

# Piloting Study on Biofouling Control of Reverse Osmosis System in Steel Mill Wastewater Reuse

Cheng Yang<sup>1</sup>, Tina Arrowood<sup>2</sup> and Jon Johnson<sup>2</sup>

1. Dow Water and Process Solutions, The Dow Chemical (China) Investment Co., Ltd., Shanghai 201203, China

2. Dow Water and Process Solutions, The Dow Chemical Company, Minneapolis 55439, USA

**Abstract:** The biofouling of RO (Reverse Osmosis) system is one of the most common problems in highly contaminated demineralization and wastewater reuse system. The biological fouling occurs due to the bacteria growth and proliferation under nutritive environment, resulting in a dramatic increase of dP (differential pressure) in the RO system, which requires frequent system shutdown for cleaning. This paper discusses the effectiveness of low-dP RO element and periodic flushing on the biofouling scheme of industrial steel mill wastewater reuse system. The low-dP RO element is able to provide low RO system dP, which is expressed to be lower biofouling starting point during the industrial system operation. However, the periodic flushing utilizes fresh water to remove the biofilm deposit along with feed channel. The long term operation performance demonstrated strong caustic is effective in removing the biofilm and recovering RO system performance. It is experimentally validated that, in the case of a high biofouling environment, low-dP RO element and periodic flushing is able to extend the cleaning cycles by 36.6% and 11.4%, respectively. Meanwhile, a joint application of both methods is proven to improve the biofouling control and extend the cleaning cycle by 62.5%, as compared to standard RO technology.

**Key words:** RO (Reverse Osmosis), biofouling, membrane, dP (Differential Pressure), wastewater reuse.

## 1. Introduction

As water scarcity and water contamination increases around the world [1], RO (Reverse Osmosis) technology is widely used to treat wastewater for reuse in industries such as steel mills, petrochemicals, coal to chemicals, textiles and municipal corporations, as one of the core water purification technologies [2-5]. However, RO systems are always at the risk of fouling in wastewater or contaminated surface water. Serious fouling is due to the high level of organics, which is often expressed in terms of COD (Chemical Oxygen Demand). The performance of an RO system is severely deteriorated by an increase in system dP (Differential Pressure) or a drop in permeate flow due to RO element fouling [6]. To recover the membrane system performance, operators need to shut down the

RO train and start a CIP (Clean-In-Place) process, using caustic and/or acidic solutions to remove the foulant. Frequent shutdowns impact the water treatment system productivity, while CIP consumes chemicals, manpower and clean water. Frequent use of extreme pH conditions during a CIP also reduces the expected membrane lifetime [7, 8].

The contaminants in different water sources vary, resulting in different types of fouling: particle fouling, inorganic scaling, colloidal fouling, organic fouling and biofouling [9]. Due to the growth of microorganisms, biofouling is one of the major types of fouling found in the operation of an RO system [10-12]. For example, about 70% of the seawater RO installations at Middle East [7] and almost 75% of more than 600 autopsied RO membranes all over world [13] suffer biological and organic fouling. Although non-oxidative biocides are often applied with continuous or shock dosage, biofouling is still the most problematic due to the quick growth rate of

---

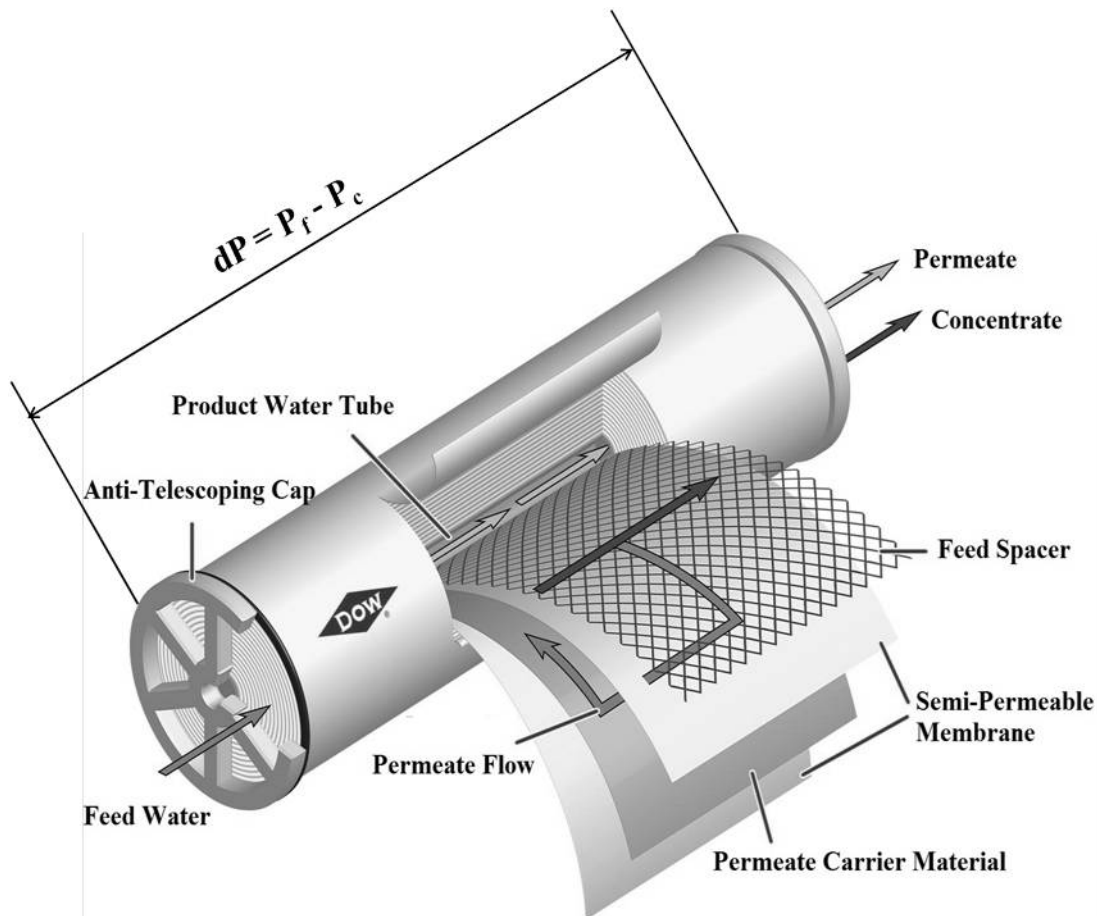
**Corresponding author:** Cheng Yang, Ph.D., research fields: membrane science, wastewater treatment, minimal liquid discharge and processing liquid separations.

bacteria. Moreover, some studies show that bacteria can develop resistance to biocides after treatment with non-oxidative biocides [14, 15].

The configuration of a typical industrial RO element is depicted in Fig. 1. The RO membrane is spiral wounded around the central permeate tube. The feed and permeate sides of the RO membrane are segregated by the feed spacer and the permeate spacer to provide water flow distribution. Both scientific research and RO elements autopsies from industrial practice indicate that the greatest harm caused by biofouling is that the biofilm “jams” the feed spacer and surrounding flow channel of the element, resulting in a rapid increase in the feed-to-concentrate dP, leading to the system shutdown for cleaning purposes [14, 16, 17].

In addition to a non-oxidative biocides dosage, low-dP RO and periodic flushing may also helpful in extending the time interval between CIPs. The latest

innovation in fouling resistant RO designs [18] uses adhesion resistant membrane chemistry and low dP module designs to more effectively manage the fouling while not sacrificing the flux and rejection performance of the RO membrane. Periodic flushing has been shown in lab studies to strip portions of weakly adhered biofilm from the feed spacer fiber [19] and has also be modeled using fluid dynamics [20]. Understanding the synergy of using both low-dP RO elements and periodic flushing operating discipline has yet to be explored. This paper investigates the combined impact of the two methods on biofouling control in an RO system treating steel mill wastewater for reuse in an industrial plant setting. Operational experience gained from this pilot study can be applied to other large wastewater reuse and demineralization systems for treating challenging water prone to biofouling.



**Fig. 1** RO element construction and dP description.

## 2. Materials and Methods

### 2.1 Raw Water Quality

The raw water source was steel mill wastewater, including the wastewater from steel smelting, rolling, flushing and cooling tower blow down, all collected in the equalization basin. The pretreatment steps of steel mill wastewater included a high speed clarifier, V-type filter, multi-media filter and ultrafiltration. The raw steel mill wastewater was first dosed with PAC (Poly Aluminum Chloride) and lime as coagulants; it then experienced sedimentation and filtration to remove colloids and suspended solids. SDI (Silt Density Index) [21] of pre-treated wastewater was lower than 5. The wastewater was then transferred to the RO system with 2,000 m<sup>3</sup>/h volumetric flow for demineralization, as boiler makeup water and steel manufacturing process water. The RO feed water quality was stabilized to 500-900 mg/L TDS (Total Dissolved Solid), 40-60 mg/L total COD (Chemical Oxygen Demand), and 19 °C-32 °C (water temperature fluctuates according to seasonal change).

### 2.2 Materials

The RO elements were acquired from Dow Water & Process Solutions (MN, USA). The FILMTEC™ BW30FR-400/34 and FILMTEC™ FORTILIFE™ CR100 type of elements were manufactured at DOW FILMTEC plant (MN, USA), and were used as the standard fouling resistant RO element and a model of the low-dP design, respectively. All the meters and sensors were purchased from Endress and Hauser AG, which is a Swiss-based instrumentation and process

automation company. The 10W40 electromagnetic flow meters and Condumax CLS21D digital conductivity sensors were selected for RO feed and concentrate water, whereas the Prowirl 72F40 vortex flow meters and Condumax CLS19D analog conductivity sensors were applied to RO permeate water, according to the supplier's product selection guideline [22]. The Deltabar PMD75 dP transmitter with piezo-resistive sensor and welded metallic membrane was used to measure the dP in each RO system. The FTNORM (Normalization of Membrane System) software by Dow Water & Process Solutions (MN, USA) was used to analyze and normalize the collected data [23]. The sodium meta-bisulfate Na<sub>2</sub>S<sub>2</sub>O<sub>5</sub> and sodium dodecyl sulfonate C<sub>12</sub>H<sub>25</sub> is purchased from Sinopharm chemical reagent corporation (Shanghai, China) as chemical grade. PermaTreat 191 (PC-191) is purchased from NaICO water (MN, USA) as antiscalent.

### 2.3 Methods

The piloting study was conducted at the wastewater reuse plant in a steel mill. The standard fouling resistant RO elements and low-dP RO elements were installed in two RO systems running in parallel, as shown in Fig. 2. Both RO systems had a single stage, which was demonstrative because biofouling tends to localize in the lead elements of the first stage of an RO system [14, 24-26]. Both RO systems were operated under the same feed water composition, system flux and system recovery, according to the design guidelines of the RO system for wastewater reuse [27]. During normal operation, periodic flushing was conducted at least once per day using RO

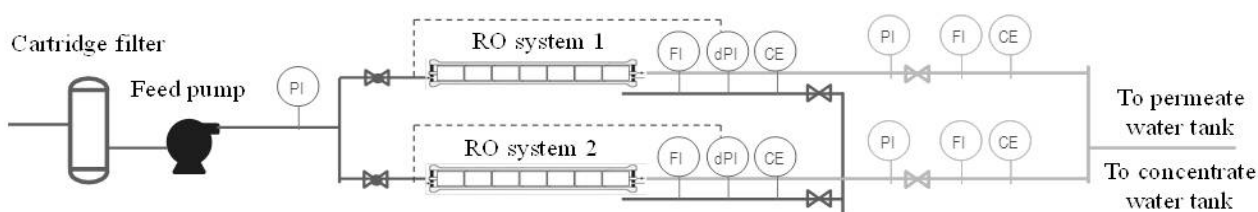


Fig. 2 Pilot system layout in steel mill wastewater reuse plant (PI—Pressure Sensor Indicator, FI—Flow Meter Indicator, dPI—differential Pressure Indicator, CE—Conductivity Meter).

**Table 1** Operation parameters of clean-in-place in steel mill wastewater reuse pilot.

Steps	Protocol
1	pH: 13.5 by NaOH, 0.035% SDS (Sodium Dodecyl Sulfonate), 35 °C circulation for 4 hours;
2	pH: 13.5 by NaOH, 0.035% SDS, 35 °C soaking for 12 hours;
3	pH: 13.5 by NaOH, 0.035% SDS, 35 °C circulation for 4 hours, RO permeate flushing for 10 mins;
4	pH: 1 by HCl, 25 °C; circulation for 1 hour, RO permeate flushing for 10 mins.

permeate water. The flush lasted 10 minutes, with a linear flushing velocity of 0.1 m/s for each pressure vessel. To investigate the effects of only the element design and periodic flushing on biofouling, no biocides were dosed into the feed water, only reducing agent (10 mg/L sodium meta-bisulfate) and antiscalant (3 mg/L) were added. When the normalized feed-to-concentrate dP of the first stage RO reached 0.3 MPa, the system was shut down. Chemical cleaning was then conducted to remove the biofilm, according to the description in Table 1.

### 3. Results and Discussion

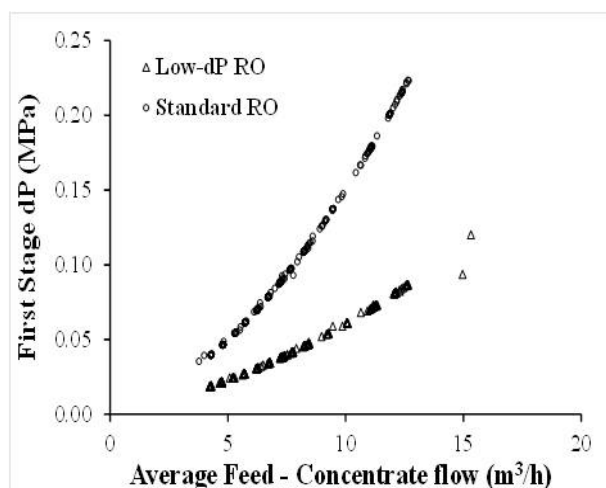
#### 3.1 Static dP

Upon the initial installation of the RO elements into the system, prior to the normal operation, the static dP was tested under different average feed-to-concentrate flow rates. The pre-treated steel mill wastewater was used for static dP testing at 0.75 MPa feed pressure and 25 °C ambient temperature. The first stage RO is tested with seven RO elements installed in-series. As shown in Fig. 3, the first stage dP for low-dP RO element is about 50% lower than that of standard fouling-resistant RO element. The advantage is obviously more significant when the average feed-to-concentrate flow rate is increased. The low initial dP supports a more uniform distribution of membrane flux in the RO system, and also provides a lower initial dP when biofouling starts up. It could be thus predicted that longer time is needed to reach the same CIP trigger value, due to a delay in both biofilm initiation and reaching the CIP threshold value of dP = 0.3 MPa.

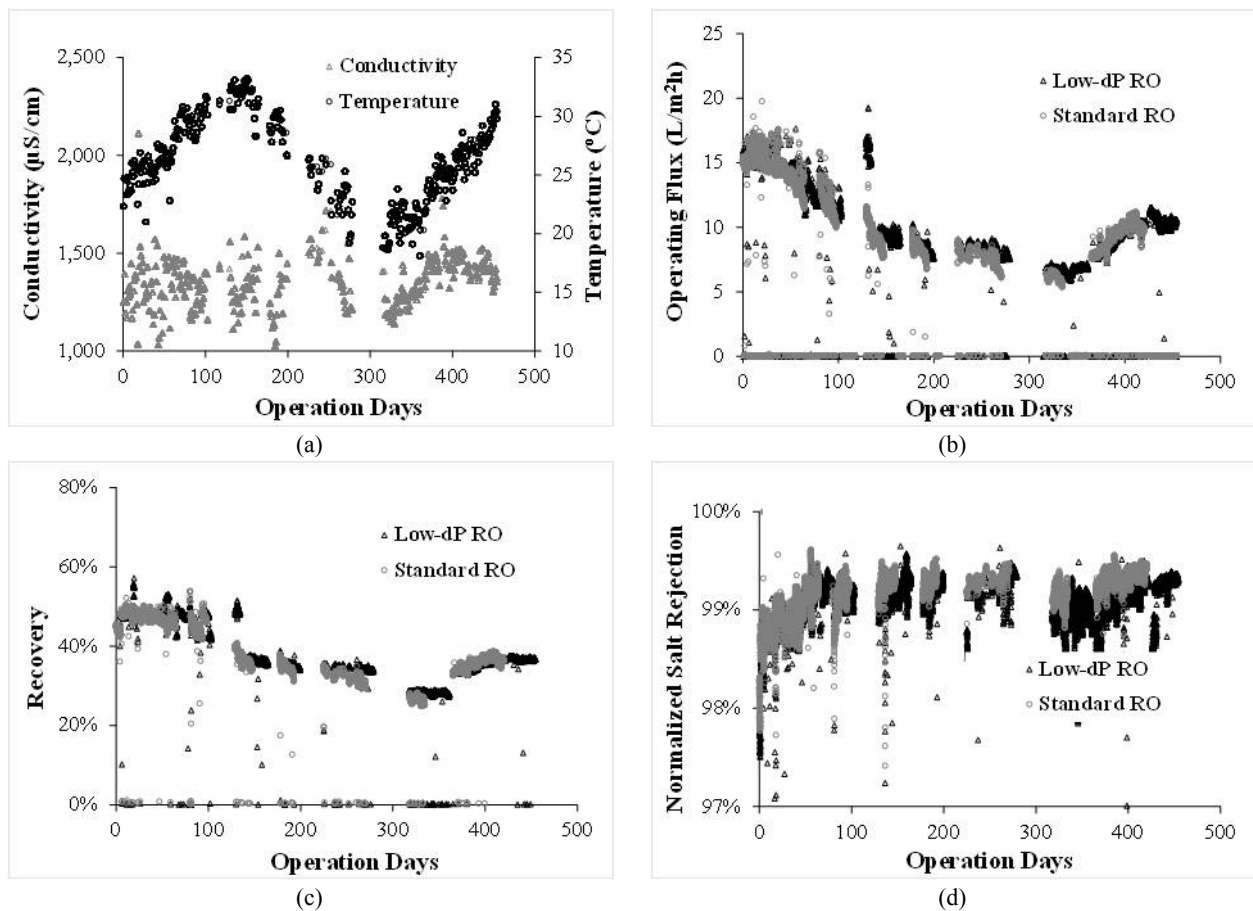
#### 3.2 Long Term Operation Performance

As shown in Fig. 4(A), since the steel mill

wastewater composition exhibited daily fluctuations and feed conductivity was recorded on a daily basis, the feed water conductivity varied in the range of 1,000-1,500  $\mu\text{S}/\text{cm}$  during the 450-days' operation. The water temperature varied seasonally from 19-31 °C. Figs. 4(B) and 4(C) displays the operating flux and recovery, which were held the same for low-dP RO and standard fouling-resistant RO. The operating flux was 8-15  $\text{L}/(\text{m}^2\text{h})$ , and the first stage recovery was 35%-45%. The long term normalized salt rejection of the two pressure vessels is shown in Fig. 4(D). Initially, the salt rejection of the two RO pressure vessels was around 98.5%, but the normalized rejection increased to 99% and then stabilized about 50-60 days after commissioning. Noteworthy is that six aggressive chemical cleanings were conducted during the 450-days' operation. Despite the use of aggressive caustic cleaning at pH 13.5 and 35 °C temperature, the salt rejection performance was not impacted, whereas the biofilm was removed to recover the RO system performance.



**Fig. 3** First stage dP of low-dP RO (FORTILIFE™ CR100) and standard fouling-resistant RO (FILMTEC™ BW30FR-400/34).



**Fig. 4** The feed water conductivity and temperature (A), operating flux (B), system recovery (C) and normalized system salt rejection (D) of the side-by-side comparison of low-dP RO (FORTILIFE™ CR100) and standard fouling-resistant RO (BW30FR-400/34).

### 3.3 Normalized dP

The normalized dP directly indicates the severity of biofouling. As shown in Fig. 5, the biofouling process was not strongly manifested during the first 30 days after installing fresh RO elements, but was intensified in the followed 30 days, as shown by a sharp increase in the normalized dP. When the normalized dP reached the CIP threshold of 0.3 MPa, the corresponding RO system was isolated, while the comparison system was allowed to continue to operate till the normalized dP also reached the 0.3 MPa CIP threshold. Then, a CIP was conducted for both systems together to remove biofouling and recover membrane performance. It was found that low-dP RO repeatedly provided extended operating time during each fouling cycle in the 450-days' operation,

covering all four seasons of the year.

Table 2 summarizes the cycle interval and the cleaning frequency per year, respectively. The CIP frequency reduction by low-dP RO, as compared to standard fouling-resistant RO, is also listed in the last column. As shown in Table 2, although the feed temperature changed seasonally, the CIP cycles of both RO systems ranged from 10 to 50 days due to the temperature dependence of bacteria growth rate. The most important finding was that the implementation of low-dP RO made it possible to reduce the CIP frequency by 35.5% on the average (ranged from 16% to 59%) and elevated the average operating cycle time from 18.9 to 31 days.

### 3.4 Periodic Flushing

During the daily operation, a continuous increase in

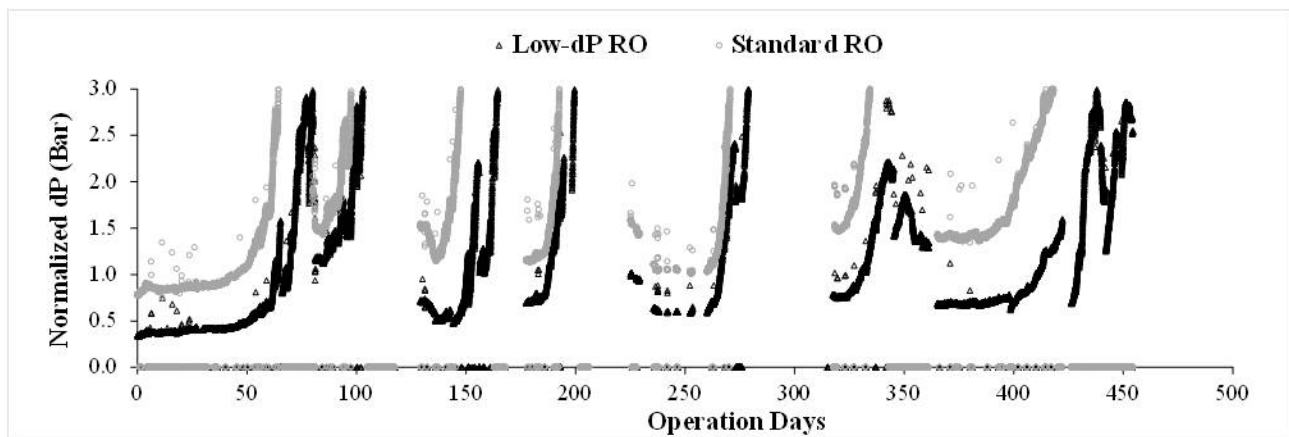


Fig. 5 The dP scheme of the side-by-side comparison of low-dP RO (FORTILIFE™ CR100) and standard fouling-resistant RO (BW30FR-400/34).

Table 2 CIP frequency reduction of low-dP RO element.

	Operating cycle, days		Annual CIP frequency		CIP frequency reduction
	Standard fouling-resistant RO	Low-dP RO	Standard fouling-resistant RO	Low-dP RO	
1	34.4	49.9	10.6	7.3	31%
2	17.6	22.8	20.8	16.0	23%
3	18.3	35.2	19.9	10.4	48%
4	15.3	18.2	23.9	20.1	16%
5	10.6	16.5	34.4	22.1	36%
6	17.0	41.5	21.5	8.8	59%
Average	18.9	31	21.8	14.1	35.5%

dP value was observed at the first-stage of RO system if operated with no interruption or flushing. However, if periodic flushing of the system with RO permeate water was conducted with a certain frequency, the system dP dropped after the flushing. This can be attributed to the fact that the disruption by RO permeate flushing caused a portion of weakly adhered biofilm colonies to be flushed away, reducing blockage within feed channel and improving the system dP when the normal operation was resumed.

Fig. 6 demonstrates the potential impact of flushing during the fouling period prior to two typical CIP cycles (namely, the first CIP cycle is CIP1 and the third CIP cycle is CIP3). The recorded data during operation with normal flushing was first plotted, and then compared against a mathematically processed version of the same data wherein the “dips” in dP due to flushing were eliminated. Each time a dip caused by the flushing sequence was removed, the data was

transformed by moving the remaining portion of the fouling curve to close the resulting time gap. By this approach, the dP curve for the hypothetical “no flushing” case was approximated. It more closely resembles a uniform exponential increase. Flushing appears to interrupt the microorganism colonies, and changes the exponential growth environment, so the dP scheme is expressed as multiple exponential increasing curves in the “with flushing” case. Considering that the biofouling in this piloting study was developed at 10 m<sup>3</sup>/h feed flow rate for an individual pressure vessel, the linear cross flow velocity within the feed channel of the first RO element was about 0.13 m/s. The results correspond well with Vrouwenvelder, J. S. et al’s work [19] on the impact of flushing on biofouling morphology, which was developed at lower flow velocity (0.06 m/s).

Fig. 7 shows the statistical average summary for the total six CIP cycles. Periodic flushing can effectively

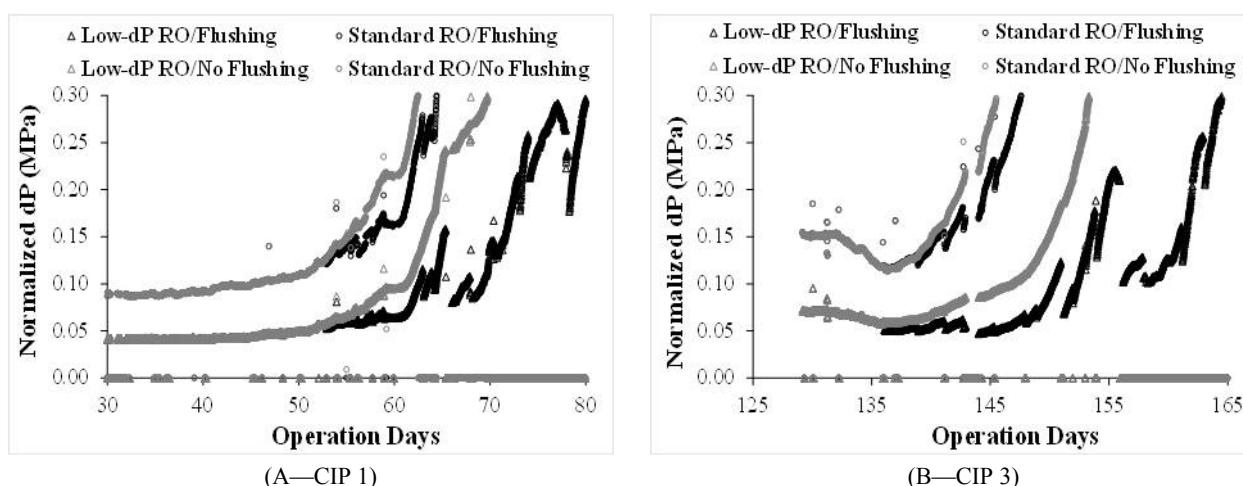


Fig. 6 The effect of regular flushing on the dP scheme of low-dP RO (FORTILIFE™ CR100) and standard fouling-resistant RO (BW30FR-400/34).

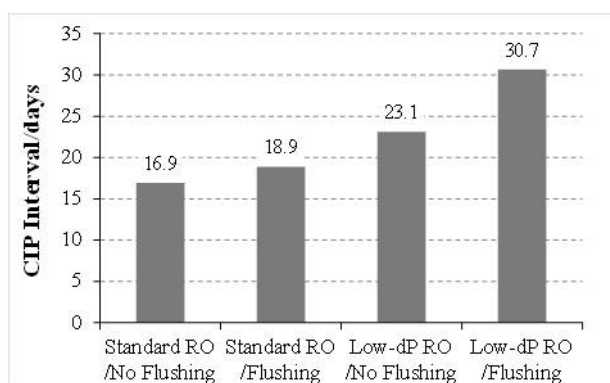


Fig. 7 The average CIP intervals for the six investigated CIP cycles.

extend the CIP cycle of the corresponding RO systems. The data suggests that periodic flushing of the low-dP RO element had a greater impact on extending the time to reach dP = 0.3 MPa CIP threshold than with standard fouling-resistant RO element. For the standard fouling-resistant and low-dP RO elements, the periodic flushing extended the CIP cycle by 11.4% and 32.6%, respectively.

In addition, when the system did not have periodic flushing, the low-dP RO element was still able to extend the CIP cycle from 16.9 to 23.1 days compared to the standard fouling-resistant RO element, an increase of about 36.6%. When periodic flushing was conducted in the system, the low-dP RO element was able to extend the CIP cycle even more, from 18.9 to 30.7 days, an increase of about 62.5%. This

corresponds to a 35.5% decrease in cleaning frequency, as described in Table 2.

#### 4. Conclusion

Biofouling is one of the most critical challenges for the application of RO technology in highly contaminated surface water and wastewater reuse systems. This paper investigates the application of low-dP RO element and periodic flushing to delay biofouling progress, thus increasing the chemical cleaning cycle time and decrease the cleaning frequency. The 450-days piloting study demonstrated that both methods could effectively extend the cleaning cycle in a high biofouling environment. The optimal result was obtained by combining the two methods, and the average CIP cycle was increased from 16.9 days to 30.7 days. The results obtained in this study suggest the proposed scheme is useful for wider industrial implementation.

#### Acknowledgement

The authors sincerely thank colleagues at Dow Water & Process Solution on providing the commercialized FILMTEC™ BW30FR-400/34 and FILMTEC™ FORTILIFE™ CR100 RO elements for the piloting trial. The authors also sincerely thank Hongshu Liang from Tangshan Steel Mill and Ning

Zhang, Liang Yue from Jining Tongrun water Co. Ltd. for their discussion and help on the pilot experiment design.

### Conflict of Interest

The authors declare that they have no conflict of interest.

### References

- [1] Shannon, M. A., Bohn P. W., Elimelech M., Elimelech, M., Georgiadis, J. G., Mariñas, B. J., et al. 2008. "Science and Technology for Water Purification in the Coming Decades." *Nature* 452 (7185): 301-10.
- [2] Dialynas E., and Diamadopoulos, E. 2009. "Integration of a Membrane Bioreactor Coupled with Reverse Osmosis for Advanced Treatment of Municipal Wastewater." *Desalination* 238 (1-3): 302-11.
- [3] Lee, J. W., Kwon, T. O., and Moon, I. S. 2005. "Performance of Polyamide Reverse Osmosis Membranes for Steel Wastewater Reuse." *Desalination* 177 (1-3): 69-82.
- [4] Madaeni, S. S., and Eslamifard, M. R. 2010. "Recycle Unit Wastewater Treatment in Petrochemical Complex Using Reverse Osmosis Process." *J. Hazard. Mater.* 174: 404-9.
- [5] Gupta, V. K., Khamparia, S., Tyagi, I., Jaspal, D., and Malviya, A. 2015. "Decolorization of Mixture of Dyes: A Critical Review." *Global J. Environ. Sci. Manage.* 1: 71-94.
- [6] Kang, G. D., and Cao, Y. M. 2012. "Development of Antifouling Reverse Osmosis Membranes for Water Treatment: A Review." *Water Res.* 46: 584-600.
- [7] Matin, A., Khan, Z., Zaidi, S. M. J. and Boyce, M. C. 2011. "Biofouling in Reverse Osmosis Membranes for Seawater Desalination: Phenomena and Prevention." *Desalination* 281: 1-16.
- [8] Nagaraja, N., Skillman, L., Xie, Z. W., Jiang, S., Ho, G., and Li, D. 2017. "Investigation of Compounds that Degrade Biofilm Polysaccharides on Reverse Osmosis Membranes from a Full Scale Desalination Plant to Alleviate Biofouling." *Desalination* 403: 88-96.
- [9] Fritzmann, C., Lowenberg, J., Wintgens, T., and Melin, T. 2007. "State-of-the-Art of Reverse Osmosis Desalination." *Desalination* 216: 1-76.
- [10] Li, C., Yang, Y., Ding, S. Y. and Hou, L. A. 2016. "Dynamics of Biofouling Development on the Conditioned Membrane and Its Relationship with Membrane Performance." *J. Mem. Sci.* 514: 264-73.
- [11] Liu, C. H., Faria, A. F., Ma, J. and Elimelech, M. 2017. "Mitigation of Biofilm Development on Thin-Film Composite Membranes Functionalized with Zwitterionic Polymers and Silver Nanoparticles." *Environ. Sci. Technol.* 51: 182-91.
- [12] Johnson, T. A., Rehak, E. A., Sahu, S. P., Ladner, D. A., and Cates, E. L. 2016. "Bacteria Inactivation via X-ray-Induced UVC Radioluminescence: Toward in Situ Biofouling Prevention in Membrane Modules." *Environ. Sci. Technol.* 50: 11912-21.
- [13] Nuria, P. G., Fernando, D. V., Stephen, C., Armstrong, M., Wilson, R., and Fazel, M. 2013. "A Study of the Physical and Chemical Damage on Reverse Osmosis Membranes Detected by Autopsies." Genesys International Ltd. Accessed December 27, 2017. <http://www.genesysro.com/ro-membrane-cleaning-chemicals-free-research-docs.php>.
- [14] Baker, J. S., and Dudley, L. Y. 1998. "Biofouling in Membrane Systems-A Review." *Desalination* 118: 81-90.
- [15] Alvarado, C., Farris, K., and Kilduff, J. 2016. "Membrane Fouling, Modelling and Recent Developments for Mitigation." In *Emerging Membrane Technology for Sustainable Water Treatment*, edited by Singh, R. and Hankins, N. Amsterdam: Elsevier.
- [16] Vrouwenvelder, J. S., Van Paassen, J. A. M., Wessels, L. P., Van Dam, A. F., and Bakker, S. M. 2006. "The Membrane Fouling Simulator: A Practical Tool for Fouling Prediction and Control." *J. Mem. Sci.* 281 (1): 316-24.
- [17] Radu, A. I., van Steen, M. S. H., Vrouwenvelder J. S. Van Loosdrecht, M. C. M., and Picioreanu, C. 2014. "Spacer Geometry and Particle Deposition in Spiral Wound Membrane Feed Channels." *Water Res.* 64: 160-76.
- [18] Dow Chemical. 2016. "DOW FILMTEC™ FORTILIFE™ CR100 Element." Accessed December 27, 2017. <http://www.dow.com/en-us/markets-and-solutions/products/DOWFILMTECFORTILIFE/DOWFILMTECFORTILIFE/CR100Element>.
- [19] Vrouwenvelder, J. S., Buijter, J., Riviere, M., Van der Meer, W. G. J., Van Loosdrecht, M. C. M., and Kruithof, J. C. 2010. "Impact of Flow Regime on Pressure Drop Increase and Biomass Accumulation and Morphology in Membrane Systems." *Water Res.* 44 (3): 689-702.
- [20] Radu, A. I., Vrouwenvelder, J. S., Van Loosdrecht, M. C. M., and Picioreanu, C. 2012. "Effect of Flow Velocity, Substrate Concentration and Hydraulic Cleaning on Biofouling of Reverse Osmosis Feed Channels." *Chem. Eng. J.* 188: 30-9.
- [21] Dow Chemical. 2017. "FILMTEC Membranes—Silt Density Index (SDI)." Accessed December 27, 2017. [https://dowac.custhelp.com/app/answers/detail/a\\_id/263/~filmtec-membranes---silt-density-index-%28sdi%29](https://dowac.custhelp.com/app/answers/detail/a_id/263/~filmtec-membranes---silt-density-index-%28sdi%29).



- [22] The Endress + Hauser Group. 2017. "Vortex Flowmeters." Accessed December 27, 2017. <https://www.endress.com/en/Field-instruments-overview/Flow-measurement-product-overview/Vortex-flowmeters>.
- [23] Dow Chemical. 2016. "Normalization of Membrane Systems (FTNORM) Software." Accessed December 27, 2017. <http://www.dow.com/en-us/water-and-process-solutions/resources/design-software/ftnorm-software>.
- [24] Camahan, R. P., Bolin, L., and Suratt, W. 1995. "Biofouling of PVD-1 Reverse Osmosis Elements in the Water Treatment Plant of the City of Dunedin, Florida." *Desalination* 102 (1-3): 235-44.
- [25] Vrouwenvelder, J. S., Manolarakisa, S. A., Van der Hoek, J. P., Van Paassen, J. A. M., Van der Meer, W. G. J., Van Agtmaal, J. M. C. et al. 2008. "Quantitative Biofouling Diagnosis in Full Scale Nanofiltration and Reverse Osmosis Installations." *Water Res.* 42 (19): 4856-68.
- [26] Vrouwenvelder, J. S., van Paassen, J. A. M., Kruithof, J. C., and Van Loosdrecht, M. C. M. 2009. "Sensitive Pressure Drop Measurements of Individual Lead Membrane Elements for Accurate Early Biofouling Detection." *J. Mem. Sci.* 338 (1): 92-9.
- [27] Dow Chemical. 2016. "FILMTEC Membranes—Design Guidelines." Accessed December 27, 2017. [https://dowwater.custhelp.com/app/answers/detail/a\\_id/3180](https://dowwater.custhelp.com/app/answers/detail/a_id/3180).