### **Perspective**

# Emerging Scientific and Engineering Opportunities within the Water-Energy Nexus

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Energy and water resources are deeply interconnected. In the United States, the water sector consumes  $\sim$ 4% of primary energy, and energy generation is the sector where the most water is withdrawn. These competing water-energy demands are global and not unique to the U.S.; this highlights an urgent role for first-principles scientific innovation. The goal of this perspective is to define the scientific context of the water-energy nexus and examine ways in which developing technologies could have an impact on the future of deriving energy from water and, in turn, water from energy. Scientists, perched upon the steep slopes of demand curves for water and energy, are charged with developing enhanced techniques to enable a sustainable water and energy future. Inevitably though, for sustainability to be achieved, there must be a pairing of these innovative new technologies with a more cognizant public perception surrounding water use and reuse.

#### **Focus Topics for This Perspective**

- \* Scientific context of the water-energy nexus (WEN): identifying the most urgent scientific and engineering challenges related to WEN
- \* Energy from water: approaches to making energy generation more water and CO<sub>2</sub> parsimonious
- \* Water from energy: opportunities to increase the energy efficiency of water production and use
- \* The dirty truth: a call to advance the science of fouling and scaling and altering our perceptions surrounding water use (and reuse)

Ocean, n. a body of water occupying about two-thirds of a world made for man – who has no gills. Ambrose Bierce, the Unabridged Devil's Dictionary

Energy and water are intimately interlaced in a yin-yang fashion.<sup>1–3</sup> At present, in the United States, energy generation withdraws more water than any other sector, and the water sector consumes ~4% of energy resources.<sup>4</sup> Critically, these figures are not unique to the U.S., but rather reflect globally entrenched approaches to energy and water management and hold true for most industrialized nations (with a few notable exceptions). However, this is hardly a new dilemma; this resource tension between energy and water has echoed true throughout recorded history and across civilizations and cultures. Given that water resources are finite, whereas global population and energy consumption are annually expanding, the competitive balance between these resources has received renewed focus (Figures 1 and 2). Today, roughly 700 million people lack access to safe drinking water, and

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#### Context & Scale

Fundamentally, energy and water resources are deeply interconnected. This presents urgent demands for impactful innovation in light of trends in population and energy consumption. Appropriate technologies can substitute for water in two of its three main roles (thermal medium, solvent, and biological medium); however, innovation is needed as these technologies have evolved over time from engineering needs, and not first-principles scientific thought.

Central research priorities in the water-energy nexus are water-free energy generation, CO<sub>2</sub> sequestration, low-energy separations, and enhanced fluids. Above all else discussed in the article, water pretreatment is presently a mystery and could transform future water and energy landscapes on an ultimate path to sustainable energy generation with no water waste.



estimates show this figure rising to 1.8 billion in just 10 years.<sup>5</sup> As of 2016, global municipal water withdrawal comprises 12% of the total global water withdraw.<sup>6</sup> Lifestyle changes at the level of each single citizen can have a significant impact on water scarcity (freshwater consumption per country per capita can be explored in the database of The World Bank<sup>7,8</sup>). Industrialized countries are also vulnerable to water scarcity. The U.S., Australia, Singapore, and many Middle East nations are coping with periods of extended drought, which is further elevating nearterm water-energy concerns. Rationally, securing potable water (and the agricultural products borne of it) is indisputably a need of existential importance, whereas energy consumption viewed through this lens is, by contrast, a want. However, post enlightenment, there are no large-scale examples of cultures or civilizations that have taken a deliberate step backward in technological progress in the name of resource conservation, given that the fruits of technology and their impact on our livelihood, health, and longevity are so positive and impactful.<sup>9</sup> Rather, many fields that have matured from lab-scale nascent technologies to globally consequential enterprises over the past 30 years (i.e., photovoltaics, energy storage) have attempted to find solutions to enable increasing energy utilization while more or less preserving current resource availability. However, in the water-energy space, this is a remarkably daunting task. The example of California provides a poignant case study.<sup>10</sup> California, in comparison with other independent nations, has the sixth largest gross domestic product (GDP) in the world. In the 22 years spanning 1990–2012, California's total energy consumption increased by just 2.6% (impressive given a population expansion of 27% and GDP expansion of 68% over this period), but the water required to produce that energy grew by 260%. This emphasizes that there are no easy fixes to be found in the tug of war between consumption targets in the water-energy nexus (WEN).

These trends, not unique to California, or the United States, have sown an increasingly prominent and growing devotion to water-energy research that crosses traditional research dichotomies (e.g., basic versus applied science, chemistry versus physics versus engineering, industrial versus academic research) in a search for ways to fundamentally change our approach to the production, transport, and utilization of water to meet our daily needs. Water has had this vital role due to its unique properties as related to energy generation and management. Redefining the role of water moving forward will require us to contend with this cluster of attributes. Namely, from the energy perspective, water has among the highest known heat capacities (4.2 J/g °C) and heat of vaporization (2.26 kJ/g) due to its strong hydrogen bonding network. Thus water is difficult to displace as an ideal thermal storage medium, cooling fluid, and for power generation cycles. Secondly, water is an exceptional solvent. It has the ability to dissolve nearly all ions in the periodic table<sup>14</sup> and many organics as well. Thus, new fluid solutions will be needed to replace its role as a solvent, not only for washing and cleaning but also for oil and gas production (enhanced oil recovery and hydraulic fracking). This article discusses the areas where innovation is most needed and poised to be most transformational; topics are outlined below. Given the colossal breadth of each of these topics, there is no way to write a comprehensive outlook that remains less than a textbook. And while policy undoubtedly has a firm hand in guiding (or hindering) the journey from technology to market, this article does not address policy levers. However, each of the areas that are discussed is a fertile territory for the sort of conversations that Joule seeks to broker: globally transformative issues in energy that cry out for basic research innovations and ways to effectively partner, stress test, and launch these innovations into the world.

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Figure 1. The Changing Landscape of Worldwide Renewable Internal Freshwater Resources from 1962 to 2014

Scale is in cubic meters per person per year by country, therefore regional water scarcity within individual countries is not reflected here. Source data from The World Bank database.<sup>11</sup>

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world electricity demand

### world population

#### Figure 2. Global Trends of Population and Electricity Demand

Source of world population from OECD Environmental Outlook to 2030.<sup>12</sup> Source of world electricity demand from International energy outlook 2016, U.S. Energy Information Administration.<sup>13</sup>

### Scientific Context of the WEN: Identifying the Most Urgent Scientific and Engineering Challenges Related to WEN

We currently use an annually increasing fraction of our available water supplies for energy generation. Reciprocally, our energy demands to produce and transport potable (and agriculturally useful) water are climbing as well. This interconnected web of water and energy is captured in Figure 3, a Sankey diagram highlighting current sources, uses, and products of both energy and water in the U.S. (not just in the U.S. but globally, although with some variance in the nature of the problems, e.g., Oman versus China). Several notable features emerge at a glance: Enormous fractions of our freshwater supplies are withdrawn (Figure 4) to cool thermally driven (thermoelectric) power generation, which is our primary driver for electricity production. Consequently, these thermally driven energy generation processes are accompanied by vast amounts of secondary "waste" power (primarily as heat) as a byproduct. Also significant is that agriculture is the single largest consumer of water (Figure 4), competing directly with water resources withdrawn for energy generation and those used for energy production itself via biofuels. Transport of water is not depicted here, but requires large energy draws, and water treatment as well is beginning to require increasing energy inputs to maintain water quality in the face of increasing draws from non-traditional and more contaminated sources in response to extended droughts across the planet.

This portrait is subject to change apace with coming technological advances. Expanding use of photovoltaics, water, and wind energy could mitigate water withdrawals for energy generation. On the other hand, other growing technologies such as carbon capture, drilling, and hydraulic fracturing could increase water demands for energy and negatively affect local water quality and availability. However, assuming no wholesale changes to this energy and water landscape are imminent, the impetus is on scientists to develop transformational approaches to have an impact on both water for energy and also energy for water. It is crucial to note that these advances span not only basic research in understanding how ions behave



Figure 3. Hybrid Sankey Diagram Showing Interconnected Water and Energy Flows in the U.S. Note that not all waters are equivalent here in terms of constituents and application-specific usability. Source data from the Water Energy Nexus report.<sup>15</sup>

at electrified interfaces out to mid-scale challenges in selective ion-capture and remediation (arsenic, lead, etc.) but also redound to large-scale concepts that might fundamentally disrupt how we produce, transport, and consume water as a global community. These questions guide the subsequent sections of this perspective: What opportunities are there to radically lower the water demands for cooling? How can we capture  $CO_2$  without water? Can we decrease the energy required for separations, while also allowing for reclamation of precious metals from treated water? Is it possible to increase the speed at which we transport water while decreasing the energy required?

If we are able to marshal a scientific response to these urgent questions, we have the opportunity to navigate our future water-energy landscape placidly, making gains in technological progress and civilizational growth while still nourishing ourselves without conflict. Many dystopian novels have been written propounding on the alternate future—Frank Herbert's novel *Dune* is a renowned example—where water and energy scarcity lead to meager existences filled with strife and war over this essential triatomic cog in our biology. Already today in 2017, the issue has been identified as the most critical scientific and technological advance needed for sustainable global development.<sup>16</sup> To alleviate global suffering and support continued global prosperity, we must alter the current ways in which we produce and use both water and energy.

Before developing the science further, it is necessary to briefly discuss some common terminology used to talk about certain sources of waters. This is vital to understanding what resources are being tapped into, and what implications these waters have with respect to a more holistic WEN perspective. Much like "energy," the concept of "water" subsumes many different categories, and the classification of waters can ultimately be fragmented in innumerable ways (Figure 5). Generally speaking, we consider only a few types of water in this article and classify these based on source and composition. From the viewpoint of



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Figure 4. Fresh Water Withdrawal Versus Consumption in the U.S. Source data from the Water Energy Nexus report. $^2$ 

source, the main primary sources to consider are surface water (which contains both seawater and freshwater) and groundwater. Around 76% of available water resources originate from surface water and the second most abundant source is groundwater, contributing another 13%. The other two sources that appear frequently are "unconventional sources," resulting after a first use of the primary resources above; these categories are produced waters (waters existing as a byproduct of oil and gas exploration and production) and wastewater (water remaining after initial contact with humans). Composition of water is another useful categorization scheme, given that from a WEN perspective, one is invariably trying to remove species from, or add species to, water. The salinity of water is a useful metric here, and water salinity is classified based upon total dissolved solids (TDS) in ppm or mg/L. Seawater and brine are the most concentrated conventional water source (with 35,000 ppm or greater), brackish water is moderately saline (defined as containing 1,000-10,000 ppm TDS), and freshwater is defined as containing 0-1,000 ppm TDS with regulated drinking water being <500 ppm. Produced water can vary widely in salinity (TDS), organic content, toxicity, and the like, depending upon the methods used. Invariably, this water is contaminated with a panoply of gellants, corrosion inhibitors, friction reducers, biocides, and the like, rendering these sources problematic from a treatment and reuse perspective.

### Energy from Water: Approaches to Making Energy Generation More Water and CO<sub>2</sub> Parsimonious

Presently, industrialized nations withdraw an enormous amount of water for cooling of thermoelectric power plants. For example, the United States is the world's largest economy and a top energy consumer, and roughly 40% of its total freshwater supply is diverted to cooling in thermoelectric power plants.<sup>15</sup> In comparison, the amount of fresh water consumed in agriculture is 40%, and commercial and residential activities combined hold 12% of the fresh water supply. In addition to water withdrawals,

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#### Figure 5. Natural Water Resources and Availability Adapted from IEEE.<sup>17</sup>

water consumption is also substantial. The U.S. Environmental Protection Agency estimates that to generate each kWh of electricity at the user end, 25 gallons of water would be withdrawn and at least 2 gallons of it would be consumed.<sup>18</sup> Therefore, thermoelectric power generation, and heating and cooling more generally, are the key pressure points that must be addressed for advanced materials, technologies, and systems to meaningfully have an impact on our current water-energy habits.

To understand where innovation may be useful, it is important to understand how water is currently used in these operations. The majority of thermoelectric power plants are water cooled, using one of two basic approaches: once-through systems and closed-cycle systems. In a once-through system, vast quantities of water (~25,000 to 50,000 gallons/MWh) are re-routed from rivers or the ocean to the plant, used for cooling, and then discharged back after going through a steam condenser. As mentioned earlier, these are withdrawals only, and the net consumption is negligible. Nevertheless, since this water is effectively removed from the use cycle, it dramatically limits water resource availability upstream, and raises environmental problems due to thermal and (to a lesser degree) chemical pollution. Arguably, this is only slightly less problematic than consumption, as a kitchen with a well-stocked (but locked) pantry would offer little comfort to soothe urgent hunger pangs. The other type of cooling is closed-cycle wet cooling. In this case, the heated water

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(instead of being directly discharged) is instead sent to a cooling tower, where cooling occurs via convective air flow and enhanced evaporation. Here, the water used for cooling is subsequently pumped back to the heat exchanger and re-used for the next cooling cycle. A closed-cycle cooling system withdraws much less water, roughly 3% that of the once-through system for a comparable amount of cooling.<sup>19</sup> However, since the rejection of heat is largely through evaporation, the net water consumption is higher. Furthermore, while it is in principle a closed cycle, there are many losses in the system, which is why they require water withdrawals despite the implications of the title, "closed cycle." The majority of these losses are due to evaporation, and the rest of the water consumption is due to replacement, as even in a "closed-cycle" system, the water needs to be replaced after a number of cycles to prevent scale formation.

Thus, there are no ideal choices here from a water-energy perspective, just different systems-level considerations. Thus, it is not surprising that among all thermoelectric power plants in the U.S., 42% are closed-cycle wet-cooling systems, while another 43% use once-through cooling.<sup>19</sup> With a total water withdrawal of 196 billion gallons per day, we estimate the total consumption to be over 6 billion gallons. To illustrate the differences between these approaches,<sup>19</sup> consider a 500 MWe coal-fired thermoelectric power plant; this plant operating in closed-cycle mode would consume more than 6,000 gallons of water per minute during its operation, far exceeding the consumption of a once-through system (ca. 2,000 gallons per minute), although the latter would withdraw a staggering 250,000 gallons of water per minute.

Given the magnitude of this challenge, and the fact that we are unlikely to dramatically supplant thermoelectric power generation in the next several decades, a combination of governmental and industrial consortia have pinpointed several priority areas where new technologies have a path to large-scale implementation to reduce water usage.<sup>15,20</sup> The most pressing problems identified (spanning from basic science to more engineering) are: (1) alternatives to water as a working fluid, (2) water-minimal carbon capture materials, (3) dry cooling, (4) more effective fuel use, and (5) better systems-level water recovery. Some innovations are already on the horizon for water recovery and fuel use. A new technology called "Air2Air,"<sup>21</sup> which uses indirect heat exchange between warm saturated air and cool dry air is under development and can enable recycling of up to 25% of water that would otherwise be lost to evaporation. Other technologies under development address seemingly banal but pernicious losses, such as water losses unrecovered from flue gas (water comprises 5%-7% of flue gas on average) or scaling, which sound minor, but at the scope of a 500 MWe power plant, lead to unacceptable water waste. For such a plant, four million pounds of post-combustion flue gas are emitted every hour, which amounts to about 500 gallons of water per minute or the amount of water used by 1,700 American households during the same time.

One of the industry's first answers to water usage reduction in power plants is implementation of water-free condensers that depend on air convection. This limits the cooling efficiency and power output on hot summer days, and in this case additional spray-on wet cooling is used. Nanostructured super hydrophilic surfaces are being developed to help improve the adhesion and heat transfer between water droplets and the heat exchanger, thus reducing the amount of water that is lost through useful evaporation.<sup>22–24</sup> These water-energy trade-offs demand increased efficiency in the face of climate change and growing populations.

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In addition to the areas mentioned above, it is possible to reduce the water consumption in closed-cycle cooling systems by engineering the working fluid itself: water. Water has historically been the coolant of choice because it has one of the highest heat capacities of any liquid, but the development of advanced fluids that can supplant the use of water is an attractive emerging research topic. Particularly attractive are new fluid options that can be engineered to improve upon the thermal properties of water while providing scaling and fouling resistance, or offer viscosities that enable ready use as hydraulic fracturing fluids (another large consumer of water). While there has been some industrial-scale research on "new waterless fluids," particularly for fracking, most of these are either  $CO_2$  or  $N_2$  foams optimized for solubility and not thermal behavior, and thus not viable options for cooling. Given the constraints of the operational conditions of power plants (i.e., we cannot use ultrahigh pressures), much of the research in advanced thermal fluids has orbited around novel additives to water that can dramatically increase its heat capacity.

These additives, commonly referred to as phase-change materials (PCM), are compounds with large latent heats (usually found between 150 and 300 J/g, greater than 2× that of the sensible heat of water over a 20 K temperature difference). Many of these PCMs are non-toxic, cost effective, and have melting temperatures slightly above ambient temperatures (see Zalba et al.<sup>25</sup> for a list of common PCMs), one example being encapsulated paraffins<sup>26,27</sup>. Historically, these have been of interest for "smart" building insulation, and heat-energy storage systems, but are now being considered for power plant cooling. In addition to buffering temperature rises in the condenser, this could also beneficially lead to more efficient heat exchange and less reliance on evaporation for heat rejection, since more heat flux is expected for larger temperature differences. In order for PCM technology to make this leap, additional engineering characteristics must be met; principally: (1) narrow phase-transition ranges (typical water temperature entering into the condenser is 28°C and that leaving is 39°C), (2) minimal thermal hysteresis in transition temperature, and (3) excellent long-term cycling stability so the enthalpy of fusion does not decrease over repeated melting and cooling cycles. Assuming these requirements can be met, the working fluid in closed-cycle cooling systems can be replaced by a "phase-change slurry,"<sup>27,28</sup> where PCMs are encapsulated in small spheres, forming a suspension with water. This would potentially reduce evaporation loss and save water.

Engineered fluids can have substantial impact beyond cooling. The second largest water consumer in the energy sector is water used in the oil industry for hydraulic fracturing and enhanced oil recovery. For the United States, hydraulic fracturing is estimated to account for over 30% of total water consumption by all energy sectors (2.2 billion gallons per day) compared with 45% for thermoelectric power plant cooling.<sup>29</sup> The production of shale gas through hydraulic fracturing is a process where pressurized water (together with granular and chemical additives) is injected into wells to break shale depositions and free the natural gas trapped within the rocks. Waterless fracking has been a known technology for a while, initiated by companies sensitive to the ramifications of such large water consumption. However, due to scientific challenges regarding optimization of viscosity, thermal stability, and fluid properties, it has only been used on a limited scale. In some cases, liquid propane is being explored as an alternative to water;<sup>30</sup> in other cases, gases such as  $CO_2$  are used for the same purpose.<sup>31–33</sup> The concept of  $CO_2$  fracking holds great appeal. CO<sub>2</sub> itself is a product of combustion and the target of carbon capture and storage (CCS),<sup>34</sup> so using it to generate additional fuel aims to reduce greenhouse gas emission at point of generation. One relevant example, which could see wider

implementation in the near term if successful, is part of the Department of Energy's initiative in "clean coal" (integrated gasification combined cycle) power plants. These plants use pressurized gasifiers to directly form syngas (a fuel mix of hydrogen, carbon monoxide, and carbon dioxide that burns more cleanly) from coal; a pilot plant called the Kemper project in Mississippi (under development) is designed to use over 60% of its captured  $CO_2$  (estimated 3 million tons per year) for enhanced oil recovery.

It is worth noting that water and energy also interact significantly in the process of CCS in less obvious ways. Today, fossil fuels (coal, gas, and oil) supply 80% of the world's energy needs and emit an unprecedented amount of  $CO_2$ . High levels of atmospheric  $CO_2$  contribute to global warming and to devastating and potentially irreversible effects via climate change. Reducing  $CO_2$  emission through CCS is technologically feasible but with significant energy and water costs. Implementing carbon capture in existing power plants results in up to 40% loss in effective power output and nearly doubled water usage,<sup>35</sup> which will inevitably intensify pressure on water resources.

Current commercial amine-based wet-scrubbing capture systems require significant guantities of water for cooling, regeneration, and other operations. So while the process is amine based, water is consumed in nearly every operational stage. To begin, cooling water is indirectly used to lower the temperature of the flue gas to about 38°C after combustion. An amine-based solution is then introduced, which absorbs CO<sub>2</sub> from the flue gas; this amine-CO<sub>2</sub> complexed solution is subsequently cleaned with water to remove any residual ammonia. The CO<sub>2</sub>-rich solution is then pumped to a stripping reactor for regeneration where the CO<sub>2</sub> is separated by the application of heat. It is only after these water- and energy-expensive steps that  $CO_2$  is released, producing a concentrated stream that exits the stripper and is then cooled and dried in preparation for compression. Therefore, a key frontier of modern R&D in CCS concentrates on development of advanced CO<sub>2</sub> capture technologies that require less water. So-called "dry CCS" methods often involve molecular design of targeted sorbents, such as those using metal-organic frameworks (MOFs). These adsorptionbased separations using solid MOF sorbents with high CO<sub>2</sub> sorption capacity<sup>36</sup> and membrane-based separations using high-performance hybrid membranes<sup>37</sup> are examples of new technologies with demonstrated success at the lab scale whose supplemental water requirements are limited, offering potential paths to dry CCS.

Another approach to the problem of emitted waste heat from power generation would be to directly use this waste heat to drive energy generation, rather than trying to mitigate these thermal losses. A huge amount of low-grade heat from industry, geothermal wells, and solar collectors below 100°C is lost each year due to the limited existing methods to harvest energy from sources with a small temperature difference between the source and environment. Typically, this might involve running a secondary thermodynamic cycle (e.g., an organic Rankine cycle using a non-aqueous low-boiling point working fluid), however these are not highly efficient and, moreover, have extremely narrow operative temperature ranges given the paucity of fluid options, although they have seen some adoption for low-temperature geothermal and produced water sources.<sup>38</sup> Another enticing possibility is that of direct thermal to electrical energy conversion using thermoelectric materials (not to be confused with the thermoelectric power plants).<sup>39</sup> Thermoelectric devices consist of highly doped n- and p-type semiconductors that are sewn together electrically in series and thermally in parallel; under a thermal bias, this impetus moves both electrons and holes in a coordinated fashion across the device, directly

generating power. From an engineering perspective, one effectively considers the electrons and holes as the "working fluid," and thus they do not require pumps, moving parts, do not undergo fouling, and do not leak. While attractive conceptually given the enormous amount of rejected heat from power plants (even a meager 5% efficient conversion of power plant waste heat would meet approximately 25% of U.S. residential electrical demands), existing materials themselves tend to be expensive, brittle, and finicky. Moreover, given that these are heat engines, the overall power generation potential is capped by the Carnot efficiency, which scales with the temperature difference between the hot and cold reservoirs, and in these low-temperature operational modes this leaves little available energy for recovery. However, emerging research into soft thermoelectrics,<sup>40,41</sup> designed to operate in these low temperature ranges and capable of woven and fibrous geometries, could rejuvenate this approach.

Alternatively, recent research has shown that it may be possible to perform lowgrade waste-heat harvesting using membrane technology. This new concept, thermo-osmotic energy conversion (TOEC), was recently introduced with the aim of passively extracting energy from low-grade heat sources.<sup>42</sup> This TOEC process utilizes temperature gradients (with a 60°C heat source and a 20°C heat sink) across the membranes to drive water vapor flux (and thus energy flux) from the warm reservoir to the cool reservoir across a hydrophobic, nanoporous membrane. The rate of vapor transport across the membrane depends upon the partial vapor pressure difference at either side of the membrane and on membrane properties. In a system where the temperature gradient is maintained across the membrane, thermoosmotic vapor transports continuously occurs across the membrane into the cold stream, transmitting thermal energy. The resulting pressurized flow in the cool reservoir can pass through a turbine to convert the low-grade heat energy to mechanical work. This is a very recent report and uses water as the fluid/vapor, however the implications here are intriguing as they can capture up to 50% of the theoretical Carnot efficiency (which is very challenging to do at low-temperature differentials). Further efficiency gains may be had by the thermal efficiency of the membrane or heat exchangers inversely proportional to the heat of vaporization of the working fluid. Therefore, fundamental understanding on the heat and mass transfer problems in confined nano-channels and how to effectively design the working fluids and porous membranes are key factors to the future development of the TOEC process.

In addition to regular wastewater treatment, a wastewater treatment system designed to be frugal on freshwater use has to deal with biological waste streams and wastewater with high chemical oxygen loads. For example, microbial fuel cells (MFC) can harvest the renewable energy produced from the organic content in waste streams to yield electricity and hydrogen gas.<sup>43</sup> Such an MFC-centered technology could recover up to 41% of the chemical energy,<sup>44</sup> which in theory could turn wastewater treatment from an energy consumer into a net energy producer.

#### Water from Energy: Opportunities to Increase the Energy Efficiency of Water Production and Use

Water, at a molecular level, is not scarce. Earth is a blue planet, and water covers 70% of our surface. The challenge is that 97% of that water exists in our oceans as a non-potable 3.5 wt % salt solution (Figure 5).<sup>45</sup> In addition to sodium chloride, these saline sources (water being a powerful solvent) contain "virtually all the elements of the periodic table."<sup>14</sup> Furthermore, in addition to metal ions, there exist a motley collection of microorganisms, humic acids, clays, silt, algae, viruses, and bacteria (see Figure 1)<sup>46</sup> in most natural sources. However, producing water goes well

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beyond processing and treatment of natural sources. Due to increasing water use for energy production, the water we consume for agriculture and drinking is becoming less and less likely to emanate from a pristine mountain spring, and increasingly likely to be heavily treated water that emerged from industrial use just days prior. Alternatively, this water may even come from more marginal sources such as produced water from the petroleum industry. There is massive potential here to mediate water needs. For example, it is estimated that the volume of produced water left unused and untreated in the United States ( $\sim$ 1–2 M acre-feet/year) roughly matches that of California's water overdrafts during an average year.<sup>47</sup> Moreover, given an appropriate technology, there exists the potential to extract many valuable resources from these waters (e.g., precious metals for catalysis or energy-relevant materials such as Li<sup>+</sup>). Peering toward the horizon, a low-energy method to extract uranium or cesium ions from water would immediately change the environmental considerations regarding use of light-water reactors and their attendant remediation. Ultimately, next-generation treatment technologies could do more than assist in meeting expanding water demands; they could powerfully aid in decarbonizing our energy production.48

Unfortunately, at present, the process of generating potable water from these less than ideal sources is incredibly costly and energy intensive. The stronger challenge of extracting resources from water for reuse is even less established. Largely, this is due to the fact that innovation in water production has remained relatively stagnant for the past 50 years due to low energy prices. We have had the luxury of transporting water hundreds of miles from its source to meet demands as opposed to being locally water resilient. "Don't boil the ocean" is a banal consulting apothegm implying that brute force methods are to be avoided at all costs, and yet these head-on collisions with physics are essentially the basis of desalination technologies today, which rely on either thermal (multiple effect distillation or multi-stage flash) or mechanical/pressure-based means (reverse osmosis).<sup>49</sup> In contrast to these methods, which currently produce the vast majority of the world's water in perpetually arid regions, future technologies based upon advanced materials that are incompletely understood promise energy-efficient solutions for producing water.<sup>50</sup> However, at present, these materials (studied at the lab scale) as of yet possess few fundamental microscopic transport theories. The transport relationships for membranes are largely empirical in general and rely upon continuum transport models coupled to statistical fluctuations; their capacity to yield meaningful predictive validity weakens considerably when investigating these new ultrathin materials with nanoscale voids. Continuum transport models and physical intuition both erode on small length scales. But it is precisely these cases where bulk intuition is violated that new phenomenology emerges; our intuitions must be revised by better fundamental understanding of transport at these nanoscale dimensions. This lays the groundwork for future transformative technologies with ultrafast water transport, selective ion sieving, and low-energy separations. It is difficult to overstate the global impact that new engineering and basic science solutions to increase the energy efficiency of producing water would provide. It is considered the number one breakthrough needed to improve the quality of life for the world's impoverished people by the LBNL Institute for Globally Transformative Technologies, ahead of other more widely championed causes such as bed nets for malaria and tuberculosis vaccines.<sup>16</sup>

The principal problem to tackle is, of course, separating the salt from the water. This is easy to state but not simple to do. Considered abstractly as a physics problem, thermodynamics provides a theoretical limit for the minimum amount of energy

required to separate pure water from dissolved ions. Independently of the purification method, this thermodynamic minimum is achieved when separation occurs as a reversible, adiabatic process. Calculations<sup>51</sup> show that the minimum energy required to extract half the fresh water out of a given volume of seawater containing 3.5 wt % (35,000 ppm) of NaCl is about 1.06 kWh/m<sup>3</sup>. As an important aside, the 50% recovery number is most commonly used as the extraction of pure water from brine becomes much more expensive as the salinity increases (which occurs as the reverse osmosis process proceeds) toward the practical reverse osmosis (RO) maximum of 7 wt % exit stream concentration. Understanding this theoretical lower bound provides a useful benchmark for comparison between different purification technologies and can help guide future efforts to reduce energy demands.

Current desalination methods can be roughly categorized by whether the external driving force is mechanical or thermal, or sometimes a combination of both (Figure 6). The common mechanical-driven methods include mechanical vapor compression (MVC), microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and RO, and the thermal-driven methods include multiple effect distillation (MED), multi-stage flash (MSF), and forward osmosis (FO). Often, MF, UF, and NF are principally used as a pretreatment to RO (Figures 7 and 8) and for water and wastewater treatment more generally. Although these approaches are all similar in principle (using a force to drive a separation), they are not equally favored from the standpoint of energy consumption. Thermal-driven desalination methods exhaust significantly more energy than those using mechanical work because the theoretical minimum heat ( $Q_{min}$ ) required to separate a mixture is, by definition, higher than the minimum work ( $W_{min}$ ) required as shown mathematically in the following relationship:

$$Q_{\min} = W_{\min} \left(1 - \frac{T_0}{T}\right)^{-1},$$

where  $T_0$  and T are the temperatures of the ambient and hot side source, respectively, in Kelvin. If the heat source is at 60°C or 100°C and the ambient temperature is 25°C, the  $Q_{min}$  (thermal-driven desalination) is 9.5 or 5.0 times greater than  $W_{min}$ (mechanical-driven desalination), respectively. In the sense of energy consumption, the mechanically driven technologies have great promise to be more efficient in treating seawater. However, as we see, considerations beyond energy balance complicate the selection of a preferred separations technology.

The mechanically driven technologies (e.g., osmosis, filtration) are mostly membrane-based separations that rely on diffusive or convective mass transfer phenomena to reject dissolved and suspended constituents from aqueous solution. Large external pressures (up to 80 bar) are applied on the feed stream, driving the salt water across a semipermeable membrane, which selectively rejects Na<sup>+</sup> and Cl<sup>-</sup> and allows water to permeate. The membrane permeability and the size of constituents rejected are in a sequence of MF > UF > NF > RO, and the membrane pore sizes have been optimized over the decades to specialize in separation of one particular species from water (Figure 7) Among these technologies, only RO and NF are intended to be used as desalination processes, which can reject a broad range of contaminants and TDS in impaired feed streams. At present, the most energy efficient among these is RO (2.34 kWh/m<sup>3</sup>), although practical efficiencies of real RO plants tend to fall within the lower efficiency regime (3.5-4.5 kWh/m<sup>3</sup>) depending on a number of influencing factors such as outdated technology, distance from ocean shore, membrane life, etc.<sup>54</sup>; this is the leading current desalination technology on these terms and is closest to the theoretic lower bound mentioned





Multiple effect distillation (MED)

Flash Unit

Flash Unit

### Mechanical vapor compression (MVC)



Figure 6. Flow Diagrams Showing Concepts Underlying Various Separations Processes, Including Feeds and Products

Figure is adapted from Vane.<sup>52</sup> RO, FO, and ED are discussed in detail in the text. RO and FO rely on pressure, either external or internal (chemical potential) in origin to guide flow; FO ultimately requires thermal means for regeneration. ED is unique in that it uses an external field (electric potential) as the driving force for separation, and further unique in that the flow is orthogonal to the separation direction. MSF, MED, and MVC are all techniques that use a combination of pressure and thermal means to purify water.

earlier (1.1 kWh/m<sup>3</sup> for 50% recovery at 25°C).<sup>55</sup> And in the case of seawater, RO is by far the most advanced water purification technology available at the industrial scale. Indeed, countries such as Israel that recently struggled with extended periods of



**Figure 7. Relevant Length Scales and Constituents in Water and Conventional Treatment Approaches for Water Treatment** Figure is adapted from Oztekin et al.<sup>46</sup>

drought, now utilize millions of cubic meters of water per day generated from RO desalination sources.  $^{\rm 56}$ 

During RO, a saline feed stream is mechanically forced across an ion-rejecting membrane. While RO technologies achieve high rejection efficiencies, they suffer from a range of problems that must be addressed by future research initiatives if this technology is to advance to a next level. Often, the limitations in membranes for water purification are not, e.g., permeance at the coupon level, but rather the robustness of those membranes over time to scaling and fouling. Comprehensively, the most prominent challenges facing RO membranes are fouling, resilience to chemicals (e.g., Cl<sup>-</sup>) and temperatures, and the fact that RO energy requirements scale poorly with the salinity of treated waters. Membrane fouling mostly occurs when the membrane surface contacts with chemical components suspended and/ or dissolved in the feed stream, leading to considerable loss of membrane performance.<sup>49</sup> Chemicals, such as chlorine, in the feed could degrade membranes and efforts have been devoted to developing chemically robust RO membranes.<sup>57</sup> In addition, RO membranes usually operate under moderate temperatures less than 55°C, and thermal resilience remains a challenge for RO membranes.<sup>57,58</sup> The scalability challenge arises from the fact that the external pressure required for RO is dictated by the osmotic pressure arising from the chemical potential difference between the concentrated and diluted streams. Thus, as the RO process proceeds, the osmotic pressure naturally rises as the salinity increases. Thus, recovery rates around 50% are cited in these energy analyses, as it often becomes impractical above this value (Figure 8). The mechanical strength of RO membrane also limits



Figure 8. Desalination Limits for RO and Opportunities for New Technologies Figure adapted from Tong et al.  $^{53}$ 

the maximum feed salinity to about one-third of the solubility limit of NaCl (35 wt %). High external pressures are infeasible in other ways as well. Mechanically based methods only are as effective as their membranes, and high-pressure methods often lead to rapid and severe scaling and membrane fouling. Despite its appeal on abstract thermodynamic grounds, many projections indicate that a future integrated water management scheme will necessarily involve much more than seawater RO, and thus much higher (and lower) TDS waters such as inland brackish waters and produced waters will need to be treated as well. These non-seawater sources are not a good fit for commercial RO as it stands today, and thus new technological solutions are demanded. It may also be the case that new implementations of RO, such as high-pressure RO (to mitigate fouling) and pressure recovery RO, can play an important role in meeting these demands as well.

These well-known limitations of RO open an opportunity for other desalination methods to emerge for less conventional sources such as high-concentration saline water (TDS varies widely across bodies of water) or highly contaminated water (Figure 8). There are two prominent technologies for these types of water: FO and electrodialysis (ED). FO is, as its name implies, the conceptual inverse of RO. In FO, the water flow is driven by the internal water potential gradient between the feed and draw streams, where the draw stream possesses a higher osmotic pressure than the feed stream, and the water in the feed will penetrate through a semipermeable membrane to dilute the draw steam (Figure 6). In essence, one selects a concentrated solution of higher osmotic pressure than that of the water to be purified. Pure water flows thermodynamically downhill across the membrane (which has very different design considerations than RO membranes) in an effort to dilute the draw solution and equalize the osmotic pressures of both feed and draw. Because this is thermodynamically favorable, FO does not require high hydraulic pressures to overcome high osmotic pressures, and it can treat highly concentrated feed streams while also experiencing less membrane fouling compared with other common pressure-driven membrane process (e.g., UF, NF, RO).

To be clear, FO is a fundamentally different technology and is not a replacement for RO. FO can be used standalone or as a pretreatment technology for highly saline

sources targeted for RO, or alternatively as a pretreatment for waters from oil and gas exploration and other wastewaters with a high fouling or scaling propensity, such as industrial wastewater.<sup>59</sup> The majority of energy consumption for FO is draw agent regeneration, i.e., separating draw agents and water in the draw stream. Adequate draw agents can substantially reduce the energy cost by reducing the electric energy usage in regeneration and replacing it with other less expensive forms of energy, e.g., thermal energy, including low-grade industrial waste-heat or geothermal sources. Although FO processes have been widely suggested and investigated in a variety of applications, FO still faces some critical challenges, including concentration polarization, membrane fouling, reverse solute diffusion, and the rational design of the draw agents.<sup>60</sup>

As mentioned earlier, all membrane-based processes largely share concentration polarization and fouling problems, and these must be considered in the design of membrane-based separation processes. However, low operational pressures signify that the FO processes experience much less membrane fouling in comparison with RO, which is a highly attractive feature. Thus, the major hurdle for FO is to compensate RO's limitations (treating feed streams with high salinity or high fouling propensity) by design of novel draw agents that can be efficiently separated from treated water by low-cost thermal energy. At present, draw agents require a significant amount of thermal energy to separate the water from the draw solute, and this amount of energy sensitively depends on the type of draw agent and the resultant fluid/draw agent thermodynamics. To benchmark, a recent report shows that the regeneration energy for a thermally responsive ionic liquid (IL) is 1.80 kWh/m<sup>3</sup> (including the thermal energy for IL solution phase separation and the electricity needed for the subsequent NF process).<sup>61</sup> The ideal draw agents should possess properties such as (1) high osmotic pressure, (2) easy regeneration with only lowgrade heat, (3) low reverse diffusion, (4) low viscosity, (5) good chemical and thermal stability, and (6) low toxicity.<sup>60</sup> According to the response toward external stimuli (e.g., heat, pH value, electromagnetic field), draw agents are categorized into non-responsive or responsive types, and the responsive draw agents shows a high potential to meet these criteria. For example, IL draw agents that exhibit lower critical solution temperature (LCST) phase behavior are a promising future direction. These ILs show a high osmotic pressure and low reverse diffusion, and the LCST phase behavior (i.e., decreasing water miscibility with increasing temperature) allows these draw agents to be regenerated straightforwardly by integration with low-cost heat sources.<sup>61,62</sup> Historically, there has been little innovation in the fundamental chemistry of ILs, however, development of an environmentally benign IL with high osmotic pressure that could undergo low-temperature regeneration would powerfully expand the scope and applicability of FO processes beyond non-potable water reuse and into other realms of treatment and even desalination.

ED is another separation concept that is ripe for reinvigoration by new materials and engineering concepts. Originally developed in the 1950s as a method of demineralizing brines at large scale, its use declined over time as RO became the central technology used for desalination.<sup>63</sup> However, ED has many merits. Its premise is electrical field separation rather than separating based upon osmotic pressure. Therefore it works at approximately the same efficiency regardless of feed concentration. ED is most efficient and cost effective working at the high end of the brackish water regime,<sup>64</sup> thus, it can now play an important role in treating water from unconventional sources or brackish pools with low TDS where RO is typically not employed (Figures 6 and 8). Importantly, it is also a cross-flow technique where the salt is pulled out through the ED membrane under the influence of an applied electric

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# Joule

field orthogonal to the direction of the feed flow. As a consequence, ED, when used at the optimal salinity regime, can operate at much lower energy cost (one is not pumping against a large chemical potential gradient), thinner membranes may be used, and as a result there is much less severe membrane fouling.<sup>65</sup> There are additional intriguing opportunities to extend the use of ED beyond merely desalting for potable water, such as employing it for the concentration of brines and capture of other species of interest. The only limitation is that membranes for ED have been optimized over many years to select for Na<sup>+</sup>, Ca<sup>2+</sup>, etc. and little else. However, this is not a fundamental barrier, and increased research, design, and synthesis of entirely new classes of membranes could enable ED to have specificity for other ions of interest. This could render ED a substantial new technology in instances where remediation may be challenging (e.g., Cs<sup>+</sup> for light-water reactors) or where recovery of crucial ions may be of strategic interest (e.g., Pd<sup>+</sup> or Pt<sup>+</sup> for catalysis applications).

The concept of desalination discussed thus far is, of course, just part of a broader portfolio of water treatment options beyond mere de-salting of the oceans. To secure the accessibility of fresh water in remote areas, where seawater is a limited resource, other water treatment strategies that better serve brackish water, seawater, and other non-traditional wastewaters, such as industrial wastewater, must be considered.

Complementary to membrane-based separation techniques, whereby water is extracted from dissolved ions, are techniques that focus on the targeted removal of ions from water. ED and capacitive deionization (CDI) are two technologies that have successfully been brought to industrial scale.<sup>44</sup> During CDI, water flows through pairs of narrowly spaced electrodes. Upon application of an electric field, the electrodes act as a charged, double-layer capacitor, and dissolved ions adsorb onto the electrode material. As more and more ions coordinate to the charged double-layer capacitor, a point of zero charge will eventually be reached. This acts as the driving factor in deionization ability of the electrodes in varying salinity environments. The result is an order of magnitude theoretical differential charge efficiency decrease when moving from brine to seawater solutions.<sup>66</sup> As can be seen Figure 9, CDI may be a more energy-efficient purification technology for brackish waters than, for example, RO. Even at very low salinities, RO requires a baseline amount of energy to establish what is called "membrane pressure," i.e., the baseline amount of pressure required to push pure water through the pores of the membrane. Electrode-based processes such as ED or CDI do not suffer from this predicament, outperforming RO in a low-salinity regime.

Membrane-assisted capacitive deionization (M-CDI) is a more energy-efficient version of traditional CDI. The only substantial difference is the implementation of ion-specific membranes to provide charge asymmetry and prevent ion ping-pong during regeneration. Regeneration proceeds similarly to traditional CDI, and the electric field is switched off or reversed to expel desorbed ions from the electrode surface and into an effluent stream between membrane and electrode. Since this technology also relies on membranes, fouling is again a problem.

Ion exchange resins (IERs) are another material commonly used for ion removal. IERs comprise polymer matrices that can be functionalized to induce the preferential binding to specific ionic species. These materials are able to draw charged species out of solution by exchanging hydrogen (or hydroxyl) ions readily present in the polymeric matrix.<sup>45</sup> This enables specific absorption of ions of various size, charge,



Figure 9. The Energy Necessary to Implement RO and CDI Techniques as a Function of the Respective Salinity of the Water Being Treated Figure adapted from Oren.<sup>66</sup>

and chemical moiety. IERs are used until saturation, then regenerated chemically for reuse. However, the efficiency of IERs declines with each regeneration, so must eventually be discarded after several cycles; extending the lifetime of IERs remains a challenge. While IERs are highly effective for removing ions from solution, the regular use of harsh chemicals for regeneration and the safe disposal of spent resins are difficult issues that IER must still confront.<sup>67</sup>

### The Dirty Truth: A Call to Advance the Science of Fouling and Scaling and Altering Our Perceptions Surrounding Water Use and Reuse

The WEN must be understood in context relative to other technologies that have made the important coordinated steps from lab-scale R&D to commercialization successfully, such as photovoltaics. The future of WEN is colossal—no less than the energy and water security of our species is at stake—and screams for commensurate support. However, while there are hundreds of research groups in the world actively and consistently funded to study the science of photovoltaics for 10+ years, there are probably no more than 20–30 such groups in the R&D aspects of the WEN. We are arguably at a crossroads where further devotion to refining the engineering aspects of how water is treated and produced now will only yield asymptotic advances in water and energy security. Now is the time to revisit the core assumptions and methodologies in light of new scientific advances and develop an aggressive R&D plan to test and implement these.

The ultimate dream of WEN soberly realizes the growing impacts of climate change and population expansion and accommodates these growing energetic and caloric needs. There should be consensus that commitment to a sensible water future is a top priority. There is still time to realize a future where it costs little to prudently produce and use water close to the point of use, and what wastewater is created can be smoothly re-introduced into the water cycle, more pristine than when it

was extracted. However, while that is a distant utopia, it is a visible one, and we must build bridges to get there. At present, many of the foundational technologies for desalination are operational to some extent, although most operate far from ultimate thermodynamic limits. There are, however, several other prominent areas where no solutions are really on the horizon. Massive inefficiencies surround the prosaic aspects of transporting water, banking and storing water, preventing evaporation loss, and preparing water for reuse.

Whether one is carrying out conventional treatment or desalination of fresh water, seawater, or brackish water, membranes play a significant role. They are becoming ubiquitous at all stages of water treatment and purification at both municipal and industrial levels as membranes offer less energy intensive separations than comparable thermal methods. They are the current technology that most closely approximates a magic box where water from any source can enter, pass through, and emerge on the other side separated into streams of potable water, usable ions and chemicals, and concentrated waste. However, membranes are not yet this "magic box" as they are crippled by problems with fouling. Membrane fouling is such a grave problem that the water must often be treated to some degree before it can even undergo a separations process to produce pure water. This is referred to as pretreatment, and analogous to washing your dishes before putting them in your dishwasher. Thus, pretreatment, and the science of fouling more generally, is one of the most underserved problems in WEN currently.

The science of fouling is immature, but some basics are clear. Fouling arises from the undesirable interaction between membrane surfaces and numerous foulants, and this ultimately impairs the performance of membrane technology by reducing water permeation flux, deteriorating separation efficiency, increasing energy consumption (operational costs), and damaging membranes. Membrane foulants can be classified by their intrinsic characteristics.<sup>68</sup> inorganic foulants, organic foulants, and biofoulants (Figure 7). Inorganic foulants mainly include inorganic scales, minerals, and colloidal inorganic matter. Organic foulants mainly include oils, grease, biomacromolecules, and natural organic matter. Biofoulants comprise various kinds of microorganisms followed thereafter by their growth and multiplication. Compared with organic fouling and biofouling, the mitigation strategies for inorganic fouling are often focused on the pretreatment of feed water or optimization of operational conditions.

Many fouling mechanisms are, at root, adhesive processes by which water-borne organisms and minerals grow or precipitate onto the active membrane layer, compromising membrane permeability and selectivity, and increasing energy consumption. While the macroscopic aspects of fouling are well known, the microscopic mechanisms and atomic details of scaling and fouling mechanisms are poorly understood and are often counterintuitive. To give an example, it may seem logical that increasing flow speeds would shear off adhering bacteria and other fouling related species; however, this is not the case. Instead increasing shear flow induces thinner but more resilient and less penetrable fouling layers. In general, this is very challenging to solve due to the fact that there are bacteria and minerals present even in potable water, and how they interact with one another introduces additional variables.

Amid all this complexity, two principal antifouling approaches, passive and active, have been developed to mitigate membrane fouling. Passive antifouling strategies rely on suppressing the adsorption or settlement of foulants from attaching onto the

membrane surface to weaken the foulant-membrane surface interactions without affecting the intrinsic features of the foulants. Active strategies target eliminating proliferative fouling by destruction of the chemical structure and inactivation of the cells. Passive antifouling can be categorized into fouling-resistant and fouling-release mechanisms. The fouling-resistant strategies aim to prevent the foulants from arriving at the surface by steric repulsion effects and formation of a hydration layer.<sup>69</sup> Freeman and co-workers have conducted seminal research on this front using a series of polyethylene glycol-based graft polymer-coated membranes exhibiting reduced fouling.

using a series of polyethylene glycol-based graft polymer-coated membranes exhibiting reduced fouling properties.<sup>70,71</sup> The fouling-release defense mechanism identified is responsible for minimizing the interactions between foulants and surfaces and operates by constructing a low surface energy barrier layer on the surfaces. Recently, construction of amphiphilic membrane surfaces consisting of optimal hydrophilic fouling-resistant domains and hydrophobic moieties with fouling domains has shown promise.<sup>72,73</sup> Passive antifouling strategies have exhibited broad applicability and great popularity against various kinds of foulants, however, the inefficiency of these strategies against proliferative biofoulants promotes the development of active strategies (i.e., antimicrobial agents) for antifouling membranes. Moreover, this is just a vignette of the state of the art in biofouling. There is no guarantee that a membrane that resists biofouling will, for example, show any resistance against inorganic foulants.

Beyond water desalination, the challenge of properly managing the wastewater of desalination (e.g., concentrated brine) and other treatment processes is a constant concern. Despite increasing oversight on the ecological impact of waste (e.g., brine) discharge,<sup>6</sup> it is inevitable that any imperfectly treated water returned to the natural environment will cause some level of pollution (e.g., increased salinization in the case of brine discharge) with deleterious effects on local ecosystems and public health. One burgeoning concept that acknowledges both our societal needs and also our role as stewards of the environment is zero liquid discharge (ZLD). ZLD is an advanced multi-step water treatment process in which all wastewater is purified and recycled leaving, as the name implies, no discharge at the end of a treatment cycle (aside from minimal solid waste). This is a powerful water management strategy to both maximize water recovery while also minimizing the liquid waste from a power generation cycle, resulting in a closed cycle of water treatment and reuse.<sup>53</sup> This is an ambitious target, and a comprehensive suite of treatment strategies at every length scale is needed to realize this goal. From the micro to the macro, ZLD involves UF, RO, ED, and nearly everything discussed in the article thus far for water treatment. At the macro end, evaporators, brine concentrators, and crystallizers are used to approach full recovery of water. Brine concentrators are able to reach a salinity of 25 wt % with water recovery of 90%-98%. The remaining water in concentrated brines produced by brine concentrators is further recovered by the brine crystallizers, which are basically thermal-driven distillation units with high energy demands. In the final tally, while ZLD ideally results in only solid waste, water withdrawals are still large and energy use increases to meet these stringent targets. There are no free lunches in the WEN as of today.

Still, opportunities remain for innovation within the framework of ZLD. FO is capable of treating high-salinity feed streams with exit concentrations >20 wt %, thus it can be used as a brine concentrator after the RO stage. Compared with distillation processes, use of FO as a brine concentrator is compelling because the phase transitions occur at moderate temperatures (e.g.,  $30^{\circ}C-60^{\circ}C$  for LCST), and are therefore less energy consumptive relative to vaporization of water. Membrane distillation (MD) is another potential option for brine concentration which requires slightly lower temperatures (feed streams are heated to  $60^{\circ}C-90^{\circ}C$ ), and the water

vapor flux is driven by the partial vapor pressure difference across a hydrophobic, microporous membrane to the colder permeate side. However, while it can treat high-salinity feed waters that cannot be desalinated by RO, MD still requires a vaporization phase change to operate. For both MD and FO, their capability of harnessing low-grade energy or renewable energy could significantly reduce the prime energy demand, operation cost, and greenhouse gas footprint of ZLD.

We are perched upon steep slopes of demand curves for water and energy that both bend upward in time as our world expands and develops. Profligate, annually expanding consumption of water and energy, with disregard for the consequences, does not lead to a viable future. It is also important to realize that solutions viable for one country may not be directly translatable to other locations due to a multitude of differences, such as environment, resources, infrastructure, and government structure. It is imperative that we, in our dual roles as citizens and scientists, work across traditional disciplinary boundaries and institutional structures to promote and develop innovations in the use and treatment of water and energy at every scale. Some nations have made this leap to a more sustainable low-water, moderate-energy future,<sup>74</sup> but there is no simple loosening of the Gordian knot that is the WEN. We must innovate our way out.

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