

The Ammonia-Carbon Dioxide Forward Osmosis Desalination Process

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Introduction

There is a finite amount of freshwater readily available for human consumption and use. This supply is already strained due to competing utilization demands for farming, industrial, commercial and domestic uses. Increasing populations place further strain on already-dwindling or otherwise impaired water sources. With the world population expected to exceed ten billion by 2040, the draw on these resources will become ever less sustainable. Growth in population necessitates the cultivation of alternative water sources.

Desalination

One such alternative is the vast quantity of saline water in the oceans and large brackish groundwater reserves often found in arid regions. These sources represent over 97 percent of the world's water and if tapped economically they would yield a virtually unlimited supply of water.

The cost associated with desalinating these types of water, however, is high. Currently, most of the world's desalination capacity is based on thermal technologies, primarily multi-stage flash (MSF) distillation and multi-effect distillation (MED). MSF and MED are popular in parts of the world where thermal energy is readily available and inexpensive. The drawbacks of these technolo-

gies are the large thermal energy inputs required to vaporize water, the brine discharges and the relatively low water recoveries, with electrical requirements that often approach those of reverse osmosis (RO).

RO continues to gain popularity as a successful desalination technology; nearly all desalination plants built today are RO plants. Its benefits include the capability of achieving higher recoveries than those typical of its thermal counterparts, while using less overall energy. However, electricity use is still high and brine discharge problems remain. The production of brine is a significant drawback and requires that the plant be located near an ocean where discarded brine has less (albeit still a considerable) impact on the environment. In brackish water applications, the quantity of brine produced precludes the use of economic solar pond evaporation and ground well injection will increase source water salinity over time. These technologies, therefore, cannot be used to desalinate inland brackish groundwater sources as the brine cannot be disposed of in a sustainable manner.

FO not RO

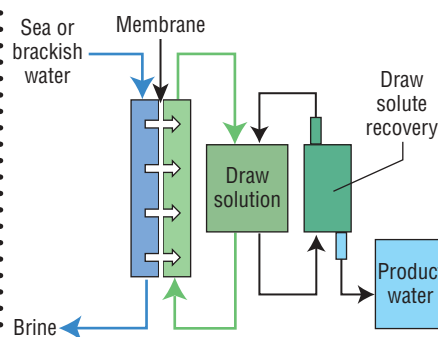
With issues of energy use and water recovery at the forefront of the desalination debate, many are investigating an alternative. Forward osmosis (FO) is a

membrane based separation process, like RO, which relies on the semipermeable character of a membrane to remove salt. However, unlike RO, the driving force for separation is osmotic pressure, not hydraulic pressure. By using a concentrated solution of high osmotic pressure called the draw solution, water can be induced to flow from saline water across the membrane, rejecting the salt. The (now diluted) draw solution must be re-concentrated, yielding potable water and recycling the draw solute.¹ Figure 1 presents the general process diagram.

The ideal draw solution

Since the recovery or utility of the draw solute is critical to the successful

Figure 1. Forward osmosis desalination process schematic diagram.



implementation of the FO process, various draw solutes may be used, depending upon the intended use of the desalinated water. One current version of FO uses an edible solute, such as concentrated glucose. In this case, the concentrated solute is diluted by the permeate water yielding a nutritious drink. This is an example of FO that utilizes the draw solute rather than recovering it. Other suggested draw solutes are those that can be chemically or thermally precipitated from solution for removal. Some propose the use of dissolved gases that can be removed by thermal means, or the use of larger molecular weight solutes that can be separated by physical means. With these two latter options, the draw solute is concentrated and recycled in a closed loop, as Figure 1 illustrates. All of these various draw solutions rely on specific chemical and physical properties of the solute which make them ideal for certain FO processes.¹

A draw solute for use in a continuous FO desalination process, in which the draw solute is recovered, must have certain characteristics to make the process economically viable. For this FO process configuration (see Figure 1) the draw solute must have a high solubility, a low molecular weight, an easy removal

mechanism and a low toxicity. High solubility coupled with low molecular weight allows for the generation of large osmotic pressures which lead to high product water flux and recovery. An easy removal mechanism is critical to the economic viability of the FO process since the overwhelming majority of the energy used in the FO process is used for draw solute recovery. A non-toxic draw solute is critical for public acceptance of a new desalination technology, as trace amounts of the draw solute may be present in the product water.

The novel ammonia-carbon dioxide draw solution

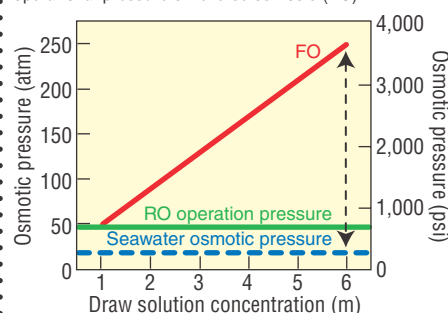
The FO process currently being investigated uses a recyclable solute composed of ammonium salts. These salts (a mixture of ammonium bicarbonate, ammonium carbonate and ammonium carbamate) are formed when ammonia and carbon dioxide gases are mixed in an aqueous solution.^{2,3} The salts are highly rejected by the semipermeable membrane used in FO and are highly soluble, leading to the reliable generation of high osmotic pressures for the FO process (see Figure 2).

Once the concentrated draw solution is used to effect separation of water from

the saline feed source, the subsequently diluted draw solution may be treated thermally to remove its ammonium salt solutes, producing fresh water as the primary product of the FO process. This thermal separation of draw solutes is based on the useful characteristic of these salts to decompose into ammonia and carbon dioxide gases when the solution is heated. The temperature at which this occurs is dependent on the pressure of the solution. If a vacuum distillation column is used for this separation, the tem-

Figure 2. Osmotic pressure as a function of ammonia-carbon dioxide draw solution concentration (FO line).

Also shown for comparison are the seawater osmotic pressure (black dashed line) and approximate operational pressure of reverse osmosis (RO).



perature of heat required can be quite low, in the range of 35-40°C (95-104°F) given an ambient temperature of 15-20°C (59-68°F).

The use of this ammonia-carbon dioxide draw solute thereby allows for effective desalination of saline feedwater sources using little more than low-grade heat (very little electricity is required for unpressurized process pumping). Furthermore, the high osmotic pressures that solutions of this type may generate allow for very high feedwater recoveries. This has the benefit of reducing brine discharge volumes, electrical requirements for feedwater pumping and process capital costs.

FO performance

Performance of the FO desalination process was measured in the lab by determining the permeate water flux and salt rejection of several commercially available polymeric membranes³. Three membranes were tested for water flux and salt rejection performance using the ammonia-carbon dioxide draw solution and a sodium chloride feed solution. Two of these membranes (TFC-1, TFC-2, thin film composite) were designed for use in RO. The other (CA, a membrane derived from cellulose acetate) was designed for FO landfill leachate dewatering. All membranes used were commercially available at the time of testing. Figure 3 shows the flux performance of each membrane under a set of specified experimental conditions.³

Figure 3 shows that water flux performance of the CA membrane was high, at around 15 gfd (gallons per square foot of membrane area per day). For comparison, typical RO systems treating water of similar salinity run between nine and 11 gfd. The NaCl rejection for the CA membrane in these conditions also exceeded 95 percent, which is reasonable considering the membrane is not designed specifically for desalination pur-

poses. Figure 3 also illustrates the poor flux performance of the RO membranes when used for FO. Similarly, NaCl rejection of the RO membranes was also low (less than 80 percent). These results beg the question: Why do the RO membranes perform poorly in FO?

Internal concentration polarization

RO membranes are designed to have a thin, dense, separating layer called the active layer, which is supported by multiple porous layers. The active layer rejects the salt while the supporting layers provide mechanical stability to the membrane during pressure-driven water flow. As salt rejection occurs, a region of increased salt concentration forms near the membrane surface. This phenomenon, referred to as concentration polarization, is reduced if turbulence is induced near the membrane surface, facilitating the diffusion of the concentrated solute back into the bulk solution. This is often accomplished by using crossflow (at relatively high velocities) and creating turbulence with spacers within the flow channels.

The same phenomenon will occur in FO on the feed side of the membrane. However, a similar but *dilutive* effect simultaneously occurs on the permeate (or draw) side, reducing the effective driving force of the draw solution. This phenomenon is intensified by the presence of the porous support, which provides a protected environment where crossflow cannot mitigate the polarized layer. Termed 'internal concentration polarization', this phenomenon severely reduces the osmotic driving force when asymmetric membranes are used in FO. Internal concentration polarization is illustrated in Figure 4.⁴

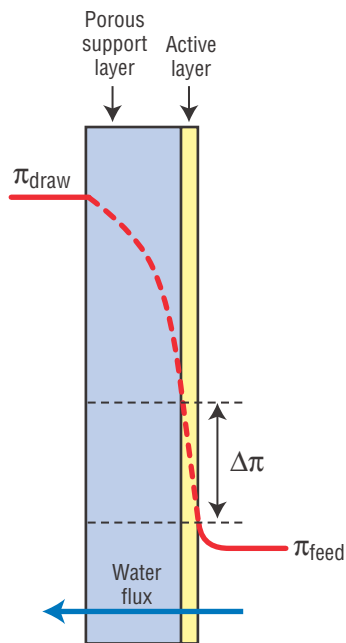
The TFC-1 and TFC-2 membranes, comprise a polymer porous support layer cast upon a thick fabric backing layer, which provides mechanical strength. The FO membrane also contains a porous polymer support layer, but it is relatively thin and the membrane lacks an additional fabric layer. Mechanical support is instead provided by a mesh imbedded in the porous polymer matrix⁵. This allows for a thinner support layer, which results in a reduced prevalence of internal concentration polarization. The reduced internal concentration polarization results in a greater utilization of the osmotic driving force which in turn leads to either higher water fluxes or increased recovery.

Draw solute recovery

The draw solutes are removed from

Figure 4. Illustration of internal concentration polarization in the FO process.⁴

π_{Feed} and π_{Draw} indicate the bulk feed and draw solution osmotic pressure, respectively. Note the external concentration polarization on the feed side of the membrane which is a result of the dilute feed solute being rejected from the membrane surfaces as water flux occurs. Also note the osmotic pressure gradients that exist inside the membrane due to the dilution of the draw solute in the porous support layer (internal concentration polarization). Both of these phenomena reduce the effective osmotic driving force, $\Delta\pi$.

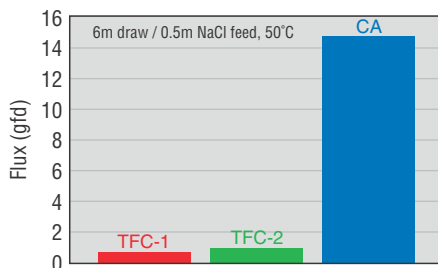


the product water and recycled within the system by a thermal separation process. The most readily adaptable technology for this purpose is a distillation column, or more specifically, a reboiled stripper. The diluted draw solution is introduced to the column at its top and heat is introduced at its bottom. The equilibrium state of a column of this type, given an appropriate height, results in a fresh water stream from the base of the column and a vapor stream at the top, containing nearly all of the ammonia and carbon dioxide present in the dilute draw stream (less than one ppm ammonia remains in the product water stream).

Along with the gaseous solutes, some water vapor is also captured in the gas stream from the column. To the degree that this occurs, the solute separation process loses a similar degree of thermal efficiency. For this reason, one important area of future research will be in achieving better separation of the draw solutes from the dilute draw stream. Possible avenues for this include membrane distillation or pervaporation (a membrane process in which a liquid is maintained at atmospheric pressure on the feed or upstream side of the membrane

Figure 3. Comparison of flux performance of two RO membranes.

(TFC-1 and TFC-2) and one FO membrane (CA).³



while permeate is removed as a vapor due to the low vapor pressure existing on the permeate or downstream side). Success in the use of an alternate solute recovery system will lead to improved efficiency overall for the FO process. It is important to note, however, that the currently available technology is already more efficient than existing thermal desalination methods.⁶

Potential benefits of ammonia-carbon dioxide FO

The use of osmotic pressure to effect the separation of fresh water from saline sources will allow for higher feedwater recoveries, lower brine discharge volumes, lower (and less expensive) energy use and a lower total water cost. Using a vacuum distillation column for solute recovery, it is possible to use very low-grade heat as the primary energy source for FO. This creates the potential to drive water desalination with used energy exhausted from power plants or industrial facilities, at near to or zero energy cost. One way to estimate the improvement this represents is to compare FO to desalination technologies on the basis of the value and quantity of energy used. A term often used for this is *equivalent work*, which uses the quantity of electricity consumed by the process plus the electricity that any thermal energy consumed could be otherwise used to make. The comparison, shown in Figure 5, makes the advantages of low-grade heat use clear.⁶

Conclusion

The high recoveries and subsequent low brine discharge volumes make it

possible to reduce the negative environmental impact of desalination of all types, but these also open up the possibility of effectively desalting inland saline water sources. With high recovery FO, it may be possible to obtain fresh water economically from brackish groundwater without producing a liquid brine stream. This could be of great benefit to arid regions with such resources, such as the southwestern US. The greatest benefit of FO, however, will be realized in its potential to reduce the total water cost. If it were economically preferable to obtain water from the ocean, rather than to ship it over long distances or from environmentally sensitive streams and fresh water habitats, it would have tremendously positive impacts on our natural environment, while enabling continued, sustainable economic growth.

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Figure 5. Comparison of desalination technologies on the basis of 'equivalent work', or the quantity and value of the energy used.

Equivalent work is a calculation giving the electricity that a given quantity of heat could create if that heat, as steam, were expanded in a turbine. Added to this is the electrical energy consumed directly by the process. MSF above refers to Multi-Stage Flash Distillation; MED-TVC for Multi-Effect Distillation with Thermal Vapor Compression and MED-LT for Multi-Effect Distillation, Low Temperature. FO-LT refers to Forward Osmosis, Low Temperature (vacuum column).⁶

