Appendix 5

AUTOPSY AND CLEANING OF REVERSE OSMOSIS ELEMENTS AFFECTED BY HARMFUL ALGAL BLOOM-CONTAMINATED SEAWATER

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1 FOULING DIAGNOSIS

Following an algal bloom, if a change is observed in the reverse osmosis (RO) performance, an initial visual plant inspection should be carried out, including looking at and removing cartridge filters and membrane elements from different positions in the pressure vessel. Fouling may be a combination of organic, biofouling, particulate, and metal hydroxide. Biofouling is often slimy or gelatinous which may be accompanied by a bad smell while iron fouling is a reddish brown deposit. Figure 1 shows evidence of biological fouling on a cartridge filter and inside a pressure vessel following an algal bloom event.

Figure 1. Severe fouling due to algal bloom. Algal fouling on a cartridge filter (L), remnants of algal fouling left inside a pressure vessel after removing the lead element (R). Note: Elements are from a brackish water reverse osmosis system, fouling may appear as different colors in a SWRO system.

If it is obvious that there is severe fouling, membrane autopsy would be the most appropriate tool for identifying the nature of the foulant, and the best cleaning protocol for removal of the foulant. Autopsy results would be interpreted in conjunction with an analysis of plant performance data.

2 PRE-AUTOPSY

The following procedure would be recommended prior to membrane autopsy:

- The first element from the SWRO first pass should be chosen for autopsy, although best characterization of plant status would be obtained by autopsying elements from both the first and last positions of the pressure vessel. Note that for two-pass seawater desalination plants, it is unlikely that harmful algal bloom (HAB) fouling will be evident in the second pass, as low fouling permeate from the SWRO is the feedwater.
- Membrane elements should be wrapped in dark plastic and taped securely to ensure that water is retained within the element. This is necessary for accurate microbiological analysis and deposit characterization. Dry membrane elements yield unrepresentative samples that can give false results.
- Do not use any chemicals for membrane preservation before sample delivery. Otherwise, microbiological count results will not be representative.
- Membrane elements should be sent for autopsy the day of removal. If membrane(s) cannot be shipped immediately, store horizontally in a cool dark place. It is important to avoid light and high temperatures.

In addition to membrane elements, further samples could be analyzed for complementary information about the algal bloom:

- Water samples from different points in the pretreatment process;
- Silt density index (SDI) membrane discs from different points in the pretreatment process; and
- Cartridge filters

3 AUTOPSY

Autopsy involves different tests and analyses that should be carried out in order to obtain a final diagnosis. This process includes the following steps that should be followed during algal bloom events:

External and internal inspection of membrane element

During the inspection, failure due to a significant presence of fouling would be verified. Fouling after an algal bloom would be expected to:

- Appear organic, with development of a biofilm on the RO membrane surface;
- Be a sticky deposit with a high content of water that would probably also adhere to the spacer material; and
- Exhibit different coloration depending upon the type of algal bloom and fouling content.

Analyses of foulant

- The LOI (loss on ignition) test is a common and widely used method to estimate the organic content of foulants. A very high organic matter content would be expected (>60%), although the high sodium chloride content in seawater systems could interfere with the measurement.
- Optical microscopy analysis for algae identification (see Chapter 3, Appendix 3).

Analyses of foulant samples and membrane surface samples

- Scanning electronic microscopy with Energy Dispersive X-ray detection (SEM-EDX): with this analytical technique it is possible to get an elemental analysis of

fouling and inspection at very high magnifications. This method can assist in identifying colloidal, scaling, and metal hydroxide fouling, but cannot identify biofouling.

- Infrared spectroscopy (IR): This technique provides information related to the presence of specific functional groups and it is a very good tool for identification of organic components. For algal bloom fouling it would verify the presence of biopolymeric substances such as polysaccharides and proteins produced during an algal bloom.
- Liquid Chromatography - Organic Carbon - Organic Nitrogen Detection (LC-OCD-OND): a very accurate tool for the characterization of natural organic matter including biopolymers (see Chapter 5).

Analyses of foulant samples and membrane surface samples for Algal Organic Matter

At present, there is no standard test protocol for determining Algal Organic Matter (AOM) deposits on RO membranes or spacers. HAB research studies have examined the accumulation of organic deposits using LC-OCD and staining of the membrane/spacer using Alcian blue in membrane autopsies (Villacorte 2014).

- TEP deposits can be identified by staining a sample of RO membranes and/or spacer with a solution of Alcian blue (see Appendix 3 for preparation) followed by rinsing with ultrapure water.
- The stained samples are then viewed by an optical microscope. The presence of a blue/green stained deposit is indicative of the presence of TEP. It cannot distinguish between TEP which may have originated from algae and/or bacteria in the feedwater or generated by biofilm growth in the membrane.
- For more quantitative information on the deposit on RO membranes/spacers following a HAB bloom, Villacorte (2014) submerged samples of membrane and spacer in a known quantity of ultrapure water and sonicated for 1 hour to extract the organic matter accumulated on the membrane.
- The extracted solutions can then be analyzed for $TEP_{0.4\mu m}$ and TEP_{10kDa} (see Appendix 3) and natural organic matter such as biopolymer concentrations using LC-OCD as described above.

The identification of NOM constituents such as TEP could assist in determining the appropriate cleaning agent/chemical.

Microbiological counts

- A very high presence of microorganisms would be expected in the biofilm on the membrane surface after an algal bloom.
- Characteristic microorganisms would be: bacteria (aerobic and anaerobic), moulds, and yeasts, etc. Results would be recorded as UFC/cm^2.

Biocide tests

Based on microbiological counts, biocide tests would be carried out to determine the most suitable biocide for biofilm removal.

Sampling for membrane performance parameters and cleaning tests

Once the nature of fouling has been identified, it is important to know the effect of the foulant on membrane performance. By working with membrane coupons on a flat sheet test

rig it is possible to examine the permeate flux and salt rejection conditions of a membrane after an algal bloom. If the membrane was not damaged during algal bloom operation and there is fouling present, a decrease in both permeate flux at constant applied pressure and salt rejection would be expected.

Different cleaning tests should be carried out in order to choose the most suitable cleaner and optimal cleaning conditions (e.g., concentration, contact time, temperature) as the incorrect cleaning agent may cause a further loss in membrane performance. Depending upon the results obtained during the biocide tests, an additional biocide step should be tested and included in the final cleaning protocol if appropriate.

Integrity tests

An important impact of fouling on reverse osmosis membranes is the damage that can be caused on the polyamide layer and on their rejection capabilities (Peña et al. 2013). Therefore, integrity tests should be carried out in order to check if the polyamide layer has suffered irreversible damage during operation after fouling due to algal bloom. Considering the nature of fouling after an algal bloom, it is very common to observe increases in differential pressure that can produce physical damage on the membrane surface.

The methylene blue test would detect this kind of damage, staining damaged areas blue. Care should be taken not to scratch or damage the membrane during the autopsy process.

4 CLEANING PROTOCOL FOR HAB-AFFECTED RO ELEMENTS

Before cleaning RO elements, operators are advised to review the technical manual, technical bulletins, or specification sheets for each element type used. Common manufacturers' literature is below:

- Hydranautics: Foulants and Cleaning Procedures, TSB-107, http://www.membranes.com/docs/tsb/TSB107.pdf
- Dow Filmtec: Filmtec Reverse Osmosis Membranes Technical Manual, Section 6, page 121, http://www.dow.com/en-us/water-and-process-solutions/resources/resource-finder
- Toray: Operation, Maintenance and Handling Manual, TMM-300, 310, 320, 330, 340, 350, http://www.toraywater.com/knowledge/pdf/HandlingManual.pdf

While general cleaning solutions are presented below, specially formulated cleaners are available from RO chemical suppliers that are more effective than standard commodity chemicals. Globally there are many common RO cleaning chemical suppliers such as (but not limited to); Genesys, Avista, PWT Chemicals, Nalco, Alkema Solutions, GE, and BASF.

It is very important always to follow membrane manufacturers' guidelines. While most SWRO elements will tolerate pH 2 - 12, care should be taken as some RO membrane elements will only withstand high pH values for short periods of time (e.g. 30min) or may only withstand lower alkaline pH (e.g. pH 11.0). Cleaning fluid volume should be on the order of 35 - 40 liters per 8" element and made with permeate water (rather than feedwater).

Table 1 shows a common cleaning procedure for HAB-affected RO elements where organic, biological plus iron fouling, may occur. Ideally the clean should consist of a high pH clean to soften and remove organics, biofilm and algae (Step 1), followed by a biocide in extreme cases to kill these organisms (Step 2), Step 1 is repeated to remove dead organisms and the remainder of the organics, and finally a low pH acid clean (Step 4) to remove carbonates and iron and generally restore the membranes. In order to restore membrane plant performance as quickly as possible after an algal bloom event has fouled the membranes, proprietary cleaners

are recommended rather than simple commodities such as caustics and acid. For instance, the alkaline cleaner in Step 1 may comprise of a mixture of detergents, penetrants, sequestrants, and other targeted components, and preferably with in-built biocidal properties. Each cleaning step is further described below.

Table 1. Common cleaning procedures for SWRO elements following a HAB event.

Stage	Cleaner	Dose rate	pH	Temperature
Flush	*Permeate*		*Ambient*	
Step 1	Alkaline detergent	~1-3% w/vol	As high as permitted (pH 11.8 – 12.3)	35-40 ^{o}C
Flush	*Permeate*		*Ambient*	
Step 2	Non-oxidizing biocide (e.g. DBNPA)	~400 ppm	5.5 – 7.0 (natural)	Ambient
Flush	*Permeate*		*Ambient*	
Step 3	Alkaline detergent	~ 1-3% w/vol	As high as permitted (pH 11.8 – 12.3)	35-40 ^{o}C
Flush	*Permeate*		*Ambient*	
Step 4	Low pH, organic acid,	~4% vol/vol	pH 2-4	25-30 ^{o}C
Flush	*Permeate*		*Ambient*	

Step 1: Alkaline detergent procedure to remove organics

- Ideally in order to prepare membranes for most efficient cleaning, heat the cleaning tank with only permeate (no chemical) to 35^{o}C and circulate around membranes for 10-15 minutes maintaining temperature. This will raise the temperature of the membranes allowing for a more efficient cleaning.
- Prepare cleaning solution as per Table 1 with chemical (strength dependent on severity of fouling), at pH 11.8 – 12.3, and at 35-40^{o}C.
- Low-flow pumping - Pump the mixed, preheated cleaning solution to the pressure vessel at low flow (3 - 4.5 m³/h per pressure vessel) and low pressure (2 - 2.5 bar to prevent permeate being produced) to displace the process water already in the membranes. Low pressure minimizes redeposition of foulants on the membrane. Reject the concentrate to prevent dilution of the cleaning solution.
- Measure pH and adjust if necessary, maintain temperature, and recycle around the system for 20 - 30 minutes. If the solution shows any sign of significant discoloration then discard and prepare fresh as per Table 1 to prevent possible membrane abrasion. Recirculating dirty cleaning solutions will lead to poor cleaning results and possible membrane damage.
- Once the pH, temperature, and color have stabilized, allow the elements to soak for as long as possible, ideally 4 - 6 hours. For difficult fouling, an extended soaking period may be required, overnight for example. Contact time is critical for organic removal.

- High-flow pumping. Feed the cleaning solution at high flow rates (8 - 10.2 m^3/h at 1.5 - 4.0 bar) for 30 - 60 minutes. The high flow rate flushes out the foulants removed from the membrane surface by the cleaning.
- Flush with good quality permeate to return to natural pH levels.

Step 2: Non-oxiding biocide to remove biofouling

- Prepare cleaning solution with non-oxidizing biocide.
- Low-flow pumping - Pump the mixed, preheated cleaning solution to the pressure vessel at low flow (3-4.5 m^3/h per pressure vessel) and low pressure (2 - 2.5 bar to prevent permeate being produced) to displace the process water already in the membranes. Low pressure minimizes redeposition of foulants on the membrane. Reject the concentrate to prevent dilution of the cleaning solution.
- Measure pH and adjust if necessary, and recycle around the system for 20 minutes. If the solution shows any sign of significant discoloration then discard and prepare fresh as per above to prevent possible membrane abrasion. Recirculating dirty cleaning solutions will lead to poor cleaning results and possible membrane damage.
- Once the pH, temperature, and color have stabilized, allow the elements to soak for as long as possible. One hour should be sufficient unless biological fouling is very severe. For difficult fouling, an extended soaking period (several hours) may be required followed by further recirculation.
- High-flow pumping. Feed the cleaning solution at high flow rates (8 - 10.2 m^3/h at 1.5 - 4.0 bar) for 30 - 60 minutes. The high flow rate flushes out the foulants removed from the membrane surface by the cleaning.
- Flush with good quality permeate to natural pH levels.

Step 3: Alkaline procedure (Repeat of Step 1)

Biocide application works best if applied between alkaline cleanings. The first alkaline application “softens” the fouling, allowing the biocide to penetrate and kill the microorganisms, and the second alkaline cleaning step optimizes their removal.

Step 4: Low pH, organic acid procedure to remove iron hydroxide fouling

If iron hydroxide fouling is present in addition to biofouling:

- Ideally, in order to prepare membranes for most efficient cleaning, heat the cleaning tank with permeate only to 30^oC and circulate around membranes for 10 - 15 minutes maintaining temperature, this will allow for more efficient cleaning.
- Prepare cleaning solution as per Table 1 with low pH, organic acid (such as citric acid), at around pH 2 - 4, and heat to 25-30^oC
- Low-flow pumping. Pump the mixed, preheated cleaning solution to the vessel at low flow (3-4.5 m^3/h per pressure vessel) and low pressure to displace the process water.
- Measure pH and adjust if necessary, maintain temperature and recycle around the system for 20-30 minutes. If the solution shows any sign of significant discoloration then discard and prepare fresh as per above to prevent possible membrane abrasion.
- Once the pH, temperature and color has stabilized allow the elements to soak for as long as possible ideally 2-4 hours. For difficult fouling an extended soaking period may be required, overnight for example.

- High-flow pumping. Feed the cleaning solution at high flow rates (8 - 10.2 m^3/h at 1.5 - 4.0 bar) for 30-60 minutes. The high flow rate flushes out the foulants removed from the membrane surface by the cleaning.
- Flush with good quality permeate to return to natural pH levels.

5 ADDITIONAL NOTES ON CLEANING

Always measure the pH during cleaning. If the pH increases more than 0.5 pH units during acid cleaning, more acid needs to be added. If the pH decreases more than 0.5 pH units during alkaline cleaning, more caustic needs to be added.

Long soak times should be broken up with short circulation periods. It is possible for the cleaning solution to become fully saturated and the foulants can deposit back onto the membrane surface. In addition, the temperature will decrease during this period, therefore the soaking becomes less effective. It is recommended to circulate the solution regularly in order to maintain the temperature (temperature should not drop more than 5°C) and add chemicals if the pH needs to be adjusted. Soaking times may be reduced if it is felt that no more deposits are being removed.

Turbid or strong-colored cleaning solutions should be replaced with a freshly prepared solution to avoid recirculating foulants around the system causing membrane damage.

6 REFERENCES

Peña, N., Gallego, S., del Vigo, F. and Chesters, S. P. 2013. Evaluating impact of fouling on reverse osmosis membranes performance, *Desalination and Water Treatment* 51, 958-961.

Villacorte, L. O. 2014. Algal blooms and membrane-based desalination technology. Ph.D. thesis UNESCO-IHE/TUDelft, ISBN 978-1-138-02626-1, CRC Press/Balkema, Leiden.