Novell and emerging food technology

Prof. Dr. Hodúr Cecília- Dr. László Zsuzsanna

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BEFEKTETÉS A JÖVŐBE

MEMBRANE SEPARATION

Membrane technology is a generic term for a number of different, very characteristic separation processes. It is a technology which selectively separates (fractionates) materials via pores and/or minute gaps in the molecular arrangement of a continuous structure. Membrane separations are classified by pore size and by the separation driving force. The membrane technology is known as a flexible adaptable technique for varying capacity and for the diverse chemical composition of processed fluids.

Although membrane processes may differ greatly in their mode of operation, structures and driving forces, some advantages are common to all. They are faster, more efficient and more economical, and their operation is easier to control and maintain than other conventional separation techniques. Further, there is only a low need for chemicals and separation is usually performed at ambient temperature, therefore allowing temperature-sensitive solutions to be treated without the constituents being damaged or chemically altered. This is important in the food industry, where temperature-sensitive products have to be processed.

Unfortunately, membrane techniques have some drawbacks too, such as high energy consumption and especially RO or the flux decline caused by membrane fouling or concentration polarization. Benefits of membrane separation are well known; many industries are utilizing various technologies to minimize fresh water purchases and wastewater disposal. Membranes are now competitive for conventional techniques: flocculation, sediment purification techniques, adsorption (sand_filters and active carbon filters, ion exchangers), extraction and distillation.

1. Membrane

The membrane is a selective barrier that permits the separation of certain species in a fluid by combination of sieving and diffusion mechanisms. Membranes can separate particles and molecules and over a wide particle size range and molecular weights.

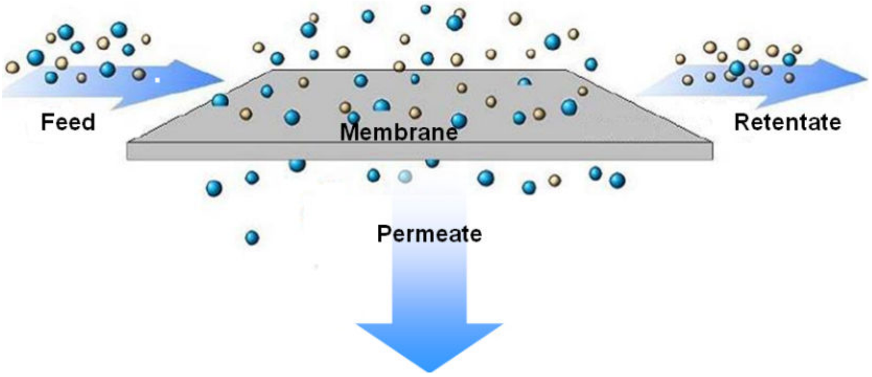


Fig.1: Membrane separation (http://www.beilstein-journals.org)

The principle is quite simple: the membrane acts as a very specific filter that will let permeate flow through, while it catches suspended solids and other substances. There are various methods to enable substances to penetrate a membrane. Examples of these methods are the applications of high pressure, the maintenance of a concentration gradient on both sides of the membrane and the introduction of an electric potential.

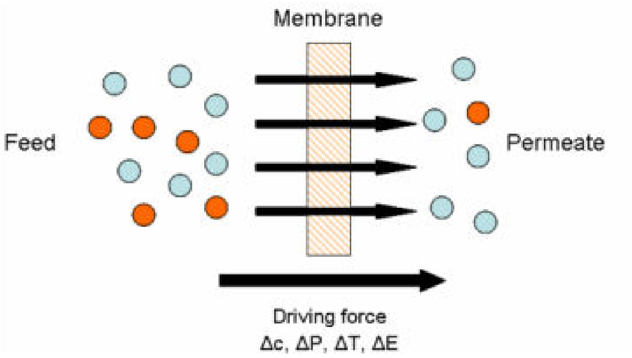


Fig.2: driving forces of membrane separations

(http://www.nanoglowa.com/membranes.html)

The most important and wilde used driving forces are: concentration difference (Δc), pressure difference (Δp), temperature difference (ΔT), chemical potential difference, or electric potential (ΔE).

Pressure requirements are based on osmotic pressure for reverse osmosis, osmotic pressure and fluid mechanical frictional head loss (straining) for nanofiltration, and purely fluid mechanical frictional head loss (straining) for ultra- and microfiltration. If clean water and water with some concentration of solute are separated by a semi-permeable membrane (permeable to only water) water will be transported across the membrane until increases hydrostatic pressure on the solute side will force the process to stop.

1.1. History of membrane separation

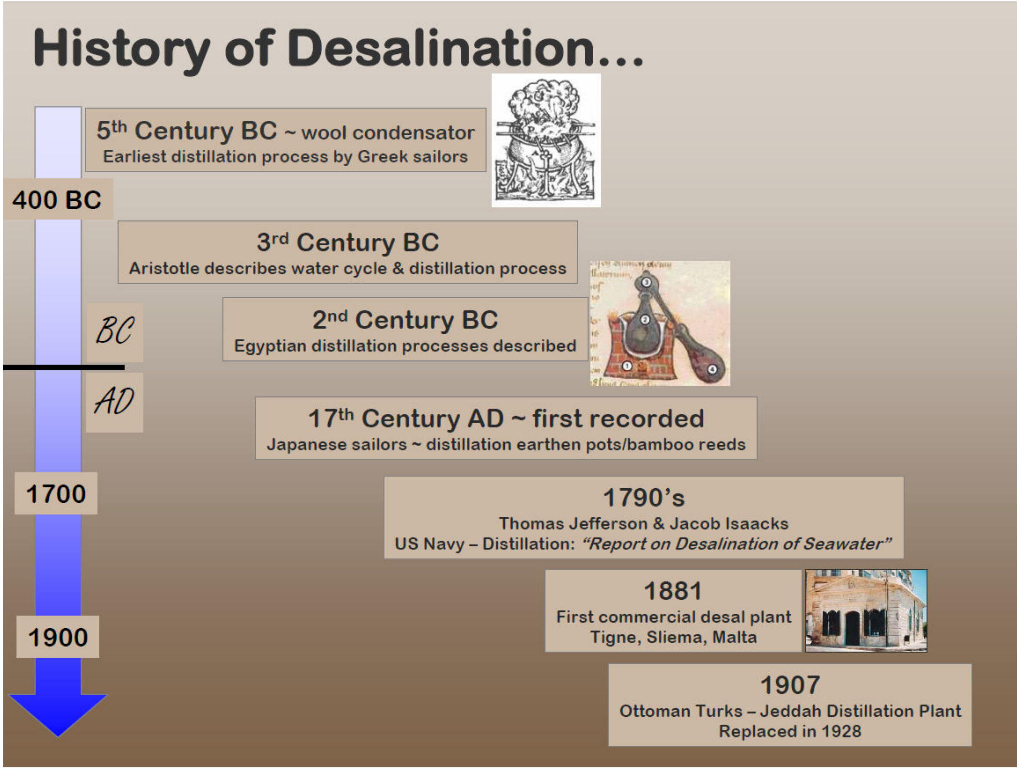
Nollet and Dutrochet (about 1750) used membranes in their osmotic pressure experiments, whereas Graham (18051869) used membranes for the separation of crystals from colloids (1854) and accomplished the enrichment of oxygen from air (1863). At the same time, Traube produced the first artificial membranes and many other researchers used membranes in their experiments (Fick, Raoult, van ‘t Hoff).

They also developed the first fundamental theories about membrane structures and transport mechanisms. In 1855, Fick introduced Fick's law of diffusion, which governs the diffusion of a gas across a fluid membrane. In 1870, he was the first to measure cardiac output, using what is now called the Fick principle. Fick managed to double-publish his law of diffusion, as it applied equally to physiology and physics. His work led to the development of the direct Fick method for measuring cardiac output.

Graham noted the importance of solubility of components in membranes and, in 1855, Lhermite showed that in principle two different membrane types do exist: porous and non-porous ones. Lhermite was also the first who stated the ‘solution theory’, i.e., permeation as the result of specific interactions between the membrane material and the pet-meant, but he also recognized that this theory and the ‘capillary theories’ merge gradually into ne another. When Bechhold in 1907, found that the porosity of nitrocellulose membranes could be influenced by the manipulation of the collodion concentration in the casting solution, more possibilities became available to study the characteristics of porous membranes thoroughly.

Bechhold also developed a technique to evaluate pore sixes in membranes, which is presently known as the ‘bubble pressure method’.

Between 1924 and 1926. Zsigmondy systematically investigated porous filter media, which eventually led to the first commercially produced membranes by the Sartorius Company. Zsigmondy left organic chemistry to join the physics group of August Kundt at the University of Berlin, and completed his habilitation at the University of Graz in 1893. Because of his knowledge about glass and its colouring, in 1897 the Schott Glass factory offered him a job which he accepted. He invented the Jenaer Milchglas and conducted some research on the red Ruby glass.



History of Desalination…

400 BC

5th Century BC ~ wool condensator
Earliest distillation process by Greek sailors

3rd Century BC
Aristotle describes water cycle & distillation process

2nd Century BC
Egyptian distillation processes described

BC
AD

17th Century AD ~ first recorded
Japanese sailors ~ distillation earthen pots/bamboo reeds

1700

1790’s
Thomas Jefferson & Jacob Isaacks
US Navy – Distillation: *“Report on Desalination of Seawater”*

1881
First commercial desal plant
Tigne, Sliema, Malta

1900

1907
Ottoman Turks – Jeddah Distillation Plant
Replaced in 1928

Fig.3: History of desalination (by H.R Ridgway)

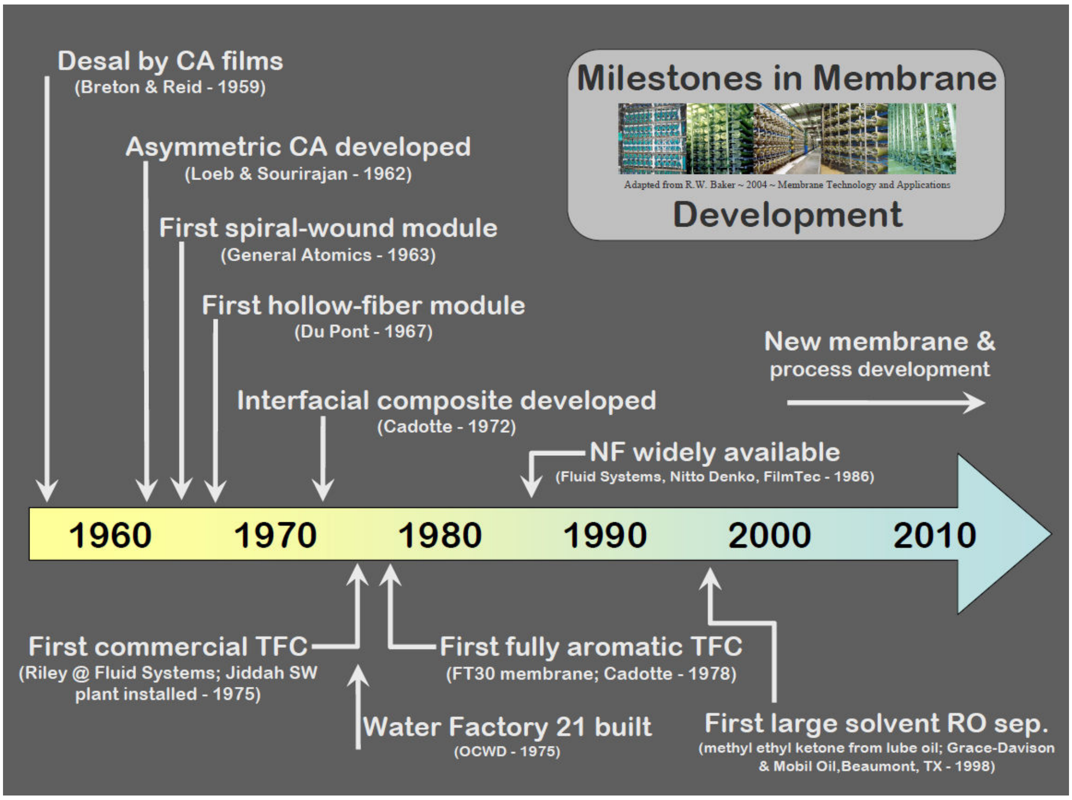


Fig.4: Milestone in membrane development (by H.R Ridgway)

1.2. Membrane materials

The membrane materials can be classification following different criteria:

- based on microstructure: porous or non-porous (dense);
- based on isotropy: symmetric (isotropic) or asymmetric (anisotropic);
- based on material nature: organic polymers or inorganic solids.

The main parts of the used membranes are organic membranes but for specific conditions of utilization inorganic (or organic-inorganic) membranes have been also developed. A lot of different organic polymers are used to prepare membrane like cellulose acetate, regenerated cellulose, polyethylene (PE), polypropylene (PP), polysulfone, Polyacrylonitrile (PAN), polyimide (PI), polytetrafluoroethylene (PTFE), polyethersulfone, polyamide, polyvinyl difluoride, polyacrylonitrile.

The main inorganic materials used for membranes are oxide ceramic, porous glasses, carbon-like solids, porous metals (like sintered stainless steel) or dense metals (like Pd or Pd-based alloys for H_2 separation). The primary materials used for inorganic membranes are: - aluminum oxide (Al2O3), zirconium oxide (ZrO2) , also being tried as membranes are materials such as- stainless steel (SUS), - glass (Shirasu Porous Glass, SPG).

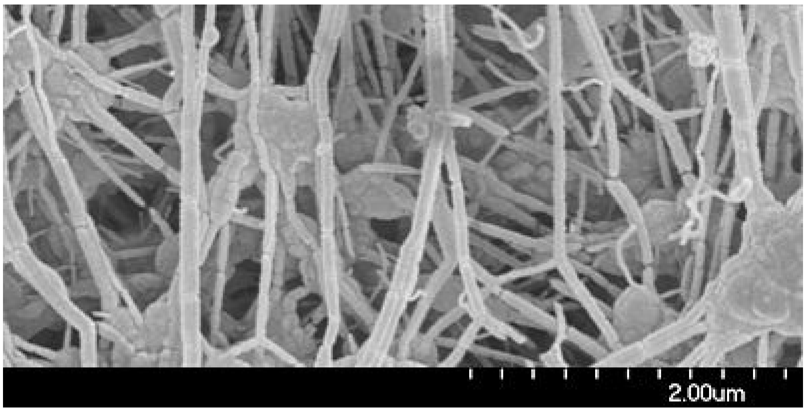


Fig.5 : PTFE membrane

In comparison with organic membranes, inorganic membranes excel in heat and chemical resistance, as well as in mechanical strength. These advantages often offset their inherent higher capital cost. The interest of the ceramic membranes is related to the intrinsic characteristics of the used materials are the mechanical strength allowing large pressure gradients without significant strain**.**

Dense organic membranes are prepared by conventional plasturgy methods like melt extrusion, compression moulding, solution casting or coating. For porous organic membranes, the most used class of techniques is called phase inversion techniques . Phase separation mechanisms can generally be subdivided in three main categories depending on the parameters that induce demixing. By posing a change in one of these parameters at one particular side of the film, asymmetric boundaries are posed on the polymer film which can be expressed in the resulting structure. By changing the temperature at the interface of the polymer solution, heat will be exchanged and demixing can be induced (temperature induced phase separation or TIPS). The original polymer solution can also be subjected to a reaction which causes phase separation (reaction induced phase separation) (RIPS). The most used technique is based on diffusion induced phase separation (DIPS). By contacting a polymer solution to a vapour or liquid, diffusional mass exchange will lead to a change in the local composition of the polymer film and demixing can be induced.

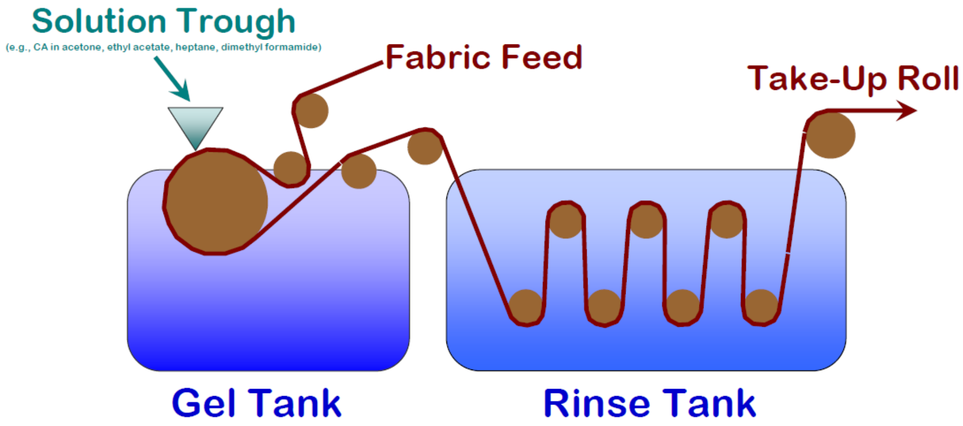


Fig.6: Membrane preparation method – phase inversion ((by H.R Ridgway)

Other methods can be used to prepare porous organic membranes like leaching (for selective removal of a porogen phase), sintering of polymer powders or track etching (irradiation followed by caustic etching).

Porous ceramic membranes for liquid treatments are usually based on a macroporous support and successive layers with decreasing thickness and pore size (Table 4 and Figure 14). The macroporous support and the macroporous intermediate layers are produced by conventional ceramic methods. The sol-gel route is well-adapted to prepare the mesoporous and microporous separative top layers required for low UF and NF membranes, respectively. Macroporous and mesoporous alumina discs obtained by anodizing aluminum foils are also commercially available.

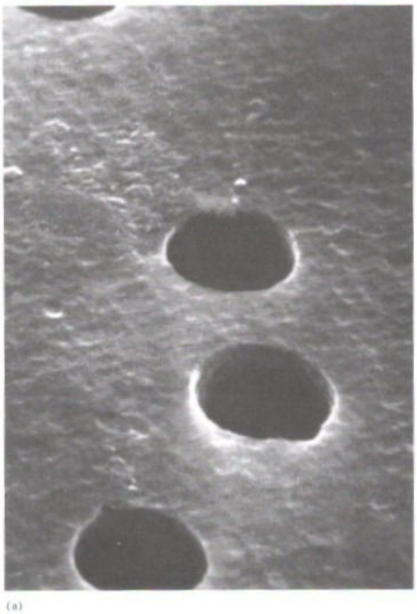


Fig.7: Track etching membrane

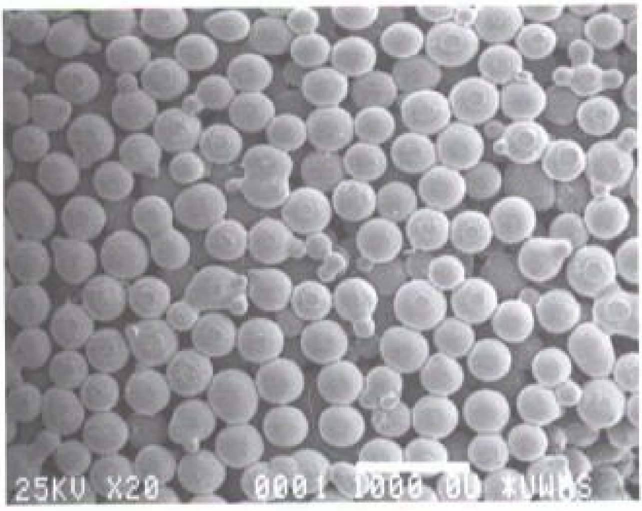


FIG. 17 Microscopic view of ordered porous ceramic.

Fig.8: Ceramic membrane

The balance between the permeability and selectivity of a membrane material with respect to specific compositions of the gases, vapors, or liquids to be separated in specific applications with substantial market potential, such as natural gas purification or CO_2 management, require an extremely high degree of optimization, which is frequently not attainable with traditional homopolymers. For this reason, multicomponent polymers are also being developed. There is little known to date concerning the relationships between the topologies and properties of these polymers.

Unlike conventional size-selective membranes, reverse-selective polymer membranes are more permeable to larger, more condensable or more polar gases and vapors (e.g., carbon dioxide, hydrogen sulfide, condensable hydrocarbons, etc.) than to smaller, less condensable gases (e.g., hydrogen). The reverse-selective membranes selectively separate carbon dioxide, hydrogen sulfide, and carbonyl sulfide from the synthesis gas as a low-pressure waste stream, leaving the hydrogen- and carbon monoxide-enriched product stream at high pressure for downstream utilization. The chemistry of these membranes has been tailored to give them high permeability and high selectivity for polar and acidic gas species. Process modeling has shown that reverse-selective membrane processes can provide significant cost advantages over amine absorption systems, the industry standard for acid-gas removal.

Molecular Weight Cut Off or MWCO refers to the lowest molecular weight solute (in daltons) in which 90% of the solute is retained by the membrane or the molecular weight of the molecule (e.g. globular protein) that is 90% retained by the membrane. This definition is not however standardized, and MWCOs can also be defined as the molecular weight at which 80% of the analytes (or solutes) are prohibited from membrane diffusion. Commercially available ultrafiltration membranes typically have molecular weight cutoffs that range from 1,000 to 300,000 Da, and larger thresholds of filtration are measured in µm.

There are two factors that determine the effectivity of a membrane filtration process; selectivity and productivity. Selectivity is expressed as a parameter called retention or separation factor. Productivity is expressed as a parameter called flux (expressed by the unit $l/m^2 \cdot h$). Selectivity and productivity are membrane-dependent.

Read more: http://www.lenntech.com/membrane-technology.htm#ixzz2qV8JgU4b

Flux (J) through the membrane is the most important design and operational parameter. Next most important is solute exclusion. Some solute will diffuse (by molecular diffusion) through the membrane because there will be a significant gradient of the solute across the membrane.

Flux would be calculated as follows:

$$J = \frac{V_{perm}}{A \cdot \tau} \qquad (1)$$

Retention (R) equation:

$$R = \frac{c_{ret} - c_{perm}}{c_{ret}} = 1 - \frac{c_{perm}}{c_{ret}} \qquad (2)$$

where V_{perm} is the volume of the permeate (m^3),, A is the membrane area (m^2), τ is the time (h),

c_{ret} is the concentration of the retentate, c_{perm} is the concentration of the permeate.

1.3. Configuration

Membranes come in four basic configurations—tubular, spiral, hollow fiber, and flat sheet. Each is configured differently, both in packaging and in the types of materials used, to address the range of physical characteristics found in process fluids. There are distinct advantages that come with each configuration, allowing you to manage your process needs effectively.

Spiral membranes consist of two layers of membrane, placed onto a permeate collector fabric. This membrane envelope is wrapped around a centrally placed permeate drain (see picture below). This causes the packing density of the membranes to be higher. The feed channel is placed at moderate height, to prevent plugging of the membrane unit.

Spiral membranes are only used for nano filtration and Reverse Osmosis (RO) applications.

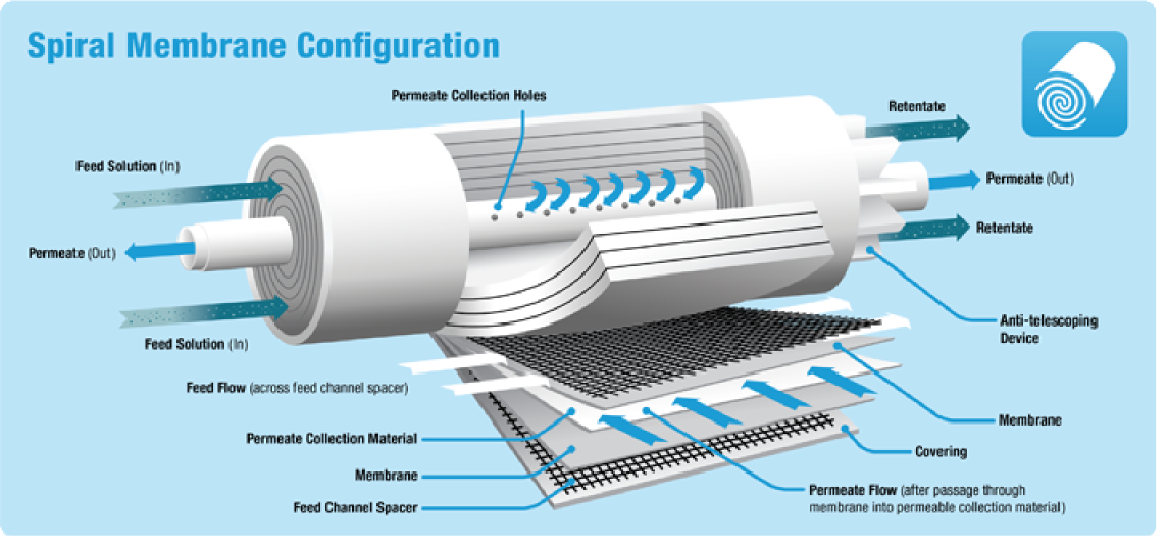


Fig.9: Spiral membrane configuration (by Koch Membrane system)

Tubular membranes are not self-supporting membranes. They are located on the inside of a tube, made of a special kind of material. This material is the supporting layer for the membrane. Because the location of tubular membranes is inside a tube, the flow in a tubular membrane is usually inside out. The main cause for this is that the attachment of the membrane to the supporting layer is very weak. Tubular membranes have a diameter of about 5 to 15 mm. Because of the size of the membrane surface, plugging of tubular membranes is not likely to occur. A drawback of tubular membranes is that the packing density is low, which results in high prices per module.

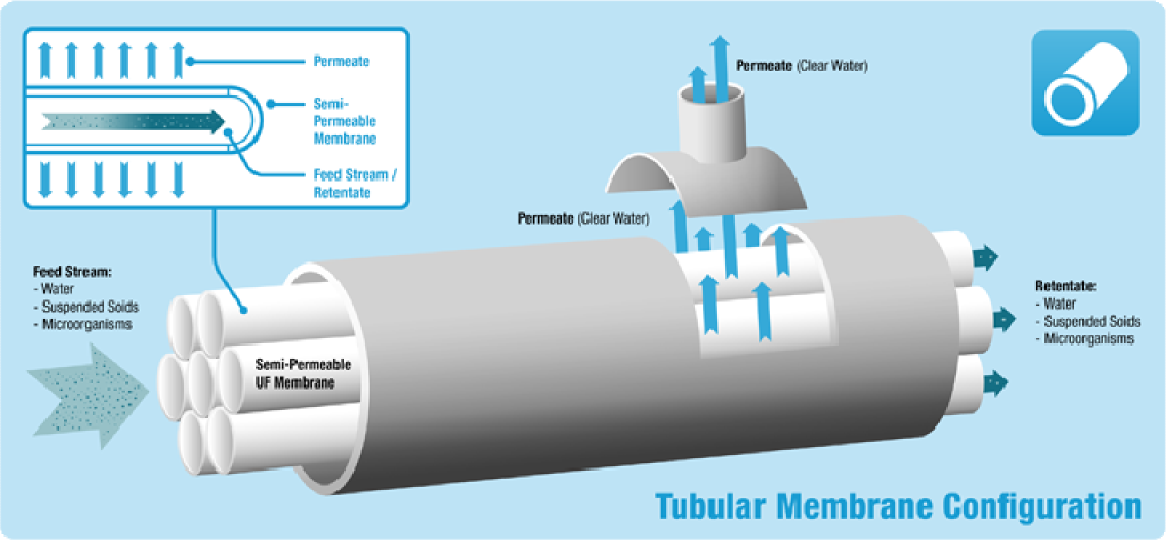


Fig.10: Tubular membrane configuration (by Koch Membrane system)

The diameter of capillary membranes is much smaller than that of tubular membranes, namely 0.5 to 5 mm. Because of the smaller diameter the chances of plugging are much higher with a capillary membrane. A benefit is that the packing density is much greater.

Hollow Fiber membranes are also densely packed and consist of extruded fibers with a small hollow portion. Filtration can occur from inside the fiber to the outside or in the reverse direction from the outside of the fiber to the inside allowing for a backwash cycle. Although more resilient to small particulates than spirals, hollow fibers will also often require pre-filtration where larger particulates or fibers are present in the feed material. Most hollow fiber membranes cannot be used at pressures above (2 bar without breaking.

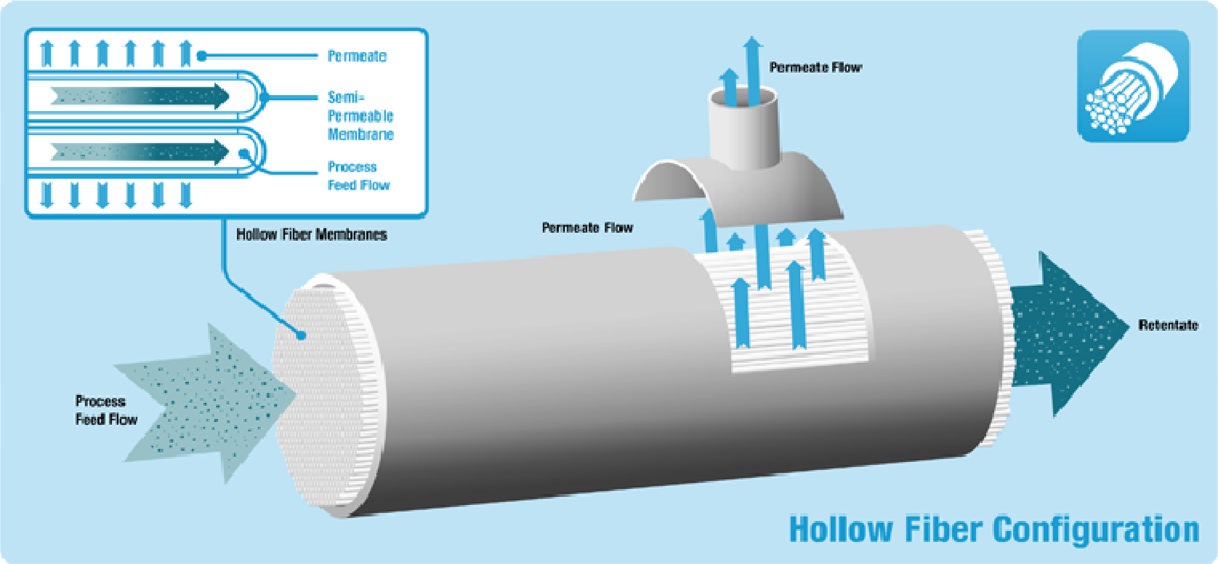


Fig.11: Hollow fibre membrane configuration (by Koch Membrane system)

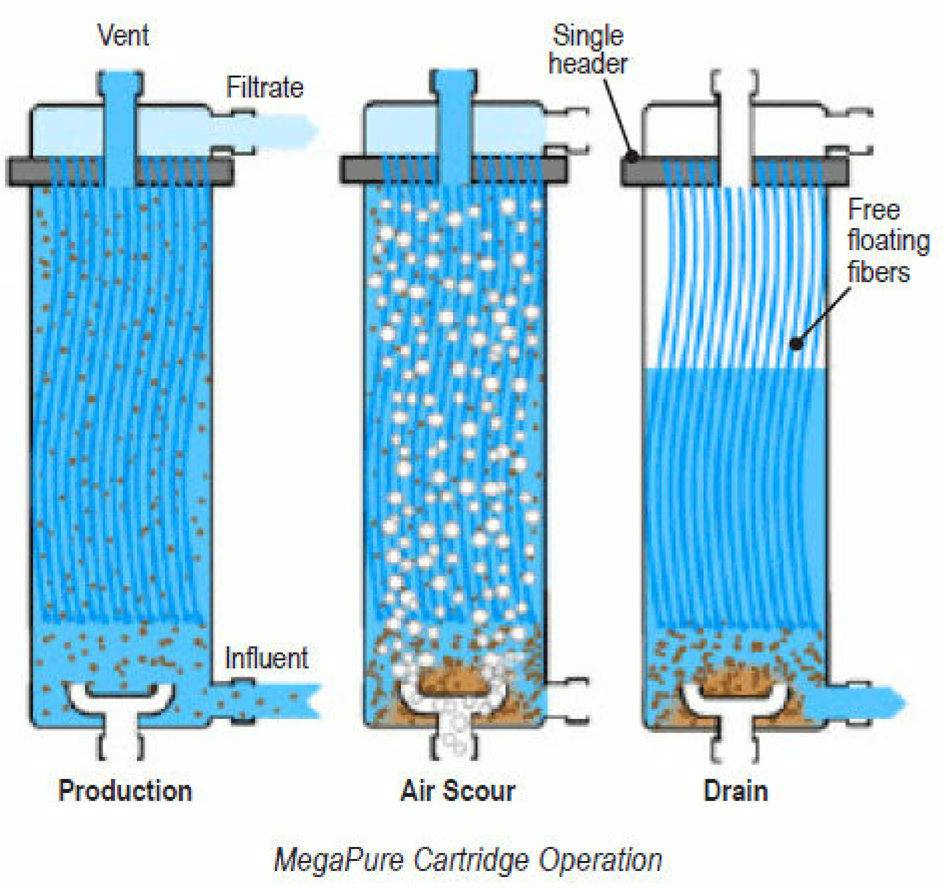


Fig. 12: Hololw fibre membrane for suspensions (http://www.desalination.com)

2. Membrane separation

Membrane technology is a generic term for a number of different, very characteristic separation processes. The main force of membrane technology is the fact that it works without the addition of chemicals, with a relatively low energy use and easy and well-arranged process conductions. Membranes are now competitive for conventional techniques.flocculation, sediment purification techniques, adsorption (sand_filters and active carbon filters, ion exchangers), extraction and distillation.

There are two factors that determine the affectivity of a membrane filtration process; selectivity and productivity. Selectivity is expressed as a parameter called retention or separation factor (expressed by the unit l/m^{2}h). Productivity is expressed as a parameter called flux (expressed by the unit l/m^{2}h). Selectivity and productivity are membrane-dependent. Read more: http://www.lenntech.com/membrane-technology.htm#ixzz2qV8JgU4b

So many different driving force could be used for separation when the membrane make a role as a separator or only a contactor. (see Table1.)

Table 1: Membrane separation processes

Membrane	Gradient			
	Concentration	Pressure	Temperature	Electric potential
Non - porous	Pervaporation PV	Gas separation GS	Membrane distillation MD	Electrodialysis ED
	Osmotic distillation OD	Reverz osmosis RO		
mikropore $d_p \leq 2nm$	Dialysis D	Nanofiltration NF		

mezopore d_p=2-50nm		Ultrafiltration UF		Electrodialysis ED
makropore d_p=50-500nm		Microfiltration MF		Fluel cells
		Membrane distillation MD		

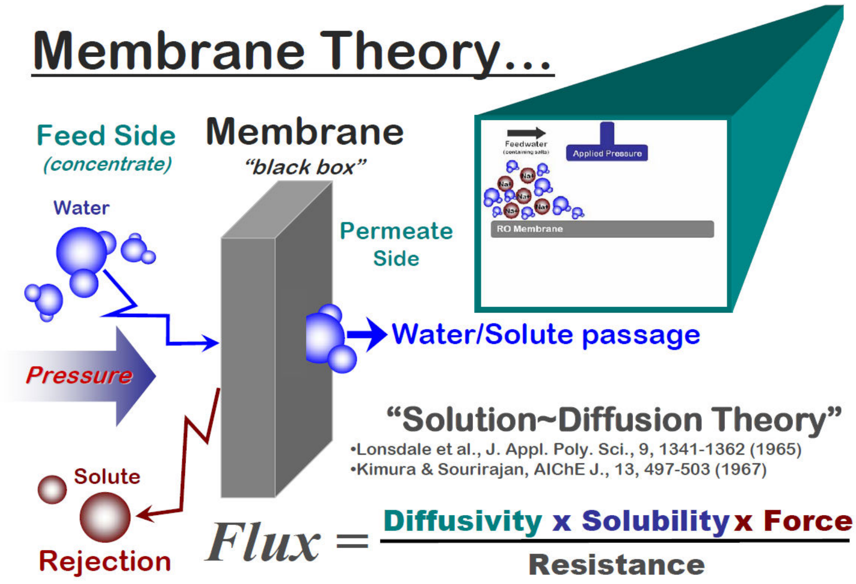


Fig.13: Membrane separation theory

There are a lot of membrane theories about how to allow pass the membrane through the molecules (Figure 13)

At the porous membrane a simple impulses transport might be the solution, but non-pore membrane can work another way.

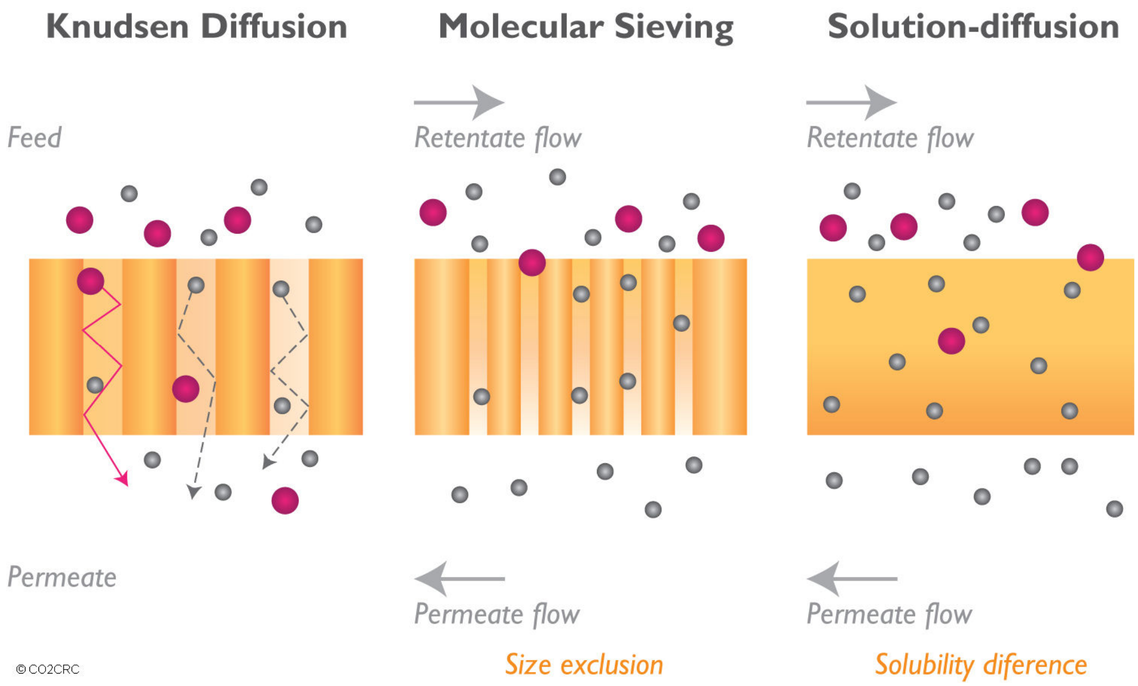


Fig.14: Basic membrane separation methods

2.1 Pervaporation

Pervaporation membranes are non porous and used for separating liquid from liquid mixtures. It enables solvent mixtures to be separated without using any third substance or entrainer. Azeotropes can be broken effectively and economically irrespective of vapor-liquid equilibrium. Molecules with high affinity are attracted by the membrane layer and are diffused through the membrane while molecules with low affinity are retained. For example hydrophilic membranes have high affinity to water molecules and so allow water to diffuse through the membrane while preventing other molecules from doing so while a hydrophobic membrane will do the opposite. The membrane separates mixtures at the molecular level, separating and driving similar type molecules in a vapor phase into one tank while redirecting the other portion of the liquid mixture back to the original tank or a third tank.

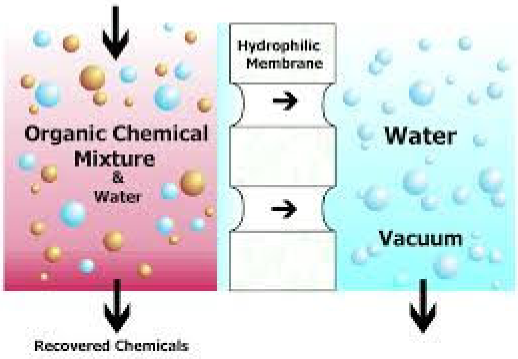


Fig.15: Pervaporation method (http://kmxcorp.com)

2.2. Membrane distillation

Membrane distillation is a thermally driven separation process in which separation is enabled due to phase change. A hydrophobic membrane displays a barrier for the liquid phase, letting the vapour phase (e.g. water vapour) pass through the membrane pores. The driving force of the process is given by a partial vapour pressure difference commonly triggered by a temperature difference.

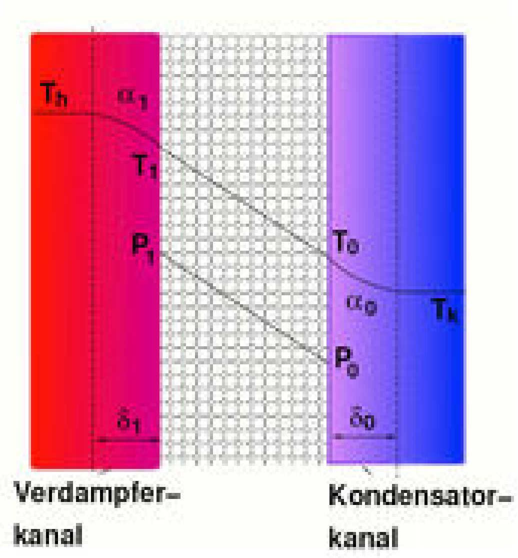


Fig.16 : Temperature and pressure diferences at membrane destillation

(by Joachim Koschikowsk)

Membrane distillation is very suitable for compact, solar powered desalination units providing small and medium range output <10000 l/day. Especially the spiral wound design patented by GORE in the year 1985 suits this application. Within the MEMDIS project, which kicked off in 2003, the Fraunhofer Institute for Solar Energy Systems ISE began developing MD modules as well as installing and analysing two different solar powered operating systems, together with other project partners. The first system type is a so-called compact system, designed to produce a drinking water output of 100-120 l/day from sea-or brackish water. The main aim of the system design is a simple, self-sufficient, low maintenance and robust plant for target markets in arid and semi-arid areas of low infra structure. The second system type is a so-called two-loop plant with a capacity of around 2000 l/day. Here, the collector circuit is separated from the desalination circuit by a saltwater resistant heat exchanger. Based on these two system types, a various number of prototypes were developed, installed and observed.

The standard configuration of today's (2011) compact system is able to produce a distillate output of up to 150 l/day. The required thermal energy is supplied by a 6,5 m² solar thermal collector field. Electrical energy is supplied by a 75 W PV-module. This system type is currently being developed further and marketed by the Solar Spring GmbH, a Spin -Off of the Fraunhofer Institute for Solar Energy Systems. Within the MEDIRAS project- a further EU-project, an enhanced two-loop system was installed on the Island of Gran Canary. Built inside a 20 ft container and equipped with a collector array size of 225 m², a heat storage tank makes a distillate output of up to 3000 l/day possible. Further applications with up to 5000 l/day have also been implemented, either 100% solar powered or as hybrid projects in combination with waste heat.

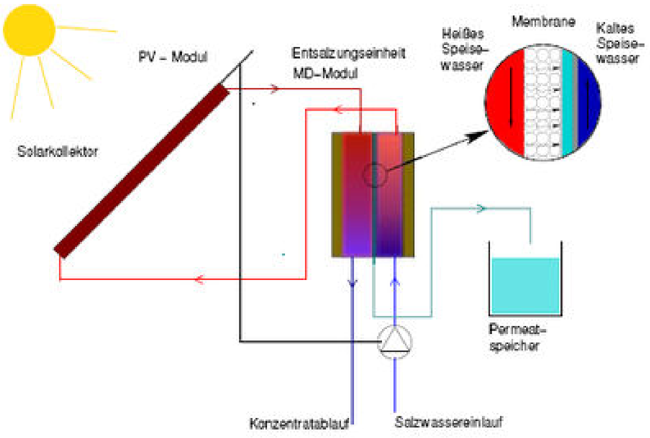


Fig.17 : Compact system of solar powered membrane distillation (by Joachim Koschikowsk)

3. Membrane filtration

Membrane filtration is said when the driving force is the pressure difference through the membrane.

The membrane as a medium is very active and effective in that intervall, so the membrane separation is very effective in food industry, mainly at liquid-industries.

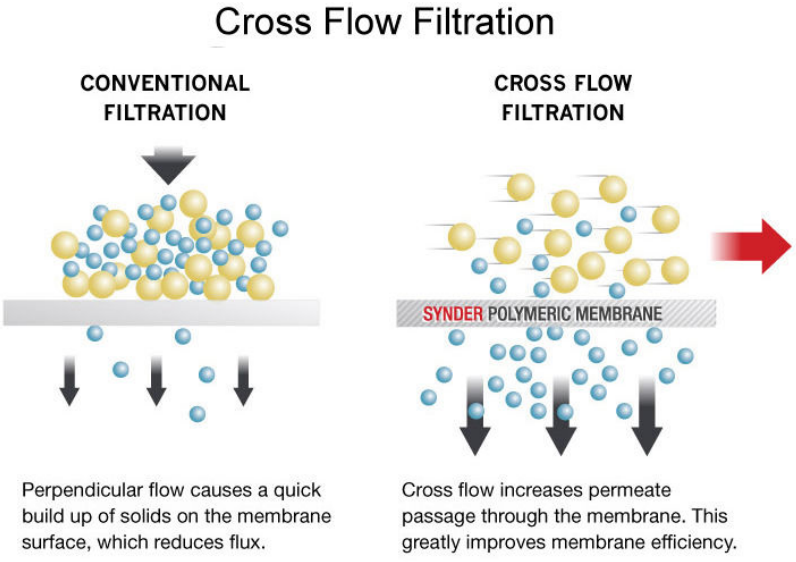
The principle is quite simple: the membrane acts as a very specific filter that will let water flow through, while it catches suspended solids and other substances. There are various methods to enable substances to penetrate a membrane. Examples of these methods are the applications of high pressure, the maintenance of a concentration gradient on both sides of the membrane and the introduction of an electric potential. Read more: http://www.lenntech.com/membrane-technology.htm#ixzz2qV86Pnby

Based on the size of the separated particles we can classified the membrane filtration (Table 1., Figure 19)

Membrane performance is characterized always by flux and selectivity. Flux is volume of permeate passing through a membrane per unit area and time. Using SI units this is given as m^3/m^2 s, but other units such as L/m^2 h, L/m^2 day are often used in the literature.

The main applications of membranes are in the dairy industry (close to 40 % , of which over 10 % are used for milk protein standardization), followed by beverages (wine, beer, fruit juices, etc.) and egg products (2%). Other fields are emerging: fruit and vegetable juices and concentrates, wate streams, co-products (recovery and recycling of blood plasma in abattoirs) and technical fluids (brines, cleaning –in-place solutions).

There are two modes used for membrane filtration - direct (or 'dead end') flow and cross-flow.



Perpendicular flow causes a quick build up of solids on the membrane surface, which reduces flux.

Cross flow increases permeate passage through the membrane. This greatly improves membrane efficiency.

Fig.18: Comparization of filtration method (http://www.synderfiltration.com)

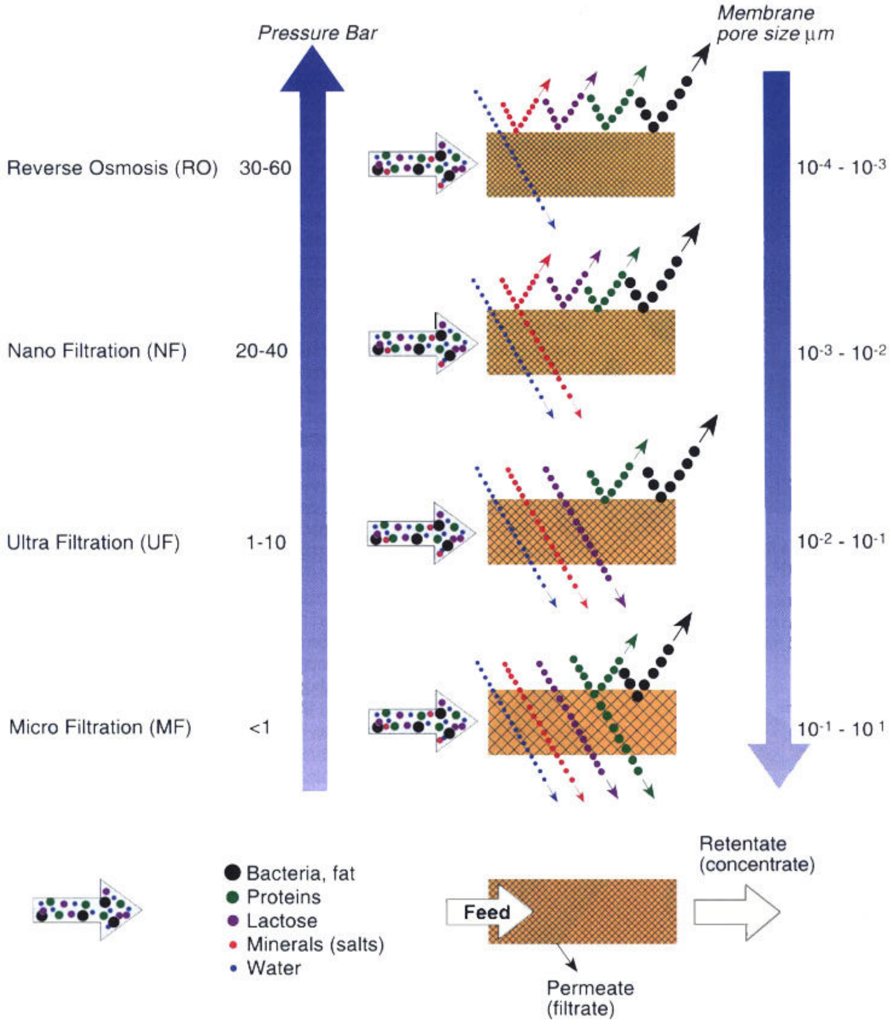


Fig.19: Most important parameters of membrane filtrations

In direct flow, the full raw water feed supply passes directly through the filter similar to conventional sand-filtration. These filters require periodic cleaning (or back washing) of membranes.

In contrast, a cross flow filtration mode employs a high velocity of raw water feed flowing in parallel over (across) the membrane surface. This flow keeps the membrane surface from fouling or accumulating solids.

The appropriate filtration mode should be selected by taking into account factors such as fluid composition, membrane material, selectivity of the membrane, filtration module geometry, and cleaning methods.

3.1. Reverz osmosis and Nanofiltration

Reverse osmosis is a high-efficient technique for dewatering process streams, concentrating/separating low-molecular-weight substances in solution, or cleaning wastewater. It has the ability to concentrate all dissolved and suspended solids. The permeate contains a very low concentration of dissolved solids. Reverse Osmosis is typically used for the desalination of seawater.

In order to describe Reverse Osmosis, it is first necessary to explain the phenomenon of osmosis. Osmosis may be described as the physical movement of a solvent through a semi-permeable membrane based on a difference in chemical potential between two solutions separated by that semi-permeable membrane.

The following example serves to demonstrate and clarify this point. A beaker of water as shown in is divided through the center by a semi-permeable membrane. The black dotted line represents the semi-permeable membrane. We will define this semi-permeable membrane as lacking the capacity to diffuse anything other than the solvent, in this case water molecules. Now we will add a little common table salt (NaCl) to the solution on one side of the membrane. The salt water solution has a greater chemical potential than the water solution on the other side of the membrane. In an effort to equilibrate the difference in chemical potential, water begins to diffuse through the membrane from the water side to the salt water side. This movement is osmosis. The pressure exerted by this mass transfer is known as osmotic pressure.

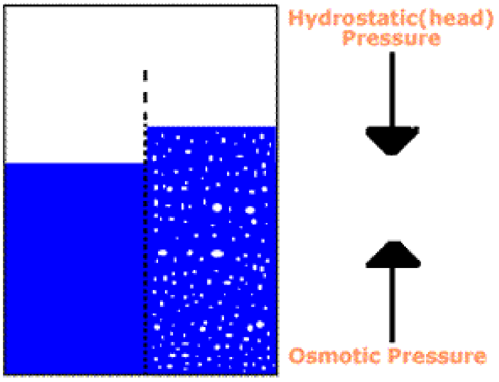


Fig. 20: Osmosis

By exerting a hydraulic pressure greater than the sum of the osmotic pressure difference and the pressure loss of diffusion through the membrane, we can cause water to diffuse in the opposite direction, into the less concentrated solution. This is reverse osmosis. The greater the pressure applied, the more rapid the diffusion.

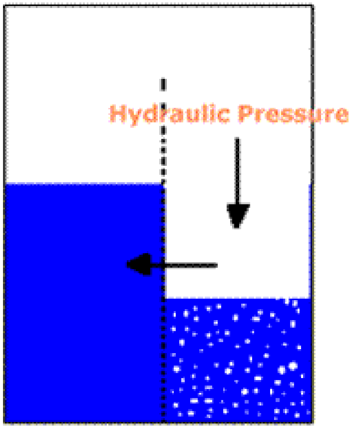


Fig. 21: Reverse osmosis

The RO membrane is semi-permeable with thin layer of annealed material supported on a more porous sub-structure. The thin skin is about 0.25 micron thick and has pore size in the 5 – 10 Angstrom range. The porous sub-structure is primarily to support the thin skin. The pore size of the skin limits transport to certain size molecules. Dissolved ions such as Na and Cl are about the same size as water molecules

However, the charged ions seem to be repelled by the active portion of the membrane and water is attracted to it. So adsorbed water will block the passage and exclude ions. Under pressure attached water will be transferred through the pores.

The flux of RO could be calculated by the knowledge of the membrane permeability (K), the transmembrane pressure difference (Δp) and the transmembrane osmotic pressure difference (Δπ):

$$J = K(\Delta p - \Delta \pi) \tag{3}$$

Nanofiltration can perform separation applications such as demineralization, color removal, and desalination. In concentration of organic solutes, suspended solids, and polyvalent ions, the permeate contains monovalent ions and low-molecular-weight organic solutions like alcohol. Today, nano filtration is mainly applied in drinking water purification process steps, such as water softening, decolouring and micro pollutant removal.

3.2. Ultrafiltration

Ultrafiltration is a selective fractionation process using pressures up to 145 psi (10 bar). Ultrafiltration is widely used in the fractionation of milk and whey, and in protein fractionation. It concentrates suspended solids and solutes of molecular weight greater than 1,000. The permeate has low-molecular-weight organic solutes and salts.For complete removal of viruses, ultra filtration is required. The pores of ultra filtration membranes can remove particles of 0.001 – 0.1 µm from fluids. Examples of fields where ultra filtration is applied are:

- Concentration of milk
- separation of whey,

- fruit juice clearing
- emulsion separation,
- The metal industry – dare recovery

In the case of ultrafiltration instead of classical flux equation,

$$J = K(\Delta p - \Delta \pi) \tag{4}$$

the simplified version could be used:

$$J = K(\Delta p) \tag{5}$$

because of the large molecule weights of separated molecules, the the low mol.conc.of solutes/permeate, so the the effect of osmotic pressure difference is minimal.

But there is developed a big concentration difference between the membrane wall's boundary layer at the feed side and the bulb solution. It creates a reversed diffusion flow. The two reversed flow the flow through the membrane and the flow back from the membrane wall to the bulk make a balance. It means their difference is zero. The diffusion flow to the bulk is determined by the concentration gradient difference between the wall and the bulk (dc/dx), and by the diffusion coefficient (D):

$$J - D\frac{dc}{dx} = 0 \tag{6}$$

$$J = \frac{D}{\delta}\ln\frac{c_w}{c_b} = k\,\ln\frac{c_w}{c_b} \tag{7}$$

After integration of the equation between c_w – concentration at the wall and c_b- concentration at the bulk in distance δ, we get the mass transfer coefficient (k) in our equation, which would be calculated by the Sherwood equations and Sherwood number (Sh).

$$Sh = \frac{kl}{D} \tag{8}$$

$$Sh = f(\mathrm{Re}, Sc) \tag{9}$$

$$\mathrm{Re} = \frac{lv\rho}{\eta} \tag{10}$$

$$Sc = \frac{v}{D} \tag{11}$$

Re is the Reynolds number, Sc is the Schmidt number, ν is the kinematics viscosity , η is the dynamical viscosity, ρ is the density.

Example: Milk is concentrated by UF at 20 °C. The TSS of the feed is TSS: 3,1 %, the diameter of the tubular membrane is:d = 1,1 cm, the milk is flowing through 10 pieces of tube with mass flow rate: 150 kg/min, density.1030 kg/m^3, viscosity: 0,8 cP.

Calculate the permeate flux if the diffusion coefficient: 7x10^{-7} m^2/s and the pressure is:

6895 kPa

As we know the permeate flux could be calculated by Eq.7 :

$$J = k_m \ln \frac{c_w}{c_b}$$

At first we have to calculate k via Sherwood number (Eq.9):

$$\mathrm{Sh} = \frac{\mathrm{kl}}{\mathrm{D}} = \mathrm{const.Sc}^{0,33}\,\mathrm{Re}^{0,8}$$

$$\mathrm{Sh} = 0{,}023\left(\frac{\nu}{\mathrm{D}}\right)^{0.33}\left(\frac{\mathrm{d}\cdot\mathrm{v}\cdot\rho}{\mu}\right)^{0.8}$$

$$\mathrm{Sh} = 1440$$

$$Sh \;= 1440 = \frac{k \cdot d}{D}$$

$$k_m = \frac{1440 \cdot 7 \cdot 10^{-11}}{0{,}011} = 9{,}16 \cdot 10^{-6}\; m^2 / s$$

and this way we can calculate the flux:

$$J = 9{,}16 \cdot 10^{-6} \cdot 998{,}2 \cdot \ln\frac{0{,}22}{0{,}031} = 0{,}018\,\frac{kg}{m^2 s}$$

3.3. Microfiltration

Microfiltration is a low-pressure cross-flow membrane process for separating colloidal and suspended particles in the range of 0.05-10 microns. Microfiltration is used for fermentation, broth clarification and biomass clarification and recovery. Membranes with a pore size of 0.1 – 10 µm perform micro filtration. Microfiltration membranes remove all bacteria. Only part of the viral contamination is caught up in the process, even though viruses are smaller than the pores of a micro filtration membrane. This is because viruses can attach themselves to bacterial biofilm.

Micro filtration can be implemented in many different liquid treatment processes when particles with a diameter greater than 0.1 mm need to be removed from a liquid.

Examples of micro filtration applications are:

- cold sterilization of beverages and pharmaceuticals
- clearing of fruit juice, wines and beer
- cell separation
- brightness filtration of liquids
- continuously fermentation
- oil-water emulsion separation
- gentle product treatment due to moderate temperature changes during processing;
- high selectivity based on unique separation mechanisms, for example sieving,
- solution-diffusion or ion-exchange mechanism;
- compact and modular design for ease of installation and extension;
- separation of bacteria from water (biological wastewater treatment)
- low energy consumption compared to condensers and evaporators.

4. Membrane fouling

The key disadvantage of membrane filtration is the fouling of the membrane causing a reduction in flux and thus a loss in process productivity over time. The effect of fouling can be minimized by regular cleaning intervals. In the food industry it is common to have at least one cleaning cycle per 24-h shift. Other actions to reduce fouling are directly related to plant design and operation. During the plant design, the selection of a low-fouling membrane, for example hydrophilic membranes to
reduce fouling by bacteria, and membrane modules with appropriate channel heights.

Membrane fouling is a process where solute or particles deposit onto a membrane surface or into membrane pores in a way that degrades the membrane's performance. It is a major obstacle to the widespread use of this technology. Membrane fouling can cause severe flux decline and affect the quality of the water produced. Severe fouling may require intense chemical cleaning or membrane replacement. This increases the operating costs of a treatment plant. There are various types of foulants: colloidal (clays, flocs), biological (bacteria, fungi), organic (oils, polyelectrolytes, humics) and scaling (mineral precipitates).

Fouling can be divided into reversible and irreversible fouling based on the attachment strength of particles to the membrane surface. Reversible fouling can be removed by a strong shear force or backwashing. Formation of a strong matrix of fouling layer with the solute during a continuous filtration process will result in reversible fouling being transformed into an irreversible fouling layer. Irreversible fouling is the strong attachment of particles which cannot be removed by physical cleaning.

Factors that affect membrane fouling:

1. Membrane properties such as pore size, hydrophobicity, pore size distribution and membrane material.
2. Solution properties such as concentration, the nature of the components and particle size distribution.
3. Operating conditions such as pH, temperature, flow rate and pressure.

Table 2: Summary of common types of fouling and their respective chemical treatments

Foulant	**Reagent**	**Time and Temperature**	**Mode of Action**
Fats and oils, proteins, polysaccharides, bacteria	0.5M NaOH with 200 ppm Cl2	30-60 min 25-55°C	Hydrolysis and oxidation
DNA, mineral salts	0.1M – 0.5M acid (acetic, citric, nitric)	30-60 min 25-35°C	Solubilization
Fats, oils, biopolymers, proteins	0.1% SDS, 0.1% Triton X-100	30 min – overnight 25-55°C	Wetting, emulsifying, suspending, dispersing
Cell fragments, fats, oils, proteins	Enzyme detergents	30 min – overnight 30 – 40°C	Catalytic breakdown
DNA	0.5% DNAase	30 min – overnight 20 – 40°C	Enzyme hydrolysis

There are various ways to reduce this fouling such as:

- Periodic pulsing of feed
- Periodic pulsing filtrate (backwashing)
- Increasing shear at by rotating membrane
- Vibrating membrane (VSEP technology)

Vibrating shear to prevent fouling

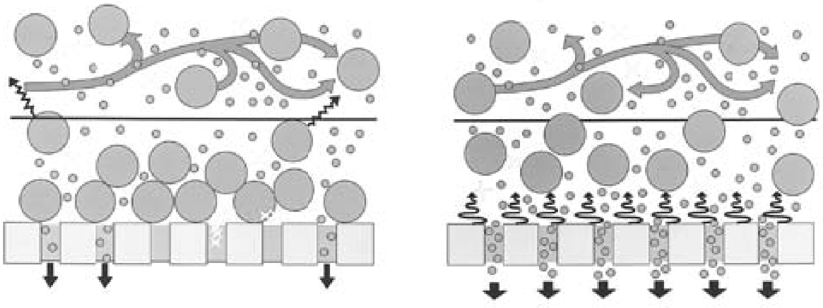


Fig. 22: VSEP technology

5. Mathematical modeling:

5.1. The resistance-in-series model for RO

When clean water is filtered, the membrane material is the only resistance caused (Rm). The flux is than called the clean water-flux. As a result of the accumulation of particles on the membrane through the filtration of water with a certain level of suspended solids, a cake will form on the membrane (Rc; particles). When particles block the membrane pores, this is called pore plugging (Rpb; scaling). Resistance as a consequence of adsorption in or on the membrane is called biofouling (Ra).

Th ersistance in series model of membrane separation defines pure water flux as the quotient of the trans-membrane pressure - driving force (ΔpTM, Pa) - and the resistance (R_M, m^{-1}, calculated by water dynamic viscosity, η_W, Pas) arising from the pore size of the membrane material feature.

The fouling resistance of the applied membranes can be determined from the water flux (J_F, ms^{-1}) - measured on a fixed temperature - after flushing the membrane with tap water after concentration test using the following formula:

$$J_w = \frac{\Delta p_{TM}}{R_m \cdot \eta_w} \quad (dm^3 m^{-2} h^{-1}) \tag{12}$$

$$R_F = \frac{\Delta p_{TM}}{J_F \cdot \eta_w} R_m \quad (m^{-1}) \tag{13}$$

The total resistance is composed of three resistances:

$$R_T = R_M + R_F + R_P \quad (m^{-1}) \tag{14}$$

where R_P (m^{-1}) is the polarization layer resistance.

At membrane filtration of liquid mixtures the osmotic pressure model is valid, which determines the flux (J, ms-1) as the quotient of difference of the trans-membrane pressure (ΔpTM, Pa), the osmotic pressure difference (Δπ, Pa), and the total membrane resistance (RT, m-1). The effect of temperature is integrated into the equation knowing the permeate (practically water) viscosity (□w, Pas).

$$J = \frac{\Delta p_{TM} - \Delta\pi}{R_T \cdot \eta_w} \quad (dm^3 m^{-2} h^{-1} \tag{15}$$

It is possible that the glucose molecules in the boundary layer near the membrane play a role in the creation of the osmotic pressure. The van't Hoff model can be applied for this phenomenon which determines the osmotic pressure dependence on the difference of concentrate (cR, kmol m-3) and permeate (cP, kmol m-3) concentration (R=8314.472 J $kmol^{-1}K^{-1}$ universal gas constant, T= 298.15 K temperature of experiment).

.

$$\Delta\pi = \left(c_r - c_p\right) RT \quad (Pa) \tag{16}$$

The concentration of the permeate side (c_P) in all experimental runs was very low~/0.1°Brix, two order of magnitude lower than the retentate concentration. Neglecting the permeate side concentration and introducing the concentration polarization β=/c_M/c_R in the previous equation, the following formula is obtained:

$$\Delta\pi = \beta \cdot c_R RT \quad (Pa) \qquad (17)$$

By the combination of the above equations, the following one is obtained:

$$J = \frac{\Delta p_{TM}}{R_T \cdot \eta_w} - \frac{\beta RT}{R_T \cdot \eta_w} c_R \quad (dm^3 m^{-2} h^{-1}) \qquad (18)$$

Plotting the permeate flux versus c_R , from the intercept of the fitted straight line the average values of the total resistances during the concentration of the blackcurrant juice can be estimated/calculated.

4.2. Makardij's modeling

For determination of the rate constants characterizing the ultrafiltration process itself, the method of Makardij et al. (2002) could be followed with the initial conditions specified as follows:

$$t = 0 \quad J = J_0, \quad \text{and} \quad k_1 c_0 J \text{ »k2Ren} \qquad (19)$$

On approaching a steady state:

$$\frac{dJ}{dt} \Rightarrow 0, \quad \text{and thus} \quad k_2 \approx k_1 \left(\frac{c_0 J}{Re^n} \right)_{equilibrium} \qquad (20)$$

Equation (5) could be used to calculate the values of k1 from the measurement of the initial flux decline.

Reynolds' number in the case of mixing was calculated as follows:

$$Re_{mix} = \frac{d^2 n \rho}{\eta} \tag{21}$$

where ρ is the retentate density (kg m-3), n is the rotation rate of the stirrer (s-1), η is the viscosity of the retentate (Pas), and d is the diameter of the stirrer (m).

Ozone treatment in food technologies

Ozone as a strong oxidizing agent is widely used in water treatment and its beneficial properties like sanitizing effect or that excess ozone decomposes to oxygen leaving no chemical residues in foods make it a very attractive "green" food additive. The recent regulatory approval and the increasing acceptance of ozone have made it a new environmentally friendly technology in food processing. It has increasing number of applications in sanitizing, washing and disinfecting equipments, odour removal, fruit, vegetable, meat and seafood storage and processing.

Properties of ozone

Ozone is a triatomic oxygen molecule with the chemical formula O_3. Clear ozone is a blue gas at ordinary temperature when generated from dried air, but colourless, when generated from high-purity oxygen. However at normal production concentrations for most applications, including food processing, the colour is not noticeable. Below −112 °C, ozone is a dark blue liquid. Liquid ozone can be detonated if >20% ozone–oxygen mixtures occur.

The three atoms of oxygen in the ozone molecule are arranged at an obtuse angle, a central oxygen atom is attached to two equidistant oxygen atoms. The structure of ozone is as follows (Fig.1.).

Figure 1. Stucture of ozone

The symbols $\delta^+$and δ^- show, that ozone molecules are short of electrons on the locations where these signs occur. This means that ozone is a dipolar molecule. This causes ozone to have characteristic properties. Ozone is not stable, generally rapidly decomposes to produce atomic oxygen which may oxidize organic and inorganic compounds. Ozone reacts very selectively and is electrophilic.(Rice and Netzer 1982).

Ozone has high oxidizing potential (+2.07V), which is higher than oxygen (+1.23V) or chlorine (1.36V). The mechanism of ozone decomposition in water leads to formation of hydroxyl radicals, which have even higher oxidising potential (2.80V) than ozone.

At room temperature ozone is an unstable gas, it readily degrades; however it has a longer half-life in gaseous phase than in aqueous phase. The components of water determine the half-life of aqueous ozone: impurities cause more rapid decomposition of ozone.Ozone solubility in wateris 13 times higher than that of oxygen at 0-30°C and it is more soluble in colder water; at 0°C the solubility is 0,64 g/L water, while in 60°C ozone is insoluble in water. Ozone decomposition is faster in higher water temperature. (Rice, 1986)

Ozone is a toxic gas, toxicity is dependent on concentration and length of exposure. At lower level exposure (0.1-1.0 ppm) the symptoms may be headaches, eye and respiratory irritation. At higher exposure level (1-100 ppm) it may cause asthma-like symptoms or tiredness. (Pascual et al, 2007.)

To prevent the above-mentioned health risks, a maximum amount of ozone has been established for areas where one uses ozone. This is the so-called Maximum Admitted Concentration, or MAC-value. This value describes the maximum concentration of a substance that a human can be exposed to for a given period of time. For a normal working week of five days, eight hours per day, ozone has a MAC-value of 0,06 ppm (parts per million, or mg/L). For 15 minutes, the MAC-value is 0,3 ppm. (Metzger, 2009) .

Chemical reactions of ozone

Since ozone is an unstable gas, it has to be generated at the point of use (Rice and Netzer, 1982). The decomposition of ozone in water cannot be described in an easy way, because many chemical reaction can occur simultaneously. Ozone can react

(1) indirectly, by decaying via a chain-reaction mechanism of hydroxyl radicals, or

(2) directly, via selective reactions with substrates in the water or foodstaff materials. (Masschelein, 1992)

The efficiency of ozonation caused by the simultaneous presence of direct and indirect reactions, and depends on the chemical composition of the matrix, chemical nature of dissolved substrate and pH.

In the presence of organic compounds ozone reacts with the C-H bonds of alkanes, alkenes or amines (Adachi, 2001). It decomposes the aromatic rings, and may oxidise the primary amine nitrogen atom. Ozonation of lipids form peroxides. Ozone also attacks the S-H bonds of sulphhydryl groups. Proteins are generally resistant against ozone, the S-cotaining and aromatic amino-acids are easily oxidisable (Cataldo, 2003); while the main polyamide chain of the protein is not affected by ozone.

Generation of ozone

There are several ways to produce ozone; commercially it is generated by passing an oxygen containing gas through either a high energy electrical field or a source of ultraviolet (UV) radiation. There are several other methods like electrolysis, radiochemical processes, etc., but for food processing technologies the corona discharge caused by high electrical field and the photochemical (UV) methods are economical.

The ozone generators operating by corona discharge (Fig. 2) work by passinga dried, oil- and dust-free oxygen containing gas through a high-energy electrical fieldbetween two electrodes: one of them is the ground electrode; the other is the current bearing dielectric medium. As oxygen molecules pass through the electric field between electrodes, they are decompodes forming active oxygen atoms. These oxygen radicals can combine with oxygen molecules to produce molecular ozone:

$O_2 + e^- \rightarrow 2O\cdot$

$2O\cdot + 2O_2 \rightarrow 2\ O_3$

The quality of feed gas to an ozone generator can be a critical factor, particularly if ozone is produced by CD or plasma techniques. Ambient air contains nitrogen, water vapour (moisture) and in many instances hydrocarbons. Ozone can react rapidly with such impurities, causing fouling of dielectric surfaces, increased downtime and the need for increased maintenance of equipment. To avoid this, air that has been through some treatment may also contain traces of oils picked up from improperly maintained gas cleaning equipment.

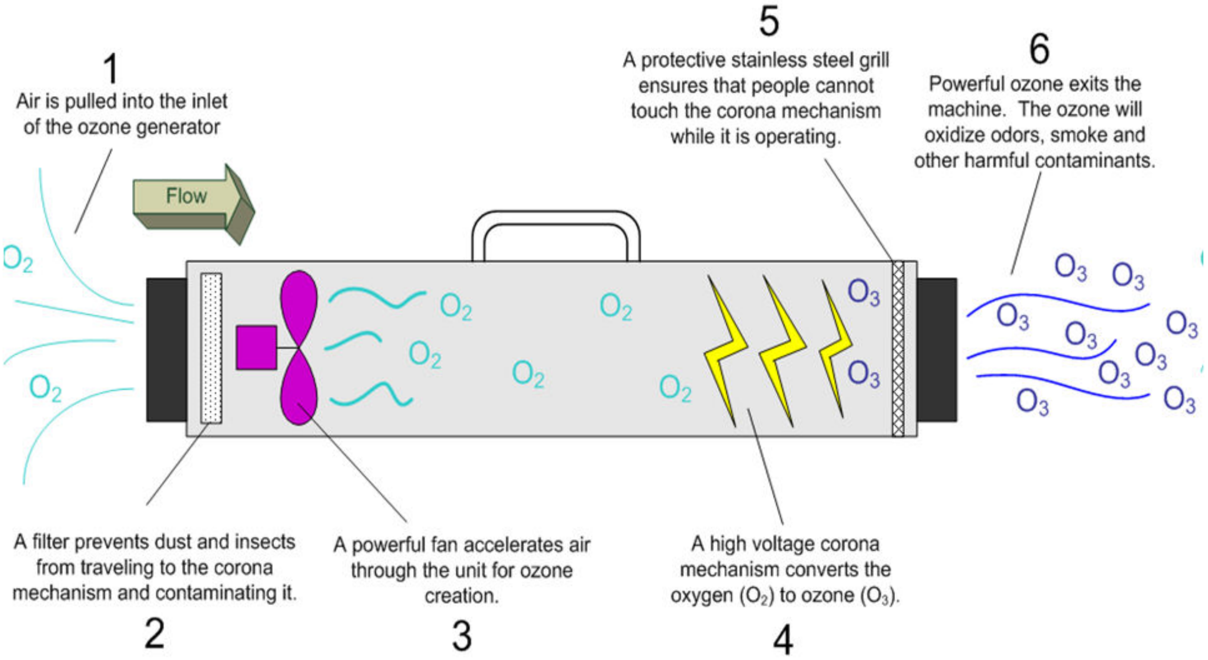


Figure 2. Operating of the ozone generator (Source of the picture: http://www.ozonesolutions.com/info/how-ozone-generators-work)

Ultraviolet (UV) ozone generation bases on similar reactions, ultraviolet light below 200 nm wavelength decomposes molecular oxygen to oxygen atoms which then form ozone by reacting molecular oxygen.

Generally low-pressure mercury UV lamps are used for ozone generation. The mercury lapms have two resonance lines (radiate mainly at these wavelengths) of 254 and 185 nm. The photons with 185 nm wavelength have enough energy to break O-O double bond thus it is responsible for ozone production. The commercial so-called germicidal lamps (used for inactivation of microbial contaminants) generally made from quartz, but their material can not transmit the 185 nm UV light, only radiating at 254 nm, thus can not be used for ozone generation. Ozone producing UV lamps radiate not only at 254 but 185 nm too, are made from special quality of quartz (e.g. Suprasil).

In these ozone generators feed gas (usually ambient air) passes through the high energy UV_{185nm} irradiance field surrounding the lamp. Oxygen atoms are forming during photodissociation of O_2, finally resulting O_3 molecules by reacting with molecular oxygen.

(Tapp and Rice, 2012)

Biocidal behaviour of ozone

Ozone is a strong biocidal agent; there are several pathogens what can be inactivated by ozone, like all known bacteria including *Salmonella enteritidis, E-coli, Listeria monocytogenes, Shigella dysenteriae, Micrococcus aureus or Clostriduim botulinum;* molds, like *Botrytis, Rhizopus, Penicillium* or *Aspergillus*, and all known protozoas, parasites and amoeba.

Inactivation by ozone is a complex process in which ozone react with cell-membrane and cell-wall constituents (like unsaturated fats), or cell-content (like enzymes and nucleic acids). The major mechanisms of ozone destruction of microorganisms:

1. ozone oxidises polyunsaturated fatty acids to acid peroxides in cell membranes, then
2. ozone oxidises sulfhydyl groups and amino acids of peptides, proteins or enzymes. (Victorin, 1992)

Microorganisms are inactivated by disruption of the cell-envelop and disintegration leads to cell lysis. (Fig.3.)

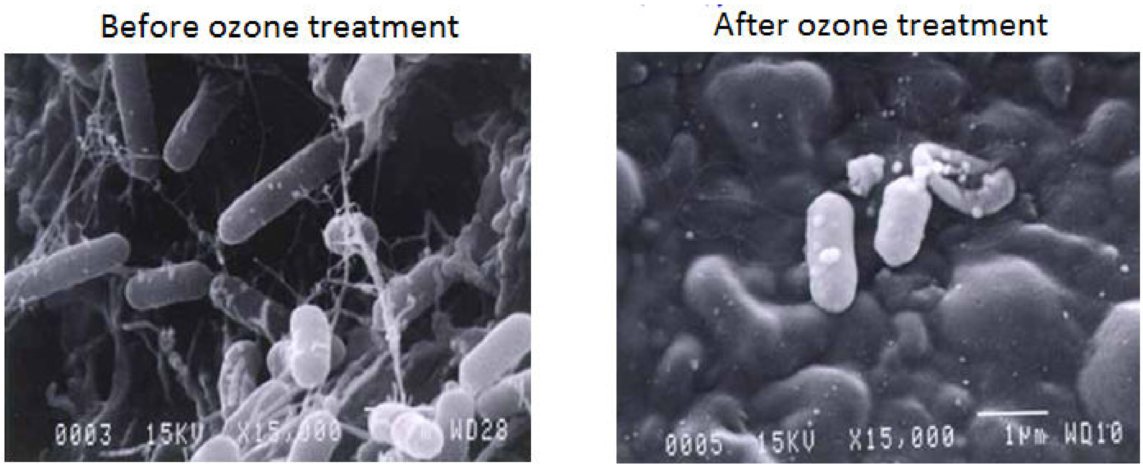


Figure 3. Cell disruption after ozonation (Air Liquid America Corp. Chicago Research Centre, James T.C. Yuan, PhD Thesis, 2000)

Spores also can be inactivatedby ozone, in this case ozone degrade spore coat. Both molecular ozone and free radicals play a part in the inactivation mechanism, but the exact mechanism may vary between microorganisms.

Ozone is effective against enveloped and non-enveloped viruses in water. Enveloped viruses are more susceptible to ozone inactivation than those lacking lipid envelopes.

In case of biofilms ozone also may be effective in destroying the organisms and capable of removing exopolysaccharides in the biofilm matrices.

While ozone has a wide antimicrobial spectrum, its effectiveness depends on the nature of the target microorganism (Khadre et al, 2001), e.g. in case of bacteria it can be assumed that Gram-negative bacteria are more sensitive to ozonation than Gram-positive bacteria, and ozone is more effective against vegetative cells than against bacterial and fungal spores.

The effectiveness of ozone against foodborn microorganisms depends on several environmental factors: temperature, humidity (due to the reaction of ozone with water), pH, and other components like surfactants, sugars, fats and other organic compounds (Pascuale et al, 2007). The biocidal effect also depends on the amount of applied ozone (the applied concentration and the contact time also may affect on the effectivity and the non-desirable changes of food quality.This means that since ozone is generally safe and effective method for processing e.g. fruits and vegetables, the treatment conditions must be developed and optimized for each product prior to adaptation of this method.

Ozone generally recognised as safe

Ozonation first used for water treatment in the early 1900s, soon after it was commenced in food processing. In the United States ozone in the gaseous form was approved for the storage of meat by the USDA from 1957, then in 1975 FDA recognized ozone treatment to be a Good Manufacturing Practice (GMP) for the bottled water industry. The minimum ozone treatment for GMP is “0.1 part per million (0.1 mg/l) of ozone in water solution in an enclosed systems for at least 5 minutes.” (Code 21 of Federal Regulations, Section 129.80 d.4 Federal Register 11566, 12 March 1975). The use of ozone in food industry has been widespread since the FDA gave ozone GRAS (Generally Recognized As Safe) approval in November 1982 (21 CFR 184.1563), then a panel of experts from food science, ozone technology, and other related fields has declared Generally Recognized as Safe (GRAS) status for ozone use in food processing in 1997. The use of ozone as a surface sanitizer and for direct contact with food has also grown more recently. In 2001, ozone was give GRAS approval for direct contact with all meat and poultry products (FSIS Directive 7120.1).

Figure 4.**Generally recognised as safe sing in US**

In Europe there is no specific legislation applied for ozone; the general rules can be applied are the Labeling directive (2000/13), which concerns to indication on the label of the specific treatment undergone by a product, and the Novel Food regulation (258/97) which concerns the premarket authorization for foods which have undergone a novel treatment process. The use of ozone is now permitted to separate unstable elements (like iron, manganese and sulfur components) from natural mineral waters. The European Council Direcitives (89/107/EEC) on food additives lists the substances which legally may be added to food but ozone currently is not on this list. The European Commission will develop more detailed regulations about the use of processing aids; currently legislation is not harmonized at the EU level. (Tiwari and Rice, 2012)

Use of ozone in food processing

There are several application area of ozone in food processing. It may disinfect water before it is bottled, because of its biocidal behaviour. It kills bacteria, yeast and protozoa on food-contact surfaces such as fresh fruits, vegetables, grains, seeds, nuts, legumes, and all animal meats. It kills yeast and mold spores that float in the air in food processing plants. Ozone in its gaseous phase is a proven deodorizer for a variety of odorous materials. Ozone is used as a food preservation agent by destroying the aging compounds (like ethylene), oxidize and degrade many organic pollutants including pesticides, herbicides and other persistent environmental chemicals.

Application of ozone in water treatment

Water plays a fundamental role in many of the common processing methods, and unit operations employed in the food industry. Ozone's properties provides multiple benefits in water treatment. It oxidises organic pollutants, decrease the chemical oxygen demand or TOC, oxidise the ferrous and manganese compounds and hydrogen sulfide. It may eliminate the colour, taste and odour from water. Ozone can be added at several points throughout the treatment system, such as during pre-oxidation, intermediate oxidation or final disinfection. Generally it is used for pre-oxidation, before a sand filter or an active carbon filter (GAC). After ozonation these filters can remove the remaining organic matter, but due to high instability of ozone the final disinfection (e.g. with chlorine) is necessary.(Rice and Netzer, 1982)

All water sources contain natural organic matter (NOM). Concentrations usually measured as dissolved organic carbon, DOC or expressed in chemical oxygen demand (COD). Presence of these compounds in drinking water sources cause non-desirable odour and taste in water, orthe organic disinfection byproduct formation, support of bacterial regrowth in the distribution system, etc. Ozone may completely mineraliseNOM. If organic matter is partly oxidized it becomes more easily biodegradable, resulting higher BOD (Biochemical Oxygen Demand) of water. As a result, ozone improves the removal process of NOM by a subsequent filter, when it is used as a pre-oxidant. (Rice and Netzer, 1982)

Non-desirable odour and taste in drinking water have several sources: these compounds can be present in raw water, but they can also be formed during water treatment. These compounds may be a result of the activity of living organisms present in the water. Inorganic compounds such as iron, copper and zinc can also generate some taste. Another possibility is that the chemical oxidation (chlorine treatment) leads to an unpleasant tastes and odours. These compounds are often very resistant, and can be eliminated only by very intensive processes: ozone can oxidize 20–90% of these compounds depending on the type of compound. Ozone is more effective for the oxidation of unsaturated compounds, because ozone is attracted to break organic double bonds. As more of these double bonds are eliminated, the colour of organic matter in water disappears.

Ozone is a more effective disinfectant than chlorine, chloramines, and even chlorine dioxide. Several studies proved that ozone, unlike chlorine products, can deactivate resistant micro-organisms, including even *Cryptosporidium parvam* and *Giardia lambia* with some limitations. However, as ozone rapidly decomposes in water, its life-span in aqueous solutions is very short (less than one hour). Therefore ozone is less suitable for residual disinfection and can be used only in particular cases (mainly in short distribution systems), thus chlorine or chlorine dioxide must be used as a final disinfectant. (Rice and Netzer, 1982)

Sanitisation with ozone in the food industry

Effective cleaning and sanitisation methods are required to achieve an appropriate level of hygiene in food industry. **Cleaning** is defined as the removal of soil (food residues) from food contact surfaces. It means that the surfaces are visually clean, don't have bad odours, or greasy touch. **Sanitisation** means that there are no pathogenic microorganisms or undesirable number of spoilage microorganisms on the surface. (Cullen and Norten, 2012)

On food contact surfaces there are food soil (food residues from the process), residues from water minerals, cleaning compounds or microbiologically active residues, like biofilms. Such films are complex aggregations, which may enhance the growth of microorganisms and are very difficult to remove – mechanical cleaning or chemical detergents must be used before disinfection. After cleaning the surface, it has to be sanitised. Sanitising agents are: chlorine and its derivatives, iodine derivatives, ozone, hydrogen peroxide or quaternary amines. Sometimes in food industry thermal sanitation methods or irradiation also are used. Thermal sanitation is very effective method, bat the costs are high due to the energy demand of steam and hot water production. Chemical sanitation methods (mainly chlorine and derivatives) are more economical, very effective due to their broad spectrum germicidal effect, but the chlorine byproducts may be corrosive to many metal surfaces, and they can cause health and safety problems, like skin irritation, moreover the chlorinated organic derivatives may be potentially carcinogenic (e.g. trihalomethanes, THMs).

The bactericidal properties of ozone, and the fact that it decomposes to oxygen take it applicable for alternative sanitisation age instead of chlorine. In water ozone decomposes to free radicals which can attack organic compounds, and oxidise them forming finally carbon dioxide, water and oxygen, thus ozone can readily inactivates microorganisms in aqueous solutions. In sanitisation procedures in the food industry ozone is generally used in an aqueous solution. Since the organic components deplete the ozone the ozone concentration must be followed during the cleaning and sanitisation procedures by an appropriate detection technology. The efficacy of the ozone sanitisation procedure depends on temperature, pH, and quantity of organic matter. It was found (Lagrange et al, 2004) that ozone containing water was not effective in disinfecting food contact surfaces in the presence of protein, thus efficient cleaning methods must be applied before ozone sanitising.

Beside its good disinfection properties ozone has several advantages using in industrial cleaning procedures: it does not leave chemical residues, and since it must be generated on demand, it requires no storage or handling considerations. However the main benefits of ozonation emerge using as part of a clan-in-place (CIP) system. CIP is a closed system where recirculating cleaning solution is applied that cleans, rinses and sanitises equipment. The CIP system is usually automatically controlled and the cleaning sequences are given the optimum timing for efficient cleaning of all parts of the plants. Ozone-containing water can be used in CIP systems by directly injecting it into a fluid distribution network.

The advantages of using ozone a CIP systems is that widespread using of chemicals (chlorine or other sanitizers) can be eliminated, thus reduced quantity of chemicals discharged into sewer systems, and reduced amounts of water necessary to rinse out residual chemicals from the machines. It saves cost and labor in handling/transporting chemicals. CIP rinse/cleaning cycles can be combined using ozone; saving water and time. This may allow for more processing time due to shorter CIP cycle time. Ozone sanitation may replace hot water cycles lowering energy costs. An other benefit of ozone is that no residual or by-products production during disinfection thus it does not require a final rinse to remove any residual disinfectant.

Ozone has been used extensively in the beverage and newly in dairy industry for disinfection of the product, bottles, and fillers, or it was found to be effective in CIP systems of wineries (Guillien et al, 2010) and breweries (Porter, 2002).

Ozone storage

There are several applications of ozone in food storage; it can be appled for extending shelf-life of fruits, vegetables, meat products, or preservation of fish and seafood. Ozone can be used as gas, aqueous solution or in frozen ice.

Ozone gas is used in coolers or other cold storage facilities In these cases ozone containing gas is distributed throughout a pipe system (Fig. 5). Ozone generator (1) creates the necessary ozone for storage and maintains the ozone level. An ozone sensor (2) monitors and controls the ozone levels in the storage facility. Fans (3) pass ozone containing gas throughout PVC pipes (4) dispersing ozone in the container or building (5).

Low level (< 0.3 ppm) ozone concentration may inhibit microbiological growth in the air and it can be used e.g. in meat coolers to extend shelf-life of the products. Different products require different ozone concentrations to achieve effective preservation without decreased sensorial quality of products. Low level ozone gas also can be used in containers to prolong shelf life upon delivery, while high levels can be used for disinfectionwhen room is empty. In latter cases surface sanitation can be maintained by eliminating mould growth from storage area or by inhibiting growth of pathogens on surfaces.

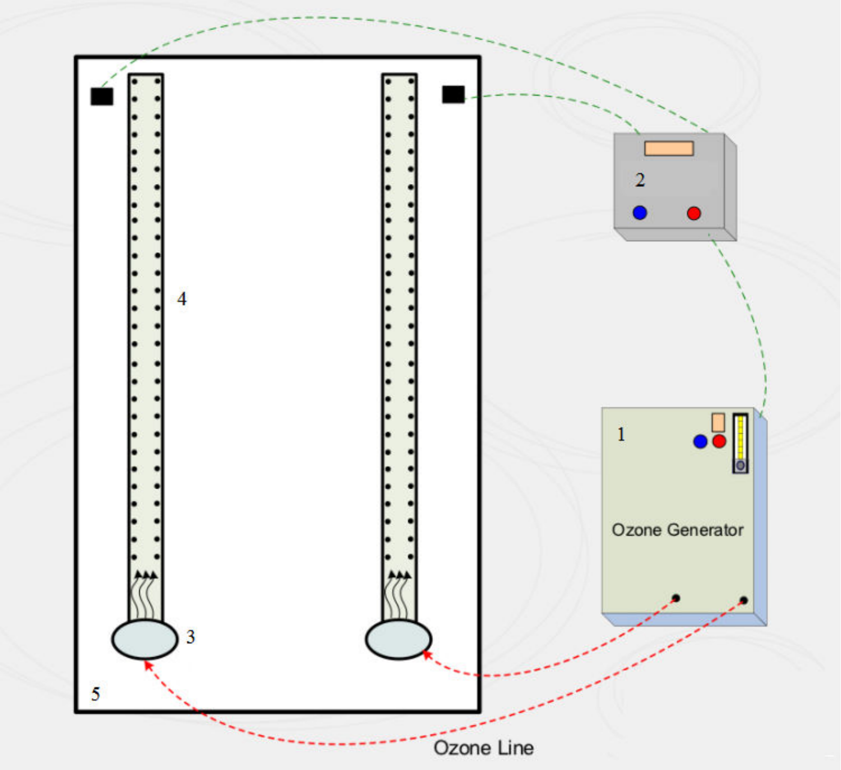


Figure 5. System design for food storage(www.ozonesolutions.com)

By application of ozone in gas phase in storage containers or rooms an odour-free area can be maintained and parallel keep odours from cross-contaminating between products.

Food storage facilities are commonly higher humidity areas. Ozone rapidly decomposes in high humidity resulting increasing oxidising efficiency; but it also means that ozone must be rapidly refilled and distributed throughout the area.

Ozone-sterilised ice can be used to pack fresh fish and seafood to prolong freshness.

Ozone also can be used by dissolving in water to wash food surfaces, both fruits and vegetables, and meat and poultry products to remove bacteria and extend shelf life of refrigerated products.

Human safety also must be ensured, ozone levels must be below safe levels when workers are in the area. Humidity can be used for quick destroying of ozone, allowing employees to return to the previously ozonated area.

Ozone applications in fruit and vegetable processing

Fruits and vegetables will carry bacteria and mold directly out of the field, which reduces shelf life and can cause serious health issues. While nearly all food processing facilities rinse produce with clean water, rinsing alone does not adequately sanitize against mold and bacteria.Typically the minimal oxidant present in the water rinse (usually chlorine) is quickly consumed by the bacteria and mold leaving significant contamination behind to spread to other produce in the processing line. The resulting spoilage quickly leads to lower profits.

The ozonated product has a longer shelf life and less spoilage occurs during transit and on the customer's shelf.Ozone treatment within the fruit and vegetable processing industry has been carried out for surface decontamination of whole fruits and vegetables by either gaseous treatment or washing with aqueous ozone. Aqueous ozone has been applied to fresh-cut vegetables for sanitation purposes, reducing microbial contamination. (Beltrán, 2005). Increased shelf life and lower weight loss was observed in case of ozone treated apples and oranges (Achen and Yousef 2001), and these results had been attributed to the oxidation of ethylene. (Many fruits and vegetables release ethylene, this gas accelerates the ripening process. Ozone rapidly oxidises ethylene.) Ozone containing water was found to reduce bacterial content of shredded lettuce, blackberries, grapes, black pepper, broccoli, carrots and tomatoes. Microbial studies typically show a 2 log reduction of total counts, and significant reduction in spoilage and potentially pathogenic species in fruits and vegetables.

Fungal deterioration of blackberries and grapes was decreased by ozonation of the fruits (Beuchat, 1992)

Washing of fruits and vegetables was also reported to degrade pesticide residues (Wu et al, 2007). It was found that rinsing at dissolved ozone of 1.4 mg/L for 15 min effectively removes 27-34% of residual pesticide from vegetables; moreover, higher degradation of pesticides can be obtained with an increased concentration of ozone.

Storage of fruits and vegetables in ozone-rich atmospheres was found to reduce or eliminate odour, and control microbial and fungal spoilage of apples, cherries, carrots, kiwi, onions, peach, plum, potatoes, grapes, tomatoes, blackberries and strawberries. Ozone can be used as a relatively brief pre-storage treatment in air or water, or it can be added continuously to the storage room or container.

The effect of ozone during storage is strongly depends on the type of microorganism, commodities and storage conditions (temperature, humidity). High ozone concentrations during storage may cause surface discolouration, e.g. in case of carrots.

Ozone in meat processing

Meat related illnesses caused by *E. coli, Salmonella, Campylobacter, Listeria* or other pathogens are a serious problem in meat processing technologies. Number of industries applies multiple intervention technologies from live animals to finished product to prevent microbial incidences. To avoid the presence of pathogens several sanitation methods had been evaluated including carcass washing, lactic or acetic acid application, other organic acids such as gluconic acid, hot water or steam, or ozone.

The antimicrobial treatments not only should be effective against pathogens, but the meat quality characteristics also must be preserved: safety must be improved without deterioration to colour, appearance, aroma, taste and textural properties of the meat. The generally used antimicrobials such as organic acids provide against microorganisms by decreasing pH. Some of them, like lactic acid naturally occur in beef, and the others also considered safe for consumption at applied levels. On the other hand the reduced pH have negative impacts on meat colour or lipid oxidation; the low H caused by organic acids can modify the molecular structure of myoglobine (pigment in meat related to the red colour) causing a darking of colour.

Other antimicrobials, such as trisodium phosphate or sodium metasilicate shift pH t neutrality, thus thy have little impact on colour or lipid oxidation. On the other hand, trace amounts or residues of antimicrobials may remain in the meat.

Ozone can be used in meat processing due to its antimicrobial properties. Since it is a gas, it can be used in gaseous or aqueous phases; residues remaining after meat product treatment are negligible

Ozone successfully can be used for surface decontamination of red meat; ozone significantly decreases microbial count. Ozone also has been used as a pre-treatment before cooking(Novak and Yuan, 2004) resulting decreasing number of pathogens (e.g. *E. coli* and *Listerium monocytogenes*) on beef.

Ozone also has been evaluated for poultry surface decontamination. Ozone treatment of poultry generally is most effective for reducing gram-negative rods; it is effective against *Salmonella* and ozone treatment may enhance the shelf life by 1-2 days. (Pohlmann, 2009)

Ozone also was reported to be effective against contamination of natural casings, which are generally contaminated with several microorganisms. (Steffen and Rice, 2010).

Although ozone is an effective agent against microorganisms, due to its high oxidation potential retaining meat quality is challenging. Oxidation in meat systems can influence meat colour and lipid stability characteristics. Ozone may cause brownish colour due to pigment oxidation (red colouring oxymyoglobine is converted to brown-colouring metmyoglobine) and this may affect to consumer acceptance negatively.

Meats consist of lipid or fatty acid profile with saturated and unsaturated compounds. The double bond-containing unsaturated fatty acids are susceptible to oxidation, and so an oxidising environment may induce lipid oxidation and formation of oxidation by-products. The lipid oxidation and by-product formation may cause undesirable aroma and flavour changesin meat. This means that ozone must be applied very carefully to avoid sensorial deterioration.

Ozone in grain processing

Due to its properties, ozone has been used to control pest development in stored grains, to disinfect flours and to degrade potentially toxic molecules. It can be applied in the gaseousor aqueous state and has been demonstrated to be at least as efficient a disinfectant as chlorine, and more convenient, because it quickly decomposes into O_2 and hence does not leave residues (Graham 1997).

Storage of grains are very susceptible due to a number of insects (e.g. Tribolium, Sithophilus and moths) cause damage of grains, and could be resistant to the currently used insecticides. Since in the USA or Europe and other countries the amount of permitted pesticides reduce, ozone have become an interesting alternative to applied chemicals for the control of insect development. The gaseous ozone used in fumigation (fr 3-5days at 25-50 ppm) increases the insect mortality up to 100%. The lower doses also are efficient but lead to a lower insect mortality. (Kells et al, 2001).

Ozone conditions are critical for ozone efficiency: apparent air velocity necessary to disperse the ozone in the grain mass; increasing temperature (up to 40°C) results increased insect mortality.

Fungi development in grains depends on field weather conditions, resistance of the plant or storage conditions. After harvest the fungi growth and mycotoxin production can be reduced by drying grains or maintaining moisture content below 14% and a low storage temperature. The fungicidal efficacy of ozone was observed in the case of *Aspergillus parasiticus* (Kells et al, 2001), or *Fusarium* (Kottapally et al, 2005).

Ozone also was found to be effective in decreasing the level of *Bacillus* and *Micrococcus* microorganisms, and a significant decrease of total bacteria can be achieved in both soft and hard wheat type grains.

Ozone considered not only helping to reduce mycotoxin accumulation during grain storage, but its oxidant properties could also be used for degradation of mycotoxins (e.g. aflatoxin B1) (McKenzie et al, 1997).

Since ozone is a powerful oxidant, its potential negative effects on the grain compounds also must be studied before using this technology. Generally it can be state that lower ozone doses (below 50 ppm) has no significant effect on lipid content, or low molecular weight components, but there are observable oxidation effects at higher doses. However, while these changes could alter the protein and lipid qualities of grains, this effects had not been observed in metabolism and physiological status of grains and had no significant effect on development of fed animals.

Another task is to study the effect of ozone on grain germination. Studies in this field showed that the effect of ozone on the germination capability of grains is dose-dependent, above 0.98 g/mg·min ozone dose the germination capability decreased, and it is more pronounced if grain integrity has been damaged due to e.g. *Fusarium* infection.

Aqueous ozone can be used in the grain temper process to inactivate mold and bacteria at the first point of the milling process. Many grains are tempered to increase the moisture content of the grain by adding water to the grain. Since most pathogens are found on the exterior of the grain, and only fewer pathogens are found within the grain, ozone use in the temper process lowers all pathogen levels. Water used in tempering process passes through an ozone injection system to provide aqueous ozone at very high dissolved ozone levels (Fig 6). A minimum of 10 ppm of dissolved ozone is used to ensure residual aqueous ozone can soak completely through the outer part of the grain. Ozone half-life in water is 20 minutes in 20° C water. After 60 minutes ozone level in water may still be above 2.0 ppm. Aqueous ozone at 2.0 ppm is sufficient for antimicrobial intervention. Aqueous ozone at 2.0 ppm will achieve a four (4) log reduction of bacteria in one (1) second of contact time.

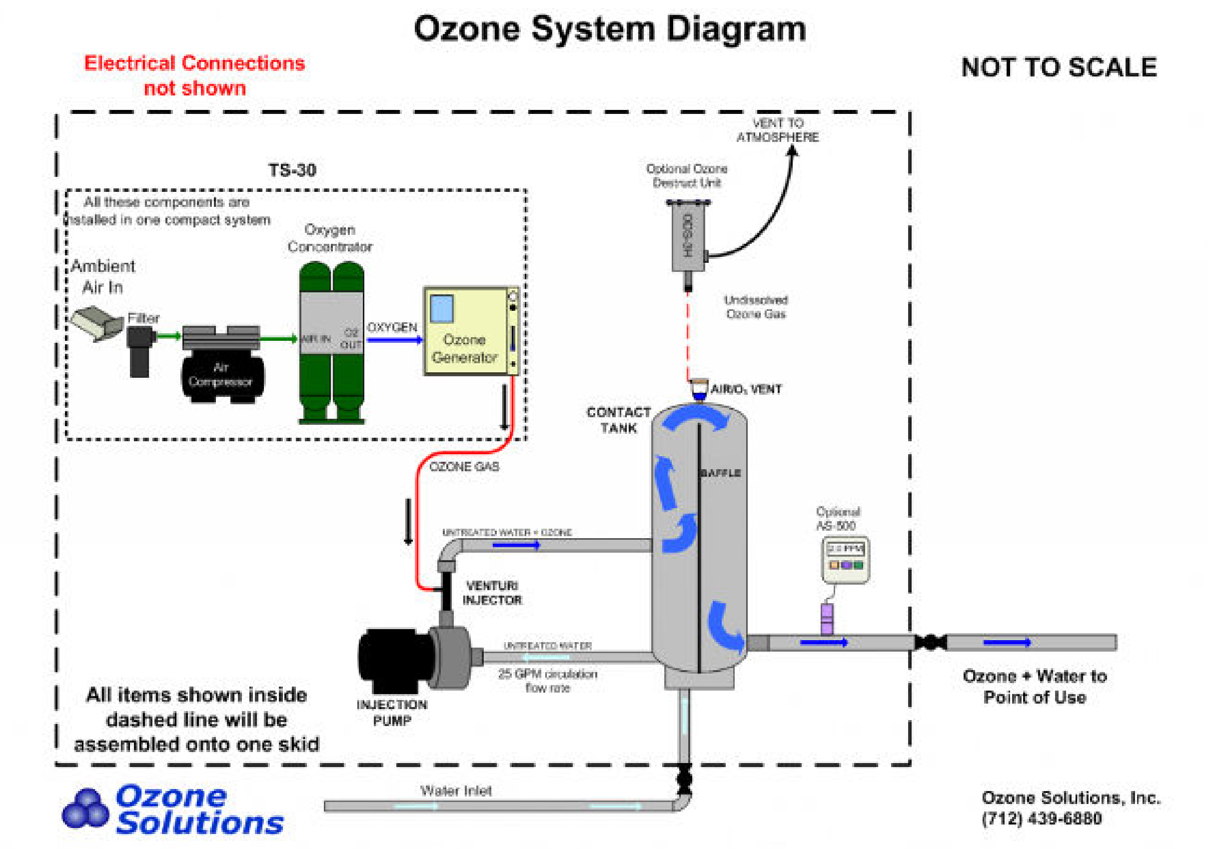


Fig. 6. Ozone system diagram for tempering process

Studies dealed to investigate the effect of ozone tempering of grains on the quality of milled flour have not founded and significant effect on quality of flours (Ibanoglu, 2001, Mendez, 2003), while the mechanical properties of grains changed: enhanced friability of the outer layer was observed, and this explain the reduction of required energy for grain milling. (Mariotti et al, 2006).

In cases when not the grain but the milled flour is treated by ozone (and/or UV light) quite different results can be obtained: the combined treatment resultedin a whiter flour suitable for consumption, while ozone or UV treatment alone cause decreased sensorial quality. Changes in the quality of the dough is observable, similar by as in response to other oxidizing agents used in milling processes. The treatments significantly reduced the microbial count, which also decreased significantly during storage. (László et al, 2008)

Summary

Ozone is a chemical that can provide many benefits in food processing, by itself and in combination with other treatment procedures. Equipment is commercially available to generate, apply, monitor and control ozone in both the aqueous and gaseous phases for a variety of applications within a food processing plant. A panel of food experts concluded that when used under Good Manufacturing Practices, ozone is safe for plant workers to use, and does not impart detrimental effects to foods processed with ozone. The use of ozone as an antimicrobial food additive or ozone-containing water for spraying in food processing plants for a number of washing applications has been conducted under conditions that provide 4–6 log reductions of microorganisms typically found in food processing plants.
Consequently there are several benefits of use of ozone in the food industries:

- it extents the shelf life of food products.
- Is much safer for employees than any conventional chemicals. It is chemical-free, because it decomposes to oxygen.
- It may eliminate the use of hot water and conventional sanitizer.
- Is generated on-site, thus eliminating the transporting, storing and handling of otherwise hazardous material and finally permits recycling of wastewater.

However there are some limitations the use of ozone is food industry: Taste and sensory properties may be change – it must be considered prior to any potential food application, and due to its oxidising effect the colour of foods may be change. The potential hazards of ozone based technologies also must be understood and appropriate precautions be designed into the processes that use them.

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