MEMBRANE Technology Applications in Power Plants

OVERVIEW

Membrane processes for water treatment applications in the world's power plants are relatively new when compared to conventional treatment processes, such as granular media filtration and ion exchange demineralization. Membrane processes commonly used in power plants include microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), reverse osmosis (RO), electrodialysis (ED)/electrodialysis reversal (EDR), and electrodeionization (EDI). Newer developments include forward osmosis (FO), membrane distillation, and electrodialysis metathesis (EDM). These membrane processes are used to remove solids (suspended, colloidal, and dissolved) from water while membrane contactor (MC) is a membrane process used to separate gases from water.

The power industry recognized the value of membrane technologies in water treatment more than 30 years ago and embraced the unique technological and economic benefits of RO. Those initial applications have continued to evolve. At present, there are five key areas in power plants that benefit from membrane technology use. These include:

- Boiler feed and NOx injection water treatment
- Removal of dissolved gases in water for boiler feed
- Recycled water treatment (municipal and industrial)
- Cooling tower blowdown recovery
- Concentration of solids for zero liquid discharge (ZLD)

BOILER FEED AND NO_X INJECTION WATER TREATMENT

Power plants typically require highly purified (demineralized) water for use as makeup water to steam generators (boilers) and/or for injection into the turbine combustors to control the formation of environmentally undesirable nitrogen oxides (NOx) in the turbine exhaustion gas. As the boiler pressure increases, the requirement for enhanced water quality also increases, especially as it relates to silica and total dissolved solids (TDS) concentrations. Conventional power plant water treatment processes using surface water sources include coagulation, flocculation, sedimentation, granular media filtration (GMF), granular activated carbon (GAC), cation exchange, degasification, anion exchange, and mixed bed ion exchange (MBIX). The product water is basically ultrapure water. A modern power plant may use coagulation, MF/UF, RO, and EDI to achieve similar water quality objectives as conventional treatment processes. However, the advantages of using membrane processes include higher water quality, more reliable performance and reduced handling and storage of hazardous chemicals.

MF/UF. MF/UF are low pressure membrane filtration processes that remove fine particles physically by size exclusion. The MF/UF membrane pore size is highly uniform and, therefore, capable of very high, or "absolute," removal of a targeted particle size or microorganism. The nominal pore sizes of MF and UF are 0.1 and 0.01 micron, respectively. However, MF and UF are considered equivalent in most water treatment applications, including the power industry. Since the early 1990s, there has been rapid growth in the use of MF/UF for the treatment of drinking water. In wastewater reclamation and power industry uses, MF and UF have enjoyed a similar level of growth, where they have essentially replaced lime softening and GMF as the preferred methods of pretreatment prior to RO for advanced reclamation projects. The use of MF/UF as pretreatment for RO has also been applied in power plant water treatment for more than 20 years.

RO. The use of RO as pretreatment for downstream ion exchange (IX) to reduce chemical regeneration costs has also been practiced for many years, especially since 1987 when polyamide membranes were introduced to the marketplace. RO elements made with polyamide membranes lowered the cost of producing water from a RO/IX system. This is because there is a breakeven point in TDS above which it is more economical to use IX or RO/IX. The breakeven point depends on a number of factors, including costs of chemicals, resins, membranes, energy, operating labor, maintenance, and capital-related items. In 1994, the TDS breakeven point was 130 mg/L as $CaCO_3$ (Beardsley et al., 1994). As most feedwaters supplying the deionized (DI) system are above this TDS level, RO/IX offered clear economic benefits, and installations became quite common in power plants.

EDI. RO-EDI has replaced RO-Mixed Bed IX (MBIX) in many power plants worldwide (Hernon et al., 1994). EDI is continuous in nature and sometimes referred to as Continuous Electrodeionization (CEDI) or Continuous Deionization (CDI). There are several different commercially available EDI products with varying design, but

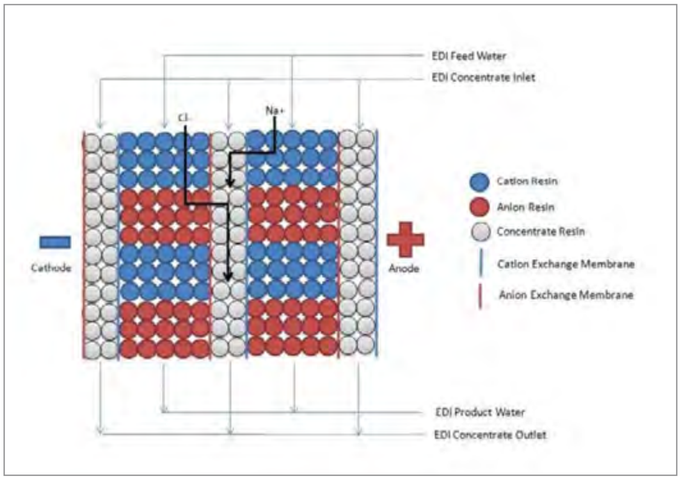

Figure 1: Schematic of Internal Process of One Type of EDI Device

all operate using the same principles of chemistry. EDI modules are electrochemical devices, driven by electrical energy from an external direct current (DC) power supply. Each EDI module consists of five primary components: ion exchange resin, two ion exchange membranes (cation and anion exchange), and two electrodes (cathode and anode). **Figure 1** shows a schematic diagram of the internal process of one type of EDI device.

As water flows through the EDI module and power is applied, three processes occur simultaneously: 1) the DI process where the water is purified by IX; 2) ion migration where the ions are removed from the resin; and 3) continuous regeneration of the resin. The regeneration of the cation and anion resins is by the H+ and OH- ions, respectively, which are split from H_2O by the electric current, and hence acid and caustic are not needed for regeneration. EDI standard systems can produce water of 17 megohm-cm. All EDI manufacturers market a product water of up to 18 megohm-cm, but a product quality at that level will greatly depend on the EDI feed water quality. For certain raw waters, two pass RO may be needed before EDI to produce the necessary product water quality.

EDI has several advantages over IX. These include:

- No storage or handling of hazardous chemicals (acid and caustic)
- No regeneration waste neutralization needed
- Continuous operation without interruption for regeneration
- Simpler operation and maintenance

BOILER FEED WATER DEGASSING USING MEMBRANE CONTACTORS

Membrane contactors have been used to remove dissolved oxygen (DO) in boiler feed water systems for years. More recently, they have been installed in power plant water treatment systems to remove carbon dioxide (CO_2) to extend MBIX resin life or to reduce capital cost and energy use by eliminating an RO pass in a RO-RO-EDI system. MCs are devices that utilize microporous, hydrophobic hollow fiber membranes that contain a large surface area, which promotes ideal mass transfer. In a typical design, water flows on one side of the microporous hollow fiber membrane, and gas flows on the other side of the membrane. Since the membrane is hydrophobic and the pores are very small, liquid will not pass through the pores. Pores in the membrane fiber provide a very stable gas/liquid interface. Manipulation of partial pressures at the interface allows gases to be added to or removed from the bulk water flow. In the MC design as shown in **Figure 2**, water enters the assembly via the distribution tube (Miller et al., 2005).

At the distribution tube midpoint is a liquid-side baffle that forces the water to flow through perforations in the distribution tube and across the fibers in a flow path that is 90 degrees from its original flow direction. The water then takes a tortuous path across the fibers until reaching an annular space between the fiber cartridge and the housing wall. Traveling along this annular space the water will reach the baffle and make a 180-degree turn around the baffle, continue back across the fibers and enter the collection tube, and then exit the MC assembly.

In addition to application for boiler makeup water treatment, MCs can also be used in the boiler system to remove DO from boiler water. With the proper configuration and system design MCs can remove essentially all DO present in the water stream. MCs can be used as a standalone deoxygenation system, or they can be used with existing technology as a hybrid system. Traditional deaerators may only remove gasses to 7-10 parts per billion (ppb), and this small amount of oxygen is still corrosive to the system. Installing a MC system in conjunction with the traditional vacuum deaerator will allow the lowest possible levels of dissolved gasses to the boiler. It is also possible to replace the traditional steam deaerator with the MC system in new installations. There are several advantages of this configuration:

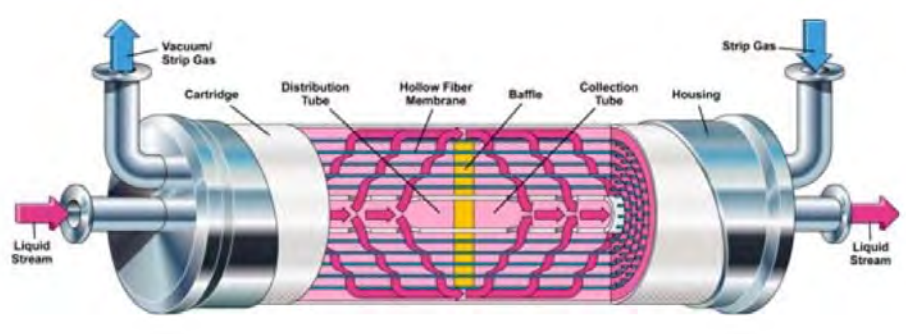

Figure 2: The Inside of a Membrane Contactor *(courtesy of Membrana)*

- Smaller space requirement because MC systems are modular and easily adaptable to a given footprint
- MC systems are more easily controlled. No special controls are required
- Lower energy consumption
- The MC system has a lower cost than a steam deaerator.

MEMBRANES FOR USE IN TREATING RECYCLED WATER USED AS BOILER FEED WATER

MF/UF and RO processes have been used for treating municipal wastewater effluent for reuse as boiler feed water in refineries and power plants for more than 20 years. The El Segundo, CA, Chevron refinery has been receiving 4.3 million gallons per day (mgd) of reclaimed water to feed its boilers since 2000 (Wong and Hng, 2004). MF and RO is used to treat secondary effluent from the Hyperion Wastewater Treatment Plant and provides low-pressure boiler feedwater while a two pass RO is used to produce high-pressure boiler feedwater. The Richmond, CA, Chevron refinery has a similar arrangement with the East Bay Municipal Utilities District (EBMUD) using MF/RO to produce boiler feed water from secondary effluent. The refinery provides the two pass RO to polish RO permeate from the EBMUD MF/RO system for boiler feed. The Delta Energy Center in Pittsburg, CA, uses UF/RO to treat filtered secondary effluent from the Delta Diablo Sanitation District to supply purified water to the power plant's DI system for boiler feed makeup. There are many other similar applications in power plants worldwide, according to a membrane vendor supplying some of those UF/RO systems (Shin, 2017).

A large steel complex in the Far East installed an advanced treatment system to reclaim its industrial wastewater effluent as boiler feed water for the power/steam plants onsite (Wong, 2014). The treatment processes include coagulation, flocculation, sedimentation, UF, RO, two bed IX, and MBIX. The product water has near ultrapure water quality and is supplied to the steam plant to produce steam for power generation and for sale to other industrial plants near the steel complex.

MEMBRANES USED IN POWER PLANT COOLING TOWER BLOWDOWN RECOVERY

Power plants use high volumes of water in cooling towers to dissipate waste heat that results from power generation. In some arid areas, power plants are trying to implement zero liquid discharge (ZLD) for environmental sustainability. Cooling tower blowdown (CTBD) recovery/reuse is one of the important elements of ZLD. A typical CTBD recovery treatment schematic includes a pretreatment process followed by RO for TDS removal. The RO system is designed to remove 90 to 95% of the TDS. Operating the RO at maximum water recovery minimizes the expense of the brine concentration process, which usually involves evaporation/crystallization for further water recovery and solids disposal. The RO permeate and evaporator/crystallizer condensate generated from the treatment processes can be reused as cooling tower/boiler makeup. Effective pretreatment for RO is critical in CTBD recovery as CTBD contains many potential membrane foulants including suspended solids, calcium precipitates, silica and various organics.

A coal-fired power plant in Southern California installed a CTBD recovery system in 2004. The average CTBD flowrate is 300 gallons per minute (gpm). The treatment process starts with chemical softening (no clarifier) and MF 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 in landfills, the distillate is used as makeup water for the heat recovery steam generators, and the balance is returned to the cooling tower with an evaporation rate of more than 3,000 gpm.

Figure 3 shows a process flow diagram of the CTBD and ZLD system for this power plant (Lander and Chan, 2010).

The MF system used in this project is a tubular MF system that can handle high influent solids concentration (as high as 5,000 mg/L TSS). The membranes are made of PVDF and cast on the surface of porous polymeric tubes to produce nominal pore size of 0.1 micron. Bleach (5% NaOCl) and hydrochloric acid (10% HCl) are typically used for membrane cleaning in the CTBD application. The chemically pre-treated CTBD 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. 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 recirculation loop are periodically purged for further dewatering. An automatic back-pulse mechanism is an integral part of the operational design, providing physical surface cleaning by periodically reversing the filtrate flow direction. The CTBD recovery system has been operating successfully since 2004.

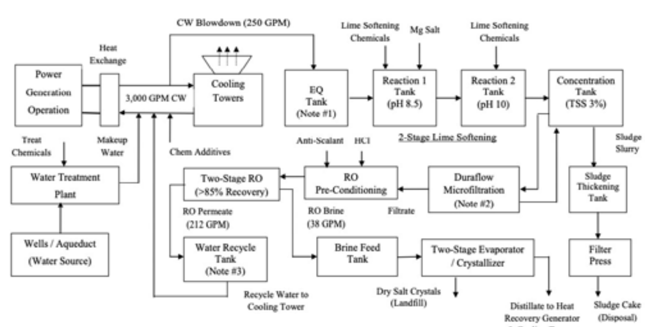

Figure 3: Power Plant – Cooling Tower Blowdown Water Recycle Flow Diagram Example

USE OF FORWARD OSMOSIS IN POWER PLANT ZERO LIQUID DISCHARGE

A newer development in membrane application for power plants is the use of Forward Osmosis (FO) as a brine concentrator to replace thermal evaporator in a ZLD system. Unlike hydraulic pressure-driven RO, FO relies on osmotic pressure differences to drive water permeation across a semi-permeable membrane. In FO, water flows from the feedwater to a concentrated draw solution with an osmotic pressure that is higher than the feedwater. The produced brine can be sent to a brine crystallizer or an evaporation pond, whereas the draw solutes are separated from the desalinated water to regenerate the concentrated draw solution. Since the driving force in FO is osmotic pressure, FO can treat waters with much higher salinity than RO. In addition, FO operates at low pressure, resulting in foulant layers that are less compact and more reversible than hydraulic pressure-driven RO systems. Accordingly, FO has a much lower fouling propensity than RO, which not only reduces the operational costs related to fouling prevention and cleaning but also extends the applicability of ZLD to wastewaters with high fouling potential.

The development of thermolytic draw solutes, such as NH_3 and CO_2, paved the way for ZLD systems. The NH_3/CO_2 draw solution generates very high osmotic pressure driving forces and can be regenerated by low-temperature distillation. Because the thermolytic NH_3/CO_2 draw solution decomposes at moderate temperature (approximately 60°C at atmospheric pressure), low-grade thermal energy, such as waste heat from power plants, can be utilized to regenerate the concentrated draw solution. A recent study estimated that U.S. power plants produced 803 million gigajoules of waste heat at temperatures greater than 194°F or 90°C in 2012 (Gingerich and Mauter, 2015). The available waste heat in power plants makes it ideal for FO technology use in power plants to treat water and wastewater necessary for boiler feed makeup. The thermolytic FO process can be used as a brine concentrator after the RO stage. Compared to thermal brine concentrators, the NH_3/CO_2 FO can be cost competitive because a small volume of the more volatile draw solutes, as opposed to water, is vaporized to regenerate the concentrate draw solution. Furthermore, the modularity of FO results in a smaller area footprint and also renders ZLD systems more adaptable to fluctuations in the flow rate and quality of feedwater.

A power plant in Changxing in China treats a mixture of flue gas desulfurization (FGD) wastewater and CTBD at an average flow of 116 gpm. The softened feedwater is first concentrated by RO to a TDS concentration of approximately 60,000 mg/L. The NH_3/CO_2 FO process is then used as a brine concentrator to further concentrate the RO brine to above 220,000 mg/L TDS, while a high-quality product water (TDS < 100 mg/L after polishing by a secondary RO) is produced for reuse as boiler makeup. The FO reject is treated by the crystallizer. The overall water recovery is between 93 to 97 percent. **Figure 4** shows a process flow diagram of this plant.

SUMMARY AND CONCLUSIONS

Membrane technologies have been used for water treatment in power generating plants for several decades. Effective applications include boiler feed makeup water treatment using MF/UF, RO, and EDI, and boiler feed water degassing using MCs. As water quality and scarcity becomes a worldwide problem, wastewater reclamation and reuse have become more commonplace, and ZLD has been applied to address these issues in power plants worldwide. The relative newcomer in membrane applications is FO, used as a brine concentrator and, potentially, a more economical alternative to traditional thermal brine concentrators such as mechanical vapor compression and multi-flash distillation systems. The abundant availability of low-grade waste heat generated by power plants offers reduced operating costs for the thermolytic FO process. More installations like these are expected to be prevalent in power plants located in arid regions. Other developing membrane technologies such as membrane distillation also make use of low-grade waste heat for operation and may one day find their niche application in the power generating industry.

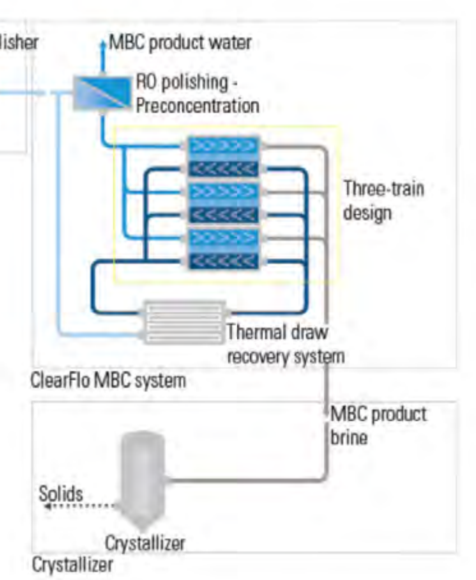

Figure 4: Power Plant ZLD Process Flow Diagram

Figure 5: Power Plant MBC System

FOR MORE INFORMATION:
American Membrane Technology Association (AMTA)
PO Box 14918
Tallahassee, FL 32317
Phone: (772) 469-6797
Email: custsrv@amtaorg.com
www.amtaorg.com

@AmericanMembraneTechnologyAssociation

@amtaorg

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