PROSIMPLUS APPLICATION EXAMPLE

MEMBRANE FILTRATION

EXAMPLE PURPOSE
This example presents the simulation of two membrane filters: the first one is dealing with a liquid-liquid filtration and the second one with a gas-gas filtration. The main objective of this example is to illustrate the use of membrane filters in the ProSimPlus software.

ACCESS	☑ **Free Internet**	☐ **Restricted to ProSim clients**	☐ **Restricted**	☐ **Confidential**

CORRESPONDING PROSIMPLUS FILES	*PSPS_EX_EN–Oxygen-Nitrogen-Membrane-Separation.pmp3* *PSPS_EX_EN–Seawater-Desalination.pmp3*

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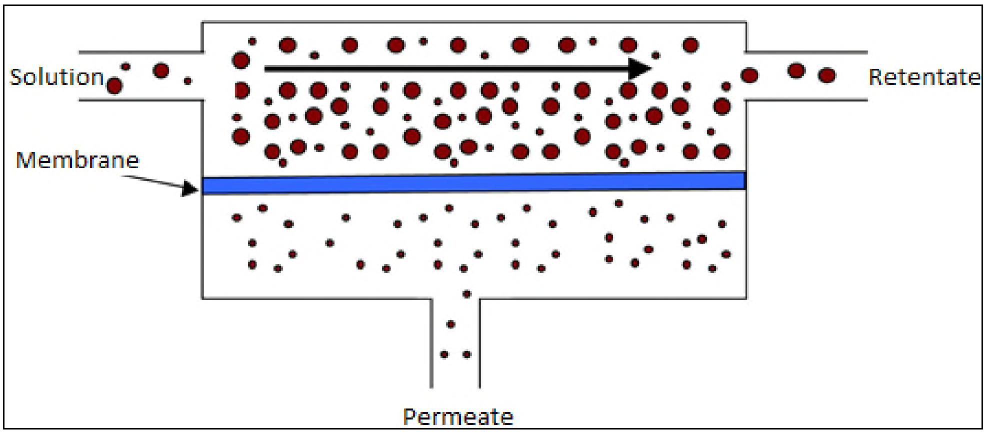
1 PROCESS MODELING

1.1 Process description

This example presents the use of membrane filters applied to 2 cases of membrane filtrations: liquid-liquid filtration (filtration of an aqueous solution of sodium chloride) and gas-gas filtration (separation of oxygen and nitrogen from air).

Membrane filtration is a physical separation process. It is based on the principle of permeation through a permselective membrane. This permselective membrane, depending on its intrinsic characteristics and its use, constitutes a barrier allowing (or favoring) some transfers of matter and limiting others. The driving forces allowing permeation through the membrane can be diffusion (active transport) but also pressure, concentration, or electrical potential differentials (passive transport). In the case of the liquid-liquid filtration as presented here, the effect of reverse osmosis is also taken into account as a driving force (see Appendix 1: Reverse Osmosis).



Depending on the pore size, the filtration membrane is an absolute physical barrier for molecules or particles above a certain size threshold. This is the main advantage of membrane filtration compared to conventional methods (sand filter, activated carbon...) since these ones do not constitute an absolute filter [CAU17].

With a membrane filtration operation, two streams are generated:

- The retentate (or concentrate) where the molecules and/or particles retained by the membrane are concentrated.
- The permeate, free of retained molecules and/or particles.

Membrane filters can be used for:

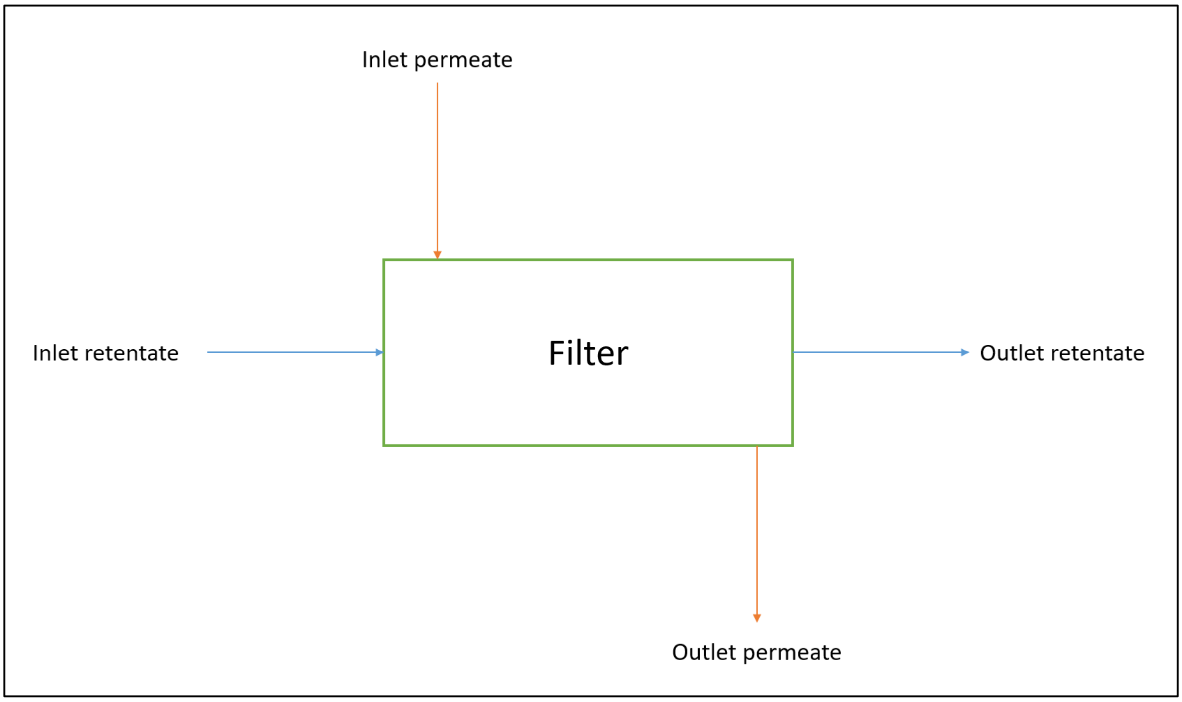
- Gas dehumidification/air drying;
- Gas/air humidification;
- Treatment of gaseous (VOC: Volatile Organic Compound) or liquid pollutants;
- Biogas purification;
- Separation of air components (O_2/N_2);
- ...

1.2 Process flowsheet

The 2 membrane filtration processes presented in this document are created from a membrane filter module.

The stream to be treated enters through the retentate side. This stream is split in two outlets through the filter. The components passing through the filter exit in the permeate while the retained phase exits on the retentate side.

The stream of interest can be the permeate, the retentate, or both in some cases. For the seawater filtration (see 3 Seawater desalination), the stream of interest is the permeate (desalinated water). Whereas for air filtration (see 2 Oxygen/nitrogen filtration), both streams have an interest (N_2 and O_2 purified on both sides of the membrane).

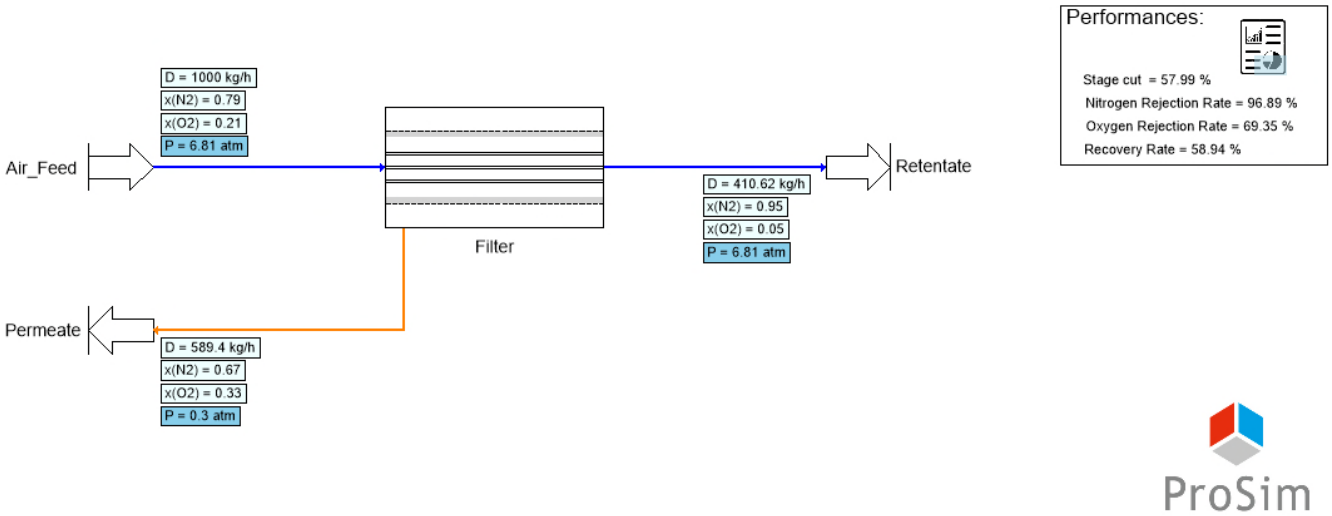


In many cases, there is no inlet on the permeate side. In configuration where this permeate-side inlet stream exists, it is a sweep stream, which is especially used for gas-gas filtration applications. The sweep stream is a neutral gas (*i.e.,* not involved in permeation) and is used to "sweep" the membrane surface to increase the concentration differential across the membrane and increase the transfer.

2 OXYGEN/NITROGEN FILTRATION

The following example is based on the separation of oxygen (O_2) and nitrogen (N_2) from air. This example is extracted from [PER08].

2.1 Simulation flowsheet



Simulation of an oxygen/nitrogen separation unit

2.2 Compounds

Compounds considered in the simulation, their chemical formulas and CAS[1] numbers are presented in the following table. Pure components physical properties are extracted from the ProSimPlus standard database [WIL21].

Compound	**Chemical formula**	**CAS Number[1]**
NITROGEN	N_2	7727-37-9
OXYGEN	O_2	7782-44-7

[1]*CAS Registry numbers® are the intellectual property of the American Chemical Society and are used by ProSim SA with the express permission of ACS. CAS Registry Numbers® have not been verified by ACS and may be inaccurate*

2.3 Thermodynamic model

The system studied is a mixture of N_2/O_2 which can be considered as air. Under process pressure conditions (0.3 to 6 atm), the thermodynamic profile chosen is the “ideal” profile.

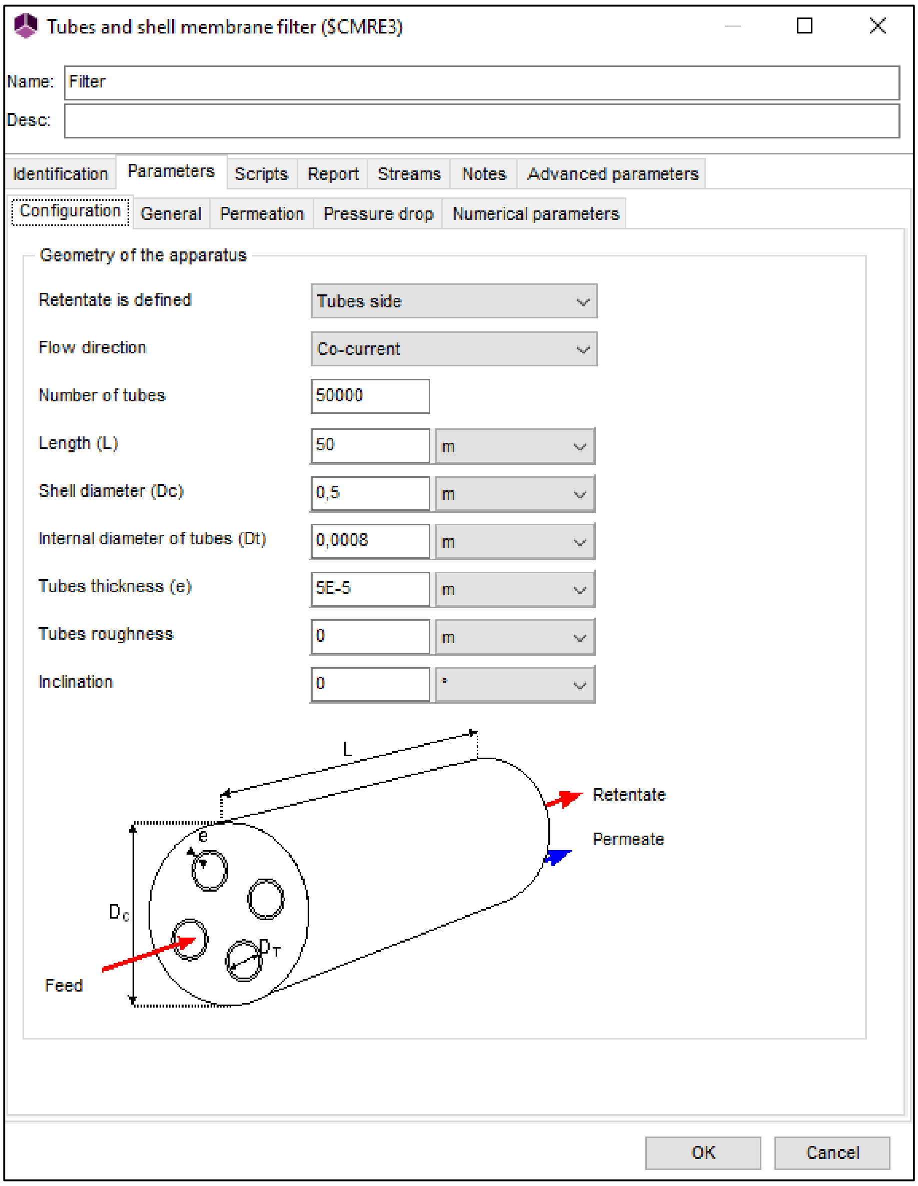
2.4 Operating conditions

✓ Process feed

Air of the tube-side		
Molar fraction (%)	**O_2**	21
	N_2	79
Inlet temperature (°C)		25
Inlet pressure (kPa)		690
Total mass flowrate (kg/h)		1000

✓ Tubes and shell membrane filter

The configuration of the filter is made throught the 5 tabs presented below:



Tubes and shell membrane filter ($CMRE3)

Name: Filter

Desc:

Geometry of the apparatus

Retentate is defined: Tubes side

Flow direction: Co-current

Number of tubes: 50000

Length (L): 50 m

Shell diameter (Dc): 0,5 m

Internal diameter of tubes (Dt): 0,0008 m

Tubes thickness (e): 5E-5 m

Tubes roughness: 0 m

Inclination: 0 °

1. Configuration

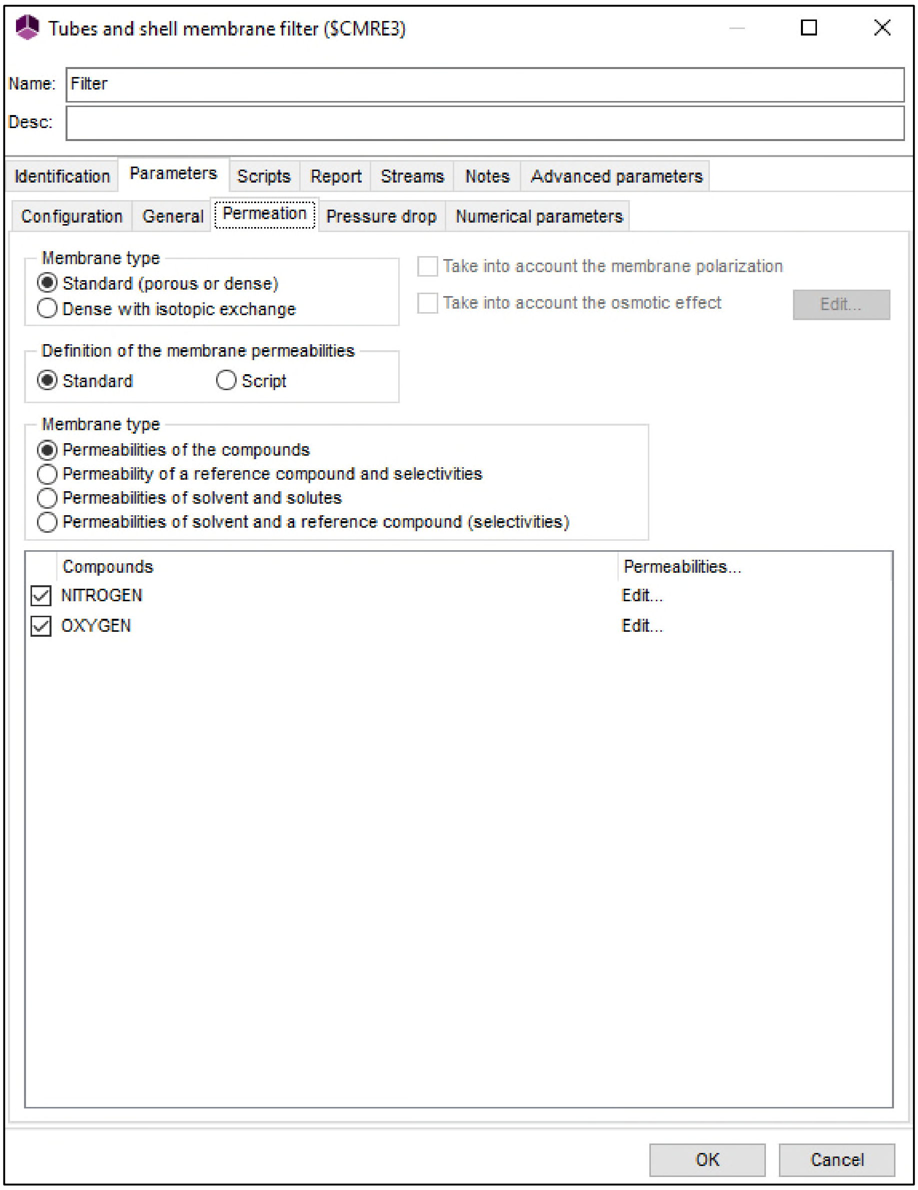
Retentate defined	Tubes side
Flow direction	Co-current
Number of tubes	50 000
Length (m)	50
Shell diameter Dc (m)	0.5
Internal diameter of tubes Dt (m)	0.0008
Tubes thickness (m)	5×10^{-5}
Tubes roughness (m)	0
Inclination (°)	0

2. General

Temperature (°C)	25
Physical state	Vapor
Permeate side pressure (atm)	0.3

3. Permeation

All the following checkboxes must be ticked:



Tubes and shell membrane filter ($CMRE3)

Name: Filter

Desc:

Membrane type
● Standard (porous or dense)
○ Dense with isotopic exchange

☐ Take into account the membrane polarization
☐ Take into account the osmotic effect

Definition of the membrane permeabilities
● Standard
○ Script

Membrane type
● Permeabilities of the compounds
○ Permeability of a reference compound and selectivities
○ Permeabilities of solvent and solutes
○ Permeabilities of solvent and a reference compound (selectivities)

	Compounds	Permeabilities...
☑	NITROGEN	Edit...
☑	OXYGEN	Edit...

In this example, the membrane is a porous silicone membrane. All components of the air penetrate and cross through this kind of membrane. However, this type of membrane is selective because the permeabilities of the components are different (see Appendix 2: Permeability Database):

- O_2 permeability : 650 barrer equivalent to 2.0×10^{-13} mol/(s.m.Pa);
- N_2 permeability : 155 barrer equivalent to 4.76×10^{-14} mol/(s.m.Pa).

The permeabilities values of oxygen and nitrogen are the following:

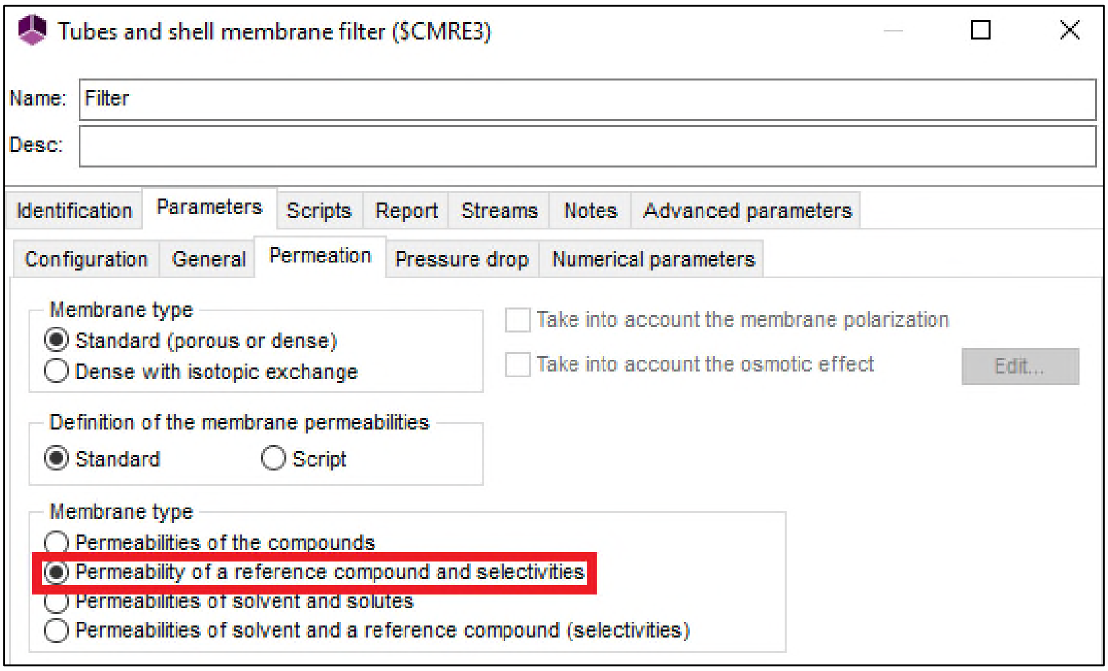
N_2 permeability	
Permeation model	Partial pressure
Definition type	Constant
Type	Molar
Molar permeability (mol.m/m²/s/Pa)	4.76×10^{-14}

O_2 permeability	
Permeation model	Partial pressure
Definition type	Constant
Type	Molar
Molar permeability (mol.m/m²/s/Pa)	2×10^{-13}

Note: For a binary mixture (A/B), ratio between the permeability of compound B and the permeability of compound A (separation coefficient: α) and the permeability of one of the two compounds are frequently used:

$$\alpha = \frac{Permeability\ of\ A}{Permeability\ of\ B}$$

This feature is also available in the « Permeation » tab of the membrane filtration module:



Tubes and shell membrane filter ($CMRE3)

Name: Filter

Desc:

Membrane type
● Standard (porous or dense)
○ Dense with isotopic exchange

☐ Take into account the membrane polarization
☐ Take into account the osmotic effect

Definition of the membrane permeabilities
● Standard ○ Script

Membrane type
○ Permeabilities of the compounds
● Permeability of a reference compound and selectivities
○ Permeabilities of solvent and solutes
○ Permeabilities of solvent and a reference compound (selectivities)

4. Pressure drop

Default values are used.

5. Numerical parameters

The number of cells, the maximum number of iterations and the convergence criterion are respectively modified to 150, 500 and 1×10^{-9}.

✓ Script

The following script is used in the module («Stage Cut» Windows Script).

```
Function OnCalculation()
    With Project.Modules("Filter")
      ' Get streams
      F_RET_E = .InputStream(1).MolarFlowrate
      F_PER_S = .OutputStream(2).MolarFlowrate
    End With
    ' Stage cut calculation
    Stage_Cut = (F_PER_S/F_RET_E)*100.0
    Module.parameter(1) = Stage_Cut
    OnCalculation = True
End Function
```

2.5 Results

- ✓ Balance

		Retentate side		Permeate side
		Inlet	**Outlet**	**Outlet**
Temperature (°C)		25	25	25
Pressure (atm)		6.8	6.8	0.3
Velocity (m/s)		1.38	0.58	2.77
Mass flowrate (t/h)		1000	411	589
Molar composition (%)	**NITROGEN**	0.79	0.95	0.67
	OXYGEN	0.21	0.05	0.33

- ✓ Performances (see Appendix 3: Definition of filtration results)

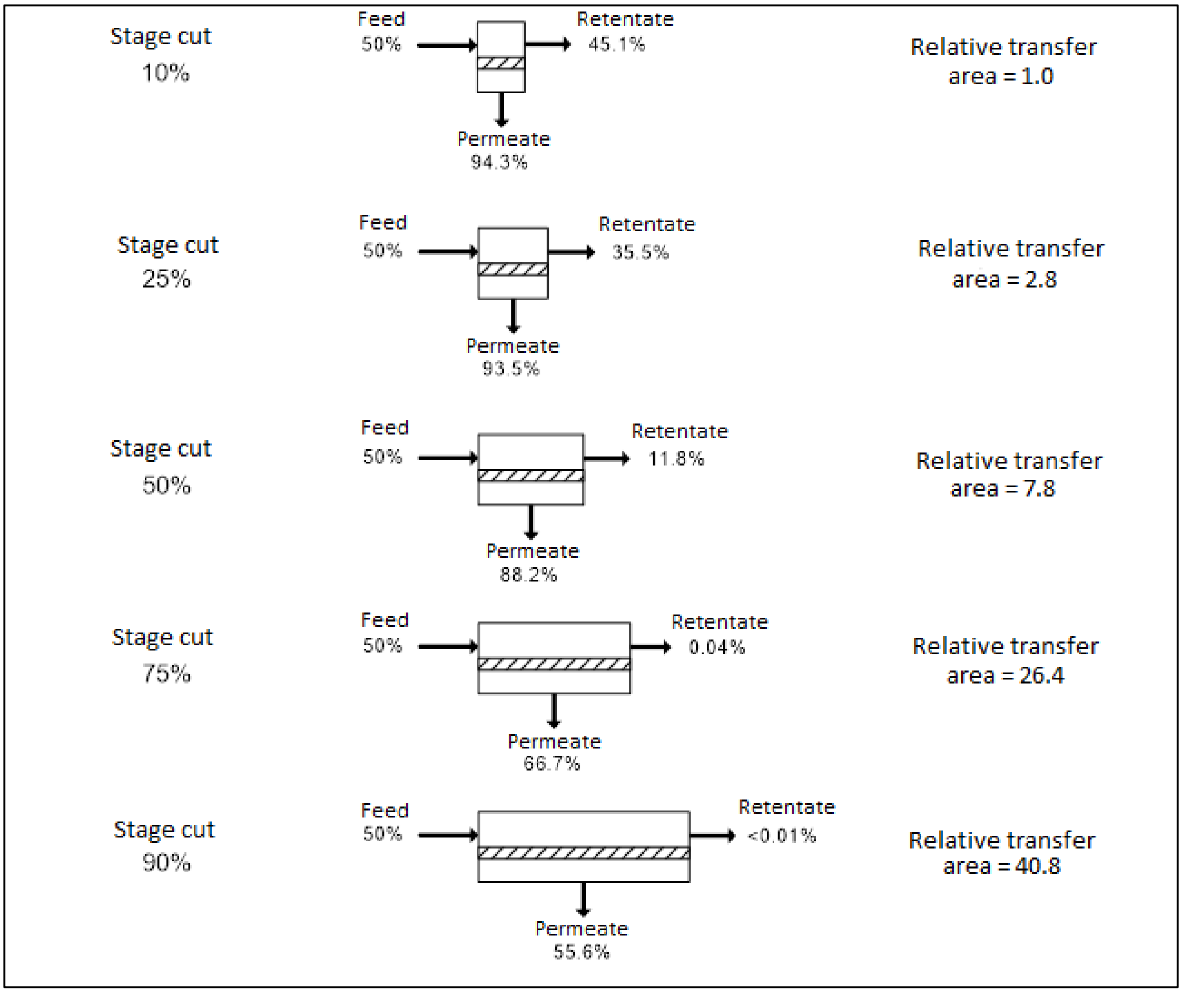
N_2 rejection rate (%)	96.89
O_2 rejection rate (%)	69.35
Recovery rate (%)	58.94

The membrane rejects ≈ 97% of the oxygen and ≈ 70% of the nitrogen. The retentate stream is so more concentrated in nitrogen and the permeate more concentrated in oxygen.

- ✓ Comparison with experimental data

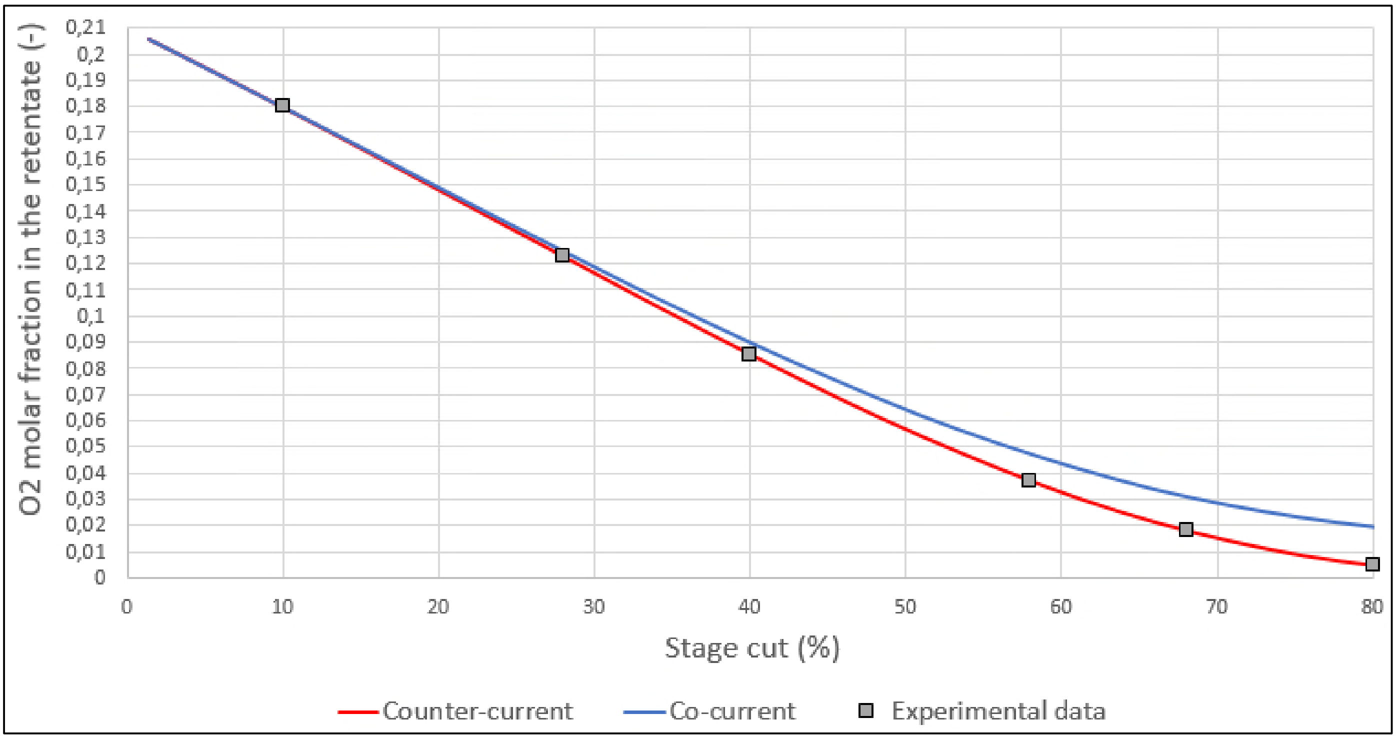
The results of the simulation such as the recovery rate (see Appendix 3: Definition of filtration results) and the O_2 composition of the retentate are compared to the experimental data from [PER08].

The more the filtration rate (recovery rate) is significant (the more the transfer area is significant), the less the permeate stream is enriched in the most permeant species.



Relationship between surface transfer area, stage cut and purification

The comparison of the experimental data and the ProSimPlus simulation results for O_2/N_2 separation is presented below:

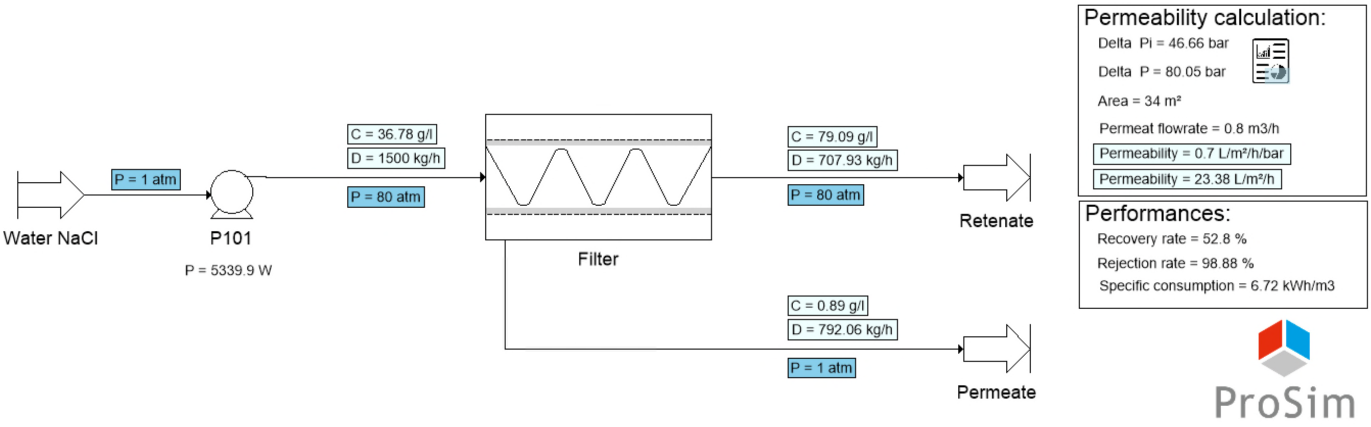


The results are consistent with the experimental data. It should be noted that the "co-current" model is less effective than the "counter current" model for filtration rates above 30% [PER08].

3 SEAWATER DESALINATION

The following example is based on the separation of water (H_2O) and sodium chloride (NaCl). This type of filter is particularly used for the desalination of seawater.

3.1 Simulation flowsheet



Simulation of seawater desalination

3.2 Compounds

Compounds considered in the simulation, their chemical formulae and CAS[1] numbers are presented in the following table. Pure components physical properties are extracted from the ProSimPlus standard database [WIL21].

Compound	Chemical formula	CAS number[1]
WATER	H_2O	7732-18-5
SODIUM CHLORIDE	NaCl	7647-14-5

[1] *CAS Registry numbers® are the intellectual property of the American Chemical Society and are used by ProSim SA with the express permission of ACS. CAS Registry Numbers® have not been verified by ACS and may be inaccurate*

3.3 Thermodynamic model

The system is composed of an aqueous solution of sodium chloride. Therefore, the thermodynamic profile “Sour water” is used to model this electrolytic solution.

3.4 Operating conditions

The operating conditions of the different modules are presented as follows:

- ✓ Process feed

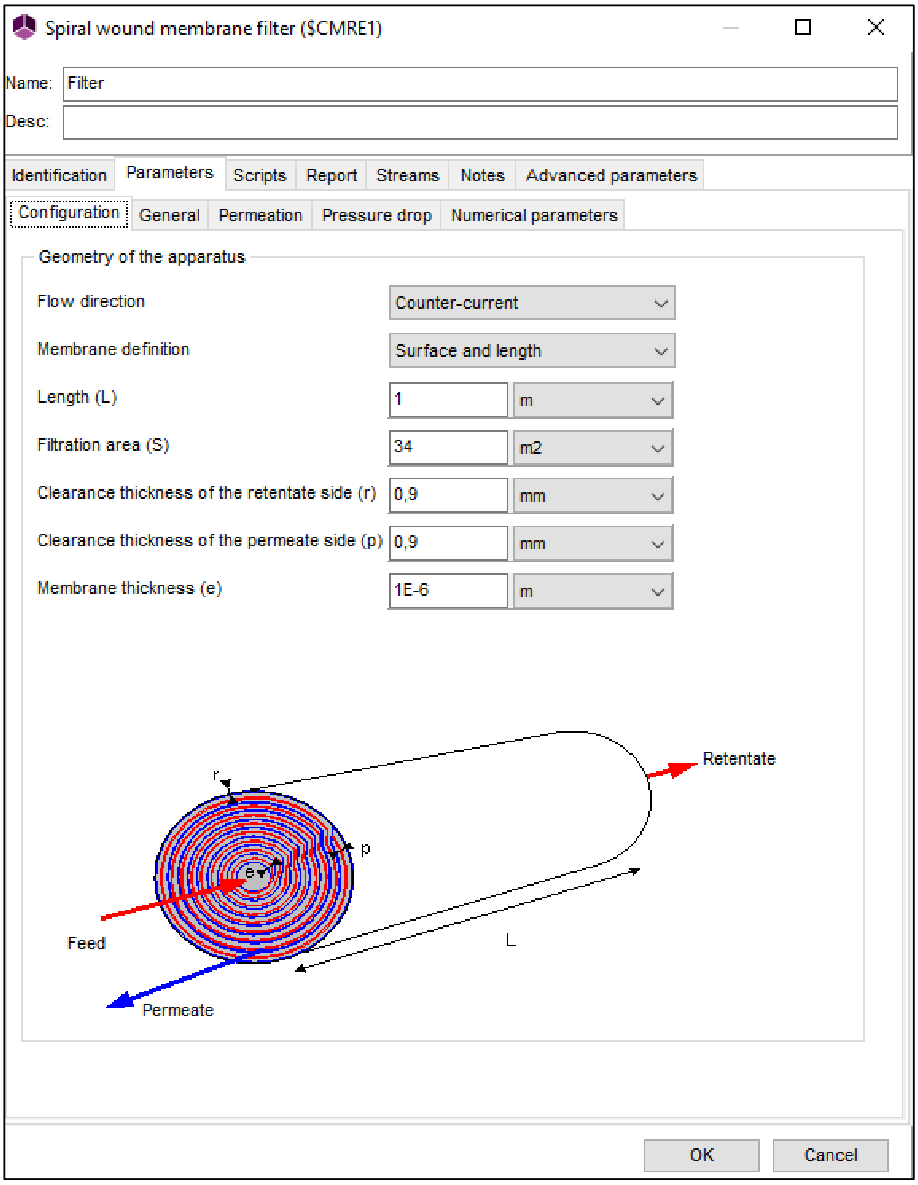
		Water NaCl
Mass fraction (%)	**WATER**	96.4
	NaCl	3.6
Concentration (g/l)		36.8
Mass flowrate (t/h)		1.5
Temperature (°C)		30
Pressure (atm)		1

- ✓ Centrifugal pump

Exhaust pressure (atm)	80
Volumetric efficiency	0.65
Mechanical efficiency	0.95
Electrical efficiency	0.99

✓ Spiral wound membrane filter

The configuration of the filter is made throught the 5 tabs presented below:



Name: Filter

Desc:

Geometry of the apparatus

Flow direction: Counter-current
Membrane definition: Surface and length
Length (L): 1 m
Filtration area (S): 34 m2
Clearance thickness of the retentate side (r): 0,9 mm
Clearance thickness of the permeate side (p): 0,9 mm
Membrane thickness (e): 1E-6 m

1. Configuration

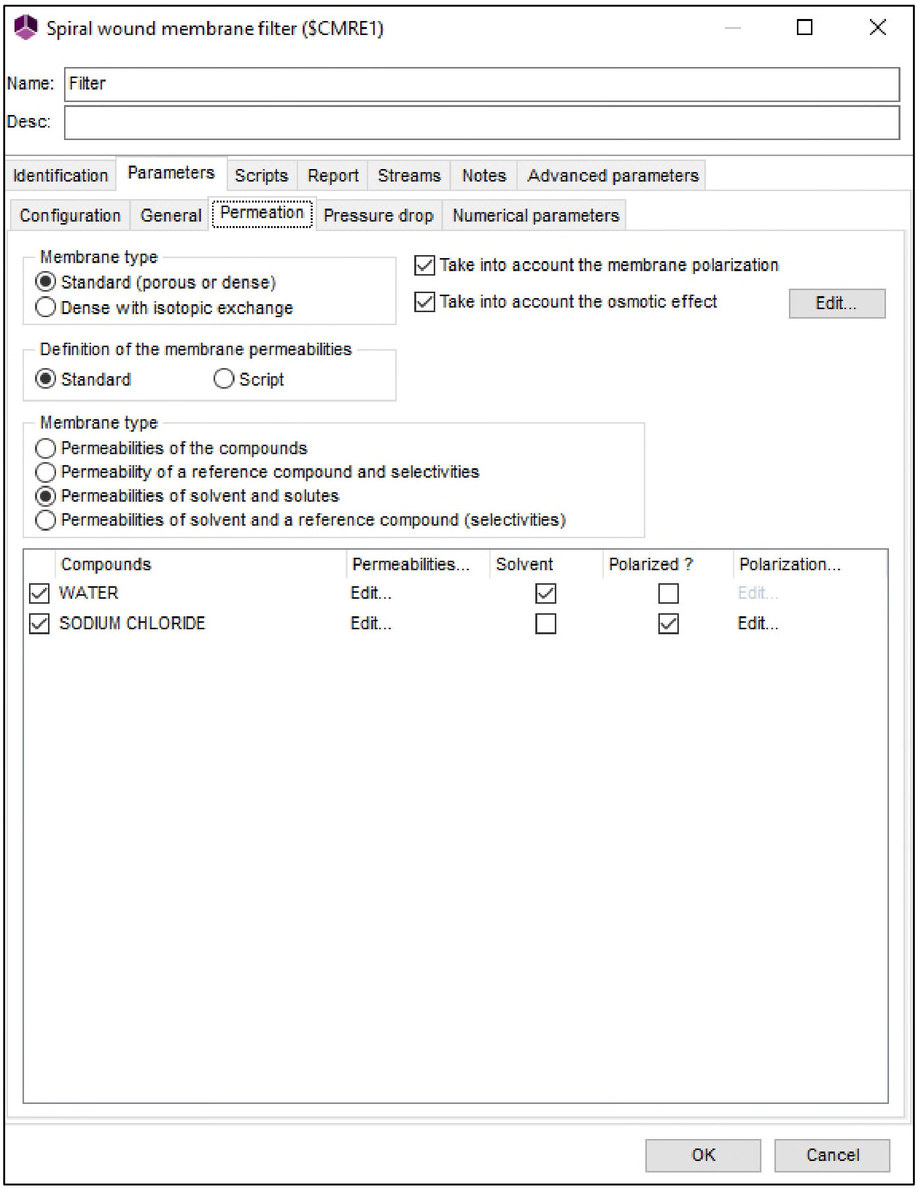
Flow direction	Counter-current
Membrane definition	Surface and length
Length (m)	1
Filtration area (m²)	34
Clearance thickness of the retentate side (mm)	0.9
Clearance thickness of the permeate side (mm)	0.9
Membrane thickness (m)	1×10^{-6}

2. General

Temperature (°C)	30
Physical state	Liquide
Permeate side pressure (atm)	1

3. Permeation

All the following checkboxes must be ticked:


Spiral wound membrane filter (SCMRE1)

Name: Filter

Desc:

Membrane type
● Standard (porous or dense)
○ Dense with isotopic exchange

☑ Take into account the membrane polarization
☑ Take into account the osmotic effect

Definition of the membrane permeabilities
● Standard ○ Script

Membrane type
○ Permeabilities of the compounds
○ Permeability of a reference compound and selectivities
● Permeabilities of solvent and solutes
○ Permeabilities of solvent and a reference compound (selectivities)

	Compounds	Permeabilities...	Solvent	Polarized ?	Polarization...
☑	WATER	Edit...	☑	☐	Edit...
☑	SODIUM CHLORIDE	Edit...	☐	☑	Edit...

For this type of filtration, permeability values can be taken from the literature ([MAU74] and [OKA19]).

The default values for the osmotic effect definition are used (calculation of the osmotic pressure by the thermodynamic model). The values of permeability and polarization, for water and sodium chloride, are supplied as follows:

Water permeability	
Permeation model	Partial pressure
Definition type	Constant
Type	Volume
Volume permeability (m²/h/atm)	7.1×10^{-10}

NaCl permeability	
Permeation model	Concentration
Permeability (m/s)	1×10^{-7}
NaCl polarization	
Model for the mass transfer coefficient (ki)	Chen and Qin
Di (m²/s)	1×10^{-6}
α	0.031
β	0.9243
γ	0.3495

4. Pressure drop

Default values are used.

5. Numerical parameters

Only the number of cells is changed to 20.

✓ Script

The following script is used in the «Permeability calculation» Windows Script module. This script allows to calculate the average permeability and the average osmotic pressure drop of the filter:

```
With CreateObject("Scripting.FileSystemObject")
  ExecuteGlobal .OpenTextFile(Project.ApplicationPath & "Scripts\UnitConversion.vbs", 1).ReadAll()
End With

Function OnCalculation()
  '
  ' Parameters
  Filter_Name = "Filter"
  '
  With Project.Modules(Filter_Name)
    ' Streams
    Set Feed     = .InputStream(1)
    Set Permeate = .OutputStream(2)
    'Osmotic pressure
    Nb_Cells = .GridCellsNumber
    a = (.OsmoticPressureDifferenceProfile(1) + .OsmoticPressureDifferenceProfile(Nb_Cells+1)) / 2
    a = ConvertFromProSim("pressure", a, "bar")
    'Membrane transfer area m2
    S = .TransferTotalArea
  End With
  '
  'Pressure deviation
  b = Feed.Pressure - Permeate.Pressure
  b = ConvertFromProSim("pressure", b, "bar")
  '
  'Permeate flowrate  m3/h
  F = Permeate.VolumeFlowrate
  '
  'Permeability L/m²/h/bar
  Perma2 = F*1000.0/S
  Perma1 = Perma2/(b-a)
  '
  'Save of the parameters
  Module.Parameters(1) = a
  Module.Parameters(2) = b
  Module.Parameters(3) = S
  Module.Parameters(4) = F
  Module.Parameters(5) = Perma1
  Module.Parameters(6) = Perma2

  OnCalculation = True

End Function
```

3.5 Results

- ✓ Balance

		Retentate side		Permeate side
		Inlet	**Outlet**	**Outlet**
Temperature (°C)		32.9	30.0	30.0
Pressure (atm)		80	80	1
Volume flowrate (m^3/h)		1.47	0.67	0.79
Velocity (m/s)		1.33×10^{-2}	6.12×10^{-3}	7.19×10^{-3}
Mass flowrate (t/h)		1.50	0.71	0.79
Concentration (g/l)		36.84	79.02	0.89
Mass fraction (%)	**WATER**	0.964	0.925	0.999
	SODIUM CHLORIDE	0.036	0.075	0.001

- ✓ Performances (see Appendix 3: Definition of filtration results)

Recovery rate (%)	52.8
NaCl rejection rate (%)	98.9
Specific consumption (kWh/m^3)	6.7

4 CONCLUSION

This example has presented liquid-liquid and gas-gas membrane filtrations by using membrane filters in ProSimPlus. There are 3 different types of membrane filters in ProSimPlus: a plate and frame membrane filter, a tubes and shell membrane filter and a spiral wound membrane filter. The purpose of this example was to illustrate the use of these membrane filter modules.

The examples presented in this document are voluntarily simplified compared to industrial filtration plants. More complex configurations (series and/or parallel filters configurations depending on the purity and flowrate specified) are presented in the PSPS_EX_EN-Seawater-Desalination example.

5 REFERENCES

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[CHA05] CHAY L., « Etude comparative des membranes utilisées en production d'eau potable : microfiltration, ultrafiltration, nanofiltration et osmose inverse », Office International de l'eau SNIDE, (2005).

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[OKA19] OKAMOTO Y., LIENHARD J. H., « How RO membrane permeability and other performance factors affect process cost and energy use: A review », Desalination, (2019).

[PER08] PERRY R.H., « Perry's Chemical Engineers's Handbook », 8th edition, 2008, Membrane permeation processes, 20-57.

[POL21] Site internet de Polymem, fabriquant de membranes, https://www.polymem.fr/produits/membranes , consultée le 10/11/2021.

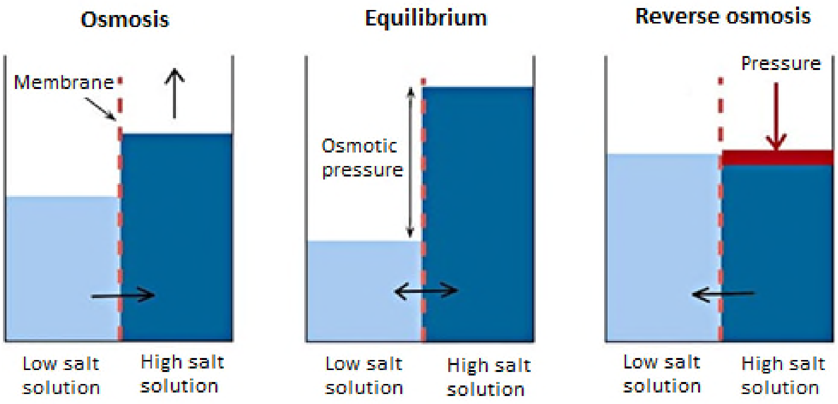
[ROB68] ROBB W. L., « THIN SILICONE MEMBRANES-THEIR PERMEATION PROPERTIES AND SOME APPLICATIONS », Annals of the New York Academy of Sciences, vol. 146, issue 1 Materials in , pp. 119-137, (1968).

[WIL21] WILDING, W. V.; KNOTTS, T. A., GILES, N. F., ROWLEY, R. L. « DIPPR Data Compilation of Pure Chemical Properties »; Design Institute for Physical Properties, AIChE, New York, NY (2021).

APPENDIX 1: REVERSE OSMOSIS

Reverse osmosis (RO) is a technique that can be used to replace a distillation step or associated to a distillation plant to increase the production.

To understand the reverse osmosis, it is necessary to explain the osmosis phenomenon. Osmosis is a natural phenomenon that occurs when a solution diluted in solute(s) is separated from a concentrated solution by a semi-permeable membrane. Water (the most used solvent), under the action of a force generated by the concentration gradient, passes through the membrane from the less concentrated solution to the more concentrated one. This transfer is done until the concentrated solution is diluted. When the concentrations on both sides of the membrane are equal, osmotic equilibrium is reached. The difference in concentration creates a pressure, called the osmotic pressure (noted π). During this equilibrium, the pressure prevents any further transfer to balance the concentrations ([BER02], [CHA05], [POL21]).



Principle of the osmotic effect

If a pressure greater than the osmotic pressure is applied on the side of the concentrated solution, the normal direction of the osmotic flow is reversed. Pure water passes through the membrane from the most concentrated solution to the least concentrated solution. Thus, the water is separated from its contaminants. This is the basic principle of reverse osmosis.

Reverse osmosis is often used with dense membranes that allow water to pass through by stopping all the salts unlike the MF (Micro Filtration) and UF (Ultra Filtration) membranes. This type of dense membrane has a thickness of a few microns (0.2 µm) [POL20].

The main industrial applications of RO are [DEO20]:

- Desalination of seawater;
- Desalination of brackish water;
- Elimination of pesticides and herbicides;
- Production of ultra-pure water (electronics, pharmaceuticals…);
- Production of process water…

APPENDIX 2: PERMEABILITIES DATABASE

This appendix presents a database of permeabilities of gaseous components.

The table below shows the permeabilities of some gaseous components through a silicone membrane [ROB68]:

Name (gas)	Chemical formula	Permeability coefficient in silicone (Barrer)
Nitrogen	N_2	280
Carbon monoxide	CO	340
Oxygen	O_2	600
Nitric oxide	NO	600
Argon	Ar	600
Hydrogen	H_2	650
Helium	He	350
Methane	CH_4	950
Ethylene	C_2H_4	1350
Ethane	C_2H_6	2500
Carbon dioxide	CO_2	3250
Propane	C_3H_8	4100
Nitrous oxide	N_2O	4350
Acetone	C_3H_6O	5860
Ammonia	NH_3	5900
Nitrogen dioxide	NO_2	7500
Octane	$n\text{-}C_8H_{18}$	8600
Butane	$n\text{-}C_4H_{10}$	9000
Toluene	C_7H_8	9130
Hexane	$n\text{-}C_6H_{14}$	9400
Hydrogen sulfide	H_2S	10000
Benzene	C_6H_6	10800
Methanol	CH_3OH	13900
Sulfur dioxide	SO_2	15000
Pentane	$n\text{-}C_5H_{12}$	20000
Water	H_2O	36000
Carbon disulfide	CS_2	90000

APPENDIX 3: DEFINITION OF FILTRATION RESULTS

The main results of a membrane filtration are summarized with coefficients traditionally used in the field of filtration:

- ✓ Recovery rate:

$$Recovery\ rate = \frac{F_{p,out} - F_{p,in}}{F_{r,in}}$$

If there is no inlet connection on the permeate side, the formula is simplified as follows:

$$Recovery\ rate = \frac{F_{p,out}}{F_{r,in}}$$

$F_{p,out}$: Permeate outlet mass flowrate (kg/h)

$F_{p,in}$: Permeate inlet mass flowrate (kg/h)

$F_{r,in}$: Feed mass flowrate (retentate inlet) (kg/h)

- ✓ Compound i rejection rate:

$$Rr_i = 1 - \frac{C_{p,i,out}}{C_{r,i,out}}$$

$C_{p,i,out}$: Permeate outlet mass concentration of compound i (kg/m^3)

$C_{r,i,out}$: Retentate inlet mass concentration of compound i (kg/m^3)

- ✓ Specific consumption (kWh/m^3)

$$Specific\ consumption = \frac{Pw}{F_{p,out}}$$

Pw: Total electrical power consumption (kW)

$F_{p,out}$: Permeate outlet volume flowrate (m^3/h)