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Control of severe membrane silica scaling: investigation and trouble shooting

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ABSTRACT

Reverse osmosis (RO) continues to develop into an important means for water purification. The increase in RO applications has forced many projects to contend with water sources containing higher levels of sparingly soluble minerals. In many parts of the world, membrane silica scaling is becoming a limiting parameter for the design and operation of RO systems using brackish feed water. Located in the northeast of China and established since 2009, the LiaoNing Panjing power company is the only energy supplier of the Panjing Lioabin economic zone (400 km^2). The power generation requires demineralized water coming from the power plant water treatment facility, which consists of a primary filtration step followed by RO trains and ion exchange resins. At the end of 2011, the RO plant performance severely dropped—normalized flux declined by 50%—indicating an occurrence of fouling or scaling on the membranes. Membrane autopsies have shown evidence of silica scales resulting from high levels of silica (50 ppm) in the feed water. This paper describes the investigation and troubleshooting processes used to restore membrane performance. The process utilized thorough scientific analysis, deposit removal via very efficient proprietary membrane cleaners, and dosing a novel antiscalant developed specifically to reduce silica deposition on RO membranes. To date, the chemical-based solution used to curb scaling has been effective in ensuring smooth operation of the membranes in the power plant water treatment facility.

Keywords: Reverse osmosis; Silica scale inhibition; Antiscalant; Cleaning

1. Introduction

In the field of reverse osmosis (RO) design and operation and maintenance, silica can become a constraint at high levels due to low solubility in most water systems, and it often leads to costly membrane scaling. The precipitation of silica is difficult to predict because the formation of amorphous or colloidal silica depends mainly on its concentration, temperature, pH, and induction time. To complicate the issue, silica is also strongly influenced by other species such as iron, aluminum, and magnesium, and they too can co-precipitate on a membrane's surface with silica.

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Located in the northeast of China and established in 2009, the LiaoNing Panjing power company is the only energy supplier of the Panjing Lioabin economic zone (400 Km^2). The power generation requires demineralized water coming from the power plant water treatment facility, which consists of a primary filtration step followed by RO trains and ion exchange resins.

At the end of 2011, the RO plant performance severely dropped—normalized flux declined by 50%—indicating an occurrence of fouling or scaling on the membranes. The performance change triggered initiation of a technical investigation in order to restore RO performance. Detailed feed water quality analysis, RO plant inspection, and deposit analysis were carried out, and severe silica scaling was found as the cause.

This paper describes the investigation and troubleshooting processes used to restore membrane performance. The process utilized thorough scientific analysis, deposit removal via very efficient proprietary membrane cleaners, and dosing a novel antiscalant developed specifically to reduce silica deposition on RO membranes.

2. Water treatment facility and feed water quality

2.1. LiaoNing Panjing power water treatment facility description

The LiaoNing Panjing power water treatment facility was commissioned in 2010. The plant capacity is 11,500 m^3/day of demineralized water for power generation. Demineralized water needs to be produced in accordance with the water quality guidelines are described in Table 1. In order to meet the required water quality, the water treatment facility setup is composed of three steps of coarse filtration followed by four RO trains and four ion exchange mixed beds as shown in Fig. 1.

The raw water feed is a blend between well water and factory water. After the chemical addition of chlorine and inline coagulant, the first step is to regulate the temperature between 20 and 30℃ through a heater. The water is then filtered through three steps of filtrations: multimedia filters, activated carbon filters (GAC), and cartridge filters (Cart.Filter). Sodium metabisulfite is added before GAC, and antiscalant is dosed prior to the cartridge filter. The filtered water is then pumped into and further filtered by a two-stage RO system with a recovery of 75%. Four RO trains produce 120 m^3/h each of RO permeate to supply two degassers and four ion exchange mixed beds.

Table 1
Demineralized water quality requirements

Demineralized water	SiO_2	μg/L	≤20
	Cond. 25℃	μs/cm	≤10
	Hardness	μmol/L	≈0
	pH		8.8–9.3

2.2. LiaoNing Panjing power water treatment feed water quality

The plant was designed to produce 120 m^3/h of RO permeate water per train with a recovery of 75% based on feed water with the known quality listed in Table 2 (column A). Starting in early 2012, RO performance began to deteriorate. The feed water quality was reanalyzed, and it was found to have changed. The new water analysis is listed in columns B and C in Table 2.

The initial water analysis was used as a reference for design and operation of the plant and was confirmed via additional analyses prior to February 2012. Comparison between the historical results and the new results obtained in February 2012 show a dramatic and sudden change in the feed water quality. The silica concentrations increased by a factor of 10, calcium, magnesium, fluoride, and chloride concentrations were reduced by a factor of 2.5–3, and bicarbonate concentration increased twofold. Levels of sulfate and phosphate were found to be negligible.

2.3. Scaling tendency of RO brines

Table 3 shows the scaling tendency of the brine before and after the feed water quality changes. Both water qualities (Table 2, Columns A & B) were analyzed by using Corola T software provided by Italmatch.

The Corola T software showed the changes with regards to the potential of mineral scaling. Initial brine water quality (A) is over saturated for calcium carbonate and calcium fluoride while the changed brine water quality (B) presents calcium carbonate and silica scaling issues.

The changes in feed water quality and brine saturation data weren't without consequences on the RO performance. The operation team faced difficulties in maintaining the permeate quality and flow as required by production.

3. RO performance

As shown in Fig. 2 below, the RO performances started to drop at the end of the year 2011 with a fast decline observed at the beginning of the year 2012.

Normalized parameters [1] were calculated with 2011 parameters as a reference. In February 2012, normalized parameters showed a permeate flow

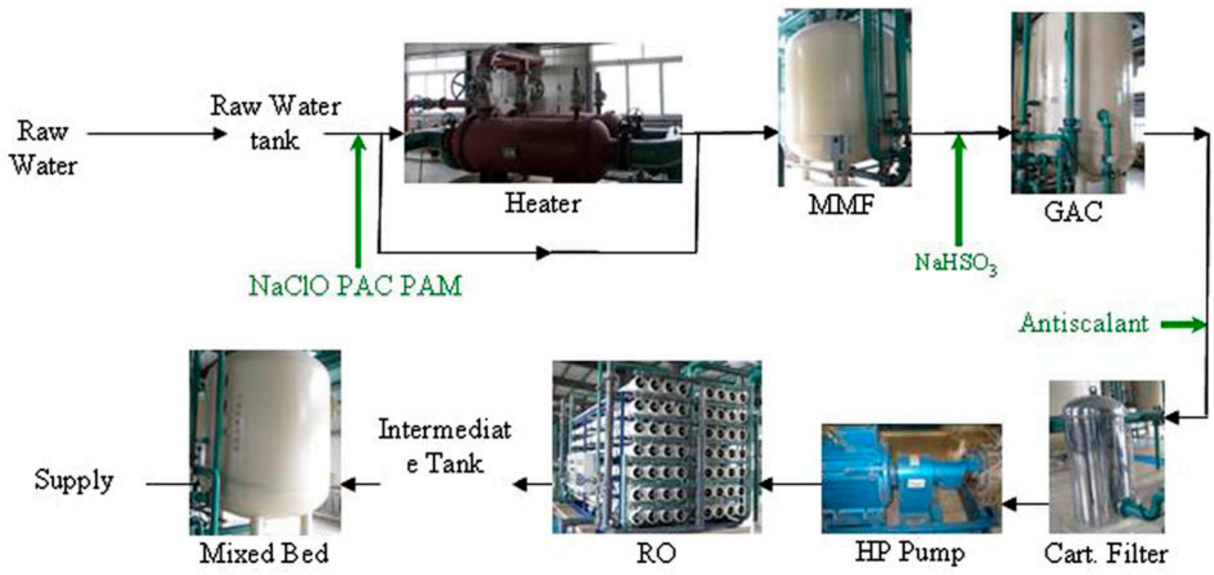


Fig. 1. Plant setup.

Table 2
Raw water quality

Parameter	A Initial raw water	B Raw water Feb 2012	C GAC effluent Feb
Al (mg/L)	0.01	0.01	0.01
Ba (mg/L)	0.01	0.01	0.01
Ca (mg/L)	48.37	15.06	13.56
Fe (mg/L)	0.01	0.01	0.01
K (mg/L)	2.95	1.27	1.29
Mg (mg/L)	13.01	5.96	5.54
Mn (mg/L)	0.01	1	0.01
Na (mg/L)	78.03	74.98	75.01
Si (mg/L)	4.87	45.01	58.76
Sr (mg/L)	0.55	0.32	0.32
Cl^- (mg/L)	83.41	44.72	39.92
SO_4^{2-} (mg/L)	12.09	1.29	0.89
HCO_3^- (mg/L)	185.41	341.08	328.52
NO_3^- (mg/L)	3.05	0.57	1.89
PO_4^{3-} (mg/L)	0.15	<0.1	<0.1
F^- (mg/L)	0.62	0.31	0.31
pH	8.12	8.06	8.36
COD_{Mn} (mg/L)	1.12	1.14	1.04
Cond. (ms/cm)	0.65	0.64	0.63

decrease by 50% (Fig. 3), a slight increase in salt passage, and a fluctuating pressure drop.

In February 2012, the general RO performance was tremendously negatively impacted.

4. Investigation

Several tests were conducted to investigate the cause of the drop in permeate flow.

4.1. Visual inspection on RO B

RO pressure vessels in the first stage and second stage were opened at the feed (inlet) and brine (outlet) sides. A thin layer of white deposit was found on the end caps, upon evaporation. The white deposit is more obvious on first stage brine side and second stage inlet side as shown in Fig. 4 below.

Table 3
Brine saturation data calculated before and after the change of feed water quality

Project :	Liaobin power compagny	Project :	Liaobin power compagny
Notes :	Initial feed water (A)	Notes	Feed water quality February 2012 (B)
Water source	Brackish Water	Water source	Brackish Water
Membrane type:	Thin film/High rejection	Membrane type:	Thin film/High rejection
Permeate flow :	120 m^3/h	Permeate flow :	120 m^3/h
Recovery:	75 %	Recovery:	75 %
Feed water pH:	8.12	Feed water pH:	8.06

Brine Saturation Data (A)

Name	Value	Treatment
LSI	2.21	NEEDED
S&DSI	2.06	
CaSO4	0.02	
BaSO4	0.19	
SrSO4	0.01	
SiO2	0.12	
Fe	39.96	
CaF2	1.18	NEEDED
CaPO4	0.03	

Brine Saturation Data (B)

Name	Value	Treatment
LSI	1.92	NEEDED
S&DSI	1.75	
CaSO4	0.00	
BaSO4	0.02	
SrSO4	0.00	
SiO2	1.13	NEEDED
Fe	39.96	
CaF2	0.10	
CaPO4	0.00	

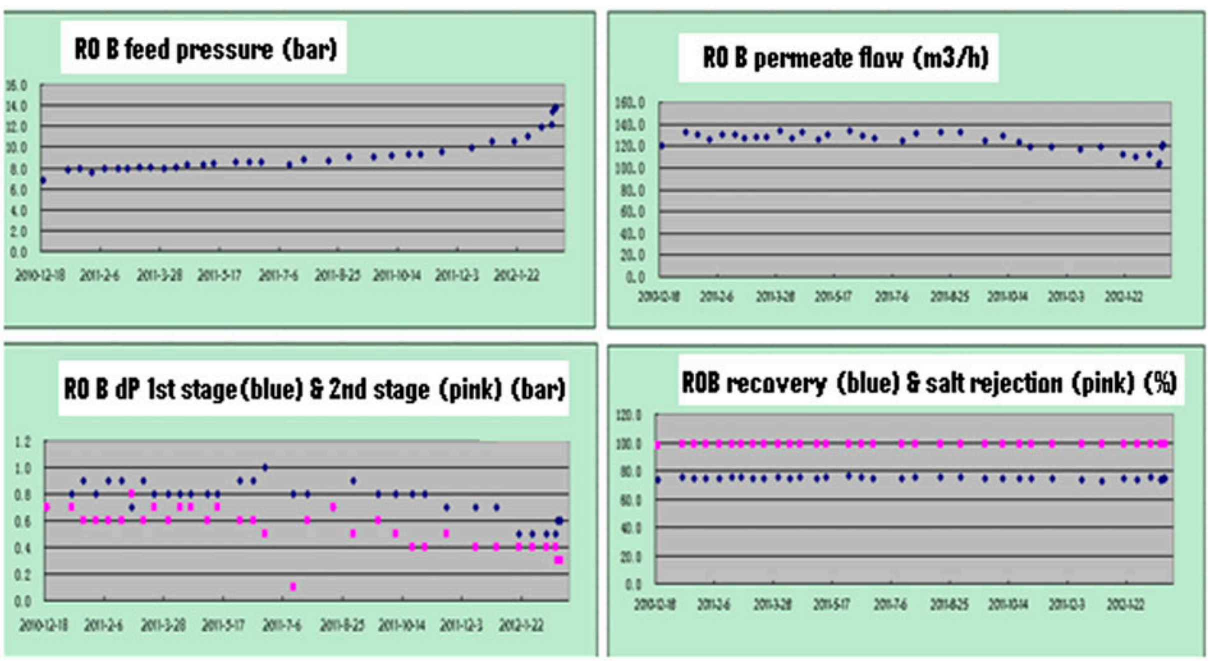


Fig. 2. RO operational parameters monitoring.

4.2. Membrane probing

Membrane probing was done on the first stage and second stage membrane elements. Results show abnormal conductivity of second stage permeate.

4.3 Scanning electron microscopy (SEM) analysis

The white deposit (second stage feed side) was sent for SEM analysis in order to screen its mineral composition. The results are in Table 4.

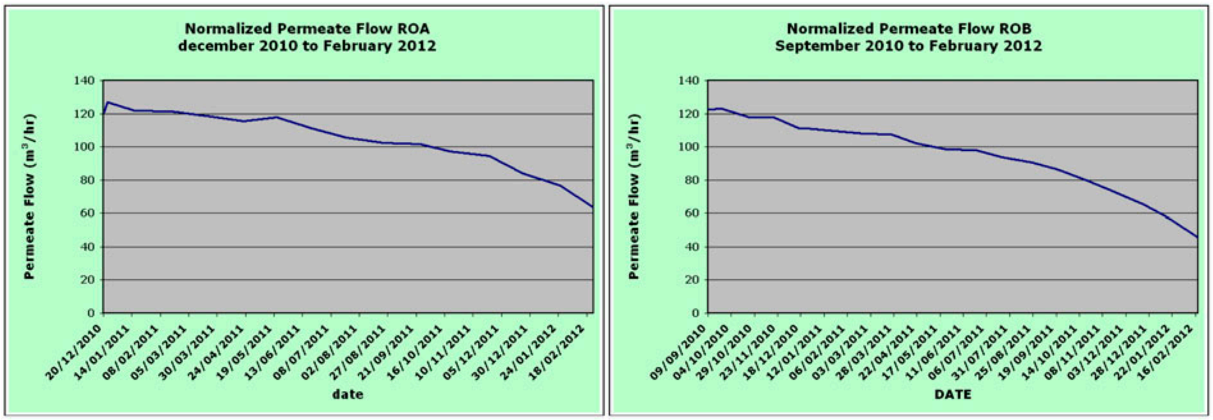


Fig. 3. RO normalized permeate flow year 2010–February 2012.

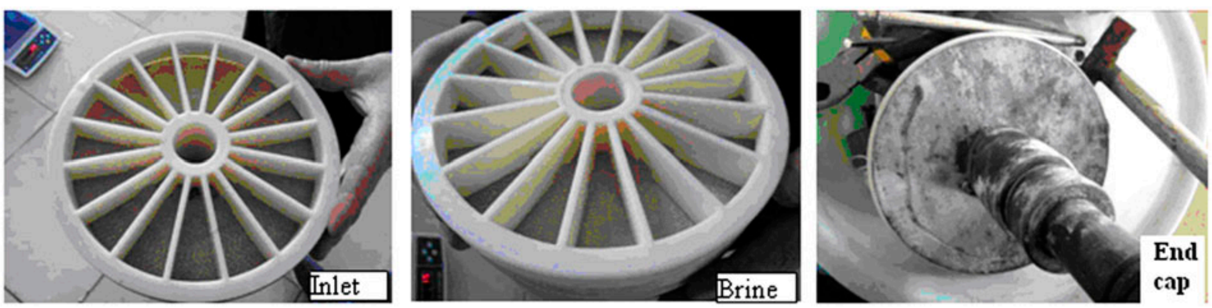


Fig. 4. Membranes pictures.

The deposits contain mostly silicon and oxygen with traces of aluminum and calcium

5. Trouble shooting

Investigations confirm that the loss in RO performance is due to a silica-based scale with a co-precipitation of aluminum and calcium.

Based on the various analyses [2–4], two optimization steps were adopted. First, an efficient cleaning protocol was requested and developed in order to avoid membrane replacement. Secondly, the application of a powerful silica scale inhibition antiscalant was needed to reduce further scale development.

5.1. Cleaning protocol

Several cleaning tests were conducted in order to find a solution to restore membranes performances, but the results were ineffective :

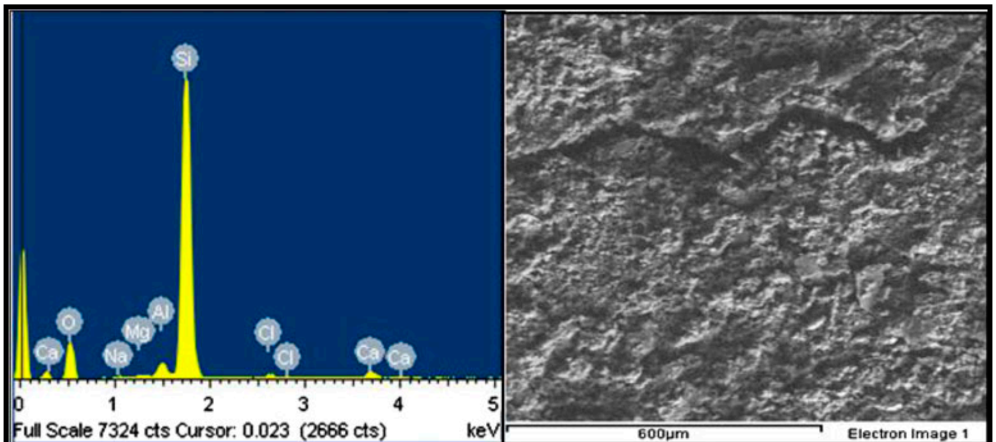
(1) Beaker tests based on caustic soda and hydrochloric acid were performed. The deposits were soaked overnight in both chemical and heated solutions, but no conclusive results were achieved.
(2) The plant generic cleaning [5] was not effective (Fig. 5).

A new cleaning protocol was tested based on proprietary cleaners blended with a chelating agent in the following manner:

(1) Step 1: Alkaline cleaning solution composed by MCC241 [6] commercialized by ShiBoHengYe company mixed with STPP (sodium tri polyphosphate).
(2) Step 2: Alkaline cleaning solution is composed by MCC241 commercialized by ShiBoHengYe company mixed with Na4-EDTA (tetra sodium salt of ethylenediaminetetraacetic acid).
(3) Step 3: Acid cleaning done with citric acid.

During each step of the protocol the cleaning solution was heated at 35˚C, and the pH was

Table 4
SEM results



Spectrum	In stats.	Na	Mg	Al	Si	Cl	Ca	O	Total
Spectrum 1	Yes	0.19	0.21	1.7	43.57	0.82	1.53	51.97	100
Spectrum 2	Yes	0.4	0.28	1.73	43.47	0.76	1.4	51.95	100
Spectrum 3	Yes	0.22	0.31	1.99	43.39	0.59	1.45	52.06	100
Mean		0.27	0.27	1.81	43.48	0.72	1.46	51.99	100
Std. deviation		0.12	0.05	0.16	0.09	0.12	0.06	0.06	
Max.		0.4	0.31	1.99	43.57	0.82	1.53	52.06	
Min.		0.19	0.21	1.7	43.39	0.59	1.4	51.95	

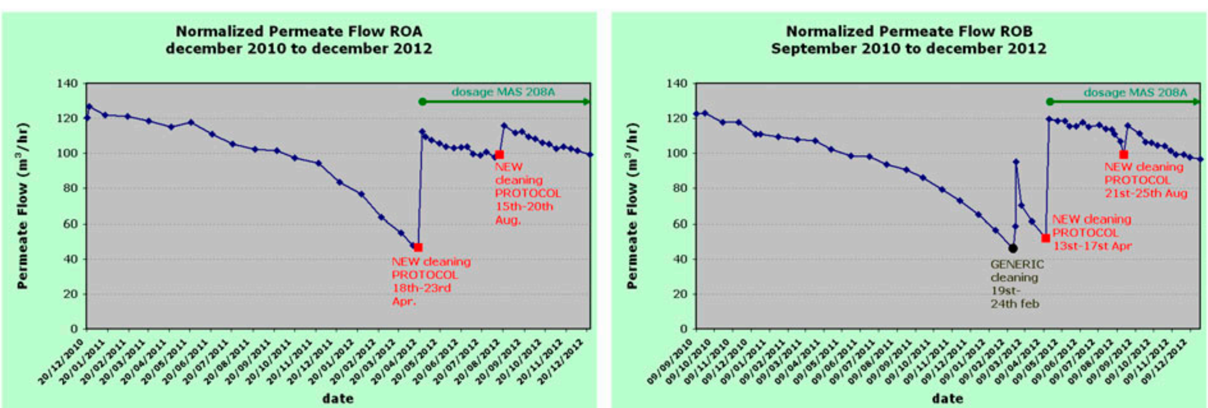


Fig. 5. RO normalized permeate flow before and after the trouble shooting year 2010–December 2012.

monitored in order to adjust it to approximately 11.3 during the alkaline cleaning and to approximately 3 during the acidic cleaning.

The proprietary cleaner MCC241 was chosen because of its effectiveness against a wide range of organic-based foulants. This cleaner is also highly effective against aluminum and colloidal silica foulants. Furthermore, MCC241 is approved by the major membrane manufacturers, which helps to limit the risk of damaging the membranes by using inappropriate cleaner levels.

Fig. 5 shows the effectiveness of the cleaning by comparing operational parameters before and after this new cleaning protocol. After cleaning, the RO performances were restored to normal operational ranges.

5.2. Choosing the correct antiscalant

The LiaoNing Panjing power water treatment facility was designed to treat a feed water quality as outlined during the planning of the facility. From 2010 to 2012, the feed water quality changed and silica fouling occurred.

After the change of feed water, the original antiscalant was found to be inefficient against silica-based scale to avoid the membrane fouling. The choice was made to do a field trial with the antiscalant MAS 208A [6] which was developed in conjunction with the Italmatch Belgium technical center. After development, it became a trademark of the ShiBoHengYe Company.

The MAS 208A antiscalant is known as a powerful silica scale inhibitor; however, the silica feed water level is extremely high. The levels in the feed water are up to 50 ppm; therefore, the levels in the brine can reach 200 ppm.

MAS 208A was instituted immediately after the new cleaning protocol in April 2012. Fig. 5 shows that RO performance was stable since cleaning, and the MAS 208A antiscalant is still currently being used with success.

6. Conclusions

The LiaoNing Panjing Power Plant water treatment facility experienced a drop in RO performances characterized by a loss of normalized permeate flow by 50%. Deposit analysis has shown that the reduced performance is due to severe silica scaling.

The RO operational performance was successfully restored by the implementation of a new membrane cleaning protocol and the selection and correct application of a new powerful proprietary silica scale inhibitor called MAS 208A.

The use of MAS 208A antiscalant stabilized the RO operational parameters and is ensuring smooth operation even with high concentrations of silica, up to 200 mg SiO_2/L in the RO brine in the presence of aluminum.

The proprietary cleaner MCC241 was confirmed to be an efficient cleaner against aluminosilicate deposits on the membranes. The combination of MCC241 and addition of chelants showed nice synergies for efficient removal of silica fouling.

Moreover this case study shows that:

(1) It is important to apply the most appropriate RO antiscalant to ensure a prolonged stable operation.
(2) Optimized cleaning protocol should be carried out at the very early stages of membrane performance deterioration.
(3) Partnership with a professional service provider is key for troubleshooting and performance restoration.

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