

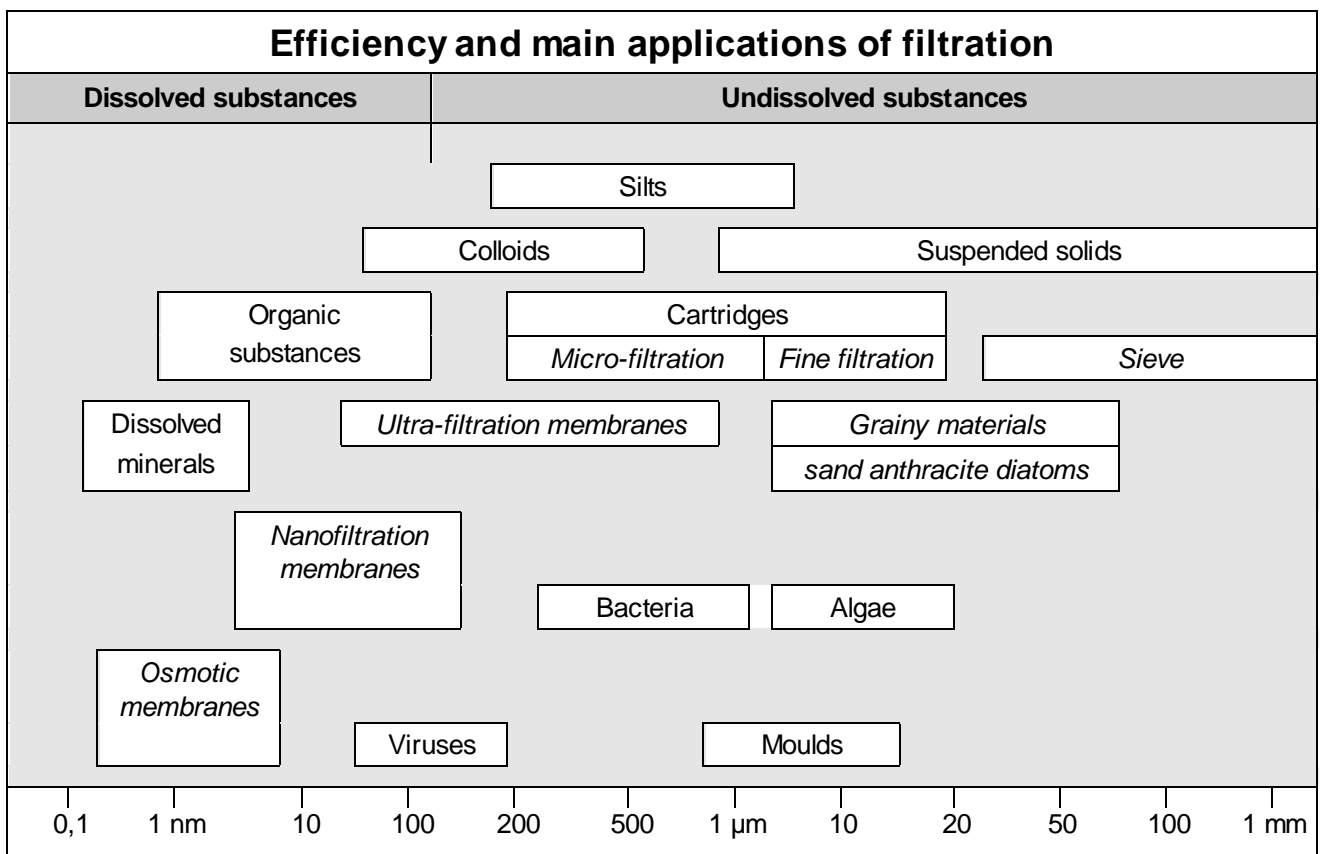
SEPARATION TECHNIQUES USING MEMBRANE FILTERS

GE 9

In the history of water treatment, filtration techniques have evolved towards the development of finer filtration processes : from gravel filters used in ancient times to the porous, sterilising ceramic cartridges developed by Pasteur and Chamberland last century and re-marketed after the World War II in the form of wound cartridges.

The very recent development of separation techniques using membranes started strangely enough with the finest inverted osmotic membranes.

It was only in the last decade that coarser ultra-filtration membranes appeared on the market, followed very recently by nanofiltration membranes.



Front-end filtration

In this mode of filtration, the water flows perpendicularly to the membrane surface.

Particles tend to accumulate on this membrane surface, forming an increasingly thick layer.

Front-end filtration is used to achieve high conversion rates (up to 95 % in some cases).

Microfiltration and ultrafiltration membranes can be unclogged by a backflow of filtered water.

For these reasons, front-end filtration is reserved for water with a very low solid and colloid content (physical and microbiological finishing treatments, demineralisation by reverse osmosis of microfiltered or ultrafiltered water).

Tangential filtration

In tangential filtration, the filtered water flows parallel to the membrane surface.

Solids and colloids do not tend to accumulate on the membrane surface, but rather to drain off towards the outlet. As a result, fouling is much slower than in the case of front-end filtration.

However, tangential filtration can only achieve relatively low conversion rates (seldom above 50%).

This mode of filtration is always used when the filtered water has a high fouling capacity.

Ultrafiltration and nanofiltration

Ultrafiltration membranes have porosities ranging from approximately 0.5 μm to 0.2 μm .

Obtained through mineral synthesis (ceramics) or organic synthesis, these membranes have been widely used to concentrate liquids by separating organic macromolecules from water, in the farm-produce industry (e.g. whey concentration), the pharmaceutical industry (antibiotic concentration in fermentation juices) and in the metallurgic industry (treatment of cutting oils).

It is only since ultrafiltration membranes have been tested for application to surface water purification for the preparation of water for human consumption, as a substitute for the conventional processes of flocculation and decanting.

Applications are also possible in finishing treatments after conventional purification or in sterilising filtration.

Aside from their purifying properties, ultrafiltration membranes eliminate germs present in the water as well as colloids and organic compounds with a high molecular mass.

These membranes are used for the front-end filtration of water with very few suspended solids and colloids, and for tangential filtration when the water has a high solid and colloid content.

When the membranes become clogged, they are washed out with ultrafiltered water, either in tangential or upstream mode.

Practical conversion rates range from 50 % (for murky water) to 95 % (for clear water).

Organic synthesis has led to the development of nanofiltration membranes similar to those used for reverse osmosis, with porosities somewhere between those of ultrafiltration and reverse osmosis.

Not only do these membranes trap all solids, colloids and living organisms, but also viruses and organic or organometallic micropollutants.

They also reduce the bivalent and trivalent ion content. However, they do not significantly modify the monovalent ion content.

Reverse osmosis

The osmotic phenomenon

Osmosis is a natural phenomenon whereby a solvent passes through a semi-permeable membrane separating solutions of different concentrations.

A semi-permeable membrane is a film of material that is permeable to water but not to the dissolved mineral elements, colloids, and bacteria.

Let us consider a system comprising a container divided into two compartments by a semi-permeable membrane, the one compartment containing pure water and the other salt water. We observe that the pure water passes through the membrane and lowers the concentration of the salt water (fig. 1).

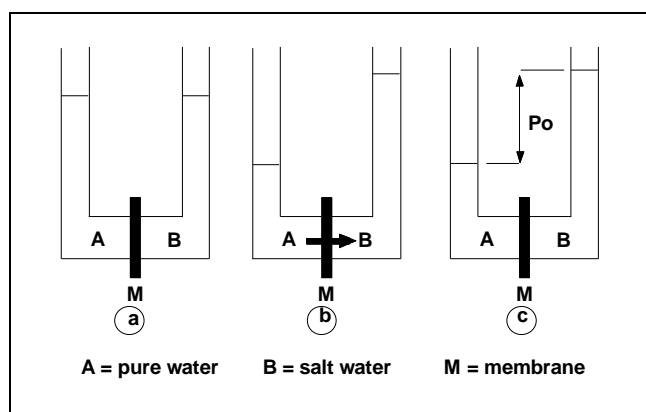


Fig. 1 - Osmotic principle

The migration of pure water to the saline solution increases the volume of the saline solution and creates a water column of which the physical effects include the exertion of greater pressure on the salt water side of the membrane.

As a result of this increase in pressure, there comes a time when this pressure stops the pure water from passing through the membrane to the saline solution.

The system is then in equilibrium (liquids at rest).

The hydrostatic pressure required to create this equilibrium is called the osmotic pressure of a given concentrated solution.

Osmotic pressure

The osmotic pressure of a solution with concentration C is defined by the equation :

$$P_o = C \cdot R \cdot T$$

where

R = ideal gas constant

T = absolute temperature in ° Kelvin

C = rate of concentration defined by the ratio $\frac{N_i}{N}$ where N is the molar concentration of the dissolved element and i its dissociation constant at equilibrium.

Osmotic pressure is therefore a physical property which depends on the concentration of each solution and thus increases with it.

In the example of an aqueous solution of sodium chloride, the osmotic pressure increases theoretically by 0.7 bar per saline g/litre.

Reverse osmosis

Osmosis is reversible. It suffices to subject the stronger solution to a higher pressure than its osmotic pressure O_p in order to reverse the direction of the pure water flow.

As soon as this is done, the saline solution produces pure water.

This is known as reverse osmosis (fig. 2).

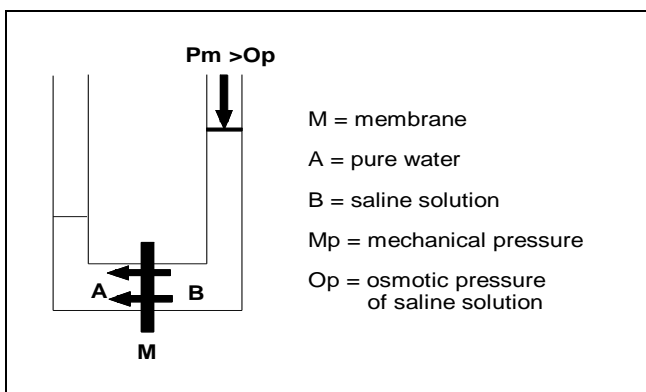


Fig. 2 - Osmotic principle

Reverse osmosis mechanism

Several theories have been devised in order to explain the separation of water and mineral salts by a semi-permeable membrane in this type of treatment.

The most widely recognised theory is that of solubilisation - diffusion.

According to this theory, each constituent of the solution dissolves in this type of treatment.

Two forces contribute to the migration of a constituent through a membrane : the concentration gradient and the pressure gradient.

Reverse osmosis membranes

Composition

Various materials have been used to manufacture membranes. The most frequently used materials are cellulose acetate and polyamide.

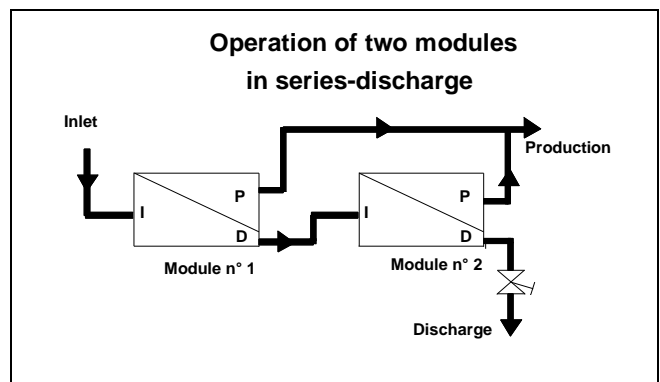
They are produced in the form of hollow fibres with an external diameter of about 80 to 100 micrometres, or in the form of a double spiral wound around a collector.

Several generations of membranes have been produced, each outdoing its predecessor in terms of quality (salt separation) and quantity (pure water flow rate at a given pressure).

Configuration of the reverse osmosis unit

For best results, discharges from the first stage of osmosis can be reprocessed in a second stage. This method saves a significant amount of water.

Example :



Dual reverse osmosis or biosmosis, whereby the permeate from a first stage undergoes a second stage of treatment, is designed to obtain water with a

resistance of more than 1 MΩ.cm by means of the appropriate pre-treatment.

Special case of final reverse osmosis

The *reverse osmosis unit* located at the upper end of the cycle is more particularly intended for demineralisation (90 % of dissolved salts trapped). The osmosed water is practically never used as is; it undergoes additional treatment using ion-exchanging resins (mixed beds) in order to obtain process-compatible resistivities.

In some cases, osmosis is used at the final stage as an ultrafilter. In effete, the membrane has a very low porosity (around 5 Angstroms) and achieves extremely good filtration results, not only with regard to suspended substances but also bacteria and organic molecules; these are eliminated when their molar mass exceeds 300. Final osmosis thus achieves very low organic carbon levels (5 to 15 ppb).

Membrane protection

The water feeding the *reverse osmosis units* is usually feedwater containing certain minerals (TH, TAC). When they reach the membrane, the pure water passes through (permeate) while the salts are discharged in a much higher concentration.

This high concentration could lead to the precipitation of hardly soluble salts and calcium salts in particular (CaCO₃). There are two ways in which to avoid this phenomenon :

- softening, which eliminates calcium (sodium salts are all soluble). Drawback : no pH control which could lead to problems with acetate membranes.

- acidification, which transforms TAC (HCO₃) into CO₂, thus preventing the formation of carbonates. Drawback : all the resultant CO₂ passes through the membrane and must therefore be eliminated.

Furthermore, the water undergoing treatment contains suspended particles which are liable to clog the membranes ; for this reason, a filter will always be installed upstream of the membranes.

Other treatments can be considered depending on the nature of the membrane :

- chlorination (cellulose acetate)
- dechlorination (polyamide)

- decarbonisation of resins.

Cleaning membranes

When a membrane is soiled by any pollutant whatsoever, the membrane must be decontaminated. This entails injecting a chemical substance onto the membrane in a closed loop (vessel + pump). Fouling is detected by an increased pressure loss (max. charge loss : 3 bars).

Pollution	Chemical substance
CaCO ₃	Citric acid
Al, Fe Hydroxide	Tartaric acid
Hydrocarbons	Detergent
Bacteria	Chlorine, Formol, Hydrogen peroxide

Quality of water treated by reverse osmosis

Physical quality

The water obtained by using reverse osmosis membranes is free of all solid particles and colloids.

The physical quality of the treated water does not depend on operating conditions (composition of the water being treated, inlet pressure to the module, conversion rate).

The quality of the water purified by reverse osmosis is defined in terms of physical composition, chemical composition (mineral and organic) and microbiological population.

Mineral quality

Generally speaking, the quality of the water obtained is defined by ionic leakages, by the CO₂ content in the water being treated and its pH, the last two values being very closely linked.

The determination of the chemical quality obtained by reverse osmosis incorporates a number of interlinked parameters : ionic composition of the water being treated, pH, fouling index, temperature, conversion rate, inlet pressure, etc. Calculations which include all these parameters can only be done reliably and quickly by computer.

It is obvious that reverse osmosis does not directly achieve chemical qualities which are comparable with those achieved by ion-exchanging resins.

Organic quality

Owing to the membranes' capacity to trap organic substances, water of a very high organic quality can be obtained.

Theoretically, water treated by reverse osmosis is incombustible, as combustible endotoxins with a very high molar mass are all trapped by the membranes. In practice, this theory is almost always confirmed.

Nevertheless, nothing is beyond the sudden deterioration of the whole membrane or defects in the watertight seals separating the water being treated from the purified water compartment. Consequently, it would be unwise to guarantee the obtainment of incombustible water after treatment by reverse osmosis membranes.

Microbiological quality

For the same reasons, a negligible but sudden deterioration in the membrane or seal is enough to let some bacteria through to the purified water compartment. Once they have passed through the membrane, these bacteria can then nest and reproduce.

Even if experience shows that water treated by reverse osmosis is almost always sterile, it is impossible to guarantee this sterility categorically.

