

Optimization Study of a Novel Water-Ionic Technology for Smart-Waterflooding Application in Carbonate Reservoirs

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Summary

Injection water with selective ionic content and composition is a key requirement for smart-waterflooding (SWF) application in carbonate reservoirs. Smart water—depleted in monovalent ions, but enriched in sulfates and divalent cations—is desired for incremental oil recovery in carbonates, which constitute complex water chemistry when compared with sandstones. Most of the published work available in this area is focused on addressing water-chemistry requirements for low-salinity waterflooding in sandstones. However, none of these studies describes the complex injection-water requirements of SWF in carbonate reservoirs. Also, injection-water chemistry has a known impact on several tertiary enhanced-oil-recovery (EOR) processes among the three major categories of chemical, gas, and thermal EOR. The main purpose of this study is, therefore, to identify and optimize a novel water-ionic technology that can serve as a “one-shop solution” to generate desired water chemistries suited for different improved-oil-recovery (IOR)/EOR processes, including SWF in carbonates.

A novel water-ionic technology, comprising nanofiltration and reverse-osmosis membrane-based processes, was identified for optimization in this study. The proposed technology makes use of these two membrane-desalination processes in parallel configuration to provide multiple water streams of widely varying ionic strength and content. Different water streams obtained from this novel solution can be blended effectively to yield a smart-water cocktail of desired ionic strength, composition, and monovalent- to divalent-ion content suited for carbonates.

Smart-water cocktails obtained from the proposed solution are also suited for application in other EOR processes such as polymer flooding, alkaline/surfactant/polymer flooding, low-salinity surfactant flooding, dilute surfactant flooding, carbonated waterflooding, and miscible gasflooding, and are suited for boiler feedwater in steamflooding. The optimized scheme thereby offers a novel one-shop solution to meet the complete suite of desired water-chemistry requirements for different IOR/EOR processes. In addition, comparative evaluation-study results between novel water-ionic technology and other already-known advanced-desalination schemes highlight the major advantages of the new solution in terms of better water-ion-tuning flexibility, higher recovery efficiency, lower energy requirement/footprint, and ease of operation.

Introduction

The oil industry is currently showing renewed interest in improved-oil-recovery/enhanced-oil-recovery (IOR/EOR) technologies to re-

cover a portion of left-behind-waterflood residual oil. Higher and stable oil prices in the market, diminishing chances of finding big discoveries, and declining oil from matured fields are three major reasons for these renewed interests. Recently advanced waterfloods are receiving good attention for both sandstone and carbonate reservoirs under the two tag names low-salinity flooding (LSF) and smart waterflooding (SWF), respectively. These processes depend on the tailoring of salinity and ionic composition in the injection water to release more oil from the pores in the reservoir rock. Injection-water chemistry is important not only in offshore waterfloods but also for several tertiary EOR processes among the three major EOR types—chemical, gas, and thermal. Offshore waterfloods are not tolerant of certain detrimental ions in the injection water because of their adverse reactions with resident in-situ materials present in the reservoir. All source waters are not optimally suited for chemical EOR because of chemical interference with salinity and specific ions in the injection water. Water is injected as alternating slugs with gas in miscible carbon dioxide EOR, and water chemistry impacts gas utilization efficiencies because of the adverse gas/water solubilities in the reservoir. The source water required to generate steam for thermal floods should be fresh, with almost zero hardness ions to meet boiler feedwater quality specifications. In this section, we provide an overview of SWF technology followed by some background on the desired injection-water-chemistry requirements for different IOR/EOR processes to define major objectives for this study.

SWF Technology. Recently, significant interest has been shown in advanced waterfloods for oil-recovery improvement in both sandstones and carbonates in the oil industry. The effects of water-ionic composition on oil recovery were widely recognized in the early 1990s at the University of Wyoming in coreflood tests (Jadhunandan 1990; Jadhunandan and Morrow 1995; Tang and Morrow 1997). Industry then quickly embraced this technology because of its lower capital investment compared with conventional EOR and quicker payback time associated with its early implementation during the project life cycle. Several single-well chemical-tracer tests (Webb et al. 2004; Lager et al. 2008; Secombe et al. 2010; Vledder et al. 2010; Mahani et al. 2011; Skrettingland et al. 2011) were carried out in sandstone fields during the last decade. Most of these tests showed some positive result. Injection-water salinity at less than 5,000 ppm is the desired threshold to activate oil-recovery benefits for LSF in sandstones. Expected incremental oil recoveries from the process ranged from 5 to 10% oil originally in place (OOIP). Some divalents should be included (typically less than 500 ppm) in the low-salinity water to avoid clay swelling and deflocculation in the reservoir. Clay hydration (Sharma and Filoco 2000), detachment of mixed-wet clay from pore walls (Tang and Morrow 1999), pseudoalkaline flooding (McGuire et al. 2005), multicomponent ion exchange (Lager et al. 2006), and double-layer expansion (Ligthelm et al. 2009) are some responsible mechanisms proposed for LSF incremental oil recovery in several studies.

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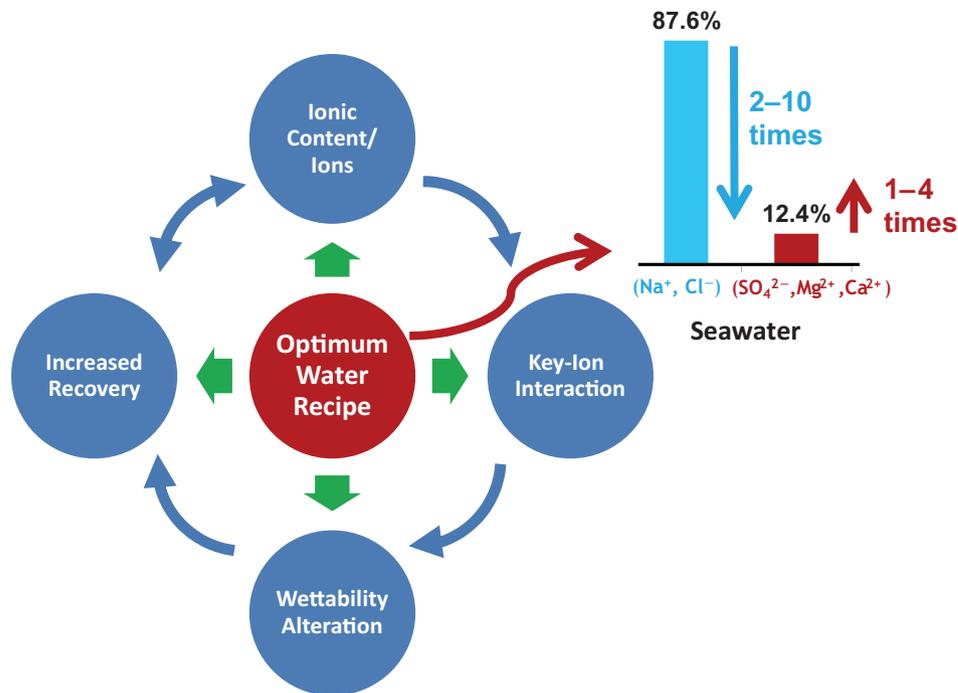


Fig. 1—Optimum injection-water recipe for SWF in carbonates.

Relatively less research work has been conducted to understand water-ionic compositional effects in carbonates when compared with sandstones. Researchers from the University of Stavanger in mid-2000 showed that sulfate ions in seawater play an important role in oil recovery from chalk reservoirs (Austad et al. 2005; Strand et al. 2006; Doust et al. 2009). Recent studies from the same research group indicated that not only are sulfates and divalents (Ca^{+2} and Mg^{+2}) important, but the amounts of nonactive salts (Na^+ and Cl^-) that affect the wettability alteration in carbonates (Fathi et al. 2011) are as well. This process is highly sensitive to temperature. Temperatures greater than 70°C seem to activate the interaction of potential determining ions with rock surface (Zhang and Sarma 2012; Austad 2013). One study (Chandrasekhar and Mohanty 2013) showed the greatest oil recoveries for limestone-rock crude oil with seawater containing 4X sulfates, 1X magnesium, and 1X calcium at 120°C . In-house research work from Saudi Aramco during 2006–09 revealed that reduced-ionic-strength seawater does work to improve oil recovery in typical carbonates (Yousef et al. 2010, 2011; Al-Yousef et al. 2013a). Results from tertiary core-flood tests showed improvements in oil recovery by approximately 8% of OOIP, with twice-reduced-ionic-strength seawater. Further reductions in ionic strength by 10 times added another 10% of OOIP to this incremental oil. The primary recovery mechanism responsible for observed incremental oil recovery was attributed to be favorable wettability alteration in this study through the results from laboratory measurements such as contact angle, interfacial tension (IFT), zeta potential, and nuclear-magnetic-resonance response. The industry’s first field trials conducted in a carbonate reservoir also confirmed the potential of smart water, with reduction of seven saturation units in residual oil saturation (Yousef et al. 2012). Reduced-ionic-strength seawater—depleted in monovalent ions, but enriched in sulfates and divalent cations—is the desired “optimum water recipe” for SWF in carbonates. These desired smart waters are either low- to moderate-salinity seawater (2 to 10 times reduced ionic strength; 28,000 to 6,000 ppm) or modified seawater depleted in monovalent ions, but enriched with divalents and sulfates (4X sulfates, 1X calcium and magnesium; <10,000 ppm sulfates and <2,000 to 3,000 ppm calcium and magnesium). The interrelationship among ionic content/composition, their interac-

tion, wettability alteration, and increased oil recovery in carbonates through optimum water recipe of the injection water are shown in Fig. 1. As can be seen, desired ionic content and composition in the optimum water recipe result in favorable interactions from key ions to cause wettability alteration, which, eventually, leads to increased oil recovery.

IOR/EOR Injection-Water-Chemistry Requirements. Sulfates in injection water are detrimental to offshore waterfloods because of their in-situ biological reactions with the resident materials present in the reservoir that cause reservoir souring and scaling. Hence, injection water needs to be tuned to remove sulfates (to concentrations ranging from 10 to 40 ppm) with low- to moderate-hardness ions (500 to 1,000 ppm). It is important to note that most of the EOR processes described in this subsection are for sandstones, unless specifically mentioned for application in carbonates. The most widely used EOR polymers—hydrolyzed polyacrylamides—are sensitive to salinity and hardness. As a result, a reduced polymer dosage is required in low-salinity water to achieve injection viscosities similar to those of high-salinity water (Raney et al. 2012). Low-salinity water also has a synergistic effect on polymer floods that results in higher incremental oil because of the combined effect of improved microscopic sweep with better mobility control (Mohammadi and Jerauld 2012). Typically, injection-water salinities less than 5,000 ppm with hardness ions less than 100 ppm (to avoid polymer degradation, clay swelling, and deflocculation) are desired for polymer floods.

Alkaline/surfactant/polymer (ASP) floods require removal of hardness ions (to levels less than 10 ppm) in injection water to prevent alkali precipitation in the chemical cocktail. Alkali reduces anionic surfactant adsorption on sandstones. It also generates natural surfactants in situ by reaction with crude-oil organic acids to reduce synthetic surfactant concentration. Injection-water chemistry is commonly matched with optimal salinity obtained from phase-behavior testing to generate the so-called middle-phase microemulsion for ultralow IFT behavior. The two popular EOR surfactant classes—propylene oxide (PO) sulfates and internal olefin sulfonates—and their different blends show poor aqueous stabilities at salinities greater than 50,000 ppm (Liu et al. 2008). Some recent

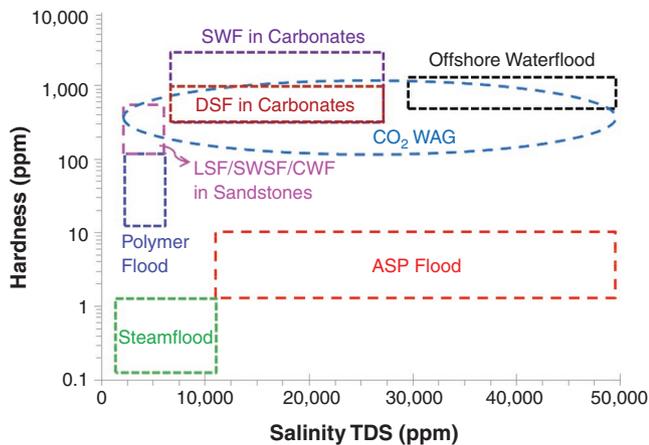


Fig. 2—IOR/EOR injection-water-chemistry-requirement diagram: salinity vs. hardness. (TDS – total dissolved solids.)

studies described the benefits of combining low-salinity water with surfactant flooding in sandstones (Alagic and Skauge 2010; Alagic et al. 2011). Mobilization of residual oil resulting from lower brine salinity because of wettability alteration combined with reduced capillary trapping caused by low IFT was attributed to be the key mechanism responsible for incremental oil recovery in smart-water surfactant flooding (SWSF). The combination of smart water with dilute surfactant (<0.1 wt %) looks attractive for carbonate reservoirs (Al-Yousef et al. 2013b). Addition of surfactant to smart water in dilute surfactant flooding (DSF) for carbonates is expected to result in better incremental oil over SWF because of additional surfactant-induced mechanisms, such as IFT reduction and improved spontaneous imbibition, coming into play. In summary, ASP floods require negligible hardness (<10 ppm) and salinities at optimal salinity (<50,000 ppm) in the injection water. SWSFs in sandstones require lower-salinity water (<5,000 ppm salinity and divalents less than 500 ppm). Two- to ten-times-diluted seawater (6,000–28,000 ppm salinity with 250–1,000 ppm hardness and 500–2,000 ppm sulfates) is one desired injection-water recipe for DSF in carbonates.

There are not many studies reported to investigate injection-brine compositional effects in tertiary miscible carbon dioxide (CO₂) water-alternating-gas (WAG) floods. Jiang et al. (2010) performed both secondary water and tertiary miscible CO₂ WAG core-floods with Berea sandstones (low clay content) and crude oil at different injection-brine salinities. Waterflood recoveries increased at lower salinities (wettability alteration effect is questionable), whereas WAG recoveries decreased as a result of the higher CO₂ solubilities in brine. However, the total oil recovery from combined low-salinity secondary waterflood and low-salinity tertiary miscible WAG is approximately 13 to 14% OOIP greater when compared with total oil recovery obtained at corresponding high-salinity conditions. A recent 1D numerical-simulation study by Dang et al. (2013) that used a compositional model showed that ultimate oil recoveries in low-salinity WAG are approximately 9% OOIP greater compared with high-salinity WAG. On the basis of these studies, it can be concluded that smart-water benefits may compensate adverse CO₂-solubility effects at lower salinities to provide an overall better incremental oil recovery in low-salinity miscible WAG. Solubility of CO₂ in brines containing divalent ions is greater compared with monovalent ions at the same ionic strength (Rosenbauer and Koksalan 2002). Hence, relatively less adverse CO₂-solubility effects are expected in miscible WAG with injection waters containing fewer divalent cations. Because there is no direct experimental evidence in the literature to support the advantage of a low-salinity effect in CO₂ miscible WAG, no specific injection-water salinity requirements are identified in this study.

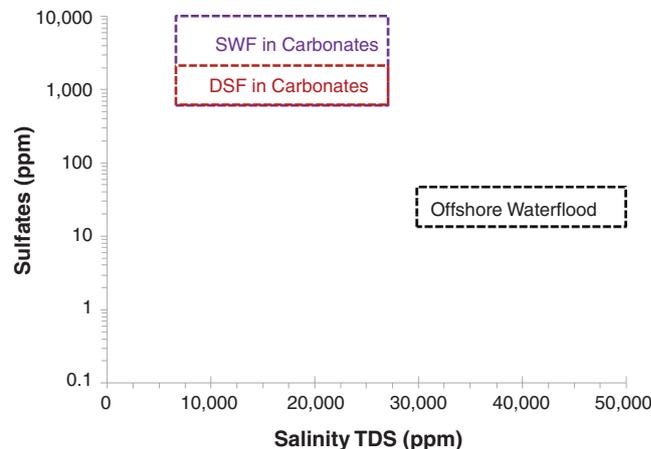


Fig. 3—IOR/EOR injection-water-chemistry-requirement diagram: salinity vs. sulfates. (TDS – total dissolved solids.)

However, lower salinity could be advantageous and also low- to moderate-hardness ions are desired.

Carbonated waterflooding (CWF) is an emerging IOR/EOR technology, and some active research is ongoing in this area. It is well-recognized that increased carbonation levels in the injection water will lead to higher incremental oil recoveries. Because more volumes of dissolved CO₂ will be available to interact with and mobilize trapped residual oil, CO₂ solubilities increase with the decrease in injection-brine salinity. This could turn out to be a “big boon” for low-salinity CWF to increase dissolved CO₂ quantities in water and improve oil recovery. The wettability alteration associated with low-salinity water may add even more to this incremental oil. The desired injection-water-chemistry requirements of CWF are similar to those of low-salinity flooding in sandstones. Thermal floods require steam, which is generated with boilers that use fresh water. Removal of hardness ions from source water is one critical parameter to meet steamflood-boiler-feedwater quality-specification requirements. Typically, boilers used for steam generation require essentially zero hardness (<0.5–1.0 ppm) and low salinity (<10,000–12,000 ppm) in the source water (Pedenaud et al. 2005).

The IOR/EOR water-chemistry-requirement diagram, shown in Figs. 2 and 3, summarizes all the desired injection-water salinities and compositions required for different IOR/EOR processes. The total salinity is plotted against hardness in Fig. 2 and against sulfates in Fig. 3. The data presented in these figures indicate that injection-water chemistry plays an important role in IOR/EOR business, which illustrates the need to develop appropriate water-treatment solutions to address these requirements. Therefore, the objectives of this study are to identify a fit-for-purpose water-ionic technology for SWF application in carbonates, optimize on the identified technology to provide a novel one-shop solution to generate desired water chemistries suited for different IOR/EOR processes, compare the novel solution with other advanced technologies to generate rough-order-of-magnitude estimates for offshore facilities, and provide path-forward recommendations on future work to qualify this novel technology for application in SWF field pilots.

Novel Water-Ionic-Optimization Technology for Smart Waterflooding (SWF) in Carbonates

In this section, we present a detailed description of the methodology that we used to identify novel water-ionic technology, followed by optimization of the chosen solution with selected examples. A technology evaluation is then performed to compare the novel solution with other already-known advanced technologies and provide rough-order-of-magnitude estimates for offshore facilities. Finally, path-forward recommendations are provided for the next steps to qualify this novel technology for possible field application.

Reference	Description	Key Attributes
Collins (2008) US Patent No. 7,455,109 B2 BP	Proposes to use “forward osmosis” to generate low-salinity water in the range of 200–5,000 ppm total dissolved solids (TDS) from high-salinity water. Salinity is adjusted by adding minor amounts of feedwater or concentrated reject.	<ol style="list-style-type: none"> 1. Uses desalination technology other than RO and NF. 2. Reservoir objectives are different (i.e., targeted for LSF in sandstones).
Collins et al. (2010) US Patent No. 7,726,398 B2 BP	Describes selection of suitable RO and NF membranes based on the Sourirajan model. It proposes obtaining desired low-salinity water in the range of 500–5,000 ppm by use of a plurality of RO units. The combined permeate from all units will provide the desired low-salinity water.	<ol style="list-style-type: none"> 1. Uses either RO or NF. 2. Plurality of desalination units or permeate flux control in a single unit to achieve desired salinity. 3. Targeted for LSF in sandstones.
Christopher et al. (2009) US Patent No. 7,600,567 B2 BP	This patent describes submerging an RO unit in the water or downhole in the injection well to make use of hydrostatic-head pressure. Plurality of RO units or a single RO unit with selected permeate flux can be used to generate desired low-salinity water in the range of 500–5,000 ppm TDS.	<ol style="list-style-type: none"> 1. Uses only RO desalination. 2. Plurality of desalination units or permeate flux control to achieve desired salinity. 3. Targeted for LSF in sandstones.
Curole and Greene (2009) US Patent Ap. 12/295,183 Shell	This patent application combines different desalination technologies, such as sulfate removal, NF, and RO, in series to remove the ions from seawater. A viscosifying agent is then added to the processed water for injection into the reservoir.	<ol style="list-style-type: none"> 1. Uses NF and RO in series. 2. Targeted for polymer flooding.
Ayirala et al. (2010b) US Patent Ap. 12/425,311 Shell	Proposes a method for generating low-salinity water by removing multivalent and monovalent ions with NF and RO technologies in series. Multivalent ions from NF reject are then added back to low-salinity water before injection into the reservoir.	<ol style="list-style-type: none"> 1. Uses NF and RO in series. 2. Targeted for LSF in sandstones.
Ayirala et al. (2012) US Patent Ap. 13/505,001 Shell	Describes the use of multiple NF modules to generate desired low-salinity water in the range of 1,000–10,000 ppm TDS.	<ol style="list-style-type: none"> 1. Uses NF technology alone. 2. Targeted for LSF in sandstones.
Ligthelm et al. (2012) US Patent Ap. 13/272,965 Shell	Describes injecting lower-ionic-strength waters into a carbonate formation to increase oil recovery. NF and RO units used in series are shown as one way to achieve lower-ionic-strength water from a high-salinity feedwater.	<ol style="list-style-type: none"> 1. Uses NF and RO in series. 2. Criticality of having divalents and sulfates in injection water—not addressed. 3. Targeted for LSF in carbonates.
Williams (2012) US Patent Ap. 13/519,057 BP	This patent describes the use of NF and RO units in parallel to generate desired low-salinity water in the range of 500–5,000 ppm TDS by mixing RO and NF permeates.	<ol style="list-style-type: none"> 1. Reservoir objectives are different (i.e., targeted for LSF in sandstones). 2. Discards RO and NF rejects as “waste.”
Ayirala et al. (2010a) SPE-129926-MS Shell	Describes the use of NF and RO in series to generate desired low-salinity water for offshore LSF and polymer flooding. Also, different blending options are provided with NF and RO reject streams to avoid clay swelling, souring, and scaling.	<ol style="list-style-type: none"> 1. NF and RO application in series 2. Targeted for LSF in sandstones and polymer flooding, both offshore.
Henthorne and Wodehouse (2012) SPE-154281-MS Water Standard	Provides results from pilot testing of brackish RO-membrane element for seawater-based EOR applications, including LSF, polymer flooding, and ASP flooding.	<ol style="list-style-type: none"> 1. Uses brackish water RO. 2. Targeted for LSF in sandstones and chemical EOR.
Henthorne et al. (2013) SPE-165241-MS Water Standard	It describes a proprietary RO/NF technology and its ability to produce a wide range of effluent qualities with the same water-treatment infrastructure.	<ol style="list-style-type: none"> 1. RO/NF proprietary technology. 2. Targeted for offshore EOR applications, primarily chemical EOR.
Henthorne and Movahed (2013) US Patent Ap. 2013/0161256 A1 Water Standard	It proposes the use of a plurality of NF and RO units in a parallel configuration and blending of various permeate streams to meet the water-quality requirements of LSF and chemical EOR floods.	<ol style="list-style-type: none"> 1. NF and RO in parallel configuration. 2. For LSF and chemical EOR applications in sandstones.

Table 1—Summary of prior work on IOR/EOR injection-water-treatment schemes.

Identification of Novel Water-Ionic Technology. Existing seawater-desalination methods can be categorized into two groups: thermal-based and membrane-based. Multistage-flash distillation, multi-effect distillation, thermocompression distillation, and mechanical-vapor compression are the popular thermal-based desalination methods. Reverse osmosis (RO) and nanofiltration (NF) are the two membrane-based desalination methods available in the market. Ayirala et al. (2010a) reviewed various seawater-

desalination methods for application in offshore environments and concluded that thermal-based methods are not suitable for these environments because of large space, weight, and energy/steam requirements. This study also pointed out that membrane-based RO is the most suitable method for offshore.

RO uses a much tighter membrane, with pore sizes less than or equal to 0.0005 μm . These membranes reject all the monovalent and divalent ions from seawater with greater than 99% rejection

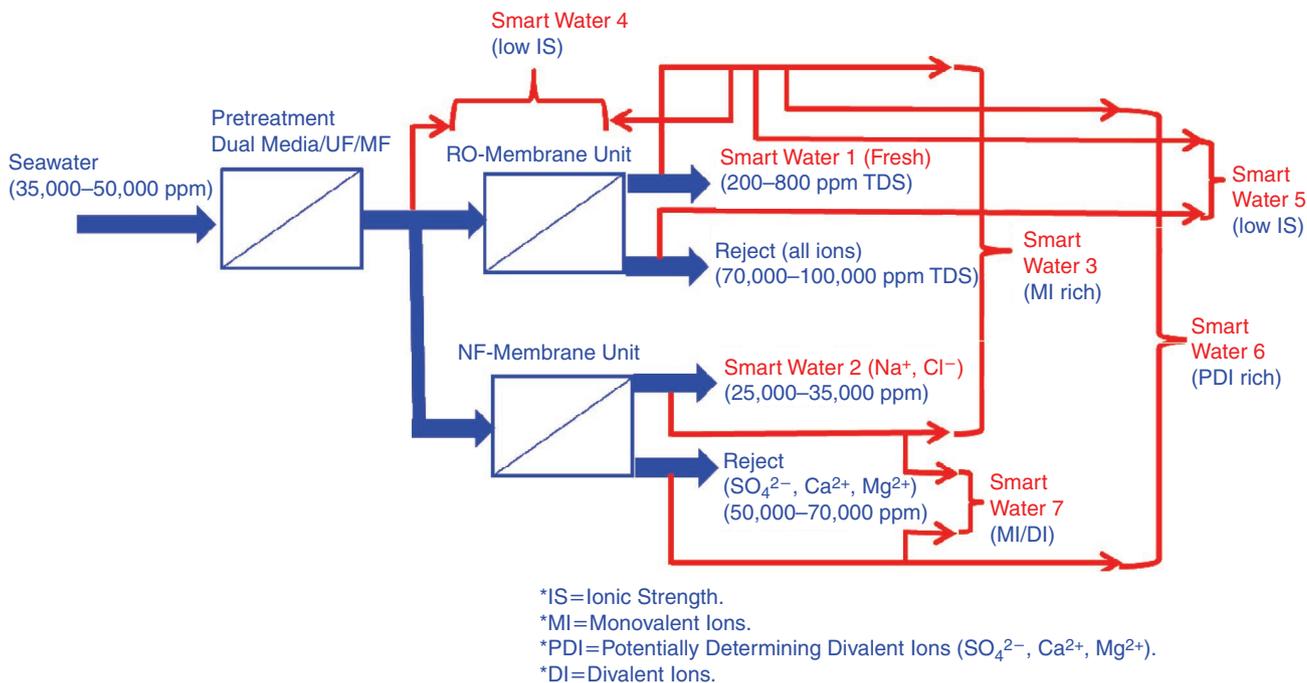


Fig. 4—Novel water-ionic technology for SWF application in carbonates. (TDS – total dissolved solids.)

efficiencies. As a result, the product water from RO membranes is fresh, with negligible salt ions (<500 ppm). Reject water is concentrated in both monovalent and divalent ions. NF membranes, on the other hand, are looser, with pore sizes ranging from 0.05 to 0.005 μm . NF membranes selectively reject divalent cations and sulfates with greater than 90 to 99% rejection efficiencies. Consequently, the product water from NF membranes is rich in monovalent ions and the reject water is concentrated in divalent ions. Both NF and RO membrane-based desalination processes are widely used today for seawater desalination, and some of the existing installations are cited as examples in the following list.

1. Ashkelon seawater RO plant in Israel is one of the largest desalination facilities in the world. This plant's capacity is 330 000 m^3/d , and it produces approximately 13% of the country's domestic water needs (Sauvet-Goichon 2007).
2. Another seawater RO desalination plant is operated in Sydney, Australia. This unit is another of the largest desalination facilities in the world, with a capacity of approximately 250 000 m^3/d (El Saliby et al. 2009). The Rabigh Independent Water, Steam, and Power project in Saudi Arabia is one more example of a large RO seawater-desalination plant, and it has a maximum production-water capacity of approximately 192 000 m^3/d (Tanaka et al. 2009).
3. There are approximately 50 seawater sulfate-removal NF desalination units on offshore oil platforms currently either operating or in the design phase, with a total estimated capacity of approximately 600 000 m^3/d (Walsh et al. 2008). These fields include Brae, Heidrun, and Girassol in the North Sea.

On the basis of the preceding cited reference list, it becomes quite evident that RO systems are common in the water industry to provide potable water. On the other hand, NF systems are used in the oil industry to remove sulfates and divalents for offshore waterfloods. In view of the suitability of these two technologies for both onshore and offshore environments, several of the advanced water-treatment schemes proposed in the literature for low-salinity flooding (LSF) and chemical enhanced oil recovery (EOR) used them in either standalone RO or NF/RO hybrid configurations. The summary and key attributes of all these published studies on improved oil recovery (IOR)/EOR injection-water-treatment schemes

are provided in **Table 1**. Interestingly, patent applications by BP (Collins 2008; Christopher et al. 2009; Collins et al. 2010; Williams 2012) propose the use of either RO alone or NF/RO in a parallel configuration. Patent applications from Shell (Curole and Greene 2009; Ayirala et al. 2010b; Ayirala et al. 2012; Ligthelm et al. 2012) suggest the use of NF alone and NF/RO in a series configuration to generate desired low-salinity water. One recent patent application (Henthorne and Movahed 2013) from the water company Water Standard advocates the use of a plurality of NF and RO units in a parallel configuration. It advocates the blending of various permeate streams from these units to meet the water-quality requirements of low-salinity and chemical-EOR floods. However, none of these patent applications and papers describe carbonate-reservoir applications or address complex water-chemistry requirements of SWF in carbonates. Furthermore, NF/RO water-treatment schemes in the parallel configuration proposed so far in the current art used only NF and RO permeates that are either rich in monovalent ions or lacking in all ions (fresh water) for blending to generate desired low-salinity water for sandstones. The major advantage associated with the other two critical water streams (i.e., NF reject and RO reject) are not identified and they are disposed of as "waste." These two reject streams are of great importance to SWF in carbonates because they have unique water chemistries in that NF reject is rich in divalent-ion content and RO reject is rich in both monovalent- and divalent-ion content. As a result, these prior studies do not seem to capture the importance of tuning injection-water chemistry in terms of divalent cations and sulfates to enable SWF in carbonates.

One key challenge for SWF application is to design a fit-for-purpose selective seawater-ion-removal technology to meet injection-water-chemistry requirements pertinent to a specific reservoir. As a result RO/NF technology arranged in a parallel configuration was investigated in this study for SWF application in carbonates. This configuration was selected after detailed evaluation because the resulting desalination solution is capable of generating the desired water cocktails covering the entire range of ionic content and salinity variation. It provides four different water streams to include monovalent-ion-rich (NF permeate) water, divalent-ion-rich (NF reject) water, fresh water (RO permeate), and monovalent- and divalent-ion-rich (RO reject) water. The availability of these four widely varying water streams renders great flexibility in the water-

Smart Water Number	Cocktail Proposition	Cocktail Characteristics	IOR/EOR Suitability
1	RO Permeate	Fresh water with no MI and PDI	LSF, polymer flood, CWF, and steamflood
2	NF Permeate	Modified seawater with only MI	Offshore waterflood, ASP flood, and miscible WAG
3	RO Permeate + NF Permeate	Low-salinity water with MI	LSF, polymer flood, SWSF, and CWF
4	RO Permeate + Seawater	Diluted seawater, low-salinity water with MI and PDI	LSF, SWF, polymer flood, DSF, and CWF
5	RO Permeate + RO Reject	Diluted seawater, low-salinity water with MI and PDI	LSF, SWF, polymer flood, DSF, and CWF
6	NF Reject + RO Permeate	Modified seawater with only PDI	SWF
7	NF Permeate + NF Reject	Modified seawater with MI and PDI	SWF, offshore waterflood, and miscible WAG

MI = monovalent ions.

PDI = potentially determining divalent ions.

Table 2—Summary on applicability of smart water to different IOR/EOR processes.

treatment system. It becomes easy to customize a desired salinity or an ionic-content water cocktail that is rich in either monovalent or divalent ions or both or with the desired monovalent-/divalent-ion ratio. More importantly, the proposed scheme makes use of both NF and RO reject streams as source water to come up with different water recipes in terms of desired quality and to yield relatively better economics.

Optimization of Novel Water-Ionic Technology. Fig. 4 shows a schematic of novel water-ionic technology investigated in this study for optimization in generating the desired water salinity and composition. As shown in the figure, pretreated seawater (35,000 to 50,000 ppm salinity) from a dual-media/ultrafiltration (UF)/microfiltration (MF) unit is split into two water streams. One of the streams flows into a reverse-osmosis (RO) unit and the other stream flows into a nanofiltration (NF) unit for selective water-ion removal. NF removes primarily the larger divalent ions, and the permeate stream from the unit is hardness- and sulfate-free water consisting of monovalent ions (25,000 to 35,000 ppm salinity) only. The reject stream from the NF unit is a concentrated stream (50,000 to 70,000 ppm salinity), which is rich in divalent ions (Ca^{2+} , Mg^{2+} , and SO_4^{-2}).

RO membranes are tighter than NF membranes, and, as a result, the RO unit removes both monovalent and divalent ions. The permeate stream from the RO unit is almost fresh, with low salinity (200 to 800 ppm). The reject stream is concentrated with both monovalent and divalent ions (70,000 to 100,000 ppm salinity). Two stages can be used in NF to reach recovery efficiencies up to 75% (Ayirala et al. 2010). In a two-stage system, the reject stream from the first stage is further processed in a second stage, and product waters from the two stages are then merged to provide the final permeate stream. The reject stream from the second stage provides the final concentrate.

Therefore, the different water streams generated in the investigated RO/NF seawater-desalination scheme are RO fresh water, with negligible monovalent and divalent ions; RO concentrated reject water, rich in both monovalent and divalent ions; NF water, rich in only monovalent ions; and NF reject water, rich in divalent ions. Blending the NF reject with the RO permeate provides one desired cocktail for smart waterflooding (SWF) in carbonates that is rich in divalents and sulfates, but depleted in monovalent ions. Blending RO permeate with RO reject or pretreated seawater provides another desired injection-water cocktail to mimic seawater dilution. Also, one of the four water streams generated from the treatment scheme can be blended selectively with any other water stream, including the pretreated seawater, as described in the following, to tailor the desired injection water suited for different IOR/EOR processes. Furthermore, a complete suite of injection-water compositions can be generated with the investigated solution, varying on total ionic strength, monovalent-ion content, divalent-ion con-

tent, and monovalent- to divalent-ion content to avoid both clay swelling and reservoir souring in underground formations.

- Smart Water 1: Fresh, low-salinity water from RO. Almost all monovalent and divalent ions are removed, and the water is essentially salt free. If there are no swelling clays in the reservoir, it could be suited for LSF in sandstones, polymer flooding, and carbonated waterflooding (CWF). A downstream ion-exchange resin can be used as a polishing unit to remove residual hardness from RO permeate. The resulting water can be used as boiler feedwater to generate steam for thermal flooding.
- Smart Water 2: Modified seawater with monovalent ions only. All divalent ions are removed. This water is suitable for offshore waterfloods, ASP flooding, and miscible carbon dioxide (CO_2) WAG.
- Smart Water 3: Lower-salinity monovalent ion-rich water obtained by blending RO fresh water with NF permeate. This water contains no divalents/sulfates and is well-suited for injection into reservoirs that pose a reservoir-souring risk. Small volumes of NF reject or RO reject can be added to Smart Water 3 to avoid clay swelling. Such water is suited for reservoirs that pose both clay-swelling and reservoir-souring issues. Smart Water 3 could be preferred for LSF in sandstones, polymer flooding, smart-water surfactant flooding (SWSF), and CWF.
- Smart Water 4: This water is obtained by blending RO fresh water with pretreated seawater. The resulting water is of low-to-moderate ionic strength and represents one version of diluted seawater. Any ionic strength can be obtained by changing the blending ratio appropriately. This water is suitable for LSF in sandstones, SWF in carbonates, polymer flooding, dilute surfactant flooding (DSF) in carbonates, and CWF. Desired amounts of divalents are also included in water to avoid clay swelling in the reservoir.
- Smart Water 5: This water is obtained by blending RO fresh water with RO reject. It can also be classified as low-to-moderate-ionic-strength water and represents another version of diluted seawater. Smart Water 5 is more preferred than Smart Water 4 because of nonconsumption of pretreated seawater (pretreatment savings) and use of concentrated reject (which otherwise has to be disposed of as waste) in the blending scheme. Because RO reject is concentrated, blending requirements are lower, with fewer volumes. Hence, this water is preferentially suited over Smart Water 4 for LSF/SWF in sandstones and carbonates, polymer flooding, DSF in carbonates, and CWF. It offers other advantages similar to those of Smart Water 4 to avoid clay swelling in the reservoir.
- Smart Water 6: This water is obtained by blending RO fresh water and NF reject to create a smart water that is rich in potentially determining divalent ions (sulfates, calcium, and magnesium), but depleted in monovalent ions. This water is suited specifically for SWF in carbonates.

Feed Seawater		NF (ppm)		RO (ppm)	
Ion	ppm	Permeate	Reject	Permeate	Reject
Mg ²⁺	1,400	309	4,673	4	2,796
Ca ²⁺	400	330	610	1	799
Na ⁺	11,200	10,688	12,736	81	22,319
SO ₄ ²⁻	2,650	48	10,456	8	5,292
Cl ⁻	19,750	19,000	22,000	136	39,364
TDS	35,400	30,375	50,475	230	70,570

TDS = total dissolved solids.

Table 3—Typical resulting water compositions from NF and RO.

Ion	RO Permeate/NF Reject (vol%/vol%)	50/50	75/25	90/10	25/75
		Smart Water A	Smart Water B	Smart Water C	Smart Water D
Mg ²⁺		2,339	1,171	471	3,506
Ca ²⁺		306	153	62	458
Na ⁺		6,408	3,244	1,346	9,572
SO ₄ ²⁻		5,232	2,620	1,053	7,844
Cl ⁻		11,068	5,602	2,322	16,534
TDS		25,352	12,791	5,254	37,914

TDS = total dissolved solids.

Table 4—Example optimization on injection-water recipes for SWF in carbonates.

Ion	Smart Water A	Smart Water B	Smart Water C	Smart Water D
Mg ²⁺	1.67	0.84	0.34	2.50
Ca ²⁺	0.76	0.38	0.15	1.14
Na ⁺	0.57	0.29	0.12	0.85
SO ₄ ²⁻	1.97	0.99	0.40	2.96
Cl ⁻	0.56	0.28	0.12	0.84
TDS	0.72	0.36	0.15	1.07

Data given in this table for different ions denote the change as "number of times" with respect to seawater.
TDS = total dissolved solids.

Table 5—Relative changes in smart-water ionic distributions compared with seawater.

- Smart Water 7: This smart-water cocktail is obtained by blending NF permeate with NF reject. The monovalent/divalent-ion ratio in the water recipe can be suitably varied to meet the injection-water-chemistry requirements of a specific reservoir. This water could be suitable for SWF in carbonates, offshore waterflood, and miscible CO₂ WAG.

The applicability of various smart waters obtained from investigated RO/NF solution to different IOR/EOR processes is summarized in **Table 2**. As can be seen, a full suite of smart-water cocktails that are suitable not only to secondary offshore waterfloods but also to different IOR/EOR processes, such as LSF in sandstones, SWF in carbonates, polymer flooding, ASP flooding, low-salinity surfactant flooding, DSF for carbonates, CWF, miscible CO₂ WAG, and steamflooding, can be generated with this technology. As a result, the investigated technology can be termed as a novel one-shop IOR/EOR smart-water solution.

Now, we provide more details on injection-water-recipe optimization by use of novel water-ionic technology. **Table 3** shows typical seawater composition and expected permeate/reject ionic distributions from both NF and RO membrane-desalination systems. These data on feed seawater, NF, and RO permeate compositions are obtained from Davis and McElhiney (2002) and Ludwig

(2010), respectively. The corresponding reject compositions are then determined from mass balance on different ionic species with recovery efficiencies of 75% for NF (two stages) and 50% for the RO unit. Hence, the overall recovery efficiency of the system becomes 62.5%. NF permeate compositions used in this optimization can be treated as somewhat conservative because of the recent advancements in the technology to obtain better membrane-rejection efficiencies for sulfates, calcium, and magnesium. It is also possible to achieve partial rejection of sodium and chloride ions by use of some of the newer NF membranes available currently.

Table 4 provides a summary of the optimization example for the selected case of SWF in carbonates. **Table 5** shows relative changes in the different ionic species present in various smart waters when compared with seawater. As can be seen, blending 50% volume RO permeate and 50% volume NF reject provides a modified seawater (Smart Water A) of approximately 25,000-ppm salinity, with retention of only one-half of the sodium and chloride ions present in seawater. Key ions, sulfates, and magnesium are almost doubled (2X, with reference to feed seawater) and calcium is retained almost at the same level. Adding 25% by volume NF reject to 75% by volume RO permeate results in a moderate-salinity water (Smart Water B) with only 12,000-ppm salinity. Sodium and chloride ions are depleted by approximately 4X, whereas key ion sul-

fates and magnesium are retained almost at the same level as feed seawater. The volumetric blending ratio of 90:10 for RO permeate/NF reject results in low-salinity Smart Water C ($\approx 5,000$ ppm total dissolved solids), but it still contains significant amounts of sulfates (1,000 ppm) and calcium and magnesium (500 ppm). Mixing 75 vol% NF reject with 25 vol% RO permeate results in Smart Water D, with salinity similar to that of seawater, but sulfates are increased by 3X, magnesium by approximately 2.5X, and calcium by approximately 1X. The two monovalent ions (sodium and chloride) in the water are depleted by nearly 15% when compared with seawater. Note that the sizing capacities of both NF and RO units need to be designed appropriately to meet the desired blending-ratio requirements of various water streams generated depending on specific IOR/EOR application.

Technology Evaluation and Offshore-Facility Rough-Order-of-Magnitude (ROM) Estimates. As discussed previously, either RO desalination or NF/RO desalination in series configuration are suggested in most published studies to generate desired injection water for low-salinity waterflooding in sandstones. Both of these systems have some inherent shortcomings for SWF application in carbonates, as described in the following, which can be overcome with the novel water-ionic solution investigated in this study.

RO desalination will provide only two water streams—fresh water and monovalent-/divalent-ion-rich concentrate—with an expected recovery of approximately 50%. Hence, this system will not be able to provide flexibility to alter water chemistry to obtain either monovalent-ion-rich or divalent-ion-rich water. It is important to note that tuning on sulfates and divalent ions is critical for SWF application in carbonate reservoirs. Therefore, the RO system alone will not provide that capability.

NF/RO desalination in a series configuration will provide three different water streams: monovalent-ion-rich (NF permeate/RO reject) water, divalent-ion-rich (NF reject) water, and fresh water (RO permeate). Hence, if smart water to mimic seawater dilution is required, then fresh water should be blended with pretreated seawater, which adds more capital expense because of the extra seawater pretreatment. Because the permeate stream from the NF unit is further processed in a downstream RO unit, the final product recoveries tend to be lower (typically less than 50%). This results in larger-capacity systems for both NF and RO, which would increase capital/operating expenditures and the weight and space requirements on the platform. For example, if individual recoveries from NF and RO units are approximately 75 and 66% each (Ayirala et al. 2010a), then the overall product recovery becomes 49%. Also, NF and RO processes are interdependent on each other in series configuration. As a consequence, removal of large NF-permeate quantities for blending could become cumbersome and could result in some equipment downtime.

RO/NF desalination in a parallel configuration will provide four different water streams to cover the entire spectrum of salinity and ionic-content variation. These streams include monovalent-ion-rich (NF permeate) water, divalent-ion-rich (NF reject) water, fresh water (RO permeate), and monovalent- and divalent-ion-rich (RO reject) water. The availability of these four widely varying water streams provides better flexibility to customize a desired salinity or ionic-content smart water. RO reject can be used for blending with RO permeate to obtain smart water to mimic seawater dilution. As a result, savings in pretreatment costs are expected. Because NF and RO units are operated in parallel, the overall product-water recoveries are expected to be higher (i.e., in the range of approximately 60%). It requires relatively compact NF and RO units to achieve the same product-water volume requirement. Product and reject streams can also be withdrawn with much ease for blending to make up the desired smart-water cocktail. Even the energy requirements are expected to be lower because less power is required to force water through NF relative to RO and compact facilities. The comparative evaluation on these three desalination schemes

Comparison Parameter	RO	RO/NF Series	RO/NF Parallel
Recovery efficiency	Medium	Medium	High
Ease of operation	High	Low	Medium
Ion tuning flexibility	Low	Medium	High
Energy requirement	Medium	High	Low
Footprint	Medium	High	Low

Table 6—Comparative evaluation of novel ionic technology with other schemes.

with respect to ion tuning flexibility, recovery efficiency, energy requirement, footprint, and ease in operation is provided in Table 6 on the basis of the same product-water capacity. As can be seen, the novel water-ionic solution looks attractive in all key aspects compared with other schemes in addition to providing a one-shop solution to address improved/enhanced oil recovery injection-water-chemistry requirements.

Verbeek and Matzakos (2009) presented facility estimates for offshore low-salinity waterflooding with desalination equipment consisting of NF and RO in a series configuration. The case described in their study used ultrafiltration for seawater pretreatment, and facilities were designed as retrofit to seawater injection at 10 000 m³/d. These estimates included incremental facilities such as seawater lift, pretreatment, and desalination. The study results showed an operating weight of 340 t with a 726-m² footprint and a power consumption of 2 MW for NF/RO series configuration in the offshore environment. These authors also provided breakdown of life-cycle costs for large-scale seawater RO desalination and these data indicated RO-desalination costs to be USD 0.80/m³ of treated water (onshore) and greater than USD 2.2/m³ of treated water (offshore).

ROM estimates are generated for novel-water-ionic-technology offshore facilities by use of the preceding data from Verbeek and Matzakos (2009) on similar facilities, as a basis. Expected water recoveries in the NF/RO series configuration are approximately 50%. As a result, these systems need to handle feedwater capacities of twice the product-water volume requirement (i.e., 20 000 m³/d for the case-study example). The NF/RO parallel configuration used in the novel water-ionic technology can provide product water at approximately 62.5% recovery. Hence, these systems process approximately 16 000 m³/d of feedwater to generate 10 000 m³/d of product water. The well-known exponential scaling with an exponent 0.70 (used to scale process equipment and capital costs) has been adopted to determine scaled facility estimates on the basis of feedwater capacities with the following equation:

$$SP = RP \times \left(\frac{SF}{RF} \right)^{0.70}, \dots \dots \dots (1)$$

where *SP* is the scaled parameter, *RP* is the reference parameter, *SF* is the scaling-flow rate, and *RF* is the reference-flow rate. We also assumed that this scaling equation is applicable to all three facility parameters (weight, space, and power) to provide reasonable estimates. These scaled data indicate an operating weight of 290 t, a 620-m² footprint, and a power consumption of 1.7 MW for the novel-water-ionic-technology offshore facilities to produce 10 000 m³/d of treated water. It is reasonable to consider the water-treatment costs (USD/m³ of product water) of this technology to be almost similar to those of seawater RO desalination as a good first-hand approximation in both onshore and offshore environments. However, it is important to note that these conservative costs are expected to come down with more-detailed estimates because of increased water recovery and lower power consumption in novel water-ionic technology.

Recommendations and the Path Forward

The significance of the need discussed in this paper to address improved-oil-recovery/enhanced-oil-recovery (IOR/EOR) injection-water-chemistry requirements gives rise to the following major recommendations:

1. The water industry should recognize the oil industry's complex IOR/EOR water needs, and similarly, the oil industry should look to the water industry to come up with novel solutions. This calls for close collaboration between two industries to render these partnerships to be win-win for both.
2. Some critical thought should be given on research and development to alter water compositions of produced water for reuse in IOR/EOR to address current challenges on water scarcity and environmental concerns.
3. New emerging and cost-effective alternative technologies currently under development should be examined for selective removal of specific ions from saline water.

Preliminary technology-evaluation data on the novel water-ionic solution presented in this paper look promising. As a result, the following path forward is suggested for next steps.

1. Identify an appropriate nanofiltration (NF) membrane to provide the most efficient tailoring of injection water in terms of key ions for smart-waterflooding (SWF) application in carbonates.
2. Carry out small-scale continuous-flow-loop experiments to validate membrane-performance projections.
3. Design a water-treatment system with proper sizing of NF and reverse-osmosis units to generate the desired blending requirements and meet optimized injection-water composition of a specific carbonate reservoir.
4. Perform a thorough economic analysis to provide more-detailed weight, space, power, and cost estimates for the designed water-treatment system.

All these path-forward steps are critical to further optimize and qualify this novel water-ionic technology for application in SWF field pilots.

Summary and Conclusions

1. A novel water-ionic-composition optimization technology was investigated in this study by use of nanofiltration and reverse-osmosis membrane processes in a parallel configuration. The beauty of this configuration is that it can generate multiple product-water streams to cover the entire range of ionic content and variation. As a result, great flexibility is provided to tailor smart water of desired composition and ionic content for injection into the reservoir either by itself or in combination with other improved-oil-recovery/enhanced-oil-recovery (IOR/EOR) fluids.
2. Desired low-ionic-strength water cocktails that are rich in either monovalent or divalent ions or both or with the desired monovalent/divalent-ion ratio can be custom made with the investigated technology to suit both low-salinity water and smart-waterflooding applications in sandstone and carbonate reservoirs, respectively.
3. Smart waters obtained from the technology are even suited for application in other EOR processes such as polymer flooding, alkaline/surfactant/polymer flooding, smart-water surfactant flooding, carbonated waterflooding, miscible gas flooding, and dilute surfactant flooding for carbonates, and as boiler feedwater in steamfloods. The technology thereby offers a novel one-shop IOR/EOR smart-water solution.
4. The investigated technology also offers savings in seawater pretreatment (because of nonusage of pretreated seawater for blending) and compact surface facilities/lower energy requirements when compared with other advanced desalination schemes already advocated in other works.

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