting precipitates and generation of a high-quality feed stream prior to the RO membrane filtration. To a large extent, membrane fouling management is based on scientific data and methodology. However, the know-how developed from empirical field experience is essential to the overall result of a successful CTBD recycle system.

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