Use of Isothiazolin and DBNPA to Control Biofouling of RO Membranes Used for Side-Stream Circulating Water Treatment

Shawn S. Simmons

ABSTRACT

Mountainview Generating Station in Redlands, California, uses a reverse osmosis system to deconcentrate the total dissolved solids of the circulating water in the cooling towers. Since the generating station started operation in 2006, the reverse osmosis membranes to the system have rapidly fouled, repeatedly. The primary foulants have been calcium hardness, iron, and bacteria slime. Fouling from calcium hardness and iron was reduced by modifying the water treatment processes upstream of the reverse osmosis (RO) trains. Fouling from iron was reduced by decreasing ferrous chloride feed to the clarifier, which is also upstream. Adding 2,2-dibromo-3-nitrilopropionamide (DBNPA) biocide to the RO membrane cleaning solution and extending the soak period for the alkaline cleaner has improved the effectiveness of membrane cleanings. Addition of isothiazolin biocide to the RO feedwater during operation and shutdown has improved permeate flux rates and extended the life of cartridge pre-filter elements from 1–2 weeks to 2–3 months.

INTRODUCTION

Since commissioning in 2006, the reverse osmosis (RO) membranes to a cooling tower side-stream treatment system have required frequent replacement compared to conventional systems. Since 2013, microbiocide treatment has been helpful in improving membrane permeate flow and reducing the frequency of cartridge pre-filter change-outs. Optimization of the application of the microbiocide treatment is still ongoing.

BACKGROUND

Mountainview Generating Station in Redlands, California, is a 1 080 MW capacity, combined cycle, gas-fired facility owned and operated by Southern California Edison. There are two 2-on-1 heat recovery steam generator (HRSG) units. Each unit has two banks of three heat recovery boilers (high pressure (HP), intermediate pressure (IP), and low pressure (LP)) and a steam turbine. The circulating water systems have open recirculating cooling towers fabricated from treated lumber. Scaling is controlled by limiting the concentration of dissolved solids in the circulating water ($< 6\,750\ mg \cdot L^{-1}$), adding sulfuric acid to control alkalinity (pH 7.4 to 8.2), and treatment with a proprietary dispersant. Microbiological activity is controlled primarily by adding sodium hypochlorite (0.2 to $2.0\ mg \cdot L^{-1}$ free chlorine). The makeup water to the circulating water system is a 1+1 blend of tertiary treated reclaimed water and local groundwater. A side-stream water treatment plant enables Mountainview to limit the total wastewater discharge to $68.14\ m^3 \cdot h^{-1}$ (300 gpm). Without the water treatment plant, the discharge rate from cooling tower blowdown alone would be $> 227.12\ m^3 \cdot h^{-1}$ (1 000 gpm).

The water treatment plant includes a side-stream softener system sized to treat up to $454.25\ m^3 \cdot h^{-1}$ (2 000 gpm) circulating water. Components include a $75.71\ m^3$ (20 000 US.liq.gal.) premix tank and a $681.37\ m^3$ (180 000 US.liq.gal.) clarifier. The silica and hardness concentrations in the water from the cooling towers are reduced by chemical precipitation using sodium hydroxide and sodium carbonate (soda ash). Ferric chloride (coagulant) and a polymer (flocculent) are added to promote solids formation and settling. The bottom slurry from the clarifier containing 1 to 2 % solids is piped to a $529.96\ m^3$ (140 000 US.liq.gal.) settling tank. The bottom blowdown from the settling tank contains 5 to 12 % solids and is piped to three sludge filter presses. The sludge from the presses is collected in bins and taken to a landfill.

Clarified water collected from the top of the clarifier splits in two directions. The larger portion is partially softened water that is returned to the cooling towers. The smaller stream is filtered and collected in a sump that undergoes additional treatment by the HERO process. This additional treatment process culminates in two RO trains, whose permeate returns low dissolved solids water to the cooling towers. The RO reject is discharged to waste.

TREATMENT SYSTEM DESCRIPTION

The HERO system is a process supplied by Aquatech International [1]. It comprises the filtered water sump, two 0–172.6 $m^3 \cdot h^{-1}$ (0–760 gpm) forwarding pumps followed by three softeners containing weak acid cation resin, a decarbonator followed by two 0–172.6 $m^3 \cdot h^{-1}$ forwarding pumps, two cartridge filter vessels, two 0–86.3 $m^3 \cdot h^{-1}$ (0–380 gpm) RO feedwater booster pumps, two RO trains, and a storage tank for RO permeate (Figure 1).

Water from the filtered water sump is first passed through ion exchange softeners containing weak acid cation resin. The water is treated with sodium bisulfite to remove chlorine before it reaches the softeners. The water quality at the weak acid softener inlet is described in Table 1.

There are three softener vessels and each vessel contains 3.9 m^3 (138 ft^3) of weak acid cation resin in the sodium form. A freshly regenerated softener is first put in service as the lead softener. After processing 2 271.2 m^3 (600 000 US.liq.gal.), it then becomes the lag softener and processes an additional 2 271.2 m^3. The total hardness limit for the lag softener effluent is 0.7 $mg \cdot L^{-1}$ maximum.

Following softening, the water is dealkalized by adjusting its pH using acid and passing it through a fiberglass decarbonator. A pH of 4.1 to 4.5 is required to convert the carbonate/bicarbonate alkalinity to carbonic acid.

Following the decarbonator and prior to the decarbonator forwarding pumps, caustic is added to adjust the pH to 10.0 to 11.3 prior to the RO trains. Antiscalant and biocide may also be added at this point.

There are two full-flow cartridge filter vessels. Each vessel has 67 individual cartridge filters rated for the removal of particles ≥ 3 μm. Since each filter is capable of 34.5 kPa (0.5 psid) of differential, there is a total vessel differential of 2 309.7 kPa (33.5 psid) before there is a decline in performance or a filter failure.

There are two reverse osmosis membrane trains (Trains A and B) arranged in two stages. Each membrane vessel contains seven 20.32 cm (8 in) membrane elements and the reject from the six membrane vessels in the first stage feeds the three membrane vessels in the second stage. The RO trains are designed to operate at 75 % maximum water recovery and at high pH (10.0–11.3) to increase silica solubility. Operating at high pH should also cause higher rejection of chemical oxygen demand (COD), less biological growth, and greater tolerance to suspended matter and organic fouling. Because running at high pH increases the tendency for alkaline earth carbonates to foul the membranes, the pretreatment addresses calcium, magnesium, and carbonate removal.

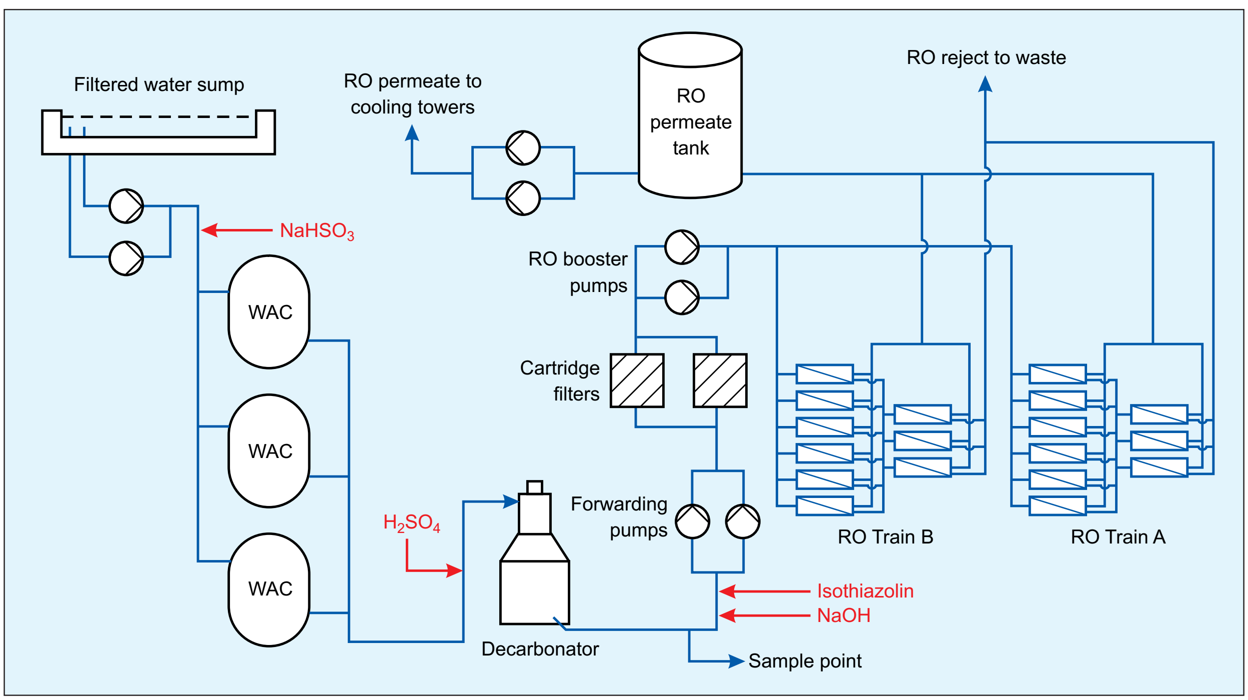

Figure 1:
Simplified flow diagram of the HERO process.
WAC weak acid cation resin softener

Parameter		Value
pH at 25°C		8.5–9.5 (8.8)
Specific conductivity at 25°C	[$\mu S \cdot cm^{-1}$]	3 000–10 000 (7 200)
Turbidity	[NTU]	5 max. (2.0)
Calcium as $CaCO_3$	[$mg \cdot L^{-1}$]	50–150 (105)
Total hardness as $CaCO_3$	[$mg \cdot L^{-1}$]	60–200 (130)
Silica as SiO_2	[$mg \cdot L^{-1}$]	40–60 (52)
Total iron	[$mg \cdot L^{-1}$]	0.02–1.0 (0.16)

Table 1:
Water quality at the weak acid softener inlet.
Data in parentheses in the table are average values.

When there is high demand both trains run simultaneously; otherwise, only one train is in service, and they are alternated weekly. At shutdown, RO product from an additional system (with a product water conductivity of ~ 25 $\mu S \cdot cm^{-1}$) is passed through a RO train for two hours.

RO MEMBRANE HISTORY BEFORE MICROBIOCIDE ADDITION

The initial membranes were Hydranautics ESNA1-LF-4040. They were completely replaced December 2006 after less than one year of service. A membrane autopsy identified calcium as the principle foulant. Studies done on the weak acid cation (WAC) softeners indicated they were leaking high hardness levels, especially during the first 10 % of the service run. Initially, freshly regenerated softeners operated in the lag position, then in the lead position. After the membranes were changed out with Dow Filmtec BW30-400, a significant process improvement was achieved by changing the operation to have freshly regenerated softeners first run in the lead position, then in the lag position.

During October 2008, the first stage membranes to both trains were replaced after cleaning them did not improve their performance. The membranes had been in service 22 months. The second stage membranes were not replaced since cleaning them partially restored performance.

Since a membrane autopsy report identified iron as the principle foulant, an iron testing program was initiated. Iron test results showed that the RO feedwater was averaging 110 $\mu g \cdot L^{-1}$ total iron and 30 $\mu g \cdot L^{-1}$ suspended iron. Chemical testing determined the particle size of the suspended iron to range from 0.45 µm to 1 µm.

On a temporary basis, the "5-micron" cartridge filters in the pre-filter vessels were replaced with "1-micron" cartridge filters; however, there was no improvement in iron removal efficiency and the 1-micron filters needed changing more frequently.

During May 2010, after 17 months of service, the first stage membranes to Trains A and B were replaced again. Also, the second stage membranes to Train B were replaced. A membrane autopsy report identified iron, calcium carbonate, and gelatinous organic matter as the primary foulants. The replacement membranes were Dow Filmtec BW30-400 and GE AG8040F.

Because of iron fouling to the RO membranes, the ferric chloride used for coagulation in the clarifier came under scrutiny. Field tests were done using several polymer products in place of ferric chloride for coagulation; however, none of the polymers tested were found to be a suitable replacement for ferric chloride.

The next complete membrane change-out was done September 2011, 16 months after the previous membrane replacement. A membrane autopsy report identified gelatinous organic matter and iron as the primary foulants and the autopsy report highlighted biological fouling (Figure 2). The replacement membranes were changed to Dow Filmtec BW30-400/34i elements because they are recommended for high-fouling, challenging feed conditions.

At the recommendation of a vendor, the station began injecting 2 to 5 $mg \cdot kg^{-1}$ antiscalant into the RO feedwater. Also, the type of cartridge pre-filter was changed. Mountainview switched from using 5 µm string-type filters, to 3 µm honeycomb-polymer filters. Although the new filters do not reduce iron passage, they can be operated to a differential pressure of 2 309.7 kPa (33.5 psid) versus 103.4 kPa (15 psid) for the string-type.

By the end of November 2011, the permeate flow through the new membranes installed September 2011 had declined by 50 %.

During the early months of 2012, the station found they could run the clarifier with less ferric chloride. Except for startup, when 40 to 45 $mg \cdot kg^{-1}$ is still needed to build up the sludge bed, the dose can be lowered to 25 to 30 $mg \cdot kg^{-1}$. Testing showed that reducing ferric chloride from 40–45 $mg \cdot kg^{-1}$ to 25–30 $mg \cdot kg^{-1}$ reduced dissolved iron levels in the RO feedwater by more than 50 %.

During May 2012, the stage-one membranes to Train A were replaced after 7 months of service and the station discontinued adding antiscalant because there was no evidence it was helping.

During November and December 2012, half of the stage-one membranes to Train A were replaced after 6 to 7 months of service. One-sixth of the stage-one membranes to Train B were replaced after 14 months of service.

In February 2013, 17 % of the stage-one and 33 % of the stage-two membranes to Train B were replaced. The spent membranes had been in service 17 months.

The next complete membrane change-out was done in April 2013, 19 months after the last complete replacement. The membrane autopsy identified brown and orange gelatinous material as the primary foulant (Figure 3). It was apparent that fouling by bacteria slime was a greater problem than fouling by iron.

RO PERFORMANCE USING MICROBIOCIDE ADDITION

Isothiazolin biocides are used in a variety of industrial water treatment applications for control of microbiological growth and biofouling [2]. The most frequently used product is a 3:1 ratio of 5-chloro-2-methyl-4-isothiazolin-3-one (CMIT) and 2-methyl-4-isothiazolin-3-one (MIT). The biocide functions as an electrophilic agent, reacting with critical enzymes to inhibit growth within minutes, and causing cell death after several hours of contact. In experiments reported by Williams [2], the minimum concentrations of biocide as active ingredient required to inhibit

Figure 2:
Feed scroll end (left), concentrate scroll end (center), and exposed membrane surface (right) of membrane removed September 2011.

Figure 3:
Feed scroll end (left), concentrate scroll end (center), and exposed membrane surface (right) of membrane removed April 2013.

growth for two types of test bacteria were 0.4 and 0.7 mg · L^{-1}. The minimum biocidal concentrations were 0.5 and 0.8 mg · L^{-1}. Above a pH of 9.0, isothiazolin degrades rapidly; however, increasing pH does not impact its effectiveness, only the rate of degradation [3]. Typical dosages in closed cooling water systems are 1 to 5 mg · L^{-1} as active ingredient.

After changing out all the membranes in April 2013, Mountainview found a tote of an isothiazolin product on station, moved the tote to the chemical injection skid, and started injection at 15 mg · L^{-1} of product. The product formulation was 1.1 % CMIT and 0.4 % MIT. The product had been on site six years and was initially purchased to treat the closed cooling water system, but since the station had switched to using glutaraldehyde to treat the closed cooling water, the isothiazolin was no longer needed. Because of company policies there are many steps to follow when wanting to qualify a new hazardous chemical. Using a chemical already registered in the company system is easily the most convenient route. On April 16, 2013, samples were collected for heterotrophic plate count, and the bacteria plate count (colony forming units (CFU)) results were high (Table 2).

The isothiazolin product was fed continuously from April 11, 2013 to May 17, 2013. The station started out feeding 15 mg · L^{-1} of the product, then adjusted the feed rate to 10 mg · L^{-1} and continuously added biocide until the tote was empty. In hindsight, it can be concluded that the treatment was ineffective because the isothiazolin tote was past its shelf life.

At the recommendation of a vendor, on May 22 the station added 50 mg · L^{-1} of 20 % 2,2-dibromo-3-nitrilopropionamide (DBNPA) (10 mg · L^{-1} as active ingredient) to the RO feedwater for one hour. The chemical addition of DBNPA caused the differential pressure across the cartridge filters to rapidly increase and this was thought to be from the dislodging of bacteria foulant material.

On May 23, 2013, samples were collected for heterotrophic plate count. There was no biocide treatment and results for the RO feedwater and reject were very high (Table 3).

On June 4, 2013, Mountainview began injecting a fresh isothiazolin solution (Biotrol 102). The product formulation is the same as that of the initial tote. The feed concentration was 7 to 10 mg · L^{-1}. Starting in June, the station also began the practice of pumping 700 mg · L^{-1} Biotrol 102 into the flush water passed through the RO trains when they are shut down.

Based on bacteria count results for samples collected June 18, July 12, and August 15, 2013, isothiazolin addition in conjunction with the cartridge filters seemed to be helping although the treatment concentration was only 0.15 mg · L^{-1} as active ingredient (Table 4). The heterotrophic plate count results for the RO booster pump sample following the cartridge filters were less than the results for the decarbonator outlet.

In early December 2013, the station replaced the Train A, first stage, and Train B, second stage membranes.

Sample Point	CFU · mL^{-1}
Decarbonator outlet	2 500
RO booster pump (RO feed)	1 900
Train A RO reject	1 100

Table 2:
Results for heterotrophic plate count samples collected April 16, 2013.

Sample Point	CFU · mL^{-1}
Decarbonator outlet	> 5 700
RO booster pump	> 5 700
Train A RO reject	> 5 700
Train B RO reject	> 5 700

Table 3:
Results for heterotrophic plate count samples collected May 23, 2015.

Sample Point	CFU · mL^{-1}		
	6/18/13	7/12/13	8/15/13
Decarbonator outlet	480	20	2 400
RO booster pump	57	<1	13
Train A RO reject	100	50	6
Train B RO reject	130	2	4

Table 4:
Results for heterotrophic plate count samples collected 6/18/13, 7/12/13, and 8/15/13.

EFFECT OF ISOTHIAZOLIN ADDITION ON CARTRIDGE FILTERS

Isothiazolin treatment has dramatically extended the service life of the cartridge filter elements even though the treatment concentration is quite low (at an average of 12 mg · L^{-1} as product). Before biocide addition, cartridge filter life was several days and never longer than two weeks. Conservatively, it is now six weeks with both trains running and three months with one train running. In several cases the cartridge filters have lasted much longer than three months.

The cartridge filters added to Train A on June 3, 2013 and May 30, 2013 did not need changing until six months had passed. The filters added to the Train A vessel on February 22, 2014 lasted five months. The filters added to the Train B vessel on September 15, 2014 and February 18, 2015 also lasted five months.

Because of the isothiazolin treatment, the color of the solids on the filter elements changed from orange to beige. The theory is that the orange color was caused by iron adhering to the biofilm on the cartridge filters.

In conclusion, the addition of isothiazolin has dramatically reduced the amount of biofilm that develops on the filter elements.

EFFECTS OF DBNPA ADDITION AND EXTENDED SOAKS FOR RO CLEANINGS

DBNPA interacts with enzymes and interferes with cell respiration and metabolism, achieving a significant kill in 1–3 hours [3]. Typical dosages are 0.5 to 10 mg · L^{-1} as active ingredient. In the 1990s, Southern California Edison found it effective for treating biofouled RO membranes.

Since 2006, Mountainview has been cleaning the RO membranes every six to nine months with disappointing results more often than not. Results for cleanings performed February 2015 and July 2015 that included the use of DBNPA and an extended soak period have been the most effective cleanings to date.

The cleaning procedure first uses a 2 to 3 % solution (pH 2.5–3.5) designed to remove metal foulants (such as iron, manganese, and calcium carbonate) followed by a solution (pH 11.5–12.8) designed to remove silica, organics, and bacterial slime. The cleaning solutions are recirculated through each membrane array for 1 to 2 hours at 46.1 °C; the membranes are left to soak, and then rinsed to neutral pH.

For cleanings done in February 2015 and July 2015, the metals cleaning solution was spiked with 50 mg · L^{-1} DBNPA (as active ingredient) and the soak period for the silica/organics cleaning solution was increased from 2 to 20 hours (left overnight).

For cleanings done February 2015, when the temperature of the RO feedwater was 25 °C, permeate flows increased from 26.1 to 41.6 $m^3 \cdot h^{-1}$ (115 to 183 gpm) for Train A and from 37.0 to 45.7 $m^3 \cdot h^{-1}$ (163 to 201 gpm) for Train B. For cleanings done July 2015, when the temperature of the RO feedwater was 34 °C, permeate flows increased from 39.3 to 49.5 $m^3 \cdot h^{-1}$ (173 to 218 gpm) for Train A and from 40.2 to 50.4 $m^3 \cdot h^{-1}$ (177 to 222 gpm) for Train B. The permeate recovery was 71 % in all cases.

RO PERFORMANCE, SEPT 2012 TO APR 2013 VS. APR 2013 TO OCT 2015

The graphs in Figures 4 and 5 highlight the permeate rates through the RO trains from September 2012 to April 10, 2013 and from April 11, 2013 to October 2015. Flux is used to express the permeate rates and the units are liters per square meter of membrane area per hour (LMH) (gallons per square foot of membrane area per day (GFD)). Values are normalized for net driving pressure and temperature. Net driving pressure is calculated from the inlet pressure, feed conductivity, permeate pressure, and average pressure (ΔP) [4]. The normalization values used are 1 379 kPa (200 psi) inlet pressure, 6 200 µS · cm^{-1} inlet conductivity, 41.4 kPa (6 psi) permeate pressure, 137.9 kPa (20 psid) average pressure (ΔP), and 25 °C. For both case histories, the permeate recovery averaged 71 %.

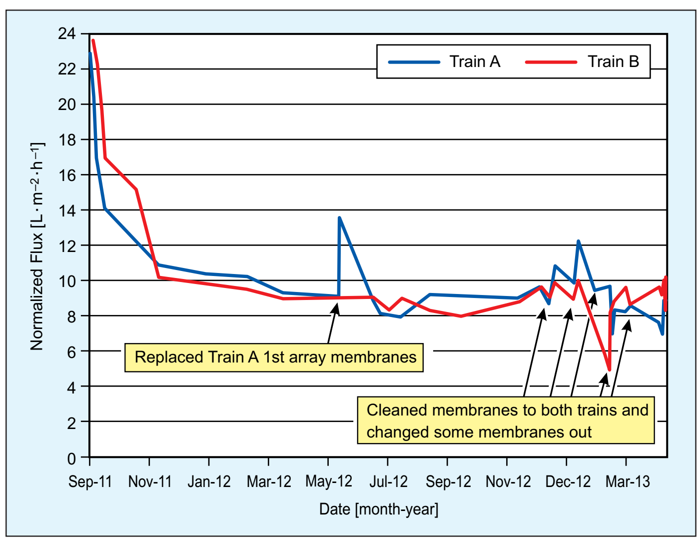

Figure 4:

RO permeate, normalized flux, September 2012 to April 2013 (no microbiocide treatment).

Following membrane replacement in September 2011, the flux for both trains declined from 23.8 LMH (14 GFD) to 10.2 LMH (6 GFD) after only two months. For the next 18 months, permeate flux was largely maintained within a range of 6.8 to 10.2 LMH (4 to 6 GFD). During the review period, no microbiocide treatment occurred.

Following membrane replacement in April 2013, flux declined rapidly the first two months, from 23.8 to 13.6 LMH (14 to 8 GFD) for Train A and from 23.8 to 17 LMH (14 to 10 GFD) for Train B. For the next 26 months, permeate flux was largely maintained within a range of 11.9 to 17 LMH (7 to 10 GFD). Microbiocide treatment measures were taken to feed a small amount of isothiazolin during operation (0.1 to 0.3 $mg \cdot L^{-1}$ as active ingredient), inject a moderate amount of isothiazolin for layup (10 $mg \cdot L^{-1}$ as active ingredient), and add DBNPA during membrane cleanings (50 $mg \cdot L^{-1}$ as active ingredient).

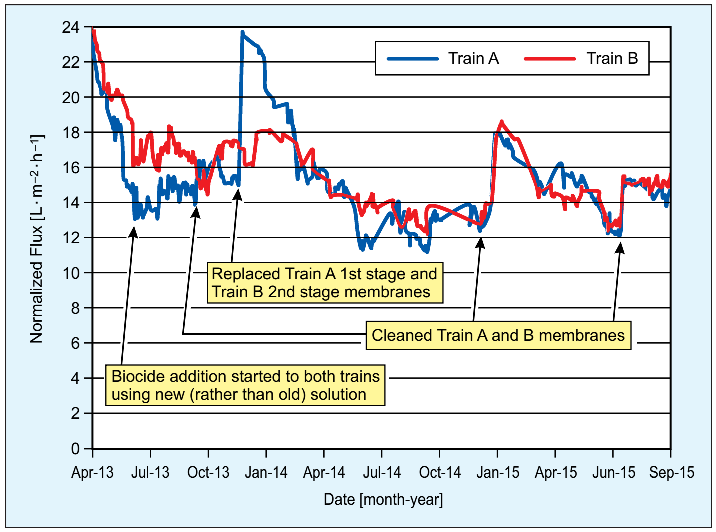

Figure 5:
RO permeate, normalized flux, April 2013 to October 2015 (with microbiocide treatment).

Since 3.4 LMH (2 GFD) represents 7.95 $m^3 \cdot h^{-1}$ (35 gpm) permeate flow, the cumulative volume is substantial in improving the efficiency of dissolved solids control in the cooling water.

Optimization of the application of the microbiocide treatment is still ongoing.

ACKNOWLEDGMENTS

Major contributors are Dan Abutin, the primary operator and troubleshooter for Mountainview's water treatment systems, Liza Aznar, who diligently collected much of the data, and Steven Johnson, the key decision maker for making process improvements at the plant.

REFERENCES

[1] *Water and Waste Water Treatment System, Training Manual for Mountainview Power Project Prepared for Bechtel Power Corporation*, **2005**. Aquatech International Corporation, Canonsburg, PA, U.S.A., Aquatech Project No. 01-1072.

[2] Williams, T. M., *PowerPlant Chemistry* **2007**, 9(1), 14.

[3] *Closed Cooling Water Chemistry Guideline, Revision 1*, **2004**. Electric Power Research Institute, Palo Alto, CA, U.S.A., EPRI 1007820.

[4] *RO Monitoring and Troubleshooting*, **2005**. Michael Bukay & Associates, Richmond, CA, U.S.A.

THE AUTHOR

Shawn S. Simmons (B.A., Biological Science with Chemistry minor, California State University at Fullerton, U.S.A.) has more than 35 years of experience in power plant chemistry and laboratory services. From 1996 to 2013 he served as the laboratory director of Southern California Edison's corporate water chemistry group. He is currently working for KAAM Group, Inc. His areas of expertise are water treatment in general, environmental/analytical chemistry, and online instrumentation.

CONTACT

Shawn S. Simmons
The KAAM Group, Inc.
Division Chemical Services
674 Aberdeen Drive
Placentia, CA 92870

E-mail: shawn.simmons@kaamgroup.com; divchem@att.net