Water, Energy and Salt: interrelations and sustainability

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Abstract

Due to depletion and salinization of fresh water resources, in a world with a growing population and demand for fresh water there is an increasing need for desalination technology. The sustainability of desalination is governed by energy consumption and brine volume. In this paper we discuss reversed osmosis, electro dialysis, capacitive deionisation and super critical fluid extraction as energy efficient desalination technologies. Sustainability aspects and fields of application are identified. Blue energy is discussed as a source of energy for desalination, readily available in salinized regions.

Keywords

Desalination Reversed Osmosis, Electro Dialysis, Capacitive Deionization, Super-critical Fluid Extraction, Blue Energy, Sustainability

INTRODUCTION

The average fresh water consumption of the worlds' population is approaching 6000 km^3 per year (2010), from which about 1200 km^3 is used for drinking water and 4000 km^3 is used for agriculture. About half of the world fresh water resources are threatened by depletion or salinization, especially in larger delta areas, coastal regions and agricultural production areas. In the future salt concentrations in fresh water reservoirs will further increase, if no measures are taken, due to sea level rise, fresh water depletion due to consumption and agricultural use due to the growing world population, and regional reduced precipitation due to climatic change. Fresh water availability including production of fresh water out salt impacted water systems by various new technologies is therefore a prime global issue, now and in the future. Desalinization costs energy. Technologies used and in development for desalinization are Reversed Osmosis, Electro Dialysis, Capacitive Deionization, and Super-critical Fluid Extraction, each having a different energy-efficiency dependency related to the salt concentrations of used and produced water.

The fresh water supply in the Rhine/Meuse basin and delta, (incl. the Netherlands) is an increasingly important issue in the western Europe region. In other EU or world regions the situation is even more pressing, such as the Mediterranean and sub Saharan regions, South East Azia (i.e. the Mekong Delta countries, South East China, India, Bangladesh), and larger agricultural (irrigation) regions in China, Australia, California, and West Andes countries in South America. The world economic damage of salt water to agriculture is estimated to be about 800 billion dollar per year. The amount of energy used to desalinate water is tremendously increasing, consuming higher and higher amounts of (fossil) energy. The energy demands consist of the reversible energy that is thermodynamically needed for the separation, and irreversible energy due to non-optimal operation of desalination plants. The latter can be optimized by proper choice of technology and optimization of the efficiency of processes. The reversible energy can be harvested by blue energy.

Like fresh water resources, the demand for energy increases globally. Since fossil sources will be eventually depleted and at this moment cause economic dependence on specific regions in the world other approaches need to be developed. Local and regional harvesting, like blue energy, and distribution of energy is part of that.

Water, Energy and Salt are interrelated topics. Desalinization of water costs energy, salinization of water yields energy. Energy produced locally (from wind, tide or solar energy) can be transferred into fresh water. Energy can be retrieved from residual biomass, but in too saline systems energy is needed to reduce salt concentrations. Water, Energy and Salt need to be related in an integrated model to obtain sustainable solutions. This presentation will present ideas for that model and compare the various technologies in their efficiency and sustainability.

REVERSED OSMOSIS AND ELECTRO DIALYSIS

Any desalination system will be most energy efficient if it involves a reversible thermodynamic process, which is independent of the techniques and mechanisms used. It can be calculated that the lower limit of specific energy consumption for seawater desalination is 1.4kWh per m^3 of fresh water produced (Post, Huiting et al. 2011). The water recovery is in this case 80%, which means that each m^3 of fresh water is produced from $1.25m^3$ of seawater. This small surplus of seawater is necessary to prevent precipitation of sparingly soluble salts when fresh water is extracted from the system (‘scaling’). These numbers for energy consumption and water recovery could be used as the ideal standard for any desalination scheme.

Seawater Reverse Osmosis (SWRO) is currently the only non-thermal technique for seawater desalination. In a SWRO system, water is forced through a semi-permeable membrane from the seawater side (‘concentrate’) to the fresh water side (‘permeate’) of the membrane by applying a hydrostatic pressure in excess of the osmotic pressure. The water recovery is at best 50% as the osmotic pressure of the concentrate is then close to the maximum applicable pressure (Kurihara, Yamamura et al. 1999). This means that for each produced m^3 of permeate at least $2m^3$ seawater need to be pressurized and extensively pre-treated. With this low water recovery, the thermodynamic minimum required energy is about 1.0 kWh/m^3 (see figure 1). The irreversible system losses are mainly determined by the conversion of electrical energy to mechanical energy by the high-pressure pump and by the water-permeation resistance of the dense membranes. State-of-the-art SWRO has a specific energy consumption of $3\text{-}5kWh/m^3$ (Shannon, Bohn et al. 2008). In theory, the energy requirements of a state-of-the-art single-staged SWRO with a water recovery of 50% could be optimised to 1.6 kWh/m^3 when operated at an applied hydrostatic pressure P_h equal to the osmotic pressure of the concentrate Π_c (with the assumption of ideal equipment, i.e., membranes without permeation losses, 100% efficient pumps and energy recovery devices; and with the assumption of ideal process conditions, i.e., no concentration polarization, no frictional losses down the channel) (Elimelech and Phillip, 2011).

In an ED system, ions are forced through ion-selective membranes from the seawater side of the membrane (‘concentrate’) to the fresh water side (‘diluate’) by applying an electrical potential difference in excess of the electrochemical back-force. The water recovery as well as the extent of desalination can be set to any value. The water recovery could be in the range of 50-90%, depending on the transport of multivalent ions through the membranes. Supersaturation of sparingly soluble salts in the concentrate could well be prevented by the use of monovalent-selective membranes. For example, with a water recovery of 80% and a desalination degree of 80%, the thermodynamic minimum required energy is about 0.89 kWh/m^3 (see figure 1). ED needs no conversion from electrical energy to mechanical energy (only an efficient AC/DC conversion). The irreversible system losses are mainly determined by the ion-permeation resistance of the ED cell-pairs. The main contributor to this resistance is the diluate between the membranes when it becomes too diluted. Therefore, ED is probably less efficient than SWRO for the entire process of desalinating, i.e., from seawater quality to fresh water quality, but could well be used to the extent of the desalination process in which it has the best characteristics.

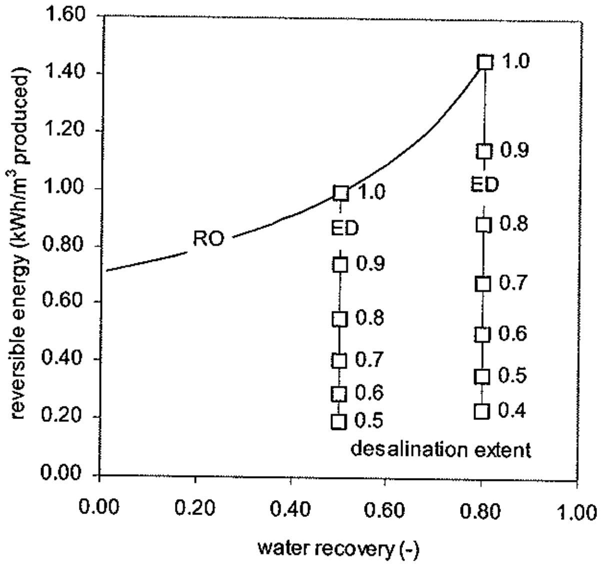

Figure 1. Reversible energy consumption as a function of water recovery and desalination extent for RO (desalination extent is 1.0 in all cases) and ED (variable desalination extent)

According to Elimelech and Phillip (Elimelech and Phillip 2011), the real incentive for research and development in desalination is not any longer the energy efficiency of the primary desalination process. Future research should focus on the pre-treatment and post treatment stages of desalination. Reducing the pre-treatment demands would substantially reduce the energy consumption, capital cost, and environmental impact of desalination plants. Their recommendation is to develop high-performance, fouling-resistant desalination membranes, or to look for new energy-efficient desalination technologies that are inherently less susceptible to fouling. To our opinion, the use of electrochemical desalination instead of pressure-driven desalination could be a good direction. ED could be used as a first desalination step (Post, Huiting et al. 2011), reducing the salt content to 0.2-0.5 of the salt content of seawater, leaving the conductance of the diluate (and thus the irreversible losses) to an acceptable level. A second desalination step after the ED could be any desalination process capable of efficient desalination of brackish water. Such a hybrid scheme with ED could have two benefits: a higher overall water recovery and consequently a lower capacity of the pre-treatment and a less extensive pre-treatment and post-treatment scheme (depending on the second desalination step).

CAPACITIVE DEIONIZATION

State-of-the-art desalination technologies, such as reverse osmosis and multistage flash distillation, produce fresh water from concentrated saline streams, like sea water. When desalinating less concentrated saline streams, e.g., with salt concentrations below 3,000 ppm, these technologies become less energy efficient when energy is expressed per amount of salt removed.

Instead of removing water molecules from the salt solution, capacitive deionization (CDI) removes the salt ions from the solution, which can be energetically advantageous at low ionic strength. Additionally, CDI can also selectively remove one specific ion from a multicomponent solution, i.e., CDI is capable of ion fractionation.

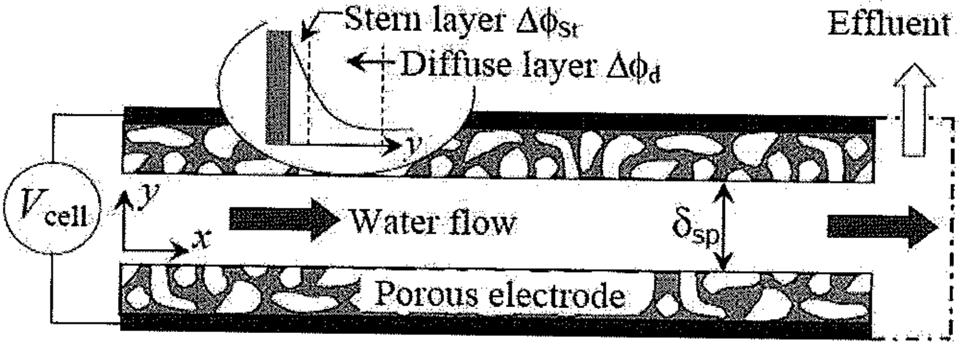

Figure 2. Schematic representation of a CDI cell, in which salt is removed from the spacer (flow) channel and is stored in the electrostatic double layers inside porous activated carbon electrodes.

CDI is an electro kinetic process where an electrical potential difference is applied between two porous electrodes placed on both sides of a flow channel that passes water to be desalinated (Figure 2). The flow channel is located parallel to the electrodes. Due to the applied electric field, ions are removed from the water and accumulate in the electrical double layers (EDLs) that form inside the micro pores in the porous carbon particles which are the major constituent of the porous electrodes.

In CDI an electrical current runs in one direction during ion adsorption (the water purification step), namely from cathode to anode (electrons run in the reverse direction) and runs in the other direction during the release of the stored salt in the regeneration step. An advantage of CDI is that the electrical energy invested in charging the cell during purification, and which runs 'backward' during regeneration can be used to partially charge up another cell running in purification-mode. To achieve a high water recovery (volume of produced water relative to total inflow water) the regeneration step is typically shorter in duration than the purification step and/or has a lower water flow rate, resulting in high salt concentrations in the waste water stream.

Many parameters can be used to define the operating costs and energy/salt performance of a CDI system. Here we focus on the energy expenditure per removed salt molecule, X, and the charge efficiency, Λ (Zhao 2010, Biesheuvel 2009a, 2009b). Both parameters require first of all analysis of the current(time) signal. The integration of this curve over the duration of the purification step gives the total charge transferred, Σ, which can be expressed in Coulomb per gram of electrode. Multiplying current with the cell voltage, V_{cell} and integration over time, results in the input energy per cycle, E, which can be expressed in Joule/gram. Salt removal Γ_{salt} (in mol/gram) is calculated from data for the effluent salt concentration vs. time-curve. Now, the charge efficiency Λ is defined as $\Lambda=(\Sigma/F)/\Gamma_{salt}$ (where F is Faraday's number), while the energy per removed salt molecule is defined as $X=E/\Gamma_{salt}$. In Fig. 3 we show some example results of X and Λ as function of inlet salt concentration in a CDI cell operating at $V_{cell}=1.2$ V.

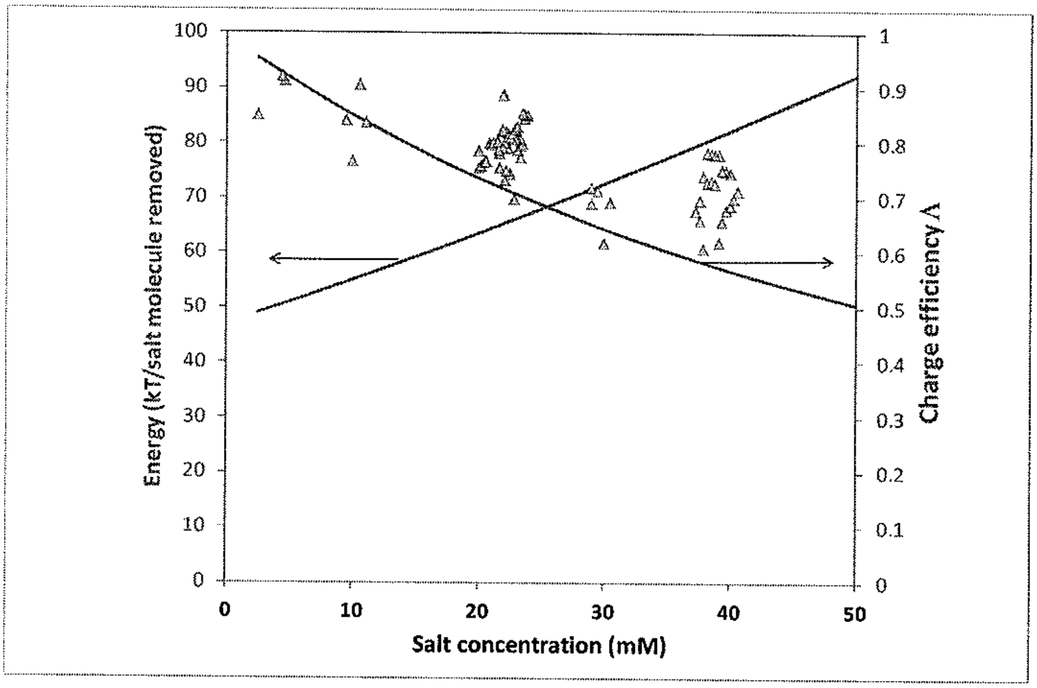

Figure 3. Energy per removed salt molecule (left y-axis) and charge efficiency (right y-axis) in a CDI cycle as function of inlet salt concentration (pure NaCl; lines: theory; points: data for charge efficiency from Biesheuvel 2011.

As Figure 3 shows, the lower the salt concentration, the higher the charge efficiency, which implies that less electrons need to be transferred per salt molecule stored. At the same time the input energy per removed salt molecule goes down. Thus CDI can be applied for inlet salt concentration of below ~30 mM (1750 ppm for NaCl). Current developments are to place ion-exchange membranes in front of both electrodes: an anion-exchange membrane in front of the anode (where anions are stored), and a cation-exchange membrane in front of the cathode. It has been found that implementing such membranes (MCDI) increases the charge efficiency, Λ, to values close to unity (Biesheuvel 2011, 2010a), thereby extending the application range of this technology to regions of higher ionic strength.

SUPER-CRITICAL FLUID EXTRACTION

The commonly applied technologies for the treatment of saline streams of all concentrations focus on the removal of the liquid phase, which represents the main part of these streams, from the saline part instead of aiming to remove the salt fraction. Furthermore, these technologies are limited to a certain low to medium concentration range (1000 - 40000 ppm) and inevitably produce a brine stream as waste product as consequence of the respective separation principle (Semiat 2000). This brine stream is considered as the major bottleneck in the sustainable application of desalination next to the energy demand (Einav *et al.* 2003).

The supercritical phase of a compound is considered as additional phase to the three common ones:

solid, liquid, vapour. In the case of water, water reaches its supercritical state of 647 K and 22.1 MPa. Coming along with this transition, the majority of the properties change tremendously. Water is an excellent solvent for salts at ambient conditions, while supercritical water is hardly able to keep salts in solution. Due the change of the dielectric constant from ~ 80 at 293 K / 0.1 MPa to < 5 at 673 K / 23 MPa, water becomes a nonpolar medium. Consequently, the solubility of inorganic compounds decreases to almost zero in the supercritical state (Knox 2005, Figure 4). The excess amount of salt precipitates and forms an additional solid phase. These solid particles can then be separated from the liquid phase by common solid phase separation technologies such as hydrocyclones.

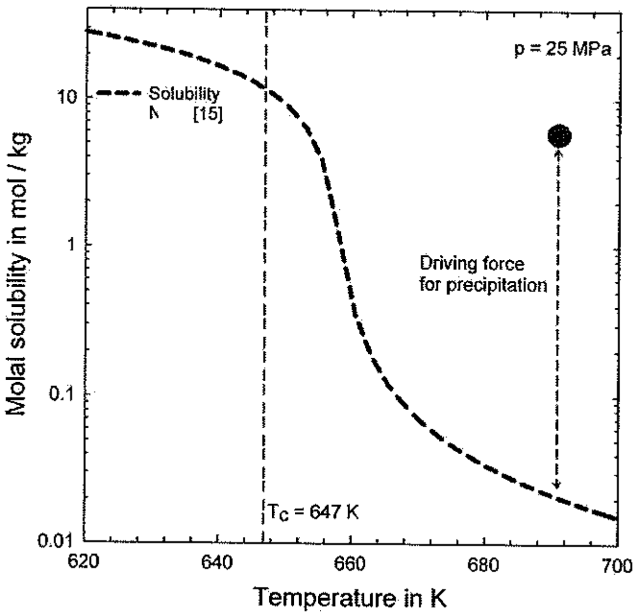

Figure 4. Solubility of sodium chloride at 250 bar and driving force for precipitation (Leusbrock *et al.* 2008)

For the process and the precipitation, it is beneficial – in contrast to all other desalination technologies -, if the feed stream has a high salinity. The difference between this high salinity and the solubility at supercritical conditions acts as driving force for the precipitation, meaning that a higher feed concentration enhances the precipitation. Furthermore, no liquid brine stream has to be treated as a waste stream as the formed solid phase is removed from the system. On the contrary, these removed salts can be used for later application and can represent a value product of the process. In this context, it is interesting to mention that all salts have solubilities depending on temperature and pressure what enables to separate different salt fractions by multi-step design comparable to distillation columns for organic compounds (Leusbrock 2011). Resulting from the feed concentration independence, this technology can be applied to treat brine streams from RO or comparable desalination technologies or other waste streams with a high salinity, for which no efficient technology for the post-treatment is available.

The quality of the effluent of a SCR process depends on two aspects: the current solubility at the conditions in the setup (usually determined by temperature and pressure regulation) and the efficiency of fluid / solid removal step. While the efficiency of the separation step is mostly determined by its design parameters, easy adjustments are possible in temperature and pressure and thereby solubility. It can be concluded that the energy demand of such a process is on the one hand side is independent of the feed concentration, while on the other side the quality of the product stream determines the overall energy demand. The production of high quality water (< 100 ppm) requires a substantial increase in temperature and thereby in energy. The production of an output stream with a concentration of ~1000 ppm on the other hand needs a comparably small amount of energy while still offering a viable solution for the treatment of high salinity streams (Leusbrock 2011). Here, smart process options are possible, where several technologies are combined (e.g. recycle of the SCR liquid product stream to the feed of a RO unit), while the energy demand is reduced (in combination with energy recovery units for heat and pressure), a brine stream is avoided and the salt fractions are separated and can be used as value products.

BLUE ENERGY

Salinity-gradient energy is a renewable energy source that was recognized already in the 1950s (Pattle 1954). It was mentioned that besides the gravitational potential, the natural runoff in coastal areas has a huge physical-chemical potential. This potential is the result of the salinity-gradient between the mainly-fresh runoff (river mouths) and the receiving mainly-saline reservoirs (seas and oceans). When a river runs into a sea, spontaneous mixing of fresh and salt water occurs. This natural process is irreversible; no work is attained from it. However, if the mixing is done (partly) reversibly, work can be obtained from the mixing process. In literature (Norman 1974; Weinstein and Leitz 1976) it was assumed that from each cubic meter of river water 2.3 MJ of work could be extracted. According to Norman (Norman 1974): *The tremendous energy flux available in the natural salination of fresh water is graphically illustrated if one imagines that every stream and river in the world is terminated at its mouth by a waterfall 225 m high...* For the Netherlands, a geographically low-lying flat country with about 27% of its area and 60% of its population located below sea level (Rosenberg, no date), this provides an extremely interesting opportunity to harvest energy from the estuary of two important European rivers, which together with their distributaries form the Rhine-Meuse-Scheldt delta. As an example, keeping in mind the words of Norman, the 30-km long Afsluitdijk that dams up the river mouth of the river IJssel (a distributary of river Rhine) becomes comparable to a huge power dam of over 200 m high. The 1,100-km^2 Lake IJssel (the artificial estuarine reservoir of river IJssel) becomes comparable to an enormous energy reservoir with over a billion m^3 storage capacity (assuming a level difference of only 1 m).

The energy can be made available from controlled mixing of two solutions with different salt concentrations. The mixing process can be controlled by means of selective membranes. The use of selective membranes means that the mixing is limited to one of the components, either the solvent (i.e., water) or solutes (i.e., dissolved salts). In the literature, several techniques for energy conversion of the salinity gradient have been proposed, either based on the use of water-permeable membranes as in Pressure-Retarded Osmosis (PRO) (Post, Veerman et al. 2007), or based on the use of ion-selective membranes as in Reverse Electro Dialysis (RED) (Post, Hamelers et al. 2008) and a Membrane-Modified Supercapacitor Flow Cell (Sales, Saakes et al. 2010). It is tempting to compare these technologies with their 'mirror image', the previously discussed reversed operated desalination technologies: Reverse Osmosis (RO), Electro Dialysis (ED), and Capacitive De Ionization (CDI). To get a grasp on the principles and the process technology this would help, even for imagination, but it is too easy to translate the design rules and economic figures of a desalination plant to a salinity-gradient power plant.

INTER RELATIONS AND SUSTAINABILITY

Salinization of fresh water resources requires desalination techniques that are optimal with respect to the degree of salinization. To produce drinking or irrigation water from brackish water (500 – 3000 ppm) RO and CDI can be applied. Energy optimized RO is economically feasible at large scale operation. CDI is a less complicated operation and can be well applied at small scale at the end users site. For brackish water the water recovery is high and the volumes of the brine are limited.

For production of fresh water from seawater RO is the state of the art technology. ED is efficient at high concentrations but is not capable of reaching low salt concentrations. ED as a pre-treatment to RO, producing brackish water as a feed for RO, is a very promising process. The overall recovery can be higher that when using RO alone, and brine volumes will be reduced.

In closed loops water systems, e.g. in horticulture, selective desalination, retaining nutrients in the water cycle, can strongly decrease the demand of fresh water. ED and CDI technology can be developed to make selective desalination possible.

Sustainability of desalination is determined by energy consumption and brine volume. The brine is a waste stream that threatens groundwater and marine environment. Super critical fluid extraction converts a brine to brackish water and solid stream. In this way desalination yields salt with economic value, and anti-scalants, that end up the solid stream is can be reused.

Salinization of delta regions and arid regions can lead to salt gradients that are a source for blue energy production. Super saline water in dead end lakes like the Dead Sea can be combined with seawater, or seawater can be combined with brackish or fresh water to produce electric energy.

Proper choice, optimization, and combination of technologies in series or parallel will lead to a sustainable way to deal with salinized delta regions.

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