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Authors: Alexander Fayer[1]

Affiliations: Alexander Fayer ha-Nadiv Str Israel[1]

Orcid ids: 0000-0003-3224-3560[1]

Contact e-mail: alxpfayer@yahoo.com

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Continuous Cycle of Water Desalination Utilizing Hydrogel as Draw Agent.

Alexander Fayer

This document discusses operation of desalination system permanently extracting water from hydrogel draw agent by specially selected wicks. Due to its peculiarity the system combines advantages of both forward and reverse osmosis approaches such as, low power consumption, passive process of a freshwater extraction, continuous duty cycle and scaling possibility. While in modern systems an energy consumption of seawater desalination reaches of about 3 kWh/m^3 , including pre-filtering and ancillaries [1], the same parameter for the specific system expected to be as low as for local fresh water supply i.e., 0.2 kWh/m^3 .

In order to facilitate the description, but without limiting the generality, we will consider a notional one-dimensional water desalination processes that can take place in a vertical vessel divided into three parts. Let the upper third of the vessel be filled with running saline water and separated from the middle part by a semipermeable membrane for forward osmosis desalination. The middle part crowded with unsaturated hydrogel material and separated from the bottom part of the vessel intended for collection of the fresh water by a partition. A wick passes through the partition, and its upper part is immersed in the hydrogel and the lower part hangs freely. Saline water pressure P_f at upper vessel's part does not exceed pressure values in ordinary drink water supply systems i.e. of about 0.5 MPa .

Only water molecules penetrate through the membrane and cause swelling of the constrained hydrogel material. The swelling leads to an increasing of hydraulic pressure and probably efflux of part of water through the wick starting from some pressure value. Hydrogels consist of two phases, the polymer network which is constant in quantity, and the aqueous phase, which is variable. The system under consideration would not reach the state of thermodynamic equilibrium between this phases if a part of the desalinated water flux entering the hydrogel is diverted through the wick to the lower part of the vessel. An implementation of the described above scheme with effective value of out-coming flux of the freshwater imposes

number of specific requirements to the properties of utilized materials. These requirements are discussed below.

Hydrogel draw agent hydration.

One of most prominent properties of hydrogels is their ability to absorb large quantity of water without dissolving and to swell in consequence of this process. Water molecules accommodated by hydrogels have different properties depending on the position and interactions within the hydrophilic network. A model presented in 1973 by John and Andrade [2], defines three types of water in hydrogels - non-freezing or bound water, free or bulk water and freezing interfacial or intermediate water. Molecules of free water are not affected by the polymer and freeze / melt similarly to pure water; molecules of bound and in some degree intermediate water are immobilized by binding to the polymer chains through hydrogen bonds. Other properties of the bound and the intermediate water (relaxation time, polarization, etc.) also differ from properties of free water.

Diffusion in hydrogels is affected by the level of hydration. Experiments with tracer molecules dissolved in water elucidate that at high level of hydration, the process occurs primarily as the free water diffusion; however, at low hydration, it takes place as diffusion in the bound water.

Note that the thermodynamic equilibrium between hydrogel and external aqueous solution corresponds to the strictly defined amount of all three types of water retained by the hydrogel in the given conditions.

The excess pressure of water in hydrogel relative to the pressure of the pure external in this state is defined as the osmotic pressures difference and can be expressed through the difference of the corresponding chemical potentials [3,4] for ideal elastomeric gels.

The hydrogel's osmotic pressure that can be called the "driving force" of the hydration process is a complex parameter.

The total osmotic pressure in a swelling hydrogel Π can be divided into three separate parts using the Flory–Rehner theory. This theory [5] states the perfect separability of the total free energy, (ΔF), into an elastic, mixing and ionic contributions, each with an associated osmotic pressure (Π_{elastic} , Π_{mixing} and Π_{ionic}),

$$\Pi = \Pi_{\text{ionic}} + \Pi_{\text{mixing}} + \Pi_{\text{elastic}}. \quad (1)$$

The mixing and ionic contributions are commonly seen as the cause of gel swelling whereas the elastic portion restricts the large expansion of the material.

The mixing osmotic pressure refers to the attraction of solvent molecules in the external solution to the hydrophilic polymer chains and can be expressed [6] by the Flory–Huggins equation

$$\Pi_{\text{mixing}} = - \frac{RT}{V} [\ln(1-\varphi) + \varphi + \chi \varphi^2] \quad (2)$$

where φ is the molar volume of the solvent, R is the universal gas constant, T is the temperature (Kelvin), V is the current solid volume fraction and χ is Flory–Huggins parameter derived from the solid-fluid interaction. This parameter is material and environment dependent and defines deswelling properties of hydrogels.

For $\chi > 0.5$ the hydrogel solution is unstable for small fluctuations [7] and gives off water relatively easily.

The equilibrium pressure for real hydrogels is different from the osmotic pressure and refers here as osmotic swelling pressure. Its value as well as equilibrium swelling ratio and swelling kinetics are different for free standing and confined hydrogels. According [10,11] the constrained hydrogels reach equilibrium with external solution at higher osmotic swelling pressure than free-swelling ones.

A steady state water flow if such established along the porous medium like confined hydrogel can be described by following equation [8]:

$$Q \approx \frac{SoK(\Delta\Pi - \Delta \mu)}{d\mu} \quad (3)$$

where Q is the rate of water flow, K is the hydraulic conductivity of the hydrogel block, d is the hydrogel layer thickness, S_0 is the hydrogel cross section, μ is the solvent viscosity, ΔP and $\Delta \Pi$ are the hydraulic and osmotic pressure differences between the input and the output edges of the hydrogel block, respectively. Note that only movement of unbounded water contributes to flow, while liquid molecules held by absorptive forces is essentially immobile [9].

Forward osmosis membrane assembly – hydrogel interface.

A flow of water through the semipermeable membrane can be described by Darcy's law in its complete form [12]:

$$Q = \frac{SD_w C_m}{\lambda} \left(1 - \exp \left[\frac{V_w}{RT} (\Delta \pi - \Delta P) \right] \right) \quad (4)$$

where Q is the rate of water flow, S is the effective cross section of membrane, D_w is the average water diffusion coefficient in the membrane, C_m is the equilibrium concentration of water in the membrane, λ is the membrane thickness, V_w is the partial molar volume of water, R universal gas constant, T is the temperature (Kelvin), ΔP is the pressure difference across the membrane assembly i.e., $\Delta P = P_p - P_f$, where P_p is hydraulic pressure at the cross section of hydrogel located at the distance of free path of water molecules from the membrane assembly and P_f is the feed pressure, and $\Delta \Pi$ is the “the driving force” of water flow i.e. difference of osmotic pressures Π_p and Π_f at the above mentioned cross section and the feed solution respectively. Fick's law gives the dependence of Π_f on the solution concentration [18]:

$$\Pi_f = \frac{n}{V_c} x_i RT \quad (5)$$

In this equation, n are the moles of dissolved molecules (e.g., NaCl), V_c is the volume of solvent, and i is the van't Hoff factor (e.g., $i = 2$ for NaCl). As follows from (5), the osmotic pressure Π_f increases linearly with increasing salt concentration at low concentrations.

Elliot J. Carr [13] defined the characteristic timescale for a diffusion process τ as the maximum value of the mean action time across the layer

$$\tau = \frac{1}{2} \frac{l^2}{D} \quad (6)$$

where l is the layer's thickness and D is the coefficient of diffusion.

The characteristic timescale of water diffusion in hydrogel block exceeds by many orders of magnitude the same parameter for the membrane assembly. As a result, a gel layer with a thickness approximately equal to the pore size in a rigid membrane's base and immediately adjacent to it approaches the state of local equilibrium with the feeding solution however does not reach it [14]. In this the water flow through the membrane decreases significantly compared to its value in the absence of a hydrogel (effect of the concentration polarization). Because of osmotic flow and hydraulic flow require the same pressure drop along the membrane pore to generate equal flow [19] this effect can be expressed by system of Equations (7)

$$\left\{ \begin{array}{l} \Pi_p = \Pi_f - \Delta\Pi_{\text{eff}} \\ P_p = P_f \end{array} \right. \quad (7)$$

A magnitude of $\Delta\Pi_{\text{eff}}$ depends on the properties of both the membrane assembly and the hydrogel and lies in the range of 1200-2200 kPa [20]

Considering the relations given in (7) Eq. 3 for steady state water flow along the hydrogel block can be rewritten as:

$$Q = \frac{KSo[\Pi_l - (\Pi_f - \Delta\Pi_{eff}) - P_l + P_f]}{d\mu} \quad (8)$$

Since the resistance of the hydrogel block is at least four orders of magnitude greater than the analogous parameter of the membrane assembly (an asymmetric membrane normally consists of a dense layer of 0.1–1 μm thick and supported by a highly porous, 100–200 μm thick support layer [21]) the same equation can be used to describe the water flow through complete membrane-hydrogel block subsystem.

Based on Eq. (8), water flow is decreasing function of P_l and reaches zero at its ceiling value (or upper limit) $P_l^{\max}$

$$P_l^{\max} = \Pi_l - \Pi_f + \Delta\Pi_{eff} + P_f \quad (9)$$

Water efflux from the hydrogel draw agent

Fresh water extraction is a bottleneck in the hydrogel-based desalination technology because number of reasons described in literature.

Quit a few methods have been tested to solve the problem, however none of them has been able to provide the energy-efficient process with a continuous duty cycle [16,17].

The proposed system provides the desired effect in two-stage process:

- outflow of water from the hydrogel medium into o the wicking material;
- dripping or evaporation of water from the wick.

The evaporation-based system implies the presence of additional subsystems controlling temperature, humidity, vapor transport and condensation. It has an elevated cost and will not be discussed in prospect.

Wicking is a spontaneous movement of liquids into porous media under the action of the capillary suction pressure. Value of the suction forces is governed by the

properties of the liquid, liquid-medium surface interactions, and geometric configurations of the pore structure in the medium.

At the conditions of steady state all liquid entering to the wick per unit of time will leave it in the same period by the drops flow (evaporation protected wicks).

Recently invented types of wicks can drain fresh water with corresponding suction pressure P_{sw} as high as hundreds of kilopascals. However, the implementation of the wicking process is complicated in the case since water retaining component of the osmotic pressure (“suction pressure of hydrogel”).

The lowest hydraulic pressure P_t (“threshold pressure”) starting from which the water enters the wick is determined from the balance of promoting and hindering forces acting on an element of free water at the hydrogel-wick interface. At real desalination system this pressure can be unavailable i.e., its value exceeds the upper limit pressure $P_{Lmax} < P_t$. Fig.1 illustrates the positive difference between P_{Lmax} and the threshold pressure P_t ($P_{Lmax} > P_t$) which corresponds to nonzero water entering the wick at the operating point W.P.

Figure1. Schematic diagram of the inlet (line 1) and outlet (line 2) flows as function of the hydraulic pressure at hydrogel/wick interface.

Both sign and magnitude of the difference depend on the sort of the hydrogel, residual concentration of salt in the water passed through the membrane and concentration polarization properties of membrane.

The method of desalination presented above theoretically possible but difficult to implement since there is a problem with the selection of a hydrogel providing the relation $P_{Lmax} > P_t$ [20,22]. Progressing rapidly family of gradient hydrogels [28] is a promising candidate for this mission. However, an alternative approach was developed in presented below e experimental part of the work.

The object of the experimental study was stimulus sensitive hydrogels with a goal to induce local release of water from the hydrogel granules to intergranular space where the hindering forces are neglected.

Potassium polyacrylate SAP (an anionic polyelectrolyte with negatively charged carboxylic groups in the main chain) was selected as the material to be tested.

Superabsorbent polyacrylate hydrogels are a unique family of swellable polymeric materials. Due to three-dimensional crosslinked polymeric network structure, they can absorb disproportionately large quantities of different activation fluids during swelling and their specific chemical crosslinks comprised of both hydrogen and ionic bonds. As a result of their non-toxicity, versatility, suitability and high pH sensitivity polyacrylate hydrogels have increasingly been used in a wide range of applications over the past decade.

The local release of water from hydrogels under such factors as laser pulse and mechanical puncture was observed in works [24] and [25]. However, these methods cannot provide collection of the released water. Our technological approach was to use wicks with surface pH different from the pH of hydrogel medium for both the local release of water from hydrogel granules and its collection from the intergranular space.

Experimental Part

Materials

As part of the experiment, there was a need for hydrogel and wick samples with different pH levels. This problem was solved by ordering multiple portions of these

materials from the same supplier: Technical grade Hydro Crystals of Potassium Super Absorbent Polymer INCEPTION-Y-21574 from Inception and Absorbent Nonwoven Mesh Fabric Roll from WINCLEAN. 1/4 Inch Self Watering Wick Cord was pursued from ORIMERC. FTSH20 Seal Water Filter-Single Use Pouches from Fluid Technology Solutions were emptied of the contents, cleaned and used as forward osmosis membranes. Analytical grade NaCl used for preparation of solutions of sodium chloride— 2.5g, 5g, 7.5, 10g and 35 g of NaCl per 1000 ml of distilled water. Analytical grade sodium bicarbonate used for preparation of 0.3 M buffer solutions (25.2g CHNaO_3 per 1000 ml of distilled water).

Methods

The SAPs was supplied to the laboratory in the form of dry, irregularly shaped crystal granules. The crystals were mixed with distilled water in order to form a hydrogel and then to wash it from a soluble phase as that of linear polymers repeatedly.

A verification of water extraction feasibility from swelled hydrogel granules preceded by complete removal of liquid from the intergranular space of the washed hydrogel.

The procedure used for this purpose described below:

Stage1. Placing of the washed hydrogel enriched by intergranular water into a pouch formed by sealed forward osmosis filter and measurement of its starting pH level and mass.

Stage2. Placing of the pouch with hydrogel into large reservoir filled by 35 g of NaCl per 1000 ml of distilled water solution and monitoring of hydrogel's pH value and mass change.

As follows from our preliminary experiments the difference in the osmotic pressures between hydrogel and solution in the reservoir if applied 24 hours leads to full extraction of the intergranular water and partial water depletion of the hydrogel granules due to forward osmosis process.

Stage3. Transfer of the pouch to a reservoir filled by distilled water to make sure that the hydrogel is swollen partially (according to the direction of the water flow).

Stage4.

Transfer of the pouch with the hydrogel to reservoir with the aqueous NaCl solution of a certain concentration: 0g, 2.5g, 5g, 7.5g or 10g per 1000 ml of distilled water and its exposure in this state till equilibration between two subsystems

separated by the forward osmosis membrane.

Stage5.

Transfer of the equilibrated hydrogels to glass beakers for the following investigations.

The pH level of Absorbent Nonwoven Mesh Fabric from different rolls have been tested following testing procedure #2 described at [27] by digital pH meter (Digita). According to the test results, two rolls of fabric were selected for the experiments. The surface pH levels of the selected fabrics were 7.8 and 7.2 while the front rate advancement of a distilled water in both laid in the range of 3000 ± 50 mm/hour.

Results and discussion

The effect of the wick's surface pH-initiated water release was investigated by simultaneous immersing of one end of each of the two test wicks into the bicker filled by hydrogel while the other end of the wicks hung loosely down. The measurement of average rate of the liquid front advancement along the wicks has been performed by optical image analysis method [26]. (The wicks were protected from water evaporation). The phenomenon of water extraction by wicks has been detected experimentally by measurement of liquid front propagation rate at various pH values of the wick and hydrogel media as well as the salinity of equilibration solution.

Fig. 2 reflects an exponential drop in the rate of the water front advancement occurring with increase in the concentration of the equilibrating solution and a corresponding decrease in the amount of water in the hydrogel characterized by pH value equal to 6.5.

Two wicks 1 and 2 differing in the values of their surface pH (7.8 and 7.2 respectively), were used in this experiment. As can be seen from the same graph, the rate of water extraction by the first wick W1 is higher than by the second one ($W1-W2 > 0$). There are two possible reasons for this phenomenon: inequality of the suction forces of two wicks and inequality of local hydrogel shrinking since wicks pH difference. In the first case the sign of difference ($W1-W2$) is independent but in the second case must be dependent on the hydrogel PH value change in a certain range. The results of the experiment with a change in the pH value of the hydrogel presented at Fig. 3.

Figure 2. Water front rate as function NaCl content in the equilibration solution

Figure 3. Rate of water front propagation along wicks 1 and 2 inserted in hydrogels equilibrated with distilled water and having different pH values.

About the same ratio between the extraction rates is maintained for hydrogel with pH equal 6.5 and 6.9. However, the test provided with hydrogel whose pH was 7.6 (7.6) resulted in a change in the sign of the difference ($W1-W2 < 0$). Note that the Crystals of Potassium Super Absorbent Polymer were mixed with Sodium Bicarbonate of 0.3 M buffer solutions in order to obtain the hydrogel with the specified value of pH

Thus, it can be concluded that the obtained experimental results confirm the possibility of extracting water from pH sensitive hydrogels using specially selected wicks. Unfortunately, a special literature does not contain relevant data about the potassium polyacrylate hydrogels/buffer solutions equilibrium which could confirm or deny the conclusions made.

The effects described above have been used to build a prototype of continuously operating forward osmosis desalination system. The schematic arrangement and appearance of this completely passive device presented at Fig.4.

Figure 4. The schematic arrangement a) and photo of the desalination system prototype.

The authors have observed a spontaneous flow of fresh water outflowing from the container with saline water and consistently passing through the semi-permeable membrane, the hydrogel block, and system of the specified wicks. At the conditions then the salinity of the source water is in the range of 0 to 10 gram per liter the potassium polyacrylate hydrogel acts as a “water pump” and a “water bridge” simultaneously. This phenomenon can be used for desalination of underground water for needs of irrigation whereas desalination of sea water requires application of pH sensitive hydrogels with higher osmotic pressure.

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