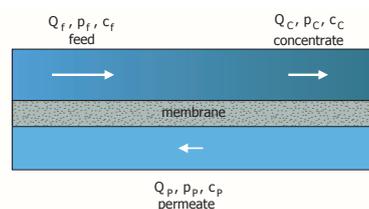
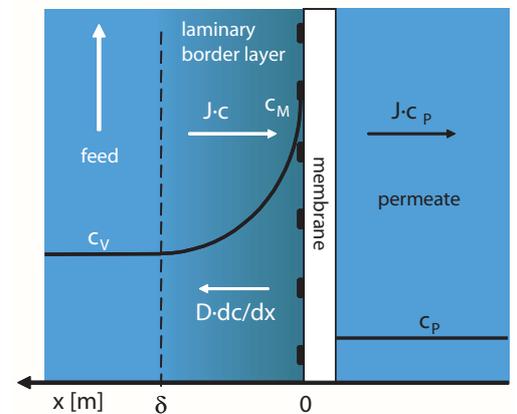
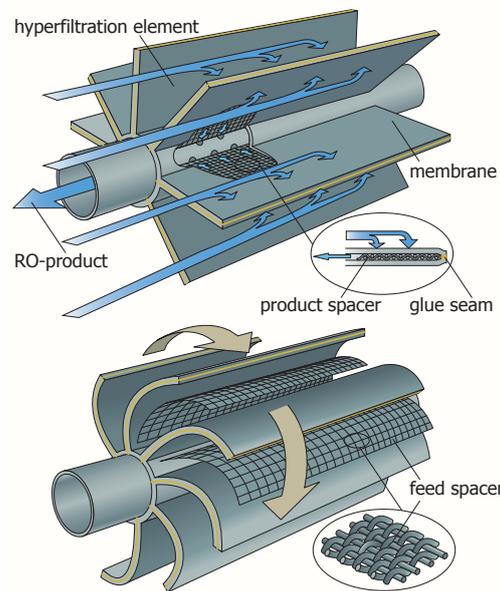


# Nanofiltration and reverse osmosis



**Framework**

This module examines nanofiltration and reverse osmosis.

**Contents**

This module has the following contents:

1. Introduction
2. Principle
  - 2.1 (Reverse) osmosis
  - 2.2 Fouling of membranes
  - 2.3 Membrane configuration
  - 2.4 Feed, permeate and concentrate
  - 2.5 Cross-flow operation
3. Theory
  - 3.1 Mass balance
  - 3.2 Kinetics
  - 3.3 Concentration polarization
4. Practice
  - 4.1 Nanofiltration
  - 4.1 Christmas tree configuration
  - 4.2 Cleaning
  - 4.3 Field installations

## 1 Introduction

Reverse osmosis is one of the membrane filtration processes. The process is used to remove salts and organic micropollutants from water.

Because reverse osmosis is able to remove very small particles from water, fouling of the membrane can easily occur. Reverse osmosis is therefore always preceded by a pre-treatment step to remove particulate matter. This pre-treatment can be a conventional pre-treatment (coagulation, flocculation, sedimentation, filtration) or an ultrafiltration pre-treatment.

In reverse osmosis almost all dissolved particles present in water will be retained, so the produced flow (permeate) has a low mineral content. Therefore, the permeate is sometimes conditioned (limestone filtration or aeration) to correct the pH and the aggressiveness of the permeate.

In nanofiltration almost all divalent ions are retained; the monovalent ions are only partly retained.

## 2 Principle

### 2.1 (Reverse) osmosis

Osmosis is a natural process of flow through a semi-permeable membrane. When pure water of the same temperature is present on both sides of a membrane and the pressure on both sides is also equal, no water will flow through the membrane. However, when the salt on one side is dissolved

into the water, a flow through the membrane from the pure water to the water containing salts will occur (Figure 1, left and middle). Nature tries to equalize concentration differences.

When pressure is applied on the side where the salts are added, a new equilibrium will develop. The extra pressure will result in a flow of water through the membrane, but the salts do not flow through.

This phenomenon is called reverse osmosis (Figure 1, right).

The driving force for reverse osmosis is the applied pressure minus the osmotic pressure.

The energy consumption of reverse osmosis is directly related to the salts concentration, since a higher salt concentration has a higher osmotic pressure.

### 2.2 Fouling of membrane

The fouling of a reverse osmosis membrane is almost inevitable.

Particulate matter will be retained and is an ideal nutrient for biomass, resulting in biofouling.

Another important fouling process is scaling, the formation of salt precipitates.

Both fouling processes (scaling and biofouling) should be avoided as much as possible to efficiently operate reverse osmosis.

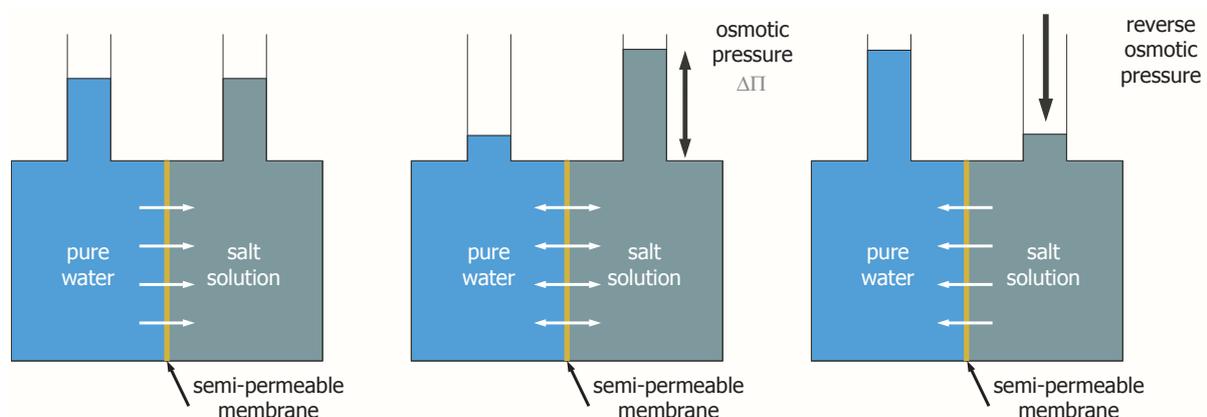


Figure 1 - Principle of osmosis and reverse osmosis

**2.3 Membrane configuration**

The application of large flat membranes is not practical, because a large footprint is needed to obtain the necessary permeate production. Therefore, a system is used with a high specific surface (membrane area per volume).

**Spiral-wound membranes**

Almost all reverse osmosis membranes are of the spiral-wound configuration.

Water is fed from one side into a module. Via spacers (supporting layers between membrane sheets), the water is distributed over a membrane element. An element is a number of membrane sheets twisted around a central permeate collecting tube (Figures 2 and 3).

The length of a membrane element is normally one meter, so one person can replace it from the installation. After passing one element the water flows to a second element.

To withstand the high operating pressures, a pressure vessel (membrane module) is used. It is not economically feasible to have a pressure vessel for every element and, therefore, six elements are generally placed in one membrane module (Figure 4).

Spiral-wound membranes have a large specific area (1000 m<sup>2</sup>/m<sup>3</sup>).

A disadvantage of spiral-wound membranes is that rapid fouling of the spacer channels with particulate matter can occur.

Reverse osmosis membranes cannot be hydraulically cleaned like ultrafiltration membranes and



Figure 2 - Open spiral-wound membrane

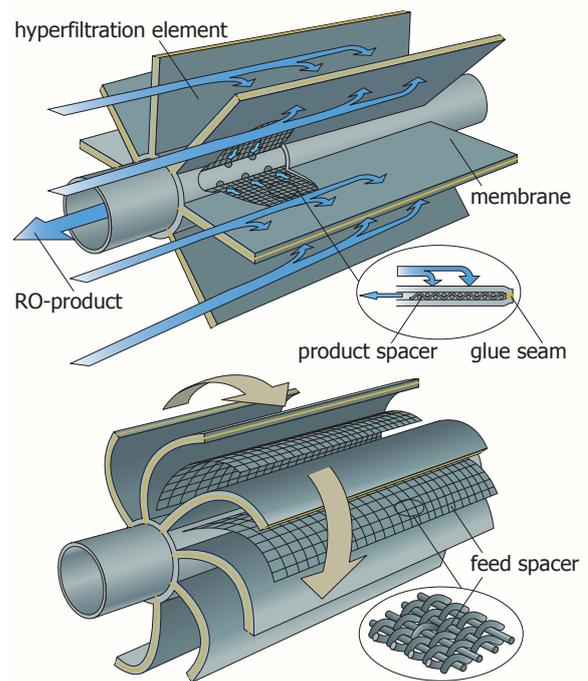


Figure 3 - Principle of spiral-wound membranes

fouling of the membranes should therefore be avoided.

**2.4 Feed, permeate and concentrate**

In membrane filtration processes, three different types of flow are distinguished.

The feed flow is separated by the membrane into a permeate (or product) flow and into a concentrate (or retentate) flow.

The salt concentration in the permeate flow is lower than the salt concentration in the feed flow.

In the concentrate flow the salt concentration is higher than in the feed flow.



Figure 4 - Membrane modules

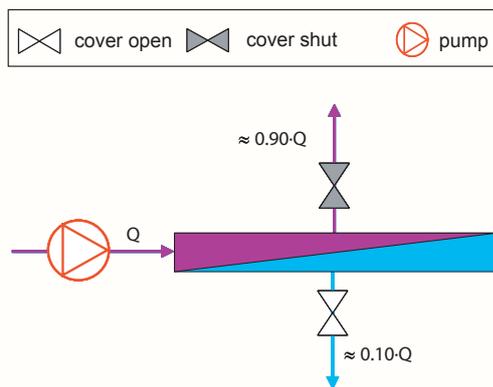


Figure 5 - Cross-flow operation

It is not possible to have an unlimited concentration of salts in the concentrate flow, because at certain salt concentrations precipitation of salts will occur.

### 2.5 Cross-flow operation

Reverse osmosis modules are always operated in cross-flow mode (Figure 5).

This means that only a small part of the feed flow is produced as permeate (between 1 and 10% per element), while most of the feed water flows along the membrane surface and exits the membrane element as concentrate.

Because of this large concentrate flow, the velocity in the membrane channels is high and the build up of a laminar boundary layer is disturbed.

## 3 Theory

### 3.1 Mass balance

The water mass balance for a membrane element is given by:

$$Q_f = Q_c + Q_p$$

in which:

- $Q_f$  = feed flow (m<sup>3</sup>/h)
- $Q_c$  = concentrate flow (m<sup>3</sup>/h)
- $Q_p$  = permeate flow (m<sup>3</sup>/h)

Also, the dissolved material of mass balance (Figure 6) can be derived by:

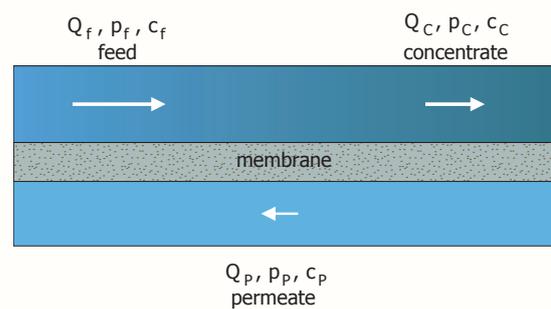


Figure 6 - Mass balance

$$Q_f c_f = Q_c c_c + Q_p c_p$$

in which:

- $c_f$  = concentration of dissolved material in feed water (g/m<sup>3</sup>)
- $c_c$  = concentration of dissolved material in concentrate (g/m<sup>3</sup>)
- $c_p$  = concentration of dissolved material in permeate (g/m<sup>3</sup>)

### Recovery

The recovery indicates the overall production of the system.

It is the relationship between permeate and feed flow:

$$\gamma = \frac{Q_p}{Q_f} 100\%$$

in which:

- $\gamma$  = recovery (%)

A recovery of 80% means that 80% of the feed flow is produced as permeate.

This also means that the concentration of salts in the concentrate is 5 times higher than the concentration in the feed flow, assuming that all salts are retained.

The recovery of one element is between 1 and 10%, therefore more elements should be placed in a series to obtain the desired recovery of 80%.

For sea water desalination, the maximum achievable recovery is about 50%.

This recovery is limited by the possibility of scaling,

caused by high salt concentrations. For groundwater, however, recoveries up to 95% can be obtained.

**Rejection**

Rejection indicates the amount of material rejected by a membrane.

Rejection is calculated by:

$$Re = 1 - \frac{c_p}{c_f}$$

in which:

R = rejection (-)

**3.2 Kinetics**

**Flux**

The flux is the permeate flow through one square meter of membrane surface or:

$$J = \frac{TMP}{\mu K}$$

in which:

- J = volumetric flux (m/s)
- K = membrane resistance coefficient (m<sup>-1</sup>)
- μ = dynamic viscosity of water (Ns/m<sup>2</sup>)
- TMP = transmembrane pressure (Pa)

The volumetric flux is often expressed as a “surface load” (flow per area (l/h/m<sup>2</sup>)).

**Transmembrane pressure**

Water does not automatically flow through a membrane. The membrane has a resistance against filtration and this resistance has to be overcome by a pressure.

The net pressure difference over a membrane is called the transmembrane pressure (TMP<sub>net</sub>) and acts as the driving force for a membrane process.

The SI-unit for pressure is (Pa), however, in membrane filtration processes, the more common (bar) is used. One bar is equal to 10<sup>5</sup> Pa.

TMP<sub>net</sub> is given by:

$$TMP_{net} = \Delta P - \Delta \pi = P_f - \frac{\Delta P_{hydr}}{2} - P_p - \Delta \pi$$

in which:

- P<sub>f</sub> = pressure of feed (Pa)
- ΔP<sub>hydr</sub> = hydraulic pressure loss (Pa)
- P<sub>p</sub> = pressure of permeate (Pa)
- Δπ = osmotic pressure difference (Pa)

The hydraulic pressure loss is the difference between the pressure of the feed and concentrate, or:

$$\Delta P_{hydr} = P_f - P_c$$

in which:

- P<sub>c</sub> = pressure of concentrate (Pa)

The TMP<sub>net</sub> is dependent on place and time. As can be seen in the TMP equation, these place and time dependent effects are averaged.

Depending on the concentration of dissolved material, the feed pressure for reverse osmosis is between 15 and 70 bar.

The pressure in permeate is often or almost 0 bar. The reason for this is the almost atmospheric conditions for permeate outflow.

**Hydraulic pressure loss**

Hydraulic losses occur in the water moving from feed (inlet) to concentrate (outlet) as a result of wall friction. Because of this wall friction, P<sub>c</sub> will always be smaller than P<sub>f</sub>.

The friction loss in spiral-wound membranes can be calculated by:

$$\frac{dP_{hydr}}{dx} = \frac{\lambda \rho v^2}{2 \cdot d_H}$$

in which:

- λ = friction factor (-)

**Hydraulic line**

In Figure 8 the hydraulic line in an RO-module containing one single element is depicted.

The storage tank with (1) feed water is open. After the storage tank the hydraulic line decreases slightly because of hydraulic losses in the feeding pipeline.

By means of a pump, the water is pressurized; a large increase in the pressure level is observed. In the membrane module, a further hydraulic loss occurs.

A valve is placed in the concentrate pipeline. This valve regulates the driving force (TMP). A large pressure drop takes place across this valve.

The concentrate flows into a second storage tank (2).

The permeate, about 10% of the feed flow, flows to tank 3.

From the permeate tank we calculate back. The permeate transported to the tank encounters hydraulic headlosses. A line has been drawn from tank 3 to the membrane module.

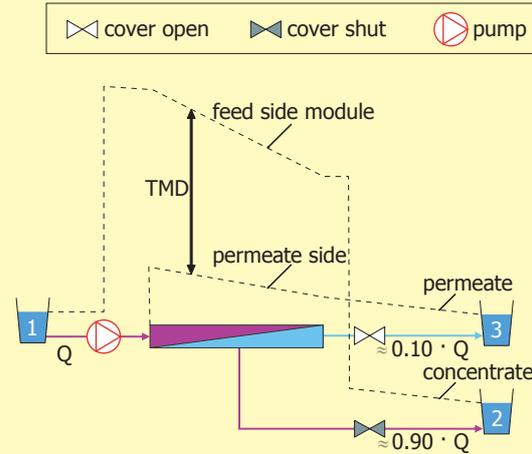


Figure 8 - Hydraulic line at permeate side (light blue line) and feed/concentrate side (dark blue line)

$d_H$  = hydraulic diameter (m)  
 $v$  = liquid velocity (m/s)

For capillary membranes the following relationship is used:

This friction loss is shown in Figure 7.

$$\lambda = \frac{64}{Re} (Re \leq 2000)$$

The friction factor  $\lambda$  for spiral-wound membranes is given by:

$$\lambda = 0.316 Re^{-0.25} (Re > 2000)$$

$$\lambda = 6.23 Re^{-0.3} (100 < Re < 1000)$$

in which:

Re = Reynolds number (-)

At smaller diameters of the membrane channels, the Reynolds number decreases and the friction factor  $\lambda$  increases.

In spiral-wound membranes the membrane channels are rectangular and there are spacers present. A spacer is a special layer resulting in more turbulence in the membrane channel and therefore creates a flow of feed water to the membrane surface.

The hydraulic diameter is dependent on the height of the spacer. In most spiral-wound membranes, a value of 0.9 mm for the hydraulic diameter is common.

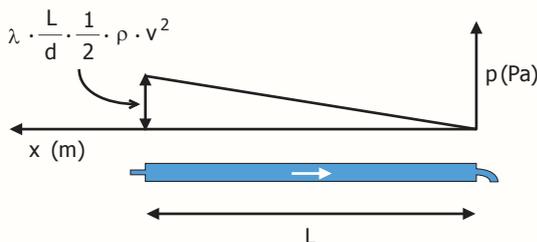


Figure 7 - Hydraulic pressure loss

**Example 1**

In a spiral-wound reverse osmosis membrane module, six elements, each with a length of 1 m, are placed.

Calculate the hydraulic pressure loss per module ( $v=0.25$  m/s (average),  $d_H=0.9$  mm, water temperature is  $20^\circ\text{C}$ ).

**Answer:**

$$T = 20^\circ\text{C}, \text{ so } \nu = 1.0 \times 10^{-6}$$

$$\text{Re} = \frac{0.25 \cdot 0.90 \cdot 10^{-3}}{1 \cdot 10^{-6}} = 225$$

$$\lambda = 6.23 \cdot 225^{-0.3} = 1.23$$

$$\Delta P_{\text{hydr}} = 1.23 \cdot \frac{1}{2 \cdot 0.9 \cdot 10^{-3}} \cdot 1000 \cdot 0.25^2$$

$$= 42603 \text{ Pa} = 0.43 \text{ bar}$$

**Osmotic pressure**

Osmotic pressure is a fluid property dependent on salt concentration and temperature and independent of the presence of a membrane.

The osmotic pressure is calculated by:

$$\pi = \sum \frac{R \cdot T \cdot c_i \cdot z_i}{M_i}$$

in which:

$\pi$	= osmotic pressure	(Pa)
$R$	= gas constant	(J/K·mol)
$T$	= temperature	(K)
$c_i$	= concentration ion	(g/m <sup>3</sup> )
$M_i$	= molecular weight ion	(g/mol)
$z_i$	= valence ion	(-)

Valence is determined by the ion. Sodium has a valence of 1 ( $\text{Na}^+$ ,  $z=1$ ), chloride also ( $\text{Cl}^-$ ,  $z=1$ ), while carbonate has a valence of 2 ( $\text{CO}_3^{2-}$ ,  $z=2$ ).

To calculate the osmotic pressure, it is sufficient to take into account the most important in water dissolved ions. These are  $\text{HCO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ ,  $\text{Na}^+$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ .

**Example 2**

In water from the IJsselmeer ( $18^\circ$ ), the following ions are present at the given concentrations:

$[\text{HCO}_3^-]$	135 g/m <sup>3</sup>	$M = 61.0$ g/mol
$[\text{SO}_4^{2-}]$	63 g/m <sup>3</sup>	$M = 96.1$ g/mol
$[\text{Cl}^-]$	95 g/m <sup>3</sup>	$M = 35.5$ g/mol
$[\text{Na}^+]$	52 g/m <sup>3</sup>	$M = 23.0$ g/mol
$[\text{Ca}^{2+}]$	60 g/m <sup>3</sup>	$M = 40.1$ g/mol
$[\text{Mg}^{2+}]$	11 g/m <sup>3</sup>	$M = 24.3$ g/mol

$$R = 8.314 \text{ J/K} \cdot \text{mol}$$

Calculate the osmotic pressure of the IJsselmeer water.

$$\pi = \sum \frac{RTc_i z_i}{M_i}$$

$$= 8.314 \cdot (273 + 18) \cdot$$

$$\left( \frac{135.1}{61} + \frac{63.2}{96} + \frac{95.1}{36} + \frac{52.1}{23} + \frac{60.2}{40} + \frac{11.2}{24} \right)$$

$$= 0.3 \cdot 10^5 \text{ Pa} = 0.3 \text{ bar}$$

By comparison, the osmotic pressure of brackish groundwater (2000 mg/l NaCl) is  $1.7 \times 10^5$  Pa (= 1.7 bar), the osmotic pressure of sea water (35.000 mg/l NaCl) is  $30 \times 10^5$  Pa (= 30 bar).

**Osmotic pressure difference**

The osmotic pressure difference over a membrane is given by:

$$\Delta\pi = \frac{\pi_f + \pi_c}{2} - \pi_p$$

in which:

$\Delta\pi$	= osmotic pressure difference	(Pa)
$\pi_f$	= osmotic pressure of feed	(Pa)
$\pi_c$	= osmotic pressure of concentrate	(Pa)
$\pi_p$	= osmotic pressure of permeate	(Pa)

The pressure difference is averaged to be independent of the position in the membrane and, thus, there is no dependency of  $\pi$  on the position.

**Example 3**

Why is the osmotic pressure in the concentrate higher than in the feed?

**Answer**

The feed is separated into permeate and concentrate flows. The concentrate flow contains the same amount of salts as the feed flow, however, they are dissolved in less water. A higher salt concentration means a higher osmotic pressure.

Because the concentration of salts in the permeate is very low, the osmotic pressure in the permeate is almost always neglected.

On the other hand, the osmotic pressure of the concentrate is higher than the osmotic pressure of the feed.

The following equation is valid:

$$\pi_c = \pi_f \frac{1}{1-\gamma}$$

Combining this with what we saw before of the osmotic pressure difference over a membrane, we see:

$$\Delta\pi = \pi_f \cdot \frac{2-\gamma}{2 \cdot (1-\gamma)}$$

**3.3 Concentration polarization**

During filtration a concentration build-up of the retained material will occur in the boundary layer close to the membrane.

This effect is called concentration polarization and results in an initial rapid decline in flux.

However, this decline will not continue in time, like in the case of fouling (Figure 9). Concentration

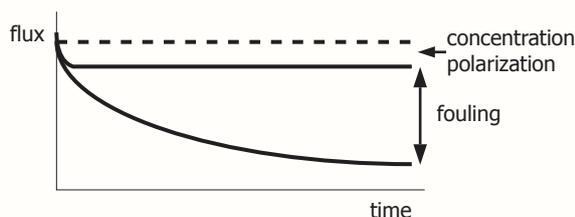


Figure 9 - Concentration polarization and fouling in time in a cross-flow operation

polarization is reversible and will disappear as the driving force becomes zero.

The concentration polarization can be limited by disturbance of the boundary layer, for example, by enhancement of the velocity along the membrane surface.

The relationship between concentration close to the membrane surface and in the feed (Figure 10) is represented by the concentration polarization factor  $\beta$  which is given by:

$$\beta = \frac{c_m - c_p}{c_f - c_p} = \exp \frac{J\delta}{D}$$

in which:

- $\beta$  = concentration polarization factor (-)
- $c_m$  = concentration at membrane surface (mg/l)
- $c_p$  = concentration in permeate (mg/l)
- $c_f$  = concentration in feed (mg/l)
- $J$  = permeate flux ( $m^3/m^2 \cdot s$ )
- $\delta$  = thickness of boundary layer (m)
- $D$  = diffusion coefficient ( $m^2/s$ )

Because  $c_p \ll c_f < c_m$ ,  $c_p$  can be neglected, and when coefficient  $k$  is taken for the mass transfer, the following relation can be used:

$$k = \frac{D}{\delta}$$

in which:

- $k$  = mass transfer coefficient (m/s)

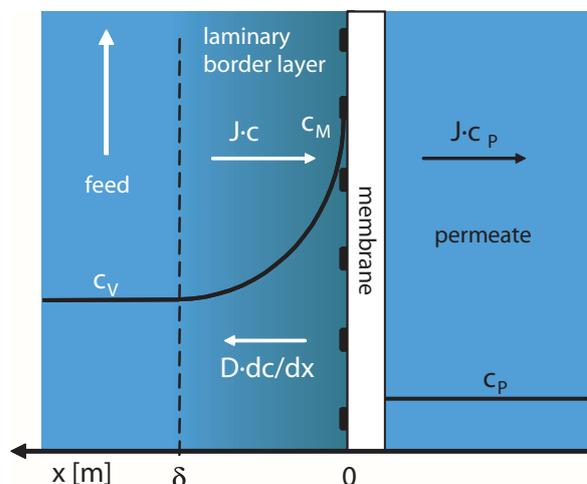


Figure 10 - Concentration polarization

Then  $\beta$  can be rewritten to:

$$\beta = \frac{c_m}{c_f} = \exp \frac{J}{k}$$

Concentration polarization results in a higher osmotic pressure difference across the membrane.

**Scaling**

Scaling can occur when the transport of salts, as a result of convection to the membrane, is larger than the transport of salts from the membrane by diffusion.

Scaling is the precipitation of inorganic salts caused by exceeding the solubility product (super saturation).

Whether scaling occurs depends on numerous factors, like pH, temperature and the presence of other ions.

Super saturation is defined by the saturation index SI:

$$SI = \log \frac{IP}{K_{SP}}$$

in which:

- SI = saturation index (-)
- $K_{SP}$  = solubility product salt (mol/l)
- IP = ion product (mol/l)

The solubility product  $K_{SP}$  is temperature dependent.

The value of the ion product of a salt is determined by the ion strength, pH and the ion affinity.

Scaling can be prevented by the dosing of acids or anti-scalants, by removal of seeding material and by not exceeding the solubility product.

Limiting the concentration polarization layer by increasing the cross-flow velocity helps to prevent exceeding the solubility product. However, this results in a higher energy consumption.

**4 Practice**

**4.1 Nanofiltration**

It is not always necessary to remove all dissolved ions. For example, when water has to be softened nanofiltration will be sufficient.

Nanofiltration removes divalent ions (like  $Ca^{2+}$ ,  $Mg^{2+}$  and  $SO_4^{2-}$ ), while monovalent ions are not rejected.

Nanofiltration membranes have larger pores than reverse osmosis membranes, resulting in a lower resistance for filtration and also lower operational pressures (2 - 10 bar).

The pores of nanofiltration are smaller than ultra-filtration pores.

Nanofiltration membrane modules can be constructed as spiral-wound membranes, and now as capillary membranes as well.

**4.2 Christmas tree configuration**

To obtain a high recovery, several modules are placed in a series in an RO/NF-membrane filtration installation to concentrate the concentrate even further.

This in-series placement of membranes is called staging. Normally, two to three stages are used.

The osmotic pressure in the first stage will always be lower than the osmotic pressure in the second stage; the osmotic pressure in the second stage will always be lower than in the third stage.

It is clear that when scaling occurs this will be in the stage where the concentrations are highest.

To prevent scaling, the cross-flow velocity in the last stage should be higher than in the first stages. Therefore, a Christmas tree configuration is often used. The number of modules in a stage decreases when the stage number increases. So, for example, in the first stage there are three modules, in the second stage there are two modules, and in the third stage there is only one module (Figure 11).

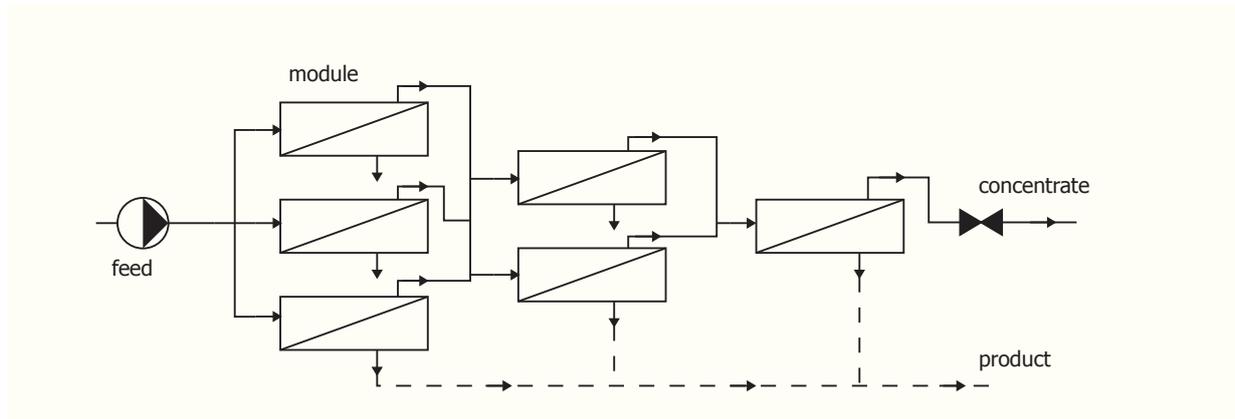


Figure 11 - Christmas tree configuration

### 4.3 Cleaning

To prevent a flux decrease (or increase in TMP) in spiral-wound NF/RO-systems, different techniques can be used:

- dosing of acids and anti-scalants
- chemical cleaning
- increasing the cross-flow velocity by recirculation.

Some anti-scalants have biofouling (growth of microorganisms in a membrane module, resulting in flux decrease) as their side effect, especially when the anti-scalants are not 100% pure and contain some organic material.

When the flux at a certain standard TMP becomes too low, the membrane is cleaned chemically. Depending on the type of fouling (biofouling, scaling or particulate fouling), a certain chemical will

be added.

After soaking, the chemicals are flushed from the module and filtration can start again.

“Preventing is better than curing.” Therefore, it is necessary to have a high cross-flow velocity to limit the concentration polarization layer. However, larger cross-flow velocities result in more energy consumption.

To overcome the high energy consumption, recirculation of the concentrate can take place.

A special configuration for this is semi-dead-end nanofiltration. The installation is operated in a dead-end configuration, but the concentrate is continuously recirculated (Figure 12). After some time the concentrate is disposed of. In this way the energy consumption is limited.

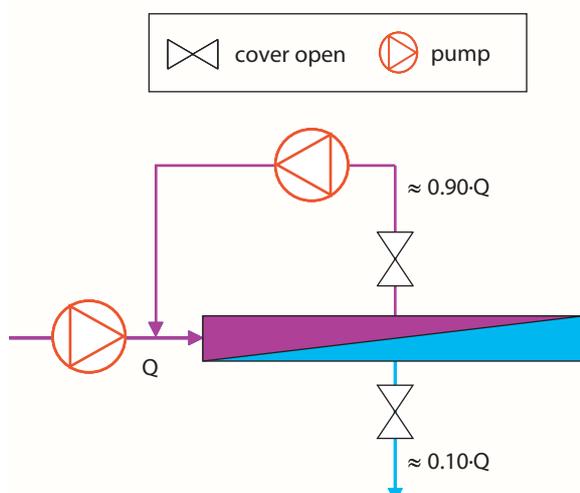


Figure 12 - Semi-dead-end operation

### 4.4 Field installations

#### Heemskerk, PWN North-Holland

Water from the IJsselmeer is conventionally pre-treated by coagulation, sedimentation, filtration and activated carbon filtration, and then transported over 70 km to Heemskerk. Here, a large surface water membrane treatment plant has been built with a capacity of 3000 m<sup>3</sup>/h.

The water is first treated by ultrafiltration to remove suspended material, bacteria and viruses. The permeate of the ultrafiltration is feed water for the reverse osmosis installation.

This RO installation consists of two stages. In the first stage, 24 modules are placed; in the second

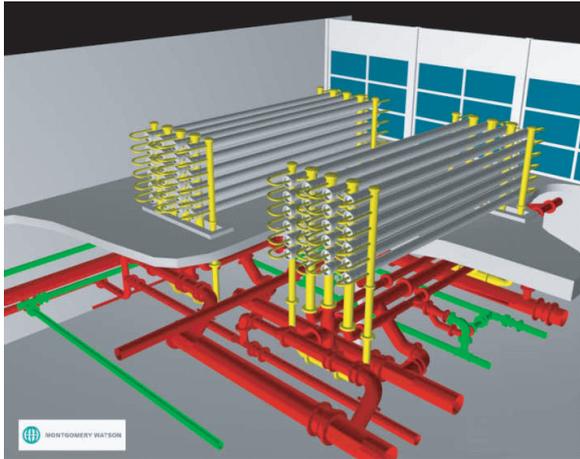


Figure 13 - 3D-engineering Heemskerk

stage only 12 modules are present (2:1 staging). The permeate of the RO is conditioned by pH-correction and, after mixing with water treated in the dunes is transported to the customers. This mixing with dune water takes place because permeate from an RO is low on necessary minerals for humans and dehydrates the human body.

**Schiermonnikoog, Vitens**

On the island of Schiermonnikoog, anaerobic groundwater is treated to produce drinking water by means of nanofiltration. Nanofiltration is used because the groundwater has a high color content and hardness level.

The groundwater is treated while it is still anaerobic, because iron and manganese are still present in dissolved form.

If oxygen were present, iron and manganese would directly precipitate and form flocs that would foul



Figure 15 - Anaerobic NF-installation

the installation.

After the NF the water is aerated and treated by slow sand filtration before it is distributed.

**Industry**

There are many industrial applications of NF/RO in the Netherlands.

Small scale laundries, slaughterhouses and green houses use NF/RO installations.

On a larger scale, chemical industries (DSM in Geleen (2000 m<sup>3</sup>/h) or Heineken in Zoeterwoude (500 m<sup>3</sup>/h)) use NF/RO membranes.



Figure 14 - Membrane installation at Heemskerk



*Figure 16 - NF at Schiermonnikoog*

In waste watertreatment NF/RO is not yet used.

---

---

### Further reading

- Water treatment: Principles and design, MWH (2005), (ISBN 0 471 11018 3) (1948 pgs)

