Electrostatic Desalination of Seawater

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Abstract: By electrostatic force, ions are bound to the surface of electrodes, whereby the salt content of the electrolyte liquid decreases. A multistage cascade desalination can remove the ions completely. The process uses no chemical transformations and requires only conventional components.

Introduction

So far, about 150 different procedures have been developed to desalinate seawater. The oldest, simplest, but also the most expensive method is vacuum distillation. This method is rarely used in the operation of powerful large plants because of the enormous energy demand. For small amounts of water, the radiant heat of the sun can be used. But nowhere is possible to supply the population with potable water with this method.

Technical standard on land and on ships is the method of reverse osmosis, in which the salt water is forced through extremely fine filters, which are impermeable to ions. One disadvantage is the required pressure of about 80 bar, which must be produced by powerful electric pumps and the formation of deposits on the filters. Exotic methods such as freezing, electrodialysis or centrifugation fail either on the power demand or they require too much time.

The new method is based on electrostatic force, it requires neither high temperature nor high pressure and therefore it has the potential for low power consumption. The plant can be produced economically with conventional components such as pumps, carbon fibers or activated carbon, pipes and valves. The process is no electrolysis and therefore it does not generate unwanted and problematic by-products. It is based on the property of the Helmholtz layer to fix ions on the surface of electrical conductors under the influence of a low electric voltage. When switched off, the Helmholtz layers dissolve and the ions diffuse back into the liquid. The process is reversible.

The electrostatic force

Since sea water is a strong electrolyte, dissolved salts such as NaCl are completely split into electrically charged ions. According to their charge, the ions may be moved by electric fields (charge separation). If the space between the plates of a charged capacitor is filled with sea water, the dissolved ions are attracted by the oppositely charged electrodes and move in their direction. Each ion is surrounded by a hydrate of H_2O dipoles which reduces the mobility of the ions in seawater, but can not neutralize the charge. Once ions reach an electrode, two cases must be distinguished:

- 1. When the electrodes are covered by an insulating layer, the attracted ions collect in a thin layer on the insulator. Once the amount of charge on both sides of the insulator is equal, no additional ions are attracted. Then the gap between the electrodes is filled with seawater (the salinity is reduced) and free of electric fields. The number of bound ions is proportional to the electric capacity and the level of the electric voltage between the electrodes. As long as the breakdown strength of the insulator is not exceeded, there is no electrolysis.
- 2. For non-insulated electrodes, two cases can be distinguished. When the voltage between the electrodes is below the decomposition voltage of the sea water (approximately 1.23 volts), the electrodes are enveloped by an insulating layer of oriented water dipoles (Helmholtz layer). Then, the considerations as described in point 1 apply. If the decomposition voltage is

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exceeded, this corresponds to an electrical breakdown, followed by electrolysis, which leads to gas formation and undesired change of the electrode surface.

The desalination described below is carried out with operating voltages below the decomposition voltage of seawater.

The Helmholtz Layer

The electrostatic binding of many ions to the surface of the charged electrode corresponds to a large total charge Q that rises proportional to the voltage between the electrodes. The proportionality factor is called capacitance C, the formula is $Q=C \cdot U$. As the voltage U is less than the decomposition voltage of the sea water, the capacitance C must be made as large as possible in order to achieve a significant desalting. From the formula $C=\varepsilon_r\varepsilon_0 A/d$ follows that the electrodes must have extremely high surface area A and the insulating layer must be extremely thin.

As the electrode material, for example, lends itself to activated carbon and as an insulating layer, a monolayer of oriented H₂O molecules, acting as a Helmholtz layer. For simplicity it is assumed that the permittivity ε_r and the thickness *d* of the Helmholtz layer are immutable.

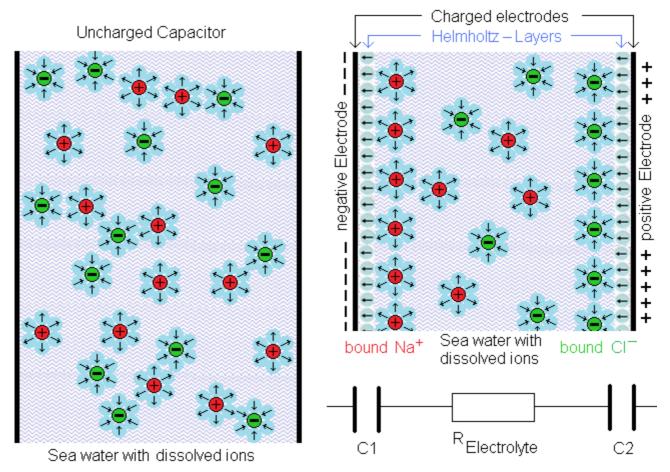


Figure 1: The left image shows the random distribution of ions in seawater. In the charged capacitor (right), the ions are concentrated in the vicinity of the electrodes.

Once the electrodes of the capacitor are charged, the H_2O dipoles rotate in the immediate vicinity of the electrode, without changing their place and spontaneously form the Helmholtz layers. These are the insulators of C1 and C2. With little delay, the ions move in the sea water towards these insulators and form the counter electrode of C1 and C2. They are fixed by the electrostatic force. At high salt concentration, this ion migration occurs only in the thin surface layer of the electrolyte beneath the electrodes and takes a short time to a standstill. With decreasing salt concentration, the

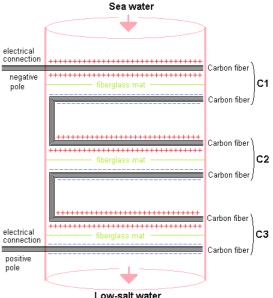
thickness of the boundary layer grows and, at constant ionic mobility, the ions need more time to reach their destination. The sum of the (singly charged) ions, fixed to the Helmholtz layers is exactly the same as the number of electrons on the negatively charged plate of the capacitor, which are supplied from the power supply. Since all the fixed ions are extracted from the sea water, they reduce the number of free moving ions in the electrolyte, corresponding to a desalination.

The term "double layer" comes from Hermann von Helmholtz (1853) and referres to an extremely thin insulating layer of oriented water molecules, which separates the electrodes from the ions. The layer thickness is about 1 nm. Film insulators are at least 10,000 times as thick, reduce the capacity (with the same area of the electrode) by this factor and can accordingly bind fewer ions. This huge difference can not be compensated by an increase in voltage.

The Desalination Unit

In seawater, different types of ions are dissolved, which need to be removed by electric fields. There are commercially available <u>supercapacitors</u> with capacities between 10 F and 3000 F and very low volume. The volumetric energy density of supercapacitors reaches 10 Wh / dm³ at a cell voltage of 2.5 V. That means that one dm³ can store the total charge 14,400 As, corresponding to $9 \cdot 10^{22}$ singly charged ions. Since sea water contains about $5 \cdot 10^{23}$ Na and Cl ions per liter, an appropriate structure should be able to capture about 15% of the ions contained in seawater.

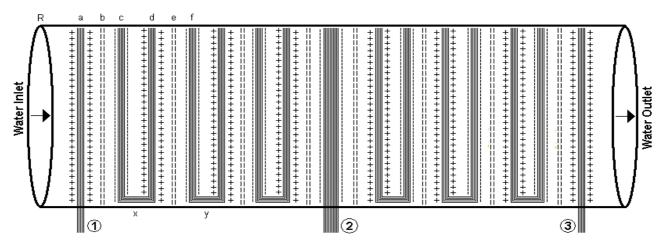
It is probably impossible to achieve complete removal of salt in a single step. Therefore, the entire system consists of several desalination units (DU), which are connected to a particular system.



Electrically, a DU contains a series connection of many

capacitors (the picture shows only three of them) whose voltage is changed periodically between zero and a fixed value in order to remove the ions from the water. All capacitors of the DU are in an insulating tube which is traversed by the seawater. Only the connections of the first and last capacitor are available and necessary.

Each capacitor consists of two layers of carbon fibers or plates of activated carbon, which are insulated from one another by a separator (e.g., fiberglass) so that the sea water can flow therethrough. The flat structure across the flow direction of the water allows rapid and complete charging and discharging of all capacitors within the cycle time of a few seconds.



The DU described above has the electrical disadvantage that there is a potential difference of several volts between the input and output. This leads to complications in construction and maintenance, because sea water conducts electricity. The potential difference disappears when two DUs with opposite polarity form one unit. The capacitor terminals at the accessible ends of a DU are electrically grounded ((1) and (3)) and are therefore safe to touch. The electrical voltage for the internal capacitors is fed in the middle of the DU (2) and is well insulated. The different profile of the electric field lines within a DU does not change the operation.

Structured surfaces of the electrodes

If one wants to withdraw many ions from the seawater, the capacitors must bind a large electric charge. Since the voltage on any capacitor must not exceed the decomposition voltage of the seawater, the (electrical) capacity must be maximized. The permittivity and thickness of the Helmholtz layer remain approximately constant. Therefore, the wetted surface area of the electrodes must be increased.

Activated carbon: The number of electrostatically bound ions is proportional to the surface of the electrodes. It can be increased enormously by the use of a porous material such as activated carbon $(2000 \text{ m}^2/\text{ g})$ or carbon airgel. A capacity of about 250 Farad per gram is possible. Connecting a voltage equal to the decomposition potential, a charge of 250 As per gram is bound. This corresponds to $1.6 \cdot 10^{21} \text{ Na}^+$ ions with the total mass of 0.06 g. One gram of seawater contains $5 \cdot 10^{20} \text{ Na}$ or Cl ions, therefore, the reduction of the salinity of sea water to zero should be possible. A further improvement using carbon nanotubes or graphene appears possible.

Although activated carbon has an extremely large (inner) surface, it is poorly electrically conductive. The narrow cavities delay the replacement of the water. Hours of heating to about 3000 °C ("graphitization") improves the conductivity, but it is hard to achieve a satisfactory level. The huge electric capacity of the activated carbon and the high bulk resistance lead to a large time constant $t = R \cdot C$ for the necessary voltage changes.

Carbon fibers: A fabric made of carbon fibers has high electrical conductivity, but – at a given mass – the surface and thus the capacity is significantly lower than that of activated carbon. This reduces the time constant to a few seconds.

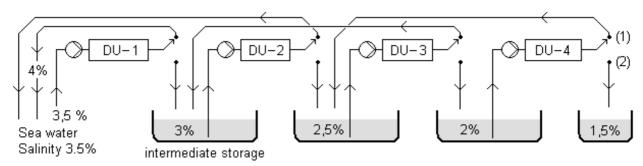
A 1 m long bundle of 10,000 fibers, each with 6 micron diameter, has a surface of 0,19 m² and a series resistance of 57 ohms. The current flow through this relatively low resistance produces little waste heat, warming the surrounding water.

One square meter of carbon fabric of thickness 0.5 mm has approximately 400 g mass and is woven from 222 cm³ fiber. At a density of 1.8 g / cm³, the total yarn length of 7900 km with a surface area of 150 m². The specific surface area is 0.4 m² / g and is about a factor 5,000 less than activated carbon. The capacitance to the surrounding sea water is about 10 F and, applying a voltage just below the decomposition voltage, a charge of 10 As is bound. This corresponds to $6 \cdot 10^{19}$ Na⁺ ions. The carbon fabric can accommodate 280 grams of sea water, which contains $1.4 \cdot 10^{23}$ Na or Cl ions. With about $2 \cdot 2300$ m² carbon fabric, all ions should be electrostatically bind in electrical double layers.

At a constant mass and reducing the diameter of the carbon fibers to 2 microns, one must choose longer fibers, whereby the entire surface area increases by a factor of 27. While this reduces the required active area of 2.83 m^2 , the series resistance of the fibers, however, would increase by a factor 81. The disadvantage is the increased time constant t = R·C for electrical charging and discharging, reducing greatly the working speed. This variant may be useful in a small system with reduced water flow.

Desalting cascade

Full desalination of sea water takes place stepwise. The picture shows the the pipeline plan of a cascade of four identical desalination units. Each unit consists of a centrifugal pump at the beginning of the DU and a hydraulic switch at the end.



The numerical values are valid under the assumption that each desalination unit can reduce the salt content by 0.5%. The actual separation factor must be determined experimentally. The cascade may be extended to the right until in the last stage, the desired salt content is achieved. The reuse of partially desalinated water reduces energy requirements.

Desalting is carried out in the following steps:

- 1. The DU is filled with sea water, the salt content is 3.5%. The DU is connected to the voltage supply. When the tube includes *n* capacitors, the total voltage is *n* times as high as the decomposition voltage of seawater. If one uses identical capacitors, the correct individual voltages set automatically and you can usually do without a balancing device.
- 2. The Na⁺ ions envelope the negative electrode and are fixed by electrostatic forces on top the thin Helmholtz layers which are formed around the carbon fibers. The positive pole binds as many Cl⁻ ions. The same applies to other types of ions such as Ca and Mg. These bound ions come from the water outside the Helmholtz layer, which corresponds to a desalination. More carbon fiber can bind more ions, but also increase the flow resistance.
- 3. With unchanged voltage, the water in the DU is replaced. By pumping in sea water (3.5%), the partially desalted water volume (3% salt content) is passed into a reservoir. With the power supply on, the tightly bound charge carriers adhere to the carbon fibers (separated by the Helmholtz layers) and can not be washed away by the movement of the water.
- 4. The DU is disconnected from the power supply and is controlled discharged (not shorted). This recovery of energy increases the efficiency of the plant. The Helmholtz layers disappear, the ions dissolve from the electrodes, diffuse back into the water and the salinity in the DU rises to 4%. Sea water is pumped in to force this highly saline water out of the tube into a container or back to the sea. Then the DU is filled again with sea water (3.5% salt).

By cyclically repeating these steps, the DU separates the water volume into two parts with different salinity, leaving the DU one after another. The separation is effected by deflection of the water flow. The fraction with reduced salinity flows into a catch basin. The part with increased salinity is called "brine" and is either pumped back into the sea or is reused in a multilevel system. The caching of partially desalinated water in reservoirs allows asynchronous operation of successive DUs and simplifies the monitoring of the operation.

Depending on the technical implementation and the salinity, the degree of desalination of adjacent DUs may differ. This can be adjusted by the number of cascade stages.

The water passes through a tube of length L with velocity v and therefore requires the time L/v. A simple timing controller does not respond to inaccuracies of these values. Therefore, the valve at the end of the tube will not always switch at the right time and some water is directed into the false reservoir and the yield decreases. A control circuit can adapt the optimal timing by measuring the

conductivity at the output of the DU and increase the yield of desalinated water. The log of the measurements can also document creeping changes.

Recycling the water

Because of the recirculation, the processed quantities in successive desalination units differ. In the table, the two pairs of arrows show, from where the stages receive the water. This amount (salinity 2.5%) is separated by every DU into two equal subsets that differ in salinity and are therefore treated in adjacent stages.

Salinity		3,5%	3,0%	2,5%	2,0%	1,5%	1,0%	0,5%
	from the sea	Stage 1	Stage 2	Stage 3	Stage 4	Stage 5	Stage 6	Stage 7
Input	1000	1750	1500	<mark>a</mark> 1250	_ 1000	750	_ 500	250
Out - 0,5%		875	750	625	500	375	250	125
Out + 0,5%		875	750	625	500	375	250	125
		4% into the sea						

In this structure of the cascade, most of the pre-purified seawater is passed as Brine back into the sea, only a small portion (125 units) leaves the cascade as potable water (green box to the right). The water turnover within the cascade is

 $u = \frac{7000}{125} = 56$ Per liter of potable water, 56 liter saline water must be filtered.

If the amount of seawater is limited, the salinity of the brine can be increased by a symmetrical cascade. This increases the expenditure on equipment and the circulation rate within the plant and reduces the dissipated amount of concentrated saline.

The following table shows the amounts of water in a symmetrical cascade with the same amount (1,000 units) prepurified seawater fed into the seventh stage, along with two times 3000 units water from the two adjacent stages.

Salzgehalt	6,5%	6,0%	5,5%	5,0%	4,5%	4,0%	3,5%	3,0%	2,5%	2,0%	1,5%	1,0%	0,5%
	Stufe 1	Stufe 2	Stufe 3	Stufe 4	Stufe 5	Stufe 6	Stufe 7	Stufe 8	Stufe 9	Stufe 10	Stufe 11	Stufe 12	Stufe 13
Input	1000	2000	3000	4000	5000	6000	7000	6000	5000	4000	3000	2000	1000
Out - 0,5%	500	1000	1500	2000	2500	3000	3500	3000	2500	2000	1500	1000	500
Out + 0,5%	500	1000	1500	2000	2500	3000	3500	3000	2500	2000	1500	1000	500
	7% in das Meer												

A comparison with the asymmetrical cascade shows that symmetrical cascade contains seven times the amount of water and is correspondingly larger dimensioned. The amount of potable water rises from 125 to 500 units, and the specific energy demand increases by 75%, because the water turnover within the cascade is now

$$u = \frac{49000}{500} = 98$$

Final remark

Perhaps the described method can reduce the energy costs for the desalination of sea water so far that the end product can be used for irrigating fields. This would revolutionize the food situation in many parts of the world.