

A Critical Review of Alternative Desalination Technologies for Smart Waterflooding

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Summary

The importance of tuning injection-water chemistry for upstream is moving beyond formation-damage control/water incompatibility to increasing oil recovery from waterflooding and different improved-oil-recovery (IOR)/enhanced-oil-recovery (EOR) processes. Smart waterflooding through tuning of injection-water salinity and ionic composition has gained good attention in the industry during recent years for IOR in carbonate reservoirs. The water-chemistry requirements for IOR/EOR have been relatively addressed in the recent literature, but the key challenge for field implementation is to find an easy, practical, and optimum technology to tune water chemistry. The currently available technologies for tuning water chemistry are limited, and most of the existing ones are adopted from the desalination industry, which relies on membrane-based separation. Even though these technologies yield an achievable solution, they are not the optimum choice for altering injection-water chemistry in terms of incorporating selective ions and providing effective water management for large-scale applications. In this study, several of the current, emerging, and future desalination technologies are reviewed with the objective to develop potential water-treatment solutions by use of both seawater and produced water that can most efficiently alter injection-water chemistry for smart waterflooding in carbonate reservoirs.

Standard chemical-precipitation technologies, such as lime/soda ash, alkali, and lime/aluminum-based reagent, are only applicable for removing certain ions from seawater. The lime/aluminum-based reagent process looks interesting because it can remove both sulfates and hardness ions to provide some tuning flexibility for key ions included in the smart water. There are some new technologies under development that use chemical solvents to extract salt ions from seawater, but their capabilities to selectively remove specific ions need further investigation.

Forward osmosis (FO) and membrane distillation (MD) are the two emerging technologies, and they can provide good alternatives to reverse-osmosis (RO) seawater desalination for the near-term. These technologies can offer a more cost-effective solution in which there is availability of low-grade waste heat or steam. The two new desalination technologies, based on dynamic vapor recompression and carrier-gas extraction (CGE), are well-suited to treat high-salinity produced water for zero liquid discharge (ZLD), but they may not be able to provide an economical solution for seawater desalination. Carbon nanotube-based desalination, graphene sheet-based desalination, and capacitive deionization are the three potential future seawater-desalination technologies identified for the long term. Among these, carbon nanotube-based desalination is more attractive, although the technology is still largely under research and development.

The results of this review study show that there is no commercial technology yet available to selectively remove specific ions from seawater in one step and optimally meet the desired water-chemistry requirements of smart waterflooding. As a result, different conceptual process configurations involving selected combinations of chemical precipitation, conventional/emerging desalination, and produced-water-treatment technologies are proposed. These configurations represent both approximate and improved solutions to incorporate specific key ions into the smart water selectively, besides presenting the key opportunities to treat produced-water/membrane reject water and provide ZLD capabilities in smart-waterflooding applications. The developed configurations can provide an attractive solution to capitalize on existing huge produced-water resources available in carbonate reservoirs to generate smart water and minimize wastewater disposal during fieldwide implementation of smart waterflood.

Introduction

Advanced waterflooding processes of lower salinity and tuned ionic composition are currently becoming attractive in the oil industry to recover more oil from both sandstone and carbonate reservoirs onshore and offshore. Laboratory studies and field pilots in sandstones indicate that threshold salinities lower than 5,000 ppm are desired to result in 5 to 7% incremental oil recovery over normal waterflooding (Jadhunandan and Morrow 1995; McGuire et al. 2005; Lager et al. 2008; Ligthelm et al. 2009; Secombe et al. 2010; Vledder et al. 2010; Mahani et al. 2011). The research studies carried out so far to investigate the effects of water ionic composition in carbonates are relatively less pronounced when compared with sandstones. Water ionic compositional effects appear to be more complex in carbonates not only because lower salinity is important, but also because certain key ions, such as sulfates, calcium, and magnesium, play an important role in impacting oil recovery. Injection waters of lower salinity, but enriched with divalent ions and depleted in monovalents, were shown to be the most-desired water chemistry to result in better incremental oil recovery in carbonates (Fathi et al. 2011; Yousef et al. 2011a; Yousef et al. 2012a; Austad 2013; Chandrasekhar and Mohanty 2013).

Saudi Aramco is strongly engaged in studying the role of water ions and their effects on oil recovery in carbonates under the in-house strategic research program tagged “SmartWater Flood.” Numerous laboratory corefloods confirmed the potential of smart waterflood in carbonates (Yousef et al. 2010, 2011a, 2011b, 2011c). The first-ever single-well chemical-tracer tests performed in a carbonate reservoir also promisingly showed 6 to 7% reduction in residual oil saturation resulting from the injection of chemistry-optimized waters (Yousef et al. 2012b). As a result, a multiwell pilot is currently being designed to demonstrate smart-water effects in carbonates at larger scale and to overcome expected problems during the pilot operation in the field.

Seawater is the most-abundant water resource on Earth, and is thereby the most-convenient source water for both offshore and onshore waterflooding projects. Similarly, plenty of produced-water

resources are also available from existing carbonate oil fields. Therefore, water-chemistry alteration and removal/enrichment of certain ions from both seawater and produced water are the keys for successful implementation of smart waterflooding in carbonate reservoirs. Desalination is the readily available water-chemistry-alteration process used to remove dissolved ions from seawater. Membrane-based technologies are used routinely to desalinate seawater and have been developed over many years in large-scale commercial applications to provide both drinking water and treated injection water for waterfloods on offshore platforms. There are also some variations in the design application of these processes, such as using energy recovery devices and larger-diameter membranes, among others. These design variations have not yet reached commercial or widespread acceptance, but in certain circumstances can be considered potentially useful. Two types of membranes, RO and nanofiltration (NF), are available in the market today for removal of ions from seawater to reduce the salinity.

Both RO and NF are pressure-driven processes, with the pressure applied used for separation, allowing the water to pass through the membrane while the selective salts remain. RO involves a much-tighter membrane with pore sizes less than 0.0005 μm . These membranes reject all the salt ions—both monovalent (sodium and chlorides) and divalent (calcium, magnesium, and sulfates)—from seawater with rejection efficiencies greater than 99%. Fresh water containing a negligible amount of salt ions (<500 ppm) is the final product water from RO. The reject water from RO is a concentrate, which is rich in both monovalent and divalent ions. In contrast to RO, NF membranes are relatively looser, with pore sizes in between 0.05 and 0.005 μm and 200-Dalton molecular-weight cutoff. These membranes reject only divalent cations and sulfates with >90 to 99% rejection efficiency. As a result, the product water from NF membranes is rich in monovalent ions, whereas the reject water stream contains mostly divalent ions.

The oil industry first realized the importance of water-chemistry alteration in injection water specifically for low-salinity waterflooding and chemical-EOR projects (Christopher et al. 2009; Collins et al. 2010; Ayirala et al. 2010, 2014, 2016; Williams 2015; Ligthelm et al. 2012; Henthorne and Movahed 2013; Henthorne et al. 2013; Curole and Greene 2014). Most of these studies quickly tapped on existing and commercially available membrane-based technologies from the desalination industry. These studies suggested the use of either a standalone RO or another hybrid membrane-based process involving both NF and RO technologies. More importantly, none of these studies addressed the complex water-chemistry requirements of smart waterflooding in carbonates. The optimum injection-water chemistry for smart waterflooding requires not only depleting monovalent ions (sodium and chlorides), but also maintaining sufficient concentration of certain key ions (sulfates, calcium, and magnesium) in seawater. Because there is no commercial technology currently available in the industry to remove selectively specific ions from seawater to enrich the so-called key ions, one possible way to generate smart water is through mixing of seawater with fresh water obtained from RO. This scheme can provide one viable approach to deplete monovalent ions, but to keep adequate concentration of key ions in the injection water. It is important to note that such a scheme will provide only an approximate solution to achieve seawater dilution for smart waterflooding.

Ayirala and Yousef (2015) performed a comprehensive review to summarize the impact of injection-water chemistry on oil recovery in different IOR/EOR processes. This review analysis pointed out that the importance of tuning injection-water chemistry in the upstream is moving beyond formation-damage control/water incompatibility to increasing oil recovery from waterflooding and IOR/EOR. It was also emphasized that there is a need for close collaboration between oil and water industries to develop fit-for-purpose water-treatment solutions to address those complex injection-water-chemistry requirements associated with different IOR/EOR processes. The recent work of Yousef and Ayirala (2014)

proposed NF/RO technologies arranged in a parallel configuration as one potential solution to generate more-favorable chemistry-optimized waters suited for smart waterflooding in carbonates. It was shown in this study that multiple water streams of widely varying ionic strength and content obtained from such technology can be blended effectively to yield any smart-water cocktail of desired ionic strength, composition, and monovalent-to-divalent ion content suited for different IOR/EOR processes. The applicability of different smart-water cocktails obtained from the proposed technology was also demonstrated to several other EOR processes, including polymer flooding, surfactant flooding, dilute-surfactant flooding, carbonated-water flooding, miscible-gas flooding, and as boiler feedwater in steamfloods. Even though this scheme yields a much better solution compared with RO, it is not yet the optimal choice to alter water chemistry in terms of incorporating selective key ions in the smart water for large-scale applications. This major deficiency is due to the reason that the ionic content can only be varied collectively as either monovalent or divalent ions without providing any flexibility to tune on individual key ions. These membrane-based processes are not suited to treat high-salinity waters greater than 60,000-ppm salinity and are also not tolerant to contaminants in produced water, such as water-soluble organics, free oil, and particulates. As a result, this technology has serious limitations to treat high-salinity/produced waters and meet environmental regulations in locations where water-reinjection/disposal facilities are not available.

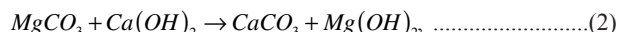
The major goal of this study is to perform a state-of-the-art literature review on current, emerging, and future desalination technologies to achieve the following objectives: (1) investigate chemical-precipitation/extraction technologies and evaluate their significance for smart waterflood, (2) identify emerging alternative technologies to conventional membrane-desalination processes, (3) explore potential technologies under development for future applications, and (4) develop several water-treatment-process configurations involving selected combinations of identified technologies to provide feasible and practical solutions for the use of both seawater and produced water in smart-waterflooding applications in carbonates.

Chemical-Precipitation Technologies

As the name implies, these technologies involve supersaturating dissolved salts in the water by adding suitable chemical reagents to cause precipitation from seawater. The chemical-precipitation technologies are most commonly used in the water industry to soften water (i.e., to remove hardness-causing calcium and magnesium ions). Precipitation of these hardness ions is achieved by raising the pH of source water to values greater than 10 or 11, and two types of softening-treatment schemes are typically practiced in the water industry today: (1) lime/soda ash and (2) caustic soda. There are some technologies available to even precipitate sulfates by use of chemical reagents, but their practical applicability to seawater-treatment applications is not very clear and needs detailed evaluation.

Lime/Soda-Ash Softening. Lime/soda-ash softening is the most widely used chemical-precipitation method in the water industry. In this technology, lime (calcium hydroxide) is used to precipitate carbonate hardness, and soda ash (sodium carbonate) is added for removing the noncarbonate hardness.

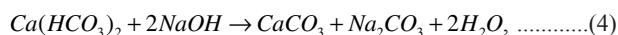
The carbonate and bicarbonate salts of calcium and magnesium constitute the so-called carbonate hardness, whereas noncarbonate hardness is primarily caused by the hardness of ion salts such as sulfates and chlorides. Calcium hardness is precipitated as calcium carbonate and magnesium hardness as magnesium hydroxide during the treatment process, and both of these precipitates are nearly insoluble. They can be made resolvable in water by adding dilute amounts of acids such as HCl and H_2SO_4 . Some key precipitation chemical reactions taking place in the lime/soda-ash softening process are listed in the following (Mountain Empire Community College 2009; Zaghaffari and Asr 2013):



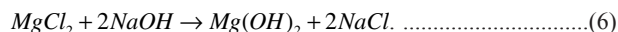
and



Caustic-Soda Softening. The single chemical “caustic soda” (sodium hydroxide) is used in this technology to precipitate both carbonate and noncarbonate hardness. As with lime/soda-ash softening, the hardness ions are precipitated as calcium carbonate and magnesium hydroxide in this process. The major chemical reactions occurring in the precipitation process are as follows (Zadghaffari and Asr 2013):



and



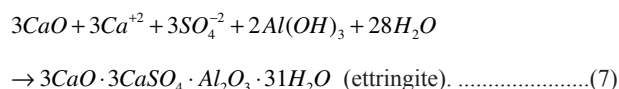
Both these softening chemical-precipitation technologies have some inherent disadvantages, such as high upfront chemical costs and major issues associated with precipitated-sludge removal and disposal. Lime/soda-ash softening is relatively less expensive compared with the caustic-soda process, and it also slightly decreases the total dissolved solids (TDS) in the treated water. The caustic-soda process produces lower sludge volumes, but sodium-ion concentration will be slightly increased in the treated water.

Pellet-softening technology is used extensively in some locations to effectively combat sludge-formation/handling issues in chemical-precipitation methods (Mahvi et al. 2005; Snedecor et al. 2008; Winklmann and McCreary 2014). In this technology, crystallization of precipitated calcium carbonate and magnesium hydroxide (to a lesser extent) occurs on a fluidized bed of sand grains. This will minimize sludge formation and the produced gravel-sized pellets can be removed from the reactor as a solid byproduct.

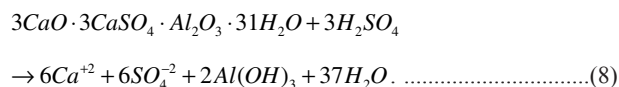
Sulfate Precipitation With Chemical Reagents. Howell (2004) and Usinowicz et al. (2005) reviewed all the available technologies to remove sulfate ions from mine water. Both these studies concluded that sulfate removal through precipitation of ettringite can provide one most-efficient treatment solution. This technology is based on the principle that addition of aluminum trihydroxide and lime at pHs ranging from 11.5 to 12.0 can precipitate sulfates in the feedwater as the sulfate-ion-based mineral ettringite. It can reduce sulfate ions from feedwater to levels below 50 ppm, and can even remove calcium ions during the treatment process.

The two commercial processes that use ettringite precipitation for sulfate-ion removal from industrial waters obtained from mining and mineral processing are SAVMIN™ and cost-effective sulfate removal (CESR). Both of these processes are basically developed to treat polluted mining waters having sulfate concentrations greater than 2,000 ppm. These are multiple-step chemical-treatment processes, and, during the initial step, calcium sulfate and metals are precipitated using lime. In the next step, either aluminum oxide (SAVMIN) or a proprietary aluminum-containing chemical (CESR) is used for sulfate precipitation as ettringite. In the SAVMIN process, aluminum is recovered for recycling from ettringite, whereas the CESR process disposes of the precipitated ettringite as sludge without aluminum recovery. The key precipita-

tion reaction occurring in both of these sulfate-removal processes with industrial water is as follows (Usinowicz et al. 2005):



In the SAVMIN process, the aluminum in the precipitated ettringite is recovered by dosing with sulfuric acid at a target pH of approximately 6.5, as per the following chemical reaction:



The aluminum trihydroxide solids are separated from the calcium sulfate by elutriation (decanting) by use of high internal mixing, and can be potentially recycled. A small makeup of only approximately 2 to 3% is required to the recycled aluminum trihydroxide. It is also important to note that all these chemical reactions occur at ambient conditions, and, as a result, the process requires only chemical additives and normal agitation to precipitate sulfate/calcium ions and recover the chemical reagent for reuse.

Banerjee et al. (2015) proposed a two-stage advanced sulfate-removal process on the basis of ettringite precipitation to treat NF-membrane reject from a mining site. The high-sulfate and calcium-containing mine water was first treated with NF membranes, and then the proposed advanced-sulfate-precipitation process was used on NF reject to produce treated effluent water. The feedwater from NF reject contained approximately 2,500 to 4,000 ppm sulfates and 800 to 1,800 ppm calcium. The ettringite precipitation was able to reduce sulfates to < 100 ppm by removing both calcium and sulfates as calcium sulfate sludge. Also, more than 95% of the aluminum-based reagent used for precipitation was recovered and reused in the process for sulfate reduction.

The two basic softening/chemical-precipitation technologies described in this subsection can be used only to remove hardness ions without showing much impact on total salinity. As a result these technologies look promising in the seawater pretreatment stage to remove hardness ions. These processes cannot stand on their own in water desalination, but they can complement the most widely used membrane and thermal-based desalination processes for better efficiency. The treated water after softening can be fed into a membrane- or thermal-based-desalination unit downstream to reduce membrane fouling/scaling and increase water recovery. El-Manharawy and Hafez (2003) performed experimental investigation to evaluate seawater alkalization as a promising pretreatment step for the RO desalination method using Red Sea surface water. These results confirmed that this pretreatment method has several technical and economic advantages in RO desalination such as hardness-ion precipitation, removal of suspended solids and colloids, bacterial disinfection, increased permeate recovery, and lower sludge volumes.

The aluminum-based ettringite-precipitation process seems to remove both hardness ions and sulfates from feedwater and, consequently, looks much more attractive. The process has been predominantly used in mining operations to remove sulfates, and as a result, the suitability and cost-effectiveness of the process in seawater applications needs to be evaluated in detail. In view of considering the importance of sulfates and divalent ions in the optimized water chemistry of smart water in carbonate reservoirs, these chemical-precipitation processes may provide one possible route to extract key ions from seawater with greater than 90% water recoveries as a first step in the water-treatment scheme. The insoluble and partially soluble precipitates rich in calcium, magnesium, and sulfate ions can then be used for blending with the desalinated fresh water to control the key-ion content in the smart water. Small amounts of dilute acid can be used to dissolve these precipitates in fresh water, which can enhance the performance of smart

Technology	Pros	Cons
Chemical precipitation	<ul style="list-style-type: none"> • Less scaling and fouling in the main desalination unit • Some water-ion-tuning flexibility for smart waterflood • Greater than 90% recoveries • Acidity may enhance smart waterflood 	<ul style="list-style-type: none"> • Only partial desalination to remove certain ions • Upfront chemical costs • Sludge handling and disposal • Additional facility costs
Salt extraction	<ul style="list-style-type: none"> • No scaling and lower energy requirements • Greater than 80–85% recoveries • Selective ion removal for smart waterflood is possible • Some expected suitability to treat high-salinity concentrates and produced water 	<ul style="list-style-type: none"> • Technology still under development • No details on costs and chemical solvents used • Chemical solvent use/recycling is uncertain • Technology scaleup needs to be demonstrated
FO	<ul style="list-style-type: none"> • Lower energy requirements • Reduced brine discharge • Can treat high-salinity water • Could become cost competitive compared with RO 	<ul style="list-style-type: none"> • Still being commercialized • Continuing developments with membranes and draw solution • Regeneration of draw solution is not yet optimized • Selective ion removal for smart waterflood is not possible
MD	<ul style="list-style-type: none"> • High water recoveries • Excellent salt separation • Can treat high-salinity water • Could become cost competitive compared with RO 	<ul style="list-style-type: none"> • Only pilot scale, not yet commercialized • Requires low-grade waste steam or heat • Ongoing further optimizations • Selective ion removal for smart waterflood is not possible
CGE	<ul style="list-style-type: none"> • High water recoveries up to 85–90% • Can treat high-salinity water and produced water • Modular design • Can offer a potential ZLD solution 	<ul style="list-style-type: none"> • Still being commercialized • No details on costs, energy requirements, or footprint estimates • Selective ion removal for smart waterflood is not possible • May not be cost-effective compared with RO for seawater desalination
Dynamic vapor recompression	<ul style="list-style-type: none"> • High water recoveries up to 97% • Can treat both high-salinity concentrates and produced water • Minimal pretreatment and no scaling • Can provide an excellent ZLD solution 	<ul style="list-style-type: none"> • Only small-scale demonstrations, and scalability needs to be determined • No details on costs, energy requirements, or footprint estimates • Selective ion removal for smart waterflood is in question • May not be cost-effective compared with RO for seawater desalination

Table 1—Pros and cons of reviewed water-chemistry-alteration technologies.

waterflood because of favorable acid interactions with the limestone. The major disadvantage of these chemical-precipitation technologies is that they can only accomplish partial desalination by removing certain water ions. After the chemical treatment, the feedwater needs to be separated into two streams: treated effluent and precipitated residue. The treated effluent water stream should be further processed in a downstream desalination unit, such as membrane desalination or any other suitable technology to achieve complete desalination and produce fresh water. The precipitated residue should then be mixed with fresh water to provide some control on tuning the key-ion content in smart water. The pros and cons of chemical-precipitation technologies are summarized in **Table 1**.

Chemical-Based Salt-Extraction Technologies

The technologies in this category depend on some type of chemical solvents to extract salt ions from seawater. There are some newer technologies being developed that use liquid solvents to extract salts from seawater continuously. The technology developed by Adionics constitutes one good example of such a salt-extraction process. The Adionics process removes salts and associated ions from feedwater by use of selected chemical solvents on the basis of the liquid/liquid

extraction principle (Adionics 2014). The salts are extracted at ambient pressure without any scaling, but at the same time with low energy requirements and high water recovery. Three different versions of this technology are under development: AquaOmnes®, SMARTEX®, and SELECTEX® (Water Online 2015). AquaOmnes removes all salt ions from high-salinity brines and seawater to generate fresh water. The SMARTEX process can smartly extract only families of cations on the basis of the valency. SELECTEX can facilitate extraction of selective water ions while leaving other ions untreated in the product water. It can treat high-salinity waters, including the produced water, to remove certain ions, such as calcium, barium, strontium, and sulfates, while leaving behind the other ions, such as sodium and chloride, in the treated water. The SELECTEX process seems to be of high relevance to the oil and gas industry when EOR applications are considered.

These extraction-based technologies can be attractive. Their capabilities are also broad, starting from fresh water to divalent/sulfate-ion removal and specific-ion removal to include even produced-water desalination for IOR/EOR. A few small-scale pilot plants that use AquaOmnes are under construction/operation, with the objective to demonstrate the desalting capabilities of this

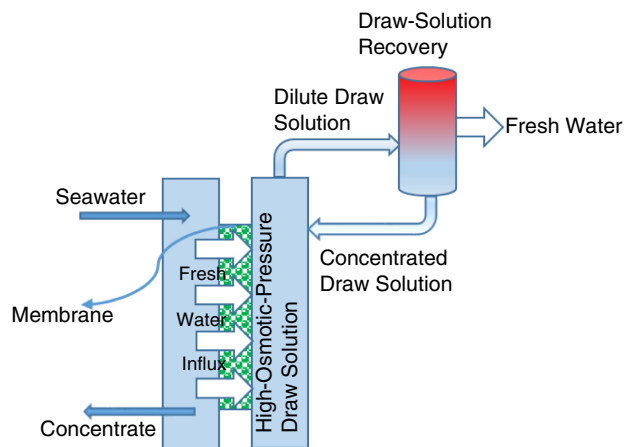


Fig. 1—Schematic of FO desalination process.

technology to generate fresh water (AMEinfo 2015). The other major capabilities of technologies such as SMARTEX and SELECTEX still need to be demonstrated. The suitability of these technologies for treating produced water is not clear. Also, not many details are available on the technology scaleup, type of chemical solvents used, solvent use/recycling capability, and expected costs per barrel of treated water. These technologies, once developed, look attractive because they can selectively remove specific ions, even from high-salinity produced water for reinjection into different IOR/EOR processes, including smart waterflood in carbonates. The pros and cons of chemical-extraction technologies are included in Table 1.

Emerging Alternative Desalination Technologies

The two emerging seawater-desalination technologies of FO and MD are described in this section to evaluate their pros and cons in comparison with the most widely used RO desalination method. The other two new technologies based on CGE and dynamic vapor recompression are also included to assess their capabilities and determine the suitability for seawater desalination and smart waterflooding.

Forward Osmosis (FO). FO desalination is also called “direct osmosis,” and it uses a semipermeable membrane and a high-osmotic-pressure concentrated “draw” solution to generate fresh water from saline source water. In other words, osmotic pressure is used as a “driving force” to separate water across the membrane rather than the hydraulic-pressure gradient used in conventional membrane-desalination processes. A schematic of the FO desalination process is shown in Fig. 1.

As shown in Fig. 1, fresh water passes through the membrane and dilutes the draw solution. The draw solution is then concentrated in a recovery system to produce fresh water. Development of appropriate membranes with low fouling and high water flux, identification of suitable draw solution, and its efficient recovery/recyclability are the keys to the success of FO technology. These three parameters have a critical impact on the technology development and economic viability. The draw solution should also exhibit high osmotic pressure, must be environmentally benign, and should be easily recoverable.

Some breakthrough was achieved in FO during the mid-2000s, and a recyclable concentrated draw solution consisting of ammonium salts was successfully used to provide high osmotic pressure (McCutcheon et al. 2006). The resulting dilute draw solution was thermally separated to produce fresh water. This thermal separation was achieved by use of the unique characteristics of the salts in the draw solution to decompose into ammonia and carbon dioxide (CO_2) gases when heated. The low-grade waste heat can be used in this recovery system to yield high water recoveries and lower energy requirements.

Mehta et al. (2014) performed cost comparisons between FO and RO technologies, and these results indicated that forward osmosis

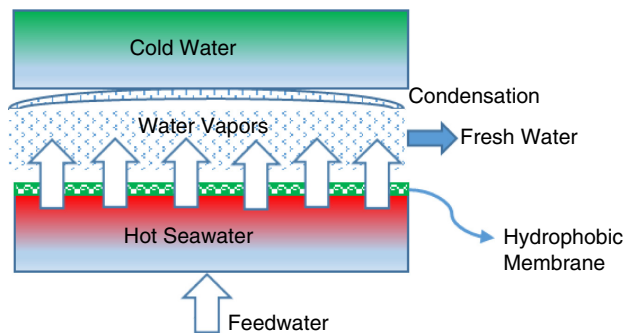


Fig. 2—Schematic of MD process.

could be economically better. The water companies, such as HTI Water Technology, Oasys Water, and Modern Water, are involved in the commercialization of FO technology. HTI is developing the technology on the basis of readily available concentrated draw solutions such as oilfield produced water, waste mud from drilling wells, concentrated rehydration drinks, and potentially fruit juice concentrate. In contrast, Oasys Water is developing FO technology using the concentrated solute containing ammonium carbonate salts. The other company, Modern Water, deployed their modified FO technology [manipulated osmosis desalination (MOD)] for seawater desalination using a proprietary osmotic agent (Thompson and Nicoll 2011). A membrane-based regeneration system is used in the MOD process. The MOD process has been implemented at commercial scale with a 100 m³/d desalination plant in Al Khaluf and another 200 m³/d desalination plant at Al Najdah, both in Oman (Thompson and Nicoll 2011; Chaudhry 2013). Because there is no osmotic-pressure limitation in FO technology, it can also be well-suited to treat much-higher-salinity water. McGinnis et al. (2013) demonstrated successfully through a pilot study that NH_3/CO_2 FO desalination can be used to desalinate the fracture flowback and produced water (73,000 ppm average salinity) from natural-gas-extraction operations in the Marcellus shale region. The pros and cons of FO desalination technology are summarized in Table 1.

Membrane Distillation (MD). MD is a hybrid desalination method that combines both thermal and membrane-based desalination concepts in one process. In this technology, vapor pressure is used as a “driving force” to pass evaporated vapors across the membrane. The membranes used are hydrophobic in nature, and as a result, they allow only water vapor to pass through, while leaving liquid water with salts behind. The desired vapor-pressure gradient for the process is created by heating the source feedwater. A schematic showing the working principle of MD is shown in Fig. 2. As can be seen, a temperature gradient is created across the membrane between cold and hot sides. The vapors from hot water pass through the membrane to the cooler side, and ultimately condense there to form fresh water. The process thereby requires some heat to produce fresh water from seawater by use of a membrane module and vaporization/condensation cycles.

Memstill® is one major MD process (Hanemaaijer et al. 2006, 2007) developed by a consortium of nine parties at the Netherlands Organization for Applied Scientific Research (TNO), which is currently gaining some attention. In this desalination process, seawater is first heated in a condenser by use of the heat of condensation from water vapor, and then it flows through a heat exchanger into the membrane evaporator. Only water vapor diffuses through the membrane while rejecting the liquid water. The water boiling point is adjusted in the membrane evaporator by reducing the ambient pressure of the water. This promotes boiling at reduced temperatures from top to bottom in the evaporator system.

Several small-scale Memstill pilots on seawater/brackish-water desalination have been successfully carried out starting from 2006.

First was a 2-m³/d seawater pilot in Singapore, then two pilots on brackish-water desalination in the Netherlands, and a recent trial was performed at BASF (Badische Anilin und Soda Fabrik), a port in Antwerp in 2011 (Jansen et al. 2010; Camacho et al. 2013). There are also some plans to build a 100-m³/d demonstration pilot at a refinery in Singapore (Camacho et al. 2013). Memstill looks especially attractive when compared with RO for treating high-salinity waters because the energy demand in the process is independent of salt concentration (Tarnacki et al. 2012). The cost of treated water from Memstill technology seems to be much lower compared with thermal desalination and relatively less expensive than RO desalination. The process is expected to decrease the desalination costs considerably in large-scale applications that use low-grade waste steam or heat. Excellent salt-separation efficiency, small footprint, limited fouling/corrosion, and simple modular construction are some major advantages associated with this desalination process. The pros and cons of this emerging desalination technology are summarized in Table 1.

Carrier-Gas Extraction. The new desalination process CGE is based on the humidification/dehumidification principle. This technology involves atmospheric pressure/moderate temperatures and uses a carrier gas to extract fresh water (<100 ppm salinity) from high-salinity brines. It was developed by Gradient Corporation, a Massachusetts Institute of Technology (MIT) spinoff company. The saline water is first heated and sprayed onto porous material of large surface area, which comes directly into contact with carrier gas such as dry air. The air saturated with water vapor is then processed in a multistage bubble column (which acts as both a heat and mass exchanger), wherein the humid air is passed as bubbles through a series of holes into water-filled trays. During this exchange process, the water vapor in the bubbles becomes cooled and condensed to create more fresh water in the trays (Whitfield 2014). The energy is recovered by using the heat of condensation to preheat incoming feedwater.

CGE technology can treat hyper-saline produced waters (>200,000 ppm TDS) from oil and gas production. It requires rigorous pretreatment for produced water to remove oil/grease residual content and solid particles. The process is currently being commercialized in the Permian basin to treat produced water and create the fresh water required for hydraulic-fracturing operations in unconventional resources (Passut 2014). This modular pilot plant has a capacity to treat approximately 5,000 to 10,000 B/D of produced water. The technology can also be used for seawater desalination and to treat contaminated waters. The output water from CGE (i.e., fresh water) is of the same quality as other well-established technologies, such as membrane (RO) and thermal desalination. The treatment of produced water (up to and more than 200,000 ppm TDS) in remote areas, where reinjection/disposal facilities are not available, is one direct application for this technology. It could provide one potential solution to meet the environmental regulations of ZLD in oilfield applications.

CGE technology will not be able to provide a cost-effective solution for seawater desalination in comparison with RO. The advantages of CGE technology (in terms of cost, footprint, and energy requirements) over the most widely used RO membrane-based seawater desalination are not well-defined. The scalability of this technology to large-scale applications has also not been demonstrated. The resultant product water is fresh (<500 ppm TDS); consequently, optimum water-ion tuning without blending with feed seawater is not possible. This technology could be attractive for desalination of oilfield produced water, and highly saline waters in remote locations where reinjection/disposal facilities are not available. The pros and cons of CGE technology are described in Table 1.

Dynamic Vapor Recompression. Dynamic vapor recompression, developed by Salttech (based in the Netherlands), involves thermal distillation in a modular system. It is a type of mechan-

ical vapor recompression in principle, and water is evaporated at moderate temperatures by applying vacuum, which is subsequently condensed. A heat exchanger is used to transfer heat of condensation to the incoming water stream to reduce energy requirements. The key feature of this technology is that a cyclone is used in the evaporation stage to provide maximum separation of crystallized salts from brine through centrifugal force. The system requires no pretreatment, and it can be operated without any scaling and fouling (BlueTech Research 2015).

The energy requirements of this technology are expected to be lower than those of conventional thermal-desalination processes. The recoveries as high as 97% clean water can be achieved (Water-Technology.net 2015). The remaining low volumes of reject (3% and higher) are collected in the system as either crystallized salts or high-concentration brine. The process is capable of handling high-salinity waters containing up to and more than 300,000 ppm TDS, which includes fracture flowback, oilfield produced water, seawater, and reject streams from conventional membrane desalination (Business Wire 2015). The high water recoveries obtained with seawater compared with existing membrane-based processes look attractive because they can minimize the discharge of concentrated brines into the environment. The cost-competitiveness of this technology and footprint estimates in comparison to more-popular membrane-based desalination processes are still unclear, and need further investigation.

The dynamic-vapor-recompression technology could be promising for the treatment of high-salinity contaminated waters, including oilfield waters, because it requires minimal pretreatment and can provide high water recoveries. The process also has merit for providing a ZLD solution with existing membrane-desalination technologies to meet environmental regulations. There are limited small-scale applications of this technology, mainly to desalinate gypsum-contaminated brackish waters to provide a drinking-water resource (SaltTech 2014; McEwen 2015). It appears that several demonstrations were conducted to confirm the applicability of this technology to treat ocean and oilfield fracture-flowback waters. The capabilities of this technology to remove specific salt ions selectively from brine solution needs detailed evaluation. The pros and cons of dynamic-vapor-recompression technology are summarized in Table 1.

Future Desalination Technologies

Carbon-nanotube-based desalination, graphene-sheet-based desalination, and capacitive deionization are the three potential future seawater-desalination technologies identified for the long term. A brief summary of these three technologies is provided in this section.

Carbon-Nanotube-Based Desalination. This technology looks to be one of the most-promising desalination processes being developed for the long term. Researchers at Lawrence Livermore National Laboratory developed a membrane consisting of carbon nanotubes and silicon with the objective of accomplishing less-expensive seawater desalination (Stark 2006). These hollow nanotubes are approximately 50,000 times thinner than human hair, and potentially serve as pores in the membrane. The spaces between the nanotubes are filled with a ceramic material to provide good strength and enable adherence of nanotubes to the silicon chip. The smooth and tiny holes in the membrane allow liquids to drain rapidly through with improved flux while blocking larger salt molecules. Appropriate pore diameters can facilitate rejection of salt ions while allowing water to pass through the nanotube hollow structure (Das et al. 2014; Corry 2008). The carbon-nanotube pores can also be modified to reject ions selectively by use of size-controlled separation (Das et al. 2014; Balcajin et al. 2009).

It is anticipated that these high-permeability nanotube membranes will reduce energy-requirement costs of conventional RO membrane-based desalination by up to 75%. The feasibility of desalinating seawater with this technology has been tested in the

Technology	Selective Ion Removal	Seawater	Produced Water	High-Salinity Water	Maturity	Technology Selection
NF	Yes	Yes	No	No	High	Yes
RO	No	Yes	No	No	Very high	Yes
Chemical precipitation	Yes	Yes	No	No	Medium to high	Yes
Salt extraction	Yes*	Yes	Yes*	Yes	Low	No
FO	No	Yes	Yes	Yes	Low to medium	Maybe
MD	No	Yes	No	Yes	Medium	Maybe
CGE	No	Yes**	Yes	Yes	Medium	Maybe
Dynamic vapor recompression	No*	Yes**	Yes	Yes	Medium	Maybe

*Needs further evaluation
**May not be cost-effective

Table 2—Summary of technology selection criteria used for both available and reviewed technologies.

laboratory and the technology has been licensed exclusively to a California-based company for commercializing carbon-nanotube membranes for water desalination and CO₂ capture from power plants. The process is still under research and it may take several years down the road to develop this technology.

Graphene-Nanosheet-Based Desalination. This technology is based on the use of graphene sheets with accurately controlled nano-sized pores for desalination (Spasenovic 2013). MIT researchers proposed this new approach with sheets of graphene, which is a one-atom-thick form of elemental carbon. These graphene sheets are approximately 1,000 times thinner than the conventional desalination membranes, and as a result, much lower pressures are required to force the water through the membrane. Creating holes of specific size with precision on graphene sheets is the critical step in the technology development, which could be quite challenging. MIT demonstrated the feasibility of this technology by use of computer simulations, and started testing actual membranes in the laboratory. Theoretically, it was found that pore sizes of at least 0.7 to 0.9 nm in diameter were very effective in passing water molecules through the membrane while rejecting sodium ions. This technology is still in the early stages of research and development.

Capacitive Deionization. Capacitive deionization is electrochemical-based salt-ion-splitting technology for desalination. Selective electrostatic adsorption of ions from seawater onto a charged electrode is the main working principle. The adsorption of water ions by the charged plates reduces the total salinity of treated water. A pair of carbon electrodes is used, and each set of these electrodes contains the flow channel for seawater. When direct-current voltage is applied, charged ions from the passing ionic source water are attracted to the appropriate electrodes to form an electric double layer (Al-Rawajfeh and Zarooni 2008). These ions are then removed by temporarily changing the polarity during the regeneration step. This technology has so far been economically applied only in brackish-water desalination. Recently scientists from South Korea have modified this technology to desalinate seawater on a larger scale by developing small-sized flow electrodes from suspended carbon materials (Newton 2013). The approach is more energy efficient, does not require a discharge step as is needed in conventional capacitive deionization, and can easily be scaled up for a large-scale operation. The proof of concept for this modified capacitive deionization technology is demonstrated, and it is expected that further optimization in the system design may provide a better solution for large-scale desalination in the long-term future.

Development of Conceptual Water Ionic Composition Optimization Process Configurations for Smart Waterflooding

A summary of the technology selection criteria used for all the available and reviewed water-chemistry-alteration technologies in this study is given in **Table 2**. As can be seen, NF and chemical-precipitation technologies are able to provide selective ion removal, although they are not suited to handle high-salinity water/produced water, and their desalination capabilities are also limited to produce fresh water. RO has very high maturity, and can generate fresh water. It will not be able to provide any selective ion removal, and it is not suited for high-salinity-water/produced-water treatment. The capabilities of salt-extraction technologies appear broad enough to cover selective ion removal and seawater/high-salinity-water/produced-water desalination, but the technology is still in the early stages of development with low maturity. FO and MD technologies are in the pilot stage (low to moderate maturity), and these can generate fresh water from both seawater and high-salinity water without any selective ion removal. The two technologies of CGE and dynamic vapor recompression are suited to treat seawater, high-salinity water, and produced water. On the basis of the chosen screening criteria, all the technologies (except extraction-based processes) were selected for the development of conceptual water-treatment configurations to generate smart water from both seawater and produced water.

Seven different water-treatment-process configurations are developed for smart waterflooding in carbonates by use of the selected technologies. Some of these configurations involve seawater desalination only to generate smart water. Other complex configurations include both produced-water treatment and further treatment of conventional membrane rejects to even provide a practical ZLD solution in locations where produced-water-reinjection/-disposal facilities are not available. Such configurations can become an attractive solution for the eventual use of produced water and the minimization of wastewater disposal during fieldwide implementation of smart waterflood.

Configuration 1 represents a simple approximate solution, as shown in **Fig. 3**. The fresh water from RO/FO/MD is blended with seawater to generate smart water. The treatment configuration shown in **Fig. 4** provides an improved solution over Configuration 1 to generate better smart water. The fresh water obtained from RO/FO/MD is blended with NF reject to provide some tuning flexibility on divalent-ion content and sulfates. NF permeate is recycled back to mix with feed seawater. Configuration 3 provides another improved solution that uses ettringite-based chemical precipitation,

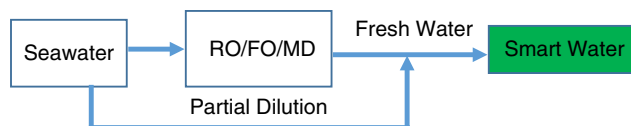


Fig. 3—Water-treatment process, Configuration 1 (approximate solution).

followed by any desalination process such as RO, FO, and MD (shown in Fig. 5). The hardness ions and sulfates are removed during the first chemical-precipitation step, whereas the next desalination step separates the treated water into fresh water and monovalent-ion-rich reject. The precipitated residue rich in calcium, magnesium, and sulfates can be used to control key-ion content in the smart water by blending with fresh water.

The next water-treatment process, Configuration 4 (Fig. 6), consists of three steps. Lime/soda ash or alkali is used as the first step in the water-treatment process to remove hardness ions from seawater as hardness-rich insoluble precipitate. The hardness-free water is then passed into an NF membrane unit in the second step to extract only sulfate ions as concentrate and a monovalent-ion-rich stream as permeate. A split stream of hardness-free water from the first step, together with the monovalent-ion-rich stream from the second step, is finally passed into a suitable desalination unit (RO, FO, and MD) during the third step to remove all the salt ions from the feedwater as reject and provide fresh water as the product. Sulfate removal and the desalination units operate in a parallel configuration. The different available water streams from the proposed scheme are hardness-rich precipitate, sulfate-rich stream, and fresh water. The two key salt-ion-containing streams can be used for blending with fresh water to tune water chemistry for precisely controlling the salinity, sulfates, and divalent ions desired for smart waterflooding in carbonates.

The newer emerging technologies, such as FO and MD, are being commercialized and could become cost-effective alternatives to RO desalination in the near future. As a result, these processes are included in the full-desalination step with RO in Configurations 1 through 4. The partial or low solubility of salt products obtained during the chemical-precipitation step of Configurations 3 and 4 may necessitate the use of dilute acids such as HCl or H₂SO₄ to dissolve these precipitates in fresh water. It is believed that the presence of small volumes of these acids in water may be able to further enhance smart-water performance because of the favorable acid interactions expected with carbonates. Adoption of the chemical-precipitation step in both these treatment schemes not only removes certain important ions from seawater, but also improves the performance of the downstream desalination unit in terms of better tuning flexibility, reduced scaling, better membrane life, and increased recovery efficiency. The major difference between the two process configurations is that all the key ions are precipitated together in

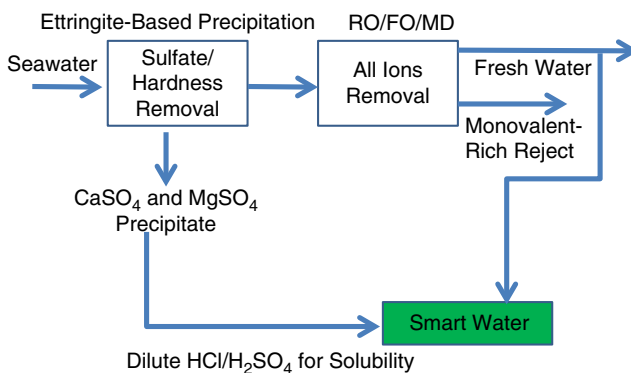


Fig. 5—Water-treatment process, Configuration 3 (improved solution).

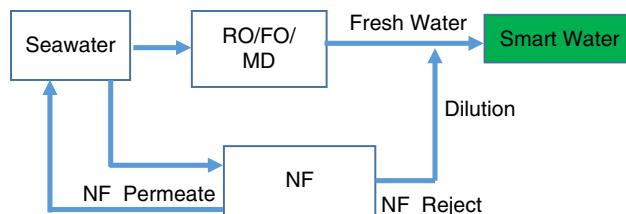


Fig. 4—Water-treatment process, Configuration 2 (improved solution).

the two-step technology, whereas the three-step technology separates out sulfates from calcium and magnesium to provide relatively better water-ion-tuning flexibility for smart waterflooding.

Fig. 7 presents the approximate solution with almost ZLD. The reject stream from RO is further treated using CGE/dynamic vapor recompression (labelled DyVaR in this and subsequent figures) to generate fresh water. This fresh water joins with RO permeate stream before blending with seawater. Figs. 8 and 9 summarize the two conceptual process configurations, which provide a potential solution to treat produced water to accomplish ZLD in one system. Fig. 8 gives an approximate solution with both produced-water treatment and ZLD capabilities. Seawater is treated in RO, and a parallel stream of produced water is first pretreated to remove oil, grease, and solids. This pretreated produced water is blended with RO reject, and then desalinated downstream by use of CGE or dynamic vapor recompression. The pretreatment step could be different for these two desalination processes, and it appears that dynamic vapor recompression requires minimal pretreatment when compared with CGE. The fresh desalinated produced water is finally mixed with RO permeate before blending with seawater to generate approximate smart water.

The water-treatment-process configuration shown in Fig. 9 provides an improved smart-water ZLD solution on both seawater and produced-water streams. First, seawater is split into two different streams, and then each one is processed separately in RO and NF systems operated in a parallel configuration. NF reject, rich in divalents and sulfates, is blended with RO permeate, whereas NF permeate (monovalent-ion-rich stream) is recycled back to mix with feed seawater. Another produced-water stream is pretreated in parallel, and then the pretreated produced water, along with RO and remaining NF rejects, is desalinated by use of CGE/dynamic vapor recompression to provide fresh water. This fresh water is blended with RO permeate and NF-reject streams to yield improved smart water.

It is important to note that Configurations 6 and 7 (shown in Figs. 8 and 9) consider both produced-water treatment and further treatment of conventional membrane rejects to essentially provide a practical

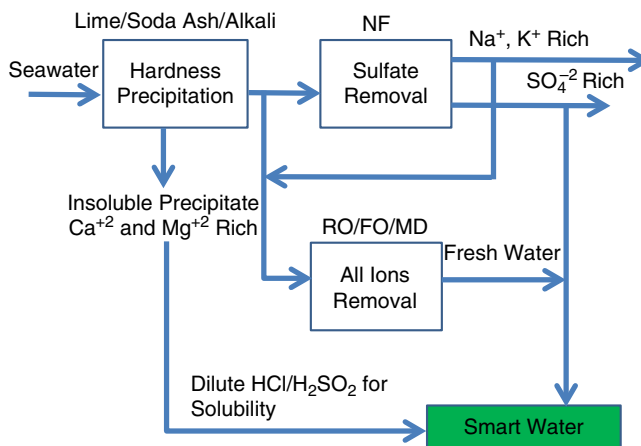


Fig. 6—Water-treatment process, Configuration 4 (exact solution).

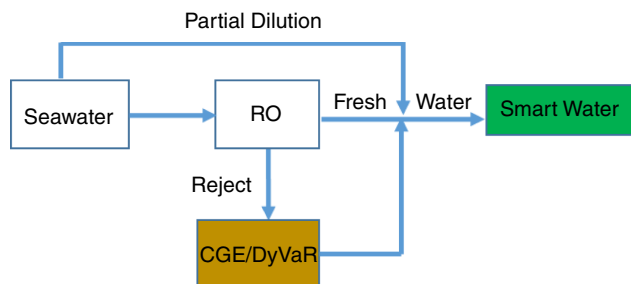


Fig. 7—Water-treatment process, Configuration 5 (approximate solution with ZLD).

ZLD solution in locations where produced-water-reinjection/-disposal facilities are not available. These two novel schemes would provide a potential solution to capitalize on existing huge produced-water resources in carbonate reservoirs to generate smart water and minimize wastewater disposal in field applications.

Currently rigorous in-house fundamental research studies are being carried out at atomic/molecular/Darcy scales to optimize injection-smart-water compositions in terms of specific individual water ions. Such optimized injection-water recipes, once developed, can result in more-favorable interactions at both fluid/fluid and rock/fluid interfaces to yield better oil recoveries in smart-waterflooding processes. In addition, the use of produced water is also being examined as a means to use large produced-water resources available in carbonate reservoirs and, consequently, provide efficient water management during fieldwide implementation of the smart waterflood. From these two perspectives, Configurations 6 and 7 (shown in Figs. 8 and 9) look highly attractive; however, more-detailed studies should be performed in the next phase to evaluate their technical robustness and economic viability. The major path-forward steps include performing in-depth technical and economic analysis on these two water-treatment-process configurations to generate some valid estimates on surface facilities.

Summary and Conclusions

Different chemical-precipitation/extraction technologies and current, emerging, and future desalination processes are reviewed in this study to evaluate their suitability for smart waterflooding in carbonates; the following are some important findings:

- Chemical-precipitation technologies such as lime/soda ash, alkali, and lime/aluminum-based reagent will not stand on their own for desalination applications, but they can be used in an initial pretreatment step for existing desalination technologies. These technologies are useful for extracting key ions from seawater before treatment in the main desalination system. As a result, they can provide some water-ion-tuning flexibility for smart waterflooding.
- The technologies that are based on chemical-solvent extraction have some potential to remove specific ions selectively from sea-

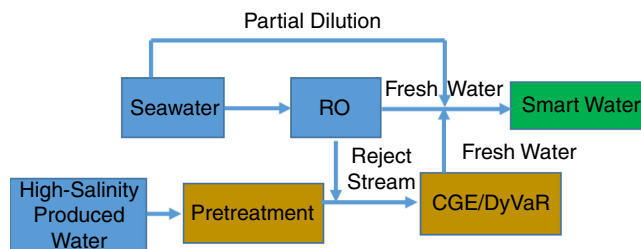


Fig. 8—Water-treatment process, Configuration 6 (approximate solution with ZLD and produced water).

water. These technologies are still in the early stages of development. More studies are required to assess their full capabilities and evaluate the economics.

- The emerging desalination technologies, such as FO and MD, are being commercialized, and are expected to become potential alternatives to conventional RO desalination for the near term. These technologies can offer a cost-effective solution to RO, in which there is availability of low-grade waste heat or steam.
- The two new desalination technologies, based on dynamic vapor recompression and CGE, are suited for treating high-salinity water, produced water, and conventional membrane-reject streams for ZLD. These technologies may not provide a cost-effective solution for seawater desalination.
- Carbon-nanotube-based desalination, graphene-sheet-based desalination, and capacitive deionization are the three potential future seawater-desalination technologies identified for the long term. Among these, carbon-nanotube-based desalination is attractive, but the process is still being researched, and these membranes are being developed for water desalination and CO₂ capture from industrial power plants.
- There is no commercial technology yet available to remove specific ions selectively from seawater in one step and optimally meet the water-chemistry requirements of smart waterflooding. As a result, seven different process configurations involving selected combinations of chemical precipitation, conventional/emerging desalination, and produced-water-treatment technologies are proposed.
- These configurations provide several approximate and improved solutions to generate smart water. Some of them include produced-water treatment and further treatment of conventional membrane rejects to provide a practical ZLD solution in locations where produced-water-reinjection/-disposal facilities are not available.
- The conceptual water-treatment configurations developed in this study would provide an attractive solution to capitalize on existing huge produced-water resources in carbonate reservoirs to generate smart water and minimize wastewater disposal during fieldwide implementation.

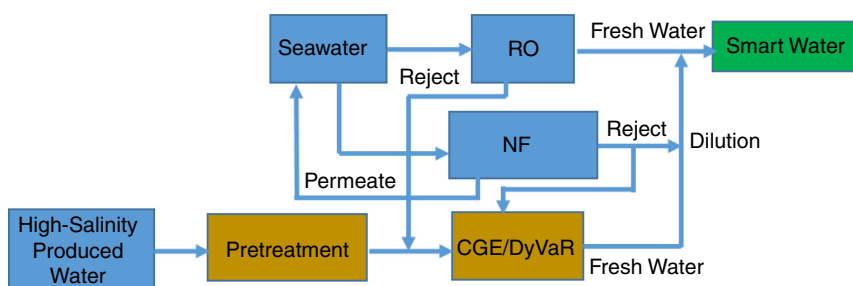


Fig. 9—Water-treatment process, Configuration 7 (improved solution with ZLD and produced water).

Acknowledgments

The authors would like to thank Saudi Aramco for providing permission to present and publish this work. They would also like to thank management of EXPEC Advanced Research Center for the great support.

References

- Adionics. 2014. AquaOmnes Technology, <http://aquaomnes.adionics.com/en/homepage/technology> (accessed 10 December 2015).
- Al-Rawajfeh, A. E. and Zarooni, M. A. 2008. New Processes in Seawater Desalination. *Recent Patents on Chemical Engineering* **1** (2): 141–150. <http://dx.doi.org/10.2174/2211334710801020141>.
- AMEinfo. 2015. Adionics Adapts Its AquaOmnes Disruptive Desalination Technology to Existing Desalination Plants and to the Oil and Gas Industry, <http://ameinfo.com/energy/oil-and-gas/extraction/adionics-adapts-aquaomnes-disruptive-desalination-technology-existing-desalination-plants-oil-gas-industry/> (accessed on 10 December 2015).
- Austad, T. 2013. Water Based EOR in Carbonates and Sandstones: New Chemical Understanding of the EOR Potential Using Smart Water. In *Enhanced Oil Recovery Field Case Studies*, ed. J. Sheng, Chapter 13, 301–335, Elsevier. <http://dx.doi.org/10.1016/B978-0-12-386545-8.00013-0>.
- Ayirala, S. C., Chin, R. W., Curole, M. A. et al. 2014. Water Injection Systems and Methods. US Patent Grant No. US8794320 B2.
- Ayirala, S. C., Chin, R. W., Matzakos, A. N. et al. 2016. Water Injection Systems and Methods. US Patent Grant No. US9234413 B2.
- Ayirala, S. C., Uehara-Nagamine, E., Matzakos, A. et al. 2010. A Designer Water Process for Offshore Low Salinity and Polymer Flooding Applications. Presented at the SPE Improved Oil Recovery Symposium, Tulsa, 24–28 April. SPE-129926-MS. <http://dx.doi.org/10.2118/129926-MS>.
- Ayirala, S. C. and Yousef, A. A. 2015. A State-of-the-Art Review To Develop Injection-Water-Chemistry Requirement Guidelines for IOR/EOR Projects. *SPE Prod & Oper* **30** (1): 26–42. SPE-169048-PA. <http://dx.doi.org/10.2118/169048-PA>.
- Balcájin, O., Noy, A., Fornasiero, F. et al. 2009. Chapter 6—Nanofluidic Carbon Nanotube Membranes: Applications for Water Purification and Desalination. In *Nanotechnology Applications for Clean Water: A Volume in Micro and Nano Technologies*, eds. N. Savage, M. Diallo, J. Duncan et al., Chapter 6, 77–93. Norwich, New York: William Andrew Inc. <http://dx.doi.org/10.1016/B978-0-8155-1578-4.50015-9>.
- Banerjee, K., Howell, C., Blumenshien, C. et al. 2015. An Innovative Process To Reduce Sulfate in Membrane Concentrate Enhances Mine Water Recovery. *Proc.*, 10th International Conference on Acid Rock Drainage & IMWA Annual Conference, Santiago, Chile, 21–24 April.
- BlueTech Research. 2015. Innovation Tracker—Company Snapshot: Saltech, <http://inside.bluetechresearch.com/tools/innovation-tracker/salttech/> (accessed 10 December 2015).
- Bowell, R. J. 2004. A Review of Sulfate Removal Options for Mine Waters. In *Proceedings International Mine Water Association Symposium*, Vol. 2, 75–91, Newcastle Upon Tyne, UK.
- Business Wire. 2015. STW Resources To Present Its Saltech Water Desalination Technology to Texas State Capitol May 13 and 14, <http://www.businesswire.com/news/home/20150511006283/en/STW-Resources-Present-Saltech-Water-Desalination-Technology> (accessed 17 April 2016).
- Camacho, L. M., Dumée, L., Zhang, J. et al. 2013. Advances in Membrane Distillation for Water Desalination and Purification Applications. *Water* **5** (1): 94–196. <http://dx.doi.org/10.3390/w5010094>.
- Chandrasekhar, S. and Mohanty, K. K. 2013. Wettability Alteration With Brine Composition in High Temperature Carbonate Reservoirs. Presented at the SPE Annual Technical Conference and Exhibition, New Orleans, 30 September–2 October. SPE-166280-MS. <http://dx.doi.org/10.2118/166280-MS>.
- Chaudhry, S. 2013. An Overview of Industrial Desalination Technologies. Presented at the ASME Industrial Demineralization (Desalination): Best Practices & Future Directions Work Shop, Washington, DC, 28–29 January.
- Christopher, C. A., Collins, I. R., Frampton, H. et al. 2009. Desalination Method. US Patent Grant No. US7600567 B2.
- Collins, I. R., Li, K., Livingston, A. G. et al. 2010. Water Flooding Method. US Patent Grant No. US7726398 B2.
- Corry, B. 2008. Designing Carbon Nanotube Membranes for Efficient Water Desalination. *J. Phys. Chem. B* **112** (5): 1427–1434. <http://dx.doi.org/10.1021/jp709845u>.
- Curole, M. A. and Greene, E. B. 2014. Water Injection Systems and Methods. US Patent Grant No. US8789594 B2.
- Das, R., Ali, M. E., Hamid, S. B. A. et al. 2014. Carbon Nanotube Membranes for Water Purification: A Bright Future in Water Desalination. *Desalination* **336**: 97–109. <http://dx.doi.org/10.1016/j.desal.2013.12.026>.
- El-Manharawy, S. and Hafez, A. 2003. Study of Seawater Alkalization as a Promising RO Pretreatment Method. *Desalination* **153** (1–3): 109–120. [http://dx.doi.org/10.1016/S0011-9164\(02\)01110-4](http://dx.doi.org/10.1016/S0011-9164(02)01110-4).
- Fathi, S. J., Austad, T., and Strand, S. 2011. Water-Based Enhanced Oil Recovery (EOR) by “Smart Water”: Optimal Ionic Composition for EOR in Carbonates. *Energy & Fuels* **25** (11): 5173–5179. <http://dx.doi.org/10.1021/ef201019k>.
- Hanemaaijer, J. H., van Medevoort, J., Jansen, A. E. et al. 2006. Memstill Membrane Distillation – A Future Desalination Technology. *Desalination* **199** (1–3): 175–176. <http://dx.doi.org/10.1016/j.desal.2006.03.163>.
- Hanemaaijer, J., van Medevoort, J., Jansen, A. et al. 2007. Memstill Membrane Distillation: A Near-Future Technology for Seawater Desalination. Presented at the International Desalination Conference (IDC), Aruba, 10–22 June.
- Henthorne, L., Martin, C., and Johnson, H. 2013. Developing and Piloting Water Treatment Technologies To Address Offshore EOR Challenges. Presented at the SPE Enhanced Oil Recovery Conference, Kuala Lumpur, 2–4 July. SPE-165241-MS. <http://dx.doi.org/10.2118/165241-MS>.
- Henthorne, L. and Movahed, B. 2013. Method and Control Devices for Production of Consistent Water Quality From Membrane-Based Water Treatment for Use in Improved Hydrocarbon Recovery Operations. US Patent Application No. US2013/0161256 A1.
- Jadhunandan, P. and Morrow, N. R. 1995. Effect of Wettability on Waterflood Recovery for Crude Oil/Brine/Rock Systems. *SPE Res Eng* **10** (1): 40–46. SPE-22597-PA. <http://dx.doi.org/10.2118/22597-PA>.
- Jansen, A., Hanemaaijer, J. H., Assink, J. W. et al. 2010. Pilot Plants Prove the Feasibility of a New Desalination Technique. *Asian Water*, 22–26. http://www.earto.eu/fileadmin/content/10_Hidden_Pages/Case_Studies_2011/TNO-Memstill_Asian_Water_pub.pdf.
- Lager, A., Webb, K. J., Collins, I. R. et al. 2008. LoSal™ Enhanced Oil Recovery: Evidence of Enhanced Oil Recovery at the Reservoir Scale. Presented at the SPE/DOE Improved Oil Recovery Symposium, Tulsa, 19–23 April. SPE-113976-MS. <http://dx.doi.org/10.2118/113976-MS>.
- Ligthelm, D. J., Gronsveld, J., Hofman, J. P. et al. 2009. Novel Waterflooding Strategy by Manipulation of Injection Brine Composition. Presented at the SPE EUROPEC/EAGE Annual Conference and Exhibition, Amsterdam, The Netherlands, 8–11 June. SPE-119835-MS. <http://dx.doi.org/10.2118/119835-MS>.
- Ligthelm, D. J., Romanuka, J., and Suijkerbuijk, B. 2012. Water Injection Systems and Methods. US Patent Application No. US/2012/0090833 A1.
- Mahani, H., Sorop, T. G., Ligthelm, D. J. et al. 2011. Analysis of Field Responses to Low-Salinity Waterflooding in Secondary and Tertiary Mode in Syria. Presented at the SPE EUROPEC/EAGE Annual Conference and Exhibition, Vienna, Austria, 23–26 May. SPE-142960-MS. <http://dx.doi.org/10.2118/142960-MS>.
- Mahvi, A. H., Shafiee, F., and Naddafi, K. 2005. Feasibility Study of Crystallization Process for Water Softening in a Pellet Reactor. *International Journal of Environmental Science & Technology* **1** (4): 301–304. <http://dx.doi.org/10.1007/BF03325846>.

- McCutcheon, J. L., McGinnis, R. L., and Elimelech, M. 2006. The Ammonia-Carbon Dioxide Forward Osmosis Desalination Process. *Water Conditioning & Purification* (October 2006), http://www.yale.edu/env/elimelech/News_Page/wcp_oct2006.pdf.
- McEwen, M. 2015. Midland Firm Demonstrates Water Treatment System. *Midland Reporter-Telegram* (26 January 2015), http://www.mrt.com/business/oil/article_e3195846-a5b0-11e4-8f14-0b2faadebe66.html (accessed 10 December 2015).
- McGinnis, R. L., Hancock, N. T., Nowosielski-Slepawron, M. S. et al. 2013. Pilot Demonstration of the NH_3/CO_2 Forward Osmosis Desalination Process on High Salinity Brines. *Desalination* **312**: 67–74. <http://dx.doi.org/10.1016/j.desal.2012.11.032>.
- McGuire, P. L., Chatham, J. R., Paskvan, F. K. et al. 2005. Low Salinity Oil Recovery: An Exciting New EOR Opportunity for Alaska's North Slope. Presented at the SPE Western Regional Meeting, Irvine, California, USA, 30 March–1 April. SPE-93903-MS. <http://dx.doi.org/10.2118/93903-MS>.
- Mehta, D., Gupta, L., and Dhingra, R. 2014. Forward Osmosis in India: Status and Comparison With Other Desalination Technologies. *International Scholarly Research Notices*, Vol. 2014, Article ID 175464, 9 pages. <http://dx.doi.org/10.1155/2014/175464>.
- Mountain Empire Community College. 2009. Lime Softening. <http://water.me.vccs.edu/concepts/softeninglime.html> (accessed 10 December 2015).
- Newton, J. 2013. Flow Electrodes May Enable Large-Scale Sea Water Desalination. *Chemistry World* (27 March 2013): Royal Society of Chemistry, <http://www.rsc.org/chemistryworld/2013/03/sea-water-desalination-capacitive-deionisation> (accessed 10 December 2015).
- Passut, C. 2014. Texas Plant Deploys Promising Technology To Clean Produced Water. *NGI's Shale Daily* (11 July 2014), <http://www.naturalgasintel.com/articles/98981-texas-plant-deploys-promising-technology-to-clean-produced-water> (accessed 10 December 2015).
- SaltTech. 2014. Loving County Media Availability for Desalination Project (22 May 2014), <http://www.salttech.com/news/LOVING-COUNTY-DESALINATION-PROJECT.php> (accessed 10 December 2015).
- Secombe, J., Lager, A., Jerauld, G. et al. 2010. Demonstration of Low-Salinity EOR at Interwell Scale, Endicott Field, Alaska. Presented at the SPE Improved Oil Recovery Symposium, Tulsa, 24–28 April. SPE-129692-MS. <http://dx.doi.org/10.2118/129692-MS>.
- Snedecor, J., Peters, T., and Larsen, M. 2008. Pellet Softening: Hardness, Iron and Manganese Removal. Presented at the 2008 PNWS-AWWA Conference, Vancouver, Washington, USA, 1 May.
- Spasenovic, M. 2013. Water Purification With Graphene Sheets - Surprising, Yet Commercially Feasible. *Graphenea* (22 April 2013), <http://www.graphenea.com/blogs/graphene-news/7714771-water-purification-with-graphene-sheets-surprising-yet-commercially-feasible> (accessed 10 December 2015).
- Stark, A. M. 2006. Nanotube Membranes Offer Possibility of Cheaper Desalination. Lawrence Livermore National Laboratory (18 May 2006), <https://www.llnl.gov/news/nanotube-membranes-offer-possibility-cheaper-desalination> (accessed 10 December 2015).
- Tarnacki, K., Meneses, M., Melin, T. et al. 2012. Environmental Assessment of Desalination Processes: Reverse Osmosis and Memstill®. *Desalination* **296**: 69–80. <http://dx.doi.org/10.1016/j.desal.2012.04.009>.
- Thompson, N. A. and Nicoll, P. G. 2011. Forward Osmosis Desalination: A Commercial Reality. Presented at the IDA World Congress, Perth, Western Australia, 4–9 September. IDAW/PER11-198.
- Usinowicz, P. J., Monzyk, B. F., and Carlton, L. 2005. Technical and Economic Evaluation and Selection of Sulfate ION Removal Technologies for Recovery of Water From Mineral Concentrate Transport Slurry. *Proceedings of the Water Environment Federation*, WEFTEC 2006, Session 1 through Session 10, 139–153. <http://dx.doi.org/10.2175/193864706783710695>.
- Vledder, P., Fonseca, J. C., Wells, T. et al. 2010. Low Salinity Water Flooding: Proof of Wettability Alteration on a Field Wide Scale. Presented at the SPE Improved Oil Recovery Symposium, Tulsa, 24–28 April. SPE-129564-MS. <http://dx.doi.org/10.2118/129564-MS>.
- Water Online. 2015. Adionics Unveils SELECTEX, A New Approach in Desalination Based on a Selective Extraction Solution for Water Deionization. *Water Online* (31 August 2015), <http://www.wateronline.com/doc/adionics-unveils-selectex-a-new-approach-in-desalination-based-on-a-selective-extraction-solution-for-water-deionization-0001> (accessed 10 December 2015).
- Water-Technology.net. 2015. STW Water Process To Showcase Salttech Water Desalination Technology in Texas, US (12 May 2015), <http://www.water-technology.net/news/newsstw-water-process-to-showcase-salttech-water-desalination-technology-in-texas-us-4574993> (accessed 10 December 2015).
- Whitfield, S. 2014. Unconventional Resources: New Facilities Find Solutions to Limited Water Resources. *Oil and Gas Facilities* **3** (6): 11–20. SPE-1214-0011-OGF. <http://dx.doi.org/10.2118/1214-0011-OGF>.
- Williams, J. D. 2015. Process of Supplying Water of Controlled Salinity. US Patent Application No. US20120261340 A1.
- Winklmann, A. and McCreary, S. 2014. Pellet Softening Treatment: Is it Right for Your Community? Presented at the One Water Ohio Technical Session, 27 August. http://www.onewaterohio.org/docs/1300_pellet_softening_treatment_McCreary.pdf.
- Yousef, A. A., Al-Saleh, S., Al-Kaabi, A. et al. 2010. Laboratory Investigation of Novel Oil Recovery Method for Carbonate Reservoirs. Presented at the Canadian Unconventional Resources and International Petroleum Conference, Calgary, 19–21 October. SPE-137634-MS. <http://dx.doi.org/10.2118/137634-MS>.
- Yousef, A. A., Al-Saleh, S., and Al-Jawfi, M. 2011a. Smart Waterflooding for Carbonate Reservoirs: Salinity and Role of Ions. Presented at the SPE Middle East Oil and Gas Show and Conference, Manama, Bahrain, 25–28 September. SPE-141082-MS. <http://dx.doi.org/10.2118/141082-MS>.
- Yousef, A. A., Al-Saleh, S., Al-Kaabi, A. et al. 2011b. Laboratory Investigation of the Impact of Injection-Water Salinity and Ionic Content on Oil Recovery from Carbonate Reservoirs. *SPE Res Eval & Eng* **14** (5): 578–593. SPE-137634-PA. <http://dx.doi.org/10.2118/137634-PA>.
- Yousef, A. A., Al-Saleh, S., and Al-Jawfi, M. 2011c. New Recovery Method for Carbonate Reservoirs Through Tuning the Injection Water Salinity: Smart Waterflooding. Presented at the SPE EUROPEC/EAGE Annual Conference and Exhibition, Vienna, Austria, 23–26 May. SPE-143550-MS. <http://dx.doi.org/10.2118/143550-MS>.
- Yousef, A. A., Al-Saleh, S., and Al-Jawfi, M. 2012a. The Impact of the Injection Water Chemistry on Oil Recovery From Carbonate Reservoirs. Presented at the SPE EOR Conference at Oil and Gas West Asia, Muscat, Oman, 16–18 April. SPE-154077-MS. <http://dx.doi.org/10.2118/154077-MS>.
- Yousef, A. A., Liu, J., Blanchard, G. et al. 2012b. SmartWater Flooding: Industry's First Field Test in Carbonate Reservoirs. Presented at the SPE Annual Technical Conference and Exhibition, San Antonio, Texas, USA, 8–10 October. SPE-159526-MS. <http://dx.doi.org/10.2118/159526-MS>.
- Yousef, A. A. and Ayirala, S. C. 2014. Optimization Study of a Novel Water-Ionic Technology for Smart-Waterflooding Application in Carbonate Reservoirs. *Oil and Gas Facilities* **3** (5): 72–82. SPE-169052-PA. <http://dx.doi.org/10.2118/169052-PA>.
- Zadghaffari, R. and Asr, S. S. 2013. Water Softening Using Caustic Soda: Privileges and Restrictions. *Polish Journal of Chemical Technology* **15** (2): 116–121. <http://dx.doi.org/10.2478/pjct-2013-0033>.

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