Energy and Water Factual Status Document

Resource Document for the Workshop
on Basic Research Needs for

Energy and Water

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Introduction

Importance of water

Water is arguably the most important material on earth. Living things rely on water to survive; it is also the hidden backbone of essentially all economic activity. Figure 1 reveals the diverse ways in which we use water. Whereas our daily interactions with water, such as drinking, bathing, and sanitation, are perhaps the most visible, the vast majority of water withdrawals are for other purposes. Largest among these is cooling associated with the generation of electricity in thermoelectric power plants, whether they be coal, natural gas, nuclear, or geothermal, representing nearly half of all withdrawals. Water and energy resources are deeply intertwined. Not only does meeting energy needs require vast amounts of water for fuel production, mining, hydro-electricity, and the aforementioned cooling in power plants, but also energy is needed to pump, treat, and distribute water as well as for collection, treatment, and discharge of wastewater. This interrelationship is often referred to as the "energy-water nexus."

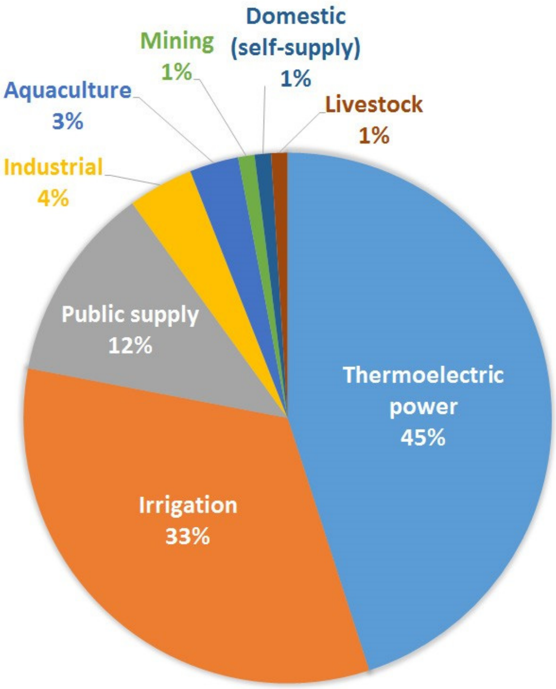

Figure 1. Water withdrawals by sector in the U.S. Data from USGS.gov, 2010.

Energy use for water can vary dramatically from one region to another. The specific combination of factors, such as water source (surface vs. aquifer; fresh vs. saline), intended end use, climate, distribution distance and topography, and wastewater treatment requirements, is unique to any given location. Most energy consumed for water is in the form of electricity, estimated at anywhere from 4% to 13% of the nation's electricity generation, although such consumption is far from homogeneous around the country. California, for example, uses nearly 20% of the state's electricity for water-related purposes. Improvements in water use efficiency translate directly to energy savings, and the reverse is true as well. Moreover, saving water mitigates carbon emissions by reducing energy otherwise required to transport and treat water.

While power generation is the largest water *withdrawal* sector, the largest water *consumption* sector is agriculture. This is because most of the cooling water in power plants is returned to waterways after use. Water applied to farmland, in contrast, is largely lost to evaporation and evapotranspiration. Irrigation is essential to supplement natural precipitation on crops. Throughout human history, overall food production has been a determining factor in population and prosperity. Countries with the largest populations (China, India, and the U.S.) are also those with the largest water withdrawals for agriculture. As with energy, aspects of the interrelation between water and food production are reciprocal. Not only is a lot of water used for irrigation; agricultural activity also has a large impact on water quality. Fertilizer applied to crops contributes nutrients to runoff from farmland, which can pollute drinking water supplies and lead to algae blooms and eutrophication of water bodies. Other food production also relies heavily on water. Direct water use in the aquaculture and livestock industries, for example, represents large absolute amounts, although they are comparatively small relative to agriculture. The food and beverage industry is also a major water consumer.

The third largest sector for water use is public supply, representing about 12% of overall withdrawals. This is the water that comes to homes and businesses, provided by city, county, and private water utilities. Within and around the home, water has many applications (Figure 2). In drier climates, irrigation of yards and landscaping can dominate consumption; this particular application, however, contributes a smaller fraction to wastewater streams. Wastewater produced in homes and businesses is among the most challenging to treat, given the diverse range of contaminants introduced during use.

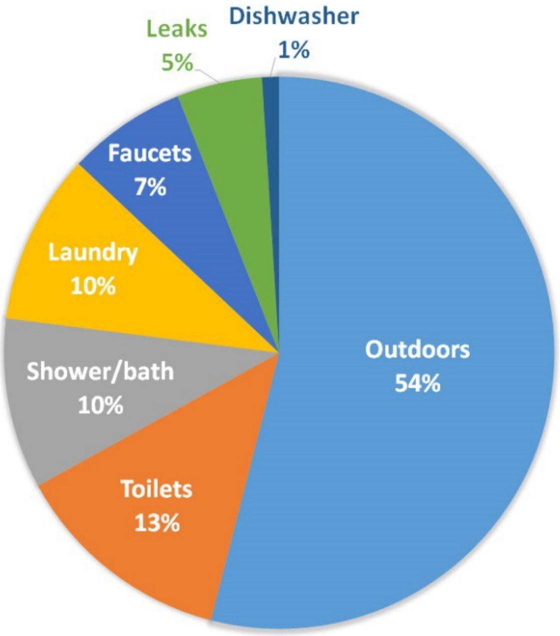

Figure 2. Example breakdown of water use in the home.

Although it represents a small fraction of overall water use, industrial activity would be impossible were it not for water. All goods manufactured today involve water during at least some stages of production. A given product undergoes many steps of manufacturing, from extraction of raw materials through numerous processing and transportation stages. Each of these stages carries with it a direct water footprint, whether it is washing, cooling, or actual incorporation of water in the product. Some industrial consumers rely on public supply, but many large consumers are self-supplied in order to lower costs and control water quality to meet their individual needs.

The sectors described above constitute direct uses of water, but it is also important to consider how these goods and services are folded into subsequent activity, embodying water indirectly. The term often applied to this concept is “virtual water,” which is further classified as blue, green, or gray. Blue water is extracted from surface or groundwater sources; green water is natural precipitation in soil and plants; and gray water refers to the impact on waterways through pollution associated with the processes under consideration. Each product will have a total water footprint with unique contributions of blue, green, and gray footprints. Direct water use in one stage of production is incorporated into the indirect, virtual water footprint of subsequent stages. When such an analysis is performed comprehensively, the final tally offers an assessment of the efficiency and sustainability of a given product. Such information is critical in deciding how best to use limited global resources.

Water crisis

Water’s centrality to the health and prosperity of people and our surrounding ecosystem heightens growing concerns regarding looming water crises. U.S. water systems were once the envy of the world, but infrastructure is aging. Waterways are increasingly polluted, as recently highlighted by the drinking water crisis in Flint, Michigan, the wastewater spill from Gold King Mine in Colorado, and the Elk River chemical spill in West Virginia. Recent developments have also brought attention to the connections between water and energy infrastructure. Harsh drought in 2012 constrained the operation of power plants and other energy production undertakings. Devastating weather events, such as Hurricanes Katrina, Sandy, and Matthew, revealed the vulnerability of vital water infrastructure to loss of power. Hydraulic fracturing and horizontal drilling have propelled domestic unconventional oil and gas development while at the same time underscoring new challenges in the relationship between energy and water resources.

Overall population growth, both within the U.S. and worldwide, is driving up demand for water. Regional migration trends indicate population in arid areas such as the Southwest and concentration of populations in urban centers will continue to increase [1]. Economic development further accelerates demand for water, projected to be 55% higher globally by the year 2050 [2]. Exacerbating increasing demand are new threats to water supplies, which are already stretched to their limit in many regions. Foremost among the supply threats is climate disruption, which is affecting precipitation and temperature patterns across the U.S. [3], melting glaciers, and raising sea levels to the point of saltwater intrusion into coastal fresh aquifers. Other groundwater resources, a major source for leading agricultural centers, are being unsustainably exploited in many instances. Figure 3 summarizes these factors.

Figure 3. Factors contributing to water crisis both domestically and worldwide.

Water's essentiality, coupled with the impending supply-demand mismatch, suggests an increasing risk for conflict. Human history is rife with connections between social instability and water scarcity. Recent drought-induced food shortages contributed to current unrest in the Middle East and North Africa. Central and southern Asia provide numerous recent examples of violence surrounding water challenges. Future national security for the U.S. will depend upon managing water security worldwide. About one-third of the global population currently lacks access to basic water and wastewater services, contributing to millions of preventable illnesses and deaths each year. Drinkable water can be viewed as a fundamental right for all people, a sentiment codified in the national constitutions of more than a dozen countries around the world.

These trends present daunting challenges, but they also constitute opportunities for new strategies to address water-energy issues with impact at both the national and global scale.

Strategies to address water challenges

The easiest and lowest-cost means to address water crises is to reduce the amount of water used for particular tasks through improved efficiency or implementation of alternative, less water-intensive technologies. In a residential context, simple options range from installing low-flow fixtures to fixing leaks to planting native species outdoors that require little or no watering. In a manufacturing setting, eliminating wasteful processes, such as continual spray devices on stop-start production lines or using mechanical cleaning rather than rinsing, can have large impacts. Efficient agricultural practices, such as drip irrigation, can dramatically cut demand for water. Finally, any efforts that reduce energy consumption will also have water-saving benefits.

A parallel strategy is to identify new, non-traditional sources of water to expand supply. A prime example would be saline sources, such as seawater or brackish groundwater, which have been tapped only sparingly to date. Often, upgrading the quality of such sources to meet the needs of a given application requires substantial amounts of energy using current technologies. As water scarcity heightens, more difficult sources become attractive targets for utilization. Innovation in water treatment technologies has potential to revolutionize this undertaking.

The final approach is also, in a sense, identifying new water sources, namely, water reuse and recycling. The simplest form of reuse is to train together several applications for water in order of decreasing water-quality needs. Potable water can be used for one purpose, rendering it less clean but of sufficient quality for a subsequent process, and then another, before proceeding to a treatment facility. Mother Nature has performed the task of recycling for eons via the water cycle. The goal here is to short-circuit that process, transforming gray water back into a stream that is fit for use. Treatment of urban wastewater to bring it up to drinking water standards has been successfully demonstrated. In the U.S., the Orange County Water District cleans sewage and provides it for indirect potable reuse by injection into an aquifer. This plant uses microfiltration (to remove solids, oils, and some bacteria) followed by reverse osmosis (to eliminate viruses and many micro-pollutants). Finally, the water is treated with ultraviolet (UV) light to degrade remaining organic compounds. Direct potable reuse systems operate successfully in countries such as Singapore, and numerous additional systems are at various stages of planning and development around the world.

Understanding water sources and use

Agriculture water and nutrients

The productivity of agriculture is the backbone of society and the primary driver in population growth and advancing civilization. Water availability is often the limiting factor in crop production. While irrigation accounts for 33% of freshwater withdrawals in the U.S., virtually none of it is returned to its source. Irrigation accounts for over 80% of water consumption [4].

The U.S. Department of Agriculture (USDA) has documented the demand for water for a large range of crops and food. In addition, there is extensive documentation of water sources including rain, irrigation from surface waters, and irrigation from groundwater (e.g., Figure 4). While rain-fed crops cause the least stress to other uses of water, rain-fed crop productivity is subject to regional and seasonal weather patterns. Animal production is dependent on grain crops or grass, which correlates meat production to weather variability. Livestock demand for water rises during heat and drought, when water and crops are most stressed.

Agriculture experiences large variability in water availability, both temporal and spatial (Figure 5) [5, 6]. In the short term, agricultural productivity can vary by orders of magnitude based on seasonal water availability. In the long term, water scarcity can disrupt society: Advanced ancient societies in Meso America and the Middle East collapsed when agricultural productivity failed because of climate-induced water scarcity. Extended drought in the “dust belt” in the 1930s caused a collapse of the cotton industry and exacerbated the Depression.

In the 21st century, the U.S. is starting to experience similar impacts from water availability. In the summer of 2012, a large heat wave across the Midwest decreased overall grain production by 25% [7]. Before the advent of advanced seed technology a generation ago, a similar drought could have caused a 90% reduction in productivity. Over the past decade, the West has experienced extended droughts. California is the primary producer of fruits, vegetables, and nuts. The industry has “weathered the storm” by using an increasingly large supply of surface water and overdrawing from deeper groundwater sources. One of the primary factors driving the water shortages is the long-term loss of snow-melt water from the Sierra Nevada. Over the past two years, the Southeast of the U.S. has been experiencing an extended drought. Impacts are just emerging in late 2016.

Nutrient loading in water is a primary driver of agricultural productivity, a critical cost element to farmers, and potentially a critical factor in agriculture’s impact on the environment. There are more than 15 essential chemical elements for growth of plants. Hydrogen, carbon, and oxygen,

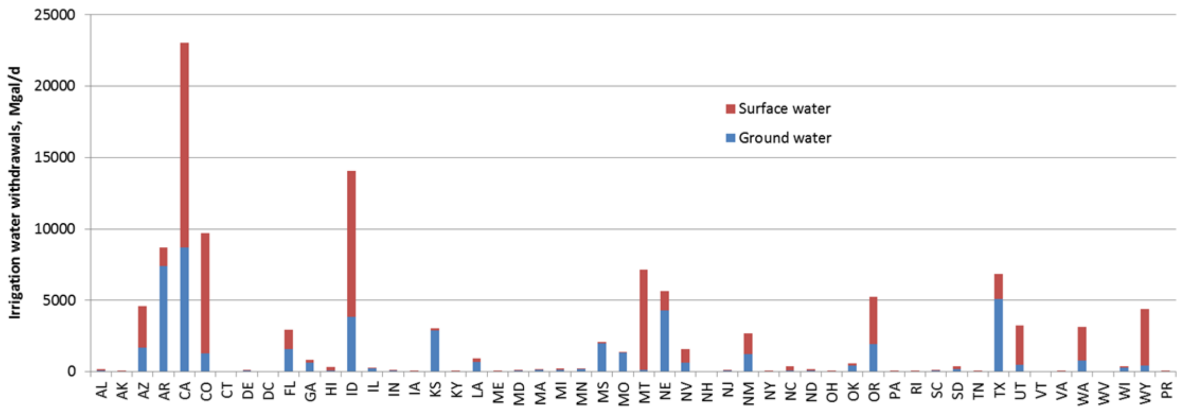

Figure 4. Surface and groundwater use for irrigation in agriculture in the U.S., broken down by state [4].

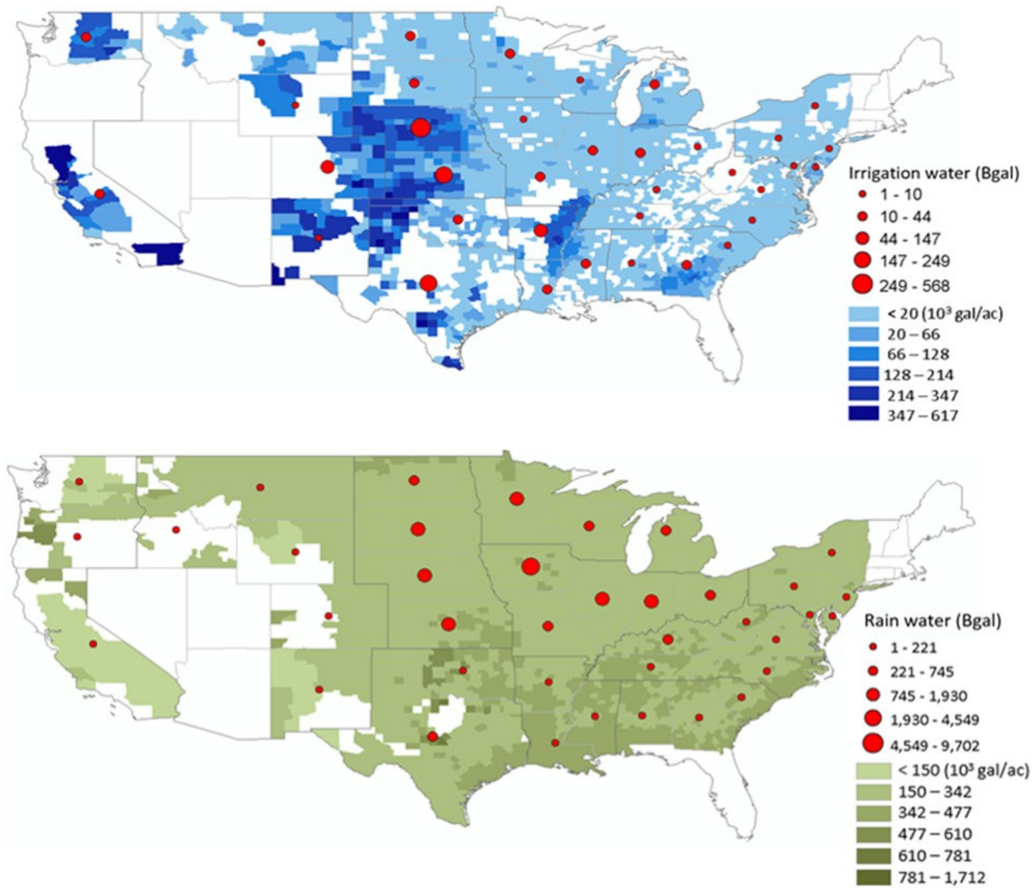

Figure 5. Blue and green water use representing 40% of current major crops (corn and soybeans) in the U.S. in 2015 [5, 6].

acquired from water and air, constitute the bulk of plant dry matter, but these are not considered "nutrients." Nutrients such as nitrogen, phosphorus, potassium, calcium, magnesium, sulfur, iron, manganese, zinc, copper, boron, molybdenum, and chlorine come from the soil. Sodium, silicon, and nickel are essential elements for certain plant species and benefit others. Legumes need cobalt for nitrogen fixation. All essential nutrients are critical for plant growth, but there is large variation in the quantities required. Crops typically need 50–150 lb/acre of the primary macronutrients nitrogen, phosphorous, and potassium. Secondary macronutrients, such as calcium, magnesium, and sulfur, are required in amounts of tens of pounds per acre. Micronutrient requirements, in contrast, are generally <1 lb/acre. The fate and transport of nutrients is of critical importance.

The water-nutrient system interfaces with divergent solid surfaces, including soil, minerals, and living matter, and with agriculture pipes, valves, and other devices. Nature uses water and nutrients at its own rate and optimizes around survival of genes into the next generation. For agriculture, we choose to optimize around productivity and use of resources.

Effective nutrient management aims to provide adequate plant nutrients to optimize growth and quality while also limiting nutrient movement away from the plant-root zone and into the off-farm environment. Biological processes control nutrient cycling, and, by extension, management of crop and livestock systems. Soil organic matter and biological nutrient flow management is challenging, because organic nutrient sources vary in composition, release nutrients in myriad ways, and, with regard to nutrient cycling, are influenced differently by surrounding environmental conditions. Chemical processes in soil control solution pH, binding to soil particle surfaces, mineral solubility, and cation exchange. When considered together with biological processes, complexity increases because inorganic nutrients are rapidly incorporated into and released from biological cycles. On most farms, inorganic fertilizer will be the largest nutrient input. Inorganic fertilizers can enable more efficient use of other available resources, such as water and sunlight, by excluding nutrient supply as a limiting factor in crop yield.

Better immobilization, uptake, and use of water and nutrients would enhance the efficiency of agriculture. These changes could advance the next generation of agriculture by improving the sustainable use of water while reducing net energy use and life-cycle greenhouse gas emissions. In the long term, improvements in water-nutrient interactions could provide a backbone for reducing the impact of agriculture on the environment. A notable example would be the hypoxia zone in the Gulf of Mexico that arises from nutrients arriving from the Mississippi River via runoff on Midwest farms.

Sensing

Water sensing has a wide charter, which includes applications related to geographical management, such as surface (lakes, rivers, wetlands, ice caps), below surface (agriculture, aquifers) and deep waters, as well as human use needs, such as those related to water purification and urban water management. Almost all water sensing can be categorized into two types: 1) sensing of chemical content and composition or 2) measurement of flow and volume. Each of these types can span a diverse target range of applications. Flow sensors, for instance, are of value for urban applications, such as city water leak detection[8], and for the measurement of aquifer charging rates in the vadose zones [9]. The measurement of chemical content, as another example, can apply to measuring nitrogen dissolved in the water contained in soil (for agriculture), carbon emissions given off from the melting of ice caps (for environmental management), or arsenic in drinking water [10]. Measurement of volume applies in the characterization of changes in water bodies (such as lakes and reservoirs) over time and of the levels of groundwater. There are also varied demands upon the cost, performance, size, and detectivity levels of sensing technologies. Levels of *E. coli* in developed nations, for instance, are limited to maximum permissible limits of 400 colony-forming units (CFUs) per 100 ml of water. Detection techniques need to be sophisticated enough to measure such low levels, often translating into increased cost. From a different perspective, for rivers in developing nations, such as the Ganga in India, *E. coli* numbers have been measured in the range of one million per 100 ml [11], a figure that can accommodate different—and cheaper—techniques. Figures 6 and 7 provide overviews of sensing technologies.

Techniques for water sensing fall into two categories: 1) remote techniques that are based on electromagnetic radiation, such as satellite and aerial imagery or dielectric response measurements, and 2) those that are reliant on proximity- and/or contact-based evaluation. In the first category, satellite hyperspectral imagery is increasingly popular, and data are obtainable—in many cases without charge—from any region of the world and over a range of wavelengths from the thermal infrared bands to the visible. Such data allow for detection and geographical distribution mapping of color- and reflectance-sensitive parameters, such as chlorophyll content, algae blooms, and total suspended solids. Microwave radar techniques are used for measuring water levels in large water bodies. In the second category, there are several major types of measurements: electrochemical or electrical techniques; optical techniques (increasingly using semiconductor light emitters and detectors); chemical reaction- and assay-based techniques; and ultrasonic- or pressure-based sensing techniques for measuring levels and flow. There are often combinations, such as chemical functionalization of surfaces to selectively attract certain ions to the gate of a transistor whose concentration is then measured by the current

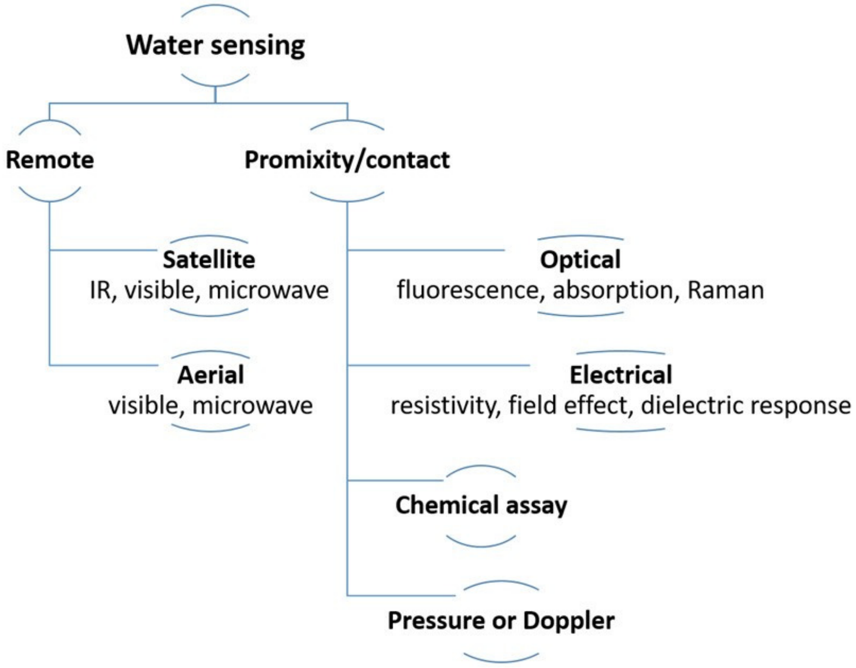

Figure 6. Methodologies for water sensing according to location of the sensor with respect to the target.

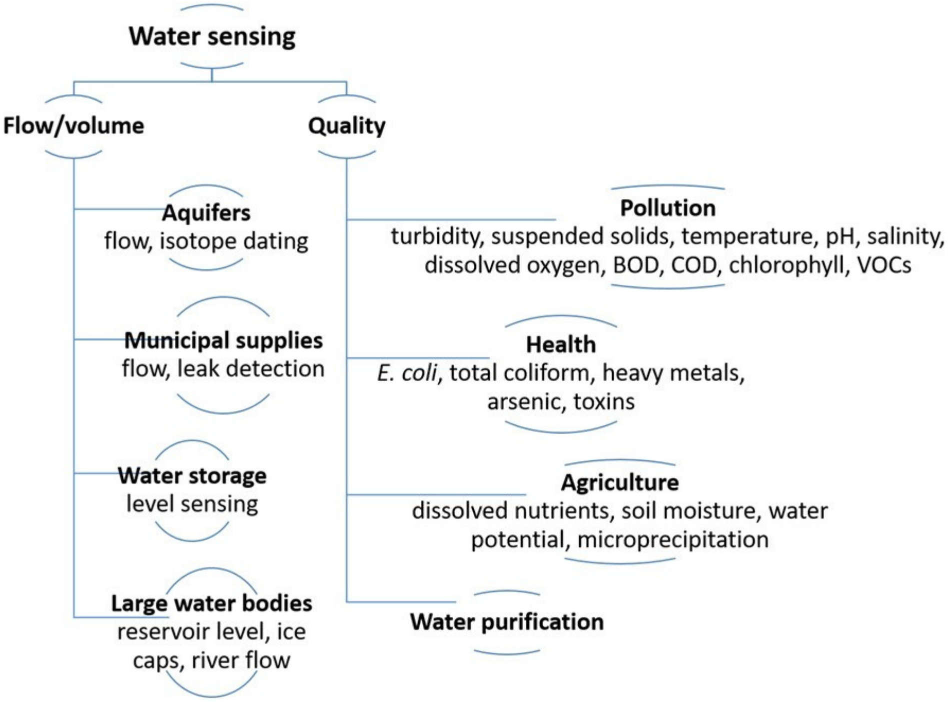

Figure 7. Methodologies for water sensing according to type of information collected.

modulation in the transistor due to the charged ion species (ion-sensitive field-effect transistor) [12].

Satellite imagery options have been rapidly increasing, with the advent of new satellites and expanded wavelength bands for analysis. They are typically useful for monitoring large bodies of water at resolutions from tens of meters to kilometers, and some representative examples include monitoring chlorophyll, algae blooms, sub-surface moisture content, and melting of ice caps. Sensing technologies have been focused on photon detectors and models for accurate interpretation of the data.

A list of important sensing elements and current techniques in use for proximal sensors is shown in Table 1. The key challenges in sensing technologies are cost, sensitivity and specificity, field usability, and automated in-line measurements. Almost all of the techniques shown in the table have a more accurate chemical assay-based established method, along with emerging rapid in-line techniques that may not yet be as accurate or proven or cost effective. Measurement of biochemical oxygen demand in water (BOD), a widely used measure for monitoring water pollution and judging the effectiveness of sewage

Table 1. A list of typical water-sensing technologies.

Sensing	Technique	Applications
turbidity	optical light scattering	environment, health
total suspended solids	sediment weight, acoustic Doppler backscatter	environment, health
pH	electrochemical	
dissolved oxygen	electrochemical; optical (dye luminescence quenching)	environment, health, agriculture
biochemical oxygen demand (BOD)	5-day incubation-based test	health, environment
chemical oxygen demand (COD)	Chemical tests; UV-Vis absorption spectroscopy (200–400 nm)	health, environment
salinity	electrical conductivity	environment
heavy metals	X-ray fluorescence (XRF), atomic absorption spectroscopy, mass spectroscopy	health
fecal coliform	most probable number, membrane filter tests: 1- to 5-day incubation, relies on inoculating media	health, environment
dissolved nitrates	chemical tests	agriculture, environment
harmful algal blooms	satellite spectral signatures, enzyme-based assays	environment
water level/water flow	ultrasonic pulsed Doppler, pressure, microwave radar	agriculture, aquifers, environment, water management
fluoride	ion selective electrodes, fluorescence & colorimetry, nuclear magnetic resonance	health
arsenic	colorimetry, portable XRF	health
hydrocarbons	extraction additives, infrared, UV absorption, fluorescence, light scattering	health

treatment plants, is a classic example. The U.S. Environmental Protection Agency (EPA)-approved test for BOD is a 5-day test during which bacteria oxidize organic matter using dissolved oxygen in the water samples. Chemical analysis of the dissolved oxygen consumed gives an indication of the amount of organic matter in the water. Newer tests based upon respirometry have been developed, in which the sample water is mixed with controlled activated sludge and air; the test measures the amount of oxygen consumed in the reactor cascade. Testing times can be a few minutes, but equipment costs are high, and the tests are not yet widely accepted. A second example is *E. coli* testing, where the accepted test again is one where the *E. coli* bacteria are cultured over a period of time and the number of CFUs counted, resulting in—again—a time-consuming, labor-intensive process. Faster (20-hour), semi-quantitative tests based upon *E. coli*-specific enzymatic reactions to break down nutrients that change color (Colilert) are now EPA-approved but are expensive. Selective biofluorescent indicators that detect the reaction of *E. coli* enzymes with specific substrates have resulted in even shorter (8-hour) test times and more compact footprints, but these tests are considered less reliable. These are just two examples to indicate what may be considered to be a general trend in water sensing, towards quicker tests with smaller footprints, but cost and reliability remain a challenge.

Recent developments in nanotechnology and materials science are helping meet these challenges. Inexpensive semiconductor optoelectronics (light-emitting diodes, lasers, detectors) have emerged in the UV to infrared (IR) bands. Highly sensitive field effect transistors will improve gate-driven electrical sensing. Advances in nanophotonics for plasmonic and Purcell effects can enhance detection. Functionalization chemistry and nanomaterials are enabling the use of selective adherence. Optical discriminatory techniques, such as Förster resonance energy transfer and other fluorescent techniques, are enabling a new generation of optoelectronic sensor devices.

Water and geologic systems

A critical aspect of water-energy systems is the need to manage the deleterious impacts of energy use on water resources, in terms of both water quality and extent. The hydrosphere includes approximately 1.3 billion cubic meters of water, of which less than 3% is fresh water. Subsurface energy operations have the potential to deplete or degrade local freshwater resources. Water needs for all oil and gas (O&G) extraction are mostly supplied by surface waters (such as rivers and lakes), but groundwater is used when these are not available. Some of the roles of water may be augmented by additives or replaced by non-aqueous alternatives.

Water geochemistry

Earth's near-surface region is a highly complex multiphase system with rock formations in contact with fluids (including aqueous phases, hydrocarbon liquids) and gas (Figure 8). Reactions of the aqueous fluids with the rock matrix include adsorption of dissolved species, mineral growth and precipitation on existing grains, and mineral

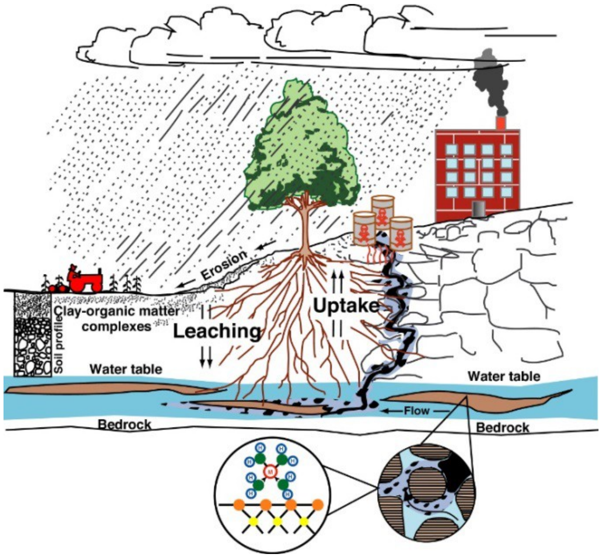

Figure 8. Schematic showing how elemental transport of nutrients and toxins in Earth's near-surface region is ultimately controlled by the porosity of the rock matrix and interactions of species with individual mineral–water interfaces. From the Advanced Photon Source (Argonne National Laboratory).

dissolution and dissolution/reprecipitation reactions that can modify the composition of existing mineral grains. These reactions effectively control the transport of both nutrients needed to support life and toxins (either natural or anthropogenic). Thus, reactions between the solid and fluid phases effectively control the transport and cycling of elements near Earth's surface.

The interaction of dissolved metals with rock surfaces is controlled by the nature, charge and distribution of surface functional groups that are present at a mineral surface. Solid-water interfaces are sites for adsorption reactions with dissolved species driven by a specific interaction with a site on the surface, displacing interfacial water. In particular, mineral surfaces typically exhibit a surface charge, which is often controlled by the water pH. The electrostatic fields associated with the charged surface are screened by ions in the electrolyte solution, leading to a surface excess of the charge-compensating ions indicating the formation of an "electrical double layer." More complex reactions occur when the solid and water phases are not in equilibrium, such as occurs with dissolution of the mineral matrix (releasing metal ions such as Ca^{2+} and Mg^{2+}) as well as precipitation of new phases. Consequently, relevant reactions, mechanisms, and rates would be components of validated predictions of field-scale behavior over extended time periods.

Disposition of energy byproducts in geological repositories

The use of geological repositories for energy byproducts (e.g., CO_2 from burning of fossil fuels, spent fuel from nuclear energy) represents a longer-term impact of energy use on water sources. Elemental transport in the geosphere is enabled by the flow of fluids that respond to gradients in, e.g., composition, pressure, or stress. As such, the use of geological repositories relies, ultimately, on a robust and validated understanding of the structure and reactivity of the geological subsurface to maximize the repository effectiveness and minimize secondary deleterious impacts. The introduction of energy byproducts into the geosphere as a repository necessarily creates additional disequilibria that need to be managed.

Subsurface CO_2 storage. Geologic carbon sequestration (GCS) is considered by the Intergovernmental Panel on Climate Change to be a critical approach to reducing the accumulation of anthropogenic carbon dioxide (CO_2) in the atmosphere during the transition to a low-carbon energy economy [13]. The water and energy costs for separation and transportation are given elsewhere in this document. For those costs to be net beneficial, the feasibility of indefinite sequestration of megatons of carbon annually must be ensured. An important issue concerns the trapping of CO_2 by dissolution, capillary forces, and impermeable cap rock long enough for mineralization reactions to occur [14]. Heterogeneous and reactive mineralogy may be beneficial. In a site in west Texas where CO_2 was injected over a period of 35 years for the purpose of enhanced oil recovery, fractures sealed with calcite can be observed in well casing cement [15]. During CO_2 injection in the Columbia River basalts, it appears that mineral precipitation begins immediately after injection, to the extent that pumps can become clogged [16]. Pre-mixing of CO_2 and water in the CarbFIX project led to rapid mineralization [17], but the water requirements of this approach would be extreme.

Disposal of spent nuclear fuel. The properties of the geological matrix will determine the robustness of sequestration of high-level radioactive materials. Issues related to contaminant transport would include reactions that lead to adsorption and precipitation reactions of contaminants, as well as the impact of dissolution and reaction with existing minerals in the rock matrix. Another consideration is how the geological environment can effectively inhibit the transport of species once technical engineering barriers have failed. This is especially crucial for elements whose behavior in natural environments is poorly constrained owing to the lack of any historical precedent in the geological record (e.g., transuranics), especially under conditions where intense radiation fields may perturb the geochemical system, such as through the presence of radicals in the aqueous phase and through changes to the morphology and mineralogy of the rock matrix.

Energy use for water extraction, transportation, and storage

The energy used for pumping groundwater and for transporting fresh water from all sources is considerable. In California, for example, the State Water Project (SWP) transports water from Northern Californian rivers to the more populous Southern California. The SWP, one of three inter-basin transfer systems in California, accounts for 2–3% of all electricity consumed in the state. Direct pumping of groundwater, which has increased dramatically in recent years as a result of California's ongoing drought, is estimated to be a still larger energy burden for the state. In addition, overreliance on groundwater for domestic, agriculture, and industrial uses can have adverse consequences, including increased pumping and facility costs due to lowering of the water table, water quality degradation through saltwater intrusion, impacts on surface water systems, and damage to infrastructure due to subsidence.

Groundwater pumping and pipe flow. Energy is required for water pumping and transportation to lift fluids against the Earth's gravitational field and to counteract resistance to flow in aquifers, pipes, and aqueducts [18]. Groundwater extraction initiates complex hydrological, geochemical, mineralogical, and mechanical changes in subsurface systems. Unforeseen impacts upon aquifer permeability, often associated with clay-water interactions, can limit rates of recharge and further use. Compaction from groundwater pumping can also result in contamination as water is expelled from fine-grained units [19].

Groundwater banking and water reuse. The managed replenishment of groundwater and conjunctive groundwater-surface water use could provide a lower-cost alternative to the construction of dams or other infrastructure, and can limit these adverse consequences of groundwater depletion and reduce the reliance on surface water. Introduction of treated water or water otherwise non-native to the aquifer can stimulate a host of fluid-rock interactions that may impair or improve water quality.

Fluid transportation. Fluid transport through pipes continues to be the most energy-efficient method for long-distance fluid transport, and is considerably safer than train or truck shipping of flammable hydrocarbons.

Water use for fuel and energy extraction

A recent trend is the transition from conventional to non-conventional sources of fossil fuel and geothermal energy. These rapidly developing technologies involve the injection of fluids—almost exclusively aqueous fluids—into subsurface rock formations. There are acknowledged challenges for the optimization of these approaches that directly affect their productivity for energy, their water intensity, and their potential to adversely affect freshwater resources.

Oil and gas systems

Conventional O&G resources. Subsurface O&G reservoirs are pressurized by the weight of the overlying rock, and initial production is due to pressure-driven flow. Flushing a depleted oil reservoir with water (called "water flooding") is effective at extracting additional oil. Because oil and water are immiscible, this process occurs through the replacement of oil by water in reservoir pores. The efficiency is dictated by how completely water replaces oil, which can often be predicted (but not easily maximized) for porous aquifer rock, provided mineralogy and porosity are known, but which is not predictable for flow through fractures. Moreover, chemical aspects of the solutions can enhance production in ways that are poorly understood. For example, it is well-established that lowering the salinity to less than 5,000 ppm can increase oil recovery, but no consensus has been established as to the mechanism [20]. Species partitioning at interfaces will play an important role in dynamic wetting and flow processes in O&G and GCS reservoirs (Figure 9).

Enhanced oil recovery uses additional approaches to mobilize residual hydrocarbons through several mechanisms, such as the introduction of steam to decrease the viscosity of oil, or the injection of gas (such as CO_2) that both reduces viscosity and can dissolve some hydrocarbons.

Unconventional O&G resources. The U.S. shale gas revolution was enabled by advances in horizontal drilling (which allows large areas of shale seams to be accessed) and hydraulic fracturing (which stimulates methane transport out of the nanoporous matrix into fractures). Estimates of water use for hydraulic fracturing vary, but there is a clear trend of increasing use of fresh water for this industry (Figure 10) [21]. Hydraulic fracturing of one well typically requires between 7 and 19 million L of water [24]. Production has increased with more sophisticated drilling and completion technology, but geological factors have a larger impact on production than technological improvements, and only 5–10% of the oil in place is recovered [22].

Almost all fracturing fluids used currently are aqueous solutions that contain polymers, such as polysaccharides or polyacrylimide, to alter viscosity, a range of chemical additives to suppress microbial activity and other reservoir processes, and colloidal particles called proppants that prevent the induced fractures from closing once the initial pressure stimulation has ceased. The complex mixtures display features of non-Newtonian fluids [24]. Non-aqueous fluids, particularly supercritical CO_2 (sCO_2), have been used for enhanced oil extraction and have been considered for hydraulic fracturing. The low viscosity of sCO_2 is a problem for flow fracture initiation and proppant transport, but it can be increased by adding surfactants to create foams.

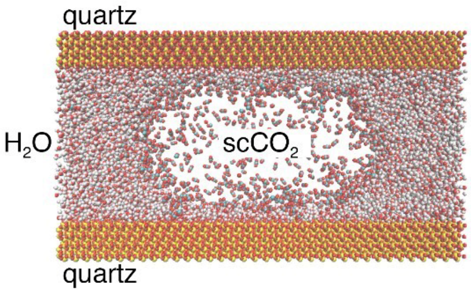

Figure 9. Molecular dynamics simulation of the interfacial tension in the quartz-brine-CO_2 system.

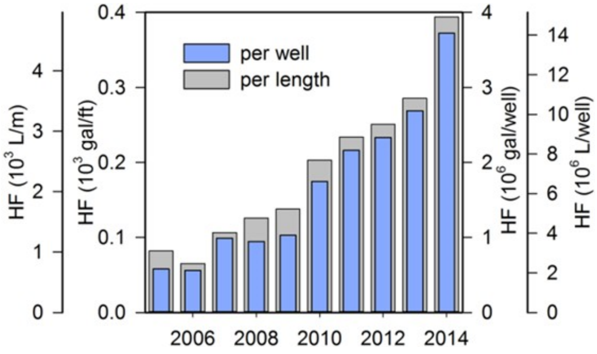

Figure 10. Mean water use for hydraulic fracturing (HF) in the Bakken formation, USA, ranging from 0.58×10^6 to 3.7×10^6 gal/well (2.2 to 14×10^6 L/well) (2005−2014) and mean water use/ft of lateral ranging from 82 to 394 gal/ft (1020 to 4890 L/m) (2005−2014). From Scanlon et al. 2016 [21]. Further permissions related to the material excerpted should be directed to the ACS.

Geothermal energy

Enhanced geothermal systems (EGS). Massive thermal energy reserves are present in all locations of the subsurface [25]. In rare locations of Earth's surface, access to geothermal energy is provided by water flowing through naturally fractured rock. In other locations, a combination of deep drilling, water injection, and hydraulic fracturing of hot dry rocks could allow access to geothermal energy. Drilling and fracturing at depth has been demonstrated, but the creation of such enhanced geothermal systems represents one of the most difficult subsurface operations [26]. Efforts are ongoing in creating a suitable fracture network, monitoring (i.e., imaging) changes in permeability, and managing flow of fluid and heat to optimize electricity generation, minimize water use, and maximize lifetime. The Frontier Observatory for Research in Geothermal Energy (FORGE) provides a facility to explore these issues (https://www.energy.gov/eere/geothermal/what-forge).

Control of fracture network permeability and fluid properties is critical to optimize heat extraction and to minimize water loss. New fluid pathways must penetrate a large rock volume through a closed system that does not leak water. Fracture aperture dimensions should be uniform to avoid fast transfer pathways. The viscoelastic behavior of high-temperature stressed rocks affects fracture formation and evolution. Alteration of water heat capacity through the addition of particulates, as demonstrated in nanofluids, could increase heat capacity.

EGS has extreme materials challenges because of its high temperatures and potential for corrosion and scaling. For example, hydrothermal fluids can dissolve minerals, such as carbonates or silicates, that may reprecipitate in fractures, altering flow, or within wells and pipes. The mobilization of corrosive gases, such as HCl or H_2S, from subsurface reactions will degrade electricity generation infrastructure. A substantial empirical effort at the Salton Sea conventional geothermal field in California, studying materials performance and precipitation, successfully mitigated corrosion and scaling [27]. Nanostructured precipitates from geothermal water may have unusual structures and commercial uses as sorbents [28].

Management of brines and produced/flowback water

Produced water from oil and gas extraction. At some stage of their operational life, O&G reservoirs co-produce water that was either present in the formation or injected during water flooding or hydraulic fracturing. In some oil fields in southern California, 10–15 barrels of water are produced with each barrel of oil. Following hydrocarbon separation, the residual water may contain salts, heavy metals, and oil field additives, such as biocides [29]. Although hydraulic fracturing fluids can be recycled, the produced and flowback water must either be disposed of by injection into a deep saline aquifer or treated for beneficial reuse, such as irrigation. O&G companies are facing challenges of increased water production, declining options for subsurface disposal, and increasing scrutiny of water quality for reuse. The technical, geological, and regulatory uncertainties associated with production water management threaten to delay U.S. O&G growth and similarly add burdens to any new application, including GCS, which may produce subsurface brines.

Extracted water from GCS. The injection of sCO_2 into a subsurface aquifer generates a pore pressure increase that subsides when injection ceases, owing to flow and dissolution. For the buoyant CO_2 to remain trapped, the pressure increase due to injection must be controlled to prevent over-pressuring and fracturing of low-permeability caprock above the aquifer. During the injection of CO_2, extraction of brine from a well situated elsewhere in the aquifer is a strategy for pressure control. The extracted brines likely have a salinity significantly higher than seawater (100,000 mg/L or higher), with a chemical composition that depends upon the geologic history of the aquifer. Extraction of brines influenced by the CO_2 injection should be avoided, but may occur, depending on the pressure response of the aquifer. CO_2 dissolution into brine lowers the pH, creating solutions that can dissolve carbonates and oxides and mobilize metals.

Treatment or disposal of produced/flowback water. Production waters typically have salt concentrations similar to or far exceeding seawater levels. They are typically processed through a two-stage treatment process [30]. First, selected contaminants such as heavy metals, arsenic, boron, or oil field chemicals such as quaternary ammonium compounds are removed through sorption, biological treatment, or other separation steps [31]. Second, if required, the fluid is treated for salt removal. Membrane desalinization is the most common procedure, but faces challenges with fouling caused by initial composition or primary treatment steps. Alternatives that are being developed include membrane-free capacitive desalination and thermal desalination for very-high-salinity fluids. As the quantity and diversity of produced and flowback waters increase, novel, effective, economic, and approved methods for specific and non-specific treatments may be used to provide waters fit for a range of industrial or agricultural uses. Transportation between production, treatment, and secondary use sites, however, can significantly increase energy costs [22]. Later sections in this document outline the full spectrum of treatment technologies.

Disposition of brines

Fluid injection into the subsurface is widely used to dispose of unwanted brines; there are tens of thousands of active disposal wells in the U.S. Wastewater injection carries risks of groundwater contamination, typically associated with above-ground operations, and of induced seismicity. The 40-fold increase in seismicity within Oklahoma from 2008 to 2013 as compared to 1976 to 2007 has been attributed to wastewater disposal rather than to extraction operations [32]. Best practices for managing seismicity risk during subsurface operations are provided by recent reviews [33, 34]. Other surface operations involving large–scale water storage or extraction can also induce seismicity. Efficient use of subsurface systems will require manipulation and monitoring of the permeability of rock formations and prediction of the flow of fluids within them. The permeability of a porous material describes the rate of flow of a fluid in response to a pressure difference.

Permeability, k (m^2), is a macroscopic quantity that averages over the details of pore or fracture geometry. Useful empirical relationships between porosity and permeability are established for porous materials, but less so for porous media containing fracture networks. An overview of the challenges for visualizing changes that occur to subsurface systems as a result of fluid injection or removal is provided in a recent U.S. Department of Energy (DOE) report [35].

Hydraulic fracturing and shearing. Hydraulic fracturing and shearing are achieved by injecting a fluid that creates a pressure front that extends into the formation [36]. Shale rocks are reasonably described as linear elastic materials in which tensile failure (i.e., fracture opening) requires the pore pressure to exceed lithostatic stress from the overburden and the fracture toughness of the shale. Fractures open in the direction of the minimum compressive stress, which is typically horizontal unless altered by rock anisotropic and tectonic history. Polymer addition is required to increase viscosity, favoring laminar over turbulent flow to reduce resistance to flow [24]. Proppant particles prevent fracture-aperture closing when injection pressure is reduced. Hydraulic shearing of deep crystalline rock formations suitable for EGS opens preexisting fractures and the strain from the overlying rock causes slip, so that natural asperities prop open the fracture [37].

Fluid flow in porous and fractured porous systems. Predicting fluid transport through complex geologic media is challenged by the inherent uncertainties of remotely characterizing the 3D geometry and connectivity of pores and fractures, and requires the development of efficient geometric descriptors of relevant flow network properties and their influence on transport processes so that large-scale modeling is feasible. Although accurate reservoir-scale modeling of flow is routine for many geosystems, there are limitations in the reliability of predicting the flow of two or more immiscible fluids, and the flow of fluids that alter pore geometry by water-rock reactions. Moreover, safe and efficient utilization of subsurface systems for water and energy benefits requires the control of fluid flow and fluid chemistry to manipulate and preserve permeability. Accurately modeling fluid transport that is highly coupled to mechanical processes in stressed rock that alter permeability, including fracture formation, slip, creep or mineral dissolution, also plays an important role [35].

The Navier-Stokes equation, an expression of the conservation of mass and momentum for an incompressible fluid, precisely describes the flow of a single fluid phase within an arbitrary geometry. For porous media, Darcy's law, an empirical flow equation, accurately describes single-phase flow when the permeability is known. The presence of fracture networks adds considerable complexity to all transport models [38]. Fracture surfaces and fracture networks are both believed to exhibit self-affine geometric properties. The

Richard's equation, derived for flow through parallel plates, describes flow as a function of pressure and aperture (the distance between fracture surfaces). As illustrated by Figure 11, applied stress and the changes to fracture geometry strongly influence fluid pressure and flow.

Materials chemistry in aqueous environments

Metal components in energy and water systems can be seriously degraded by corrosion or by the precipitation of deposits on surfaces. Degradation carries a large economic cost, may have ecosystem or human health impacts, and reduces energy and water security. Precipitation reactions can increase energy requirements for fluid flow through pipes and can prematurely end the useful life of O&G and geothermal infrastructure and reservoirs. Tied to predicting corrosion and precipitation is a quantitative understanding of the interfacial aqueous chemical and materials processes at play. Reducing corrosion can be aided by improved separation of impurities from process fluids, by selecting bulk and surface materials properties for the relevant conditions, and sometimes by the addition of surface treatments.

Corrosion

Corrosion of steam turbines. Steam turbines convert heat to electricity. Modern turbine rotors are designed and fabricated to strict tolerances, and the most common causes of reduced efficiency or failure are corrosion, erosion, and deposition. Low levels of impurities, such as sodium hydroxide, chloride, sulfate, and sulfides, can cause damage. Steam turbines are particularly susceptible to impurity-driven corrosion because the solubility of impurities drops significantly with temperature, such that condensation on surfaces can concentrate chemicals and significantly alter the pH and oxidation/reduction potential of surface fluids.

Corrosion of high-level nuclear waste canisters. Long-term storage of high-level radioactive waste in subsurface rock formations will almost certainly be used to safely dispose of the growing nuclear waste stockpile [40]. The U.S. is studying the feasibility of deep bore-hole disposal, in which canisters are loaded vertically several kilometers down into solid rock. France, Japan, and other nations are considering storage in low-permeability shale. A common feature of these containment strategies is the use of metal containers intended to resist water entry and radionuclide release over time scales relevant to the very long half-lives (10,000 to 1 million years) of certain isotopes. In anaerobic surface formations, steel or copper reacts slowly with water, producing hydrogen, at rates that can be assessed in the laboratory. However, corrosion reactions with species such as chlorides or sulfides may degrade canister integrity at rates that depend sensitively on aqueous chemical conditions and that cannot currently be confidently measured or predicted over sufficiently long time scales.

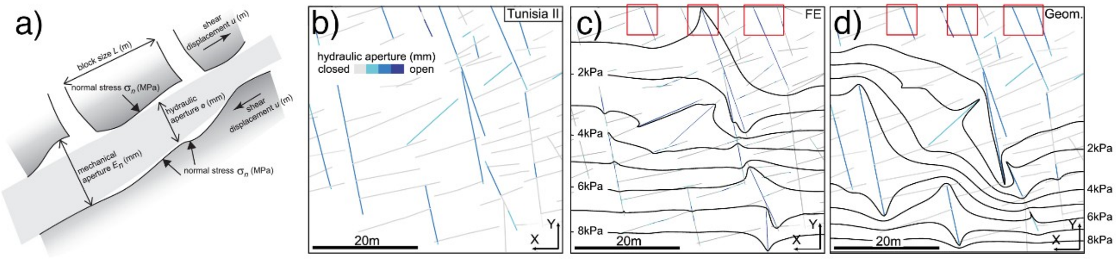

Figure 11. Predicting the effect of pressure on aperture width and flow using a discrete fracture network model. a) Scheme of fracture aperture. b) Fracture distribution and aperture in a Tunisian carbonate pavement. c) Pressure contour lines assuming closed fracture terminations (red boxes). d) Pressure contour lines assuming open terminations (red boxes). From Bisdom 2016 [39], AAPG Bulletin, AAPG © 2016, reprinted by permission of the AAPG whose permission is required for further use.

Corrosion of water pipes. The recent public health event in Flint, Michigan, was initiated when a change in drinking-water chemistry provoked an onset of lead pipe corrosion [41]. Until 2014, water sourced from Lake Huron and treated with orthophosphate maintained a lead phosphate coating on lead pipes. A switch to Flint River water lacking orthophosphate but with elevated chloride (to treat *E. coli*) and lower pH rapidly dissolved the phosphate coating, enabling oxidative corrosion and toxic $Pb^{+}(aq)$ release. Restoration of a protective phosphate coating was expected to take at least one year. The U.S. is estimated to possess 3–10 million lead water pipes.

Nucleation from solution. The precipitation of solids from solution may occur through homogeneous nucleation, where nuclei form directly in solution, and heterogeneous nucleation, where materials form at the interface between a liquid and another liquid or solid. Which mechanism of precipitation is favored depends on both thermodynamic favorability and kinetic factors that are governed mainly by solubility and temperature.

Heterogeneous nucleation is often more energetically favorable than homogeneous nucleation and so tends to occur at lower solution concentrations and is the principal cause of scale formation. Highly supersaturated solutions favor nucleation of substances that are less stable thermodynamically, such as amorphous phases. Either these dissolve and reprecipitate as the more thermodynamically stable phase, or the system resides in a metastable state. Close to equilibrium, nucleation is usually not observed, and the only growth of material is on pre-existing crystals.

Precipitation and scale formation

Scale formation in O&G reservoirs and infrastructure. Scale formation, that is, the unintended precipitation of minerals and organic matter from aqueous fluids in pipes and O&G reservoirs, has been estimated to cost $1.4 billion dollars per year annually for removal, increased corrosion damage, and lost O&G production [42]. Predicting the extent and timing of scale formation is often not possible; analyses rely instead on post hoc rationalizations (e.g., [43]). Barite precipitation is a known cause of clogging in some tight shales exposed to oxidizing fluids that oxidize sulfates; it is the dominant scale-forming mineral in, for example, North Sea oil deposits. Other common scale-forming minerals include calcium carbonate and amorphous silica; organic scales, such as waxes and asphaltenes, can also form.

Silica precipitation from cooling water. The precipitation of silica from cooling high-temperature fluids is a significant cause of steam turbine degradation and scale formation in geothermal systems. The solubility of amorphous silica drops with temperature, and when a fluid becomes supersaturated relative to the amorphous solid, scale formation is highly favored [44]. Conditions for silica precipitation can be predicted from chemical speciation models. However, the speciation of silica in water and precipitation pathways are poorly understood on a molecular level, and the rates and products of precipitation in the presence of multiple species, including aluminum and carbonate, are not established.

Scale prevention and removal. In some cases the scale can be removed, either by using mechanical means (e.g., high-pressure fluid flow, particulate blasting) or by manipulating solvent chemistry (e.g., introducing a chelating agent, such as ethyldiaminetetraacetic acid. Scale removal is complicated when the scale formation occurs in the subsurface, since accessibility of a solvent to the locale where the scale has formed can be problematic. By far the preferred alternative to removing scale is preventing its formation. Prevention involves using a scale inhibitor, a chelating agent for sparingly soluble salts, or a corrosion inhibitor to prevent iron mineral formation due to pipe corrosion. These compounds can be mixed with working fluids, or injected into subsurface pore structures to mix with formation water.

Heat transduction

Cooling in thermopower plants

As indicated previously, cooling water needs for thermoelectric power generation account for about 45% of the total water withdrawals in the U.S., with only a fraction of that consumed through evaporation (approximated at 3–6% of total water consumed in the U.S.) [45]. Most of the water consumption occurs in closed-loop cooling operations, where outfall water from the plant is cooled via cooling towers or open ponds. In open-loop cooling, the cooling water is being used in a once-through mode so that it is returned to the water source/reservoir with minimal losses (Figure 12). Water consumption could as well rise owing to potential increased deployment of carbon capture and storage technologies that use water in various stages of the capture and storage processes. Additional fresh water is also consumed throughout the life cycle of power plant operations in the course of the extraction, processing, transport, and end-of-life of the various power plant fuels (e.g., coal, nuclear, natural gas). These operations can add some 10–20% to overall water consumption [46].

There are various approaches to reducing both water withdrawals and consumption by water-cooled power plants. The obvious solutions involve reducing or even eliminating cooling-water needs. Such approaches include deploying dry (air) cooling technologies or some form of hybrid dry-wet cooling that would dramatically reduce cooling water needs, especially in arid areas. However, such cooling approaches would result in higher initial capital costs and an energy production penalty because of the higher temperature of inlet steam cycle compressor water [45]. However, dry cooling obviates the need for water treatment. Another approach might be to increase the use of non-traditional water sources, such as produced waters from O&G operations or recycled and treated wastewater of various types. The reuse of discharged cooling water also reduces cooling-water needs. Seawater can and is used as a cooling-water source for power plants located along the coast, reducing total freshwater requirements. However, various regulatory requirements for discharge and intake of seawater and other siting constraints are expected to slow deployment of open-loop cooled plants in coastal regions. While currently over 75% of power plants use surface water for cooling, planned power plant deployment through 2022 indicates a reduction of that fraction to 20% with utilization of other cooling water sources, such as recycled/treated water and groundwater [45].

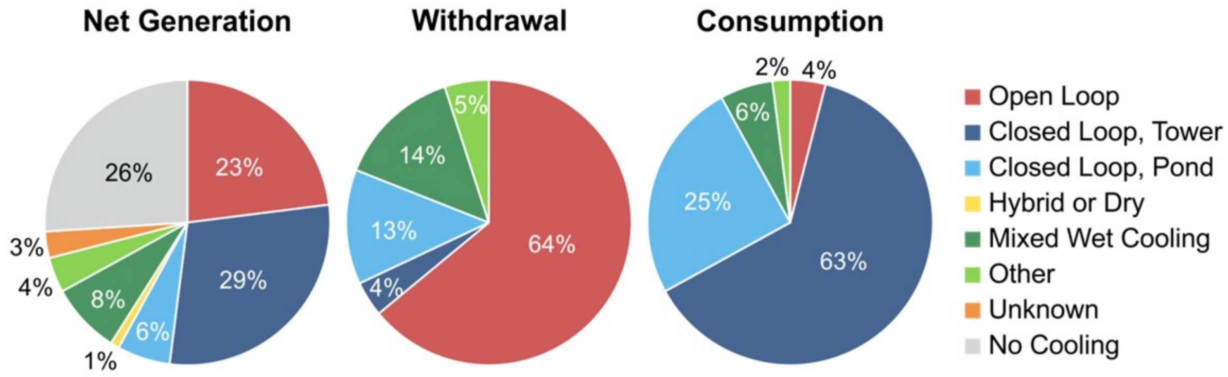

Figure 12. Relative water withdrawal and consumption for various thermoelectric power generation cooling options. From DOE 2014 [47].

In addition to using cooling approaches that reduce water use for power-plant operation, cooling-water requirements can be reduced significantly by increasing overall power-plant heat cycle efficiency, designing better heat-transfer materials and heat exchangers to improve heat exchange in the cooling process, and increasing renewable-energy generation.

More efficient power cycles can be achieved by employing those with higher heat-to-electricity conversion efficiencies, such as in the case of sCO_2, where efficiencies of combined cycle generation (natural gas-sCO_2) can exceed 60%. Materials that can withstand the harsher temperatures and pressures associated with them will be important for such advanced cycles.

Advanced heat-exchanger materials used for thermoelectric cooling hold promise for increased use of harsher, non-traditional waters, such as degraded-quality and minimally treated wastewater and produced water. These new and/or improved materials would resist the fouling, scaling, and corrosion that often result from use of impaired and low-quality waters. Further, economical surface engineering approaches could help minimize and/or eliminate fouling/scaling.

Even though the water lost in wet cooling systems is merely several percent of the total circulated, minimization of water loss from evaporation during cooling is an important issue. Cooling-tower water chemistries could reduce water evaporation while dissipating the same amount of heat. Further, use of phase-change materials, in combination with dry cooling, might reduce or eliminate the need for cooling water altogether.

The efficiencies of the various sub-systems of the power plant cooling system could also be improved. These include performance of condensers or heat exchangers for wet cooling systems. Possible options could include new designs and surface engineering/coatings in heat exchangers to enhance heat transfer and make them more efficient. For dry cooling, airside heat transfer is always challenging and needs to be improved.

Innovative approaches, such as thermosyphon coolers [47] and dew-point cooling towers [48], are being explored to reduce the load on the wet cooling towers. In the first approach, dry-heat-rejection thermosyphon technology is applied before the hot water enters the cooling tower. In dew-point cooling towers, the cold-water return temperature is reduced, and, hence, the temperature of water exiting the condenser is lower. These technologies reduce the evaporation losses and make-up water requirements. New concepts and technology development along these lines could enhance performance of cooling systems employed in power plants.

Waste heat recovery

It is estimated that approximately 59 quadrillion BTU of thermal energy is wasted [49]. The wasted energy is about 50% of the energy produced. The sectors with the largest waste thermal energy are power generation and transportation, followed by the industrial and buildings sectors. For example, in the power generation sector where the steam Rankine cycle is used for electricity production, almost two-thirds of the thermal energy generated is wasted—the majority of it to the environment.

Waste heat is typically categorized on the basis of the temperature of the medium carrying the waste heat. Usually, low-grade heat is associated with temperatures <230°C, medium-grade heat with temperatures 230–650°C, and high-grade heat with temperatures >650°C. Low-grade heat is difficult to utilize because it is challenging to convert it to usable work (low energy). Almost 75% of the waste heat falls in the category of low-grade heat. Table 2 shows the waste heat from various sectors, percent of the heat characterized, and estimated potential of work from the waste heat in quadrillion BTU (Q) [50, 51].

Table 2. Waste heat from various sectors and its effective work potential (in quadrillion BTU).

Sector	Characterized Waste Heat (Q)	Total Waste Heat (Q)	% Characterized	Estimated Work Potential (Q)
Power generation	23.1	25.4	94%	3.2
Industrial	1.6	4.9	33%	2.1
Transportation	17.2	21.9	78%	6.7
Buildings	0.0	7.0	0%	Unknown
Total	41.9	59.2	71%	12.0

As shown in Table 2, the largest amount of waste heat is generated from power plants, mostly from heat transferred to cooling water during condensation of steam exiting from the turbines in the condenser. The cooling water typically rises to about 95°C, and thus, this heat is low-grade. This hot water could have numerous uses; however, since power plants are often situated away from population centers, the cost to transport the heat is not economical. In this regard, high-energy-density mobile systems for thermal energy storage would be an attractive option.

Technologies to use low-grade waste heat fall into three categories: mechanical systems, solid-state devices, and hybrid systems. In a typical mechanical system, the heat is used to boil an organic working fluid (organic Rankine cycle), and the energy from the working fluid is used to run a mechanical system. In such systems, overall conversion efficiency from thermal to mechanical energy is critical and is dependent on the heat transfer and flow characteristics of the working fluid. Such systems have a large footprint.

For solid-state devices based on thermoelectric generators, thermoionics and multiferroic thermoelectrics are being investigated for low-grade waste heat recovery and utilization [52]. These devices are limited by their efficiencies and costs. For example, to utilize thermoelectric generators for low-grade waste heat recovery, the figure of merit (ZT) of such devices must triple from current state-of-the-art values, and the device must cost about $1/W for potential commercial viability [52].

Waste heat from cooling power plants has been explored for use in desalination. Desalination technologies such as reverse osmosis, multi-stage flash (MSF), and multiple-effect evaporation desalination (MSG) require electrical energy and/or heat. MSG requires 70°C heat, whereas other technologies (MSF) require temperatures >100°C. Thus, there may be an opportunity to use low-grade heat from cooling power plants for desalination.

For medium- and high-grade waste heat, the work potential is high, especially in the case of transportation. Systems to recover the waste heat are currently being developed. Most such systems are based on the organic Rankine cycle and have challenges related to heat transfer, uncertainties in two-phase flows, issues with heat exchanger design and efficiency, stability of working fluids, and efficiency of energy conversion systems. Further, for many of the applications, the weight and cost of the waste heat recovery systems come into play.

Separations

Membranes

Semi-permeable membranes are structures made of hard or soft matter that allow some chemical species to pass through, but not others. Such membranes are essential for many problems in energy-water systems. An obvious example is the water purification problem [53, 54], different manifestations of which are desalination [55, 56], decontamination, and disinfection of seawater, fresh water, groundwater, and wastewater. In this case the goal is to remove unwanted chemical species, be they ions, solutes, pathogens, or particles. Semi-permeable membranes that allow water to pass through but exclude undesirable species would be beneficial for separations. These purification processes often consume energy; for example, salt water must be pressurized in reverse-osmosis desalination, and so this process is central to the connection between energy and water. Another example involves hydrogen fuel cells. Therein, to complete the electrical circuit, protons must flow from the anode to the cathode. In this case one wants membranes that allow for the transport of protons but do not pass oxygen or hydrogen. A fuel cell produces energy (and water) and the membranes work in aqueous solution, and so this problem is also central to energy-water systems, although in a different way.

Membranes can be categorized in terms of the size of chemical species that are excluded [53] (Figure 13). Reverse-osmosis membranes used in the desalination process have pores small enough, and with the appropriate electrostatic properties, to exclude monatomic sodium and chloride ions. So-called polymer exchange fuel-cell membranes exclude oxygen and hydrogen molecules. Both of these membranes have pores with diameters of a fraction of a nanometer. Nanofiltration (NF) membranes have pores that are slightly larger, on the order of a few nanometers, which filter out organic molecules. Ultrafiltration (UF) membranes have pores on the order of a few tens of nanometers and filter out virus particles. Microfiltration (MF) membranes have pores on the order of a micron and filter out bacteria, red blood cells, and dust particles. Particle filtration membranes have pores on the order of a few to many microns and filter out larger particles, such as sand and pollen. Generally speaking, membranes have broad pore size distributions, with flux often dominated by the largest pathways, thereby limiting their effectiveness in efficiently filtering out targeted species. Narrowing pore size distribution is a key challenge in the coming years to reduce energy consumption and improve overall performance.

Membranes can also be classified by the materials of which they are made. Inorganic membranes are typically composed of nanocrystalline ceramics, such as TiO_2 or SiO_2, or mixtures thereof. TiO_2 membranes are particularly interesting because they are photocatalytic [58] and can be used as effective disinfectants. Another recently developed inorganic photocatalyst for disinfection is MoS_2. Many current MF, UF, and NF membranes are made from organic polymers, such as cellulose acetate and polyvinylidene fluoride. Reverse-osmosis and proton-exchange membranes are also polymeric: The former features cross-linked polyamides and the latter sulfonated fluoropolyethylenes. One can also make hybrid inorganic/organic membranes by combining polymers and nanoparticles to obtain specific tailored properties. Finally, one can use new carbon-based materials, such as carbon nanotubes and graphene (and graphene oxide), to make interesting membranes, use surfactants to make soft-matter membranes, and even incorporate proteins, such as aquaporin, into membranes [55].

Effective membranes have certain performance requirements: they must exhibit mechanical, chemical, and thermal robustness; have high water (or proton) flux; and demonstrate high solute rejection. In addition, they should be non-fouling, or at least easy to clean. Few current membranes satisfy all of these criteria.

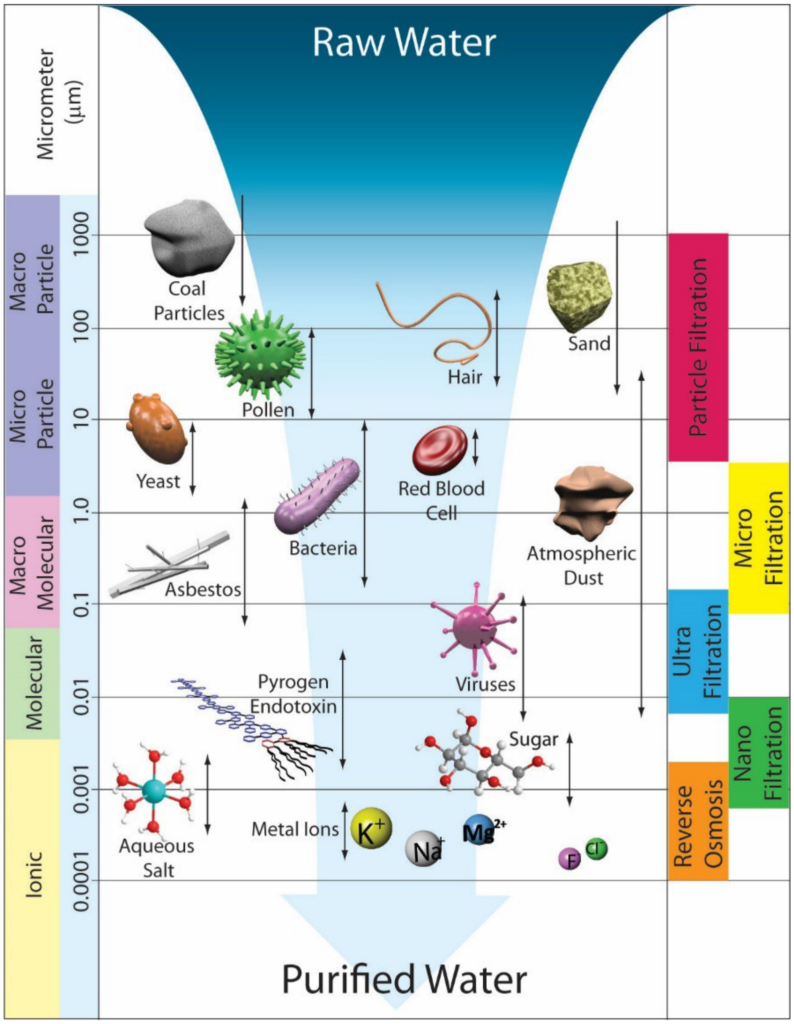

Figure 13. Schematic of membrane filtration spectrum. From Lee et al. 2016 [57].

Different factors affect membrane properties and thus would be considerations in designing membranes with tailored properties. The interactions of ions (including protons) and solutes with water are important for membrane properties and function, as are the hydration structures and dynamics of water around ions and solutes and the transport properties of ions, solutes, and water itself. Many, if not all, of these aspects will factor into tailoring membrane properties such that the full range of hydrophilic and hydrophobic interactions can be accessed as well as tuned.

Inorganic membranes are typically crystalline (or at least nanocrystalline) solids and are affected by the interactions, structure, and dynamics of water near solid surfaces. Membranes made of polymers or soft matter, such as surfactants, are similarly affected by the interactions, structure, and dynamics near the interfaces. One of the salient features of membranes is that water, ions, and solutes are confined in pores; this confinement changes the structure and dynamics—even hydrodynamics— of these species.

Nature has elegant solutions for many of the processes discussed here. For example, cell membranes made of lipid bilayers surround the cell and prevent many chemical species from entering (or leaving). However, nature also needs mechanisms to regulate matter transport in and out of cells, and it often accomplishes this with membrane protein channels—protein complexes embedded in the cell membrane. These channels can selectively transport protons, ions, or water (see below). It behooves science to take a careful look at how nature has accomplished many of the same goals in other contexts and see if "biomimetic" design principles would be beneficial, in this case for separations and membrane development.

An essential step in the development of new membranes is their characterization. Tools allow quantitative measurement of microstructure and transport such as direct visualization through microscopy of various kinds (scanning and transmission electron microscopy and scanning probe microscopy). X-ray and neutron scattering provide powerful complementary structural tools, with the latter having a unique capability to derive contrast in aqueous systems via deuteration. Vibrational spectroscopy (IR and Raman) does not typically provide long-range structural information, but since vibrations can be sensitive to local chemical environments, it can yield important local structural information. A newer variant is sum-frequency generation (SFG), which is surface-sensitive and essentially provides vibrational spectra of surface species [59]. Another advantage of vibrational spectroscopy is that new ultrafast time-domain versions are useful for probing dynamics. Two-dimensional IR spectroscopy (2DIR) has proven to be a useful technique for measuring dynamics in bulk systems, while 2DSFG is fast becoming the go-to technique for dynamics at surfaces.

Theory and computation are also important tools in the development of new membranes, related to both design and characterization. Direct simulation of condensed-matter systems can be performed on many levels, involving a wide range of time and length scales. *Ab initio* molecular dynamics simulations involve doing electronic quantum mechanics "on the fly." These methods are now quite accurate, but they tend to be expensive. Therefore, the ranges of accessible time and length scales are tens of picoseconds and a few nanometers, respectively. Molecular dynamics from empirical potential surfaces is less rigorous but substantially less expensive; with this technique, accessible time and length scales can be as long as microseconds and tens of nanometers. To achieve even longer time and length scales, theorists have developed "coarse-grained" methods, where groups of atoms are considered together [60]. Finally, to access even longer time and length scales, continuum mechanics, hydrodynamics, and fluid dynamics are valid. Just as there is a wide range of pore sizes in the membranes of interest, there are computational methods capable of exploring the same wide range of length scales.

Model systems are also a tool that allows researchers to focus on specific scientific questions. Direct comparison between experiment and theory/simulation is important in the validation of both experimental and computational methods.

The structure and dynamics of water near soft and hard interfaces, as noted earlier, is a notable aspect of separations processes and membrane development. Researchers have used SFG and 2DSFG to investigate the orientation and hydrogen-bonding dynamics of water near monolayers of positively and negatively charged, and zwitterionic, lipids and surfactants [61].

Model systems studied that involve water near hard interfaces include silica (often with templated surfaces) and graphene [62].

The effect of confinement is also a consideration for separations, with confinement by soft-matter interfaces being researched systematically. Studies include "zero-dimensional water," or "dots," which are small water pools in surfactant reverse micelles [63], as shown in Figure 14. The size of the dots can be tuned by varying the mole fraction of water and surfactant, and in doing so, the dependence of water dynamics on confinement interface curvature can be measured by 2DIR or simulation. For the smallest dots, water dynamics can be slowed down by orders of magnitude and can even display glassy behavior.

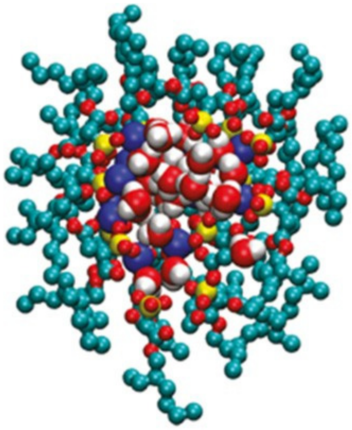

Figure 14. Simulation of water confined within a surfactant reverse micelle.

“One-dimensional” water in tubes formed by gyroid surfactant structures has also been studied. The morphology of the structures can be tuned by surfactant chemistry, including chemical dimerization to make “gemini” surfactants [64]. Water in these tubes senses interfaces of the opposite curvature from those in the reverse micelles, providing an intriguing comparison. Finally, two-dimensional water confined by the headgroups in lipid multibilayers has been studied to make a connection with water near lipid monolayer surfaces. Water dots confined in silica, metal-organic frameworks (MOFs), and zeolite pores have also been researched, as has one-dimensional water confined by carbon nanotubes; the findings in some cases reflect exceptionally high transport rates [65]. Water and proton transport in polymer membranes such as Nafion has also been explored [66, 67].

“Biological water,” has been studied in water channels formed by proteins in cell membranes, such as aquaporin; in ion channels, such as the potassium KcsA channel or similar potassium channels in nerve cells; or in proton channels, such as the M2 channel in influenza A. 2DIR studies have shown how the sites in the KcsA channel are occupied by water molecules and potassium ions and have elucidated the transport mechanism [68]. Similar investigations have also suggested a mechanism for pH gating of the M2 channel [69]. Other aspects involve the structure and dynamics of water-hydrating proteins, especially anti-freeze proteins, and the important role that water plays in biomolecular self-assembly, for example, in the aggregation of amyloid proteins [70]. These examples show how sensitive the structure and dynamics of water are to its molecular surroundings.

Sorbents

Whereas membranes most often function in separations via size exclusion, some separations are best approached using affinities to bind the targeted species. One such strategy is sorption. Sorbents are materials that absorb or adsorb other materials, either by physically trapping them or via chemical or electrostatic affinity. Absorption, where a fluid dissolves or permeates into another liquid or solid, has few applications in the water arena—although superabsorbent polymers are an important exception, with functions ranging from hygiene to waste solidification. Here the focus is on adsorption, which involves the adhesion of atoms, ions, or molecules to a surface. Often, an adsorbent is engineered to be highly porous, such that the internal surface area is large, thereby accommodating a greater number of adsorbates in a given volume. Common adsorbents include zeolites [71], activated carbon [72], silica gel [73], and polymers [74]. Zeolites are most often polar, crystalline aluminosilicates, although non-polar siliceous zeolites also exist. Their distinguishing feature is uniform, molecular-scale pore networks that can effectively and selectively bind specific ions or small molecules (Figure 15). By far the most widely used (and low cost) adsorbent is activated carbon. This material is highly porous

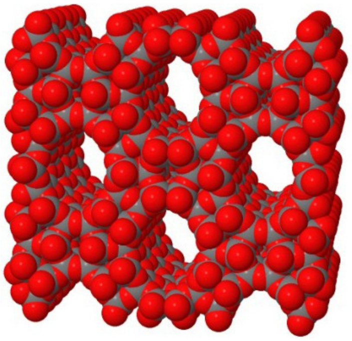

Figure 15. Atomic model of example zeolite structure.

and typically has a form factor of small pellets or powder. Heating carbon sources in an oxygen-free environment under exposure to an oxidizing agent (e.g., steam or carbon dioxide) drives reactions that form three-dimensional graphitic microstructures, with pore sizes tunable by reaction time. Activated carbon can effectively adsorb many organic and non-polar substances. Silica gel, an amorphous form of silicon dioxide, is usually prepared by reacting sodium silicate with mild acid followed by aging to adjust pore sizes. It is particularly effective at adsorbing polar hydrocarbons, although there are also reports of nanoporous silica materials for heavy metal sorption [75]. Polymer-based sorbents offer remarkable flexibility to target a broad spectrum of species through chemical functionalization of the constituent macromolecules as well as the morphology of the pore network.

In water treatment, there is an important subcategory of adsorption called ion exchange. This process involves swapping of ions between an electrolyte solution and a surface. This surface can be a porous or gel polymer called an ion exchange resin (Figure 16); a zeolite; or a natural material, such as clay or soil humus. These materials can function as cation exchangers, anion exchangers, or amphoteric exchangers that can process ions of both charges at the same time. (The same end goal can be achieved by combining anion and cation exchangers.) Selectivity of ion exchange processes can vary substantially, depending on the size, charge, and structure of the ions in solution.

Figure 16. Ion exchange resin beads.

Common applications for ion exchange include water softening, purification, and decontamination. Softening is achieved by exchanging multivalent cations, such as Ca^{2+} and Mg^{2+}, which bind tightly to the resin's anionic functional groups, for monovalent species, such as Na^+, K^+, or protons. Harmful anions in water, such as nitrates and nitrites, are also routinely adsorbed by using ion exchangers. Since the ion exchange process is consumptive, ion exchange systems have a finite operational lifetime and are typically operated on a cyclic basis. When the exchange material is exhausted of its original ions, it is regenerated by flushing it with a concentrated excess of replacement ions to wash out the accumulated adsorbed species and return the material to its original state. Because this regeneration process produces substantial volumes of waste itself, applications in large-scale operations such as municipal wastewater treatment are challenging.

The future of sorbents in water systems will rely on a collection of proven technologies, such as those outlined above, and new, innovative sorbents capable of higher specificity or scalability. Several next-generation materials have emerged with potential utility in this space. One class of compounds, closely related to zeolites, is MOFs, which consist of metal ions or clusters coordinated to organic ligands, forming microporous structures. To date, these materials have been heavily studied for gas sorption [76], but there may also be opportunities to explore use in capture of materials from water.

Recently, the extended family of two-dimensional materials, headed by graphene, has captured attention for its potential in water treatment. The reason for much of this interest is that these materials have an extremely high surface area, which offers large sorption capacity for materials (such as oils and common solvents) that are attracted to the basal planes of graphene and related materials [77–79]. These two-dimensional material sorbents can often be regenerated by heat treatment, which drives off the adsorbed species so the sorbent can be reused. Clearly, energy consumption is a drawback of such a processing strategy. Reusability, however, is indeed a potential game-changing property for sorbent materials, because it can dramatically reduce the life-cycle cost and sustainability of a treatment process. Washing is an alternative regeneration process, as implemented with ion exchange resins. Another possibility relevant for certain sorption applications is mechanical compression. There have been reports of polymeric foam sponges being used as sorbents for oil and organic solvents [80], particularly for use in water bodies where fluid selectivity is important. Once oil has been extracted from the water by using such a sponge, it can be squeezed out into a containment vessel, thereby emptying the pores of the sponge and rendering it ready for another cycle of adsorption and compression.

A consideration in using sorption technologies is the possible tailoring of surface properties for solute-specific adsorption. This characteristic would not only enable effective capture of difficult water contaminants, such as nitrate [81], phosphate [82], and heavy metals, including hexavalent chromium, lead, and mercury [83], but would also offer the tantalizing promise of pulling one specific material from a complex aqueous solution. Fabrication of sorbents capable of grabbing ions, for example, or even ions with a particular charge, is feasible using current technologies. The impact of sorbents could be notably greater if ion-specific sorption were possible, allowing increased resource recovery from waste streams and from contaminated water sources. Similarly beneficial would be the sequestration of bioactive molecules, such as endocrine disruptors, from wastewater treatment plants while non-hazardous organic materials were allowed to pass through.

Electro/capacitive technologies

Classic methods for water purification, such as filtration or membranes, separate components based on size and surface affinity. These methods can require long pathways, high pressures, and sometimes slow processes. Providing a chemical potential has significant advantages in key purification applications. Removal of charged species, including salts, ions, acids, and bases, is a core function in treatment of water streams. A specific advantage of electro/capacitive technologies is that charged species are transported and separated out of the water solution. In comparison, reverse osmosis forces water across a membrane and out of the solution. The charged species rarely exceed 5% of the total solution by weight, so electro/capacitive technologies are inherently more atom-efficient.

Electro/capacitive technologies offer some of the most atom- and energy-efficient methods to drive purification. The electromotive force acts preferentially on the charged species to drive the separation. In electromotive-based technologies, including electrodialysis (ED) and electrodeionization (EDI), an electric field provides the force to transport charged species to and across an ion exchange membrane (Figure 17) [84, 85]. Diffusion may transport water and other neutral species across the ion exchange membrane, but the driving force from concentration polarization will be significantly slower that the electromotive driving force. The major transport mechanism for water will be co-transport in the hydration sphere. Hydration sets the upper limit on concentration of the charged species in the permeate. With organic species such as acids, the upper limit is about 50 weight %.

With capacitive deionization (CDI) technologies (Figure 18), the charged species are adsorbed into a matrix electrode by an electric potential. When the material approaches saturation, the flow ports are switched, the charge is reversed, and the ions are desorbed. CDI has particular advantages when handling solutions with intermediate conductivity, such as brackish water. As with ED and EDI, CDI takes advantage of the chemical differences between ions to efficiently drive the separation.

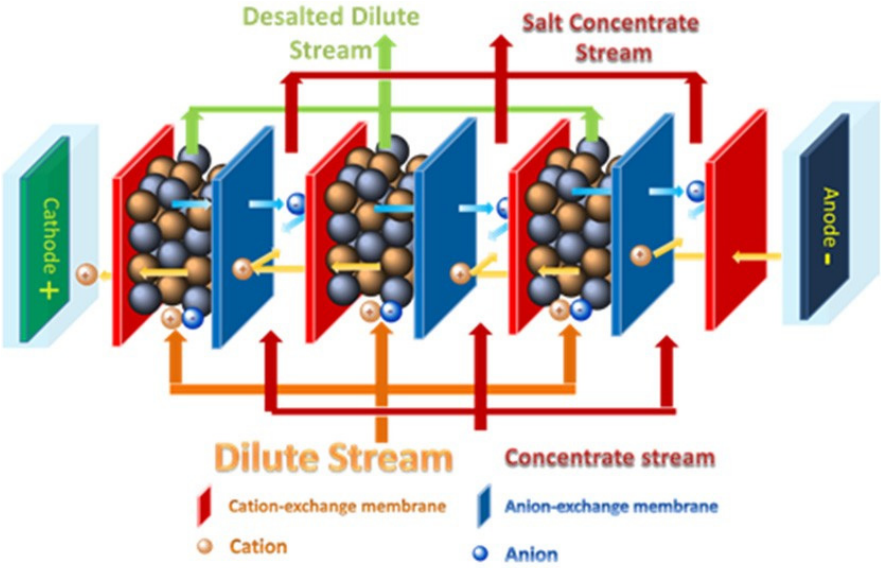

Figure 17. Schematic of electrodeionization for water treatment.

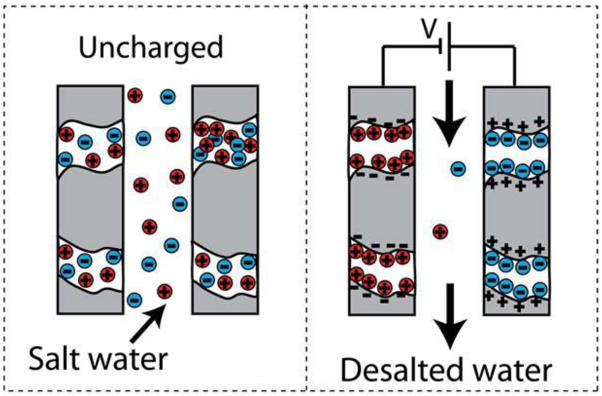

Figure 18. Schematic of capacitive deionization for water treatment. Image courtesy of M. Stadermann; modified from Biener et al. 2011 [86].

Catalysis

Water remediation chemistry must address a diverse array of soluble and particulate pollutants. These range from biologically and anthropogenically sourced organic and halogenated hydrocarbons to toxic inorganic and metal-based soluble compounds and particulates. Widely implemented membrane separation and pollutant sequestration processes are effective for the production of clean, remediated water, but they have limitations as sustainable, full-cycle water remediation technologies. As discussed in prior sections, these limitations include the costs associated with membrane fouling and the accumulation of pollutant-enriched sludge.

Water remediation chemistry based on a combination of advanced oxidative [87–89] and reductive [90, 91] catalytic processes offers the potential to develop sustainable, full-cycle remediation technologies that couple degradation of wastewater pollutants with energy and resource recovery [92] (Figure 19). Catalytic electrochemical and photochemical redox processes are significant because they provide a complement to separation and sequestration-based methodologies and can be targeted to achieve in situ, "residual-free" pollutant degradation, in situ membrane foulant degradative removal, and energy/resource recovery from wastewater and sludge residuals from separation processes.

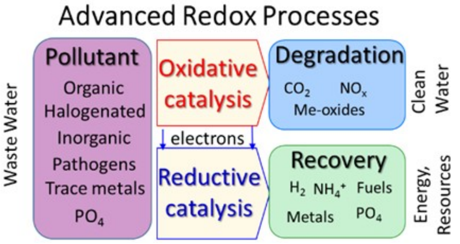

Figure 19. Advanced redox process for wastewater remediation that integrates oxidative and reductive catalysis to achieve combined pollutant degradation with energy and chemical resource recoveries.

Bio-based catalysis

Biological treatment processes are widely implemented and serve as the core of current municipal and agricultural wastewater remediation technologies. These include a toolbox of aerobic and anaerobic microbial reactors, trickle filters, lagoons, and landfill systems that are effective technologies for the removal of organics, nitrates, and bioactive compounds from wastewater and sequestration of phosphates and trace and toxic metals into biomass residuals. Evolving technologies include the development of membrane bioreactors that streamline and improve the efficiency of remediation processes by integrating MF and UF with sequential stages of aerobic and anaerobic microbial reactors [93, 94].

The limitations of these current technologies arise from incomplete processing of water-borne waste, the accumulation of sludge and biomass, the energy input needed to maintain efficiency, and the geographic footprint. Bio-based catalysis processes may offer pathways for energy recovery from wastewaters. For example, the *Biogas Opportunities Roadmap*, a 2014 report authored jointly by the DOE, EPA, and USDA, outlines strategies for utilization of organic waste as an energy resource extractable from landfills, municipal water treatment facilities, and agricultural and industrial wastewater streams (Figure 20) [95]. Further, ongoing basic research is demonstrating opportunities to extend microbial bioreactor technologies for more direct, compact, and efficient energy conversion and resource recovery. These include the conversion of biodegradable organic waste to electricity in microbial fuel cells (MFCs) [96–98] and conversion of biodegradable organic waste to hydrogen (and, conceptually, to other liquid fuel or chemical products) in microbial electrolysis cells (MECs) [99, 100].

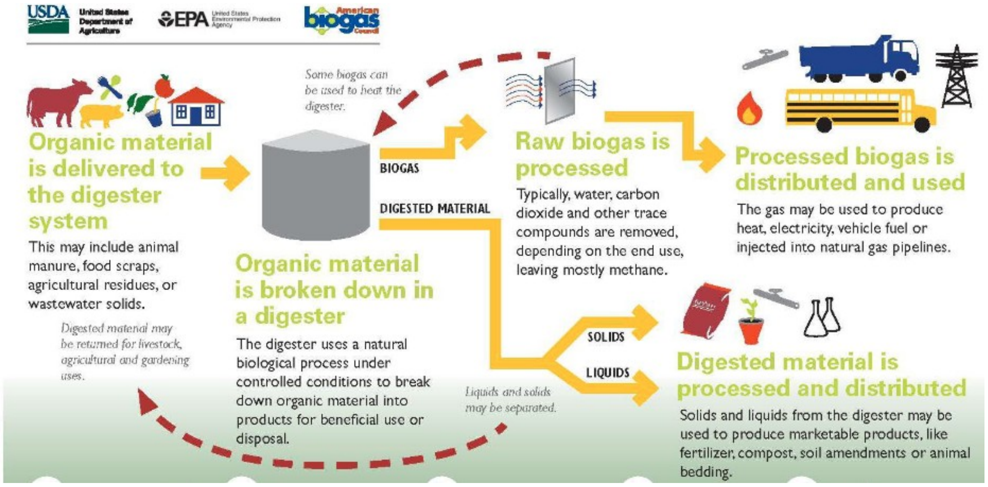

Figure 20. Overview of an anaerobic bio-catalytic digester concept. From the 2014 joint DOE, EPA, USDA *Biogas Opportunities Roadmap* [95].

Advanced bio-based catalysis. Biological catalysis is accomplished by the control of chemical processes across multiple levels of organization, ranging from the atomic-scale control of active-site structures in individual enzymes and enzyme cascades to development of microbial community networks of coordinated function. Optimization of the microbe-electrode and biological-materials interfaces will likely play a role in the development of enhanced MFC and MEC devices.

In an example of a multidisciplinary approach for modifying bio-based catalysts, a synthetic metabolic pathway for CO_2 fixation was achieved by recruiting 17 enzymes from nine organisms, including three enzymes subjected to computation-based redesign, to maximize the conversion process and improve bio-based catalytic processes for CO_2 fixation. Such multidisciplinary approaches could potentially enable novel bio-based catalyst pathways for water remediation.

In related work, remarkable successes have been achieved in the development of artificial enzymes that integrate synthetic metal complexes as active sites within protein host environments. These enzymes have been designed to carry out entirely abiotic, needs-directed catalysis within bio-based frameworks [101–103]. These accomplishments demonstrated chemistry and cofactors that are not accessed in nature but are hosted in protein frameworks that can be operated in parallel or integrated with biological redox metabolism. Hybrid materials with integrated function are also being utilized to achieve human needs-directed function. Recent examples include the development of electrode architectures and microbial strains that cooperate to perform “artificial leaf” solar-to-fuel, CO_2 conversion catalysis [104, 105].

Electrocatalysis

Electrocatalysis for water treatment generally falls into the category of advanced oxidation processes (AOPs). As summarized in the recent review article by Moreira et al. [87], AOPs promoted by electrocatalytic processes are generally referred to as electrochemical AOPs (EAOPs). EAOPs have attracted increasing attention in recent years as effective approaches for water treatment. They can be categorized into four classes (Table 3): 1) anodic oxidation (AO) [106], 2) anodic oxidation with electro-generated hydrogen peroxide (AO-H_2O_2) [107], 3) electro-Fenton (EF) process [107, 108], and 4) photoelectro-Fenton (PEF)/solar photoelectro-Fenton (SPEF) processes [106]. The first three are exclusively electro-catalytic processes, whereas the last one could also be grouped with photocatalytic processes, which will be discussed in the next section.

Table 3. Four representative electrochemical advanced oxidation processes.
Adapted from Moreira et al. 2017 [87].

Anodic Oxidation (AO)	Water Oxidation at the Anode Surface: $M + H_2O \rightarrow M(^{\bullet}OH) + H^+ + e^-$
Anodic Oxidation with Electrogenerated H_2O_2 ($AO\text{-}H_2O_2$)	Reactions of AO + H_2O_2 Electrogeneration at the Cathode: $O_{2(g)} + 2H^+ 2e^- \rightarrow H_2O_2$
Electro-Fenton (EF)	Reactions of AO, $AO\text{-}H_2O_2$ + Fenton's Reaction: $Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + {}^{\bullet}OH + OH^-$ Fe^{3+} Regeneration to Fe^{2+} at the Cathode: $Fe^{3+} + e^- \rightarrow Fe^{2+}$
Photoelectro-Fenton (PEF) Solar Photoelectro-Fenton (SPEF)	Reactions of AO, $AO\text{-}H_2O_2$, EF + Photolysis of $FeOH^{2+}$: $FeOH^{2+} + hv \rightarrow Fe^{2+} + {}^{\bullet}OH$ Photolysis of Ferricarboxylate Complexes: $Fe^{3+}(L)_n + hv \rightarrow Fe^{2+}(L)_{n-1} + L^{\bullet}_{ox}$

Anodic oxidation. AO represents a heterogeneous electrocatalytic process occurring at the anode surface. It shares traits with the oxygen evolution reaction (OER) for water splitting, but the objective here is to produce reaction intermediates, such as hydroxyl radicals, instead of oxygen as the complete OER product. Degradation of organic pollutants through AO involves multiple electrochemical steps, including direct electron transfer to the anode surface and formation of reactive oxygenated species, such as physisorbed •OH, through interfacial oxidation of water. The •OH species can react directly with organic pollutants at the anode surface or form hydrogen peroxide and release it into solution for subsequent oxidative reactions. The AOP involving H_2O_2 generation is also known as AO-H_2O_2. Degradation of organic pollutants by •OH or H_2O_2 can be achieved through either partial oxidation or total mineralization, converting them all the way to CO_2 and water. The efficiency of AO depends, among other factors, on the type(s) of catalyst materials used at the anode. The commonly accepted idea is that a higher potential for O_2 evolution at the anode catalyst will lead to weaker interaction between catalyst surface and hydroxyl groups and, therefore, higher chemical reactivity toward oxidation of organics.

Traditional OER catalysts, such as RuO_2, IrO_2, and Pt, generally have lower overpotential with stronger binding to •OH and higher cost, limiting their effectiveness as catalysts for AO. Some of the "inefficient" OER catalysts, such as transition metal oxides (PbO_2, SnO_2, TiO_2, etc.) and boron-doped diamond, produce high OER overpotential and weak binding with hydroxyl groups and are therefore considered more efficient AO catalysts [109]. Although higher catalytic overpotential could lead to more reactive oxygenate intermediate production, lower operating potential is desired since it is directly related to the operating cost. The challenge is how to produce high concentration of •OH with weak binding to catalytic sites at lower onset voltage. There has been substantial research in recent years in developing precious-metal-free catalysts with low OER potential for water splitting-hydrogen production. Such materials tend to produce two-electron process OER with low OH binding, suggesting they could serve as effective catalysts for water treatment.

In the presence of air, oxygen in the solution can often be reduced to H_2O_2 through two-electron processes. AO processes carried out with electrochemical production of this oxidant are referred to as anodic oxidation with electrogenerated H_2O_2 (AO-H_2O_2). Hydrogen peroxide is a weak oxidant that can attack certain organic pollutants. At present, porous cathodes with three-dimensional architecture and high specific surface area are preferred catalysts for H_2O_2 electrogeneration.

Electro-Fenton process. The classical Fenton reaction uses a mixture of H_2O_2 and Fe^{2+} and is a homogeneous reaction. When combined with electrochemically produced H_2O_2 and the addition of Fe^{2+} to the bulk, the process is called the electro-Fenton (EF) process. EF processes aim to produce additional •OH from H_2O_2 generated from electrocatalytic processes through interaction with ferrous ions. Since •OH is significantly more reactive than H_2O_2, EF processes could substantially improve the efficiency of organic pollutant destruction.

Photocatalysis

Photocatalysis has been investigated extensively for pollution abatement in water. Similarly to electrocatalysis, the working principle of photocatalysis is also based on the concept of AOP. Generally, the photon energy from a natural or manufactured light source is converted to highly oxidative species in the presence of water and oxygen; these species subsequently oxidize trace organic compounds and disinfect pathogens in water. An additional potential application is in degradation of organic and biological foulants on membranes and other water-system elements. Since these pollutants are usually charge neutral, photocatalysis plays an important role in water treatment technology and complements other, charge-driven treatment technologies such as the electro-capacitive methods discussed earlier. Photocatalysis offers some advantages such as ambient operating temperature and pressure, potential complete conversion of contaminants, and low operating costs. Both heterogeneous and homogeneous photocatalytic approaches have been and are continuing to be explored [110].

Heterogeneous photocatalysis. Heterogeneous photocatalysis in this context generally refers to a system with a solid-state catalyst in aqueous solution. Although several semiconductor materials, such as TiO_2, ZnO, and CdS, have been explored as the photocatalysts for water treatment, the most extensively studied system is TiO_2. Compared to others, TiO_2 is the most active for photon energies from 300 nm to 390 nm. It is also highly stable throughout multiple photocatalytic cycles without releasing toxic byproducts, such as those found in Cd- or Ga-based systems. The operating principle of TiO_2 has been widely studied and is illustrated in Figure 21. When a photon with energy greater than the band gap of TiO_2 (3–3.2 eV) strikes a titania microcrystallite, a lone electron will be photo-excited to the empty conduction band, leaving behind an unfilled valence band and forming an electron–hole pair. The light wavelength for such photon energy corresponds to <400 nm, in the ultraviolet region of the spectrum. Some studies have worked toward shifting absorption into the visible range to reduce costs, potentially even exploiting sunlight. Under ideal conditions, the electron-hole pair will separate, and the electron will react with scavenger molecules, such as O_2, before recombining with the hole to produce undesirable light or heat. The hole can react with water to form reactive species such as •OH, which is the key component to further react with and degrade organic pollutants or pathogens in water through radical oxidation and charge transfer. Various reaction paths have been proposed and investigated. The critical step is to prolong the

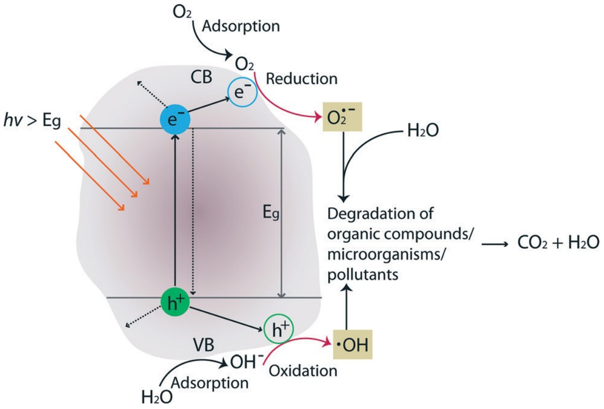

Figure 21. Schematic illustration showing degradation of organic compounds, microorganisms, or pollutants by formation of photoinduced charge carriers (e−/h+) on the surface of TiO_2. Charge-carrier pathways are indicated in a solid arrow (alternative pathways are in a dashed arrow). From Lee et al. 2016 [57].

electron-hole pair lifetime through electron scavenging.

Homogeneous photocatalysis. Homogeneous photocatalysis typically refers to PEF or SPEF reactions. Such reactions generally occur in acidified solution in the presence of soluble iron hydroxyl or iron complexes. The light source initiates a redox cycle between Fe^{+3} and Fe^{+2}, whereas the hydroxyl radical, •OH, is formed during the process. Similarly to the case of heterogeneous photocatalysis, the hydroxyl radical is believed to propagate the destruction of organic pollutants through oxidation, although the detailed mechanisms are still under debate. Unlike TiO_2, these soluble iron hydroxyl or iron complexes can absorb not only UV radiation but also visible light up to a wavelength of 600 nm, which improves the photon energy utilization. A major drawback is that the pH of the solution has to be controlled to ~3 in order to prevent the precipitation of iron compounds. Such low pH, combined with catalyst separation issues, has significantly limited the applicability of homogeneous photocatalysis to date.

Conclusions and outlook

Water crises are among the greatest risks in the coming decades. Water is essential for virtually every aspect of human existence, yet traditional supplies of fresh water are dwindling while at the same time demand is steadily rising. Sitting at the core of the water challenge is the interrelationship between water and energy, two systems that are intertwined in innumerable ways. While the challenges surrounding water are formidable, they also represent tremendous opportunities. Issues range from identifying water-source quality and quantity to reducing water consumption and pollution to removing a plethora of diverse contaminants from water streams. Chemistry, biosciences, physics, materials sciences, and geosciences all have pivotal roles to play, as does leveraging the capabilities of national user facilities. An integrated strategy incorporating innovative basic science can guide technology research and development to address water–energy issues with impact at both the national and global scales.

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