

Because of its warm water and high salinity, the Red Sea is well known as a challenging water source for seawater reverse osmosis (SWRO) processes. In particular, the warm water provides excellent conditions for growth of bacteriological organisms, and Red Sea desalination plants have a history of biofouling. The ability to apply chlorine to SWRO membranes provides a significant advantage. This article discusses combining cellulose triacetate membranes in the first pass with boron removal technology in the second pass and is based on experiences at the Shuqaiq IWPP project, which included tight specifications for chloride (18 mg/L) and boron (0.5 mg/L), in the final product water.

Matching Hollow-Fiber With Spiral-Wound Membranes: Process Compatibility and Optimization

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The Shuqaiq IWPP project consists of an 850-MW power plant and a 212,000 m³/day seawater reverse osmosis (SWRO) plant that began operating on May 29, 2010. Processes at the Shuqaiq plant have been detailed in many papers (Van der Mast et al, 2007; Al-Mahdi

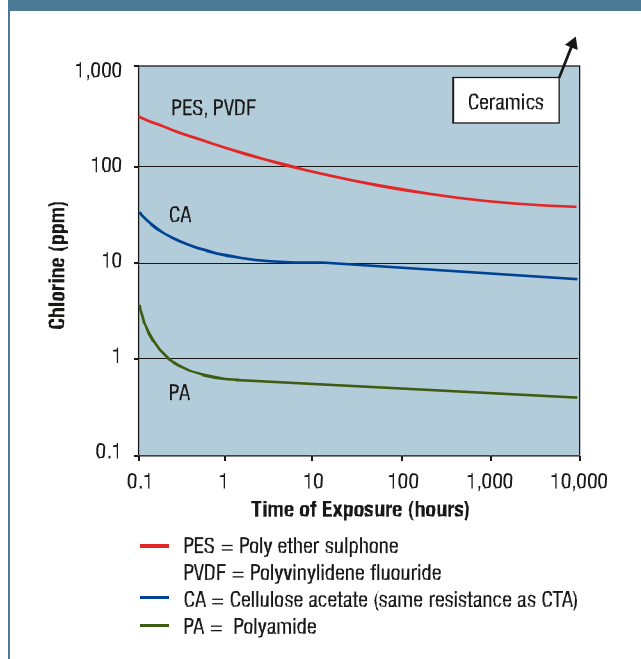
et al, 2009; Al Mohannadi et al, 2007); however, the processes described in this article relate only to combining cellulose triacetate (CTA) technology with boron removal technology.

When first-pass CTA membranes are combined with second-pass thin-film composite (TFC) membranes for boron removal, chlorine resistance of polyamide (PA) membranes is low and pH requirements for boron removal are high. Although a CTA membrane is intermittently chlorinated for 1 hour every 8 hours, chlorine in the first-pass permeate should not be allowed to enter the second-pass membranes, because this would result in rapid oxidation and second-pass performance loss. The chlorine resistance of both materials can be visualized in Figure 1 (University of Genoa, 2009–2010).

At Shuqaiq, the oxidizing effect of residual chlorine in first-pass permeate is neutralized by injecting sodium bisulphite (SBS) as a reducing agent. Caustic soda is dosed for pH elevation for boron removal, and an antiscalant is also dosed, as shown in Figure 2.

It is important that the dosing rate of each chemical used between the first and second passes is carefully controlled. If caustic soda is underdosed, the required boron standard in the final water will not be achieved. If caustic soda is overdosed, it is a waste of money, increases the system's scaling potential, and approaches the maximum pH recommended by TFC membrane suppliers (pH = 11 for continuous operation, 1 < pH < 13

Figure 1. Comparison of PA and CA chlorine resistance (concentration vs. exposure time)



Because heavy metals are usually rejected by the first pass, their presence in the second-pass feed was surprising.

for short-term chemical cleaning, maximum 30 minutes).

If antiscalant is underdosed, the second pass will scale and require chemical cleaning. However, overdosing of antiscalant represents a financial burden to the operator. It is essential that SBS not be underdosed, which would allow chlorine to enter and oxidize the second-pass membranes. The situation can be corrected only by replacing the membranes.

Because of the importance of dosing control, the process includes on-line monitoring of the first-pass permeate oxidation-reduction potential (ORP), as well as dual ORP monitors and free chlorine residual in the second-pass feed, downstream of all chemical addition. A three-way valve is installed on the first-pass permeate line upstream of the second pass so out-of-specification water can be dumped automatically, thereby protecting second-pass membranes.

Practical Experience

Because the required SBS dose is relatively low—stoichiometrically, 1.45 parts of SBS are required for every part of free chlorine, and the expected free chlorine residual in the first-pass permeate is 0.2–0.3 mg/L—and the chemical is relatively inexpensive, plant engineers decided to err on the side of caution by overdosing SBS during commissioning until the SBS system could be properly tuned. However, during the plant's initial operation, the PA membranes were damaged by oxidation. Several analyses of the damaged membranes were conducted.

Dye Test. To highlight oxidation of the membrane surface, a dye test was conducted by applying dye to the surface. If oxidation is detected, dye fixes to the surface. Figure 3 illustrates dye test results of the Shuqaiq membranes.

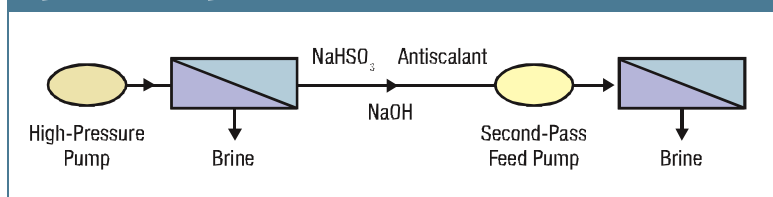
Electron Spectroscopy for Chemical Analyses (ESCA). Several membrane samples underwent ESCA analyses to evaluate the elemental composition of the membrane surface. These tests failed to identify the presence of halogens (Cl or Br) but did show an increased ratio of O:C, which might indicate oxidation.

Inorganic Analysis. An inorganic analysis was conducted on the membrane surface to evaluate the nature of potential inorganic fouling. Heavy metals (Fe, Cu, Zn, Mn, Ni) were detected.

Evaluation of Results

Testing results clearly showed that the membranes had been oxidized. However, because no halogen was found on the membrane's surface, there was no sign of oxidation

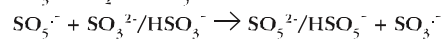
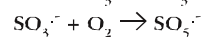
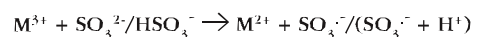
Figure 2. RO arrangement



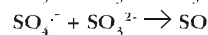
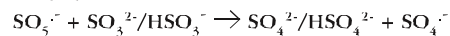
by chlorine. Therefore, an investigation to determine other potential oxidation routes not involving chlorine was conducted.

A literature review (Barron and O'Hern, 1966; Kawada et al, 1995; Nagai et al, 1994) identified a possible oxidation route in which SBS and sodium sulphite undergo auto-oxidation in the presence of heavy metals, which initiate a radical reaction. The mechanism can be expressed by the following reactions and is illustrated schematically in Figure 4.

Initiation:



Propagation:



Termination:

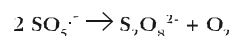


Figure 3. Dye test on oxidized membrane

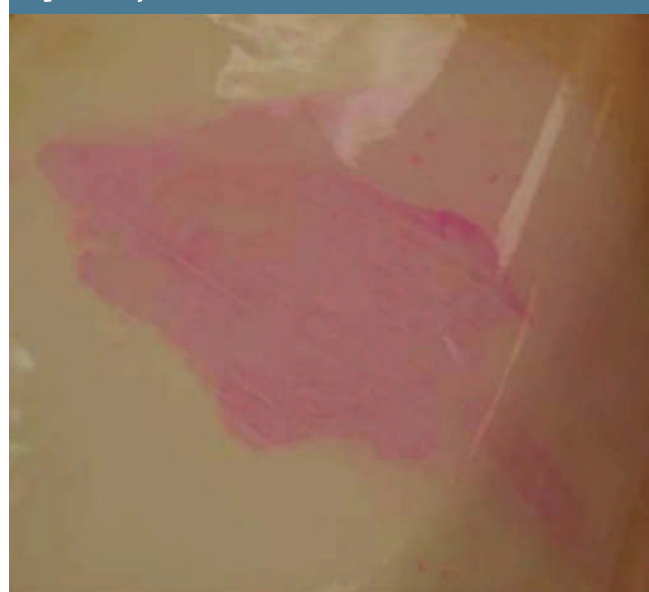
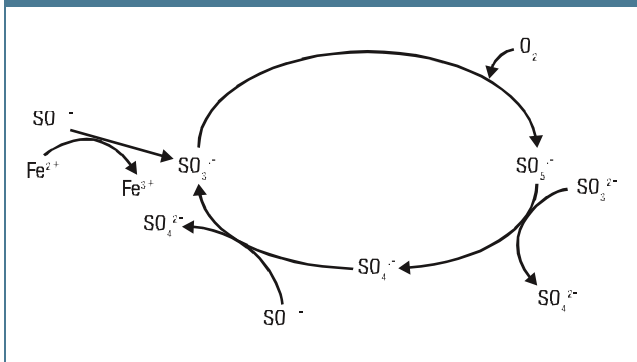


Figure 4. Reaction scheme



Considering the water's high pH resulting from the boron rejection requirement, it is also possible that hydroxyl radicals could be formed according to the following equation:



- The higher the pH, the faster the reaction, probably because SO_3^{2-} has a faster kinetic than HSO_3^- .
- The higher the concentration of the reducing agent (SBS), the faster the reaction.
- Heavy metals initiate a reaction.
- Oxygen is present.

Countermeasures

The fundamental parameters involved in the degradation mechanism are

- High pH
- Oxygen
- High SBS concentration
- Presence of heavy metals

High pH. Because of contractual requirements to produce product water with a maximum boron concentration

of 0.5 mg/L, reducing pH to slow down the reaction is not an option. If Saudi Arabian legislation adopts the revised World Health Organization (WHO) standard for boron (from 0.5 mg/L to 2.4 mg/L) and approved under the Power Water Purchase Agreement (PWPA) for Shuqaiq, it will be possible to operate the second pass at a lower pH, reducing the potential for the degradation reaction.

Oxygen Presence. Oxygen, which is involved in the first propagation step, is one of the chemical species required for the degradation reaction. Eliminating oxygen also eliminates other species such as $\text{SO}_3^{\cdot-}$. However, removing naturally present dissolved oxygen in raw seawater is not a practical solution for this plant.

High SBS Concentration. Several tests indicated that the increased SBS concentration influences the degradation reaction by causing more damage at a fixed time. It is clear that overdosing SBS during commissioning was a key factor in membrane oxidation. Therefore, the SBS concentration must be minimized as much as possible. Tightly controlling the SBS dose is critical, because underdosing results in membrane oxidation of free chlorine, and overdosing results in oxidation by the radical route.

Heavy Metal Presence. Heavy metals, which are involved in the initiation step, are required for the degradation reaction. It has been determined that concentrations as low as 10 µg/L of heavy metal (copper) can initiate degradation.

Because heavy metals are usually rejected by the first pass, their presence in the second-pass feed was surprising. However, there are other potential contamination sources, including dosed chemicals and corrosion of valves, pipes, and the second-pass feed-pump impeller.

At Shuqaiq, caustic soda and SBS were identified as the most probable source of heavy metal contamination. Therefore, the heavy metal contamination in the second-pass membrane feedwater was minimized by specifying low heavy metal concentration in the chemicals being dosed and minimizing the dose.

Using selective ion-exchange resin on the chemical line to selectively remove heavy metals was also considered but ruled out because of a concern that the caustic soda's high pH would precipitate hydroxides such as $\text{Fe}(\text{OH})_3$ and $\text{Cu}(\text{OH})_2$, which would foul the ion-exchange process.

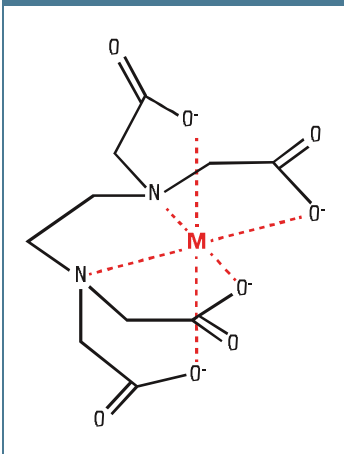
Instead of removing heavy metal contaminants from a chemical prior to injection, a chelating agent was used to form stable complexes with the heavy metal contaminants, thereby preventing them from initiating the radical oxidation reaction. Injecting a chelating agent masks the presence of heavy metals in process water and cleans the membrane surface by removing heavy metals that were previously deposited and could trigger the oxidative reaction.

Table 1. Radical species

Species	Reaction	Potential (V)
$\cdot\text{OH}^-$	$\cdot\text{HO}^- + e^- \rightarrow \text{OH}^-$	2.76
$\text{SO}_4^{\cdot-}$	$\text{SO}_4^{\cdot-} + e^- \rightarrow \text{SO}_4^{2-}$	2.6
O_3	$\text{O}_3 + 2 \text{H}^+ \rightarrow \text{O}_2 + \text{H}_2\text{O}$	2.07
$\text{S}_2\text{O}_8^{2-}$	$\text{S}_2\text{O}_8^{2-} + 2 \text{H}^+ + 2 e^- \rightarrow 2 \text{HSO}_4^-$	2.01
H_2O_2	$\text{H}_2\text{O}_2 + 2 \text{H}^+ + 2 e^- \rightarrow 2 \text{H}_2\text{O}$	1.77
ClO^-	$\text{ClO}^- + \text{H}_2\text{O} + 2 e^- \rightarrow \text{Cl}^- + 2 \text{OH}^-$	0.90

Under certain conditions, it is possible to oxidize spiral-wound membranes by overdosing the reducing agent (SBS).

Figure 5. Chelation mechanism of EDTA tetra sodium salt



The sodium salt of ethylenediaminetetraacetic acid (EDTA) was the first chemical chelant used at Shuqaiq. EDTA is widely used to chelate calcium and heavy metals. Figure 5 shows the mechanism of EDTA sodium salt chelation.

Before using the solution in the entire plant, a flat-membrane testing unit was used to evaluate EDTA's effectiveness as an

oxidation inhibitor. The reference parameter for membrane health was salt passage through the membrane (B value), which was evaluated at several SBS, heavy metal (copper), and EDTA concentrations. Table 2 summarizes the results.

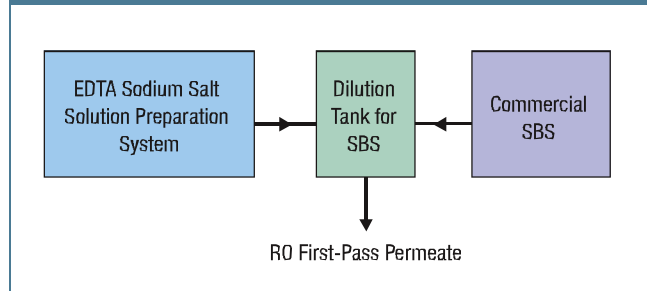
The Table 2 data illustrate that in the absence of Cu⁺⁺, the B value after the test is the same as for a new membrane. In addition, with process water containing 100 µg/L Cu⁺⁺ and a limited amount of SBS (0.75 mg/L, coincident with the design amount), the B value after the test is the same as for a new membrane.

However, when the SBS concentration was increased from 0.75 µg/L to 20 µg/L (concentration applied during the commissioning period) with 100 µg/L Cu⁺⁺, the B value increased significantly.

During the tests, EDTA concentration varied from 0.2 mg/L to 5 mg/L, keeping the Cu⁺⁺ fixed at 100 mg/L, to evaluate the minimum EDTA dose required to inhibit membrane oxidation. At 1 mg/L EDTA, there was no damage to the membrane surface. A further increase from 1 mg/L to 5 mg/L showed no improvement, and a decrease

Case	Chemical Concentration (mg/L)			Variation in B value
	Cu ⁺⁺	SBS	EDTA	
1	0	0	0	Same as new membrane
2	0	0.75	0	Same as new membrane
3	0.1	0.75	0	Same as new membrane
4	0.1	20	0	Strong increase
5	0.1	20	0.2	Strong increase
6	0.1	20	1	Same as new membrane
7	0.1	20	5	Same as new membrane

Figure 6. Arrangement for SBS dilution and EDTA sodium salt injection



to 0.2 mg/L did not prevent oxidation. Therefore, the minimum required EDTA concentration was determined to be 1 mg/L.

The experimental results provided enough confidence to increase the solution to the entire plant. To implement the EDTA sodium salt injection required a dedicated chemical injection line. The authors' experience is to combine the diluted SBS with the chelating agent as shown in Figure 6.

An alternative to injecting sodium salt EDTA is to use an antiscalant with chelating capabilities analogous to the sodium salt of EDTA, so only one chemical is injected instead of two.

Time Frame

- Nov. 9, 2009: First admission of seawater to the first-pass membranes.
- Beginning January 2010: After discontinuous operation, increased second-pass permeate conductivity was noted.
- Beginning April 2010: Injecting sodium salt EDTA in first-pass permeate was started (EDTA concentration in permeate 1 mg/L).
- Aug. 15, 2010: Antiscalant injection was started.
- From Dec. 6, 2010: The sodium salt EDTA injection was halved to 0.5 mg/L; the antiscalant injection was 2 mg/L instead of the theoretical 1.6 mg/L.
- Dec. 20, 2010: The sodium salt EDTA injection was stopped in one train as a trial.
- From Jan. 4, 2011: The sodium salt EDTA injection was stopped in all trains.

Conclusions

Under certain conditions, it is possible to oxidize spiral-wound membranes by overdosing the reducing agent (SBS). The auto-oxidation reaction can be inhibited by reducing the SBS injection rate and injecting the sodium salt of EDTA or an antiscalant with a chelating effect similar to EDTA's sodium salt.

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Editor's Note

This article is an updated, peer-reviewed version of a paper presented at IDA World Congress 2011, Sept. 4–9, Perth, Western Australia.