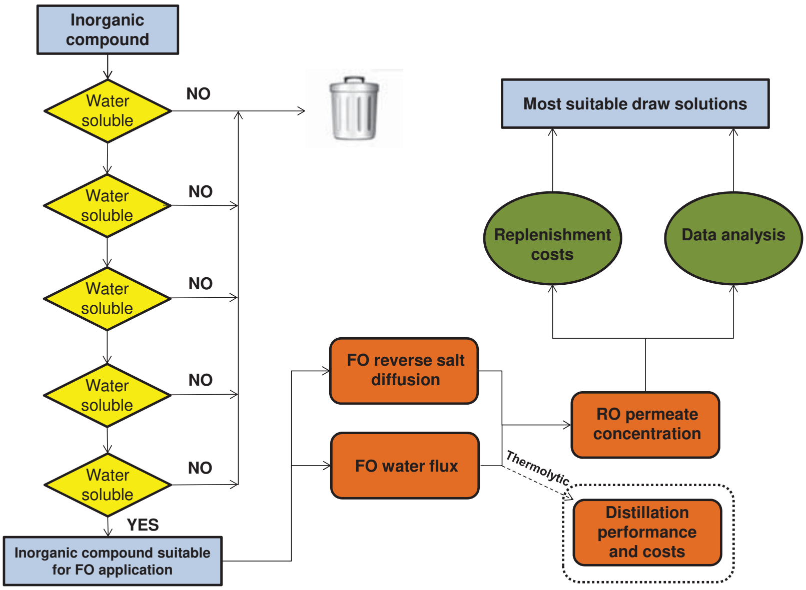

Figure 14.21. Flow chart for draw solution selection
SOURCE: Adapted from Achilli et al. 2010

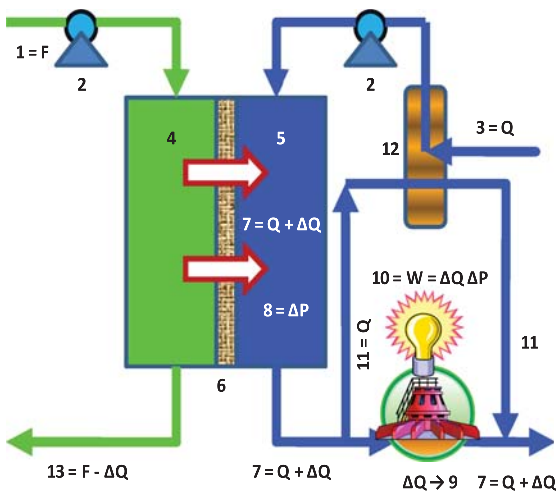

Figure 14.22. A PRO system. Fresh water (1) at a flow rate F and seawater (3) at a Q are pumped (2) into a feed (4) and draw (5) chamber separated by a FO membrane (6), which only allows water to pass through but stops salts. Osmosis transports water (ΔQ, m^3/s) from (4) to (5); the pressure difference between (4) and (5) is ΔP (8). ΔQ passes through a turbine (9) to generate power (10) (= W). The stream (11) passes through a pressure exchanger (12) to pressurize seawater (3)

In a PRO process, the power density, W (W/m^2) and water permeation flux, J_w (L/m^2-h) can be expressed as follows:

$$W = J_w \Delta P = A(\Delta\pi - \Delta P)\Delta P \quad (14.4)$$

$$J_w = A(\sigma\Delta\pi - \Delta P) \quad (14.5)$$

where J_w = volumetric flux of water; ΔP = hydrostatic pressure of the salt solution (= hydrostatic pressure of the feed, P_f – hydrostatic pressure of the permeate, P_p); A = water permeation coefficient; $\Delta\pi$ = osmotic pressure of the salt solution (= osmotic pressure in the feed, π_f – osmotic pressure in the permeate). σ=the reflection coefficient (= 1 for an impermeable solute). Notice that W_{max} can be achieved at $\Delta P = \sigma\Delta\pi/2$.

There is no detailed report about using a full-scale PRO process for blue power generation. Statkraft, an European company accelerated the PRO development in 2007 has been operating the world's first prototype PRO power plant in Norway since 2009 (Skråmestø et al. 2009); however, no detailed information about the test is available. The PRO system is limited to the estuary where seawater is used as a natural draw solute. According to Statkraft, the river-into-sea PRO system is ~66–132/MWh (at year 2015), which is comparable and competitive with the other new renewable energy sources (e.g., 82–106/MWh for wind offshore; 80–90/MWh for biomass, and 116–150/MWh for wave and tidal) (Skråmestø et al. 2009). The global potential of conventional osmotic power using seawater is about 1600–1700 TWh/year–equivalent to China's electricity consumption in 2002 (Skråmestø et al. 2009). If the additional osmotic power generated by the proposed PRO system from brackish water or fresh water is considered as suggested by Zhang and Surampalli (2012), the contribution of PRO systems to the generation of clean, renewable energy would be very significant.

Currently, the PRO system is not considered to be cost-effectively compatible with fossil fuel systems because of some major problems: a) dilution of draw solution which requires a constant replacement of draw solution; b) salt leakage from the draw chamber to the feed chamber, which reduces $\Delta\pi$; and c) CP across the salt-rejecting skin that reduces $\Delta\pi$ to some effective value $\Delta\pi_{eff}$ (Post et al. 2007; Zhang and Surampalli 2012). For most of the membranes, $\Delta\pi_{eff}/\Delta\pi$ is ~5–90% at a water flux of 2 gal/ft^2-d and 0.5–10% at a water flux of 200 gal/ft^2-d (an economically viable flux) (Lee et al. 1981). Since the maximum PRO power $W_{max} = A(\Delta\pi_{eff})^2/4$, a small reduction of $\Delta\pi_{eff}$ can reduce PRO power tremendously.

Current research about the PRO systems focuses on 1) membrane development, 2) improvement of draw solutes, and 3) enhancement of the performance of pressure recovery devices (Lee et al. 1981; Cath et al. 2006; Post et al. 2007; Peinemann et al. 2008). The break even value for the membrane performance is 5 W/m^2. Currently, CA membranes can achieve a performance of 1.3 W/m^2. TFC membranes and inner coated TFC HFMs have been tested. Yang et al. (2009) developed a dual-layer hollow fiber FO membrane with a water flux of

33.8 L/m^2-h and a salt flux <1.0 g/m^2-h using 5 M mgCl$_2$ as the draw solution. Yip et al. (2010) reported a TFC membrane with a water flux >18 LMH in a 1.5 M NaCl draw solution and a pure water feed. Modeling and tests have been conducted about the reverse diffusion of draw solute across an asymmetric membrane in FO; results indicate that the reverse flux selectivity, the ratio of the permeate flux to the reverse solute flux, is a key parameter in the design of osmotically driven membrane processes (Phillip et al. 2010).

Future Trend

Future research will focus on FO and/or PRO processes and their applications, such as good FO and PRO membranes, good FO and PRO draw solutions, combination of UF, NF, RO, FO, PRO and MBR (membrane bioreactor) for drinking water production, wastewater treatment/reuse, and blue energy generation. Some of these applications will be beyond the scope of desalination. For example, if desalination is not needed, but turbidity and bacteria in feed solution need to be removed, one can use UF or MF to replace the FO membrane in a hydrogel-based FO system (Figure 14.20). In such a system, the water flux $J_w = k_w (\Delta P + \Delta\pi_{gel})$ as UF or MF can't generate $\Delta\pi$. Zhang (2013) reported that when the HTI FO membrane was replaced by a Kubota membrane (type H-203, KUBOTA Membrane USA Co., Redmond, WA), the same hydrogels can generate a flux 80 times higher than that of the FO system shown in Figure 14.20 at a water column height of 1 m. Thus, adding hydrogels may significantly lower the ΔP that otherwise is needed in a conventional MF system. In such a new system, the function of the UF or MF is to remove unwanted materials (e.g., particles, bacteria) larger than the pore size of the membrane, while hydrogels are for lowering the energy consumption. RO or FO membranes will be used only as needed to remove salt or micro-pollutants (e.g., emerging contaminants). Thus, this new membrane process could have much wider applications (e.g., water treatment, wastewater reclamation, etc.).

14.4 CONCLUSIONS

When compared to a RO system, there are many advantages of a FO system. While RO systems involve high pressures, and therefore, high energy inputs and exotic materials, the FO process takes place at low pressures and therefore does not require the same energy input or high strength materials. However, FO systems do have additional complications when compared to RO systems. In particular, the FO process does not provide high quality water for use in a single step as the permeate is mixed with the draw solution. These are the major obstacles of the FOD process. Although the novel concept of FO was developed as early as 1968, it has not been able to advance mainly due to the lack of suitable draw solution and lack of suitable FO membranes. Therefore, future research is needed.

14.5 ABBREVIATIONS/NOMENCLATURE

CP	concentration polarization
CTA	cellulose triacetate
DO	dissolved oxygen
DOC	dissolved organic carbon
DS	draw solution
ECP	external concentration polarization
FO	forward osmosis
FOD	forward osmosis (processes) for desalination
HFM	hollow fiber membrane
HTI	Hydration Technology Innovations
ICP	internal concentration polarization
KAUST	the King Abdullah University of Science and Technology
KOPF	KAUST custom-made FO plate and frame
LMH	L/m^2-h
LPRO	low pressure reverse osmosis
MF	microfiltration
NF	nanofiltration
PRO	pressure retarded osmosis
RO	reverse osmosis
TFC	thin film composite
ΔP	hydraulic pressure
$\Delta\pi$	osmotic pressure difference
$\Delta\pi_{gel}$	osmotic pressure gradient between inside and outside of hydrogels

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CHAPTER 15

Treatment of High Salinity Waste Water from Shale Gas Exploitation by Forward Osmosis Processes

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15.1 INTRODUCTION

Hydraulic fracturing has been a key technology in producing shale gases an affordable addition to the United States' energy supply. Hydraulic fracturing is a rather water intensive process which requires 2 million to 5 million gallons of water for a horizontal shale gas well depending on the basin and formation characteristics (Ground Water Protection Council 2009). After fracturing, the hydraulic fluid begins to flow back through the well casing to the well head. This produced water contains various dissolved constituents and organic matters. Its treatment and recycling has drawn wide attention because of its health, environmental and ecological impacts. Because of the complexity in composition, high TDS, limited footprint and cost issues, new water treatment technologies are needed that can recycle the water as fracturing make-up water, or irrigation water, and in some cases pure process water.

Forward osmosis (FO) is an osmotically driven membrane process, where a chemical potential difference acts as the driving force for transferring of water across the membrane from a dilute feed solution to a concentrated draw solution (Cath et al. 2006). The semipermeable FO membrane can block the transfer of a broad range of contaminants including organic matter, dissolved solids, and suspended solids with potential applications in treatment of domestic and industrial wastewater, concentration of beverages and pharmaceutics, and controlled drug release. The most significant characteristics of FO are low energy input, low fouling propensity, high water recovery rate, and highly tolerance to high salinity water streams. FO could potentially provide a new perspective to the

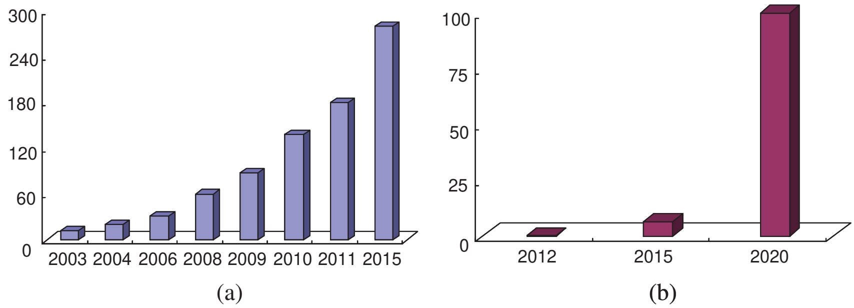

Figure 15.1. Shale gas productivity in the USA (a) and China (b) (in Billion M^3*)*

disposal of the special wastewater containing high total dissolved solids (TDS) (Shaffer et al. 2013).

This chapter reviews the state-of-the-art of the treatment of shale gas produced water with the focus on the treatment of shale gas flow-back water (SGW) by FO. A brief introduction to the origin and chemical/physical characteristics of the SGW are given, and the advantages and limitations of potential treatments methods are analyzed. The process parameters, selection of membrane and draw solutions are summarized. Finally, the potential of utilization of the FO process for the treatment of SGW in a large scale are discussed.

15.2 WATER MANAGEMENT IN SHALE GAS EXPLOITATION

15.2.1 Generation, Health and Environmental Impacts

Shale gas is an important unconventional natural resource for the energy thirsty, and its exploitation activities has been increasing. Based on the US EIA data in 2011, the reservation of the shale gas in US was about $2.44 \times 10^{4\ BM^3}$ and that in China is $3.6 \times 10^{4\ BM^3}$ (He et al. 2012). As shown in Figure 15.1, the projection of the shale gas productivity in the US will be 280 Billion cubic meter by 2015 in America and to 100 Billion cubic by 2020 in China. Between 2003 and 2010, there has been a quick and steady growth of the shale gas output in the US. It is expected that the shale gas production in China follows an even more drastic increase in the coming 10 years.

The shale gas resources in many areas had been overlooked because the production economical feasibility was not attractive enough until the development of combination of sequenced hydraulic fracture treatments and horizontal well completions for shale gas drilling. During the hydraulic fracturing process, a fracturing fluid under high pressure is pumped into a shale formation to generate fractures or cracks in the shale layer. The natural gas flows out of the shale to the well. Water and sand make up over 98% of the fracture fluid, with the rest consisting of various chemical additives that improve the effectiveness of the fracturing process. The main compositions of the fracturing fluid consist of 90.60% water, ~9% sand and other additives. The additives include biocides (sodium hypochlorite or sodium hydroxide), corrosion inhibitors, scavengers, friction reducers, surfactants, etc. The exact chemical components are the secret of the oil/gas service companies, thus not known in public. The amount of water needed to drill and fracture a horizontal shale gas well generally ranges from about 2 million to 5 million gallons of fresh water, depending on the basin and formation characteristics (Colorado School of Mines 2009).

After a hydraulic fracture treatment and relief of the pumping pressure from the well, the water-based fracturing fluid, mixed with any natural underground water, begins to flow back through the well casing to the wellhead. The time for recovering the majority of fracturing fluid ranges from several hours to a couple of weeks. In various basins and shale gas plays, the volume of produced water may account for 15–40% of the original fracture fluid volume. In some cases, flowback of fracturing fluid in produced water can continue for several months after gas production has begun. If not directly treated, the flow back water is stored in a man-made pond before further treatment or tankering. Figure 15.2 shows a typical site for shale gas mining in a remote area in the northwest China. Next to the crane, shale gas flowback water and domestic wastewater were temporarily stored in separate ponds. Both streams are of different characteristics and remains yet untreated.

The SGW contains various dissolved constituents. Initial produced water can vary from fresh (TDS < 5,000 mg/L) to varying degrees of salinity (TDS from 5,000 mg/L to 100,000 mg/L or higher). The dissolved constituents are natural compounds and vary from one shale site to the other.

The composition varies significantly as compared to the composition of produced water from Marcellus Shale drilling. The TDS in the wastewater changes

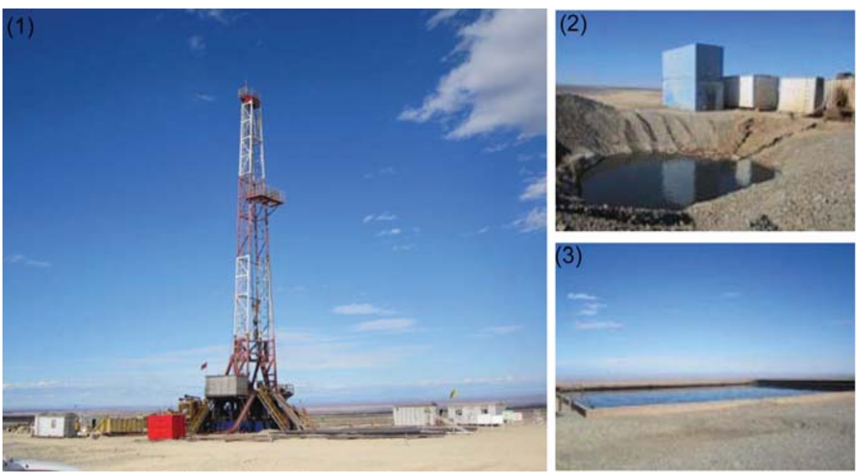

Figure 15.2. Photos of one typical shale gas exploitation site in west China. (1) Shale gas exploitation well pad; (2) domestic wastewater; (3) wastewater storage