



FILMTEC Membranes

Experiences with Fouling Resistant Membranes in Combination with Intermittent Biocide Dosage

Site Information

Location:

Germany

Purpose:

Control biofouling without using chlorine or other oxidizing agents.

Performance:

After almost 4 years of stable performance, no biofouling has been detected and the elements have required only 1 to 2 cleanings per year.



VA Tech built a new water treatment plant using intermittent biocide dosage and fouling resistant membranes, rather than chlorine, to produce process water from a nearby river, the Weisse Elster. (Photo courtesy of Infra-Zeitz)

Introduction

A new industrial park was established on the site of a former hydrogenation plant in Zeitz, Germany, 40 km south of Leipzig. Radici Deutschland GmbH, a producer of adipic acid and other intermediates for polyamide 6.6, started up an integrated polyamide plant on the site in 2001. Other companies have established production facilities since then. The local company Infra-Zeitz provides an excellent infrastructure, with facilities for supply of water, steam, and technical gases, and for the treatment of waste. Process water is made using reverse osmosis (RO) and ion exchange technologies with feed from a small nearby river, the "Weisse Elster." Other RO plants in the industrial area of Leipzig and Halle are also operating on river water, and most of them have been plagued with biofouling. For this reason, VA Tech,¹ which built the new water treatment plant for Infra-Zeitz with a capacity of 200 m³/h, decided to use a new approach. VA Tech opted for a system using no chlorine, but intermittent biocide dosage and specified FILMTEC™ BW30-365FR fouling resistant membranes.

Background

Fouling is the main threat in the smooth operation of RO plants. Fouling leads to increased energy consumption due to added water flow resistance through the membrane and through the feed spacer. It also results in the need for more frequent cleaning, which can shorten the life of elements and add cost to the process. Of the different types of fouling, the most insidious one is biofouling. Many RO plants using surface water as a raw water source suffer from biofouling. A biofilm is a matrix of living organisms that are adapted to the prevailing conditions and protected from destructive influences, such as hydrodynamic shear forces or disinfecting chemicals. The surface of an RO membrane is an ideal place for bacteria to live and grow—concentrated nutrients are delivered continuously, and the shear forces are low under the cover of the biofilm.

Background, cont.

A number of strategies have been employed to control biofouling in RO systems. The approach reported here is a combination of using a membrane surface with a reduced affinity to bacterial adhesion and the intermittent application of a nonoxidizing biocide. The synergistic effect has been demonstrated² and was applied successfully in one of the world's largest wastewater reclamation systems in Singapore.³ This case history (Infra-Zeitz) is unique in that neither chlorine nor any other oxidizing agents are being used in the pretreatment to prevent the breakdown of the natural organic matter into more biodegradable fragments.

Reverse Osmosis Membrane Element

The fouling resistant RO membrane element FILMTEC BW30-365FR is based on the construction of the standard element FILMTEC BW30-365. The main characteristics of this construction are the active membrane area of 34 m² (365 ft²), the 0.86-mm (34-mil) thick feed spacer, and a high number of short leaves. The design and the thickness of the feed spacer helps reduce the rate of feed channel plugging and improves the cleanability of the element. The reduced leaf length helps reduce the permeate flow resistance inside the leaf, so that a more uniform flux profile can be achieved. In particular, high flux values and high fouling rates close to the product water tube can be avoided. The optimized element design is realized by using automated, precision fabrication.

The membrane itself is an FT30 polyamide composite RO membrane which has been chemically modified to make the surface less prone to the attachment and colonization of bacteria. This fouling resistant (FR) membrane has a smooth surface, is hydrophilic like glass, and has a strongly negative surface charge. The membrane is as chemically stable as the standard membrane and can be cleaned at a pH range of 1 to 12. The specified performance of the FILMTEC BW30-365FR element is 36 m³/d (9,500 gpd) and 99.5% rejection with a 2,000 mg/L NaCl test solution at 15.5 bar (225 psi) and 25°C.

Biocide

DBNPA (2,2 dibromo-3-nitrilo-propionamide) is a fast-acting, nonoxidizing biocide which is very effective at low concentrations. Microorganisms that come into contact with it are rapidly killed by a mechanism that appears to involve a reaction with the protein fraction of the cell membrane and inactivation of enzyme systems. The vast majority of microorganisms are killed within 5 to 10 minutes. In aquatic environments the biocide decomposes rapidly to carbon dioxide, ammonia, and bromide, and is therefore environmentally safe. It can be applied either as a continuous low dosage, as an intermittent dosage while the RO system is in operation (shock dosage, slug dose), or offline in clean-in-place (CIP) mode. The most frequently used mode is the intermittent dosage.

Raw Water Supply and Pretreatment

The raw water is taken from the surface of the river. The Weisse Elster shows a wide variation of flow rate and water quality, see Table 1. The organic load and amount of bacteria indicate a high risk of biofouling. The relatively low specific UV absorption (SUVA) value indicates a high fraction of low molecular weight organic matter and high biodegradability.⁴ SUVA is calculated from the ratio UV-254/DOC (dissolved organic carbon).

Raw Water Supply and Pretreatment, cont.

Table 1. Flow rate and water quality of river Weisse Elster during the period from May 2001 to September 2002.

Property	Unit	Min.	Max.
Flow rate	m ³ /s	3.9	67.9
Temperature	°C	0.3	20.4
pH	—	7.7	8.8
Conductivity	mS/m	54	171
COD ^a	mg/L	16	28
DOC ^b	mg/L	3.2	6.2
UV-254	1/m	7	12.8
SUVA ^c	m ² /g	2.2	2.1
AOX ^d	µg/L	18	46
Colony count	1/mL	800	50,000
Coliform count	1/mL	20	2,000

^aChemical oxygen demand

^cSpecific UV absorption

^bDissolved organic carbon

^dAdsorbable organic halogens

In the existing water works the coarse particles are removed with screening devices, and ferric chloride is injected into the pressurized pipe of the raw water pumps at a concentration of 5 mg/L Fe. At the entry of the flocculation tanks, an anionic polyelectrolyte is added (0.25 mg/L). The flocs are separated in inclined tube settlers and open sand filters with a bed depth of 1,100 mm and a grain size of 1.0 to 1.6 mm. The specification of this utility water is ≤10 mg/L of suspended solids.

The utility water is collected in a storage tank and pumped to the site of the new RO unit. A heat exchanger can be used to maintain a temperature of not less than 14°C. Another 2 mg/L Fe is added as ferric chloride before the water enters into closed sand filters. The filtrate is further filtered by backwashable 5-µm filters and 3-µm cartridge filters. A scaling inhibitor is added into the suction side of the high pressure RO pumps (2 mg/L Aktiphos 640).

Reverse Osmosis System

The RO system is made of three independent trains, each with a permeate design flow rate of 66.7 m³/h (300 gpm) at a recovery of 80%. Each train has three stages with ten, five, and three pressure vessels respectively; each vessel houses five membrane elements. The total number of FILMTEC BW30-365FR elements is 270, and the average permeate flux is 22 L/m²/h (13 gfd).

The vessels and piping are made of stainless steel. Each vessel can be sampled and probed individually. Pressure gauges are installed before and after each stage. The RO permeate is collected in a tank. Part of the permeate (50 m³/h) is further polished in two streams of cation exchange resins, degasser, anion exchange resins, and mixed bed resins. DOWEX™ MARATHON™ resins are used for the ion exchange process.

Operation of the RO System

The first RO train started in May 2001, the second followed in July 2001, the third in July 2002. In times of low demand one of the trains is shut down. After the shutdown, the membranes are flushed at low pressure with feed water, then with permeate water. During the shutdown period the plant is flushed with permeate water every 15 hours. During operation, the concentrate valve opens every 2 hours for 10 minutes of flushing.

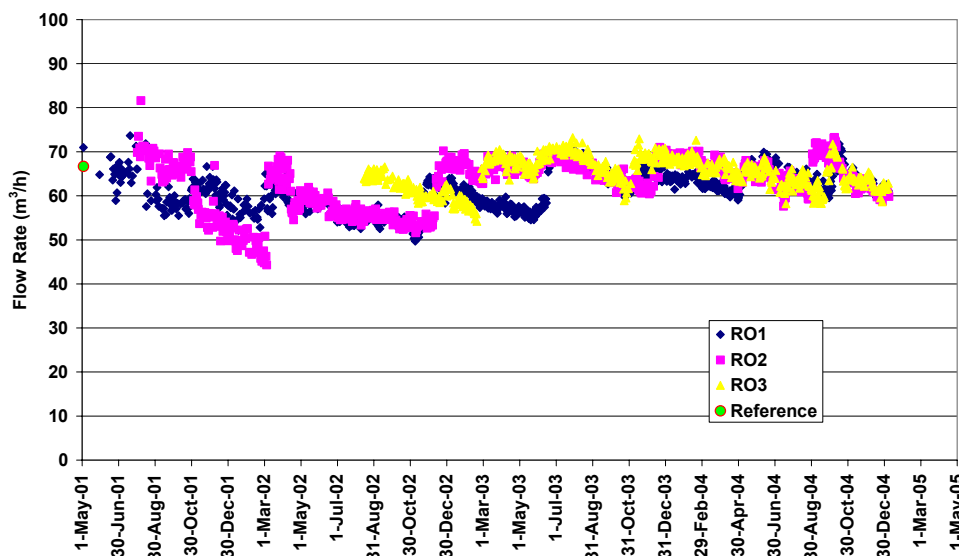
Once a week DBNPA is added to the feed water for 1 hour at about 20 mg/L during operation. The colony count in the concentrate is typically zero during dosage and can be as high as 100,000/mL before dosage.

The cleaning procedure is a sequence of three cleanings: an alkaline cleaning with surfactants and enzymes at pH 11.5, an acid cleaning with inorganic and organic acids at pH 1.8, and a final alkaline cleaning at pH 11 to 12. Each stage is cleaned separately with a fresh solution at 40°C for 45 min at a feed flow rate of 10 m³/h (44 gpm) per vessel. For better results the enzymatic alkaline cleaning solution is left in the system overnight.

Normalized RO Performance

The RO system was designed for the specified system performance at defined conditions using a typical feed water analysis and average temperatures. The design start-up performance is the projected performance of the system assuming the use of new elements performing according to the published specification. In reality, the feed water quality and temperature varies widely, and the permeate flow rate and recovery are not always maintained. The feed pressure needed to obtain the required flow rate ranged from 8 to 13 bar, and the permeate conductivity fluctuated between 7 and 20 µS/cm, making data normalization necessary to compare the observed system performance against the projected performance. The normalization program FTNORM⁵ is based on ASTM Standard D4516 and takes into account the actual operating conditions. It calculates the system performance at any time as if the system were operating under design conditions. Figure 1 shows the normalized permeate flow performance of each of the RO trains for more than three years.

Figure 1: Permeate flow performance (normalized to design start-up performance).

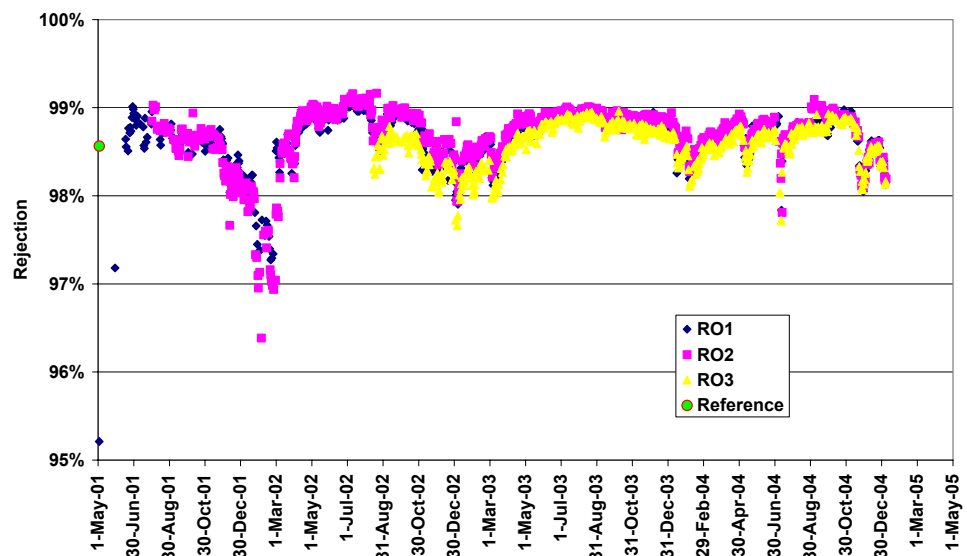


Normalized RO Performance, cont.

Each of the trains started with a performance consistent with the reference start-up design of 66.7 m³/h (300 gpm). The observed fouling rate was about 10% flow loss every 2 to 3 months during the first year, and about 10% flow loss every 6 months later on. A 10% loss of normalized flow performance indicates cleaning should be initiated. So far, RO1 has been cleaned six times in 39 months, RO2 three times in 37 months, and RO3 two times in 24 months of operation. During the first two years, the membranes were allowed to lose more than 10% flow performance before a cleaning was initiated. Since then, however, a cleaning is triggered whenever the normalized flow has lost 10% of the initial design value. In this way the system always operates in a range of 70 to 60 m³/h (308 to 264 gpm). The flow performance of all three lines in August 2004 was close to the initial performance, with the membranes performing like new according to the nominal specification.

The salt rejection of the system during the same period is plotted in Figure 2. The reference salt rejection of 98.6% is the projected salt rejection of the system under design conditions with new elements when the average element salt rejection is 99.5%. After some initial o-ring leakages had been repaired, the measured and normalized salt rejection of RO1 and RO2 matched with the reference until December 2001. Then the rejection decreased to 97%, but recovered to reference performance after cleaning. In the following months, the rejection of RO1 and RO2 stabilized at 99% and came back to the reference value by February 2003. An interesting observation is that RO1 and RO2 performed almost identically and followed the same fluctuations. RO3 is also in accordance with this rejection profile except that the rejection is slightly lower due to some o-ring leakage.

Figure 2: System salt rejection (normalized to design start-up performance).

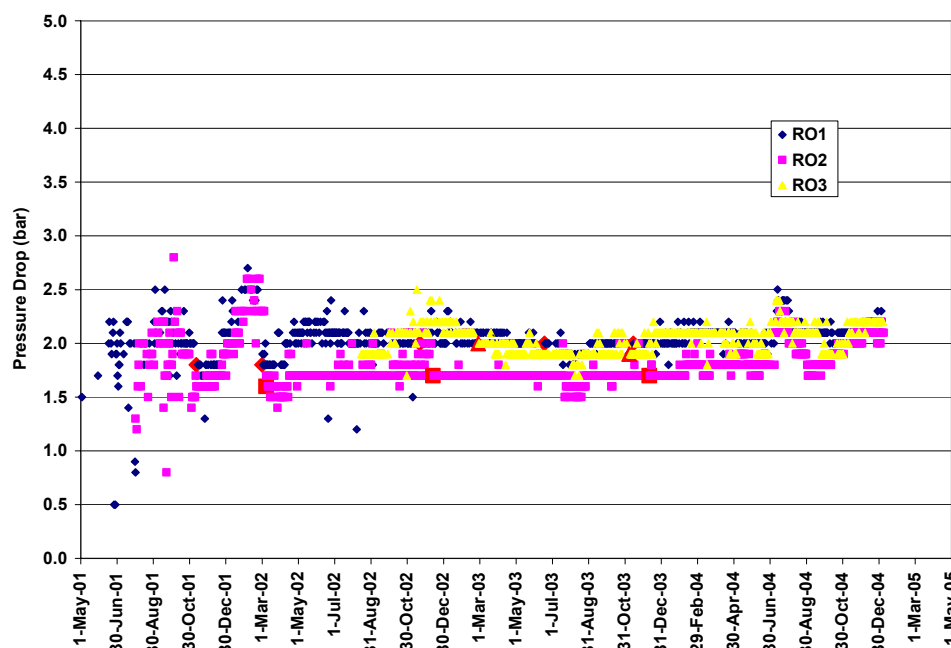


The rejection appears to follow a yearly profile with a temporary drop during wintertime. Part of the drop may be explained by fouling of the membrane, but there seems to be an influence of the raw water quality as well. The rejection drop in the beginning of 2002 coincided with a flood of the river and low raw water conductivity. After more than 3 years of operation, the rejection of all three lines still matches the initial design value.

Normalized RO Performance, cont.

The pressure drop of the system, i.e., the difference between the pressure in the concentrate and in the feed, is a sensitive measure of the degree of plugging of the feed channel spacer. Biofouling is typically first recognized by a pressure drop increase, particularly in the first stage. The pressure drop of this RO system is shown in Figure 3. The pressure drop of each of the trains was about 2 bar in a range between 1.5 and 2.5 bar. This value is across all three stages, 15 elements in series, and is below the projected pressure drop for the new system. It is mainly this result that demonstrates the absence of biofouling in this system.

Figure 3: System pressure drop from feed to concentrate.



Measured vs. Projected Performance

On November 18, 2002, just before cleaning, water samples were taken of RO1 to verify the membrane performance. The plant performance under prevailing conditions was projected with ROSA⁶ and compared with the measured results. The measured pressure was about 15% higher than the pressure calculated on the basis of new membranes. This is in agreement with the normalized flow performance before cleaning. The raw water at the time of sampling had a very low conductivity of 545 $\mu\text{S}/\text{cm}$. The measured permeate conductivity was 11 $\mu\text{S}/\text{cm}$, which corresponds with a projected permeate total dissolved solids (TDS) of 6.8 mg/L. The measured and projected permeate chloride concentrations were in agreement as well (0.6 mg/L). Nitrate and silica were measured lower than projected (1.6 vs. 2.1 mg/L and 0.07 vs. 0.14 mg/L, respectively). The DOC rejection of the membrane system at 80% recovery was 97%.

Conclusion

After more than three years of field experience, the chosen concept of using fouling resistant membranes in combination with a weekly slug dose of DBNPA has been proven successful. No biofouling has been detected, and only one to two cleanings per year are necessary. The membranes performed like new at the end of the observation period, without any permanent loss in flow and salt rejection. Harsh cleanings at pH 12 and 40°C apparently have no negative effect on salt rejection and subsequent fouling rate.

Acknowledgment

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5. FTNORM normalization software can be downloaded from www.filmtec.com.
6. ROSA FILMTEC system projection software can be downloaded from www.filmtec.com.

LENNTECH

info@lennotech.com Tel. +31-152-610-900

www.lennotech.com Fax. +31-152-616-289

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