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POSSIBLE CONSEQUENCES OF IODINE EFFECT ON REVERSE OSMOSIS MEMBRANES AND SOLUTION TO REMEDIATE AND PREVENT THEM

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Abstract:

The presence of certain forms of iodine in feed water could be responsible for complications and poor performance in operation of reverse osmosis (RO) membranes in desalination plants. A significant rapid flow loss and salt rejection increase are suspected to be related to the potential detrimental effects of iodine in membrane operation.

Based on operating experience of LG NanoH2O membranes, a study has been carried out to investigate the possible role of iodine in the performance loss of RO membranes. A suggested method to overcome and prevent those potential negative effects has been developed.

For this study the following actions were undertaken:

- Site operation data analysis;
- Individual membrane performance test;
- Membrane surface tests (autopsy and fouling analysis);
- Membrane post treatments to remediate and prevent future performance loss;
- Membrane test to corroborate the success of membrane post treatment.

This study shows the observations and results from site operation and laboratory membrane tests. It demonstrates a possible successful on-site application of the proposed post-treatment to affected membrane elements.

It appears that certain forms of iodine in seawater could be responsible for a severe effect on the membrane performance. This study evaluates this possibility in conjunction with a proposed post treatment applied to the membranes which could prevent and/or reduce the potential effects to ensure successful operation.

1 Introduction

The presence of certain forms of iodine in feed water could lead to complications and poor performance in operation of RO membranes in desalination plants. A significant rapid flow loss and salt rejection increase are suspected to be related to the potential detrimental effects of iodine in membrane operation. Based on site experience, this study has been carried out to determine the causes behind the membrane performance loss experienced at the sites where iodine has been pointed as the possible reason for such a performance decline.

1.1 Background

RO membranes are commonly used in separation processes because of their high water permeability and high selectivity against a variety of contaminants. However, their performance is vulnerable to fouling caused by accumulation of undesirable materials on the membrane surface. Foulants clog the membrane pores and reduce permeate flux. Fouling modes include formation of a cake layer, biofouling, organic fouling and inorganic fouling [1].

RO membrane operational failures are often caused by fouling or accumulation of unwanted materials on the membrane surface during the contact with the feed water. Byproducts of oxidizing agents commonly used as water disinfectants could also lead to membrane degradation [2].

Iodine is a trace element that exists in natural waters such as seawater, freshwater and rain. Iodine could be present in seawater at concentrations of 60 µg/l [3]. It is reported that the dissolved iodine species are iodine, iodate and dissolved organic iodine (DOI). These species may undergo transformations from one to another and thus affect the formation of iodinated disinfection byproducts [4]. In addition, non-volatile dissolved organic iodine (DOI) can be a major, or even the dominant, species of dissolved I in coastal, inshore and estuarine waters [5].

It is reported that iodine compounds used for disinfection might cause flux losses. They have been previously identified as responsible for improving membrane rejection and decreasing membrane permeability [6].

1.2 Objectives

This study addresses the following objectives:

- Study and identify possible causes which might be responsible for membrane performance loss;
- Develop a possible post-treatment method to recover membranes that suffered a performance loss;
- Study the effects of possible post treatment as a preventive treatment;
- Site post treatment evaluation.

2 Methodology

Based on site experience, a study was conducted to determine the reasons of the membrane performance loss in seawater reverse osmosis membranes. This study had the following steps:

- Site operation and samples evaluation;
- In-house test: individual performance test, physical inspection, fouling analysis, membrane post treatment;
- Site operation post treatment evaluation.

2.1 Site Operation Results

The operation of reverse osmosis membranes was monitored during the first months of operation after the system start up. A rapid degradation of the membrane performance was observed that manifested itself in a 40% decrease in the normalized permeate flow. Water samples from the site were sent to LG Chem Research and Development (R+D) facilities in Cheongju (South Korea) for a complete ion analysis.

2.1.1 Site operation data

Performance of the installed membranes was monitored from the start up. After the start up, a continuous and rapid loss of performance was detected. Feed pressure rose significantly, and the salt passage decreased. The following trends were observed (Figures 1-3):

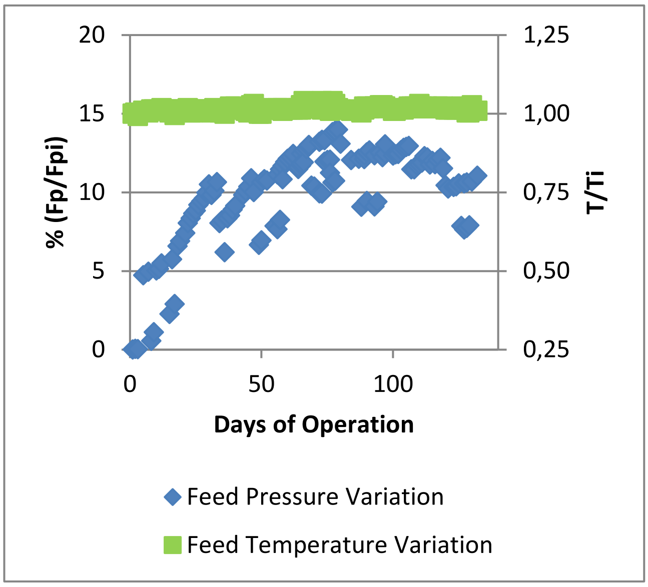

Figure 1 % Feed pressure and temperature variation increase from the start up

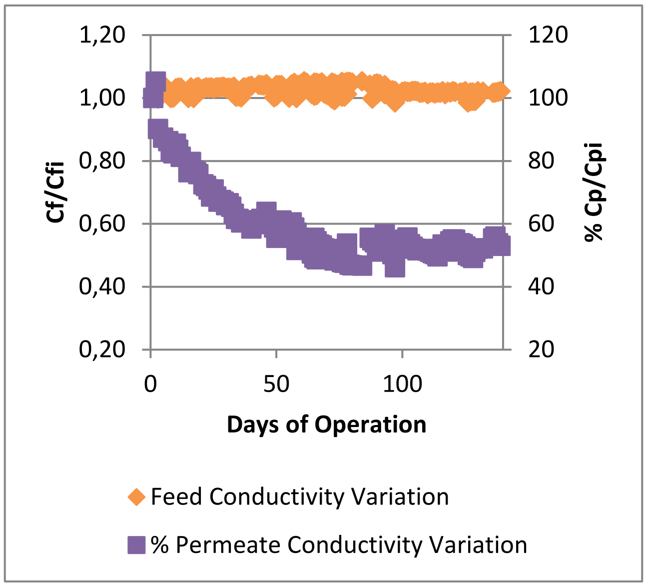

Figure 2 % Feed conductivity and permeate conductivity variation from start up

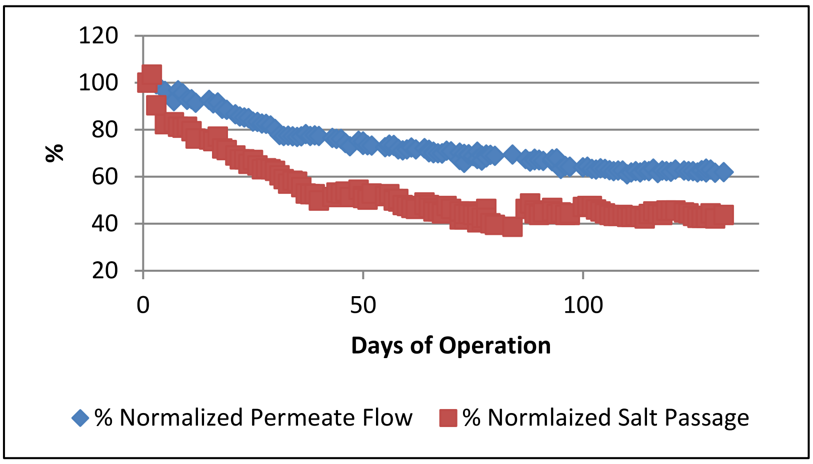

Figure 3 % Normalized Permeate Flow and Salta Passage trend from start up

Figure 3 shows a significant decrease in the normalized permeate flowrate that reached 40% after three months of operation. On the other hand, the normalized salt passage declined too (up to 60%) thus improving the rejection performance of the membranes.

2.1.2 Site water analysis

Water samples from the site where LG NanoH2O membranes had suffered loss of performance were sent to LG Chem R+D center. The objective was to determine the presence of possible elements in the water that could cause such performance degradation.

Cations in water were analyzed by ICP-OES (Inductively Coupled Plasma Optical Emission Spectroscopy). All cations without boron (B) were analyzed using ICP-OES (Optima 7300DV, Perkin Elmer) and Boron (B) was analyzed by ICP-OES (Optima 5300DV, Perkin Elmer). All anions were analyzed by IC (Ion chromatography, ICS-3000).

Table 1 Water samples from site analysis

Sampling Position	Concentration								
	Cl (%/ppm)	SO4 (ppm)	Br (ppm)	B (ppm)	Ca (ppm)	Mg (ppm)	Na (%/ppm)	Sr (ppm)	I (ppm)
Raw Water S1	2.29%	3120	79	4.9	450	1310	1.17%	6	< 1
Raw Water S2	2.32%	3210	80	5.1	460	1360	1.22%	6	< 1
RO Feed S1	2.23%	3050	75	4.9	445	1290	0.0113	6	< 1
RO Feed S2	2.30%	3220	81	5.1	455	1340	0.0119	6	< 1
RO Permeate S1	28	1	0.2	0.25	0.3	0.9	16	< 0.1	< 1
RO Permeate S2	29	1	0.2	0.25	0.3	0.9	17	< 0.1	< 1
RO Reject S1	3.86%	5640	132	8.8	760	2490	2.03%	10	< 1
RO Reject S2	3.80%	5790	136	9	775	2490	2.11%	10	< 1

The water sample analysis did not reveal the presence of any unusual element or concentration. The amount of iodine in the feed water could not be precisely determined because it was lower than the detection limit of the method employed.

2.2 In-house Test Results

A set of membranes which had suffered loss of performance were extracted from site and sent to LG Chem R+D facilities in Cheongju (South Korea) for their evaluation. The following tests were carried out:

- Laboratory membrane test: the membranes were tested individually at the standard sea water reverse osmosis (SWRO) conditions;
- Membrane surface test: a membrane autopsy and fouling/scaling test were performed:
    - Physical and visual evaluation
    - Fouling/Scaling analysis: an Electron Spectroscopy for Chemical Analysis (ESCA) was carried out.

2.2.1 Laboratory Membrane Tests

The set of membranes was tested at the SWRO conditions. Each membrane was tested individually and compared with the original wet-test results after the membrane production.

The SWRO test conditions were as follows:

- Feed TDS: 32,000 ppm NaCl;
- Feed Pressure: 800 psi;
- Temperature: 77 ˚F (25 ˚C);
- pH 8;
- Recovery 8%.

The results from the individual performance test are shown below:

Table 2 Individual performance test

Membranes	Original Wet Test		Lab Test after operation		Change Ratio	
	Flow (GPD)	Rejection (%)	Flow (GPD)	Rejection (%)	Flow (%)	SP (%)
Membrane 1	8347	99.84	5082	99.73	-39.1	72.00
Membrane 2	8299	99.76	4882	99.74	-41.2	7.0
Membrane 3	8324	99.83	4729	99.86	-43.2	-19.0
Membrane 4	8341	99.84	4689	99.9	-43.8	-37.0
Membrane 5	8249	99.83	4294	99.85	-47.9	-10.0
Membrane 6	8351	99.78	4441	99.87	-46.8	-42.0
Membrane 7	8326	99.79	4454	99.88	-46.5	-41.0

As it is seen from Table 2, the performance test results are in line with those from the operation site. In addition, one can see that the loss of performance had a higher impact on the tail elements compared to the front ones. This indicates that the compound affecting the membranes was in the feed side and, as it was getting more concentrated along the pressure vessel, the effects on the surface of the membrane were more aggressive.

2.2.2 Membrane Surface Tests

The membrane surface of the elements sent to LG Chem R+D facilities was studied by use of the following tests:

- Physical and visual inspection;
- Fouling/Scaling analysis.

2.2.2.1 Physical and visual inspection

The elements were physically and visually inspected. They were in good conditions and fairly clean. Only little debris was found in the front element.

Two elements were autopsied, and their membrane surfaces were inspected (Figure 4, 5):

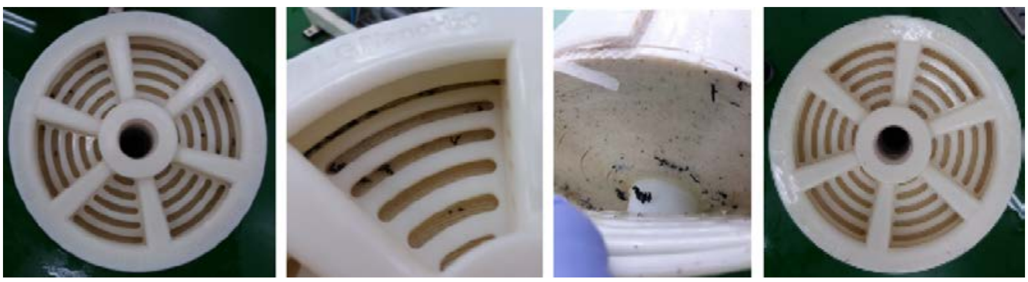

Figure 4 Autopsied membranes: external inspection

Figure 5 Autopsied membranes: membrane surface

The inspection showed that the surface was clean, and no signs of severe fouling were observed. No channeling towards the feed and brine sides was detected.

2.2.2.2 Fouling/Scaling analysis

In order to evaluate the presence of fouling/scaling on the surface of the membranes in more detail, an ESCA (also referred to as X-ray Photoelectron Spectroscopy (XPS)) was carried out. ESCA is suitable to analyze the 5 top nanometers of the surface of the membrane and to determine sources of oxidation.

This analysis was performed on the elements that had been previously autopsied.

The results can be shown in Table 3:

Table 3 ESCA individual elements results as atomic %

Elements	Membranes/Side			
	M1 Feed	M1 Brine	M2 Feed	M2 Brine
C	67.2	67.3	55.6	50.2
O	21.2	21.4	23.2	17.5
N	7.5	7.5	5.8	4.8
Na	1.3	1.2	5.2	11.4
Cl	1.3	1	5.4	12.6
Si	0.7	0.7	2.9	2
I	0.6	0.6	0.4	0.4
Al	0.3	0.3	1.5	1.1

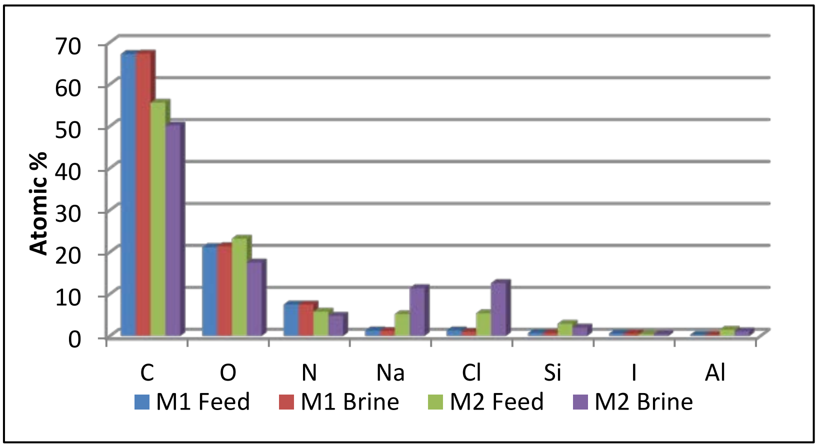

Figure 6 Individual elements results as atomic %

The results obtained from the analysis revealed small amounts of iodine (0.4 to 0.6 atomic %) on the membrane surface in conjunction with other elements such as silica and aluminum. The presence of silica and aluminum fouling was minor and therefore, not related to the membrane loss of performance.

However, iodine compounds used for disinfection had been previously reported to cause flux losses. It has been detected from the seawater membranes associated to flow decline. In addition, dissolved organic iodine is found in coastal waters and well waters. At that point it was speculated that iodine in the form of iodine-binding to polyamide layer and/or dissolved organic iodine could be responsible for these detrimental effects.

2.2.3 Membrane Post-Treatment

In order to alleviate the effects on the membranes, the countermeasures in the form of oxidative cleaning and combined treatment (oxidative cleaning with *Cleaning in Place* (CIP)) were evaluated. Oxidants are extremely successful for membrane regeneration [7]. Additionally, a comparative test of conventional CIP vs combined treatment was carried out.

The goals of this post treatment were not only to recover the membrane performance but also to test if it could also be used as a preventive treatment for future operation with membranes exposed to the same contaminant.

2.2.3.1 Oxidative Cleaning

Flat sheet from the membranes which had been sent to LG Chem R+D research facilities were tested. The following procedure was followed:

1. Membrane tested before oxidative cleaning;
2. Membrane tested after oxidative cleaning;
3. Membrane tested after oxidative cleaning with iodine treatment
4. New membrane tested with iodine treatment

The coupons were taken from the tail membrane.

The results obtained were as follows:

Table 4 Oxidative cleaning flat sheet test results

Sampling position	Test Step	Before post treatment	After post treatment
	Cell No	Flow (gfd)	
Feed Side	1	10.82	14.96
	2	11.03	15.18
	3	10.71	14.91
Brine Side	4	10.55	14.64
	5	10.50	14.64
	6	10.17	14.26

The post treatment showed promising results with a recover ratio of 39% in flow loss.

After this initial test, cells 3 and 6 were replaced with new virgin membranes without post treatment and compared with the membranes from site that had been exposed to the post treatment.

Table 5 Membranes with/without post treatment comparison test results

Sampling Position	Membrane	Test Step	Before Iodine treatment	Iodine treatment 1h	Iodine treatment 2h
		Cell No	Flow (gfd)		
Feed Side	Used with post treatment	1	15.41	15.85	16.08
		2	15.57	15.95	16.19
	New no post treatment	3	17.43	17.09	16.40
Brine Side	Used with post treatment	4	15.20	15.57	15.92
		5	15.25	15.57	15.87
	New no post treatment	6	15.51	15.19	14.66

The comparison results from the table above show the following: the membranes sent from site, which had suffered the flow loss, had recovered flow after the post-treatment. Furthermore, while the exposure to iodine did not affect their performance any further, the new membranes which had not been treated with the post treatment did show a rapid flow loss.

2.2.3.2 Comparative Test: *Cleaning in Place* vs Combined Cleaning (Oxidative Cleaning + *Cleaning in place*)

A further evaluation of the effects of standard CIP and a combined cleaning with CIP and oxidative cleaning was carried out.

Two separate tests were carried out:

1. Flat sheet membrane test using coupons from the lead membrane.
2. Individual membrane test using two elements from the middle position of the pressure vessel.

2.2.3.2.1 Flat sheet membrane Test

The results obtained from the flat sheet membrane test are shown in Table 6:

Table 6 CIP/Combine Treatment flat sheet test results

Sampling position	Test Step	Before standar CIP		After standard CIP		After combined treatment	
	Cell No	Flow (gfd)	Rejection (%)	Flow (gfd)	Rejection (%)	Flow (gfd)	Rejection (%)
Feed Side	1	12.71	99.76	14.19	99.81	16.13	99.83
	2	12.83	99.82	14.23	99.82	16.21	99.84
	3	13.06	99.78	14.50	99.82	16.30	99.84
	4	12.85	99.86	14.29	99.82	16.75	99.88
	5	13.26	99.77	7.48	99.87	16.95	99.83
	6	12.73	99.75	14.12	99.85	16.70	99.86
Average	F/S	12.91	99.79	13.14	99.83	16.51	99.85

It can be noted from the table above that the combined treatment was able to increase membrane recovery from 2% to 26%.

2.2.3.2.2 Individual membrane Test

Two membranes from the middle position of the pressure vessel were tested after standard CIP and combined treatment (CIP + oxidative cleaning).

The results obtained are shown in Figure 7:

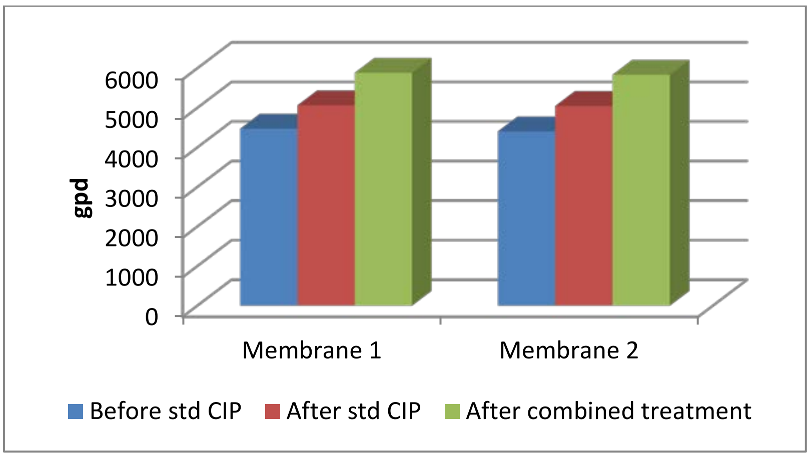

Figure 7 CIP/Combined treatment membrane element test results

The membrane performance recovery increased from 14% for standard CIP to 32% after the combined treatment.

2.3 Membrane Post-Treatment Site Results

After experiments performed at LG Chem research facilities, the membranes installed on site were treated by a combined treatment using standard CIP and oxidative cleaning.

The combined cleaning was performed between days 173 and 176 of operation.

The results obtained on site are shown in Figures 8 through 10.

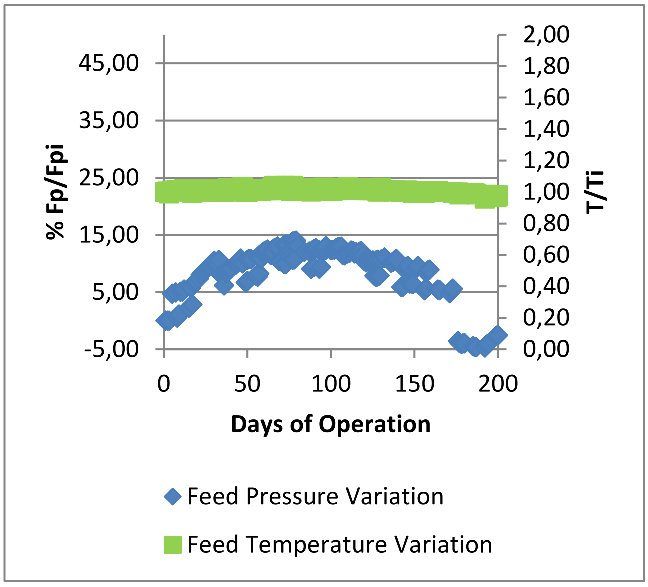

Figure 8 % Feed pressure and temperature variation increase from the start up to after post treatment

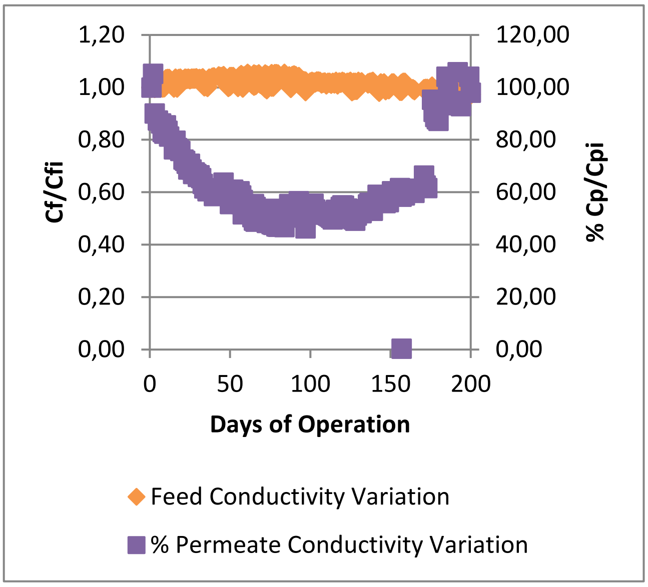

Figure 9 % Feed conductivity and permeate conductivity variation from start up to after post treatment

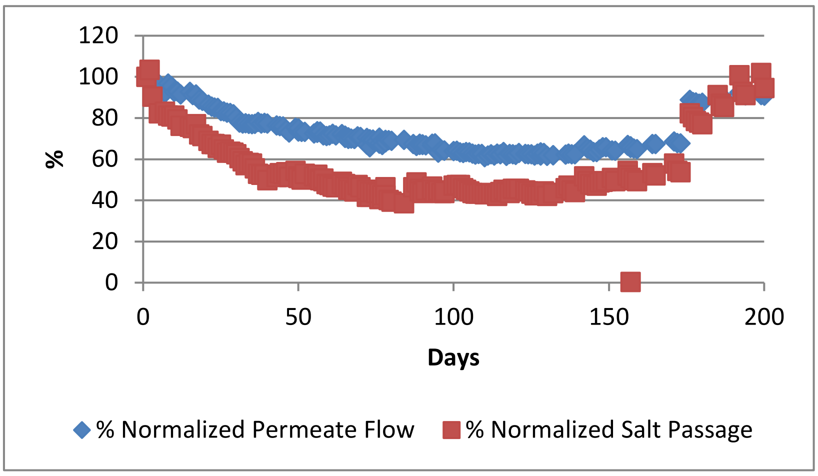

Figure 10 % Normalized Permeate Flow and Salta Passage trend from start up to after post treatment

As it can be observed from the above graphs, the results obtained on the site were quite successful. Normalized permeate flow was recovered up to 30% and normalized salt passage was increased by 50% achieving values very close to the start-up values.

3 Results

The results of the studies can be summarized as follows:

- Site operation results prior to membrane investigation and post treatment:
  - Site operation data: Normalized permeate flow and normalized salt passage declined by 40% and 60% respectively since the start up.

- Site water samples: Site samples were analyzed and the results did not reveal the presence of any unusual element or concentration. The amount of iodine in the water could not be precisely determined below 1 ppm as it was below the detection limit of the method employed.

- In-house test results:
  - Individual performance test: Individual performance test showed similar result to those observed on site. They also revealed that the loss of performance was greater in those elements installed at the end of the pressure vessel.
  - Physical inspection: The membranes studied and autopsied did not show significant signs of fouling/scaling on the membrane surface.
  - Fouling/scaling analysis: trace concentrations of iodine, silica and aluminum were detected on the membrane surface of the elements analyzed. Silica and aluminum were minor and not considered responsible for the loss of performance. However, iodine presence indicated that it could be responsible for membrane degradation.
  - Post treatment: flat sheet test using an oxidative cleaning showed a flow loss recovery of up to 39%. In addition, recovered membranes treated with oxidative cleaning and new virgin membranes without any post treatment were exposed to iodine and their performance compared. The used membranes with post treatment did not show any negative effect in their performance while the flow of the new membranes started to decrease rapidly after iodine exposure.
  - Standard CIP and a combined post treatment with CIP and Oxidative Cleaning were compared. The study revealed that the combined treatment was able to further recover the flow of the damaged membranes by 16 - 24% compared to standard CIP.
- Site operation results after combine post treatment on site: the combined post treatment on site was able to recover the normalized permeate flow and normalized salt passage by 30 and 50 % respectively.

4 Conclusions and future work

The following conclusions can be drawn after this investigation:

- Iodine, probably in a "binding form" to the polyamide layer and organic form, is suspected to be responsible for a rapid flow loss when it is in contact with reverse osmosis membranes.
- Minor concentrations of iodine in a continuous contact with the membrane surface might be a cause of the potential effects on sites with flow losses and salt passage drop up to 40% and 60% respectively.
- Oxidative cleaning has been proven to be effective against possible effects of iodine on reverse osmosis membranes and able to recover the flow loss up to 39%.
- Oxidative cleaning has been found to be a successful post treatment to avoid possible adverse effects due to RO membranes in contact with iodine forms.
- Oxidative cleaning in combination with standard CIP would be significantly more effective to recover the performance of the reverse osmosis membranes that could have been exposed to iodine fouling than standard CIP alone.
- Combined standard CIP and oxidative cleaning was able to recover membranes on site although its effectiveness was lower than the test performed on a lab scale.
- Specific data, operation conditions and concentrations have not been disclosed due to confidential reasons.

This investigation would require future work that should include the following tasks:

- Further investigation is required to confirm and determine the origin of iodine which might be responsible for the membrane performance loss.
- Further investigation is required to confirm and determine the possible membrane surface iodization mechanism.

- Determination of different iodization levels and operation conditions which could be responsible for flow loss in reverse osmosis membrane operation.

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