

## **MATCHING HOLLOW FIBRE WITH SPIRAL WOUND MEMBRANES. PROCESS COMPATIBILITY AND OPTIMISATION**

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### **Abstract**

The Red Sea is well known as being a challenging water source for seawater reverse osmosis (SWRO) processes, because of the warm temperature and high salinity. In particular, the warm temperature provides excellent conditions for the growth of bacteriological organisms, and there is a history of biofouling being a problem for SWRO plants on the Red Sea. Therefore, the ability to be able to apply chlorine to the SWRO membranes is seen as a very significant advantage, and this has resulted in the cellulose triacetate (CTA) hollow fibre (HF) membrane offered by Toyobo dominating the SWRO membrane market on the Red Sea coast of Saudi Arabia. The Toyobo CTA membrane is employed at the major plants of Jeddah, Yanbu, Rabigh and Shuqaiq along this coast.

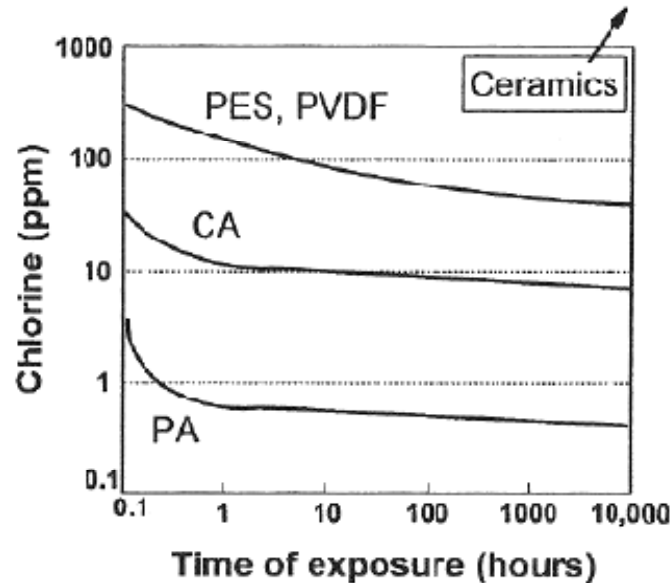
This paper discusses issues relating to the combination of CTA membranes in the first pass with boron removal technology in the second pass. The paper is based on the authors' experiences from the Shuqaiq IWPP project, which included very tight specifications for chloride (18 mg/l) and boron (0.5 mg/l) in the final product water. The Shuqaiq IWPP project was built by Mitsubishi Heavy Industries for Shuqaiq Water and Electricity Company (SqWEC) and consists of a 850 MW Power Plant and a 212,000 m<sup>3</sup>/day SWRO plant which entered into commercial operation on the 29<sup>th</sup> of May 2010. The Shuqaiq process has been described in detail in previous papers and will only be described here as far as it specifically relates to the issues of combining CTA technology with boron removal technology. At Shuqaiq, boron removal is achieved using thin film composite (TFC), polyamide (PA), spiral wound membranes.



## I. KEY ISSUES

The key issues resulting from the coupling of CTA membranes in the first pass with TFC membranes for boron removal in the second pass are the low chlorine resistance of the polyamide membrane and the high pH required for boron removal. While the CTA membrane is intermittently chlorinated for one hour every eight hours, it is absolutely essential that none of the chlorine in the first pass permeate is allowed to enter the second pass membranes, since this would result in rapid oxidation and loss of performance of the second pass.

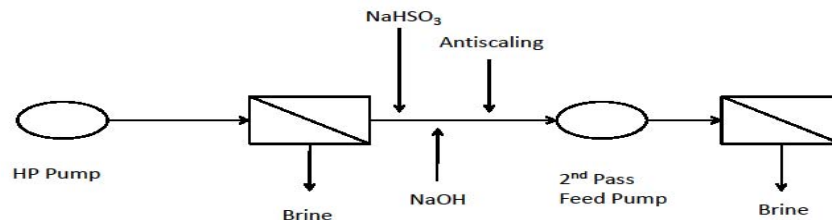
It is possible to see the chlorine resistance of both materials in Figure 1 below [1]:



**Figure 1 Comparison CTA and polyamide chlorine resistance (Concentration vs. Time of exposure)**

Note: PA = polyamide, CA = cellulose acetate (same resistance as cellulose triacetate), PES = poly ether sulphone, PVDF = polyvinylidene fluoride

At Shuqaiq, the oxidizing effect of residual chlorine in the first pass permeate is neutralised through the injection of sodium bisulphite (SBS) as a reducing agent. In addition, caustic soda is dosed for pH elevation for boron removal and an anti scalant is also dosed, as shown the figure 2 below:



**Figure 2 Reverse Osmosis Arrangement.**

It is important that the dosing rate of each of the chemicals dosed between the first and second passes is very carefully controlled. If caustic soda is underdosed, then the required boron standard in the final water will not be achieved, but if it overdosed, this is not only a waste of money, but also increases the scaling potential of the system, and gets close to the maximum pH advised by the suppliers of the TFC membranes (pH = 11 for continuous operation,  $1 < \text{pH} < 13$  for short term chemical cleaning max. 30 minutes). If antiscalant is underdosed, then the second pass will scale, and require chemical cleaning, whereas overdosing of antiscalant represents a financial penalty to the operator. It is clearly essential that the SBS is not underdosed, since this would result in chlorine entering and oxidising the second pass membranes, which can only be rectified by membrane replacement.

Because of the importance of dosing control, the process is provided with on line monitoring of the 1<sup>st</sup> pass permeate ORP as well as dual ORP monitors and free chlorine residual in the second pass feed, downstream of all the chemical addition. In addition, a three way valve is installed on the 1<sup>st</sup> pass permeate line upstream of the second pass so that out of specification water can be dumped automatically, thereby protecting the second pass membranes.

## II. 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 in the range of 0.2 to 0.3 mg/l), and the chemical is relatively cheap, the commissioning engineers decided to err on the side of caution, and overdose SBS during commissioning until the SBS system could be properly tuned. However, during initial operation of the plant, the polyamide membranes were damaged by oxidation.

Several analyses were conducted on the damaged membranes as described below.

### 2.1. Dye Test

The dye test is used in order to highlight oxidation of the surface of the membrane, by applying a dye on the surface. If there is any kind of oxidation, the dye will be fixed to the surface. Figure 3 below shows the results of the dye test on the Shuqaiq membranes.



Figure 3 Dye Test on oxidised membrane

## 2.2. ESCA analyses

Electron Spectroscopy for Chemical Analyses (ESCA) analyses were conducted on several membrane samples 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 increase in the ratio of O:C, which might be an indication that oxidation had occurred.

## 2.3. Inorganic analysis

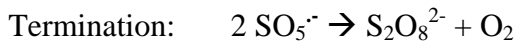
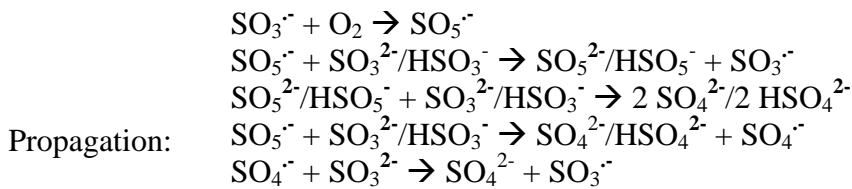
An inorganic analysis was conducted on the membrane surface to evaluate the nature of any potential inorganic fouling. Presence of heavy metals (Fe, Cu, Zn, Mn, Ni) was detected.

## III. EVALUATION OF THE RESULTS

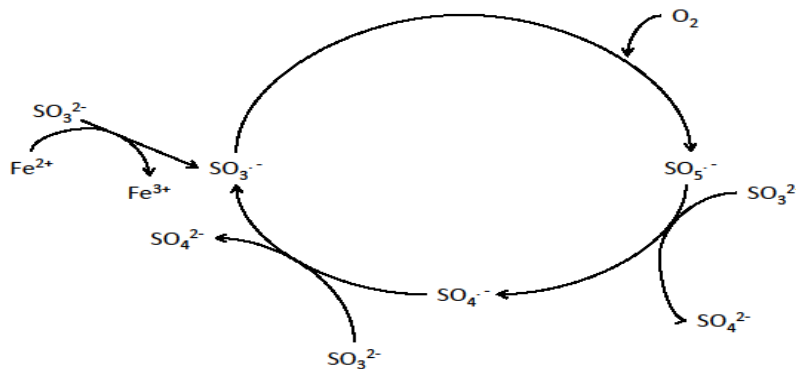
The results very clearly showed that the membranes had been oxidised, but with no sign of oxidation by chlorine, since no halogen was found on the surface of the membrane. An investigation was therefore made to determine any other potential oxidation route, not involving chlorine.

A literature review [ii, iii, iv] identified a possible oxidation route in which SBS and sodium sulphite undergo auto-oxidation in the presence of heavy metals, which act as the initiator of a radical reaction. The mechanism can be expressed by the following reactions:



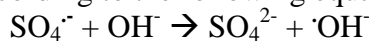


And is indicated schematically in figure 4 below:



**Figure 4 Reaction scheme**

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



As it is possible to see from the reactions listed above, the auto-oxidation of sodium bisulphite involves formation of radicals; these species are very aggressive due to their unstable nature and they show a high red-ox potential.

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

The reaction rate is function of the following parameters:

- pH, the higher the pH the faster the reaction, probably due to a faster kinetic of  $\text{SO}_3^{2-}$  than  $\text{HSO}_3^-$
- concentration of the reducing agent (SBS): the higher the concentration the faster the reaction
- presence of heavy metals, acting as initiator of the reaction
- presence of oxygen

#### **IV. COUNTERMEASURES**

The fundamental parameters involved in the degradation mechanism are, as aforementioned:

1. High pH
2. Oxygen
3. High SBS concentration
4. Presence of Heavy Metals

##### **4.1. High pH**

Due to the contractual requirement to produce product water with a maximum boron concentration of 0.5 ppm, it is presently not possible to reduce the pH in order to slow down the reaction. In future, if the revision of the WHO standard for boron from 0.5 mg/l to 2.4 mg/l is passed into Saudi Arabian legislation and the Power Water Purchase Agreement (PWPA) for Shuqaiq, then it will be possible to operate the second pass at a lower pH, reducing the potential for the degradation reaction.

##### **4.2. Oxygen presence**

Oxygen is one of the chemical species required for the degradation reaction, being involved in the first step of the propagation. Eliminating it would also eliminate other species such as  $\text{SO}_5^-$ . However, removal of dissolved oxygen naturally present in the raw sea water is not a practical solution for this plant.

##### **4.3. High SBS concentration**

Several tests indicated that the concentration of SBS influences the degradation reaction since an increase of SBS concentration results in a higher damage, at fixed time.

It is clear that the overdosing of SBS during commissioning was a key factor in causing the membrane oxidation. Therefore, the SBS concentration must be minimised as far as practically possible. Very

tight control of the SBS dose is critical, since underdosing results in oxidation of the membranes by free chlorine, but overdosing results in oxidation by the abovementioned radical route.

#### 4.4. Heavy Metal Presence

Heavy metals are required for the degradation reaction to take place since they are involved in the initiation step.

It has been determined that concentrations as low as 10 ppb (10 µg/l) of heavy metal (copper) are able to initiate the degradation.

The heavy metal presence in the second pass feed was quite surprising since all the heavy metals are expected to be rejected by the first pass. However, there are other potential sources of contamination such as corrosion of valves, piping, impeller of the second pass feed pump, or in the chemicals dosed as part of the process.

At Shuqaiq, the caustic soda and SBS were identified as the most probable source of heavy metal contamination. Therefore, the concentration of heavy metal contamination in the 2<sup>nd</sup> pass membrane feed water was minimised by the specification of very low heavy metal concentration in the chemicals being dosed, as well as minimising the actual dose of the chemicals applied.

The use of selective ion exchange resins on the chemical line to selectively remove the heavy metals was also considered, but was ruled out because of concern that the high pH of the caustic soda would precipitate hydroxides such as Fe(OH)<sub>3</sub> and Cu(OH)<sub>2</sub> which would foul the ion exchange process.

Instead of removing the heavy metal contaminant from the chemical prior to injection, it was therefore decided to use a chelating agent to form stable complexes with the heavy metal contaminants, thereby making them unavailable to initiate the radical oxidation reaction. The injection of a chelating agent not only masks the presence of heavy metals in the process water but also has the capability of cleaning the membrane surface by removing heavy metals which were previously deposited and therefore could have triggered the oxidative reaction in the future.

The first chemical chelant used at Shuqaiq was the sodium salt of EDTA, which is widely used to chelate not only calcium but also heavy metals.

The mechanism of EDTA Sodium salt chelation is shown in Figure 5

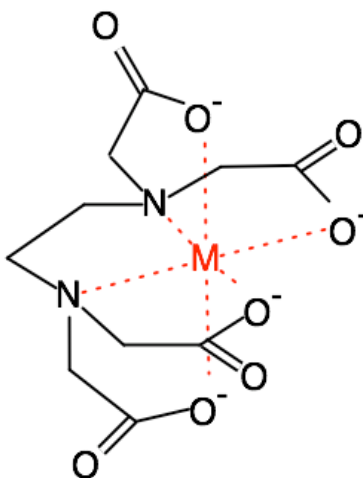


Figure 5 Mechanism of EDTA action on heavy metals

Before implementing the aforementioned solution to the entire plant, the effectiveness of the EDTA injection, as oxidation inhibitor, was evaluated experimentally with a flat membrane testing unit. The

considered reference parameter for the membrane health was the salt passage through the membrane (B value) which was evaluated at several different SBS, heavy metal (copper) and EDTA concentrations.

The results are summarised in Table 1

**Table 1 Summary of B value evaluation at several process conditions**

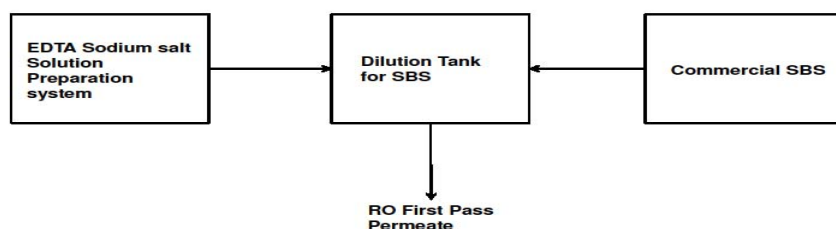
Case	Chemical concentration (ppm)			Variation in B value
	Cu <sup>++</sup>	SBS	EDTA	
1	0	0	0	As new membrane
2	0	0.75	0	As new membrane
3	0.1	0.75	0	As new membrane
4	0.1	20	0	Strong increase
5	0.1	20	0.2	Strong increase
6	0.1	20	1	As new membrane
7	0.1	20	5	As new membrane

From the table, it can be seen that in the absence of Cu<sup>++</sup> the B value after the test is the same as for a new membrane. Also, with a process water containing 100 ppb Cu<sup>++</sup> and a limited amount of SBS (0.75 ppm, 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 ppm up to 20 ppm (concentration applied during the commissioning period) with 100 ppb Cu<sup>++</sup>, there was a significant increase in the B value.

During the tests, the EDTA concentration was varied from 0.2 ppm to 5 ppm, keeping the Cu<sup>++</sup> fixed at 100 ppm, in order to evaluate the minimum EDTA dose required to inhibit the oxidation of the membrane. It was found that, at 1 ppm EDTA no damage to the membrane surface took place; a further increase from 1 to 5 ppm did not show any improvement while a decrease down to 0.2 ppm was not preventing from the oxidation. Therefore it was decided that the minimum required EDTA concentration was 1 ppm.

The experimental results gave enough confidence to scale up the solution to the entire plant. To implement the EDTA sodium salt injection a dedicated chemical injection line was required. Our experience is to combine the injection of diluted SBS with the injection of the chelating agent as shown in Figure 6:



**Figure 6 Arrangement for SBS dilution and EDTA Sodium salt injection**



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

## V. TIME FRAME

- 1st admission of seawater to the 1<sup>st</sup> pass membranes, 9<sup>th</sup> of November 2009
- After discontinuous operation, an increase of 2<sup>nd</sup> pass permeate conductivity was noted at the beginning of January 2010
- At the beginning of April 2010, injection of the sodium salt of EDTA in 1<sup>st</sup> pass permeate started (EDTA concentration in permeate 1 ppm)
- Around the 15<sup>th</sup> of August 2010 the antiscalant injection started
- From the 6<sup>th</sup> of December 2010, the sodium salt of EDTA injection was halved to 0.5 ppm (antiscalant injection 2 ppm instead of theoretical 1.6 ppm)
- From the 20<sup>th</sup> of December 2010 the sodium salt of EDTA injection was stopped in one train as trial
- From the 4<sup>th</sup> of January 2011, the sodium salt of EDTA injection stopped in all trains

## VI. CONCLUSIONS

Under certain conditions, it is possible to oxidise spiral wound membranes by overdosing the reducing agent, SBS.

The autoxidation reaction can be inhibited, by reducing the SBS injection rate and injecting either the sodium salt of EDTA or an antiscalant with a chelating effect similar to the sodium salt of EDTA.

## VII. REFERENCES

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<sup>i</sup> Second Level Master “Innovative Membrane Technologies & Conventional Processes For Waste And Drinking Water Treatment”, Module 9, University of Genoa, Faculty of Chemistry and Industrial Chemistry

<sup>ii</sup> C.H. Barron, H.A. O’Hern “Reaction kinetics of sodium sulphite oxidation by the rapid mixing method

<sup>iii</sup> I. Kawada, K. Nagura, H. Iwahori, Y. Kamiyama “Generation of certain oxidizing agents and their inhibition with higher copper concentrations in sea water desalination systems

<sup>iv</sup> M. Nagai, H. Iwahashi, Y. Hayashi, Y. Ogino “The behaviour of an oxidizing/reducing agent in seawater”

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