Desalination of Shale Gas Wastewater: Thermal and Membrane Applications for Zero-Liquid Discharge

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ABSTRACT

Natural gas exploration from unconventional shale formations, known as *"shale gas"*, has recently arisen as an appealing energy supply to meet the increasing worldwide demand. During the last decade, development of horizontal drilling and hydraulic fracturing (*"fracking"*) technologies have allowed the cost-effective gas exploration from previously inaccessible shale deposits. In spite of optimistic expansion projections, natural gas production from tight shale formations has social and environmental implications mainly associated with the depletion of freshwater resources and polluting wastewater generation. In this context, the capability of desalination technologies to allow water recycling and/or water reuse is crucial for the shale gas industry. Advances in zero-liquid discharge (ZLD) desalination processes for treating hypersaline shale gas wastewater, can play a key role in the mitigation of public health and environmental impacts, and improvement of overall process sustainability. This chapter outlines the most promising thermal and membrane-based alternatives for ZLD desalination of shale gas wastewater.

Keywords: Shale gas wastewater; Zero-liquid discharge (ZLD); Thermal desalination; Membrane desalination; Water treatment; Water reuse and water recycling.

1 Introduction

Shale gas is currently the natural gas resource whose production exhibits the largest worldwide growth. Especially in the last decade, technological developments in horizontal drilling and hydraulic fracturing (*"fracking"*) have boosted large-scale gas extraction from previously inaccessible unconventional shale reservoirs. Recent projections from the U.S. Energy Information Administration (EIA) (1,2) draw attention to the global increase in natural gas exploitation from 342 in 2015 to 554 billion cubic feet per day (Bcf day^{-1}) by 2040. The almost 62% rise in total natural gas production is mainly due to the intensification in shale gas exploration. Actually, shale gas production is expected to grow by more than 125 Bcf day^{-1} over the forecast period, reaching 30% of all natural gas produced in the world by 2040 (1,2).

Along with the depletion of conventional natural gas reserves, supply reliability and energy independence have emerged as driving forces for further development of shale gas exploration (3). Notwithstanding, the latent advance of shale gas production around the globe, notably in the United Kingdom, Argentina, Brazil, Australia, Algeria and Poland, to name a few (4); has also prompted serious concerns about environmental and social implications associated with greenhouse gas (GHG) emissions (5,6), induced seismic events (7), and quantity and quality of natural water resources and wastewater discharges (8–11). Regarding water-related impacts alone, shale gas production from tight shale formations usually requires impressive freshwater volumes and generates large amounts of polluting hypersaline wastewater. Consequently, water management is nowadays one of the biggest challenges faced by the shale gas industry for maintaining process cost-effectiveness, while accounting for environmental and human health protection (12,13).

Environmental, public health and socioeconomic risks can be significantly reduced by adequate high-salinity wastewater treatment for allowing water reuse (*i.e.*, water reinjection in new wells or existing ones), water recycling (*i.e.*, water reuse in other activities not related to hydraulic fracking operations) or safe disposal. Decreasing total dissolved solids (TDS) is the key consideration to attain water quality required for internal and/or external reuse or discharge (13). Within this framework, the application of effective desalination technologies is imperative to enhance overall shale gas process efficiency and sustainability (14,15). The main strength of desalination resides in its ability to achieve salt concentrations that comply with strict regulations, promoting cleaner shale gas production (16,17). In this chapter, the most promising thermal and membrane-based desalination alternatives for shale gas wastewater management are summarized and examined in detail. Energy and economic analyses of potential zero-liquid discharge (ZLD) processes are presented as well, to evaluate the best desalination options for more sustainable shale gas development.

2 Water Consumption, Wastewater Generation and Management Options

2.1 Water Consumption in Shale Gas Operations

Contrarily to conventional natural gas production from geological formations such as porous sandstone and carbonate reservoirs, shale gas extraction is strongly impaired by the low shale rock permeability that compels the use of additional engineered solutions for attaining cost-effective production rates (9,18). Economically viable gas exploitation from shale reservoirs is facilitated through the combined application of horizontal drilling and fracking processes (19). These techniques together have allowed access to major shale deposits and have improved permeability for releasing natural gas entrapped into tight rock formations (13).

In shale gas production, water-based fracturing fluid at very high pressure (about 480−680 bar) is injected in the shale well to unlock the existing fissures and create new artificial fracture networks, increasing the contact surface between reservoir and wellbore (20,21). The chemical composition of the hydrofracturing fluid is conditioned by geological shale formations and water supply features, as well as the gas extraction operators (20,22). Recent reports suggest that horizontal drilling and well-completion technologies demand about 7,570–30,000 m^3 (~2–8 million U.S. gallons) of water per well operation (23,24). The hydraulic fracturing process requires approximately 90% of the total water amount, while the remaining (~10%) is used for horizontal drilling (25). As a result of the exhaustive water consumption, progress in shale gas industry is greatly restricted by water availability, particularly in water-stressed regions (26,27). In these areas, the effects of water shortages can be controlled by enhancing water usage efficiency in the shale gas process. The latter is achieved via more rigorous regulations on water conservation and reuse and, finally, through the implementation of effective desalination plants.

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2.2 Wastewater Generation in Shale Gas Operations

Shale gas wastewater encompasses both flowback water and produced water (also referred as formation water). Depending on the geologic setting and the well characteristics, U.S. shale basins exploration indicates that around 10–80% of the injection fluid returns to the surface as flowback water within the first two weeks following the hydraulic fracturing operation (23,28). Afterwards, with the beginning of gas production, flowback water gradually decreases—usually, it remains in a range from ~210 to 420 U.S. gallons h^{-1}, as has been observed in prominent shale plays from North America, including Marcellus, Fayetteville, Haynesville, and Barnett (29)—and high-salinity produced water is recovered over the well lifetime (~20−40 years) (30). Recently, Kondash et al. (31) have estimated wastewater quantities ranging from 0.5 to 3.8 million U.S. gallons per well over a period of 5–10 years of shale gas production. Among other pollutants, the high-salinity nature (average values typically higher than 100,000 ppm TDS) of shale gas wastewater is extremely hazardous to the environment and human health (32), and demands energy-intensive desalination processes. **Table 1** displays the average water amounts required for horizontal drilling and fracking operations, and shale gas wastewater data from important U.S. shale plays.

[INSERT TABLE 1 HERE]

2.3 Wastewater Management Options

Different management options are available for dealing with the wastewater from shale gas operations. In the U.S., it is estimated that almost 95% of all wastewater generated in shale gas industry is currently disposed in Class II salt water disposal wells through deep underground injection (22,33). Concerning the latter procedure, waste brine can be released to the environment with or without water treatment (34). Although underground injection is the preferred practice for managing wastewater due to its economic benefits, it has lately been associated with potential induced seismic activity, and groundwater and soil contamination (7,33). Moreover, capacity of Class II disposal wells is becoming progressively more limited and, consequently, it might not be able to accommodate all produced shale gas wastewater (35). Besides water conservation policies and severe environmental regulations on discharges quality, disposal capacity constraints have also emphasized the importance of developing new alternatives for high-salinity wastewater desalination, mainly to allow its reuse or recycling (36). **Figure 1** presents the main options for wastewater management in shale gas industry.

[INSERT FIGURE 1 HERE]

Reusing wastewater in hydraulic fracking operations, commonly classified as *"internal reuse"* (13), is an economically advantageous management strategy to address current concerns about the considerable freshwater consumption and wastewater pollution risks. However, direct water reuse is unsuitable due to the high concentration of contaminants that can compromise the well exploration (37). For this reason, onsite portable units for wastewater pretreatment—which comprises primary and secondary treatment options such as filtration, physical and chemical precipitation, flotation, sedimentation, and softening—are generally used to avoid operational problems (35).

Onsite treatment plants usually include established technologies to remove total suspended solids (TSS), oil and greases and scaling materials (38). Typically, the onsite treated wastewater is blended with freshwater to reduce the high TDS contents (which are responsible for negative viscosity effects on the hydraulic fluid), allowing its reuse in hydraulic fracturing operations (13). Nevertheless, even if transportation costs are not considered in onsite plants, capacity and practical constraints alone restrict the application of this treatment alternative (35). It is also worth noting that wastewater composition and water treatment technologies employed in the corresponding system are crucial to the process cost-effectiveness. Moreover, internal reuse practice is dependent on the demand for new well exploitation and ultimately, on the industry expansion.

With the maturity of shale gas industry, drilling and fracking operations will eventually decrease, transforming the activity in a potential wastewater producer. At this point, the application of effective desalination processes will become inevitable (9,39). In this context, centralized (offsite) plants for wastewater pretreatment followed by effective desalination emerge as other options for water management. In fact, they are appealing alternatives to achieve high water quality, permitting its reuse for other beneficial purposes—for instance, water recycling for agricultural activities (40)—or even safe release to surface water bodies.

3 Challenges of Shale Gas Wastewater Desalination

Shale gas wastewater produced by hydraulic fracturing operations present physical and chemical properties that varies according to different factors, including formation geology and geographic location, fracking fluid composition, and the water's time of contact with shale deposits (13,41,42). Note that the fracturing fluid is a complex mixture, predominantly composed by proppant (sand suspension ~99.5% *v/v*) and chemical enhancers that embrace surfactants, inorganic acids, biocides, friction reducers, scale and corrosion inhibitors, flow improvers, etc. (20,43,44). Furthermore, chemical contents in shale gas wastewater may also vary throughout the time of well exploitation (13).

The selection of most suitable treatment alternatives is strongly influenced by the physicochemical composition of the wastewater (42). Apart from the chemical additives utilized within hydrofracturing fluids, shale gas wastewater is also composed by formation-based constituents, which comprises salt and other minerals (*i.e.*, scale-forming ions: Ba^{2+}, Ca^{2+} and Mg^{2+}), organic matter and naturally occurring radioactive materials (NORM) (45–48). **Table 2** shows the typical composition ranges for critical components in shale gas wastewater from Marcellus play.

[INSERT TABLE 2 HERE]

Among all contaminants, removal of the high TDS contents from shale gas wastewater is especially challenging due to the intensive energy consumption needed to accomplish with the severe regulations on water quality (particularly on water recycling and safe disposal). Additionally, besides the variations in wastewater compositions throughout the well lifetime, another complicating factor is associated with the considerable differences observed in wastewater from distinct shale basins, and even in different wellbores from the same well pad (see **Table 1**) (30). **Figure 2** displays conceptual profiles for TDS concentration and wastewater flowrate after hydraulic fracturing operations.

[INSERT FIGURE 2 HERE]

Hayes and Severin (37) have showed TDS contents in wastewater samples from Barnett shale play ranging from 5,850−31,400 ppm (average value of 25,050 ppm) in day 1 following hydraulic fracturing; and, values between 16,400−97,800 ppm (average value of 50,550 ppm) for 10−12th days from the beginning of well exploration. As reported by Acharya et al. (49), TDS concentrations in shale gas wastewater can widely vary from average values of 13,000 ppm for Fayetteville shale play (maximum value of 20,000 ppm), to 120,000 ppm for Marcellus shale play (maximum value >280,000 ppm TDS).

Also, chemical composition analyses performed by Thiel and Lienhard (30) have indicated TDS amounts in wastewater from Permian and Marcellus basins ranging from 120,000 ppm to approximately 250,000 ppm. Results presented by Barbot et al. (20) reveal even higher maximum TDS concentrations of 345,000 ppm (data from Northeast Pennsylvania basins).

Several desalination processes can be applied to treat the hypersaline shale gas wastewater, for ensuring the strict composition constraints in accordance with specific wastewater-desired destinations (*i.e.*, water reuse, water recycling or disposal). Desalination technologies include thermal and membrane-based desalination processes. Thermal technologies comprise multistage flash distillation (MSF), multi-effect distillation (MED), and single or multiple-effect evaporation (SEE/MEE) systems, which can be coupled to mechanical or thermal vapor compression (MVC/TVC); the membrane-based group includes processes such as membrane distillation (MD), forward osmosis (FO), reverse osmosis (RO) and electrodialysis (ED). **Figure 3** displays the schematic representation of main thermal and membrane-based processes for shale gas wastewater desalination.

[INSERT FIGURE 3 HERE]

High TDS contents in shale gas wastewater pose specific desalination challenges, mostly related to high energy consumption and operational problems produced by scaling, fouling and corrosion (50,51). Actually, deposition of scale forming ions on the equipment surface can compromise the system energy performance of both thermal and membrane-based technologies. Due to changes in process conditions (*i.e.*, composition, pH and temperature) during desalination, fouling and scaling surface-growth phenomena can reduce heat transfer in thermal evaporation technologies and mass transfer in membrane-based systems (51). In the last case, the presence of scaling compounds in the wastewater can severely decrease permeate flux across the membrane (52,53).

4 ZLD Desalination for Wastewater Management

4.1 Drivers and Benefits of ZLD Systems

In recent years, ZLD desalination has attracted increased interest by the scientific community and industry as a strategy for wastewater management. This is mainly due to its ability to enhance water usage efficiency, while reducing brine discharges and water and disposal-related environmental impacts (54,55). From general efficiency and environmental protection viewpoints, the ambitious goal of zero-emission desalination could be a game changer for the entire shale gas industry.

ZLD desalination systems are high-recovery processes that allow the production of high-quality treated water (*i.e.*, freshwater) and concentrate brine, by decreasing liquid contents present in the brine waste (56). Here, brine discharges salinity near to salt saturation conditions is considered as ZLD operation. Thus, ZLD alternatives are usually operated to recover ~75−90% of the total amount of water from the wastewater. The remaining water contents can be eliminated by including brine crystallizers or evaporation ponds into the system. Consequently, almost the water totality in the wastewater can be reclaimed for internal reuse in shale gas operations. In this way, ZLD desalination enhances water sustainability and diminishes the environmental pollution and social risks related to wastewater and brine disposals, as well as depletion of freshwater resources (14,54).

Although widely recognized as an important approach for reducing water impacts and improving water supply sources, the implementation of ZLD desalination systems is still limited by intensive energy consumption and high associated processing costs (54,57). However, recent studies have demonstrated the economic viability of thermal-based ZLD desalination systems applied to shale gas wastewater treatment (3,14,15,17). In Onishi et al. (15), for instance, electric-driven SEE/MEE-MVC technologies for ZLD desalination (by considering brine discharges at 300,000 ppm or 300 g kg^{-1}) have presented specific energy consumption in a range of 28.12−50.47 kWh_e m^{-3}, with operational expenses estimated between 2.73−4.90 US$ m^{-3} for 77% conversion ratio (freshwater production ratio at 7.99 kg s^{-1}). Also, the authors have shown freshwater production costs ranging from 6.7 US$ m^{-3} (MEE-MVC with thermal integration) to 10.9 US$ m^{-3} (SEE-MVC with thermal integration). It should be noted that disposal costs in Class II saline water injection wells (*i.e.*, conventional deep-well injection) are estimated to be in the range of ~8−25 US$ m^{-3} (~0.03−0.08 US$ $gallon^{-1}$)—water disposal cost for locally available injection sites in Barnett shale play—(49). These results emphasize the need for developing more realistic energy performance and cost analysis for ZLD desalination systems, to evaluate the best trade-off between their benefits, energy consumption and capital and operating costs.

Future progress in ZLD applications to shale gas wastewater will ultimately be achieved by stricter regulations on water quality and brine discharges, as well as by incrementing regulatory incentives to compensate eventual economic shortcomings (54). These factors, allied to the rising in wastewater disposal costs, will drive shale gas industry towards the implementation of cleaner ZLD desalination systems. **Table 3** and **Table 4** present the freshwater production cost and energy consumption of promising thermal and membrane-based ZLD desalination technologies for shale gas wastewater.

[INSERT TABLE 3 HERE]

[INSERT TABLE 4 HERE]

4.2 Environmental Impacts

Since both thermal and electric power used in desalination systems are usually produced from fossil fuel energy sources, the elevated energy consumption related to ZLD systems is also responsible for significant pollutant emissions to the atmosphere. These emissions are predominantly composed by GHG (Carbon dioxide), acid rain gases (Nitrogen oxides and Sulphur dioxide) and fine particulate matter (58). According to EIA (59), around 939 g of CO_2 per kWh_e are generated from burning coal. Under the latter consideration, MEE-MVC systems operating at ZLD conditions will produce approximately 26.4−47.4 kg of CO_2 per cubic meter of treated water—considering an energy consumption in a range of 28.12−50.47 $kWh_e\ m^{-3}$ (15) —. Carbon footprint and other air pollutant releases directly (*e.g.*, thermal sources as steam) or indirectly (*e.g.*, energy from electricity grids) associated with ZLD schemes can be mitigated by developing higher energy efficiency technologies, and incorporating renewable (*e.g.*, solar, wind and geothermal energy) and/or low-grade energy sources (17,54).

Additional polluting risks linked to ZLD systems are connected to brine waste production. Concentrate management strategies can include brine disposal in landfills and evaporation ponds. Apart from soil contamination possibility, the deposition of solid wastes in landfills can also compromise groundwater by leaching chemicals through the soil matrix. Likewise, brine storage in evaporation ponds can cause environmental and social impacts, due to leakage risks, odors generation and wildlife depletion (60). These negative effects on water and soil and their consequences can be prevented by the implementation of reliable monitoring systems, as well as the use of impermeable linings to isolate surface zones (54).

Major thermal and membrane-based process for ZLD desalination of shale gas wastewater are presented in the following sections.

5 ZLD Desalination Technologies for Shale Gas Wastewater

Desalination systems for the ZLD treatment of high-salinity shale gas wastewater can comprise thermal and membrane-based technologies such as SEE/MEE (with MVC or TVC), MD, FO and RO (see **Figure 3**). As described before, these technologies are able to produce high-quality water by accomplishing with the severe regulations on salt contents required for recycling opportunities (*e.g.*, irrigation, livestock watering or industrial uses). In addition, their modular feature and simple scale-up are propitious for the implementation of onsite treatment plants at shale plays constrained by infrastructure limitations (13). Thermal-based evaporation systems coupled to MVC are comparatively well-established processes, whereas MD, FO, RO and ED are promising technologies for high-salinity shale gas wastewater applications. **Table 5** shows the main advantages and limitations of thermal and membrane-based ZLD desalination processes.

[INSERT TABLE 5 HERE]

5.1 Thermal-based ZLD Processes

ZLD evaporation systems

Despite the significant research efforts on the development of thermal-based MSF and MED processes for seawater desalination (61–63), their application in ZLD systems for shale gas wastewater has not been reported in the literature to date. In general, thermal evaporation systems with MVC can be more advantageous than membrane technologies for shale gas wastewater treatment (13). Due to lower susceptibility to rusting and fouling problems, MEE-MVC demands lesser energy-intensive pretreatment processes than those required prior to membrane desalination. Furthermore, thermal systems are generally more robust and require lower cleaning frequency and intensity than membrane ones (64). On the other hand, while low-grade thermal energy can be used in membrane systems (65,66), typical thermal evaporation schemes with MVC are driven by high-grade electrical energy. Besides the related high operating costs and GHG emissions, this is also a barrier for their operation in remote areas without easy access to power grids. To surpass these limitations, geothermal or other renewable energy sources can be incorporated into the thermal systems.

ZLD thermal evaporation systems for the desalination of hypersaline shale gas wastewater have been addressed by Onishi et al. (3,14–17). In Onishi et al. (15), the authors have developed a mathematical optimization model for SEE/MEE systems design, considering single and multistage MVC and heat integration. **Figure 4** displays the MEE-MVC system proposed by Onishi et al. (15) for the ZLD desalination of shale gas wastewater. Their modelling approach is aimed at enhancing process energy efficiency, while reducing polluting brine discharges. The authors have performed a thorough comparison between the optimal systems configurations found (SEE/MEE with single or multistage mechanical compression) under a wide range of inlet wastewater salinities (10,000–220,000 ppm TDS), to evaluate their ability to achieve high water recovery ratios and ZLD operation. Energy and economic analyses have revealed the MEE process with single-stage MVC as the most cost-effective system for treatment of shale gas wastewater. Further information on ZLD desalination process of shale gas wastewater via SEE/MEE-MVR systems can be found in references (14,15).

[INSERT FIGURE 4 HERE]

Based on the latter result, Onishi et al. (14) have proposed a new rigorous optimization approach for MEE-MVC systems design, by considering more precise estimation of the global heat transfer coefficient to minimize process costs. Furthermore, their method considers the modelling of major equipment features, including optimal number and length of tubes, and evaporator diameter. Their results indicate that the MEE-MVC system can be almost 35% less expensive than SEE-MVC for recovering 76.7% of freshwater (brine discharge salinity at 300,000 ppm TDS). Afterwards, Onishi et al. (3) have focused on the high uncertainty related to well data (wastewater flowrates and salinities) from shale plays to support decision-makers in the implementation of more robust MEE-MVC systems. Distributions of energy consumption and operating expenses throughout different feeding scenarios are shown in **Figure 5**.

[INSERT FIGURE 5 HERE]

Lastly, Onishi et al. (17) have developed a mathematical modelling approach for the optimization of solar energy-driven MEE-MVC systems. The authors have considered an integrated process composed by a solar assisted Rankine cycle and a MEE-MVC desalination plant. The multi-objective optimization model allows to minimize environmental impacts, and investment and operating costs. Their trade-off Pareto-optimal solutions (especially intermediate solutions containing hybrid solar and electricity energy sources) reveal that renewable energy co-generation in desalination ZLD plants can promote significant environmental and cost savings for shale gas industry. **Figure 6** presents the zero-discharge MEE-MVC system driven by solar energy proposed by Onishi et al. (17) for the desalination of high-salinity shale gas wastewater.

[INSERT FIGURE 6 HERE]

Crystallizers

Solid waste produced by thermal evaporation systems can be further concentrated in brine crystallizers. In this case, all remaining water can be recovered from waste brine. Analogously to SEE/MEE-MVC concentrators, electrically driven mechanical compressors are used in large-scale crystallizers (*i.e.*, for treating brine flows higher than 6 gallons per minute) to superheat vapor and supply heat required for driving the evaporation process. For lower brine flows ranging 2–6 gallons per minute, steam-driven crystallizers are generally more economical (67). While horizontal-tube falling film evaporators are preferred in SEE/MEE-MVC schemes, thermal evaporative crystallizers are generally operated thru forced-circulation. Crystallization of concentrate brines is an energy intensive process, which usually demands a range of 52–66 kWh_e per cubic meter of treated water (54,60). This is mainly due to the higher salt concentration and viscosity that characterize brine wastes. However, crystallizer technology can be especially appropriate for shale gas exploration areas in which deep-well injection is not allowed or costly, the solar irradiance is low, or cost of evaporation ponds construction is excessively high (68).

Evaporation Ponds

Evaporation ponds are competitive disposal alternatives to thermal brine crystallizers. This technology uses natural solar irradiance to drive the evaporation process and eliminate the water contents from brine waste. Although the operational expenses are low, evaporations ponds implementation is constrained by its high capital investment and environmental concerns related to brine waste leakage risks (54). Additionally, since the process allows to recover only solid wastes, water cannot be reclaimed for recycling or reuse in shale gas operations. As a consequence, water usage efficiency in shale gas industry cannot be improved by evaporation ponds. Also, evaporation ponds coupled to ZLD desalination systems should be designed to ensure the deposition of all precipitated solids over the zero-discharge plant lifetime, or even the construction of new ponds (67). **Figure 7** depicts the schematic representation of a thermal-based ZLD evaporation plant coupled to the pretreatment system and crystallization or evaporation ponds.

[INSERT FIGURE 7 HERE]

5.2 Membrane-based ZLD Processes

Membrane-based technologies have recently arisen as promising alternatives for ZLD desalination of high-salinity wastewater from shale gas production. Membrane systems usually present great potential for shale gas wastewater applications due to their high efficiency, operational and control simplicity, elevated permeability and selectivity for some critical components, simple scale-up and possibility of using low-grade waste energy (69,70). **Table 6** presents process characteristics and applications of major membrane-based systems for ZLD desalination of shale gas wastewater.

[INSERT TABLE 6 HERE]

Analogously to MVC concentrators, membrane-based technologies are able to achieve (near-)ZLD conditions with brine discharge salinity higher than 300,000 ppm or 30% weight-to-volume fraction (*w/v*) (65,71,72). Note that, although these systems can theoretically concentrate the feed stream until the salt saturation conditions (~350,000 ppm or 35% *w/v*), near-ZLD operation is preferable to prevent operational difficulties related to salt crystallizing in the system (66)—In this case, crystallizer units or evaporation ponds can be considered to recover the remaining water and valuable byproducts (54)—. Also, recent studies indicate that the energy requirements and associated capital and operating costs of membrane technologies are competitive when compared to more conventional thermal ZLD desalination systems and disposal alternatives (71,72). However, the elevated pretreatment costs are still an obstacle for the broad application of membrane-based schemes in shale gas industry (64).

6 Outlook and Future Directions

Shale gas industry is responsible for elevated freshwater consumption and generation of large amounts of hazardous wastewater, which is comprised by flowback and produced waters. Developing more effective desalination systems for the treatment of high-salinity wastewater to allow its reuse and/or recycling is critical to alleviate environmental and public health impacts, and enhance the overall sustainability of shale gas process. Among all pollutants in shale gas wastewater, removal of high TDS contents (usually >100,000 ppm) is particularly challenging due to the intensive energy consumption needed to comply with strict regulations on water quality (especially on water recycling and safe disposal).

ZLD desalination systems have recently emerged as an interesting alternative for shale gas wastewater management. The main advantages of ZLD processes relies in their ability to enhance water usage efficiency in shale gas production, while reducing brine discharges and water-related environmental impacts. As ZLD desalination systems are typically able to achieve water recovery ratios up to 90% (note that the remaining water contents can be eliminated by crystallizers or evaporation ponds), almost the totality of water from wastewater can be reclaimed for internal reuse or recycling opportunities.

Several desalination technologies can be used in ZLD systems for high-salinity wastewater application, including thermal and membrane-based processes. While thermal evaporation systems with MVC are relatively well-established processes, membrane-based schemes containing MD, FO, RO and ED/EDR technologies are promising desalination systems for high-salinity shale gas wastewater. In general, membrane desalination systems present high efficiency, operational and control simplicity, easy scale-up and possibility of using low-grade waste energy.

Although widely accepted as an important wastewater management option to reduce water-related impacts, the implementation of ZLD systems in shale gas industry is still constrained by high energy demands and associated processing costs. Nevertheless, a critical review of literature has revealed the cost-competitiveness of ZLD thermal evaporation systems for shale gas wastewater desalination. Advances in membrane materials, fouling control and optimization of operating conditions should increase the application of membrane-based ZLD systems in the shale gas desalination market. More generally, the wide employment of ZLD systems depends on further development of effective and sustainable desalination technologies, regulatory incentives to compensate economic limitations, and stricter regulations on brine discharges and water quality.

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Nomenclature

AGMD	Air Gap Membrane Distillation
DCMD	Direct Contact Membrane Distillation
EC	Evaporative Crystallization
ED	Electrodialysis
EDR	Electrodialysis Reversal
EIA	Energy Information Administration
FO	Forward Osmosis
GHG	Greenhouse Gas
MEE	Multiple-Effect Evaporation
MED	Multi-Effect Distillation
MD	Membrane Distillation
MSF	Multistage Flash Distillation
MVC	Mechanical Vapor Compression
NF	Nanofiltration
NORM	Naturally Occurring Radioactive Materials
RO	Reverse Osmosis
SEE	Single-Effect Evaporation
TDS	Total Dissolved Solids
TOC	Total Organic Carbon
TSS	Total Suspended Solids
TVC	Thermal Vapor Compression
VMD	Vacuum Membrane Distillation
ZLD	Zero-Liquid Discharge

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Figure Captions

Figure 1. Wastewater management alternatives for shale gas industry.

Figure 2. Conceptual profiles for total dissolved solids (TDS) concentration and wastewater flowrate in function of time from hydraulic fracturing operations.

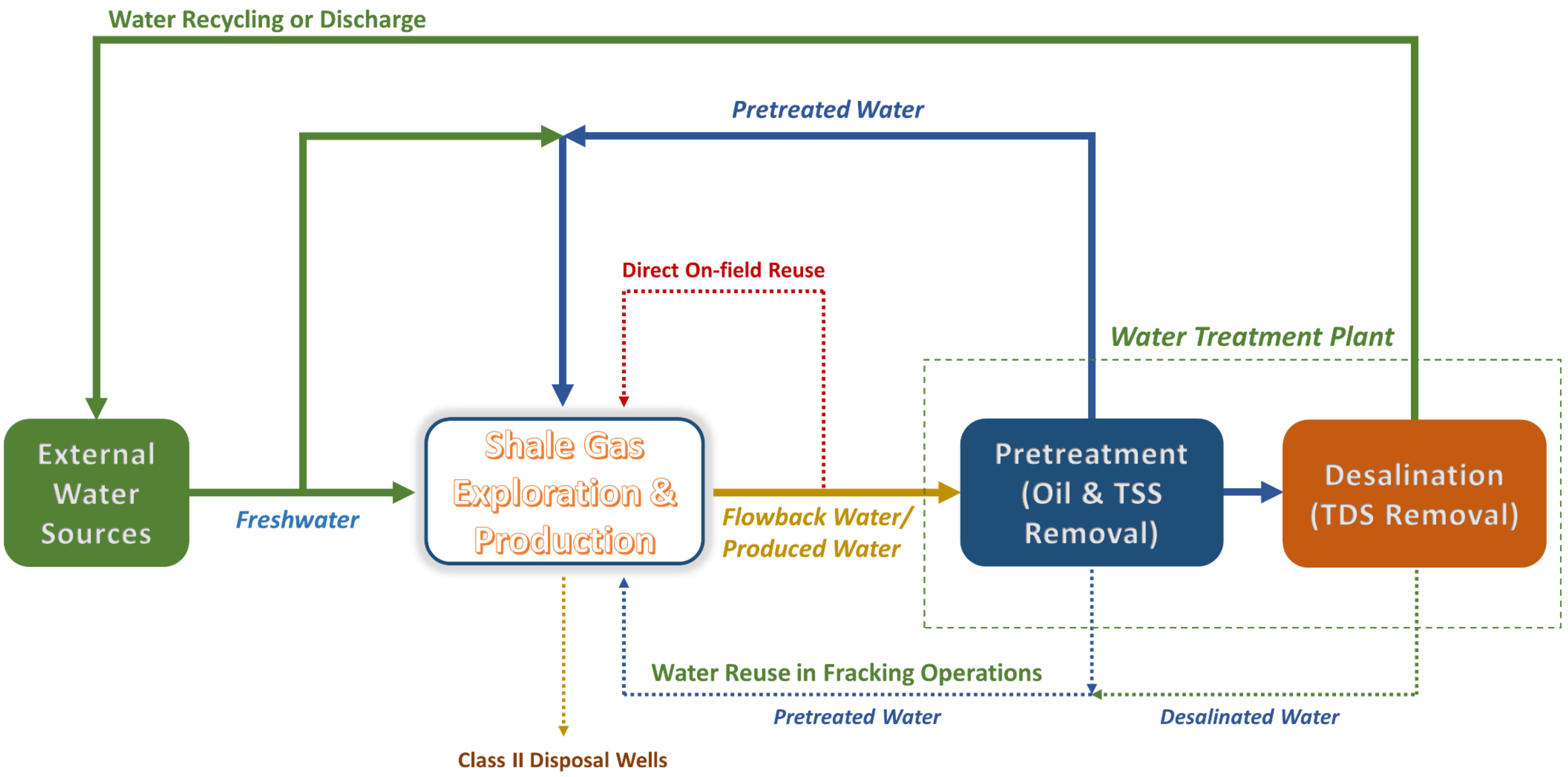
Figure 3. Schematic representation of major thermal and membrane-based processes for shale gas wastewater desalination.

Figure 4. Multiple-effect evaporation system with mechanical vapor compression (MEE-MVC) for the zero-liquid discharge (ZLD) desalination of shale gas wastewater as proposed by Onishi et al. (15).

Figure 5. Distributions throughout different feeding scenarios of zero-discharge MEE-MVC system for: (*a*) energy consumption; and, (*b*) operational expenses. Data retrieved from Onishi et al. (14).

Figure 6. Zero-discharge MEE-MVC system driven by solar energy for the desalination of high-salinity shale gas wastewater.

Figure 7. Schematic representation of a thermal-based ZLD evaporation plant coupled to the pretreatment system and crystallization or evaporation ponds.



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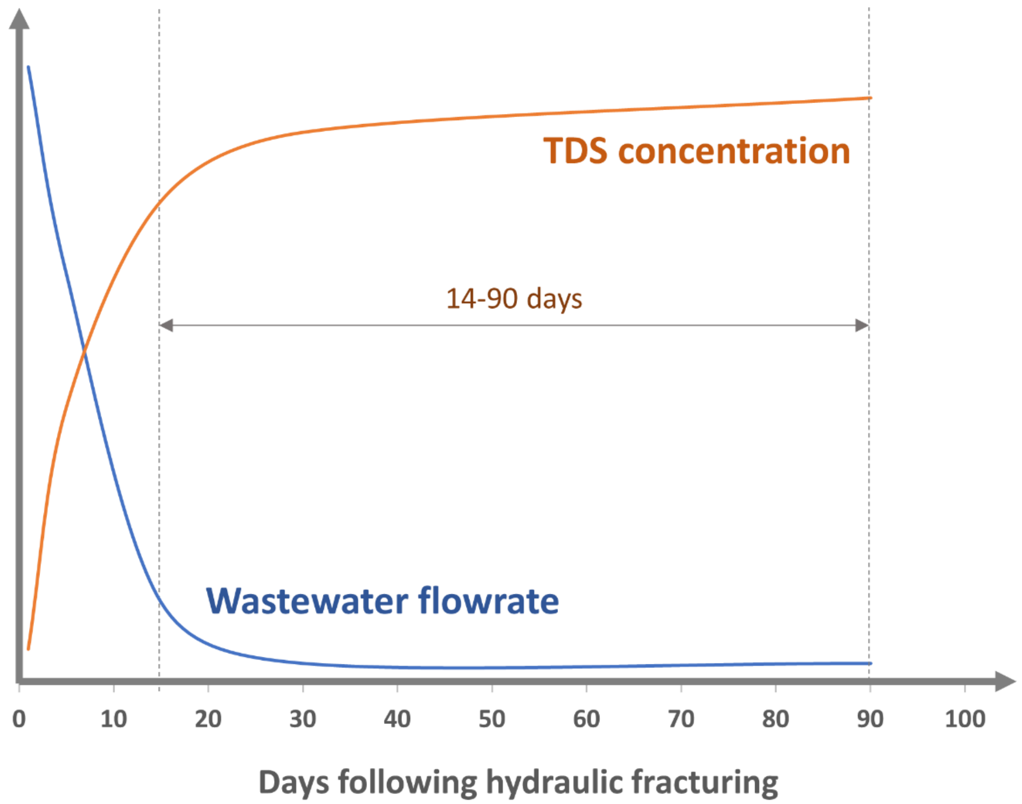

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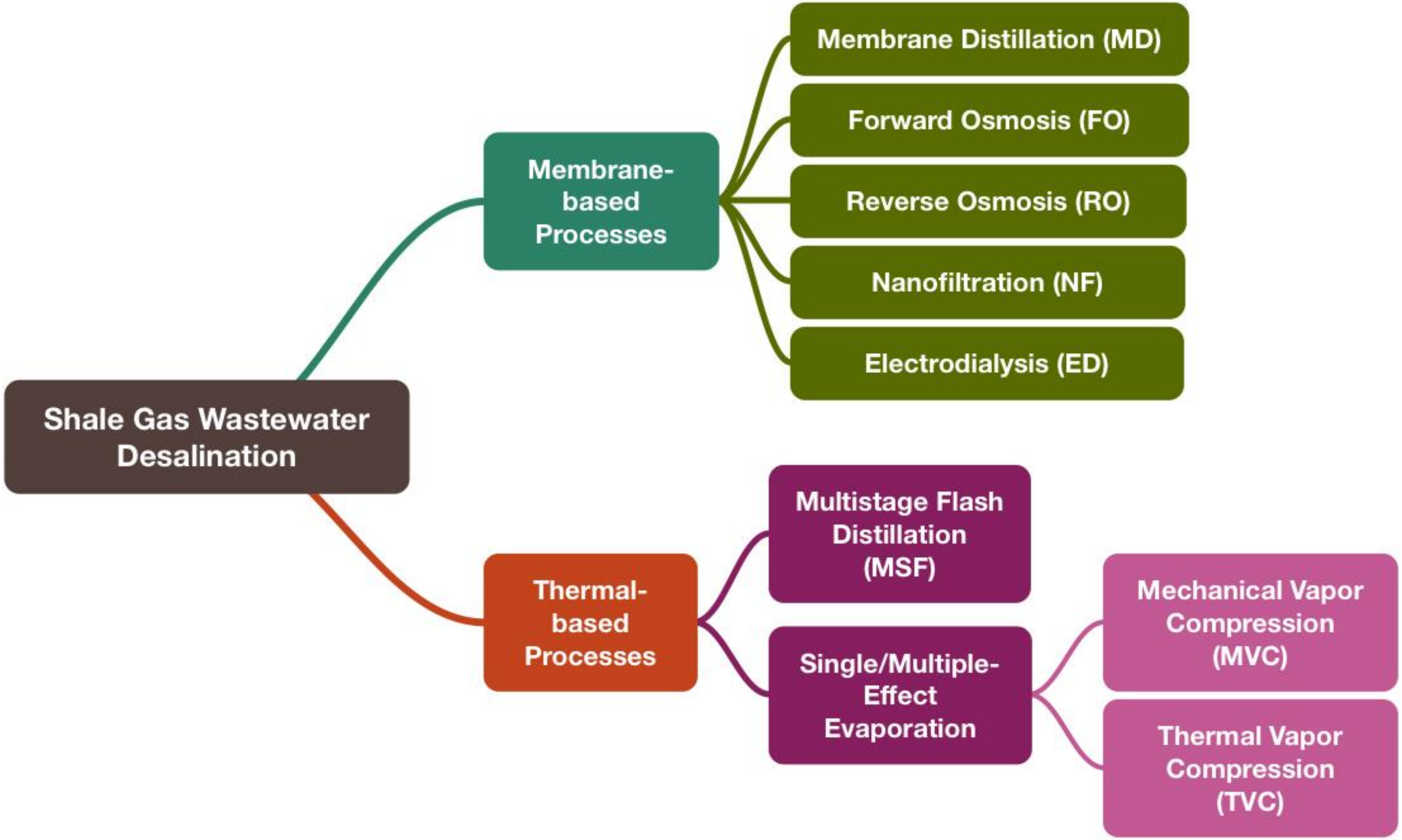

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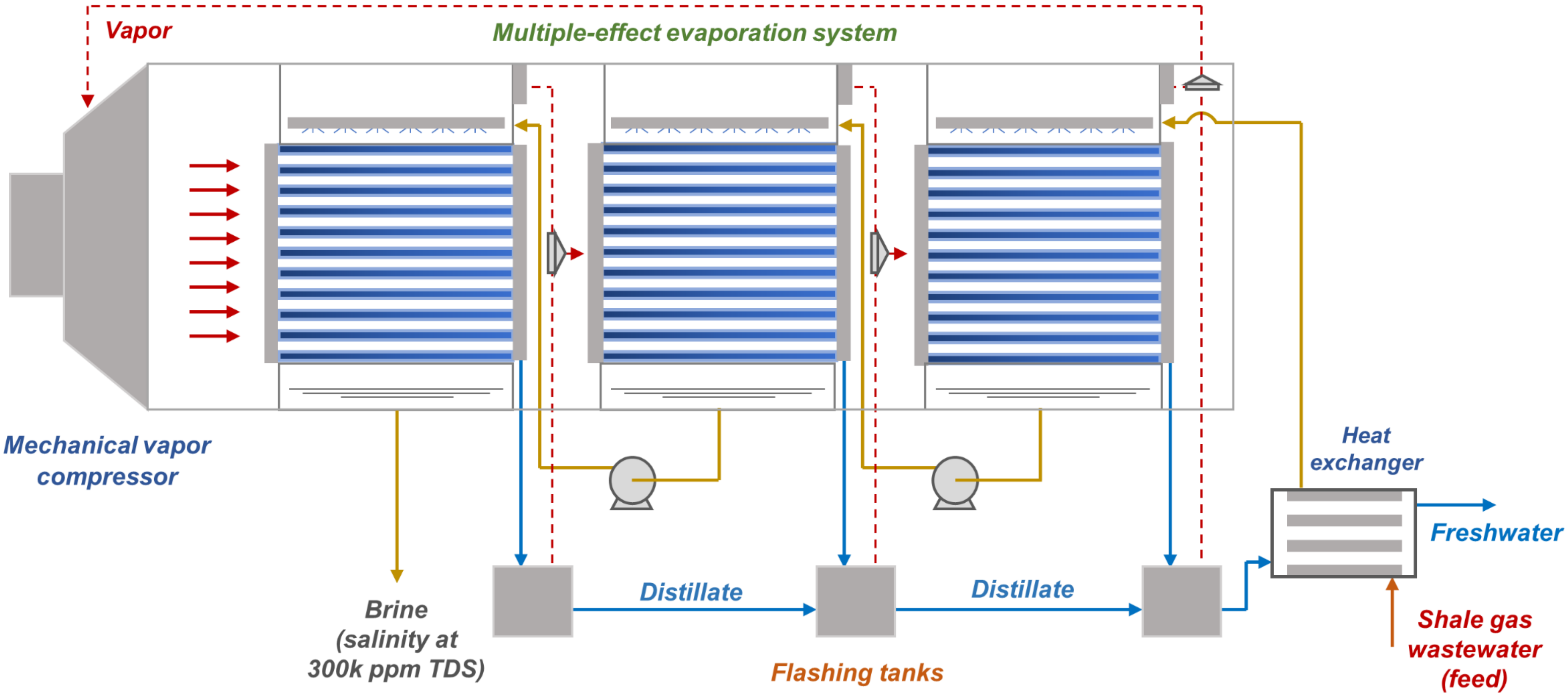

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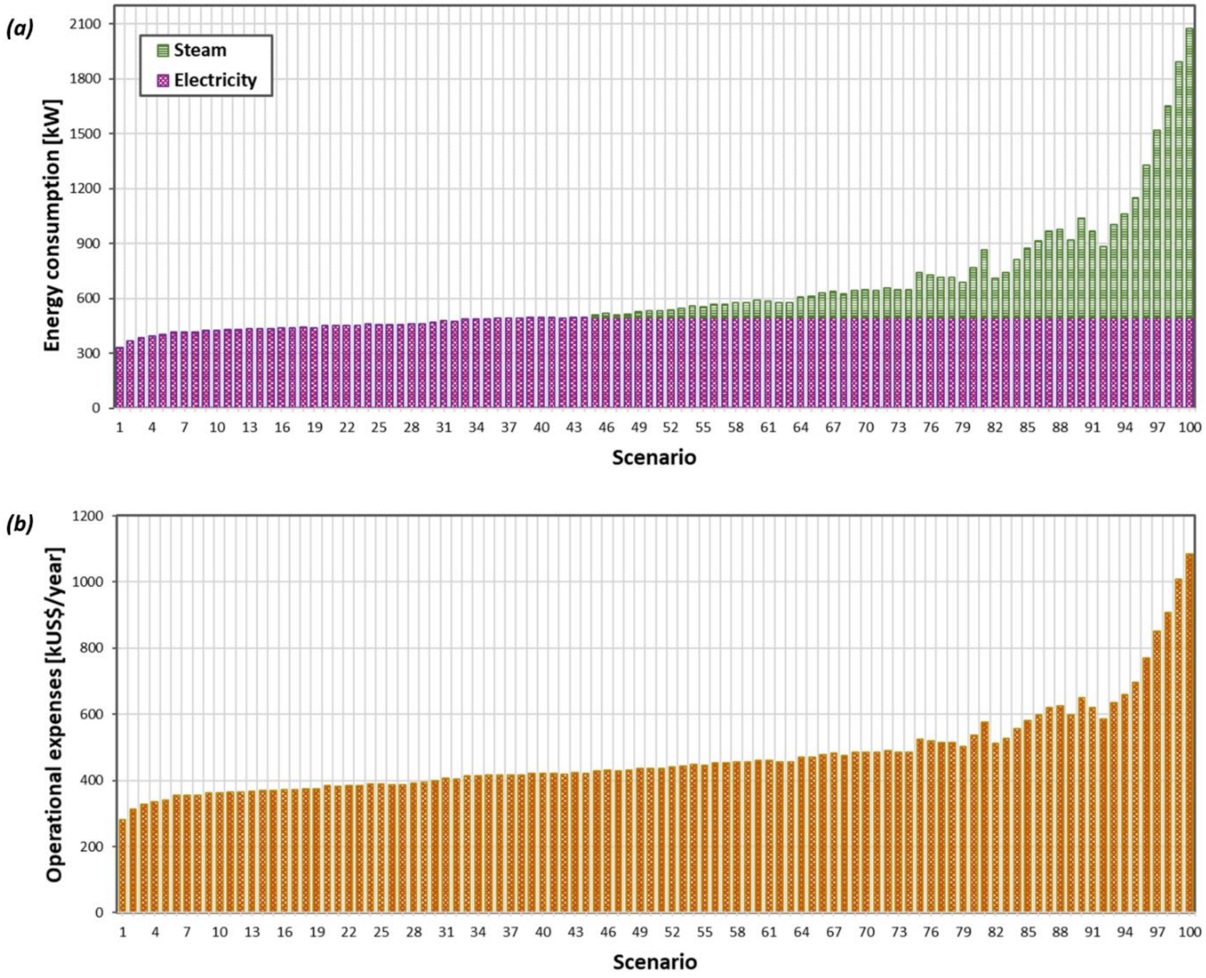

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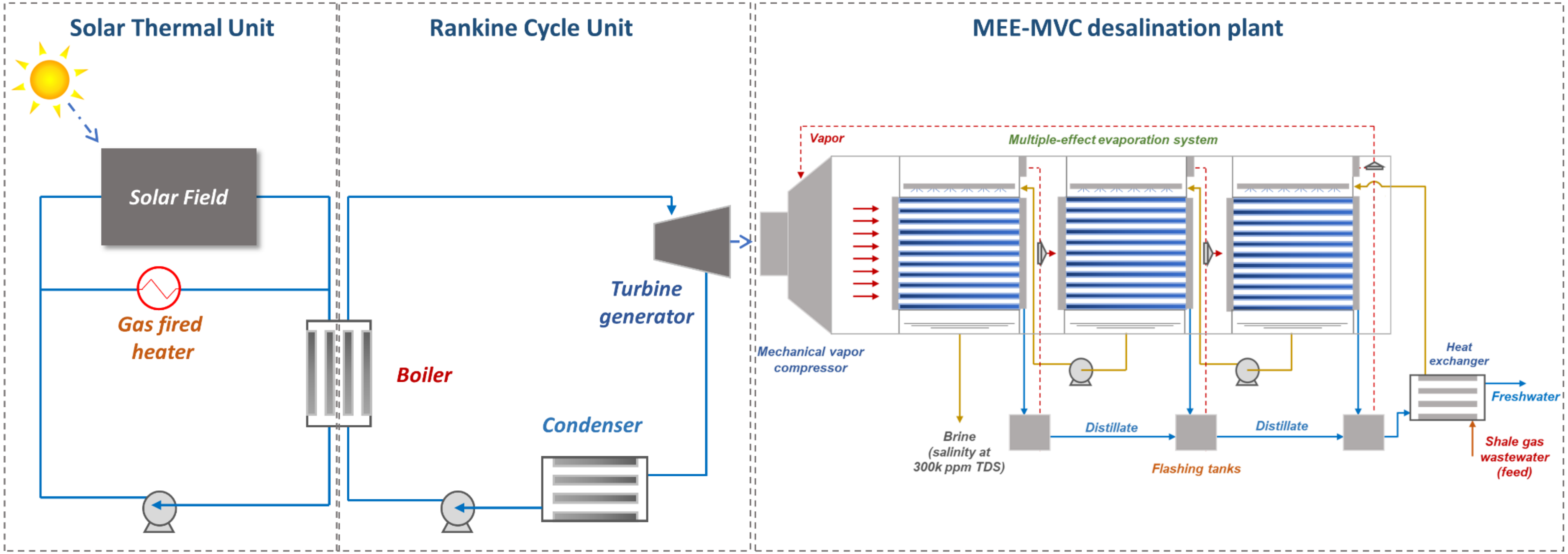

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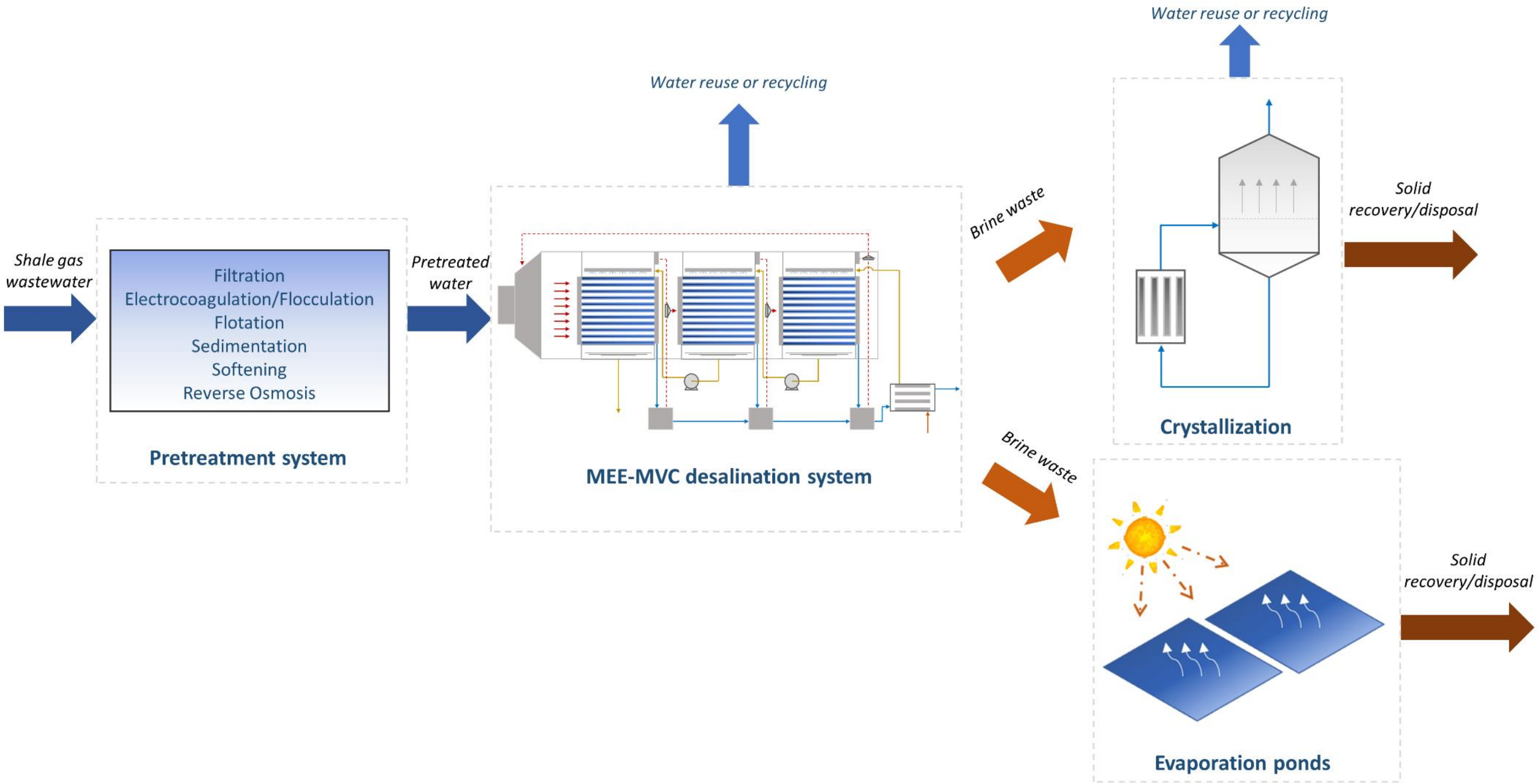

Figure 7. Schematic representation of a thermal-based ZLD evaporation plant coupled to the pretreatment system and crystallization or evaporation ponds.

Table 1. Water amount required per well for drilling and hydrofracturing processes, and shale gas wastewater information from prominent U.S. shale plays.

Data source	U.S. shale play	Water amount (m^3)	Wastewater recovery (%)	Average TDS (k ppm)
Hayes (73)	Marcellus	11,356−1,5142	25%	157 [2]
Acharya et al. (49)	Fayetteville	11,368	15−40% [1]	13
	Woodford	-		30
	Barnett	12,719		80
	Marcellus	14,627		120
	Haynesville	14,309		110
Galusky and Hayes (74)	Barnett	11,356−18,927	25−40%	~92
Hayes and Severin (37)	Marcellus	-	-	120 [2]
	Barnett	-	-	50.55 [3]
Slutz et al. (28)	-	12,700−19,000	10−40%	-
Vidic et al. (9)	Marcellus	7,570−26,500	9−53%	-
Zammerilli et al. (24)	Marcellus	7,570−22,712	30−70%	70
Rosenblum et al. (22)	Niobrara	11,000	~3%−30% [4]	18.6−18.8 [4]
Hammond and O’Grady (23)	-	10,000−30,000	40−80%	-

[1] *Overall produced water recovery after 90 days.*

[2] *TDS average values for the shale gas flowback water in 14th day following hydraulic fracturing.*

[3] *TDS average values for the shale gas flowback water in 10th to 12th day following hydraulic fracturing.*

[4] *Average values in 15th and 220th days following hydraulic fracturing.*

Table 2. Typical concentration ranges for critical constituents found in shale gas wastewater from Marcellus play [1].

Constituent	**Minimum** **(mg L^{-1})**	**Maximum** **(mg L^{-1})**	**Average** **(mg L^{-1})**
Total Dissolved Solids (TDS)	680	345,000	106,390
Total Suspended Solids (TSS)	4	7,600	352
Total Organic Carbon (TOC)	1.2	1530	160
Chloride	64.2	196,000	57,447
Sulfate	0	763	71
Sodium	69.2	117,000	24,123
Calcium	37.8	41,000	7,220
Barium	0.24	13,800	2,224
Strontium	0.59	8,460	1,695
Iron, total	2.6	321	76
Alkalinity (as $CaCO_3$)	7.5	577	165
Bromide	0.2	1,990	511
Magnesium	17.3	2,550	632
Oil and grease	4.6	802	74

[1] *Data compiled from Barbot et al. (20) for flowback water samples collected between day 1 and day 20 following hydraulic fracturing.*

857 **Table 3.** Freshwater production cost and specific energy consumption of thermal-based systems for shale gas wastewater desalination.

Desalination system	**ZLD operation**	**Freshwater production cost**	**Specific energy consumption**	**Reference**
SEE-MVC (electric-driven system with single-stage compression)	Brine salinity at 300k ppm and 76.7% of conversion ratio	10.90 US$ m^{-3}	50.47 kWh m^{-3} (4.90 US$ m^{-3})	Onishi et al. (15)
SEE-MVC (electric-driven system with multi-stage compression)	Brine salinity at 300k ppm and 76.7% of conversion ratio	10.85 US$ m^{-3}	49.85 kWh m^{-3} (4.84 US$ m^{-3})	Onishi et al. (15)
SEE-MVC (rigorous heat transfer coefficients estimations)	Brine salinity at 300k ppm and 76.7% of conversion ratio	10.07 US$ m^{-3}	49.78 kWh m^{-3} (4.83 US$ m^{-3})	Onishi et al. (14)
SEE-MVC	Not ZLD, 26% of brine salinity	-	23 – 42 kWh m^{-3}	Thiel et al. (64)
MEE (steam-driven system)	Brine salinity at 300k ppm and 76.7% of conversion ratio	12.85 US$ m^{-3}	214.19 kWh m^{-3} (10.24 US$ m^{-3})	Onishi et al. (15)
MEE-MVC (electric-driven system with single-stage compression)	Brine salinity at 300k ppm and 76.7% of conversion ratio	6.70 US$ m^{-3}	28.63 kWh m^{-3} (2.78 US$ m^{-3})	Onishi et al. (15)
MEE-MVC (electric-driven system with multi-stage compression)	Brine salinity at 300k ppm and 76.7% of conversion ratio	6.83 US$ m^{-3}	28.84 kWh m^{-3} (2.80 US$ m^{-3})	Onishi et al. (15)
MEE-MVC (rigorous heat transfer coefficients estimations)	Brine salinity at 300k ppm and 76.7% of conversion ratio	6.55 US$ m^{-3}	28.33 kWh m^{-3} (2.75 US$ m^{-3})	Onishi et al. (14)

MEE-MVC (hybrid steam and electricity energy sources)	Brine salinity at 300k ppm and 73.3% of conversion ratio	5.25 US$ m^{-3}	23.25 kWh m^{-3} (2.26 US$ m^{-3})	Onishi et al. (3)
MEE-MVC	Not ZLD, 26% of brine salinity	-	20 kWh m^{-3}	Thiel et al. (64)

Table 4. Freshwater production cost and specific energy consumption of membrane-based systems for shale gas wastewater desalination.

Desalination system	**ZLD operation**	**Freshwater production cost**	**Specific energy consumption**	**Reference**
Direct contact MD system (waste heat energy source)	Brine salinity at 300k ppm or 30% (*w/v*), water recovery ratio of 66.7%	-	527 – 565 kWh m^{-3} (depending on feed temperature)	Lokare et al. (65)
Direct contact MD system (waste heat and electricity heat energy sources)	Brine salinity at 300k ppm or 30% (*w/v*), water recovery ratio of 66.7%	0.74 – 5.70 US$ m^{-3} and 61 – 66 US$ m^{-3} (with transportation costs) [1]	-	Tavakkoli et al. (66)
Two-stage RO system	Not ZLD, 26% of brine salinity	-	4 – 16 kWh m^{-3}	Thiel et al. (64)
Hybrid EDR-RO with crystallizer system	Brine salinity at 239k ppm, water recovery ratio of ~77%	-	10 – 17 kWh_e m^{-3} (EDR-RO) and 40 kWh_e m^{-3} (crystallizer)	Loganathan et al. (55)
ED system	Not ZLD	-	49.7 kWh_e m^{-3} (wastewater with 70k ppm TDS) and 175.7 kWh_e m^{-3} (wastewater with 250k ppm TDS)	Ahmad and Williams (75)
Integrated coagulation and ED system	Not ZLD, 91% of salt removal	-	~7 – 14 kWh m^{-3} (depending on the ED voltage)	Hao et al. (76)

[1] *Values estimated based on cubic meter of feed water (with salinity of 100k ppm).*

Table 5. Comparison between thermal and membrane-based technologies for ZLD desalination of shale gas wastewater.

Desalination technology	Advantages	Drawbacks	Reference
Multistage flash distillation (MSF)	- Well-stablished technology with application to shale gas wastewater with large range of TDS contents - High-quality water product (ultrapure water or freshwater) - Technical maturity - Possibility of using geothermal or solar energy sources	- Cost and energy-intensive process, not suitable for small scale operations (77) - Intensive use of scale inhibitors and cleaning agents	NA
Single/multiple-effect evaporation with mechanical vapor compression (SEE/MEE-MVC)	- Well-stablished technology with Application to shale gas wastewater with large range of TDS contents (10 – >220k ppm) - Brine discharge salinity up to 300k ppm TDS - Use of less intensive pretreatment processes, when compared to membrane-based technologies	- Energy-intensive process - Usually operated by high-grade electric energy (for this reason, these systems present high operating expenses and indirect GHGs emissions)	Onishi et al. (3,14–17)

	- High energy efficiency - High-quality water product (ultrapure water or freshwater) - Technical maturity - Modular feature - Heat exchangers and flashing tanks can be used to further enhance energy recovery, reducing energy consumption - Possibility of using geothermal or other renewable energy sources, which allows to reduce carbon footprint	- High capital costs, due to the expensive materials (stainless steel or titanium) required to prevent rusting	
Membrane distillation (MD)	- Application to shale gas wastewater with high TDS contents - Brine discharge salinity higher than 200k ppm TDS - Modular feature and operation at low temperature and pressure - Low fouling propensity	- Energy-intensive process with energy consumption higher than RO and ED/EDR (DCMD requires 40 – 45 kWh_t m^{-3} for seawater desalination (54)) - Heat integration (by using heat exchangers and brine recycling) is critical to enhance energy efficiency to competitive levels with thermal systems (78)	Carrero-Parreño et al. (71) Boo et al. (81) Singh and Sirkar (82) Kim et al. (83) Chung et al. (84) Lokare et al. (65)

	- Possibility of using low-grade thermal energy, including geothermal or waste heat, which allows to reduce operating costs and carbon footprint	- Membrane wetting potential - Intensive pretreatment and use of cleaning agents and scale inhibitors (79,80) - Limited to commercial applications	
Forward osmosis (FO)	- Application to shale gas wastewater with TDS contents up to 180k ppm (85) - Brine discharge salinities higher than 220k ppm TDS - Modular feature - Can be used for pre-concentrating and pretreating wastewater prior RO process - High rejection of many contaminants - Propensity to membrane fouling and scaling lower than RO process (with reversible membrane fouling) - Low electricity consumption - Possibility of using low-grade thermal energy, including geothermal or waste heat, which allows to reduce operating costs and carbon footprint	- Intensive pretreatment processes (softening, pH adjustment, ultrafiltration, ion exchange, etc.) to prevent operating problems related to fouling and scaling (however, these processes are less intensive and more economical than those required prior RO) - Regular membrane cleaning	Salcedo-Díaz et al.(72) McGinnis et al. (85) Chen et al. (86) Hickenbottom et al. (87) Yun et al. (88)

Reverse osmosis (RO)	- Application to shale gas wastewater with TDS contents up to 40 – 45k ppm (38,72) - High energy efficiency - Technical maturity - Modular feature and great adaptability to wastewater treatment plants with other technologies, including water pretreatment processes (38) - Can be used for pre-concentrating wastewater prior energy-intensive thermal processes (54) - Low energy consumption of ~2 $kWh_e\ m^{-3}$, for seawater desalination (89)	- High propensity to membrane fouling and scaling, which requires intensive pretreatment processes (softening, pH adjustment, coagulant/flocculant addition, ultrafiltration, ion exchange, etc.) to prevent operating problems (90) - Intensive use of antiscalants (91) - Inability to operate at high hydraulic pressure - Stand-alone RO systems are not able to operate at ZLD conditions: brine discharge salinity up to 70k ppm TDS (crystallizer/evaporator should be included in the system) (54)	Salcedo-Díaz et al.(72) Miller et al. (53)
Nanofiltration (NF)	- Effective as softening for subsequent wastewater treatment processes - High water recovery - Energy consumption lower than RO - Mature technology	- Not effective as stand-alone process for shale gas wastewater treatment - Intensive pretreatment and scale inhibitors	Michel et al. (92)

Electrodialysis (ED) and electrodialysis reversal (EDR)	- Application to high-salinity wastewater - Ability to achieve high brine salinities (TDS > 100k ppm) - Salt removal rate ~91% (product water meets the requirements on water reclamation) - Relatively simple operation and maintenance - Low propensity to fouling (especially with coagulation pretreatment) - Long-term operation - Modular feature	- High energy consumption and related operating costs when coupled to crystallizers/evaporators to achieve ZLD conditions - Regular membrane cleaning to maintain operational production ratios - Inability to remove non-charged contaminants	Loganathan et al. (55) McGovern et al. (93) Peraki et al. (94)

Table 6. Process characteristics and applications of membrane-based technologies for ZLD desalination of shale gas wastewater.

Desalination technology	**Driving force and process characteristics**	**High-salinity application**
Membrane distillation (MD)	MD is a thermal-driven membrane desalination process, in which vapor pressure difference across the membrane acts as driving force. The vapor pressure gradient is caused by the temperature difference between the hot wastewater stream (feed stream) and the cold permeate stream (distillate) (81). In recent years, MD has gained increased attention by the literature due to its potential to efficiently deal with high-salinity wastewater from shale gas production. High purity water can be expected by applying MD treatment to the shale gas wastewater. This is due its high removal rate of salts, metals and non-volatile components. Also, MD systems present several advantages over standard thermal and pressure-based membrane processes, including their ability to achieve higher brine concentrations (ZLD operation) and potential use of low-grade waste heat or renewable energy sources	Singh and Sirkar (82) have performed an experimental study on the desalination of shale gas wastewater through direct contact membrane distillation (DCMD) at high temperature and above-ambient pressure, using hollow fibers membranes. Their results emphasize that DCMD is a cost-competitive desalination process for high-salinity shale gas wastewater, especially when compared to conventional RO. This is because the DCMD process does not require feed cooling at the operating conditions considered by the authors. Chung et al. (84) have proposed a multistage vacuum membrane distillation (VMD) for ZLD[1] desalination of high-salinity wastewater applications. The latter authors have used a finite differences-based method for numerical process simulations, by allowing brine discharge salinity near to saturation conditions. Their results indicate that

	(*e.g.*, wind, solar, geothermal, wave, etc.) (69). Typically, MD processes can be operated at temperatures ranging 40 – 80˚C (at atmospheric pressure) and driven by a low temperature difference of 20˚C between the feed and distillate streams. For these reasons, waste grade heat can provide the thermal energy required by the MD desalination process (95).	multistage VMD systems can be as cost-efficient as MSF schemes for a large range of feed water salinities. Tavakkoli et al. (66) have studied the techno-economic suitability of MD at ZLD operation (brine discharge salinity at 30% *w/v*) for desalinating produced water from Marcellus shale play. Their results reveal that the freshwater production cost is significantly affected by the initial TDS contents on wastewater, as well as by the thermal energy prices. Lastly, Carrero-Parreño et al. (71) have successfully reach ZLD operation (brine discharge salinities) by applying both DCMD and VMD systems for the shale gas wastewater desalination.
Forward osmosis (FO)	FO is an osmotically driven membrane-based technology, in which a chemical potential difference between the concentrated draw solution and a wide range of solutions (*e.g.*, shale gas wastewater) acts as driving force for salt separation (87). FO is a promising membrane process for the desalination of high-salinity shale gas wastewater. In fact, this technology presents several advantages over	Hickenbottom et al. (87) have studied the suitability of FO for the treatment of fracturing wastewater from shale gas operations. Bench-scale experiments performed by the authors reveal that the FO system can achieve a water recovery efficiency of ~80%, with high rejection of organic and inorganic contaminants. Yun et al. (88) have investigated the application of pressure assisted FO and

other membrane alternatives, such as its ability to operate at higher salt concentrations (mainly when draw solutes regeneration is considered) (85), and easier fouling reversibility when compared to RO treatment (96). FO systems can also be operated at low pressure, which can prevent fouling and reduce pre-treatment requirements and maintenance. In this process, concentrate brine can be sent to a crystallizer (or evaporation ponds) to achieve ZLD operation, while treated water is separated from draw solutes to regenerate the draw solution (54). For shale gas wastewater desalination, RO and MD can be coupled to the FO system to re-concentrate the draw solution and produce high quality water. Despite recent advances, further improvement in the development of membrane materials and draw solutions, as well as operating conditions optimization, will be critical to enhance process cost-effectiveness, and make FO a competitive alternative for high-salinity applications (39). air gap membrane distillation (AGMD) for the desalination of shale gas wastewater. Their experimental results indicate that the water flux across the membrane can be increased to 10 – 15% for wastewaters with low and medium TDS contents, by considering an external pressure of 10 bar. However, the effect of the external pressure is considerably reduced for high-salinity wastewaters. Also, the authors have shown that AGMD can be an effective process to re-concentrate draw solutes. McGinnis et al. (85) have tested a pilot-scale FO system for the desalination of high-salinity shale gas wastewater from Marcellus shale play. The authors have considered a NH_3/CO_2 draw solution to treat wastewaters with ~73k ppm TDS (and hardness of 17k ppm $CaCO_3$). The process proposed by the authors include pretreatment (softening, media filtration, activated carbon and cartridge filtration), post-FO thermal desalination, RO and brine stripper. Their results indicate water recovery of ~64% (brine discharge salinity of ~180k ppm), with an energy consumption 42% lower than conventional MVC process.

Reverse osmosis (RO)	RO is a pressure-driven desalination process characterized by the separation of dissolved salts from a (pressurized) saline water solution through a semi-permeable membrane. In this way, the flow across the membrane occurs due to a pressure differential established between the high-pressure feed water and the low-pressure permeate. In the RO process, water molecules are transferred from a high salt concentration region to the permeate side owed to an osmosis pressure. For this reason, feed water should be pressurized above osmotic condition, whilst the permeate should be at near-atmospheric pressure (90). RO is an energy-intensive process, in which the major energy requirement is related to the feed water mechanical pressurization. The efficiency of RO separation process can severely be impaired by membrane fouling and scaling. These problems can be prevented by effective wastewater pretreatments and the consideration of different membrane processes in the system (69). Salt	Jang et al. (33) have experimentally evaluated the applicability of three different techniques for the desalination of high-salinity shale gas wastewater: MD, RO and evaporative crystallization (EC). Their results indicate relatively higher efficiencies for MD and EC (>99.9%) than the RO technology (97.1–99.7%). Despite the elevated removal rates presented by the RO process, the latter has been significantly affected by the TDS levels on the wastewater, requiring four times more dilution before operation than MD and EC. In a recent study, Salcedo-Díaz et al. (72) have proposed a ZLD desalination system composed RO and FO technologies for shale gas wastewater application. The authors have developed a mathematical model for the optimal design of onsite RO-FO systems, to minimize freshwater consumption and specific fracturing water cost. Their results show that is technically possible to reduce to zero the amount of freshwater used in shale gas operations. However, due to the high freshwater production cost presented by the

	concentrations in shale gas wastewater are critical for RO desalination (33). RO systems are cost-effective for wastewaters with TDS contents lower than 30k ppm (39). In addition, RO can be included into ZLD desalination systems to enhance process cost-effectiveness. Almost 80% of wastewater volume can be reduced by using RO technology (44). Usually, RO processes are operated at low temperatures <45˚C (at 20 – 60 atm).	desalination system—in which, the cost of the cubic meter of treated water is about 100 times higher than the same amount of freshwater—, an intermediate solution can be more affordable for shale gas industry.
Electrodialysis (ED) / Electrodialysis reversal (EDR)	ED and EDR are electrochemical charge-driven membrane-based processes for the desalination of high-salinity shale gas wastewater. These technologies are characterized by dissolved ions separation across ion-selective membranes, in which the electrical potential gradient works as driving force (69,94). In EDR process, membranes polarity is changed to fouling and scaling control (69). ED and EDR systems can be used for removing salts from RO treated waters (97). The performance of ED and EDR processes is significantly affected by several factors, including applied voltage,	McGovern et al. (93) have proposed a 10-stage ED system for the treatment of high-salinity shale gas wastewater. The authors have experimentally evaluated the optimal equipment size and energy requirements to desalinate wastewater with salinities up to 192k ppm TDS. Their results emphasize the process effectiveness and the need for further investigating fouling and operating conditions (stack voltage) to minimize desalination costs. Hao et al. (76) have developed an integrated process of coagulation and ED for the treatment of fracturing wastewater. The coagulation is used for removing organic contaminants

wastewater flowrate and ions concentration, membrane density, diffusion, etc. The main disadvantages are related to high energy consumption and water production costs, and fouling propensity (75). In addition, these processes require regular membrane cleaning (alkalis or dilute acidic solutions) to keep operating conditions. The latter drawbacks must be addressed to improve competitiveness of ED/EDR for the industrial scale application to high-salinity shale gas wastewaters (69).

from the wastewater, while its desalination is performed by the ED system. Their results show ion removal rates up to 91%, reaching water reclamation regulations. Peraki et al. (94) have investigated the ED efficiency as a pretreatment alternative for desalination of high-salinity shale gas wastewater from Marcellus shale play. Their results indicate a reduction of ~27% in the wastewater TDS contents after 7 h of application of a low direct current electric field.

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[1] *Although evaporation ponds or crystallizers are required to literally achieve zero-discharge operation, brine discharges salinities near to salt saturation conditions are considered as ZLD operation in this work.*