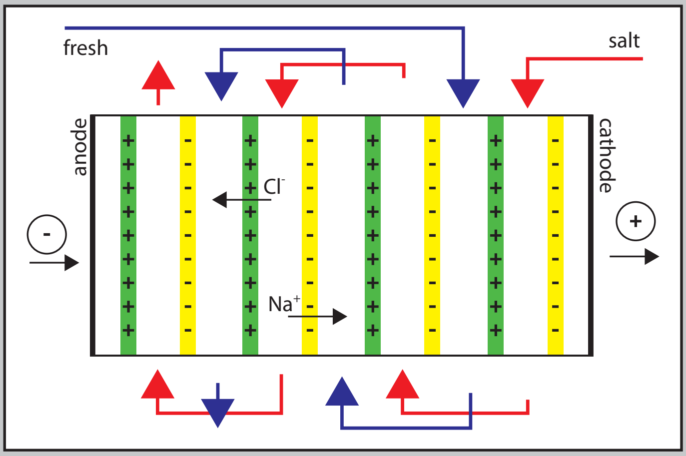
Briefing Paper

Leonardo ENERGY

Blue Energy



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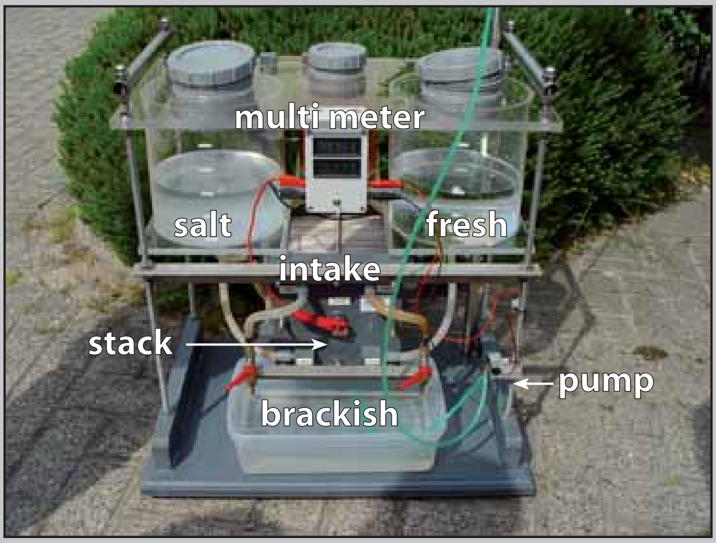

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Blue Energy

Summary

Due to the increase in oil prices or geopolitical instability in the OPEC countries, in times of energy debate, alternative sources of energy attract renewed attention. Among them we find concentrated solar power (CSP), ocean thermal energy conversion (OTEC), geothermal, nuclear fission, wave and tidal energy and salinity gradient.

There are several ways to harvest energy from the entropy of mixing fresh or river water with salt or sea water. The two most important ways, pressure-retarded osmosis (PRO) and reverse electrodialysis (RED), depend heavily on membrane development and a reduction in the price per square meter. Over the last twenty years, membrane technology has become more and more important in areas such as waste water treatment, desalination and drink water preparation, resulting in a strong reduction in prices. This has strongly supported the breakthrough of **saline power,** the brand name for PRO developed by Statkraft in Norway in 1998, and **Blue Energy**, under which name KEMA in the Netherlands started the development of the RED variant in 2002.

Starting with some historical notes, Van 't Hoff's Nobel Prize in 1899 will be described, including the physical-chemical principles. Then the current technical status and challenges will be discussed. This will include the key topic, membranes, but also other issues such as pump energy, water pre-treatment, etc. Consideration will also be given to the potential energy production in delta areas and industrial sites. This will include the necessary electrical infrastructure for Blue Energy, which generates photovoltaic DC and low voltage output.

Introduction

Energy crises lead to technological breakthrough. Some of these breakthroughs survive. The charcoal crisis in England centuries ago boosted coal mining and the development of the steam engine. More recently, the shortages of many goods such as energy after the Second World War promoted nuclear energy supported by the 'Atoms for Peace' program. The oil crisis in the seventies of the last century gave birth to modern wind energy technology. In all these periods of energy crisis, attention was given to and development spent on a number of new energy technologies. Among them we find coal gasification, nuclear fission, geothermal energy utilization, solar energy including concentrated solar power (CSP), ocean thermal energy conversion (OTEC), tidal and wave energy and salinity gradient power.

Although world oil production is predicted to peak within the next five years, there is no direct energy crisis due to shortage. Coal is still abundant throughout the world. Geopolitical instabilities in the OPEC countries in the seventies and eighties were a second factor in promoting the search for alternatives. The same geopolitical argument has continued in recent years and has reawakened interest in alternatives to oil.

But now a new incentive is contributing to the further development of other energy sources. After the initial „Limits of Growth" document published by the Club of Rome 30 years ago, climate change is now the focus of political attention. Reduction of greenhouse gases such as CO_2, formed by the production of fossil-fired power generation, is the main goal. A number of countries signed the Kyoto treaty in order to combat global warming. CO_2 now has a price, a negative price. Influenced by Al Gore's movie „An inconvenience truth" the European Union is going even further than Kyoto. In 2020, the „three 20%s" will be mandatory for all EU countries: 20% energy saving, 20% CO_2 reduction and 20% renewable energy. Each country can deviate slightly from the 20% renewable energy as part of the whole energy portfolio, but this will also drive a third factor: the development of renewable – non-CO_2 – energy sources.

A general characteristic of renewable energy sources is that they are derived from the sun and therefore intermittent, rather diffuse and need large surfaces for harvesting. The largest surface of the Earth is covered by the sea and the oceans, which capture most of the solar energy. Therefore we see that Ocean Power is one of the revived options of renewable energy. Ocean Power includes OTEC, wave and tidal energy and salinity gradient power. Salinity gradient power is also derived from the sun as can be seen when the hydrological cycle is considered. By solar irradiation and heating of the salt water of the ocean a demixing takes place and fresh or sweet water is formed in clouds. A part of this fresh water returns to the sea through rivers, where the fresh water is mixed again with the salt water and energy is released.

As the three factors, energy crises, geopolitical instabilities and the climate debate renewed the attention for earlier ocean energy techniques, a fourth factor is decisive for the success and that is technological advancements, which are mostly found in other areas. For salinity gradient power these are the enormous advances in membrane production and price for applications such as desalination and the production of potable water.

Entropy of mixing

From thermodynamics and the formulas of Gibbs free energy, ΔG including the chemical potential μ, it is known that a solution represents a lower chemical potential than the pure solvent. Nature tries to equalize the chemical potentials of two different solutions in contact which each other in order to create maximum entropy. So the driving force for the transport of a component, for example across a membrane between two solutions, is such a gradient in ΔG.

In order to obtain energy from salt water, two solutions of different concentration must be available. Such a salinity pair might be formed from sea water, saline lakes or brines left from salt manufacture, coupled with a very low concentration source such as river water. The energy that can be extracted from the two solutions is directly proportional to the absolute temperature, T (K), and the logarithm of the ratio of their concentrations (activity ratios). By mixing 1 m^3 fresh water per second with an excess of seawater, considered as a salt solution with a salt concentration c=0.5 molar, the maximum recoverable dissolution energy is ΔG = -2.35 MJ/s = -2.35 MW.

Another route for calculating this is using the osmotic pressure of sea water. Again assuming that the concentration drop in the excess of sea water is infinitesimally small when fresh water is penetrating, this results in an increase in the static pressure. The calculated osmotic pressure from

$$\Pi = 2\,RTc$$

in which the gas constant $R= 8.31\ kJ.kmol^{-1} K^{-1}$,

$T=283$ K and the concentration $c=0.5\ kmol/ m^3$

is

$$\Pi = 2.35\ kN/ m^3$$

and this gives a potential energy of $2.35\ MJ/s/ m^3$

This value is lower in practical devices when the excess of sea water above fresh water is limited due to the necessary pump energy.

The methods considered for extracting the energy are the reverse of those used for desalination. These include using the osmotic pressure difference between sea water and fresh water (20 – 25 bar), the difference in electrochemical energy which manifests itself across an ion exchange membrane (reverse electrodialysis) and the difference in vapor pressure between salt and fresh water.

Vapor pressure

The vapor pressure of a salt solution is lower than that of pure water at the same temperature. This results in a higher boiling point for salt water. People have known this for centuries.

If a dilute and a concentrated solution of brine are connected by a vacuum, the dilute solution will evaporate and condense into the concentrated solution. In this way, the transport of vapor can be used to do work. However, the process would rapidly lead to cooling of the evaporating solution, thus lowering its vapor pressure, and the evaporation would anyway tend to equalize the concentrations and stop the process. A useable device should therefore return the heat generated by the condensing vapor to the evaporating dilute liquid via a thin heat-conducting wall. This would maintain the two solutions at almost the same temperature and, if the liquid in each compartment is continuously changed, keep the concentration difference constant. Because the fluid leaving each compartment will have a different concentration to that entering, it has been suggested that a multi-stage device could be developed. Electricity would be generated by a turbine between the two compartments. This type of device is less developed than the two membrane methods: reverse electrodialysis and osmotic techniques.

Osmotic pressure

In 1784 the French priest and physicist Jean-Antoine Nollet put a pig's bladder filled with wine in a barrel of water. To his surprise, the bladder swelled and finally burst. The osmotic energy was converted into an increase in pressure. The Dutch Nobel Prize winner (1902) Van 't Hoff derived the formula for calculating the osmotic pressure Π.

A device, see figure 1, that extracts energy based on the osmotic pressure uses a semi-permeable membrane through which water can pass but not salt. Water from the compartment with the dilute solution enters the compartment with the concentrated solution through the semi-permeable membrane and raises its level. The difference in height achieved can then be used to drive a water turbine to produce electrical energy. In the fifties there was a growing interest in producing potable water from sea water. A breakthrough was made by the American Sidney Loeb by producing a semi-permeable membrane. Production of fresh water by reverse osmosis (RO) is now a major industry, especially in the Middle East. The same membranes can be used in an installation for producing electricity by pressure-retarded osmosis (PRO). In Norway the PRO method is under investigation by Statkraft.

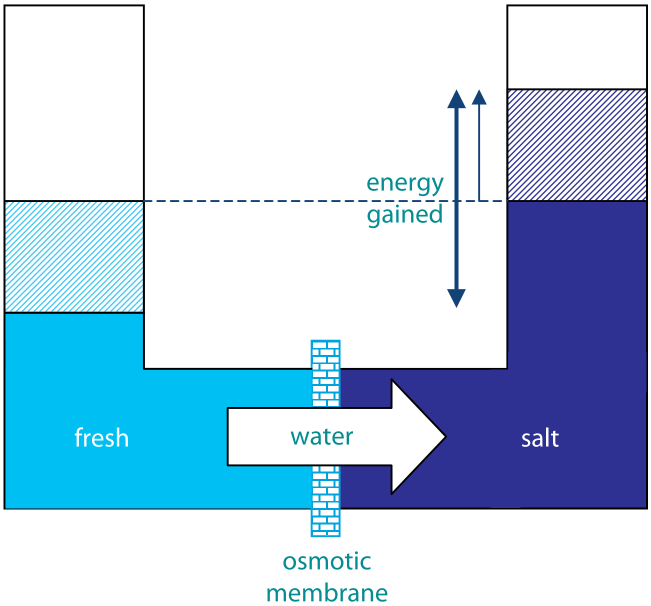

Figure 1: When fresh water permeates the semi-permeable membrane to the other seawater compartment, nature tries to equalize the salt concentration on both sides.
As a result a hydrostatic pressure is build up, which can be harvested for energy production.

Reverse Electrodialysis

A second membrane method is based on reverse dialysis. It requires two types of membranes, namely one that is selectively permeable for positive ions and one that is selectively permeable for negative ions, see figure 2. Salt water separated from fresh water between two such membranes will lose both positive ions and negative ions. This charge separation produces a potential difference that can be utilized directly as electrical energy. The voltage obtained depends on the number of membranes in the stack, the absolute temperature and the ratio of the concentrations of the solutions, the internal resistance and the electrode properties.

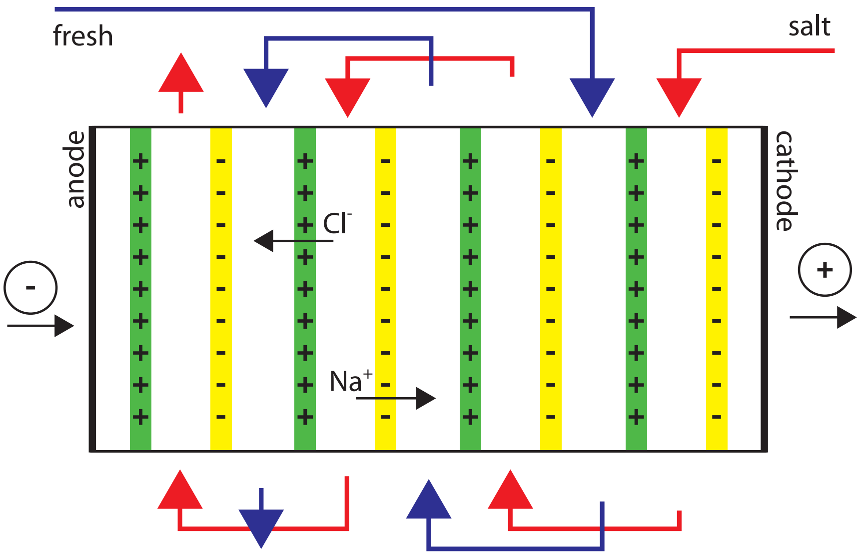

Figure 2: Using a pair of ion exchange membranes positive and negative ions from the salt solution are separated.
At the electrodes direct electrical energy can be harvested.

This electrochemical cell is also called a „dialytic battery" because it is derived from the technology currently used to desalinate blood by haemodialysis. This is achieved by passing blood between two types of membranes, each selectively permeable to positive or negative ions. On the other side of the membranes is water. Applying a voltage difference across this system drives ions out of the blood. Electrodialysis is also used to produce fresh water from brackish water.

Similar to the complementary action of an electrical engine and a dynamo, the processes of dialysis and reverse dialysis are based on the same principle. This means that a desalination plant based on electrodialysis, where an external voltage is applied, could also be used as an energy generator in reverse electrodialysis (RED) mode. The principle was described by R. Plattle in Nature for the first time (1954). Experimental results were obtained in America and Israel in the seventies. KEMA in the Netherlands revived the investigation in 2002 under the brand name „Blue Energy", focusing on the production of cheap membranes using the „Electrical Modification" (ELMO) method. KEMA won the Dutch innovation Award for 2004 in the category „Energy and Environment" for Blue Energy. The name „Blue" was chosen by KEMA in order to differentiate it from „black" – coal-fired – power generation, „brown coal" for lignite-fired power generation, and „white coal" for the water of hydropower generation, and to associate it with the blue color of (sea) water. Blue Energy is a part of the general class of renewable energy or „green energy" without the disadvantage of the unpredictable intermittent character of most forms of green energy.

Comparison of RED and PRO

Desalination by RO and ED.

The main drawback of these membrane-based energy conversion techniques was the high price of membranes. The price of membranes was by far the main factor in the final high kWh price estimated in the eighties. The increasing price of fossil fuels and the added „negative price" for the CO_2 emitted by fossil power plants made reconsideration of the available membrane-based processes for the production of sustainable power from salinity-gradient worthwhile. However, the decreasing price of membranes for desalination and water reuse applications make salinity-gradient energy even more interesting. The experience with microfiltration has been similar. Since 1985, a cost reduction by a factor 100 has been observed, see figure 3, due to increased competition, increased membrane life, the lower manufacturing costs of the membranes for increased production volumes, but of course also due to lower ancillary costs, such as submerged systems, and reduced design costs through standardized designs.

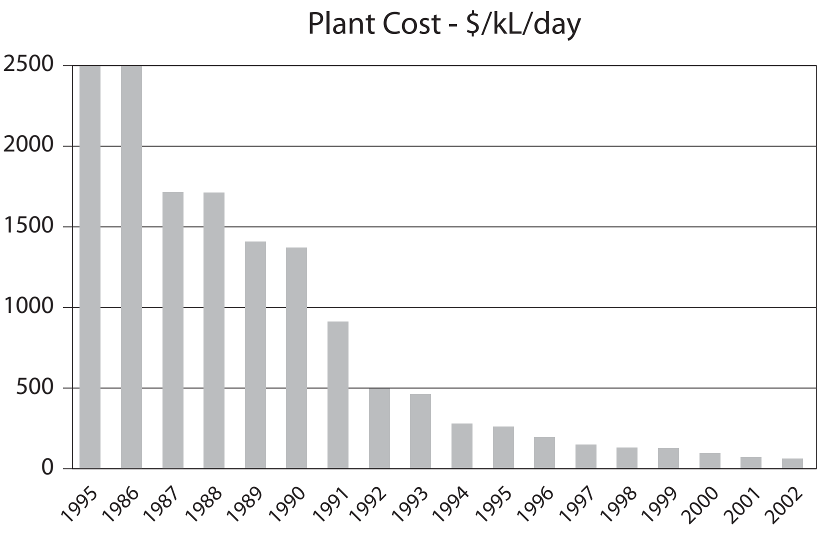

Figure 3: Tremendous reduction of plant cost of microfiltration since 1985 partly due to lowering of the membrane price.

Not only do the lessons learned from the price reduction of membranes for desalination support the development for saline gradient power but other experiences from desalination with the two membrane processes also yield relevant information. Large industrial installations for desalination, especially in the Middle East, are also based on membrane processes, reverse osmosis, and reverse osmosis is more widely used than electrodialysis. This is partly due to the more simple semi-permeable membrane (i.e. only water can permeate it) in reverse osmosis than to the two types, anion and cation, of ion exchange membranes necessary for electrodialysis.

Another aspect is the (too) high electricity consumption in electrodialysis for driving the salt ions out of high concentrated sources such as brine and sea water. Therefore electrodialysis is used more for the desalination of brackish water with a lower salt concentration. For the reverse process, power generation with reverse electrodialysis, a high electrical output with a high salt concentration is a strong advantage.

The performance of membranes deteriorates over time due to scaling and (bio)fouling. In desalination this is more the case than with reverse osmosis. The fouling can be suppressed by adding chemicals in the process. The use of chemicals is less desirable for a green energy source such as pressure-retarded osmosis. Fouling is less of a problem in desalination using electrodialysis and can be simply counteracted by short periods of reversing the electric current in the installation.

Energy production by PRO and RED

The two membrane processes for energy production based on salinity gradients, pressure-retarded osmosis and reverse electrodialysis, have the following different characteristics:

- In PRO water, 99 mass percent of sea water has to pass the membrane. In RED only 1% of the mass, the salt content of sea water, has to pass the two membranes.
- In PRO, deterioration of the membranes by fouling has to be treated by chemicals potentially, which is less environmentally friendly. However, heavy ions present in sea water can be accumulated in the ion exchange membranes of RED. At the end of the life of the RED membranes they should be treated as chemical waste.
- More development funds are spent on RO membranes, resulting in low priced membranes, with can be of short term benefit for PRO application. For RED, a longer development time of low-priced membranes is to be expected or some technical breakthrough has to accelerate this.
- In PRO, the pressure differences, 20-25 bar for sea water and fresh water put severe requirements on the mechanical strength and leakage of the membrane stack. On the other hand, in RED the pumping action of the water streams through the tiny channels between the membranes in the stack cannot be ignored. This also requires some mechanical strength of the membranes, although leakages are less detrimental in RED. For reducing pump energy losses, more emphasis should be placed on the spacing design in the membrane stack of RED.
- In PRO, pressure or high, mechanical energy, should be converted into electrical energy by the application of generators. For RED, the electrodes supply an electrical output directly.
- PRO seems to be more appropriate for highly concentrated salt streams such as brines than RED. On basis of a recent evaluation study, RED performs better for a mixture of sea water and fresh water.

Worldwide, a mixture of sea water and fresh (river) water has by far the greatest potential.

Potential of energy production by Blue Energy

The worldwide run-off of fresh water to the sea is about 4×10^{13} m^3 y^{-1} . Half of it is delivered by the 50 largest rivers. It is assumed that this will increase due to the effect of the global warming alone by 11% and an extra 6% by the reduced transpiration of plants due to the increase in CO_2 content in the atmosphere.

Earlier estimates of the River Elbe in Germany with an average run-off of 800 m^3 /s over one year gives a 1900 MW mechanical power to be harvested. Assuming that only 10% of the equilibrium value (E_{pot} = 2352 kWs/m^3) is gained and that the conversion efficiency into electrical energy is 0.5, this gives a 100 MW_e power plant.

Using the same assumptions made for the River Elbe, the worldwide production could be 150,000 MW_e or, including the effect of global warming on the run-off, up to 170,000 MW_e.

The most accessible run-offs are not open rivers. Low areas with an excess of water usually pump water to the sea in order to prevent flooding. In the Netherlands some of these points are the pumping stations at Afsluitdijk (600 m^3 /s average over the year), Velsen (90 m^3 /s) and Katwijk at the mouth of the old Rhine river (50 m^3 /s).

Blue Energy can produce the electrical power for the pumping stations and more.

Apart from the fact that the equilibrium value and thus the theoretical value is never achieved, other factors also contribute to the value below 1 of the conversion efficiency to electrical energy. In the Blue Energy variant of salinity gradient power the pumping energy could consume up to 40% when design values of desalination are used. However the cross flow velocity can be 100 times lower than for normal electrodialysis.

Other losses are due to the internal resistance in the stack. It is known that the salt concentration in the fresh water should not be too low or the internal resistance increases too much. A normal salt content of 3 g/l in river water is optimal. Internal resistance is also created by the membranes, which should be as thin as possible. The minimum compartment or spacer width in the stack between the membranes that will be used, without excessive friction losses not increasing the pump energy, should be 1 mm or lower. The compartment width also determines to which extent water filtration is required as a pre-treatment. In general, the diameter of particles should be smaller than one tenth of the compartment width. Water filtration also consumes electricity and increases the cost of the installation.

Ions are transported through the membranes from the concentrated solution to the diluted solution. For a sodium chloride solution comparable to sea water, sodium ions permeate through the cation exchange membrane in the direction of the cathode, and the chloride ions permeate through the anion exchange membranes towards the anode. Via a reduction at the electrode-cathode surface there is electro-neutrality in the cathode compartment. Similarly, oxidation takes places in the anode compartment. The final result is the transport of an electron from the anode to the cathode through an external circuit. Some resistance can also arise at the electrodes, which contributes to the losses. Therefore, larger stack configurations are considered of up to 1,000 pairs of ion exchange membranes, increasing the output voltage and reducing the relative contribution of the electrode losses and other internal losses.

The most critical component however is the membranes, as in fuel cells. Not only a high conductivity is necessary but also a high perm-selectivity, i.e. sodium ions will permeate exclusively through the anion exchange membrane and not the chloride ions, and a long lifetime. Membrane prices also have to reduce significantly since electrodialysis has never had a similar breakthrough in the desalination market as reverse osmosis.

State of development

Heterogeneous modified polyethylene containing ion exchange resin particles are used for membranes in reverse electrodialysis at a price far in excess of 10 €/m^2. Different calculations of the price per kWh generated by Blue Energy indicated a membrane price of lower then 10 €/m^2 in order to be competitive with solar energy. To be competitive with fossil-fired power generation including CO_2 this membrane price has to be reduced further to a few €/m^2.

Recent research towards low price membranes uses the method of electrical modification (ELMO) of commodity plastics such as polyolefin. ELMO is the industrial application of the water tree phenomena observed in cable insulation since 1967, see figure 4. Under the influence of an electrical field, moisture and salt nano-track growth is induced through the amorphous phase of polyolefins, yielding an oriented ionomeric structure. This can be made visible with a color agent, as can be seen in figure 5. The industrial technique is similar to the well-know galvanic techniques. An ionomeric structure of one type results in the anion exchange membrane or the cation exchange membrane.

Figure 4. Watertreeing in cable insulation.

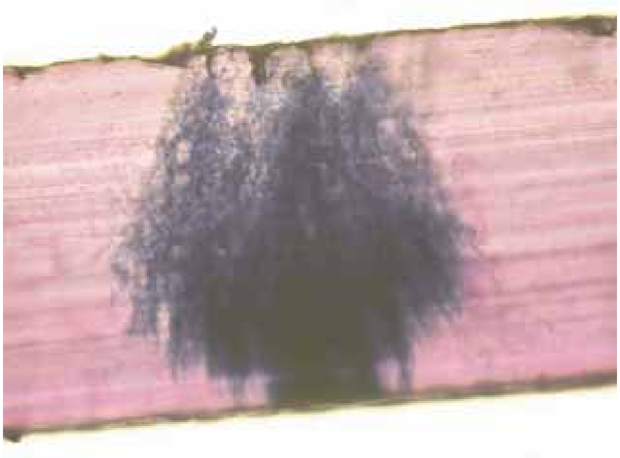

Figure 5: Grow of oriented chanels through plastic foils under influence of an electric field creates membrane properties.

Up to now only pilot Blue Energy installations have been built. A recent installation of Blue Energy at the KEMA laboratories can be seen in figure 6.

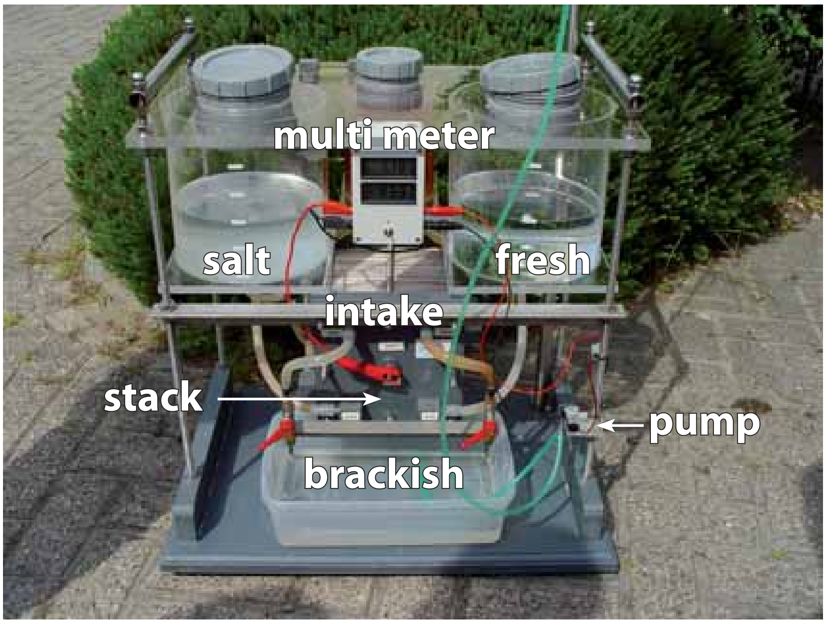

Figure 6: Blue Energy installation at KEMA.

Design studies for a Blue Energy power plant are based on a modular system. Sea containers are filled with stacks of circa 1 m^3 with more than 1,000 pairs of ion exchange membranes. With 0.078 V per pair, the output voltage is around 80 V per stack. Depending on the performance of the membranes, the electrical capacity per sea container is estimated to be 50 – 150 kW. A number of sea containers form a Blue Energy plant. All the sea containers are easy accessible. With an assumed membrane lifetime of only five years, continuous replacement procedure of the sea containers is envisaged. For a larger Blue Energy power plant in the order of 200 MW a separate membrane manufacturing installation is foreseen to produce the tens of km^2 membranes.

Integration into the electricity system

The DC (direct current) output of the Blue Energy System needs to be converted into AC (alternating current) to interconnect with the public electricity network. Depending on the power size of the individual stacks, power electronic converters will perform the required conversion. These converters will be part of the Blue Energy Plant.

The Blue Energy Plant will contain one or multiple control and protection systems in order to control the operation and to minimize the consequences of faults. The converter will also be equipped with a control and protection system that is integrated into the overall protection system.

The output power of one or multiple stacks will be collected together on a busbar system before the power is delivered to the public grid.

The technical grid connection will take place at:

- low voltage level of 0.4 kV (up to typically ~1 MVA),
- medium-voltage level of 10-35 kV (up to typically ~20-50 MVA), or
- high-voltage level of 36-170 kV.

The actual voltage level depends on the power level and the availability of transmission power in the nearby public network.

The Blue Power plant and its grid connection will need to meet several technical and non-technical grid connection requirements & conditions. For the Blue Energy plant, these requirements are not expected to limit the technical feasibility.

The cost of the grid connection and for adapting the power plant to the technical grid connection conditions are relevant for economic feasibility and are an aspect to be duly considered in the project preparation stage.

Foreseen developments

An increase in fossil fuel prices and geopolitical development will force the search for new energy sources. Because of global warming and the CO_2 price this search will be for CO_2 free energy sources. Breakthroughs in membrane technology started for desalination will open the route for salinity gradient power generation. Further development is needed, but a membrane market for power production will also significantly reduce membrane prices because of the scale. Blue Energy seems to be the most realistic salinity gradient choice for the use of the river-sea interface potential. Blue Energy can contribute to some extent to global (electricity) needs. There are several plans for erecting pilot Blue Energy plants of the size of a sea container at different locations in the coming years in the Netherlands. One of the the potential locations is the Afsluitdijk, see figure 7. Further development and up-scaling of Blue Energy will strongly depend on the success of these demonstration tests.

Figure 7: The afsluitdijk in the Netherlands with on the right the fresh water reservoir Ijsselmeer and on the left the sea Waddenzee.