MEMBRANE SYSTEMS AND WATER STRUCTURES

Jan Koppe*, Marietta Hesse

MOL Katalysatortechnik GmbH, Leunastraße 6, DE-06258 Schkopau, Germany

Abstract

Water is a vital resource for both human needs and the functioning of our ecosystem. Fresh water availability and water use have been a growing problem for centuries. This paper gives a brief overview on the current knowledge of water stress and describes possible solutions. In addition to a differentiated consideration of the various types of water stress, the special importance of water purification by membrane technology and the associated processes is discussed in detail. The economic provision of high-quality water is the focus of these considerations.

Keywords: bulk water, catalytically accelerated, catalyst, membrane filtration, catalytic water treatment, membranes, molecular water, mollik, RO, water stress, water structures

Received: August, 2019; Revised final: September, 2019; Accepted: October, 2019; Published in final edited form: October, 2019

1. Water stress – What is that?

Water stress is a topic that already filled scientific books for over 2000 years (Lee, 1951; Kenneth, 1997; Spitz et al., 2012; Reig et al., 2019). By looking deeper on this topic, three types of water stress can be differentiated (Fig. 1).

1.1. Quantitative water stress

Water covers more than 70 percent of the earth's surface - but less than one percent of the total mass is directly available for human consumption (Chauhan et al., 2015). Thus, high quality tap water is a precious commodity (Köbel et al., 2018).

According to BATES (Bates et al., 2008), quantitative water stress is present when water abstraction exceeds existing freshwater resources. That means, precipitation risk, evaporation and population growth act as direct factors on the water stress. Climate-induced dry periods have always led to an increase in the salinity and turbidity of surface water resources. This is associated with downstream ecological and economic chain reactions (Bates et al., 2008; Menzel et al., 2007).

Fig. 1. Types of water stress

1.2. Structural water stress

Any energy input on the water, which is above the osmotic pressure, could end in structural changes within water structures. Drinking water - freshly drawn from a well - will have a different taste...
than water that has been pumped longer distances through pipelines. When creating long drinks, there are differences in taste between "shaking" and "stirring". In the field of pump technology, high energy input is accompanied by the formation of cavitation bubbles. Such processes lead to corrosion phenomena and to a reduction in the lifetime of equipment. Dissolving substances also cause structural changes by creating hydration shells. Structural changes in the water are temporary in nature and are mitigated by kinetic equilibrium reactions.

1.3. Qualitative water stress

For water stress of a qualitative nature, looking back at history, it has long been recognized that marginal and less affluent areas are less able to adapt to the changes associated with qualitative water stress. Without efficient technologies combined with appropriate policy instruments, climatic change leads to greater inequality (Smits et al., 2001). The focus here is on the economic provision of high-quality water together with an optimization of usage concepts. Today, as in the past, thoughtless treatment of high-quality water in water-scarce areas is further aggravating the situation (Küffner, 2018).

2. Water stress – Which solutions?

The question therefore arises: How can you remove salts / undesirable substances from the water at a reasonable cost to obtain enough water with a desired quality? For this purpose, filter systems and biomembranes have developed in the course of the evolution – without life, as we know it, would not be possible. Springs and wells are examples of natural filtration systems. If such drinking water resources are properly maintained, then these can be used for many years to provide high-quality water. In the Middle Ages, hints were given on how far manure piles should be moved from the source to ensure a certain quality standard of the drinking water (Hoppenberg, 2017).

However frequent occurrence of temporary peaks in groundwater usage (Navarro and Carbonell, 2007; Ortuño et al., 2010), as well as less-optimized fertilization (Ehlers et al., 2018), has a negative impact on natural drinking water resources. As a result, even in Europe, today some former groundwater reservoirs only provide brackish water. To overcome water stress of a qualitative nature, sailors had already in the days of ARISTOTLE a process for drinking water production via reverse osmosis (Lee, 1951). For this purpose, a jar of terracotta was submerged in the deep-sea water. Within a few hours, the jar was filled with purified sweet water. In addition, even at that time the more energy-consuming way of getting sweet water by evaporation was known.

To reduce structural water stress, there are suitable biocatalysts available in nature. In the field of technology, a combination of pump technology and the use of suitable heterogeneous catalysts has been proven successful. The first documented applications are in the area of water supply in the Roman Empire. Here, the water was lifted instead of pumped. Another point is that volcanic ash was used at the viaduct construction as a catalytically active binder within the concrete. Today we know that this procedure has minimized the risk of deposits in distribution systems. This knowledge formed the basis for explaining the effects of technical mineral-metal catalysts for water treatment.

3. Production of high-quality water – How does it work?

The economic extraction of high-quality water by membrane filtration takes place via: pressure, temperature, electric field.

3.1. Importance of membrane technology

As natural water resources are unequally distributed, increasing qualitative water stress leads to the constant development of desalination technologies by resourceful engineers (Wünsch, 2019). More than 300 million people around the world are already getting their daily needs from desalinated water. For this purpose, currently 21,000 membrane plants in 120 countries are permanently in use (IDA Desalination Yearbook, 2017).

By the present membrane plants - can be provided in an economical manner - with a significantly reduced compared to the classic evaporation energy consumption (Lazarides and Katsanidis, 2003). Currently membrane installations for drinking water production are more economical when compared to classic evaporation processes due to the high energy consumption of the latter one. On the other hand, in membrane technology, pressures of up to 80 bar affect water structures and lead to the formation of deposits, which highly increase the operation and maintenance cost. As more chemicals added on the membranes facility as more chemicals will be found later in the concentrate discharged to the sea. Therefore, these desalination plants create an environmental impact on marine and plant life.

The use of suitable heterogeneous catalysts can suppress negative effects on water structures and at the same time extend cleaning intervals of the membranes (Kochan et al., 2019). As a result, the emitted chemical cargo from the concentrate is reduced in comparison to conventional way of operation. Thereby undesirable side effects on animal and plant life are minimized. To follow these views, let's take a closer look at the interaction of salts and water below.

3.2. Mode of action of a membrane system

What makes the processes of membrane technology so interesting? When looking more closely at membrane processes in aqueous systems, the following points are key:

• The operations are subject to isothermal conditions.
Membrane systems and water structures

Only pressure changes are found
• Osmotic processes take place in aqueous systems
• On the other hand, they are subject to the laws of the gas phase.
• Osmosis is related to ions consisting of solids.
• At the molecular level, these ions are far removed from the gas phase.
• The osmosis is independent of the type of hydrated ions.

It depends only on the number of hydrated ions.

In order to understand these interesting aspects in more detail, the processes in the water are considered in more detail below.

3.3. Salts and water

What happens when salts are dissolved? The formation of hydration shells removes molecular water from the aqueous system and the atmosphere during salt dissolution - in conjunction with a decrease in entire volume (Koppe, 2017). At the same time, there is a "stress" on the aqueous system for providing molecular water. With reference to ARISTOTLE, it follows that aqueous systems containing a larger proportion of molecular water are under higher pressure and thus automatically flow to the low-pressure region (lower proportion of molecular water). The water of hydration proportion is thus directly proportional to the number of dissolved ions. Since water of hydration is cloaking dissolved ions, the specific nature of the ions plays virtually no role.

For osmosis, this means that membranes are impermeable to larger liquid agglomerates. Only gaseous molecular water and low molecular weight gases such as carbon dioxide and chloramines can pass through the texture of membranes.

3.4. Salts, water, membranes – development of the theoretical model behind

The writings of ARISTOTLE were intensively studied in the Renaissance - good 1800 years later.

During this time most probably also accessible to Leonardo da Vinci. However, the writings of LEONARDO DA VINCI were initially lost before they emerged towards the end of the twentieth century, so that even a wider public learned about it (Schneider, 2011).

In between, the basic views on membranes processes were not accessible and thus had to be re-worked within the last 250 years. More than 2000 years after the documentation of the osmotic effect of drinking water from seawater, JEAN-ANTOINNE NOLLET described in 1748 membrane experiments in the field of experimental physics at the Collège in Paris. Only for 60 years are membrane systems available on the market, which can provide high-quality water in the technically relevant area.

At the end of the nineteenth century VAN'T HOFF succeeded in providing a theoretical model, which allowed for a calculation of the phenomenon of osmosis at the same time. The notable idea was the transfer of laws of gases to aqueous systems. For his pioneering work on the analogy of gas pressure and osmotic pressure, he was awarded with the first Nobel Prize in Chemistry in 1901. With VAN'T HOFF's model at the same time further effects, such as the boiling point increase, were mathematically developed.

3.5. Ion mobility and water structures

How does the water move through filters and membranes? Within the water, in the water clusters, which are characterized by hydrogen bonds, proton motions occur at a speed of more than 10,000 km/h. On the other hand, the slow ion migration rates in the water are a few centimetres per hour. At first glance, there is no direct correlation between the two processes.

The water structures are in a continuous thermodynamic controlled cycle. This “cycle of water structures” is determined by pressure and temperature (Samoilov, 1946; Vedamthu et al., 1994; Koppe, 2018). The energetic conditions are presented in Table 1.

![Fig. 2. Cycle of water structures](image-url)
In the bulk water, there is an ice-like structure with the well-known "hydrogen bonds". With the addition of melting and dissociation energy, the asymmetric vibrations in the hydrogen bonds increase and dissociation occurs. As a result, there are an acidic proton and a basic hydroxide anion. In the sense of an acid-base reaction, the neutral molecular water is formed. This must be thought of as a single, gaseous molecule.

If ions are present, they interact with the molecular water, resulting in LEWIS acidic and LEWIS basic water molecules. These also react again in the sense of an acid-base reaction and to form hydrogen bonds with the bulk water. Part of the molecular water leaves the system in the form of water vapor depending on the external vapor pressure. For aqueous systems, the following applies (Table 2).

**Table 1. Energetic conditions in the water**

<table>
<thead>
<tr>
<th>Energy of hydrogen bond:</th>
<th>~ 5 kcal/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Energy of O-H bond:</td>
<td>~ 100 kcal/mol</td>
</tr>
<tr>
<td>Energy of $\text{I}^{\text{cn}}$-H$_2$O bond:</td>
<td>~ 0.005 kcal/mol</td>
</tr>
</tbody>
</table>

The ion mobility should be thought of as the result of the hydration shell fluctuation, as shown in Table 3.

**Table 2. Use of supplied energy in aqueous systems**

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Supplied energy is used for</th>
</tr>
</thead>
<tbody>
<tr>
<td>below 0°C</td>
<td>Proton vibration within the hydrogen bond</td>
</tr>
<tr>
<td>0 to 100 °C</td>
<td>Dissociation of bulk water / rotational vibration H$<em>2$O$</em>\text{molecular}$ / Proton vibration within the hydrogen bond / partial evaporation</td>
</tr>
</tbody>
</table>

The ion mobility should be thought of as the result of the hydration shell fluctuation, as shown in Table 3.

**Table 3. Ion mobility – Theoretical concept**

<table>
<thead>
<tr>
<th>Step</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1$^\text{st}$</td>
<td>Provision of H$<em>2$O$</em>\text{molecular}$ from the hydrate shell by LEWIS acid-base reaction</td>
</tr>
<tr>
<td>2$^\text{nd}$</td>
<td>Formation of hydrogen bonds due to neutralization</td>
</tr>
<tr>
<td>3$^\text{rd}$</td>
<td>Formation of the cluster structure of H$<em>2$O$</em>\text{bulk}$</td>
</tr>
<tr>
<td>4$^\text{th}$</td>
<td>Dissociation of hydrogen bonding</td>
</tr>
<tr>
<td>5$^\text{th}$</td>
<td>Integration of the newly formed H$<em>2$O$</em>\text{molecular}$ into the hydration shell.</td>
</tr>
</tbody>
</table>

In this case, the ion travels the distance of a water dipole in the millisecond range. When creating an external force field (pressure / temperature / electrical potential), the migration takes place purposefully. During the provision of H$_2$O-molecular from the hydration shell, the ion is temporarily not completely electrically shielded.

The longer the formation of H$_2$O-molecular lasts, the greater the risk of precipitation processes. this explains why salts of divalent ions have a lower solubility than salts of monovalent ions. For charge shielding of such ions larger hydration shell is needed, thus the structure takes longer.

3.6. Permeability of membranes

Which molecules fit through a membrane? Looking at the performance of current membranes, it is hard to imagine hydrogen or hydroxide ions migrating through the membrane with their hydration shells. The molecular permeability of today's membranes is in the range between 80 to 150 g/mol (molecular weight of substance). This will also make it too tight for dissolved sodium and calcium ions with their hydration shells. What remains is the molecular water.

As explained above, the molecular water is a gas dissolved in the aqueous system which tends to either evaporate or hydrate (Röntgen, 1892). In order to preferentially direct H$_2$O-molecules through membranes, a pressure is needed which is above the osmotic pressure. As a result, newly formed H$_2$O-molecules are deflected from their natural migration to the ions and instead are directed to a membrane surface with higher pressure gradients. Thus, H$_2$O-molecular disappears from the system and lands on the other side of the membrane. Such deficiencies are associated with the loss of hydration shell water to restore equilibrium. If molecular water/water of hydration decrease, the formation of deposits is accelerated.

The alternatives reduce the loss of hydration shell water are:
1. Accelerated regeneration via supply of external energy (e.g., temperature increase).
2. Catalytic acceleration of the formation of H$_2$O-molecular.

3.7. Heterogenous catalysts for water treatment

The MOL®LIK catalysts consist of a special alloy – made of nickel chromium and iron. The material thickness of the unique metal foils used is about 22 microns. By an activation process, the metal foil is changed as follows (Rastetter et al., 2019):

An approximately 50 nanometre thick mineral layer is formed – with a clear demarcation to the metal structure (half of the volume of the mineral layer absorbs oxygen). As a result, areas with excess electron and electron deficiency are formed within the mineral structure. The electron-rich and electron-poor regions differ significantly in the oxygen concentration and in the number of metal cations. In the electron-rich region, the chromium concentration is higher than in the electron-poor region. In contrast, the iron and nickel concentration in the electron-poor region are higher than in the electron-rich region.

A matter of special importance is the fact that the iron ions in the mineral layer are mainly bound in tetrahedral gaps of a spinel structure. On these lattice...
Membrane systems and water structures

sites they cannot be further oxidized under normal conditions. They have an unpaired electron that is capable of interactions in the sense of a LEWIS base. As the result it comes to the expression of a band edge in the visible light area. In aqueous systems, the following processes take place on the surface of the mineral layer of the MOL®LIK catalysts (Table 4).

**Table. 4.** Processes on surface of MOL®LIK catalysts in aqueous systems

<table>
<thead>
<tr>
<th>Option</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>Reaction of electron-poor water structures (proton excess) with electron-rich regions (BRONSTED acid-base reaction).</td>
</tr>
<tr>
<td>1b</td>
<td>Reaction of electron-rich water structures (hydroxide ion excess) with electron-deficient regions (BRONSTED-base acid reaction).</td>
</tr>
<tr>
<td>3</td>
<td>Adsorption of molecular water at electron-poor regions (LEWIS acid-base reaction). This results in a bond that is more covalent. The unpaired electron on the divalent iron plays a special role here.</td>
</tr>
<tr>
<td>4</td>
<td>Further reaction of molecular water with excess protons or excess hydroxide ions by forming cluster structures.</td>
</tr>
</tbody>
</table>

In combination with visible light, the covalent bond of the molecular water is significantly weakened. This leaves the composite accelerated, so that reaction (4) is kinetically disadvantaged. As a result, then molecular water is available faster for other reactions (hydrolysis). Hydrolysis reactions can reduce COD and TOC, especially by degrading free ATP. However, the molecular water ensures a fine dispersion of lime particles, which manifests itself in a lower turbidity and a smaller number of filterable substances. It should be noted that all reactions take place only until the temperature- and pressure-dependent thermodynamic equilibrium position between the individual water structures has re-established itself in the water.

3.8. Catalytically accelerated membrane filtration – Practical experience

A homogenous catalyst for improving membrane filtration processes. Are there any results available? Effects of catalytic acceleration of the formation of H₂O-molecular were found on RO membranes on a pilot installation within the Belgium CARVE project (Chemicalønvrije Afvalwater Recuperatie in de VoEdingsindustrie). CARVE is a project in the field of zero liquid discharge (ZLD). Here purified wastewater was fed to RO (reverse osmosis) via an MBR (membrane bioreactor). Two cycles are operated (Table 5):

**Table. 5.** CARVE-Project – Description of operational mode

<table>
<thead>
<tr>
<th>Cycle</th>
<th>Description of operational mode</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Conventional operational mode</td>
</tr>
<tr>
<td>B</td>
<td>Conventional operational mode with catalyst (MOL®LIK) installed (Installation point: piping between the MBR and RO)</td>
</tr>
</tbody>
</table>

Just a few days after the start of the experiment, noticeable differences between catalysed (MOL®LIK-treated) and conventionally treated water are evident. The catalysed water stabilizes the flow rate at a higher level than conventional treatment. At the same time, fewer cleaning cycles have been necessary in the catalysed experimental cycle (Reyniers and Depuydt, 2017). This observation fits the described water model. With the following table the effect of catalytically accelerated formation of H₂O-molecular on 1 μm prefilter units in the area of industrial surface water treatment is shown (Table 6). In addition to the description of the development of the filter units, the following effects have been observed on the downstream RO membranes (Table 7).

- Improved efficiency of chemicals used
percent

Based on these facts, the use of catalytically accelerated membrane filtration in the field of surface water treatment have shown that such catalytic processes run with stable performance over periods of more than 7 years (Koppe et al., 2017).

Table 6. Performance development on 1 µm prefilters in the area of surface water

<table>
<thead>
<tr>
<th>Operational mode</th>
<th>Conventional</th>
<th>Catalytic (MOL®LIK)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flow Rate</td>
<td>[m³/h]</td>
<td>40 - 90</td>
</tr>
<tr>
<td></td>
<td>[m³/h] (stable)</td>
<td>65 - 100</td>
</tr>
<tr>
<td>Differential pressure</td>
<td>[bar]</td>
<td>0.1 - 0.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>0.05 - 0.1</td>
</tr>
<tr>
<td>Cleaning Interval</td>
<td>[days]</td>
<td>2 - 3</td>
</tr>
<tr>
<td></td>
<td></td>
<td>30</td>
</tr>
</tbody>
</table>

Table 7. Performance development on membranes in the area of surface water (Catalytic retrofitted since 2016)

<table>
<thead>
<tr>
<th>Design capacity</th>
<th>Conventional</th>
<th>Catalytic (MOL®LIK)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Permeate flow rate</td>
<td>120 m³/h</td>
<td>Decreases to 80 m³/h (in short times)</td>
</tr>
<tr>
<td></td>
<td>(stable)</td>
<td>120 m³/h (stable)</td>
</tr>
<tr>
<td>CIP-Cleanings</td>
<td>4 CIP per year</td>
<td>22 till 28 CIP per year</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10 CIP per year</td>
</tr>
<tr>
<td>Membranes life time</td>
<td>5 years</td>
<td>2 years</td>
</tr>
<tr>
<td></td>
<td></td>
<td>&gt; 3 years</td>
</tr>
</tbody>
</table>

The many years of applications with catalytically accelerated membrane filtration in the field of surface water treatment have shown that such catalytic processes run with stable performance over periods of more than 7 years (Koppe et al., 2017). Based on these facts, the use of catalytically accelerated formation of H₂O-molecular causes an increase in plant efficiency.

Adapted from on these approaches, there is a current European project INSPIRE WATER (Innovative Solutions in the Process Industry for next generation Resource Efficient WATER management). The scope of this project is checking out the extent to which a treatment of industrial wastewater - up to the use as fresh water - can be operated economically (Dambmann and Zorn, 2018).

This shows that the use of suitable catalyst technology can reduce the risk of performance-reduced deposits. With catalytic converter technology and optimized use of chemicals, economic and ecological advantages were found compared to conventional driving.

4. Conclusions

Water stress is a topic that our ecosystem has mastered since its creation. The combination of filtration and membrane technologies has been proven to separate high quality water and salts for millions of years. Humans just started using membrane technologies to provide clean water just a few thousand years ago.

The driving force for this were energetic aspects. Only for 60 years membrane technologies are available, which can provide high-quality water on a technically relevant scale.

Economic aspects are currently the driving force to make these systems more efficient. For these efforts to be targeted, knowledge about the physical-chemical processes on membranes is essential. By using the catalytically accelerated water treatment, the system performance and thus the profitability of reverse osmosis membranes is increased. At the same time, this reduces the negative impact on the ecosystem by reducing the associated use of chemicals.

References


Hoppenberg M., (2017), How much Middle Ages do we still have in us?, 2nd Int. MerWaterDays, Hochschule Merseburg, Germany.


Koppe J., Battagello G., (2017), Water Structure and Membrane Systems - Rising Performance with Catalytic
Membrane systems and water structures

Water Treatment, 2nd International MerWaterDays, Hochschule Merseburg, Germany.
Reig P., Schleifer L., (2019), Measuring, mapping and understanding water risks around the globe, Map of Europe, World Resources Institute, On line at: http://www.wri.org/our-work/project/aqueduct/
Röntgen W.C., (1892), About the constitution of the liquid water, Annals of Physics, 45, 91-97.