The Canary in a Membrane Process: An Alternative for Scale Monitoring

Jennifer C. Roque, Jayapregasham Tharamapalan, and Steven J. Duranceau

The City of Sarasota (City) owns and operates its drinking water utilities and provides service to consumers within its service area. The City's water supply comes from two sources: the Verna Wellfield located 15 miles east of Sarasota, and the downtown brackish wellfield in the northwest area. The City of Sarasota Water Treatment Facility (WTF) is comprised of two primary water treatment processes: a spiral-wound reverse osmosis (RO) process, and an ion exchange (IX) process. The capacity of the WTF is 12 million gallons per day (mgd) from a combination of 4.5 mgd from the RO component of the water treatment facility, 5.2 mgd from the IX component of the water treatment facility, and 2.3 mgd of blended bypass water from the Verna Wellfield. Schematic of the water treatment facility is as shown in Figure 1.

This article reports the results of a study where a modified two-element membrane pressure vessel assembly was designed, fabricated, and installed within a full-scale reverse osmosis (RO) process so that it could be used to monitor process operational changes. The research evaluated the effectiveness of the assembly as an online monitoring device intended to detect scale formation conditions when connected to an operating RO process train. The assembly was referred to as a "canary" sentinel monitoring device (Canary). The Canary sentinel device was controlled using the normalized specific flux of the two membrane elements fed by a portion of the second-stage concentrate of one of the City's full-scale RO process skids.

This study was implemented to support the requirements of a larger University of Central Florida (UCF) research project ongoing at the City's WTF[1]. During the time-frame of this study, the City was in the process of eliminating their sulfuric acid feed from the pretreatment system of their existing 4.5 mgd RO membrane process. The City was motivated to eliminate its dependence on sulfuric acid to reduce operating costs, as well as reduce health and safety risks associated with the use of the acid as a pretreatment chemical. Because the City was concerned with secondary process impacts associated with acid elimination, additional measures were desired in order to protect the full-scale process.

Through a pilot study developed by UCF, the WTF performance was evaluated in terms of effective operation without the use of sulfuric acid pretreatment. The results of the pilot study deemed it favorable for the City to withdraw the acid feed to the RO system at a recovery rate of 75 percent, and the City has since taken a progressive approach in eliminating its acid feed at the full-scale level. The approach has been through small dosage reductions or increases of pH of the RO feedwater until the acid feed is completely eliminated and the feedwater is at average ambient pH level. The steps include pH steps of 5.8 (original pH with acid feed), 6.05, 6.3, 6.5, 6.7, 6.9 and 7.1 (ambient pH). During the acid elimination phase, scaling conditions may take place, as there is no longer a pH suppressant. Therefore, the implementation of a "canary" pressure vessel to the third RO process train was installed prior to the City's transition from the use of sulfuric acid pretreatment, and was intended to serve as a sentinel to protect the RO process. With an aim to detect scaling or fouling at an early stage, and to protect the full-scale process from operational changes, the Canary was monitored throughout the acid elimination phase by continuously evaluating the feed pressure, differential pressure, and normalized specific flux.

Jennifer C. Roque, E.I., is a civil engineer with Tetra Tech in Orlando. Jayapregasham Tharamapalan is a doctoral candidate, and Steven J. Duranceau is an associate professor and director of the Environmental Systems Engineering Institute, both at the University of Central Florida in Orlando. The basis for this article was Roque's master's thesis at the University.

Background

In RO membrane systems, between 65 to 80 percent of the feed water is converted to permeate water; consequently, the concentrate stream will contain a high amount of dissolved salts. Some of these soluble inorganic compounds, such as calcium carbonate, may supersaturate and precipitate in the membrane, causing the membrane to scale. The more common scalants are calcium carbonate, calcium fluoride, calcium sulfate, barium sulfate, strontium sulfate, and various silica complexes[2]. Iron and manganese are also considered to be foulants when oxidized. Scaling is highly undesirable due to increases in energy consumption and chemical cleaning frequency as a result of a compromise in the permeability of the membranes. A loss of permeability will cause an increase in head loss in the feed-brine channel, which will require a manual increase in the feed pressure in order to maintain the desired flux production rate. Unfortunately, in order to maintain the flux rate at a higher feed pressure, additional energy is required and an increase in chemical cleaning frequencies will result.

The conversion ratio or recovery of membrane production is limited by scaling. However, if scaling does not occur, then the recovery ratio can be increased. Producing permeate at a higher recovery will in turn reduce the amount of energy consumption, but will also create a concentrate stream that is more concentrated with dissolved salts. Thus, the recovery ratio of the membranes is limited by the risk of precipitation of sparingly soluble inorganic compounds[2].

In order to prevent scaling and/or fouling, most membrane plants incorporate several chemical feed systems, specifically a combination of an acid (such as sulfuric acid) and a scale inhibitor as pretreatment chemicals to the RO membranes. Although scaling may be controlled physically by lowering the RO process recovery so that the solubility product is not exceeded, it is more cost-effective to control scaling chemically[2,3]. Consequently, acid is primarily used to suppress the pH throughout the system in order to limit the risk of precipitation of calcium carbonate.

Precipitation Kinetics

Scale formation, particularly scale formation by calcium carbonate, can be estimated by the Langelier Saturation Index (LSI), or more accurately through the Ryznar Stability Index (RSI). Since the LSI calculation is based upon the thermodynamic solubility of calcium carbonate ($CaCO_3(s)$), it is only an indicator of whether precipitation or dissolution will occur. The LSI does not predict how much $CaCO_3(s)$ will precipitate, whereupon, the RSI is a mathematical manipulation of the LSI and attempts to quantify the relationship between calcium carbonate saturation state and scale formation[4]. It indicates that waters with high pH values will form more scale and have positive stability indexes, which is consistent with the fact that $CaCO_3(s)$ solubility decreases with an increase in pH value and an increase of temperature[4].

In practice, membrane and scale inhibitor suppliers recommend not to exceed the solubility product, or to apply an acid and/or scale inhibitor to avoid scaling of the supersaturated carbonate compounds on the membrane surface[5]. The reason being is that the addition of acid will reduce the precipitation of the alkaline scale-forming compounds such as calcium carbonate, and scale inhibitors contain active substances that can retard nucleation or growth of the formed crystals[5]. Although there may be a considerable amount of precipitation of sulfate based scales in the membrane concentrate, this does not always result in scaling due the presence of a scale inhibitor. The complexity of these situations emphasizes the need for a method able to predict accurately whether scaling will occur or not.

Conventional Monitoring Methods

In full-scale RO processes, the detection of scaling is usually noted by a decrease in the normalized specific flux or mass transfer coefficient (MTC) of the last stage of the membrane plant. It can also be measured by mass balance of the species with precipitation potential, but this method can be very arduous and costly, and suffers from inaccuracies relative to flow measurements.

Thus, several models have been developed in order to express the flux as the product of the solute mass transfer and a net pressure differential driving force. The American Standard for Testing Materials (ASTM) standard method, ASTM D 4516 Method – Standard Practice for Standardizing Reverse Osmosis Performance Data, has been commonly used in normalizing the permeate flow (Q_P) for the assessment of long-term RO membrane performance[6]. The Homogeneous Solution Diffusion Model (HSDM) approach was used in this study for the assessment of membrane productivity. This method considers solute concentration, permeate MTC, fluxes, recoveries, and temperatures, which are transferable to other water quality environments; however, these parameters are not included in the ASTM approach[7].

The net pressure differential driving force is described as the difference between the applied and osmotic pressure differentials:

(1) $$\Delta P_{net} = \Delta P - \Delta\pi = \left[\frac{P_F + P_C}{2} - P_P\right] - \left[\frac{\pi_F + \pi_C}{2} - \pi_P\right]$$

Where ΔP is the net transmembrane pressure and subscripts F, P, and C refer to the feed, permeate, and concentrate pressure, respectively. The osmotic pressure gradient is the difference between the feed-brine and the permeate osmotic pressure and can be estimated using the total dissolved solids (TDS) method shown in equation 2.

(2) $$\pi_T = K_{TDS} \times TDS\left(\frac{mg}{L}\right) = \frac{1psi}{100\frac{mg}{L}} \times \left[\frac{TDS_F + TDS_C}{2} - TDS_P\right]$$

The water flux is normally reported as a volumetric flux (gal/ft^2-d), which describes the water flux through the RO membranes. This is shown in equation 3 at standard conditions.

(3) $$SF_{ST} = Q_P / S.A.$$

The Q_P represents the permeate flow rate through the membrane stage, and S.A. is the total surface area of the membrane elements in each stage. Membrane performance declines due to fouling, scaling, and membrane aging. To evaluate the true decline in system performance due to fouling and aging, the actual flux data must be compared at standard conditions. Standard procedures have been established for normalizing RO performance[2,3,6]. These procedures incorporate the use of temperature correction factors (TCF). The TCF values are dependent on the type of device (spiral or hollow fiber) and on the membrane type (cellulose acetate, polyamide, composite) and should be obtained from the membrane manufacturer. If data from the manufacturer is unavailable, the relationship between the standard volumetric flux at actual conditions and the fluid viscosity is approximated by the following expression:

(4) $$SF_A = SF_{ST} / (1.03)^{T-25}$$

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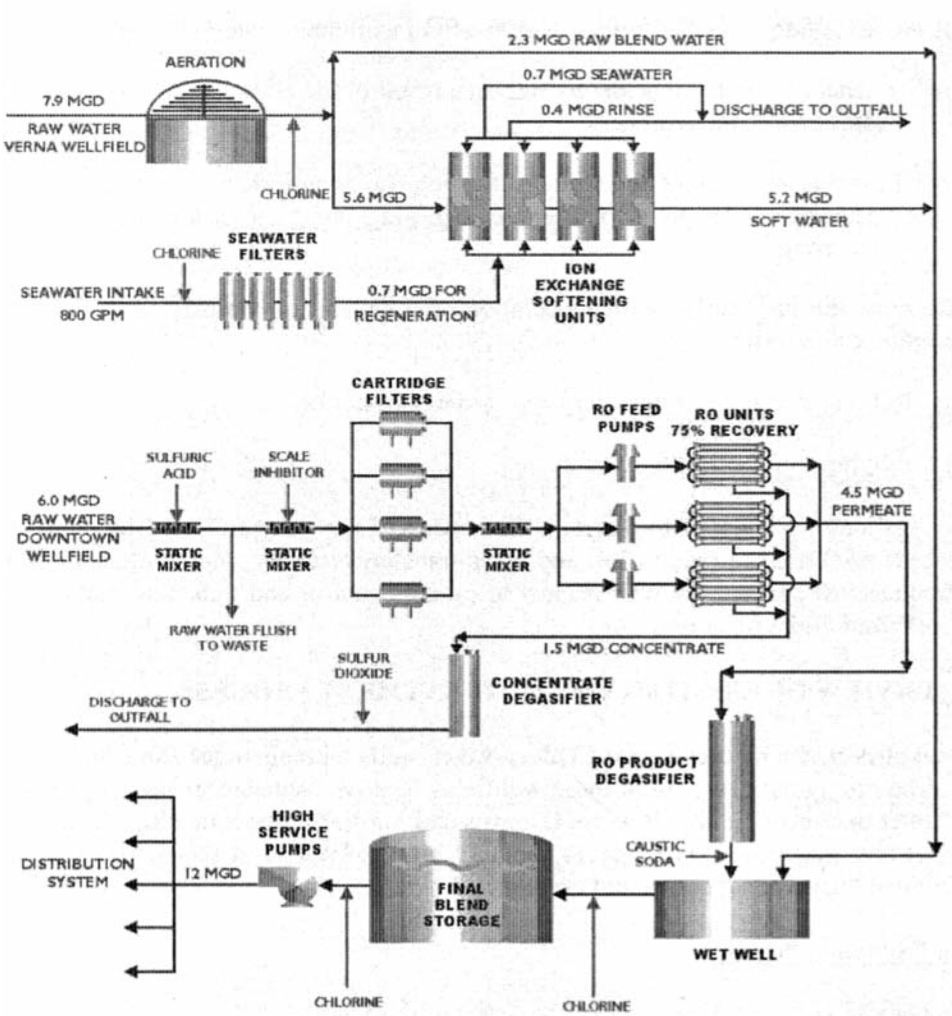

Figure 1. City of Sarasota Water Treatment Facility Schematic
(Courtesy of City of Sarasota)

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From this expression, the normalized specific flux (gal/ft^2-day-psi) through the membrane stage is calculated using:

(5) $$NSF_A = {SF_A}/{\Delta P_{net}}$$

Membrane productivity and salt passage were normalized for the experiments conducted in this work.

Water Treatment Facility Description and Layout

The City WTF is capable of producing 12 mgd of drinking water using a combination of treatment processes such as RO-IX and traditional groundwater treatment by tray aeration. However, the City is effectively limited to producing approximately 10 mgd of potable water by the Southwest Florida Water Management District (SWFWMD), which is based upon projected demand through the life of the permit[8]. Each treatment process contributes a part to the total production: the RO process contributing 4.5 mgd and the IX process contributing 7.5 mgd, of which 2.3 mgd is blended bypass water (schematic shown in Figure 1).

Reverse Osmosis Process

The City's RO system is supplied by a network of eight brackish wells, known as the Downtown Wellfield (part of the brackish Lower Hawthorn Aquifer), which is located in the northwest area of the City of Sarasota. The City is permitted to extract 6 mgd from these wells in order to produce 4.5 mgd permeate water. The wells pump into a common manifold of well piping network, which feeds into the RO system. The water quality averages approximately 2250 mg/L total dissolved solids content[1,9]. As observed from Figure 1, the raw water is first dosed with two pretreatment chemicals in order to mitigate the precipitation of sparingly soluble inorganic compounds such as calcium carbonate and strontium sulfate within the RO membranes (scaling). The first pretreatment chemical, sulfuric acid, is used to suppress the pH to roughly 5.8 in order to maintain the solubility of calcium carbonate. The acidified water is then treated with a scale inhibitor (2.0 mg/L of polyacrylic based Aquafeed®1025) to effectively and simultaneously control other types of scaling, particularly strontium sulfate scaling produced by the presence of strontium in the source water. The water is then passed through 1-micron polypropylene Fulflo® Honeycomb cartridge filters, prefiltering fine particulates that may damage or cause foulant accumulation on the membrane surfaces.

The chemically pretreated and filtered water is then pumped into the RO membrane pressure vessels at a pressure ranging anywhere from 150 to 200 psi. The arrangement of the pressure vessels are in three separate trains (numbered A through C), each designed to produce 1.5 mgd of permeate water from 2.0 mgd of raw water (a recovery of 75 percent). Each train is designed in a two-stage spiral-wound membrane process configuration with a 28:14 array using Hydranautics CPA-2 and ESPA-2 membranes in the first and second stage, respectively. Each pressure vessel contains six low-pressure membrane elements.

The RO product water is then sent through a degasifier system for the removal of excess hydrogen sulfide gases in the product water. The post-degasified water is then dosed with caustic soda for the recovery of alkalinity and for corrosion control since the RO permeate contains little to no alkalinity, resulting in an aggressive water that has a low buffering capacity.

Ion Exchange Process

The IX system is supplied by pumping raw water from the Verna Wellfield and is used for hardness removal. The city extracts 7.9 mgd from the Verna Wellfield, which is first aerated by a tray aeration system and then chlorinated before being dechlorinated and then treated by the IX system. Approximately 5.6 mgd is treated by the IX system and 2.3 mgd is bypassed before being blended with the IX soft water (5.2 mgd). The IX soft water is then blended with the raw water bypass and the post-degasified RO permeate water. This blended water is then chlorinated for disinfection purposes before being sent into the final blend storage tank for distribution to the public.

Testing Methods

A study to develop and observe a monitoring device, which detects scaling before it occurs in the second stage of the RO process, was developed by UCF in order to assess the impact of acid elimination on the membrane elements. The "canary" sentinel device measures the normalized specific flux of the two elements fed by a portion of the concentrate of the full-scale RO plant. Two membrane elements were used to provide a more accurate representation of the full-scale train, a configuration that had been previously used in a similar fashion at the City of Marco Island's reverse osmosis WTF[10]. It was reasoned that the first signs of scaling will take place on the two-element system due to a more concentrated feed flow and increased supersaturation. It was also anticipated that scaling will be detected more rapidly through the [two-membrane element device] than the full-scale plant because the normalized specific flux is measured over two elements as opposed to six.

Water Quality Assessment

The constituents listed below are evaluated on a weekly basis throughout the course of the study in order to provide profile characteristics of the RO process, the Canary, and the post-treatment process. Monitoring of these parameters was intended to help determine a deterioration of quality in the finished water and allowed a method to notify operators and management of any significant changes during and after the acid elimination phase.

- Temperature
- Calcium and Total hardness
- Potassium
- pH
- Total & Dissolved suspended solids
- Sodium
- Turbidity
- Sulfate and Sulfide
- Barium
- Conductivity
- Magnesium
- Manganese
- Total organic carbon
- Calcium
- Silica
- Total alkalinity
- Strontium
- Chloride

The frequency of monitoring varied in each pH reduction phase. A total system analysis was performed at least once during each phase.

Canary Monitoring

The normalized specific flux of the Canary is estimated through the monitoring of contributing parameters using an instrumentation panel installed aside of train C. The panel is shown in Figure 2a and portrays continuous measurements of the third-stage pressure and flow. The feed and concentrate pressure gauge is shown on the upper left and the permeate gauge and the sample ports are shown on the bottom left, indicating that the permeate and concentrate flows are on the right.

Data was collected from the Canary panel during each shift of the City operating staff for a total of three data collections per day. The parameters collected during each operations shift were the pressure, temperature, conductivity, pH and turbidity of the feed, permeate, and concentrate streams of the third

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stage. Flow data was also collected for both permeate and concentrate streams.

From the data collected by the staff, the normalized specific flux is monitored on a basis of run time (days). Other parameters needed for the determination of the specific flux are determined by weekly water quality analysis in the Environmental Systems Engineering Institute (ESEI) laboratories at UCF. For each pH change, total system analysis was performed on-site for parameters such as turbidity, conductivity, pH, temperature, and sulfide. Sulfide testing required special hosing attachments to the sample ports, which were discharged into Erlenmeyer flasks for complete submersion. This is practiced to eliminate the potential of stripping out the sulfide from the water before collection. This technique is shown in Figure 2 (b) and Figure 2 (c) for the Canary.

The normalized specific flux was observed for any significant decline. The differential pressure was also monitored as an alternative in order to better predict cleaning frequencies and provide opportunity to determine remaining membrane life. If the differential pressure did not revert to its original value from initial startup, this was considered to be an indication that irreversible fouling had occurred and membrane replacement may be required. The LSI and RSI were also monitored in comparison to the RO pilot study values.

Canary Installation

The Canary unit was first installed and commissioned on June 2, 2011. The configuration shown in Figure 3a demonstrates the piping, valves, and pumps necessary to attach the Canary to the second-stage concentrate flow. The pipe fittings are 1 ½ in. in diameter and the third-stage permeate stream is interconnected through a network to the previous RO pilot unit permeate stream.

In Figure 3b, the Canary is observed at the bottom of train C. The installation of the Canary may be at the top or bottom of the train since there is no observed hydraulic disparity. However, installing the Canary atop the train will create difficulty for membrane replacement or repair with respect to the operating staff. In order to install the Canary below the train, there must be a minimum height between the floor and the outer diameter of the pressure vessel for convenient access. As a result, an acceptable height will allow efficient installation or removal, as these both require an operator to manually bolt in the pressure vessels to the train.

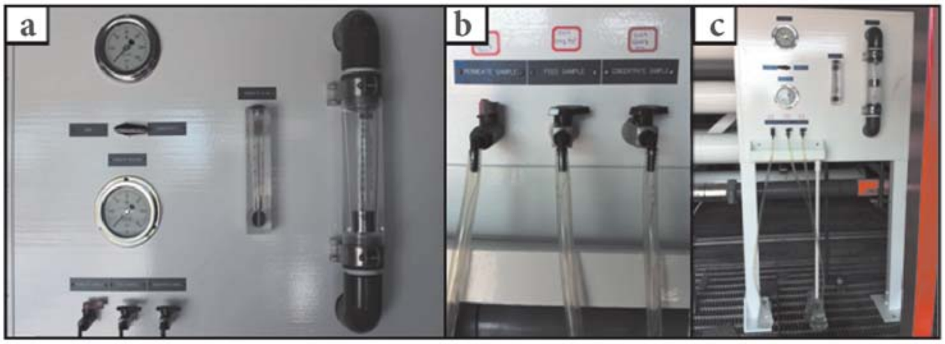

Figure 2. (a) Instrumentation Panel for Canary (b) Hose Attachments to Sample Ports (c) Canary Panel with Hoses Submerged in Erlenmeyer Flasks

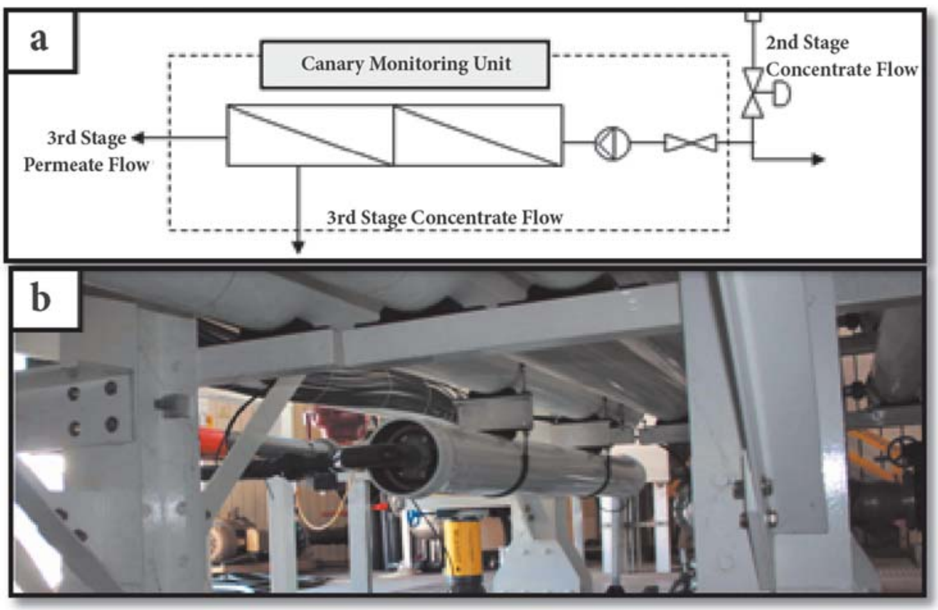

Figure 3. (a) Canary Monitor Connected to Second-Stage Concentrate (b) Canary Pressure Vessel Attachment to Train C

Results

Figure 4 presents the normalized specific flux of the two-membrane element Canary, as compared to the second-stage specific flux of the full-scale plant. It is noted that the second-stage specific flux does not experience any significant decrease during the acid elimination phase, remaining fairly consistent around a flux of 0.20 gal/ft^2-day-psi. However, the Canary device specific flux directly and continuously decreases throughout the pH changes. The Canary flux is operating at a rate of approximately four times the second-stage flux.

When the Canary was first commissioned, the feed pressure to the Canary, which is approximately equivalent to the second-stage pressure, was approximately 114 psi. The Canary concentrate pressure was 108 psi (shown in Figure 4). Between the pH increments of 6.05 and 6.7, the feed pressure to the Canary had increased to about 120 psi and the concentrate pressure to about 119 psi. The flow rates (shown in Figure 5) also experienced a decrease, where the permeate flow rate went from about 5.5 gpm to 4.5 gpm. The permeate flow did not restore to start-up conditions, possibly because conditions changed when the Canary had to be taken off-line on Sept. 16, 2011, to repair a leak that appeared on the Canary concentrate line. This activity may have altered the membrane and its appurtenances hydraulically. Both train C and the Canary were shut down for two hours prior to restart of operations. The stagnation could have caused a temporary decrease in the recovery rate that was observed, from 13.8 percent to 11.5 percent.

A chemical cleaning with a P303 low pH powder cleaner (Avista Technologies) was performed on Oct. 11, 2011, to assess whether the change in the Canary performance was due to precipitation of calcium carbonate. Ultimately, the cleaner did not restore the permeate production, which remained at approximately 4 gpm. In performing limiting salt calculations, it was observed that strontium sulfate could potentially be the limiting salt at all pH conditions between a pH of 5.8 and 7.2 (since the raw water contained a background strontium concentration of 23-26 mg/l). Therefore, an L811 high pH liquid cleaner was recommended for the potential removal of strontium sulfate accumulation on the two spiral-wound elements. This was completed on Oct. 13, 2011. A slight restoration in the flow rate and a decrease in the pressures can be observed; however, the flux rate had also been modified at this same time, so scale may or may not have been present.

The feed and concentrate pressure of the Canary were throttled down to about 116 psi and 110 psi, respectively, in order to accurately represent the original starting conditions. The permeate flow rate increased to about 4.5 gpm as shown in Figure 6 since the sulfate cleaner was applied. Another L811 sulfate clean was performed on the Canary on Nov. 1, 2011, to attempt productivity restoration. Only slight improvement was noted. Train C was cleaned on Dec. 14, 2011, and Dec. 15, 2011, for routine maintenance. It was determined that perhaps other causal factors for performance decline were present; hence, hydraulic modifications were investigated.

The LSI and RSI measurements taken from the Canary monitor are also used as estimators of the scaling potential of the water. By utilizing pH, TDS, calcium and alkalinity concentrations from the Canary, the LSI and RSI can be calculated. The LSI index is used by leading RO membrane manufacturers to guide the use of feedwater treatment chemicals[2,5]. In Table 1, it is noted that throughout the RO pilot study, the LSI became increasingly positive as expected with the acid elimination. This also indicates that there is an increased potential for $CaCO_3(s)$ precipitation. The RSI index also demonstrated a decrease in value, which indicates an increase in scale tendency. However, throughout the RO pilot study, no apparent scaling or fouling occurred as the RO pilot did not indicate a loss in performance (either in flow or in pressure). For the conditions under which this research was conducted, the full-scale process failed to show a loss in performance.

The Canary LSI and RSI values were estimated from water quality obtained in the study. The indices reflected similar trends; that is, both indices experienced an increasing positive LSI in relation to pH increase, and a decreasing RSI value. Overall, the use of LSI and RSI indices showed that calcium carbonate fouling potential on the Train C is probable, but

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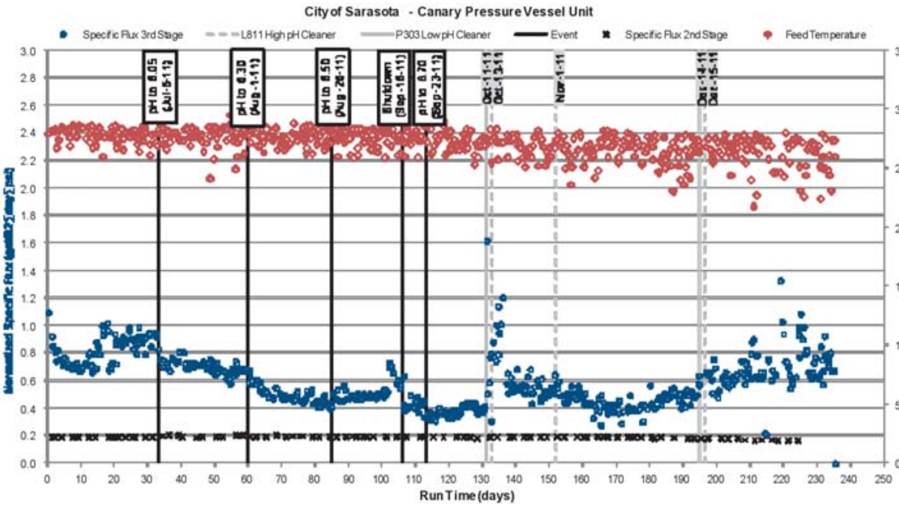

Figure 4. Normalized Specific Flux for Canary Monitoring Device

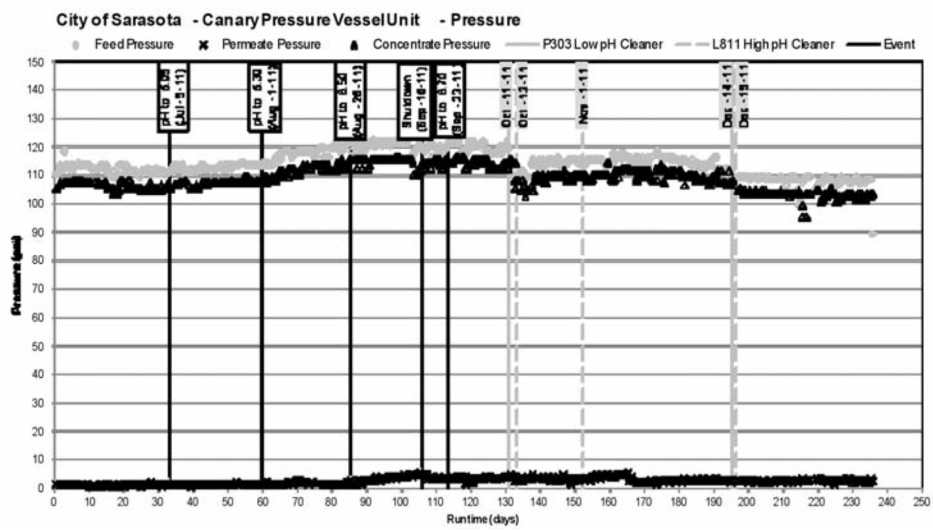

Figure 5. Canary (Third-Stage) Pressure as a Function of Time

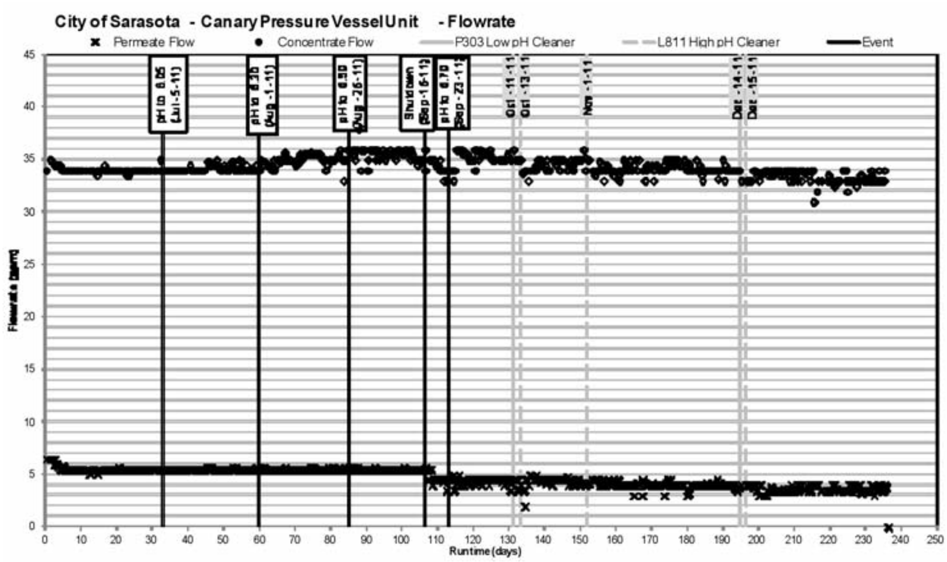

Figure 6. Canary (Third-Stage) Flowrate as a Function of Time

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it will be at a rate lower or comparable to that noted in the RO pilot and it can be cleaned using low pH cleaners. Based on results of the full-scale elimination of acid from its pretreatment operation, and taking into account the success of the pilot facility, the City eliminated acid from its brackish RO pretreatment system. Ongoing studies that focused on the secondary impacts of no-acid pretreatment with respect to post-treatment unit operations were also conducted but are not reported herein.

It was noted that the Canary was a sensitive monitoring device, and it was later determined that the Canary flux rate, as compared to the full-scale operation, was perhaps too conservative. Realistically, the flow rates on this unit were low (on the order of 5 gpm or less for the permeate stream). Hence, this lower flow rate could have explained the changes in performance that were experienced in this work. The Canary met its intended purpose, which was to serve as an early warning device; however, a sensitivity analysis showed that the Canary needed to be operated at a less conservative flux (flow) rate. After the Canary's flow rates were adjusted, and when restarted with reconditioned equipment, the device performed at the original conditions established for this project.

Summary of Findings

The cause of decline in the normalized specific flux in the Canary, which receives the second-stage concentrate as a feed, was most likely caused by hydraulic overload. A preliminary membrane autopsy report that had been made available at the time this article was developed indicated no evidence of scale. It was noted that there was no loss in performance in the second stage of the RO process; hence, it is more likely that due to the fact that the Canary operated at a higher than normal flux rate to monitor under worst-case scale conditions, the changes observed within the device were hydraulically induced and not due to scale formation. It was determined that the Canary flux rate should be established no more than 15 percent above baseline conditions, else erroneous operating data would be recorded. This demonstrated the usefulness of the Canary due to its sensitivity to changes in the RO process operation.

The Canary monitor was therefore deemed useful to serve as a monitoring device that could allow for the detection of potential scale formation without interruption of the full-scale process operation, a belief that had been supported by research where the monitoring of scale within membrane processes had been previously reported[10,11]. Based on the results of the work conducted in this study, it was realized that the Canary assembly would serve as a means to trigger chemical cleaning procedures through the observation of changes in the normalized specific flux. This work demonstrates that the implementation of monitoring devices that have the ability to provide operations and engineering staff real-time information about potential scaling conditions within the membrane elements is a useful endeavor.

Acknowledgements

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Table 1. Comparison of RSI and LSI Values between Canary Device and Reverse Osmosis Plant and Pilot Studies[1]

Canary Pressure Vessel														
pH	5.8		6.05		6.3		6.5		6.7		6.9		7.1	
	Feed	Conc.	Feed	Conc.	Feed	Conc.	Feed	Conc.	Feed	Conc.	Feed	Conc.	Feed	Conc.
LSI	0.32	0.3	0.54	0.77	0.98	1.11	1.03	1.2	1.37	1.5	1.19	1.25	1.46	1.55
RSI	6.0	5.9	5.6	5.2	5.0	4.8	4.9	4.6	4.5	4.3	4.4	4.3	4.1	3.8
Train C - Reverse Osmosis Plant														
pH	5.8		6.05		6.3		6.5		6.7		6.9		7.1	
	Feed	Conc.	Feed	Conc.	Feed	Conc.	Feed	Conc.	Feed	Conc.	Feed	Conc.	Feed	Conc.
LSI	1.35	0.03	-1.08	0.52	-0.61	0.91	-0.5	0.99	-0.2	1.23	-0.77	0.81	0.12	1.7
RSI	8.7	6.3	8.3	5.6	7.7	5.1	7.6	5	7.2	4.7	8.0	5.7	6.8	4.1
Reverse Osmosis Pilot														
pH	5.8				6.3		6.6						7.1	
	Feed	Conc.			Feed	Conc.	Feed	Conc.					Feed	Conc.
LSI	1.37	0.06			-0.57	1.00	-0.13	1.25					0.38	1.61
RSI	8.6	6.2			7.6	5.0	7.1	4.7					6.4	4.2

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