Desalination of Produced Water Using Reverse Osmosis

By Graciela Morales and Maria Barrufet , Texas A&M University

Many oil and gas wells, particularly those in mature fields, produce large amounts of brine along with the hydrocarbons. Disposing of the brine can be costly, due to its composition and large volume. For example, in the Permian Basin of West Texas and New Mexico more than 490 million gallons of water per day are produced and re-injected. The prospect of many millions of barrels of produced water from coalbed methane wells planned for the Powder River Basin has complicated development of that resource.

Historically, the oil and gas industry has not promoted on-site water desalination. The re-injection or surface discharge alternatives were much less costly and there was little demand for the water. However, growing demand for fresh water in many areas and the development of lower-cost technologies for removing contaminants from water are beginning to provide compelling arguments for produced brine desalination.

The Texas Water Resources Institute (TWRI) at Texas A&M University (TAMU) currently is supporting a multidisciplinary program, led by the Department of Petroleum Engineering to develop technologies to treat produced water and make it safe for use in agriculture and wildlife habitat restoration. The aim of the TAMU project is the development of small-scale, modular, transportable units capable of treating relatively small amounts of brine inexpensively. The team will utilize new technology in solids and oil removal and advances in remote process control to create units exhibiting low maintenance and high reliability in the field. These small scale units will utilize nanofiltration (NF) and reverse osmosis (RO) to remove contaminants from oilfield brines.

Similar pressure-driven membrane filtration equipment installations are widely used in desalination of brackish and seawater and compete successfully with traditional thermal desalination operations. However, if RO is to assume a more prominent role in produced water treatment, there is a need for sound engineering designs adaptable to modular operations.

As one portion of this effort, the TAMU team has developed a static model using parametric curves to allow scale-up of an integrated RO system. They are also developing a dynamic model that will be the basis for a control system and automatic operation. This article provides some basic background on RO systems in general, along with a brief description of the static model.

RO Desalination Process

A typical RO water treatment system includes two primary process elements: a pretreatment subsystem and the actual RO unit (Figure 1). Feed water quality determines the amount and type of pretreatment necessary to make RO economical, and as such is the limiting factor of most RO systems in operation today. Membrane surfaces are prone to fouling by particulate matter, inorganic scales (i.e. carbonate and sulfates salts of alkaline earth metals), oxides and hydroxides of aluminum and iron, organic material (i.e., humic, tannic, etc.) and biological material (e.g. bacteria, fungi, algae).

A typical pretreatment unit consists of a sand filter, an activated carbon filter and a depth cartridge filter. The sand filter is used to remove larger impurities, however, sand filters can clog quite quickly and the relative coarseness of sand allows many smaller impurities to pass through. (Osmonics Inc., Published in National Development 01, Mar 1992 – Internet source).

The activated carbon filter absorbs low molecular weight organics and reduces the amount of chlorine or other halogens, but does not remove any salts. This absorption process takes time, so service rates are limited to a maximum of about 5 gpm/ft. The accumulation of solids can require backwashing, however this can result in loss of the relatively fragile activated carbon material. Over a period of months to years, the adsorption capacity of the carbon diminishes, requiring replacement or reactivation, a process not easily accomplished in the field. These filters may also need to be changed periodically to avoid bacterial growth. Hydrocyclones, coalescing media, and organoclay materials may also be used for the removal of oil in the pretreatment portion of these systems.

In the depth cartridge filter, remaining particles (in the 1 to 100 micron range) are trapped in the complex openings of a filter material constructed of cotton, cellulose, synthetic yarns or “blown” microfiber such as polypropylene. These filters have a lower density on the outside and progressively higher density toward the inside wall. The effect of this graded density is to trap coarser particles toward the outside of the wall and the finer particles toward the inner wall. These filters are often disposable. As particles accumulate, the pressure drop across the filter increases and when the pressure difference between filter inlet and outlet has increased by 5 – 10 psi relative to the starting point, the filter is backwashed or replaced.

After pre-treatment to remove suspended particles, the incoming water is pressurized with a pump to exceed the osmotic pressure (typically 200-400 psi, depending on the RO system and the contaminants). A portion of the water (permeate) diffuses through the RO membrane leaving dissolved salts and other contaminants behind with the remaining water. This “reject” or “concentrate” is drawn off as waste. RO removes virtually all organic compounds and up to 99 percent of inorganic ions.

RO membrane fouling is a complex phenomenon involving the deposition of materials on the membrane surface rather than plugging of the system. Scaling of RO membrane surfaces is caused by the precipitation of sparingly soluble salts from the concentrated brine (especially $CaCO_3$ and $BaSO_4$). A number of chemicals may be added to prevent membrane fouling. For example, sulfuric or hydrochloric acid is employed to reduce pH and prevent $CaCO_3$ precipitation. Sulfuric acid, while safer and less expensive than HCl, will increase the content of sulfate ions in the feed water and consequently the risk of

$CaSO_4$ precipitation. The addition of polyphosphates or, more recently, polycarboxylates is employed for preventing $CaSO_4$ scaling.

Chlorination, either continuous or at intervals, is a common pre-treatment method for preventing the growth of bacteria and algae that may cause fouling in the system or degradation of cellulose acetate membranes. The amount of chlorine required is determined by the amount of organic matter in the feed water and by the water temperature.

Reverse Osmosis

Osmosis, an integral part of the functioning of all living cells, is a phenomenon in which a liquid (water in this case) passes through a semi-permeable membrane from a relatively dilute solution toward a more concentrated solution. This flow produces a measurable pressure, termed osmotic pressure. If, however, pressure is applied to the more concentrated solution that exceeds the osmotic pressure, water flows through the membrane from the more concentrated solution to the dilute solution (Figure 2). This process, reverse osmosis, results in two streams of water: one relatively large volume with a low concentration of dissolved impurities (permeate), and one relatively small volume with a high concentration (reject).

Osmotic pressure, and thus the trans-membrane pressure required to overcome it, is a function of contaminant component molecular weight and concentration. For example, the osmotic pressure for a 2 percent by volume sodium chloride stream is 250 psi, while the pressure for a 10 percent potassium chloride solution is 965 psi.

RO Membranes

During the last two decades significant advances have been made in the development and application of microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO) processes. MF membranes reject suspended particles only, UF membranes reject suspended particles and high molecular weight compounds, NF membranes also reject low molecular weight compounds, and RO membranes also reject ions (Figure 3).

The membrane itself must be physically strong in order to stand up to high osmotic pressure. Over 100 different materials are used to make RO membranes, however the two most commonly used membranes are made from cellulose acetate (CA) and polyamide thin film composite (TFC). These may come in spiral, tubular hollow fiber, plate and frame, or proprietary configurations. Hollow fiber and flat sheet are the most commonly used RO membrane configurations. Hollow fiber membrane is extruded like fishing line with a hole in the center to create a tiny (100 to 200 micron) hollow fiber strand. Flat sheet membrane, a continuous sheet rolled up like a large paper towel roll, is used in spiral wound (SW) configurations (Figure 4). Although HF RO elements provide more surface area, they are more prone to fouling (Table 1). The characteristics and performance of these membranes differ as well (Table 2).

Amjad Z. and Zibrida J., 1998, Reverse Osmosis Technology: Fundamentals and Water Applications. Association Water Technologies, Inc. Annual Convention, Washington, DC.

Spiral membrane elements are loaded in a serial configuration in a pressure vessel (1 to 7 membranes per pressure vessel) and tubular membrane elements are loaded in a parallel configuration in a pressure vessel (1 to hundreds of elements pre pressure vessel). Multiple pressure vessels may be connected in a serial or parallel flow path.

If the product flux decreases to unacceptable values (typically >10% decrease) due to membrane fouling, the membrane must be cleaned. The cleaning method and frequency depend on the type of foulant and the membrane's chemical resistance. Generally, it is easier to clean a membrane that is slightly fouled. Cleaning methods include mechanical cleaning (i.e. direct osmosis, flushing with high velocity water, ultrasonic, sponge ball or brush cleaning, air sparging, etc.), chemical cleaning (use of chemical agents), or a combination of both.

TAMU Sizing Model

The TAMU research team has developed a set of theoretically grounded parametric curves (Figure 5) that enable a designer to quickly arrive at an optimal RO unit size and operating scenario by following an iterative procedure. Primary inputs for the procedure include: feed water ionic composition, salinity, temperature, and pressure. These are used to calculate several intermediate parameters which are embedded in the equations plotted in Figure 5. By assuming a delta pressure (ΔP) and desired permeate flow rate (qP), one obtains a value for membrane area (A_m) from the left axis of the chart. Using this value, and assuming a value for membrane length/area ratio (L/A), one determines a value for feed flow rate (qF) from the right axis. This value may be too large exceeding the amount of feed water available. This value is then checked against a tolerance range and if it is not within tolerance, the procedure is repeated by changing either the proposed value of L/A or ΔP, and iterating. The procedure ends when the feed flow (qF) is within expected values, resulting in values for permeate flow rate, membrane area, and membrane length/area ratio that correspond to a particular feed rate. Following this procedure one can observe that, as might be expected, membrane area increases when increasing the brine concentration for a given permeate flow rate. (Note: A comprehensive description of the theoretical basis used to develop these parametric equations, as well as an example of their application, is available from the author.)

Ongoing RO Research

In addition to the development of this set of parametric curves, the research effort currently underway includes:

- Evaluation of different RO membrane configurations for various membrane types
- Investigation of the effects of operating conditions (pressure, temperature and brine composition) on RO membrane flux
- Experimental determination of the best diffusivity model
- Investigation of the effects of temperature and composition on osmotic pressure
- Completion of a sensitivity analysis across a range for three key variables: salt concentration and types of salts up to 200,000 ppm); temperature (100 to 200 °F) and pressure (220 to 2,000 psi).

During the past two years the TAMU team has identified and tested a hybrid system consisting of pretreatment methods, inexpensive centrifugation technologies and ceramic/polymeric RO membranes. Preliminary results indicate that the brine treatment is feasible and can be done simply and economically. The research team has been working closely with PCI Membrane Systems and Somicon A.G., who have redesigned their commercial membrane modules by changing membrane coating methods, polymer combinations and membrane element configurations. In addition PCI and Somicon developed new low fouling NF and RO membrane materials and low cost module geometries.

Using specifically formulated membrane modules, actual process water tests were completed at the university incorporating state-of-the-art pre-treatment technologies that included organo-clays, inexpensive and selective centrifuges and microfiltration systems. The test results show that the treated wastewater quality is equal or better than that of tap water.

For additional information on the status of this work or to become involved in industry efforts to support this research contact the author, Dr. Maria Barrufet, at 979-845-0314, or via e-mail at barrufet@spindletop.tamu.edu. Or members of this research team

Dr. Sefa Koseoglu ***s-koseoglu@tamu.edu (membranes)***

Dr. Graciela Morales gmorales@ciunsa.edu.ar (diffusión models)

Mr. David Burnet burnett@gpri.org (regulatory aspects)

Figure 1: Schematic of a Typical RO Treatment System

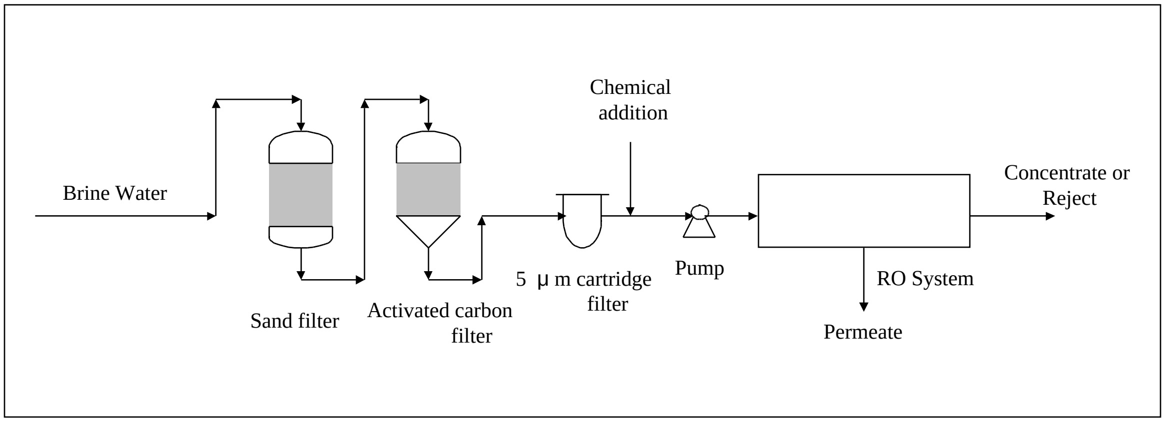


Figure 2: Schematic of Osmosis and Reverse Osmosis

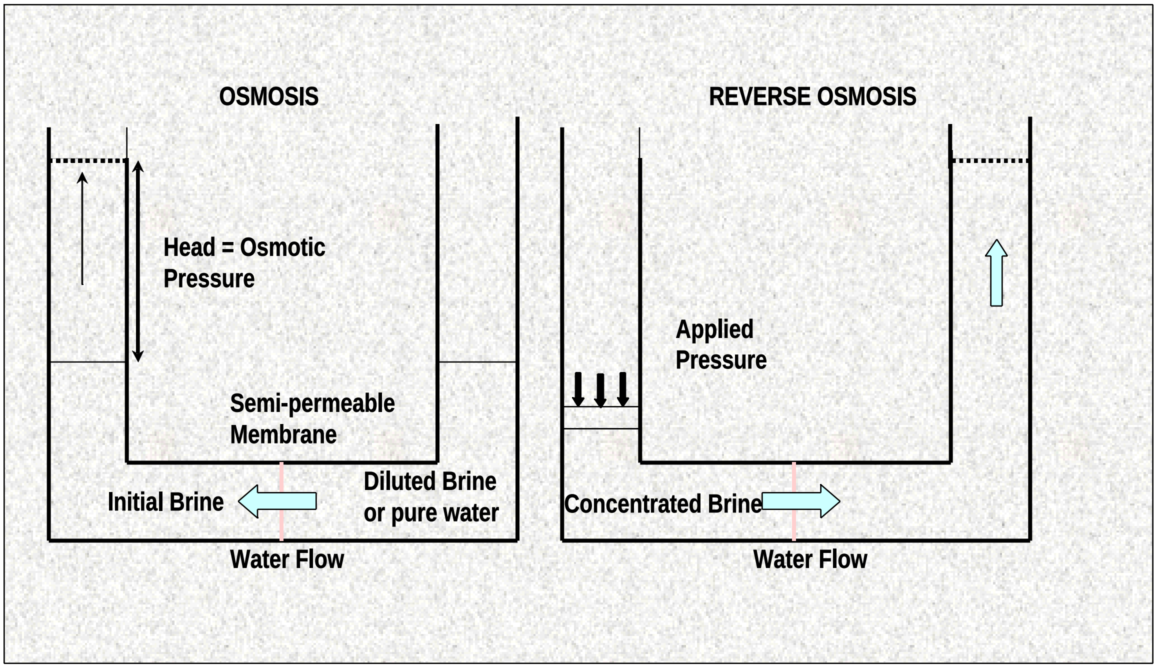
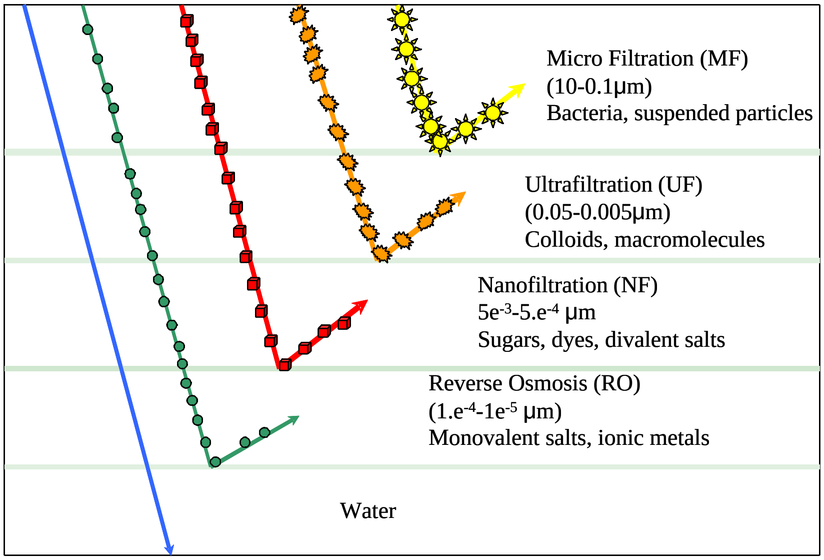


Figure 3: Pressure Driven Separation Processes



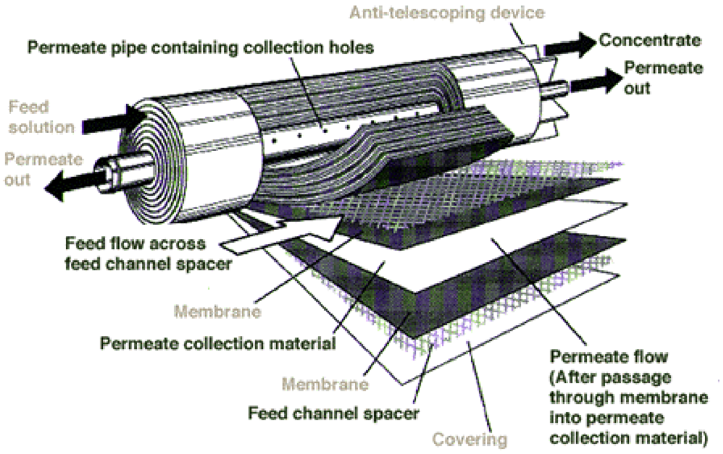


Figure 4: Spiral Wound (SW) Membrane Configuration (Source internet)

Table 1: Comparison of Hollow Fiber and Spiral Wound Membranes

Membrane	Advantages	Disadvantages
Hollow Fiber	· High membrane surface area to volume ratio · High recovery in individual RO unit. · Easy to troubleshoot · Easy to change bundles in the field	· Sensitive to fouling by colloidal materials · Limited number of membrane materials and manufactures
Spiral Wound	· Good resistance to fouling · Easy to clean · Variety of membrane materials and manufactures	· Moderate membrane surface area · Difficult to achieve high recovery

Table 2. Comparison of Cellulose Acetate and Thin Film Composite Membranes

Parameter	Cellulose Acetate (CA)	Thin Film Composite (TFC)
Operating pressure (psi)	410 to 600	200 to 500
Operating temperature (°C)	0 to 30	0 to 45
Operating pH	4 to 6.5	2 to 11
Membrane degradation potential	Hydrolyzes at low & high pHs	Stable over broad pH range
Permeate flux (gfd)	5 to 18	10 to 205
Salt Rejection (%)	70 to 95	97 to 99
Stability to free chlorine	Stable to low (<1 ppm) levels	Attacked by low levels(>0.1 ppm)
Resistance to biofouling	Relatively high resistance	Low resistance
Manufacturer	Several	Several
Cost	Lower	50 to 100 % more

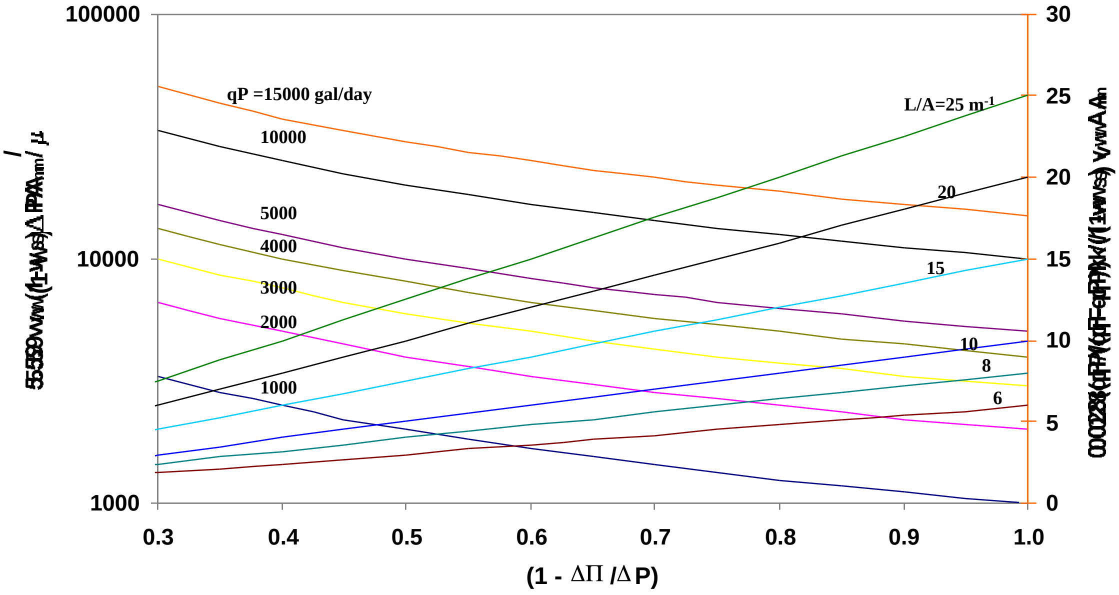


Figure 5: Parametric Equation Based Sizing Model