BASIC RESEARCH NEEDS FOR
Energy and Water

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BASIC RESEARCH NEEDS FOR
Energy and Water

REPORT OF THE OFFICE OF BASIC ENERGY SCIENCES
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Table of Contents

Executive Summary

Water is precious; it has no substitute as a vital resource. It is essential not only for life, but also for practically all forms of economic activity. The food we eat, the clothes we wear, the goods we use, and the electricity we consume all require water. Water — in both quantity and quality — is one of the world's most critical resources. The global importance of water presents enormous opportunity for innovation spurred by basic science to better understand at a fundamental level energy, water, and their interrelationship. Energy-water systems, whether manufactured or part of the natural world, exhibit extraordinary dynamics and complexities. To make possible a transformation to a future where fundamental processes underlying energy-water systems are quantified and harnessed for societal benefits, understanding of the chemical processes and materials underlying the interdependence of energy and water must be advanced. These interdependent energy and water issues (energy-water issues) intersect with national and international priorities. The challenges we face for energy-water systems are, in fact, an opportunity to shape a sustainable future for the nation and the world and present an enormous opportunity for fundamental energy science. Basic research — spanning chemistry, physics, geosciences, biosciences, and materials sciences — is essential to answering many questions related to energy and water systems.

Energy and water are deeply interrelated. The connection between water and energy means that issues with one — for instance, too much or too little water — can profoundly affect the other. The looming challenge is to address the coupled needs of sufficient energy and clean water for a thriving economy and national security. Cooling in power plants, refining petroleum, producing fuel, and extracting energy resources from the earth make up a significant fraction of water use. Conversely, water treatment, distribution, and use represent significant energy demands.

Every water source is unique, and every use of water has its own specific requirements for quality and demands on energy. Scientific understanding is needed to develop a toolbox from which stakeholders can assemble modular solutions to address distinctive, local energy-water issues and provide sufficient, fit-for-purpose water with minimal energy expenditure. Discovery of new membrane materials, for example, could offer selective filtration of targeted contaminants with minimal energy consumption and exhibit resilience to fouling and harsh environments. Deeper insights into fluid transport and reactivity in subsurface processes could enable enhanced resource recovery and better management of aquifers. Innovation based on greater knowledge of catalytic mechanisms could enhance industrial production while reducing water pollution and energy costs. A combination of separation techniques developed through new and enhanced understanding of fundamental processes could turn wastewater into a valuable, reusable resource.

It is now clear that ensuring robust and secure energy and water systems will require a significant basic scientific research effort. Science questions that underpin water resiliency and water-energy systems span 12 orders of magnitude in length scale, from the nature and implications of hydrogen bonding, to the state and movement of water through aquifers. Addressing challenging questions requires advances and integration of basic chemical, geological, biological, material, and computational sciences. Recognizing the tremendous scope and scale of basic research

needs in the energy-water domain, the U.S. Department of Energy's Office of Science, Office of Basic Energy Sciences (BES), sponsored a workshop on "Basic Research Needs for Energy and Water," which was held near Washington, D.C., January 4–6, 2017. Attended by more than 100 leading national and international scientific experts in chemistry, physics, materials sciences, biosciences, and geosciences related to the energy-water system, the workshop addressed basic research necessary to improve water use for industrial applications and energy production and to increase fit-for-purpose water availability and energy efficiency as well as crosscutting scientific research needs. The workshop identified four Priority Research Directions (PRDs) that will lay the foundation to better understand materials and processes relevant to energy-water issues and harness their potential for technological impact.

Priority Research Directions

Predict Static and Dynamic Properties of Multi-Component Fluids

Problems at the intersection of energy and water involve complex fluids, including fluids containing water, ions, gases, heavy metals, polymers, surfactants, nanoparticles, and other constituents. New molecular-level understanding is needed to reliably predict and control the emergence of structures and phases. Fundamental research is particularly needed to understand and thus ultimately predict thermodynamic, kinetic, transport, and deformation properties of complex fluids.

Achieve Mechanistic Control of Interfaces and Transport in Complex and Extreme Environments

Interfaces — and confinement of fluids by interfaces — play a central, often dominant, role in the diverse transport and reactive processes associated with energy-water issues, from membranes and catalysts to subsurface resource recovery. New fundamental insights into interfacial interactions and reactions are needed to provide a basis for design and control in natural and engineered water-energy systems. Such basic research efforts include the molecular-level understanding of reactions at pore or mineral interfaces and the role of interfacial electrostatics and charge in driving separations.

Exploit Specific Material–Fluid Interactions to Design and Discover Innovative Fluids and Materials

The predictive codesign of new materials and fluids to exploit material-fluid interactions will enable step-change improvements in tunability and selectivity of purification, transformation, and transport processes in the energy-water systems. Research will use the fundamental concepts uncovered through PRDs 1 and 2 as a foundation for the design of new materials and fluids with enhanced or new properties. Key opportunities include new complex fluids for tailored flow and reactivity and solid-state materials ranging from coatings to catalysts to separations media. Materials of this kind are critically needed to enable development of multi-functional and selective adsorbent materials and new approaches to creating self-healing and fouling-resistant membranes for water purification.

Advance Science to Harness the Subsurface for a Transformational Impact on Water

The subsurface can play a significant role in a future where water supply and demand are in perpetual, sustainable balance. Harnessing the potential of the subsurface for game-changing benefits requires not only an understanding of the challenges identified above (complex fluids, interfaces, and material-fluid interactions), but also fundamental knowledge of how the processes occurring at native scales aggregate to govern the behavior of multi-phase subsurface systems. This understanding can, in turn, make possible the ability to image, predict, and control these processes.

Detailed discussions of the four PRDs, along with guidelines and recommendations for achieving their objectives through fundamental scientific research, are provided in Chapter 2 of this report. Chapter 3 includes the detailed background information on the energy-water connections developed as part of the workshop.

1. Introduction

Water is essential to life on earth and is also the hidden backbone of virtually all economic activity, including playing a critical role in energy production. Figure 1.1 reveals the diverse ways in which we use water in the United States. The vast majority of water withdrawals are for purposes other than domestic use. 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. Not only do energy needs require vast amounts of water for fuel production, mining, hydroelectricity, and cooling in power plants, but energy is needed to pump, treat, and distribute water, as well as to collect, treat, and discharge wastewater. As discussed in more detail in the factual resource document,[1] these interdependent energy and water issues (energy-water issues) represent significant challenges that must be addressed to enable sufficient energy and clean fit-for-purpose water for a thriving economy and national security.

Energy use for water can vary dramatically from one region to another. The specific combination of factors, such as water source (e.g., surface water vs. groundwater), composition (fresh vs. saline), intended end use, climate, distribution distance and topography, and wastewater treatment requirements, varies greatly among locations. Between 4 and 13% of the nation's electricity generation is used for water purification, distribution, and point-of-use consumption, although such consumption is far from homogeneous. California, for example, consumes 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 reduces energy requirements to transport and treat water.

While power generation is the largest water *withdrawal* sector, the largest water *consumption* sector is agriculture. 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. The third largest sector for water use is public supply, representing about 12% of overall U.S. withdrawals. This is the water that comes to homes and

Figure 1.1. Water withdrawals by sector in the United States (Data from USGS.gov, 2010).

businesses from city, county, and private water utilities. 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

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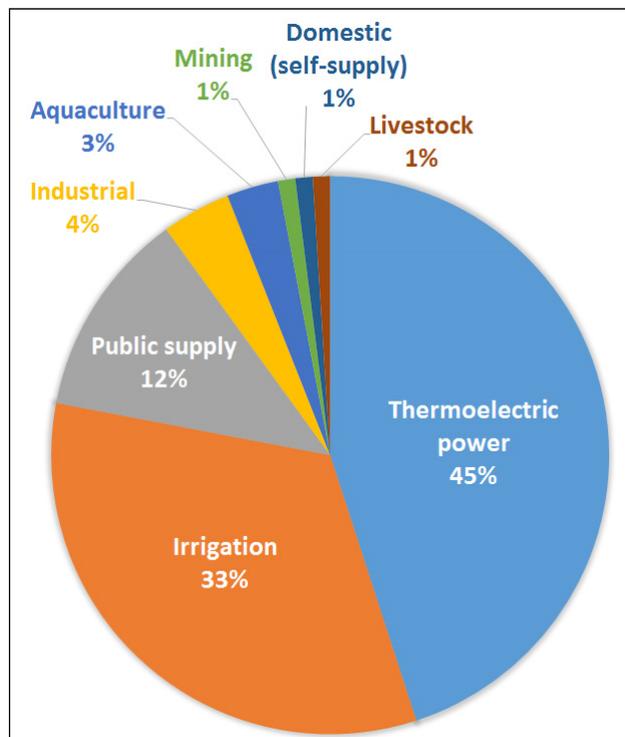[1] *Energy and Water Factual Status Document*. Resource document for the Workshop on Basic Research Needs for Energy and Water. This document is available on the DOE BES Community Resources, Reports, webpage at https://science.energy.gov/bes/community-resources/reports.

least some stages of production. A given product undergoes many steps of manufacturing, from extraction of raw materials through numerous processing and transportation stages.

The centrality of water and energy to the health and prosperity of our society, and the impact they have on our surrounding ecosystem, heightens the need to develop a deeper understanding of the connections between water and energy infrastructure. The increasing worldwide demand for these essential resources presents increasing energy, security, economic, and environmental challenges, but also constitutes opportunities. The 2014 U.S. Department of Energy (DOE) report on the Water-Energy Nexus captures many of the systems-level needs and opportunities for developing new technologies [4]. Strategic fundamental science that advances new knowledge and understanding is needed to develop these new technologies and address water-energy issues with impacts at both national and global scales. This research spans chemical, biological, geological, materials, and computational sciences, and can make exciting new uses of DOE user facilities. Leveraging its world-class facilities and expertise, the DOE is poised to provide the transformative fundamental and use-inspired science to underpin novel solutions necessary to address the wide range of energy-water challenges summarized above.

In recognition of the tremendous scope and scale of basic research needs in the energy-water domain, the Basic Energy Sciences program of the Office of Science of the DOE held a 3-day workshop on the subject near Washington, D.C., on January 4–6, 2017. The workshop, "Basic Research Needs for Energy and Water," was attended by more than 120 leading national and international scientific experts, program managers, and observers.

Four Priority Research Directions (PRDs) were identified at this workshop.

PRD 1 — Predict Static and Dynamic Properties of Multi-Component Fluids

Problems at the intersection of energy and water involve interactions of complex aqueous solutions, which can include water, gases, colloids, microbes, polymers, and other constituents. Better understanding of these fluids at a molecular level is necessary in order to reliably predict and control the emergence of structures and phases in these complex environments. We currently have an incomplete understanding of the molecular-to-macroscopic properties and aggregated behavior of complex aqueous solutions under conditions relevant to energy applications. Ion/solute solvation and speciation from dilute to concentrated non-ideal conditions are all relevant. To enable transformative advances, one needs to be able to predict the mechanisms and kinetics of nucleation, growth, self-assembly, and phase separation, which involve complex, collective molecular phenomena that are poorly understood. There is currently a limited ability to quantify and simulate these complex solutions, including providing an accurate description of intermolecular interactions, such as dispersion forces and hydrogen bonding, over sufficiently long length and timescales. Basic research is needed to predict thermodynamic properties of complex fluids and the rheological and reactive aspects of such fluids; to enable detection and speciation of trace contaminants in complex aqueous mixtures, which are of critical importance for delivering fit-for-purpose water; and to advance tools to quantify the presence and distribution of trace species in complex aqueous mixtures.

PRD 2 — Achieve Mechanistic Control of Interfaces and Transport in Complex and Extreme Environments

Interfaces — and confinement of fluids by interfaces — play a central, often dominant, role in the diverse transport and reactive processes associated with energy-water issues, from water treatment membranes and catalysts to subsurface resource recovery. Despite their prominence, the unique environments on and near interfaces in complex aqueous systems are poorly understood. Interactions between real-world subsurface, environmental, and engineered materials are dynamic. These interfacial interactions occur on many timescales, altering macroscopic transport, reaction, and mechanical properties in ways that are not currently understood. Basic research is needed to understand interfacial interactions and reactions — the processes controlling affinity/reactivity, the transport of fluids through rigid or deformable porous media, including both natural and manufactured materials, and the role of electrostatics and charge at interfaces to drive separations. Such research on these processes and materials properties can provide insights into the design and control of transport in diverse environments.

PRD 3 — Exploit Specific Material-Fluid Interactions to Design and Discover Innovative Fluids and Materials

The design of new materials that exploit specific material-fluid interactions will enable unprecedented tunability and selectivity of purification and transformation processes. Complex fluid mixtures that are prevalent in the expansive interaction of energy and water issues pose a particular and distinct challenge in materials design. Addressing this challenge will require, and build on, understanding of the intersection between, and interdependence of, inherently complex multi-component, multi-phase aqueous fluids, and multi-functional materials to control performance for separations and sorption media, coatings, and catalysts. Development of functional materials with targeted catalytic properties and advances in reactive redox approaches both have great potential. The ability to tightly control pore size distributions in membranes and to exploit novel transport mechanisms, including active pumping (meaning any mechanism that is able to drive a solute up a concentration gradient), is an important future research direction. Exploiting new insights into material-fluid interactions will allow, for instance, development of materials that have enhanced resistance to foulants and to the oxidative treatments that are widely used to regenerate membranes. Basic research is needed for the design of complex fluids and materials to tailor flow and reactivity properties.

PRD 4 — Advance Science to Harness the Subsurface for a Transformational Impact on Water

Harnessing the tremendous potential of natural environments for in situ water storage and treatment is critical for ensuring sustained future clean water supplies and water-dependent energy strategies. Realizing this opportunity will require revolutionary advances in our ability to sense, predict, and manipulate nonlinear, multi-phase physical, chemical, and biological processes in natural and designed subsurface materials. New approaches must consider the cumulative influence of the complex fluids, interfaces and transport, and materials by design PRDs described above, with an emphasis on their manifestation in the context of naturally variable geologic material and hydro-geochemical gradients. Particular challenges are associated with quantifying fluid flow and reactions in variably saturated media and engineered geomaterials, the development of 4D networked monitoring systems and multiscale mechanistic simulation capabilities, and approaches to control aggregated systems behavior through in situ manipulation of small-scale coupled processes.

2. Priority Research Directions for Energy and Water

The workshop discussions identified four Priority Research Directions (PRDs) that define the basic research needed to develop energy-relevant technologies for energy-water issues. Each PRD is discussed in depth with the associated research thrusts in this chapter. As background, Chapter 3 of the report provides an in-depth assessment of the current status of research issues in the energy-water inter-relationship.

Table 1: List of Priority Research Directions and Associated Research Thrusts

1. **Predict Static and Dynamic Properties of Multi-Component Fluids**
   How can we predict and control molecular-to-macroscopic properties and the behavior of complex, multi-component fluids?
   Thrust 1a: Thermodynamic, Chemical, and Transport Properties of Complex Fluids
   Thrust 1b: Rheology of Complex Fluids

2. **Achieve Mechanistic Control of Interfaces and Transport in Complex and Extreme Environments**
   What are the underlying mechanisms of affinity and reactivity at interfaces in aqueous systems?
   Thrust 2a: Fundamental Understanding of Interfacial Affinity and Reactivity
   Thrust 2b: Predictive Understanding of Fluid Transport through Natural and Manufactured Porous Media
   Thrust 2c: Manipulating Interfacial Charge for Separations and Reactions

3. **Exploit Specific Material-Fluid Interactions to Design and Discover Innovative Fluids and Materials**
   How can we co-design the dynamic interactions between materials and reactive fluids for unprecedented tunability?
   Thrust 3a: Designing Complex Fluids
   Thrust 3b: Designing Solid Materials

4. **Advance Science to Harness the Subsurface for a Transformational Impact on Water**
   How do we develop the ability to predict and control multiscale, multiphase, multiphysics subsurface properties?
   Thrust 4a: Fundamental Understanding of Fluid Flow and Reactions in Complex Subsurface Systems
   Thrust 4b: Understanding Reactive Geosystems
   Thrust 4c: Fundamental Advances in Multi-Scale Imaging and Simulation

2.1 PRD 1 — PREDICT STATIC AND DYNAMIC PROPERTIES OF MULTI-COMPONENT FLUIDS

Many aspects of energy–water systems involve the interactions of multi-component aqueous solutions and other complex fluids. The ability to reliably predict and control the emergence of structures and phases in these fluids requires fundamental knowledge of the underlying mechanisms, which demands a molecular-level understanding of the interactions between the components.

2.1.1 Scientific Challenges

We currently have an incomplete understanding of the molecular-to-macroscopic properties and behavior of complex fluids at conditions relevant to energy-water systems. Most of these complex fluids are multi-component aqueous solutions, but other complex fluids, such as supercritical carbon dioxide (CO_2) or oil, are also important. With water as the solvent, aqueous solutions may include ions, gases, heavy metals, hydrocarbons, polymers, surfactants, colloidal nanoparticles, radioactive materials, persistent organic pollutants, and microbes. Aqueous solutions are present in natural and engineered systems with a wide range of chemical compositions, temperatures, and pressures. For example, in water purification, the incoming water is often a complicated mixture of water, solutes, particulate matter, and microorganisms. As another example, subsurface energy applications involve complex multi-phase mixtures, often containing foams, polymers, and proppants, as well as low-water-content or non-aqueous fluids, such as supercritical CO_2. A critical aspect of water-energy challenges is to consider the aggregate reactivity and rheology of fluids containing a full range of solutes and understand how the characteristics of individual constituents influence aggregate properties. Almost all problems in energy-water systems involve the complex fluids in a confined environment or in contact with interfaces. Nonetheless, it is important to consider bulk fluids as well as more complex systems involving interfaces and confinement. It is therefore necessary to develop appropriate fundamental descriptions of these bulk fluids.

The ability to model complex solutions is limited, impeding reliable predictions for high-solute concentrations and long length and timescales. For many applications related to energy and water, it is important to be able to model or otherwise theoretically describe these complex fluids. Hydrogen bonding is the key to aqueous systems, and, even in pure water, this complicated interaction leads to a wide variety of anomalous properties. Hydrogen bonding is cooperative and depends extensively on local chemical environments. It is therefore important in any theoretical modeling that such hydrogen bonding be described properly. In ab initio calculations, the inclusion of dispersion interactions has been problematic, but its proper description is also imperative. Simulations of complex fluids often require many molecules and converge very slowly; therefore, simulations over long space and timescales are required.

Predicting ion/solute solvation and speciation from dilute to concentrated non-ideal conditions is especially important. One of the simplest, but still important, problems involves ion solvation thermodynamics and dynamics in salt solutions. Surprisingly, we do not yet know how to accurately predict solubility limits of even the simplest salts (e.g., sodium chloride [NaCl], a snapshot of which is shown in Figure 2.1.1 [1]). The isolated water molecule is well understood from experiments and quantum mechanical calculations. However, when a large number of water molecules form a liquid, we have a limited ability to model and simulate these complex solutions. For energy-water applications, it is especially important to understand the properties of water around ionic or hydrophobic solutes, which are strongly influenced by hydrogen bonding. When describing these intermolecular interactions in the presence of solutes and interfaces we need to utilize the emerging power of advanced computational strategies and massively parallel algorithms to enable high accuracy and prediction for large systems including dispersion forces and hydrogen bonding.

Another difficult problem involves elucidating water diffusion coefficients as a function of salt concentration for different salts. For example, it has been shown experimentally that this diffusion coefficient decreases as a function of salt concentration for NaCl, but increases for cesium iodide (CsI). Understanding of this interesting observation from simulation/theory has proven elusive [2]. Trends for dynamical observables are especially difficult to predict/ understand at high concentrations or in complex mixtures, when the solutions are most certainly not ideal.

Detection and speciation of trace contaminants in complex aqueous mixtures are of critical importance in any setting where water quality is of interest. A wide range of analytes are of concern as they can have an effect, even at low concentrations. In a variety of situations, the inability to routinely discriminate between multiple species of a given contaminant (e.g., oxidation states or ionic complexes) strongly inhibits the ability to regulate or mitigate these contaminants. For example, arsenic (As)(III) species are far more toxic than As(V) species, mercury methyl is taken up more readily in the food web than inorganic mercury species, and metals may be present predominantly as either cationic, neutral, or anionic species depending on the concentrations of ligands in the fluid [3]. Fundamental advances in tools to quantify the presence of trace species in complex aqueous mixtures are required to improve this situation.
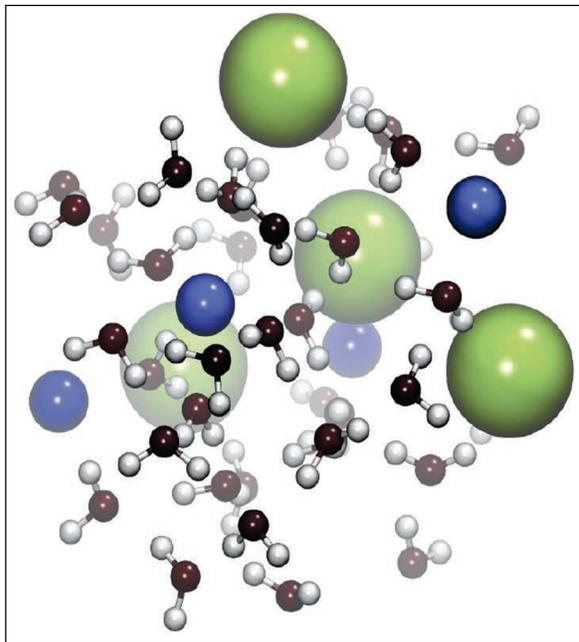

Figure 2.1.1. Modeling aqueous solvation in complex liquids. A schematic picture of water molecules interacting with cations (blue) and anions (green).

Understanding of mechanisms and kinetics for nucleation, growth, self-assembly, and phase separation is critical to allow prediction of phase behavior. Complex mixtures are often not at equilibrium, and various types of nucleation or self-assembly can occur. Examples include the nucleation of ice or clathrate hydrates or the self-assembly of surfactants into micelles. Nucleation and self-assembly can be followed by growth and even phase separation, which can lead to fouling of membranes and pipes. Thus, understanding the mechanisms and kinetics of these processes is vital.

2.1.2 Research Thrusts

PRD 1 is organized into two scientific thrusts. The first focuses on the fundamental science challenges associated with developing models capable of predicting thermodynamic properties of complex fluids (Thrust 1a). The second underscores the difficulty of understanding the fundamental interactions and processes controlling rheological and reactive aspects of such fluids in energy-water settings (Thrust 1b). The remainder of this section provides the technical details for each of these thrusts.

Thrust 1a: Thermodynamic, Chemical, and Transport Properties of Complex Fluids

A fundamental understanding of the thermodynamic, chemical, and transport properties of complex fluids forms the basis for selecting, designing, and optimizing separation and purification processes. These properties are also essential in assessing the reactivity of aqueous mixtures for fundamental science studies and in more applied processes as related to scaling, fouling, decontamination, and resource recovery, and in assessing the stability of materials in aqueous environments. Aqueous fluids pertinent to water-energy systems include very high ionic strength brines and aqueous solutions containing organic chelators, surfactants, and colloidal particles. While the chemistry and thermodynamics of these systems have been studied, much remains to be learned. Virtually all aspects of water processing in industry and electricity generation benefit from reliable data and predictive modeling of thermodynamic properties, along with advances in separation and purification technologies. Equations of state for high-salinity systems also containing soluble surfactants as a function of temperature and pressure must be developed, given their relevance in hydraulic fracturing, remediation of nuclear waste, and other aspects of energy-water systems.

CLATHRATE HYDRATES

Clathrate hydrates (or gas hydrates) are solid inclusion compounds that form when water and gas come into contact at high pressure (e.g., 60–300 bar) and low temperature (~277 K). Under favorable thermodynamic (P, T, x) conditions, water molecules hydrogen-bond together to form water cavities that encapsulate small gas molecules (e.g., methane, CO_2); the cavities are connected together in a three-dimensional (3D) crystalline lattice. These ice-like clathrate hydrate crystals can contain large amounts of gas (e.g., 1 volume of gas hydrate can contain as much as 164 volumes of gas at standard temperature and pressure). Understanding and controlling the fundamental molecular mechanisms of clathrate hydrate formation/dissociation and their interfacial properties is important in the transport of oil/gas in subsea pipelines. In these settings, clathrate hydrate formation can lead to plugging of the pipelines, with severe safety and environmental risks. The production of methane from in situ dissociation of naturally occurring methane-hydrate-bearing sediments under the ocean floor along the continental margins or in permafrost regions is of increasing interest as a future energy resource.

Gas hydrates form in pipelines in the presence of brines and polymers/surfactants (often used for hydrate crystal inhibition/slurry transport). Critically, there is still much to be learned about the molecular-level effect of these complex fluids on clathrate hydrate nucleation and growth and interfacial interactions. In addition, the interfacial properties of clathrate hydrates formation and dissociation are critically important, yet the structure, properties, and dynamics (nucleation and growth pathways) of these systems are poorly understood at the molecular level [4,5]. There is a need for strong coupling between experiment and modeling to quantify complex gas hydrate fluids and their interactions at interfaces, with the application of advanced high-resolution (temporal and spatial) molecular tools to unravel these complex structure, dynamic, and interfacial phenomena.
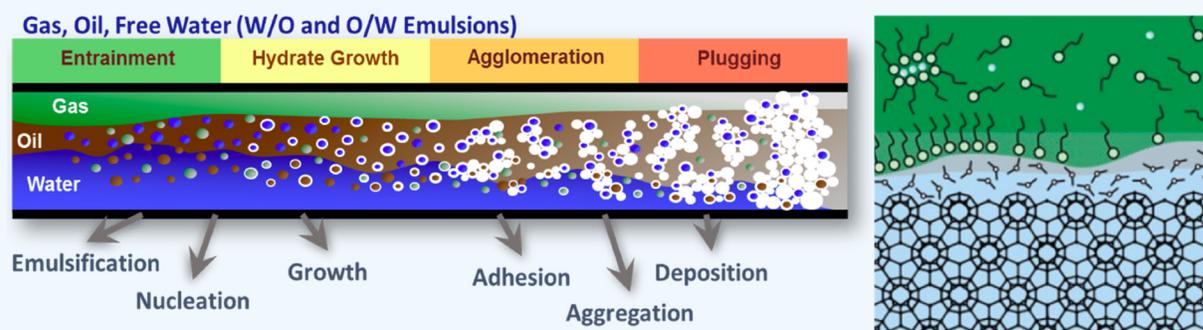
Left: Conceptual picture of gas hydrate plugging in an oil pipeline. Right: Cartoon of interfacial phenomena at the clathrate hydrate (bottom network)/water (blue)/oil (green)/surfactant interfaces.

Solutions with high solute concentrations present a particular challenge to experiment and theory. In such systems, solvent sharing and contact ion pairing likely prevail, strongly influencing solute availability and transport. Despite the importance of this situation, molecular-scale depictions of solute association structures and their effects on chemical processes remain poorly understood (Figure 2.1.2 [6]). An important goal is the extension of current technology and computational methods for these high-concentration regimes. Elucidating the fundamentals of interfacial and bulk solvent and solute dynamics, structure, and interactions will inform models of reactivity, flow, reaction mechanisms, solvation mechanisms, aggregation kinetics, and dissolution behaviors.

A critical enabler to the ability to model solution and dispersion properties is the development of new methods and descriptions of molecular interactions that capture complex solute-solute and solute-water interactions. This task will require close coupling of experimental research and computational modeling of processes in complex fluids. Given the complexities and heterogeneities that are present in the fluids and media involved, understanding the transport of water and solutes through structurally and compositionally heterogeneous media
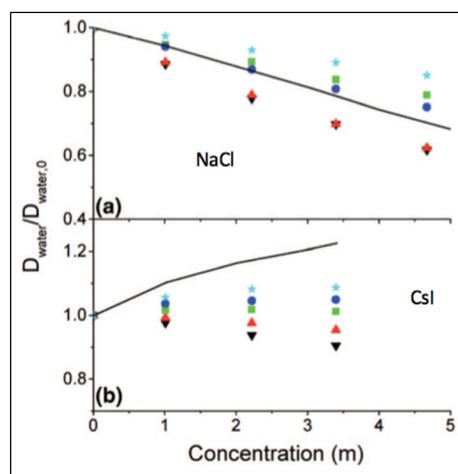

Figure 2.1.2. Comparison of measured water diffusion coefficients in aqueous NaCl and CsI electrolyte solutions (black lines) with calculated diffusion coefficients. Note the poor fidelity of theoretical models in predicting the diffusion coefficient in the CsI electrolyte.

such as those in geochemical processes is critical. These situations are complicated by complex interactions between solutes and water, as well as those with the walls of the media. Attention should also be paid to the possible structural and compositional evolution of the media as a consequence of fluid transport. In response to this challenge, laboratory models that better allow the accurate capture of fluid transport through heterogeneous media are needed. Such models should accurately capture the effects of pore size distribution and pore connectivity on fluid transport, likely requiring fundamental advances in materials characterization and representation.

In addition to modeling, significant potential exists to exploit emerging in situ spectroscopy, scattering, and imaging probes to unravel the structure and dynamics of solvation, speciation, nucleation, and self-assembly. To measure properties of these complex solutions requires the ability to take advantage of new, state-of-the-art photon, neutron, and electron experimental techniques with improved time and space resolution. These techniques include, for example, vibrational 2D infrared (IR) spectroscopy, 4D nano x-ray computed tomography, and in situ neutron and micro-beam x-ray scattering (Figures 2.1.3; 2.1.4 [7]) that are available at national synchrotron facilities.
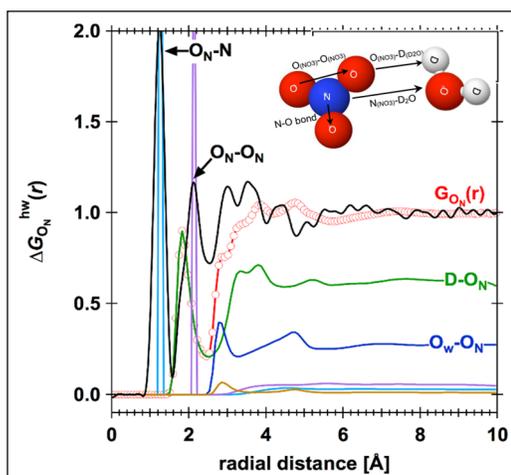

Figure 2.1.3. Combined computational simulation with neutron/x-ray scattering. Neutron pair distribution function analysis and molecular dynamics simulation of aqueous nitrate ion. The experimental data, in black, are directly compared and interpreted using the computational simulation, including peak assignments, position, and ion pair formation. New algorithm developments are enabling simulation of combined x-ray and neutron scattering data in order to understand solvation phenomena such as ion pair structure and stability. Since water is a polarizable environment, the description of some features on anion hydration behavior are improved by the use of models involving induced-dipole polarization. These data also provide an opportunity for force-field development and optimization.
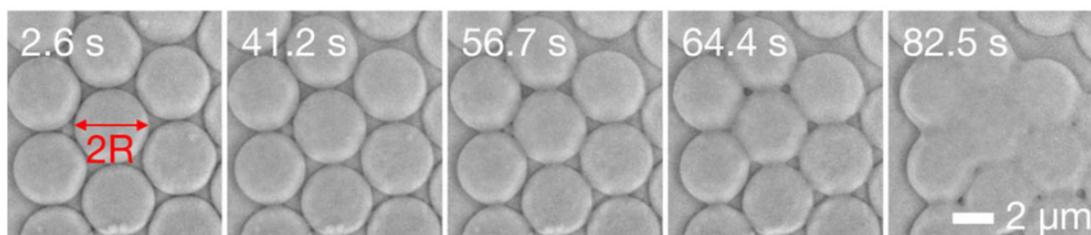
Figure 2.1.4. The structure and dynamics of solvation, speciation, nucleation, and self-assembly can be probed by exploiting emerging in situ spectroscopy, scattering, and imaging probes. As an example, synchrotron Transmission X-ray Microscopy (TXM) has been used to capture the sintering of polymer colloid particles with a spatial resolution of <30 nanometers (nm) and a time resolution of a few seconds. Other state-of-the-art photon, neutron, and electron experimental techniques include vibrational 2D IR and sum-frequency generation, in situ neutron and micro-beam x-ray scattering, and environmental transmission electron microscopy.

The development of accurate and cost-effective methods to quantitatively analyze water contaminants in complex environments is strongly limited by fundamental challenges. Although advanced analytical methods are important in research settings, there is also a great need for robust methods that can be readily used in practical settings by personnel with limited training. A key challenge in this area for both research and practical application is the ability to detect and analyze low-concentration species in complex solutions that also have high levels of non-target compounds that can obscure analysis. It is therefore vital that sensing or analysis techniques be viable in the presence of potentially confounding species. Improved techniques for contaminant detection will also be valuable in understanding the potential for methods that sometimes promote chemical transformations (e.g., disinfection with ozone) converting contaminants into even more harmful products.

One research priority is the development of tools for speciation in complex environments. Improved methods for differentiating oxidative states of species in nuclear waste streams, for example, could have significant benefits because of the differing properties of these species. Methods that ultimately allow untrained workers to quantify the presence of these species at substantially lower detection limits than are currently achievable would allow more targeted regulation of water purity and remediation activities. Significant opportunities exist in the development of sensor reagents with high-precision molecular recognition, and in the combination of these reagents with detection schemes allowing rapid and accurate measurements. Approaches to this issue could include, for example, micro- or nano-fluidic platforms. As already highlighted, it is critical that tools for this purpose be developed for use with the complex aqueous mixtures characteristic of real applications with the possibility of deployment in the field. These methods all rely on a fundamental knowledge of the chemistry of speciation and molecular signatures and their effects on material properties.

The reactivity of low-water-activity fluids is increasingly understood to play a key role in energy water systems and presents challenges for predictions of chemical transformations. Low-water-activity systems of different types occur in a remarkable number of settings. Non-aqueous fluids with low but finite water solubilities occur in methane, ammonia (NH_3), and chlorine production, and compressed air energy storage. In these systems, there is evidence that water forms nanoscale water films on solid surfaces in which corrosion and other fluid-solid reactions can occur at high rates. Water activity is highly diminished in ultrahigh concentration salt solutions as found in industrial processes, some radioactive waste stockpiles, and subsurface brines, causing unexpected solvated species formation and introducing activation barriers to processes such as mineral nucleation [8]. In addition, controlling the water concentration in synthetic complex fluids, such as room-temperature ionic liquids or deep eutectic solvents, can enable molecular structures and reactions that are unlikely in bulk aqueous solution [9].

A principal example of such a fluid with relevance to energy-water systems is the reactivity of water-wet supercritical CO_2 with metal alloys and rock-forming minerals. Water-wet CO_2 is not an inert fluid but facilitates the corrosion of metal alloys,[10,11] as well as the dissolution of basalt and precipitation of carbonates [12] (Figure 2.1.5). These reactions presumably occur in spatially confined water films at surfaces, but descriptions and models for such systems are lacking. There is a need for new tools to study the chemistry of interfacial thin aqueous films to determine the effects of confinement upon basic processes like solvation, protonation-deprotonation, and electron transfer, and the stoichiometry and the rate equations for observed reactions.

Figure 2.1.5. SEM image of the products of the reaction of forsterite, Mg_2SiO_4, in water saturated at CO_2 35°C and 90 atm pressure for 14 days. The formation of magnesite, $MgCO_3$, must involve mineral reactions in thin surface water films.

Controlling the reactivity of water-wet non-aqueous fluids will be beneficial for many energy and subsurface systems, by reducing water use in unconventional oil and gas production, reducing corrosion, and extending the lifetime of gas transport and storage infrastructure. Enhanced oil recovery operations often involve alternating water-flooding and CO_2-flooding stages. It could be possible to control the reactivity of wet-CO_2 stages to alter the surface wettability and hydrocarbon release from depleted reservoirs [13].

Accurate measurements from well-defined systems for molecular-level model development and validation:
The development of predictive models that describe chemical systems on the molecular scale may include bottom-up approaches utilizing data obtained from high-level electronic structure calculations [14], top-down approaches utilizing data from (macroscopic) experimental measurements [15], or a combination of these approaches [16]. Regardless of the approach, accurate measurements for well-defined systems are pivotal for the validation of all predictive molecular models. For the plethora of energy-water systems in general, and for the associated separation

technologies in particular, there are significant needs for additional and more accurate experimentally measured thermophysical property data.

In certain cases, like adsorption equilibrium of gases and certain two-component liquid mixtures (see Figure 2.1.6 [17]) and diffusion properties of gases in microporous materials (see Figure 2.1.7 [18]), accurate experimental data exist and have been used successfully in model development and validation. However, even simple binary water /n-alkane systems with consistent validated interfacial tension experimental data are not available (see Figure 2.1.8 [19]). Interfacial tension data for immiscible water/organic mixtures are not only instrumental for enhanced oil recovery or oil spill mitigation, but also are needed for designing industrial processes such as emulsion polymerization or biphasic reactors. The liquid–liquid interfacial tension is just an example of a macroscopic property with data needs; other relevant properties are solubility limits for ions and organics and their interdependence in multi-component mixtures, osmotic pressure data for solutions with multiple ions; and the chemical potentials of solutes at finite concentration.
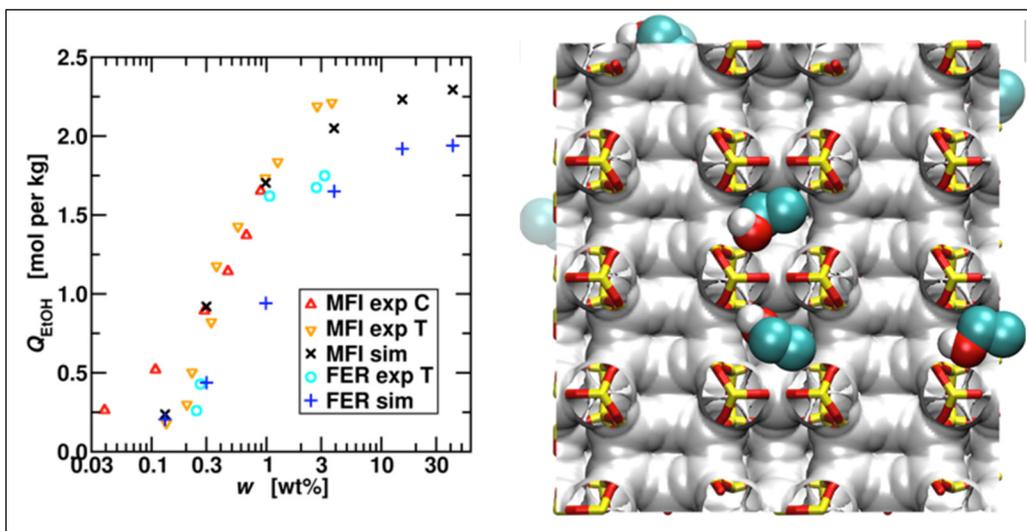
Figure 2.1.6. Experimental adsorption data provide validation for the prediction that zeolite FER (ferrierite) is a highly selective sorbent for the extraction of ethanol from aqueous solution. The snapshot on the right illustrates that ethanol molecules are preferentially adsorbed in sites that do not allow for water molecules to hydrogen bond with multiple ethanol molecules.
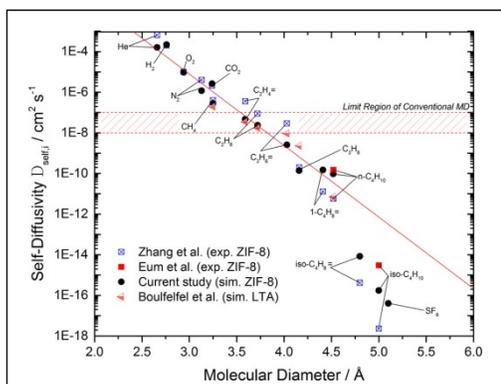
Figure 2.1.7. Comparison of measured and predicted infinite-dilution self-diffusion coefficients for small molecules and light key hydrocarbons at 308 K as a function of molecular diameter in ZIF-8, a prototypical metal-organic framework material.
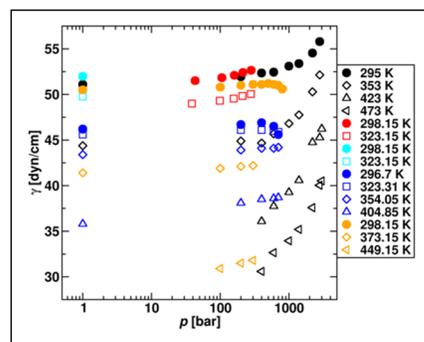
Figure 2.1.8. Compilation of experimental data for the interfacial tension of the water/n-decane system over a wide range of pressures and temperatures. The colors distinguish five literature sources, and the symbol types correspond to different temperature intervals (with filled symbols highlighting data at T ≈ 298 K). A significant data spread is found even at ambient conditions, and high-pressure data do not agree on whether the interfacial tension increases or decreases with pressure.

The examples above indicate multiple areas in which detailed characterization of complex systems could spur understanding and, ultimately, control of realistic solutions. Thorough measurements on molecular and mesoscopic scales are needed at a wide range of conditions motivated by real-world operations (including high temperature, high pressure, high salinity, and/or pH extremes) with multi-component, non-ideal solutions and multi-phase fluids in the presence of relevant substrates and confining geometries at equilibrium, steady-state, and gradient conditions. Beyond macroscopic properties, the development and/or validation of predictive molecular models [20–24] also benefits from microscopic-level property data, such as the information on the hydration structure of solutes and surfaces; the spatial and orientational distributions near interfaces, at surfaces, and in micro-heterogeneous environments; and the speciation (e.g., contact or solvent-separated ion clusters and size/shape/composition distribution for aggregates), hydrogen-bond lifetimes, and molecular or ionic transport at short timescales and/or in confined systems.

Fine-grained models and algorithms for aqueous thermodynamics and transport (molecular to continuum): The process condition space (temperature T, pressure P, $\underline{x}$) for many fluids of interest in water-energy systems lies well outside the regimes that can be described by many continuum models. For example, transport in ionic media has been described using Maxwell-Stefan relationships with the addition of an electrostatic potential field [25]. This deficiency, coupled with the constraint of net charge neutrality, sets up a field called the diffusion potential, which inhibits small ion motion (e.g., H^+) while accelerating larger ion motion (e.g., NO_3^-). While this framework correctly predicts behavior in the dilute limit, its ability to correctly describe more concentrated systems is unclear. As another example, classic continuum models, such as Fickian diffusion based on bulk properties, are inadequate for successfully describing diffusion in nanoporous materials (pore diameter d < 2 nm) [26]. This discrepancy can be rationalized in part by the knowledge that an adsorbate molecule never escapes the potential field of the pore wall and thus no bulk fluid state exists. This lack of adequate models results in not only an absence of validated experimental macroscopic measurements of, for instance, phase behavior, but also a dearth of theoretical and model frameworks for describing and accurately predicting molecular or microscopic properties of interest, such as free energies and derived properties. There is a clear need for both descriptive and predictive capabilities for aqueous systems that are far removed from conventional standard states. Overcoming this need would provide the thermodynamic and transport information necessary not only for describing fluids under conditions of interest, but also for developing engineering process frameworks to describe unit-operation performance (e.g., separations).

To address this gap, both atomistic modeling and continuum-scale frameworks will be needed. The former can be used to calculate fundamental properties of interest that can then be implemented in conjunction with, or as inputs to, continuum-scale models. Access to such approaches will also lead naturally to the revisiting of the adequacy (or inadequacy) of existing models, such as Debye-Hückel theory and derivatives [27]. New and improved frameworks need to be capable of describing systems where current models break down, including high-ionic-strength aqueous systems and the solubility/partitioning of species in aqueous systems at high temperature and pressure. Atomistic simulations of complex fluids relevant to energy-water systems are needed for a more complete description of their physical chemistry. Experimental data for well-characterized systems will enable development of force fields that serve as inputs for performing molecular simulations of the same systems. The output of molecular dynamics and Monte Carlo simulations should in turn generate thermodynamic and transport property information that can be used to develop continuum models, which will enable the engineering description of unit operations [28]. The simulations will also provide information against which model experimental fluids and systems can be designed and validated, and lead to a revisiting and/or improvement of existing continuum-level models or development of new, improved models [29].

Multi-scale integration of molecular- and process-scale models: The performance of water and energy processes, particularly separation processes, is often dependent upon multi-scale phenomena that span many orders of magnitude. Fundamental atomistic, molecular, mesoscale, and continuum models cannot individually provide insight into process performance in these systems. Where models have been linked, they rarely capture the heterogeneity inherent at each of these length scales, instead presenting highly simplified and homogeneous features of the system [30]. Thus, there is a critical need for novel integration approaches that unify models of materials chemistry and structure with those of system geometry and process conditions while maintaining the heterogeneity critical to describing complex or non-ideal systems and emergent behavior. The success of this integrated modeling approach would significantly advance potential applications in fields from oil field reservoir behavior to membrane

distillation performance — systems in which performance depends critically on the underlying heterogeneity in materials chemistry and structure.

Exascale computing capabilities, paired with improved reduced-order methods and coarse-graining procedures, will be required to make these multi-scale physics and chemistry models computationally feasible. Validation of hybridized multi-scale models must occur against both the individual model components, as well as against experiments in model and operational systems. New computational approaches for efficiently sampling multi-parameter decision spaces for improved process performance are also required in order to use these models for system design and operation. For example, a model might be used to identify the microstructural parameters that control the micro/continuum scale behavior of the material based on the atomistic/molecular structure of the chemical backbone/functional groups interacting with each other and with water-solid-air phases.

A related area of importance is the development of data-driven models to describe behaviors of realistic complex situations. Challenges related to technology development in this area include tracking and integrating data from large arrays of physical sensors, developing sensor fault detection tools, and integration of data-driven approaches with advanced optimization and control schemes. Ultimately, progress in these topics will enable the integration of machine learning models with deterministic models for real-time process optimization and control to minimize energy consumption associated with water utilization in power generation plants and water treatment/production for industrial and consumptive use [31,32].

Thrust 1b: Rheology of Complex Fluids

Liquid-phase flow and reaction can sometimes be reliably predicted for fluids that have simple rheological properties. Many fluids important in energy-water issues, however, are complex and require an increased understanding of their fundamental properties. These fluids can be highly viscous or strongly non-Newtonian; they can be suspensions, slurries, foams, emulsions, and dispersions, and often have exotic rheological behavior that is a function of temperature, composition, particulate loading, and other parameters. During reactive transport, decoupling heat evolution, hydrodynamics, and chemical changes have proven to be daunting challenges. It is likely that developing predictive insights into the rheology and reactivity of these complex fluids will require the incorporation of the fine-scale texture of compositional and thermal variations rather than treating the fluid as a homogeneous medium.

At present, hydraulic fracturing (fracking) fluids are mostly composed of water augmented by numerous additives to control rheology and chemical properties targeted for different phases of injection and withdrawal. There are numerous opportunities to use basic science to redesign fracking fluids to increase hydrocarbon yields while reducing freshwater use and reducing environmental risks. Water-based fracking fluids are either substantially lost within shale pores, or returned to the surface contaminated by salts, organic molecules, and naturally occurring radionuclides. Low-water-content fracking fluids (Figure 2.1.9) could be designed with controlled wetting properties and viscosity and that minimize perturbations to mineral equilibria.

Stimulation fluids — unlike other fracturing fluids — are commonly composed of polymers, such as cross-linked guar gum, that increase viscosity to favor laminar flow, and those that slow the settling rate of inorganic proppant particles. Such fluids exhibit non-Newtonian behavior, including viscosity variation with shear rate, such that flow and the transmission of pressure are tightly coupled to the pore or fracture morphology. Understanding and ultimately predicting the behavior of such fluids will be extremely important yet quite challenging for quantitative theories. The establishment of improved theoretical and computational models of viscoelastic fluids would be an important step toward more effective use of water-based fluids for stimulating tight reservoirs, thereby reducing overall water intensity.

Current technologies exist within academic and national laboratories to design, fabricate, model, and study innovative complex fluids for water-energy systems. Molecular design and synthesis to create fluids with desirable wetting and flow processes, advanced colloidal systems and simulations, and molecular-scale analysis of wetting under flowing conditions, all have potential for impact in this area. Surface-sensitive spectroscopy and that of buried interfaces, especially within engineered nanoporous, nano-, and micro-fluidic systems, will critically enable the elucidation of the fundamental interactions that govern low- and non-aqueous fluid properties.

NON-AQUEOUS FOAMS

Tight shale rocks host abundant quantities of oil and natural gas that can be accessed by advanced drilling and well stimulation methods that create and prop open fractures. The fluids used for hydraulic fracturing are typically composed of over 90% freshwater plus additives such as polyacrylamide to reduce flow resistance, or guar gum to suspend sand proppant particles [33]. The average water use for the lifetime of a single well is 1 million gallons [34], which not only creates significant pressure on water resources in arid regions, but can impede oil and gas flow to the surface. There are opportunities for the development of low-water foams as alternative fracturing fluids both in the fracturing and proppant delivery stages [35]. Foams and emulsions are the names conventionally given to gas-in-liquid and liquid-in-liquid colloids, respectively, although in industrial or subsurface settings either component may change between gas, liquid, or supercritical phases.

Surfactants play an extremely important role in stabilizing foam interfaces and can alter other fluid properties such as apparent viscosity. It has recently been discovered that the combination of organic surfactants, or surfactants plus inorganic nanoparticles, generates particularly stable ultra-dry CO_2 foams that can have 5% water or less [36,37]. Surfactants can act in several ways to lower the interfacial free energy of foam lamellae but the origin of favorable cooperative interactions (with or without nanoparticles) is not sufficiently understood, especially in the case in which water is replaced altogether with liquid hydrocarbons. An improved ability to predict the macroscopic rheological properties of foams and emulsions from knowledge of the nanoscale structure and interactions at lamellae would lay a foundation for tailoring low-water or even no-water (gas-in-hydrocarbon) foams for many applications. For subsurface energy and water applications in particular, achieving independent controls of properties including mineral wetting, viscosity as well as desirable stability under regimes of temperature, pH and salinity are challenging but very important goals.
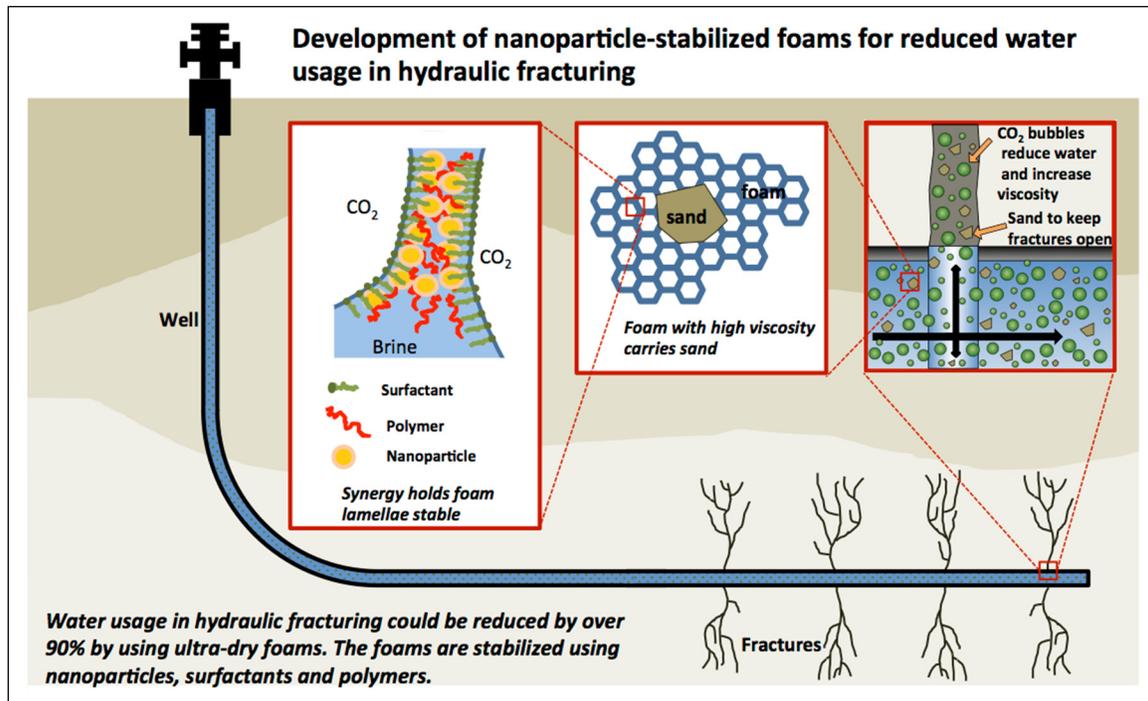
Figure 2.1.9. Replacement of standard hydraulic fracturing fluids by ultra-dry foams, composed primarily of CO_2 and organic or inorganic surfactants, could reduce water use for tight shale gas extraction by up to 90%. (Courtesy of Maša Prodanović, The University of Texas at Austin.)

2.1.3 Impacts

Research to better understand the fundamental intermolecular structure and dynamics of water molecules in the presence of solutes and interfaces will provide new insights into the properties of complex fluids and their interactions and reactivity with various surfaces. Knowledge regarding how solutes, interfaces, and confinement affect water orientation, density, and dynamical quantities, like orientational correlation times and diffusion, will emerge. Such knowledge can provide the necessary foundation for the prediction of the properties and saturation states of complex aqueous solutions over a much wider range of conditions than currently possible, including the capacity to reliably

predict and control the emergence of structures and phases. Nucleation rates and mechanisms are of particular interest, and these define an already notoriously difficult problem for simple systems. Nonetheless, to understand and control fouling and other aspects of separations, it is important to be able to make some progress even for complex mixtures. Development of new electrolyte/solute models to predict thermodynamic, hydrodynamic, and kinetic properties of concentrated multi-component aqueous solutions will be invaluable. Examples of properties of this type include molar volumes, saturation states, phase boundaries, and equations of state.

Impacts of a molecular-level understanding of complex fluids extend to a broad range of applications. Basic research that advances our understanding of the chemical reactivity of low-water-content fluids can impact energy-water issues by enabling technologies that reduce water use in enhanced oil and gas recovery and enable low-water-intensity geologic carbon sequestration. Low-water-content supercritical CO_2 can result in carbonate mineral formation in reactive geologic formations, and interactions with water-wet CO_2 influence chemical reactions with cements that seal wells that penetrate storage formations and with caprock formations. Control of chemical reactions during enhanced oil and gas recovery, as well as potential mineral recovery processes, can enable the effective use of CO_2 as an alternative working fluid to aqueous solutions. Knowledge of the corrosivity of water-wet supercritical CO_2 can lead to new methods for corrosion prevention and inhibition for our infrastructure for CO_2 storage, distribution, and injection. Reactions that occur during compressed air storage will also benefit from advances in our knowledge. Improved methods for water removal and control are also envisioned, including such ubiquitous systems as air conditioning, where small concentrations of water in fluorocarbon refrigerants lead to corrosion and failure of the compressors and other components.

Most commercial forward osmosis (FO) systems use a concentrated salt draw solution in the process. Other non-aqueous fluid concepts have been proposed and demonstrated, such as the NH_3-CO_2 system. The principal technical challenge with such systems is the need to flash the fluid phase to vapor so that water can be condensed. The resulting pressurization-depressurization cycles lower the overall exergetic efficiency. Basic research on multi-component fluids and the resulting knowledge gained of low activity water in non-aqueous fluids would help advance new non-aqueous solution concepts that could lower the energy requirements and make FO more energetically competitive with reverse osmosis (RO), while maintaining its natural low fouling benefits in terms of membrane performance.

Numerous water quality issues can arise from the use of nontraditional water sources for industrial applications, including scaling and fouling, resulting in a reduction of pollutant removal effectiveness and frequent shutdowns for maintenance. The development of thermodynamic and transport models will allow quantitative description of solute speciation, which will enable management or prevention of solids formation. This will result in a higher level of assurance that water quality and quantity requirements can be met without affecting the production process, with an end goal of using more nontraditional water sources and reducing the amount of freshwater used for industrial purposes. Nontraditional water use would reduce or even eliminate drought-related vulnerabilities to water supply. Numerous recent examples of how droughts have impacted power plant operations and hydraulic fracturing for natural gas production can be found in DOE's 2013 report *U.S. Energy Sector Vulnerabilities to Climate Change and Extreme Weather* [38]. In addition, the utilization of nontraditional water would reduce competition with other water use sectors over limited freshwater supplies. For example, consumptive water demands for siting of new thermoelectric power generation in the Western United States, where freshwater supplies are very limited, could increase by more than 30% by 2030 [39].

Current models are limited in predicting water chemistry at the high concentrations and high temperatures of zero liquid discharge (ZLD) of industrial wastewater. Most models can accurately predict a sodium-based chemistry (which occurs in natural systems such as with seawater). Wastewaters associated with energy production, however, can have significant calcium and magnesium concentrations in addition to organics and other compounds. The presence of such compounds can result in a boiling point significantly higher than sodium chloride solutions. Designing an evaporation system with uncertainty in the boiling point could result in a system that does not achieve ZLD. In addition, solids formation and scaling can be significant, especially with products from flue gas desulfurization-blowdown, which is saturated in calcium sulfate. Being able to accurately predict solids formation will enable a system designed to manage these solids. In addition, understanding the mechanisms with scale formation will enable design of a system to manage and/or prevent scale. The development of thermodynamic water chemistry models will enable a ZLD system that is "right sized" instead of "oversized" as a result of uncertainty with water chemistry [40].

2.2 PRD 2 — ACHIEVE MECHANISTIC CONTROL OF INTERFACES AND TRANSPORT IN COMPLEX AND EXTREME ENVIRONMENTS

Interfaces — and confinement of fluids by interfaces — play a central, often dominant, role in the diverse transport and reactive processes associated with energy-water systems, from water treatment membranes and catalysts to subsurface resource recovery.

2.2.1 Scientific Challenges

The unique environments on and near interfaces in complex aqueous systems are poorly understood at a fundamental level, despite their omnipresence and importance. Changes to bulk properties, for example, by additives to modify the flow or other characteristics of water, or by doping constituents in solids, can have an unexpected impact on behavior near interfaces. Interfaces of interest can be liquid-liquid, as in an oil-water interface, or liquid-solid, as in a membrane, pore or subsurface structure. The behavior of fluid constituents at interfaces governs adhesion, adsorption, wetting, and flow; the concentration, transport, and reactivity of solutes; the transmission of pressure; and the propagation of acoustic or electromagnetic wave energy. Although fluid–solid interfaces have been studied for more than a century, much remains to be learned in our basic understanding of these interactions. Current predictive models for interfacial phenomena are fully or partly empirical in the vast majority of cases. Moreover, the interfaces that are relevant to energy-water issues are distinct from simple models typically studied, exhibiting high compositional heterogeneity of both the fluid and solid phases, and a high level of morphological complexity across many spatial scales (Figure 2.2.1 [1,2]). Adding to the challenge, real-world subsurface, environmental, and technological materials are dynamic — interfacial processes evolve on many timescales, altering macroscopic transport, reaction, and mechanical properties. Increased fundamental understanding and more robust models for coupled interface dynamics and their consequences for macroscopic parameters will greatly enhance our ability to use complex systems — from membranes to reservoir fracture networks — in ways that optimize their performance, reduce water and energy requirements, and extend their useful lifetime.
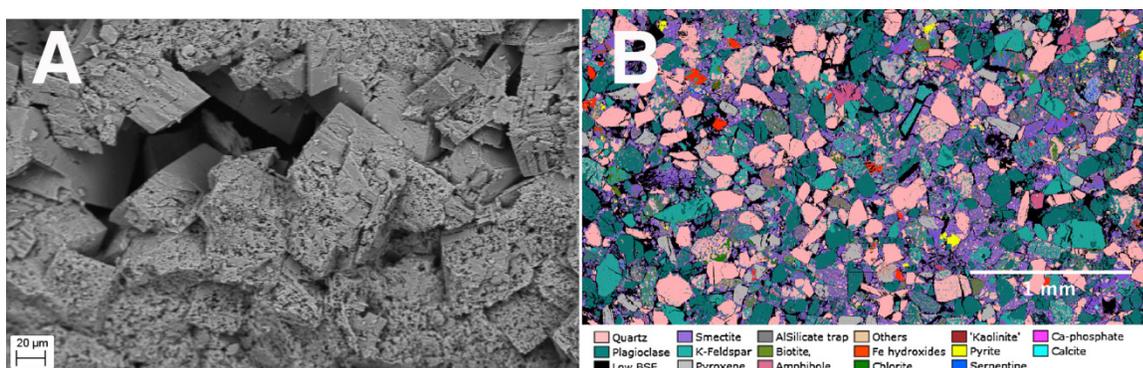
Figure 2.2.1. A – Example of a highly complex interfacial geometry created by the selective dissolution of calcite from a dolomite fracture surface exposed to CO_2-saturated acidic brine. The image shows a scanning electron microscope (SEM) combined secondary electron-backscattered electron (SE-BSE) image of dolomite from the Duperow Formation, a reservoir for proposed CO_2 sequestration sites in the state of Montana. **B** – Example of the high level of intrinsic compositional heterogeneity in a sample of volcanic reservoir rock from the pilot CO_2 sequestration site at Nagaoka, Japan. The image shows a 2D registered SEM BSE and QEMSCAN image showing the distribution of minerals identified by pixel color.

Affinity between interfaces and water or other components of aqueous systems governs scores of molecular-level phenomena in energy-water systems, ranging from transport through porous media, to sorption of ions and molecules in water purification operations, to selective sensing mechanisms. Seemingly simple surface affinity properties such as wettability and hydrophilicity are in fact the product of intricate interplay between interfacial morphology, electrostatics, mechanics, and chemistry. Such properties underpin aspects of transport through natural and manufactured porous media, rheological behavior, as well as fouling and scaling phenomena ubiquitous in energy-water systems. A major scientific challenge lies in systematically investigating each of these contributing factors, as well as their synergistic interplay.

The ability to improve our control of interfacial chemistry and morphology — especially on the nanoscale — will be vital in efforts to develop the next generation of membrane, sorbent, and sensor materials for use in energy-water systems. Precise control over pore chemistry and pore size distributions in membranes, for example, will enable exploitation of **novel transport mechanisms.** Electrostatics and various weak interaction forces (e.g., dipole-dipole, van der Waals) between interfaces and aqueous fluids become increasingly important as the surface area of contact represents a larger fraction of the overall volume of interest. Understanding these types of interactions provides a pathway to their use in the design of selective and efficient transport through porous media. Fundamental insights and tools that ultimately enable production of high-performance membranes at the scales required and in the complex operating environments in realistic applications will be critical.

Regardless of the properties of interfaces in membrane, sorbent, and sensor materials used in energy-water systems, the enormous range of solutes present in realistic water sources means that fouling of these interfaces, which is fundamentally a competitive sorption-reaction phenomenon, will always be an issue that places limits on performance and lifetime. Interfacial interactions are fundamental to both physical and biological fouling mechanisms. **Concepts that take advantage of hydrodynamic forces in operating devices or allow fouled membranes to "heal" themselves** could revolutionize efforts to mitigate fouling. At the same time, **development of interfacial materials that have enhanced resistance to the oxidative treatments that are widely used to regenerate** membranes and other components would have wide-ranging impact. Success in either of these directions will require detailed insight into the chemistry and structure associated with fouling events taking place at the complex interface between an aqueous phase (typically under flow conditions) and a surface.

Reactivity at interfaces, including corrosion (Figure 2.1.5) and other oxidative processes as well as heterogeneous catalytic reactions, is influenced by an interplay of dissolution, precipitation, adhesion, diffusion, surface structure, and ambient fields. Unpacking the relative roles of these phenomena represents a compelling basic science challenge. Mechanisms to inhibit corrosion processes under aggressive environments or even to institute self-healing properties via responsive interfaces will require new fundamental knowledge of interfacial interactions and reactivity. Catalytic function, whether to degrade challenging pollutants in water systems or to hinder bio- and organic fouling of system components, can dramatically reduce energy consumption and operating costs. Designing such function will require detailed understanding of reactivity at particular solid facets and defects to target specific solutes, as well as specific reaction products with minimal toxicity or other harmful properties.

In continuum fluid mechanics, a fluid is considered a continuous medium with a fundamental bulk density locally. The density of a fluid, however, may be non-uniform spatially, owing, for example, to temperature or concentration variations. **Density-dependent flow processes** assume an important role in many natural and engineered energy-water systems, including subsurface hydrology and reservoir mechanics. Applications include intrusion of saltwater into coastal aquifers, transport of concentrated brine with pollutants in rock formations, high-pressure membrane separations, geothermal energy extraction, and numerous others. Moreover, unlike in gas separations, **multi-body interactions** both among fluid constituents and between the fluid and interfaces further complicate mechanistic origins of transport and reactivity phenomena. Overall, the challenge is to understand at a fundamental level the relationships among — and ultimately predict and control — interfacial properties, transport, and reactivity in energy-water systems (Figure 2.2.2).
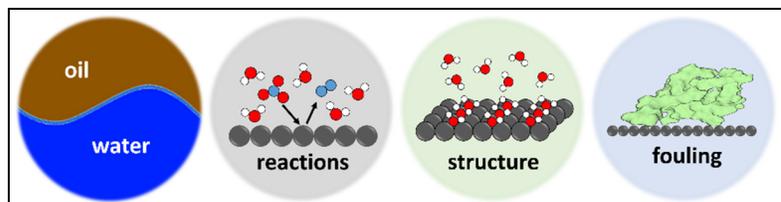

Figure 2.2.2. Illustrative roles interfaces play in energy-water systems. Interfaces between immiscible fluids, reactive and structured interfaces, and fouling via adsorption or biofilms all present new fundamental science questions.

2.2.2 Research Thrusts

PRD 2 is organized into three scientific thrusts. The first focuses on developing and leveraging new insights into multi-scale interfacial interactions and reactions into a pathway toward design and control over that affinity/reactivity (Thrust 2a). The second explores the transport of fluids through confined spaces with high interface-to-volume, such as those present in porous media (Thrust 2b). A third thrust centers on the role of electrostatics and charge at interfaces, which have relevance in many processes important in energy-water systems (Thrust 2c). This section provides the technical details for each of these thrusts.

Thrust 2a: Fundamental Understanding of Interfacial Affinity and Reactivity

Affinity of interfaces for components in a complex fluid will be dictated by synergistic effects from morphology, hydrodynamics, electrostatics, and both surface and solution chemical composition. The prospect of unpacking the relative roles of these contributing factors is tantalizing, enabling new insights into everything from hydrophilicity to fouling (Figure 2.2.3 [3]). For example, while strategies to improve fouling resistance were traditionally based on the application of highly hydrophilic surfaces, recent data indicate that chemical and charge heterogeneities at very small size scales can also prevent the adhesion of proteins and microorganisms, demonstrating the complex nature of this process [4]. Scaling, another process that leads to inefficiencies, is also affected by surface chemistry and morphology, in addition to solution chemistry and transport to and from the interface. Membranes and sorbents offer a rich palette to explore these topics. The fundamental knowledge

Figure 2.2.3. Interface fouling is a complex set of inter-connected physical, chemical and biological phenomena, which affect water transport through membranes.

resulting from basic research in these areas can be translated to a long-term goal of tailoring the affinity to tune properties related to permeability, selectivity, and stability. As an example illustrating the often unanticipated consequences of manipulations of bulk properties for interfacial phenomena, doping of membrane materials intended to alter photon harvesting has been observed to impart a dramatic influence on wetting properties [5]. Systematic studies are needed to distinguish how such seemingly unrelated properties are intertwined, in order to ultimately offer the ability to design desired — even multi-functional — behavior in such systems.

A goal to prevent adsorption of materials at an interface, such as with anti-fouling coatings, is another area in need of insights from basic research. Inorganic, as well as organic and biomaterials, such as proteins or microorganisms themselves, attach to surfaces in energy-water systems through several mechanisms, which leads to fouling. Interactions from the molecular to the mesoscale can govern the attachment of material to interfaces, and surface chemistries can be designed to interfere with such attachment mechanisms, thereby reducing the tendency for fouling. Research into the underlying mechanisms is critical, beginning with simplified systems and introducing increasing levels of complexity. One example is the use of zwitterionic polymers, exhibiting a blend of positive and negative charges, to prevent protein adsorption driven by electrostatic forces [6]. In other scenarios, adhesion to a surface is desirable. Selective removal of targeted pollutants from water streams using sorbents will require engineered affinities with surface-bound species. Such affinities can be tailored to separate an entire class of materials from water, or perhaps just one specific target. There is therefore a need to develop a library of surface chemistries spanning the spectrum of attractive and repulsive interactions, with the full gamut of constituents of waterborne materials ranging from ions (e.g., salts, heavy metals, and nutrients) to organic molecules (e.g., pharmaceuticals, hydrocarbons) to microorganisms. Such studies should provide needed insights into solid-liquid interfacial tension, which is often a controlling factor in sorption and flow processes in porous media.

While physical affinities that attach or prevent attachment to interfaces can provide value across energy-water applications, there are also situations in which chemical change at interfaces is an important consideration. Gradual decomposition of materials by oxidation and/or sulfidation is pervasive in aqueous environments such as water treatment and distribution systems as well as in subsurface environments. There is a need for predictive molecular-scale models and fundamental understanding of the dissolution and precipitation processes leading to
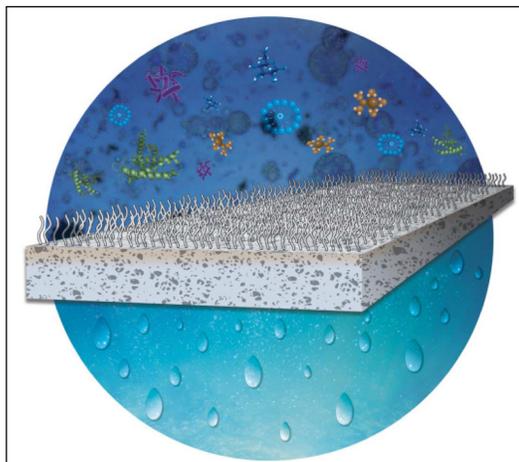
corrosion. Likewise, the interplay among adhesion, diffusion, surface structure/crystallography, and chemical reactions on catalytic interfaces in complex aqueous systems is a daunting challenge. A given catalyst, for example, can often take the form of various polymorphs, each with various possible crystalline facets. Each such surface will exhibit unique reactivity driven by differing binding of species from solution and surface-specific electronic structure, which in turn leads to distinctive reaction rates and products, offering the enticing possibility of designing systems to target both specific solutes and products.

A particularly challenging area is interfacial reactivity and characterization of non-crystalline solid phases. There are innumerable non-crystalline phases that can influence solid-water reactions in systems with an impact on energy-water issues. However, because of their poorly crystalline nature and variable compositions, there is presently insufficient information on their stability and reaction kinetics to enable predictions of their impacts on energy-water systems. An illustrative example is fly ash, a product of the combustion of coal (Figure 2.2.4A). The diverse solid phases in fly ash include the non-combustible and condensable organic and inorganic compounds of the original source coal. The phase composition within fly ash particles includes major amounts of amorphous materials (glasses). Elements of interest to energy-water systems are toxic trace elements that can leach out and diminish freshwater resources and valuable elements (e.g., rare earth elements) that could be recovered from the ashes (Figure 2.2.4B [7]). Because the behavior of these elements is not governed by their overall content in the solid phases, but rather by their chemical speciation and physical distribution within fly ash particles, new information on the molecular- and mesoscale structure properties that govern the solid-water interactions with fly ash particles is needed.
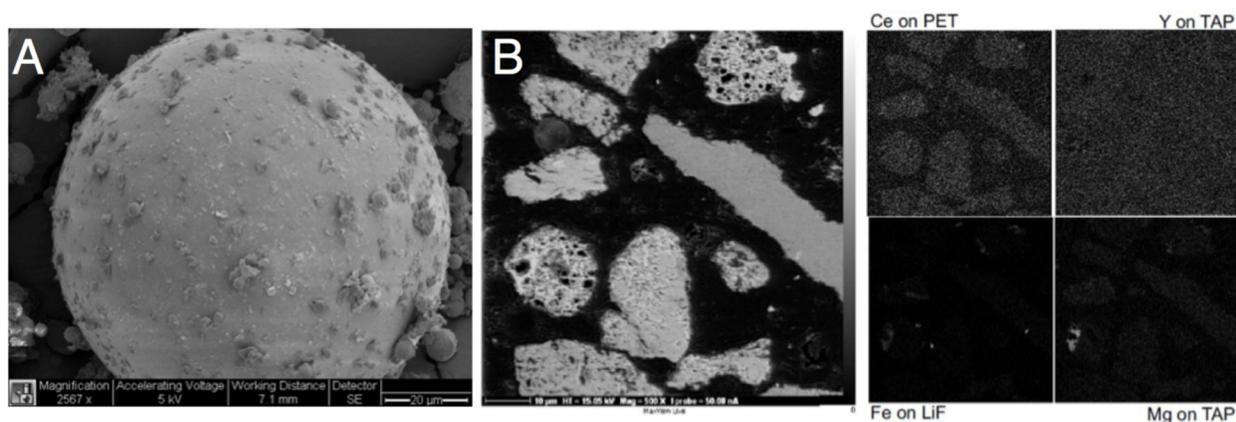

Figure 2.2.4. A – SEM of an amorphous particle obtained from coal ash. (Courtesy of H. Hsu-Kim.) **B** – SEM of sections of glass fly ash particles from a coal power plant (left panel) and associated elemental distribution maps (right panels).

A second important class of non-crystalline solid phase are the glassy inclusions in igneous rocks that react with fluids during enhanced geothermal energy recovery and carbon sequestration. For example, the basalts for which carbonate minerals have been observed following carbon injection in Wallula, Washington, and at the CarbFix site in Iceland have extensive amounts of glasses that react with water-wet CO_2 and CO_2-saturated brines. Unlike the crystalline phases present in these basalts, these non-crystalline phases do not have established equilibrium solubility parameters or dissolution rate parameters. Without such information, it is difficult to integrate the necessary chemical reactions into larger-scale simulations required to manage the sequestration of CO_2 in such environments.

Establishing the fundamental forces that control wetting will require advances in many areas of interface science. The molecular configurations and interactions that determine the enthalpy and entropy changes during interface formation or alteration are not easily accessible by existing imaging, spectroscopic, or simulation methods. Important roles are anticipated for new applications of x-ray and neutron scattering in elucidating interfacial atom distributions (Figure 2.2.5 [8]). Nonlinear spectroscopies that offer intrinsic surface sensitivity will be of broad utility for the measurement of vibrational dynamics and quantification of the electrical potential that develop at many interfaces. These approaches have elucidated solute distributions at gas-water interfaces and have the potential to address the molecular contributions to interfacial tension. Insight into non-Newtonian fluids could be obtained from studies of molecular orientations and dynamics at interfaces during flow in designed in situ fluidic cells.
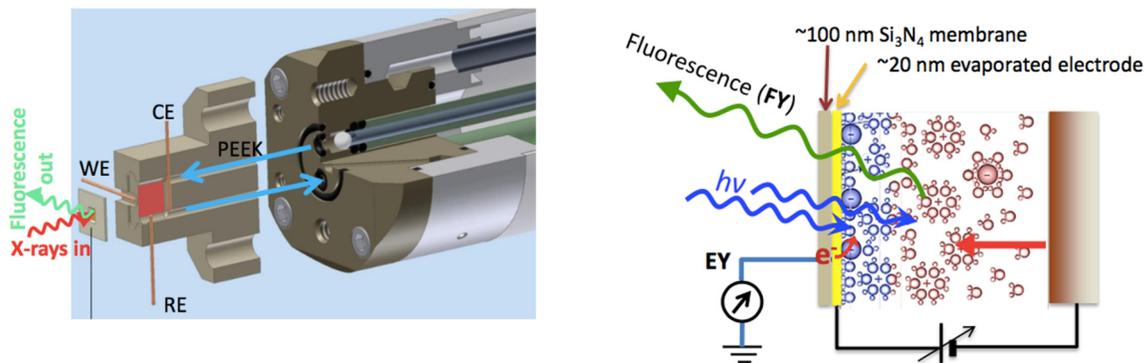
Figure 2.2.5. Synchrotron measurements can be performed on an electrochemical cell in operando. New approaches, based on the combined interrogation of the sample using high-intensity x-rays available at synchrotrons, and UV-visible photons (hv), have the potential, via simultaneous measurement of fluorescence, to provide new information on the structure of water at the interface. WE, RE, and CE are working, reference, and counter electrodes, respectively. FY and EY are fluorescence and electron yields. PEEK is polyetheretherketone, which is the material that makes up the flow cell.

Thrust 2b: Predictive Understanding of Fluid Transport through Natural and Manufactured Porous Media

Most novel materials of interest for next-generation separation membranes and sorbents feature functional nanostructures. Permeation through geological porous media and heterogeneous catalysis both involve aqueous phases interacting with pore walls in tightly confined spaces. While preliminary observations indicate that the confinement of water and solutes can further emphasize the effect of solute-wall interactions (Figures 2.2.6 [9] and 2.2.7 [10]), a good understanding is lacking of the synergistic effects of confinement and the interactions among water, solutes, and the material through which permeation occurs. These effects are at the core of understanding transport through complex systems, which deviate from traditional pore flow and solution-diffusion transport mechanisms. In addition, there is a knowledge gap in how physical and chemical heterogeneities affect transport and interfacial interactions.
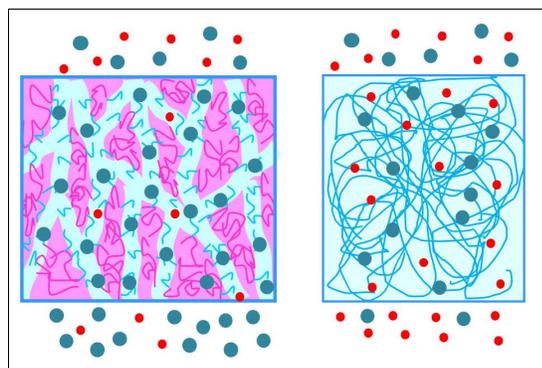
Figure 2.2.6. Different permeation selectivities can be achieved when permeation is confined into one phase only in a microphase-separated copolymer (left) in comparison with a cross-linked homopolymer (right), where traditional solution-diffusion mechanisms are in effect.
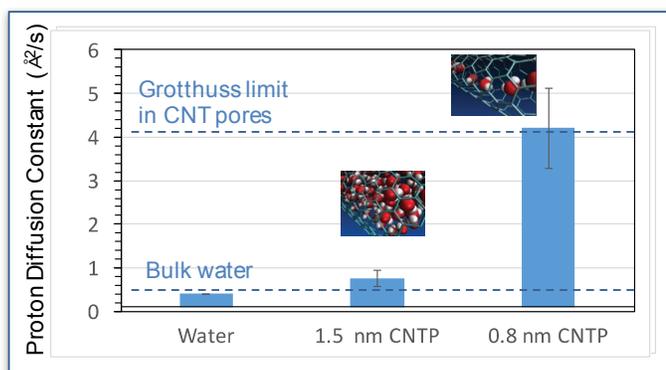
Figure 2.2.7. Confinement effects can enhance transport, such as in the significant increase in proton diffusion through small-diameter carbon nanotubes.

Given the complexity of systems of interest for energy-water issues, models are needed that capture the morphology, chemistry, and texture of natural and manufactured porous media (Figure 2.2.8 [11]), from nanoscale to microscale. Interfacial and transport processes of interest are strongly dependent on these parameters across hierarchical scales. For example, the permeability of subsurface porous media is dependent on a range of parameters that include porosity, pore sizes, pore connectivity, and throat sizes, which may further change during permeation. The same can be said for porous separation membranes, whose selectivity may be affected not only by the pore morphology but also by solute-pore interactions and fouling. Building predictive understanding of transport, reaction, and affinity in such systems requires the fundamental knowledge of processes, as well as construction and refinement of
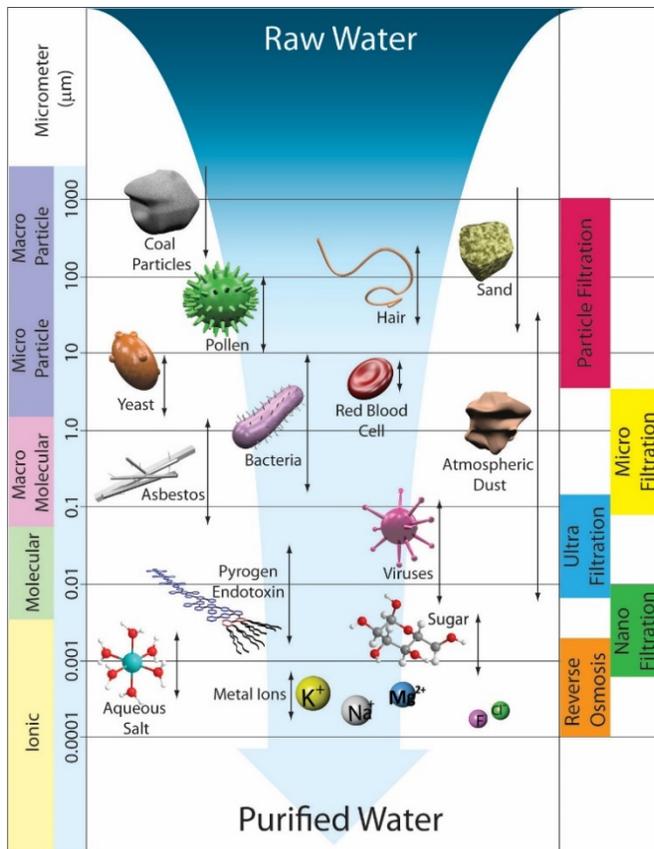
Figure 2.2.8. Size regimes of membranes.

well-designed models of these processes occurring at their native scales. It also requires consideration of how native-scale processes couple in the presence of natural geologic heterogeneity and complex gradients, and aggregate to yield a cumulative system response. Meeting these challenges will require interfacing computational and theoretical approaches, imaging, and other analytical techniques, as well as the design and synthesis of interfacial materials.

Making even modest advances in the fundamental knowledge associated with desalination and other aspects of water purification has potential to make enormous impacts on societal availability of water and use of energy. State-of-the-art RO systems are remarkably efficient, but alternative purification processes may displace RO in some operating environments, such as for brackish water or systems dominated by larger or charge-neutral contaminants, and fundamental advances are required for these processes to be fully realized. It is critical to consider the performance and characteristics of materials in the complex aqueous environments that exist in practical applications. A fundamental understanding of charged fluid-solid interfaces, especially in the regime of nanoconfinement, are critical to advance the field of capacitive and electromediated-separations to significantly increase the energy

efficiency of water treatment. These issues are explored further in Thrust 2c. Electromediated separations are not the only class of process that can potentially displace RO. Alternative processes, including FO and membrane distillation, have also been extensively studied and have potential advantages for some feed streams. Most commercial FO systems use a concentrated salt solution to draw water through the membrane. Other non-aqueous fluid concepts have been proposed and demonstrated, however, such as NH_3-CO_2 solutions. Advances in fundamental understanding of the properties of low-activity water in non-aqueous fluids would advance efforts to develop improved non-aqueous draw solutions that can lower the energy requirements of FO and related processes.

Because probing transport through complex, real-world porous media with sufficient detail to extract new insights is challenging, model systems can be used to decipher the interplay of phenomena in an environment where parameters can be controlled systematically. (See sidebar below on Membrane Pore Flow.) Use of micro- and nano-fluidic pore environments is one such research direction. Micro- and nano-fluidic devices have enabled stringent tests of flow and reaction in complex geometries [12]. Fundamental insights can be derived from systems with highly controlled, monodisperse, and tunable pore arrays. Systematically varying pore diameters through different flow regimes, where the role of the interfaces can be probed, would be a powerful tool for revealing new understanding of transport in nanoporous media. Manipulating the interfacial chemistry, such as by decorating with molecular or inorganic coatings, in such systems represents a further knob to turn in exploring the relevant parameter space.

Moving closer to real-world systems, mineral dissolution and precipitation reactions in the subsurface, which are induced by chemical perturbations from fluid injections and withdrawals, can change rock permeability and alter the stability of stressed fractures. Highly nonlinear interactions can result from the interplay of transport and reaction, due to the emergence of positive feedbacks between fluid flow and mineral reaction. These interactions manifest at large spatial scales (field scale) but depend on processes operative at the molecular and nanoscale. Processes such as hydraulic fracturing also increase rock textural complexity. Observing, understanding, and predicting the time evolution of a reacting textured geomedium is a daunting challenge for most rock formations.

Current geochemical models are typically based on the concept of the representative elementary volume (REV), which homogenizes a multi-component system and cannot reproduce certain interfacial reaction processes that occur in real systems composed of rocks, water, and other fluid phases. These approaches are now being tested by advanced imaging and computational techniques that are increasingly able to capture realistic complexity. Scale-aware modeling approaches, meaning that the model is suitable over a range of grid resolutions, are needed to simulate the influence of controlling fine-scale processes and their aggregated influence on larger geological system behavior.

Advances in x-ray and neutron imaging have made it possible to observe porous media as intact 3D systems. Originally useful only for distinguishing pore space from mineral matter, these 3D imaging methods are now useful for identifying mineral heterogeneity and capturing details of fluid flow such as contact angles. This is still a relatively new tool in the earth sciences, and there is much to be learned about 3D rock texture and pore structure. The wealth of 3D data — also called 4D data when time-lapse imaging is performed — has been described as "irreducible complexity," and is challenging traditional models of flow in porous media. Figure 2.2.9 shows how barite nucleation and growth in a porous medium closes pore throats and changes wetting behavior.

Figure 2.2.9. Measurement and prediction of the wetting angle of a CO_2 bubble within a brine-saturated porous rock. **A** — X-ray computed tomography image. **B** — Predicted contact angle from lattice Boltzmann simulation. **C** — Comparison of observed and predicted wetting angles. (Courtesy of J. Tudek et al.)

Rapidly developing "big data" interrogation methods, including machine learning algorithms, could provide new avenues for managing the wealth of digital rock data from 3D imaging and inspiring new ways to link process information to macrosystem evolution. An early example is provided by Ellis et al. 2016 [13] using a computational method to recognize one mineral phase within a heterogeneous system. Building on such approaches, the use of machine learning will play an important role in identification and classification of types of rock textures in 3D datasets and trends in 4D datasets. High-resolution 3D imaging is now a central tool for characterizing complex porous media and is increasingly used for monitoring dynamic interfacial processes such as gas trapping. Improved spatial resolution coupled to probes of composition and chemistry will enable key aspects of wetting, such as contact angles within spatially confined pore spaces, to be determined under realistic conditions (Figure 2.2.9). High-throughput time-lapse approaches will transform our ability to test models for system evolution as conditions are varied.

MEMBRANE PORE FLOW

Permeation through membrane materials is typically described either by the pore flow model or by the solution-diffusion model. The pore flow model is applicable to membranes that separate based on solute/particle size. It does not account for solute-membrane surface interactions. While some modifications that account for electrostatic interactions and pore size polydispersity exist, none account for the effects of specific/reversible interactions between the permeating species and the membrane, pore geometry, and many other parameters. On the other hand, the solution-diffusion model describes permeation through thin homogeneous polymer films. This approach is most widely applied to gas separation membranes, though recent work aims to apply this model to aqueous systems and incorporate complexities of charged species in water. This model, however, does not account for the presence of any nanostructure or specific chemical functionality in this selective layer. These two features, and their synergistic effects, are at the core of the development of many novel membrane materials whose properties, especially selectivity, can transcend conventional membrane materials. These two key features, nanoconfinement and solute-pore interactions, are also at the core of biological core function, emphasizing the importance of this knowledge gap in the development of biomimetic and bio-inspired systems. Models or even a general understanding of transport through nanostructured and chemically functional materials are lacking. This is true both for hard materials (e.g., inorganic membranes, sorbents, and rocks) and for soft materials (e.g., self-assembled polymers, pores with polymer brushes, and liquid crystals).

Thrust 2c: Manipulating Interfacial Charge for Separations and Reactions

A fundamental understanding of charged interfaces, for example, between electrode materials and complex aqueous media for capacitive processes for ionic solutes, will advance the science of separations, transport, and reactions. There is a lack of fundamental theory, models, and experimental characterization to describe and predict the properties and dynamics of interfaces and interphases in charged environments. Key challenges include understanding the structure, dynamics, kinetics, transport, selectivity, and reactivity at charged fluid-solid interfaces.

Given the emerging promise of nanoscale materials and nanostructures for water treatment, a critical science challenge centers around the effects of nanoconfinement on the double layer, space charge, and other capacitive aspects (e.g., anomalous capacitive increases) at charged interfaces. Understanding charged interfaces will enable control of charge distribution in nanoconfined regimes and during interfacial processes. At this scale, there have been observations of the double layer, space charge, and capacitance, but limited fundamental advancement in the theory behind them. New predictive models for charged interfaces and interphases need to be developed and tested to enable charged interfaces to be harnessed. Models can also provide design principles for tailored materials and ultimately lead to new approaches to synthesize and fabricate electrodes, membranes, and electrolytes. Understanding, probing, and modeling ionic conductivity and mobility at multiple scales in complex solutions over wide concentration ranges are also important.

Advancing the basic science of charged fluid-solid interfaces will enable the community to predict, design, and control systems for electromediated separations (EMSs) and reactions. In comparison to pressure-driven systems, EMS enhances atom and energy efficiency and could approach thermodynamic energy limits. Harnessing charged interfaces will enable the design of selective separations systems the recovery of value-added products from complex aqueous systems.

A wide range of research opportunities exist for spanning theory, modeling, chemistry, materials design and synthesis, and characterization. From a theory and modeling standpoint, there are many empirical models of charged interfaces, but first-principle theoretical models still need to be developed to explore, predict, and understand fundamental interactions. For example, much remains to be learned about the structure of liquid water in nanoconfined structures, pores, and channels involving electrostatics. Experimental research, including state-of-the-art structural characterization and spatial mapping of charge densities on various length scales, would lend significant new insights into EMS processes. This work would also be critical for validating emerging theoretical models. X-ray scattering shows that the interfacial water molecules exhibit potential-dependent layering and reorientation and a markedly increased density (twice bulk water) in the inner layer [14]. New models to describe and predict behavior in nanoconfined spaces, coupled with materials characterization tools (e.g., near-field techniques), would be valuable in providing fundamental understanding of phenomena that is core to the performance and efficiency of EMS processes.

Significant opportunities exist to discover and develop new multi-functional materials for charge storage and transfer, including new nanostructures. Materials-by-design approaches would benefit significantly from advances in the fundamental theory, modeling, and characterization of charged interfaces in complex aqueous environments. New approaches to materials design, synthesis, and characterization would advance a number of EMS concepts, including capacitive deionization (CDI), electrodeionization (EDI), and bipolar electrolytic capacitance (BE) (Figures 2.2.10 [15] and 2.2.11). Innovative EMS concepts can also incorporate ionic membranes, in addition to nanostructured electrodes, so avenues can also explore new organic and hybrid membranes.

EMS processes are in general not highly selective. Fundamental research could lead to the understanding needed to design, control, or induce selective affinity, binding, or other interactions of specific charged solutes with electrodes and nanostructures. In addition to enabling selective separations, controlling interfacial charge provides a pathway to design affinities to control, induce, or mitigate binding of species on surfaces. Translation of fundamental research insights to more applied research and development (R&D) in this area could also be critical to helping develop new concepts to avoid fouling, and even biofouling, of highly porous electrodes, which would have a significant impact on the need for pre-treatments.
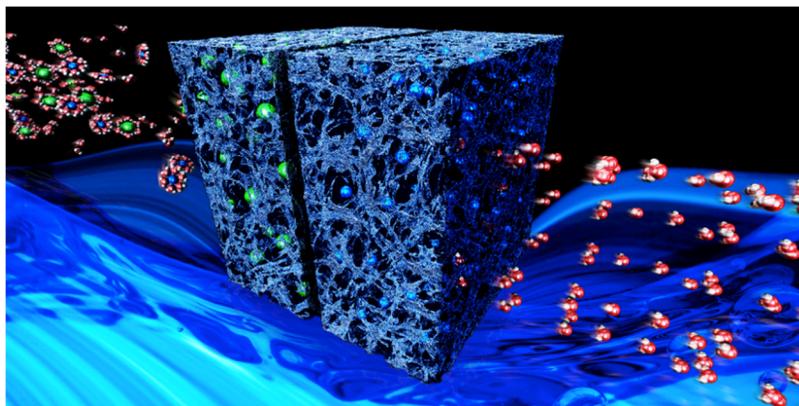
Figure 2.2.10. Capacitive deionization using flow-through electrodes in which (hydrated) salt ions are separated from a water stream.
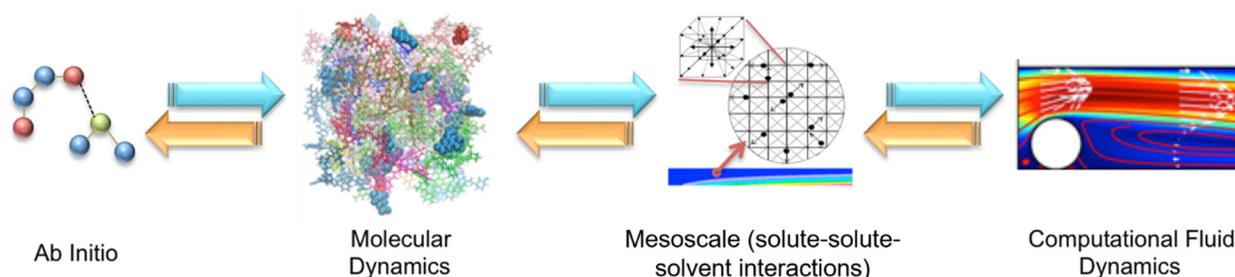

Ab Initio   Molecular Dynamics   Mesoscale (solute-solute-solvent interactions)   Computational Fluid Dynamics

Figure 2.2.11. Multi-scale modeling approaches that span ab initio to macroscale regimes. (Courtesy of R. Faibish.)

2.2.3 Impacts

Understanding relationships among interfacial properties, transport, and reactivity will require broad fundamental research spanning chemistry, physics, biochemistry, geoscience, and materials. At the core of understanding interfaces are both idealized and realistic interfacial and porous systems, controlling aspects such as morphology, charge, and composition with spatial and chemical precision. These systems can then be explored using a broad suite of existing and to-be-developed multi-modal methods spanning the theoretical, computational, and experimental space. Relevant time and length scales range from femtoseconds and atoms, for example, in light harvesting by photocatalysts, to years and macroscopic such as in the corrosion of water distribution networks. Photons, neutrons, electrons, proximal probes, and computers must all be leveraged to develop a complete understanding of the materials and chemical processes at play. Accessing long timescales will necessitate development of new accelerated methodologies capable of providing predictive insights into processes too slow to examine in real time.

A central challenge is applying novel and sufficiently robust and integrated modeling and experimental tools to study this multi-scale transport. Figure 2.2.11, for example, depicts modeling regimes that could be used to understand this range of size and timescales and the relevant transport and materials-related processes within these. A plethora of advanced spectroscopic, scattering, and imaging methods will be required to develop a full understanding of the processes at and near interfaces in energy-water systems.

The establishment of rigorous and quantitative understanding of interfacial interactions governing wetting would have a profound impact across a range of physical sciences. Control over interfacial interactions will enable implementation of resilient surfaces throughout energy-water issues, ranging from robust sorbents for fluid separations to anti-fouling/anti-scaling membranes and cooling towers, to corrosion-resistant pipes and subsurface cement casings. Research to develop concepts for charge-mediated affinity control would provide a fundamental new way to manipulate binding and create new sorbents and may also impact fouling or corrosion. Water treatment processes will be rendered more energy-efficient through selective separations, next-generation advanced oxidation

processes, low-friction transport, and other avenues. Management of subsurface resources, whether fossil, water, or minerals, will be enhanced through science-based efficient and targeted extraction.

New abilities to design, manage, and manipulate the flow of complex fluids through heterogeneous porous or fractured systems could have numerous impacts on the use of water for fuel and energy generation from earth systems. Significant uncertainties are related to the distribution and mobility of fluids trapped in the pores of sedimentary oil and gas formations, particularly tight shales. Improved understanding, modeling, and remote monitoring of reservoir operations could improve the retrieval and reuse of aqueous stimulation fluids and reduce the production of high-salinity waters that require treatment or disposal.

Harnessing charged interfaces is central to advancing EMS and the potential for selective separations processes much closer to fundamental thermodynamic energy consumption limits (Figure 2.2.12). New understanding and discoveries related to the effects of extreme confinement, the ability to create sequences of electrocatalytic reactions, and the interplay between electrostatics and selectivity among components in complex fluids could lead to significant energy and cost reductions. These opportunities are especially promising for intermediate grade water quality (2,000–15,000 ppm salt) or inland systems where waste disposal is a considerable environmental burden. In this regime, innovative capacitive technologies could outperform RO and other membrane-based technologies. The design of new materials from first principles could lead to more selective separation of the dilute components in water systems (e.g., rare earth minerals) and generate value-added products providing economic benefits beyond water purification.
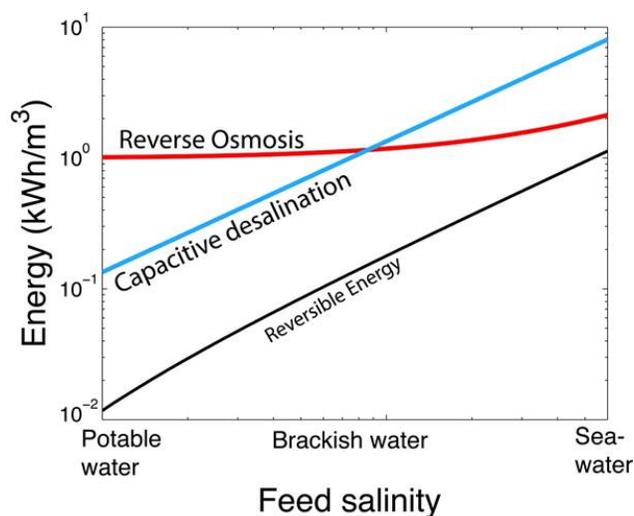
Figure 2.2.12. Calculated energy demands for desalinating water with varying salt concentrations using CDI or RO, compared to the thermodynamic limit. (Courtesy of M. Stadermann.)

Interfaces in energy-water systems represent a rich space for fundamental science exploration, particularly as they relate to affinity interactions between fluids or components within fluids and surfaces, reactions involving water at surfaces, and transport of fluids in confined geometries and in the presence of electric fields. Discoveries in these areas have potential not only to revolutionize our understanding, but also to beneficially transform our diverse uses of energy and water.

2.3 PRD 3 — EXPLOIT SPECIFIC MATERIAL-FLUID INTERACTIONS TO DESIGN AND DISCOVER INNOVATIVE FLUIDS AND MATERIALS

The co-design of new materials and fluids to exploit specific material-fluid interactions will enable step-change improvements in the design and selectivity for purification, chemical transformation, and transport processes in energy-water systems.

2.3.1 Scientific Challenges

The design of next-generation materials and fluids needed for tunable, dynamic, and selective purifications and chemical transformations in energy-water systems requires a much-expanded understanding of aqueous fluid and solute interactions with materials. Beyond the interfacial phenomena emphasized in PRD 2, there are many aspects of materials science that strongly affect energy-water systems. New understanding will enable the design of increasingly multi-functional materials with tunable properties that would harness selective and directional transport, provide for active transport to realize high-efficiency and low-energy separations, and develop new concepts for selective removal or destruction of contaminants. The **complex fluid mixtures that are prevalent in the expanding connection of energy and water issues pose a particular and distinct challenge in materials design,** which will require understanding the interdependence of inherently complex multi-component, multi-phase aqueous fluids, and necessarily multi-functional materials to control overall performance for separations, sorption, surface treatments, and catalysis.

Equally important is the ability to a priori specify and design fluids for energy-water applications with the appropriate constituents and composition for subsurface resource recovery processes. For instance, the combination of synthetic and natural systems with fluid design can provide insights into the behavior of multiphase fluids and how this behavior can be modified to enhance recovery processes. Fluid design could enable control of wetting for the reduction of flowback and produced water as well as for security of subsurface CO_2 storage. This challenge in fluid design also hinges on understanding the interactions with materials (Figure 2.3.1 [1]).

Key components in energy-water processes, including membranes for water and wastewater treatment and reuse, catalysts and sorbents to remove contaminants, and other technologies, are reliant on materials with specific chemical, physical, mechanical, and surface interactions, as well as geometrical structure, to create selectivity for separations and reactions. Most components used in energy-water processes are manufactured from a handful of

Figure 2.3.1. Metadynamics of cation attachment and detachment on materials surfaces (potassium dihydrogen phosphate is pictured).

materials, initially developed decades ago. Because of the limited knowledge available at the time, materials were typically identified through Edisonian and heuristic approaches. These materials have been tuned, modified, and optimized extensively since their initial discovery, which has led to efficient materials for specific, well-established applications related to energy-water issues (e.g., [2]). However, these incremental advances have not produced the range of selectivity and specificity necessary to deliver tunable, dynamic, and selective purifications and chemical
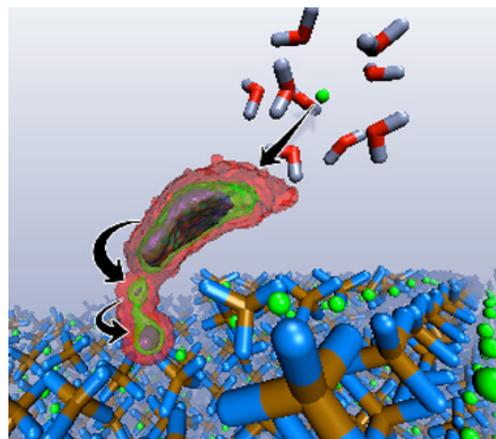
transformations. This is of particular importance given the inherently complex, multi-component, heterogeneous nature of the fluids involved in energy-water issues, which must then interact with multi-functional materials. Research in these areas is timely due to significant advances in the design, control, and synthesis of nanoscale and mesoscale materials; advanced characterization, including state-of-the art structural tools; and advanced theory, modeling, and simulation.

Additional key aspects of energy-water processes are the components in the fluid, whether they are unwanted contaminants or desired constituents. Identifying and quantifying the presence of trace contaminants is a necessary precursor to water decontamination, but new materials and processes to mitigate contaminants are urgently needed to increase efficiency of their removal. One broad approach to this task is to use materials that capture or otherwise concentrate the contaminants. **Development of multi-functional and selective adsorbents for use with complex aqueous mixtures** will widen the scope of applications that can be addressed with these approaches. A host of possible avenues exists for addressing the underlying scientific challenges in this area, including biomimetic materials exploiting the exquisite chemical specificity of biological molecules and the design principles that can be enabled by advanced computational materials and materials informatics methods. A second approach to mitigating contaminants is to use chemical conversion to remove or otherwise alter targeted contaminants. **Development of functional materials with targeted catalytic properties and advances in reactive redox approaches** both have great potential. Both of these approaches must be underpinned by the ability to synthesize and control materials at the nanoscale in ways that provide a strong foundation for the eventual deployment of low-cost materials on large scales.

As with removal of contaminants, the limited range of materials available limits the types of separations available today. Many membranes rely on flow through pore, separating through a size-sieving mechanism. Wide pore-size distributions lead to limited selection capabilities and restrict the application of membranes in a broader range of separations relevant to energy-water issues. RO and nanofiltration (NF) membranes, designed to retain ions but pass water, suffer from similar limitations that arise from structural heterogeneities. Separations of the yet more complex mixtures prevalent in energy-water systems (e.g., removal of small organic molecules, uncharged micropollutants, and selective removal and concentration of specific ions and metals) are similarly hampered by material limitations. **Thus, the ability to separate and isolate efficiently this ever-expanding list of constituents will enable many processes, including, but not limited to, water and wastewater treatment, concentrate management, and water reuse in resource extraction**. The molecular design of materials leveraging self-assembled, bio-inspired, and nano-patterned materials, selective receptors, and new synthetic approaches could provide a paradigm shift in terms of tunability and specificity in separations. Similarly, the design of materials with improved fouling and corrosion resistance relies on empirical heuristics, with much remaining unknown about the influence of foulant chemistry, charge, size, membrane pore size and size distribution, as well as membrane chemistry, topology, pore structure, and operating conditions on fouling. Activated carbon is an inexpensive, widely used sorbent that is used in water treatment because it adsorbs most organics and non-polar compounds effectively. Zeolites, metal-organic frameworks (MOFs), silica, and polymer particles all could provide more selectivity on a designer basis. Similar cases can be made for components in energy-water systems ranging from catalysts to coatings, in which the design of materials to selectively control transport and transformation could be applied to **create entirely new essential properties that would enable active, autonomous pumping** (that is, mechanisms that can move soluble constituents against a concentration gradient), **corrosion and fouling resistance, self-cleaning and healing, and robust surfaces**. Inducing reactions within the pores, channels, or surfaces of these systems by incorporating catalysts into structural motifs would lead to new concepts for selective reactive separations. For example, meeting the fundamental challenge of incorporating redox active catalytic sites into frameworks of mesoporous membranes would enable chemical oxidation of contaminants bound or adsorbed in close proximity. Whether for separation of products or removal of contaminants, at the basis of all these approaches is the need for a detailed fundamental understanding of the interrelations among structure, composition, and chemical and reactivity properties for both the liquid and solid in the interfacial region.

Materials designed for components used in energy-water processes will necessarily need to account for the multi-body interactions between the solid and the fluid. An opportunity thus exists for the synergistic design of material-fluid pairs by, for example, taking into account both molecular and nanoscopic size exclusion and adsorption effects, as well as surface and structural features of the material and its specific interactions with the constituents of the multi-phase and multi-component fluid. Similarly, atomistic-scale experiments and theory to understand water structure and

physics should be leveraged to design materials that take advantage of water confinement effects for control of the fluid transport within pores.

2.3.2 Research Thrusts

PRD 3 is organized into two scientific thrusts. The first focuses on the design of complex fluids and how flow and reactivity properties could be tailored (Thrust 3a). The second explores solid state materials design, ranging from coatings to catalysts to separations media (Thrust 3b). The remainder of this section provides the technical details for each of these thrusts.

Thrust 3a: Designing Complex Fluids

The aqueous fluids pertinent to the main challenges in energy–water issues include very high ionic strength brines and aqueous solutions containing organic chelators and surfactants, as well as colloidal particles. As noted in PRDs 1 and 2, much remains to be learned about the chemistry and thermodynamics of these systems. Equations of state for high-salinity systems also containing soluble surfactants as a function of T and P wait to be developed. The mechanisms of solvation, hydration, and chemical reactions are thus not visualized in a way that has been tested both experimentally and theoretically.

Solutions with high solute concentrations present a particular challenge to experiment and theory. In such systems, solvent sharing and contact ion pairing likely prevail, strongly influencing solute availability and transport. However, molecular-scale depictions of solute association structures, and their effects on chemical processes, remain poorly understood. An important goal is the extension of present tools and computational methods for these high-concentration regimes. Elucidating the interfacial and bulk solvent and solute dynamics, structure, and interactions will inform models of reactivity, flow, reaction mechanisms, solvation mechanisms, aggregation kinetics, and dissolution mechanistic behaviors.

Numerous challenges related to flow and reaction in a porous media could be addressed by advances in our ability to design aqueous and non-aqueous fluids to possess particular combinations of physical and chemical properties. Designer fluids could enhance the mobility of an immiscible phase; sequester or liberate contaminants or valuable species; create, preserve, or limit fracture permeability; and potentially respond to changes in environmental parameters. An aspirational goal is the design of fluids that enhance the production of oil or gas while minimizing the co-production of formation waters. Fluids in which viscosity changes reversibly with temperature may optimize heat extraction from geothermal reservoirs. Advanced design of complex fluids will require numerous advances in fundamental interfacial science as described below.

Wetting of Heterogeneous Surfaces. The permeability of a material or subsurface system is typically considered to be determined by the solid matrix. However, understanding the controls on fluid–solid and fluid–fluid interactions offers opportunities to manipulate the transport and fate of immiscible fluids and solutes within heterogeneous porous media. Impressive technical demonstrations of manipulating the release or capture of immiscible fluids in reservoirs and engineered materials illustrate the potential for science-based control of wetting and flow.

An important goal will be the development of new understanding of aqueous fluid interactions with organic solids, including separation membranes and kerogen (solid organic matter in sedimentary rocks), which are composed of mixtures of macromolecules with varying charge, hydrophilicity, and other properties. Much remains to be learned about the adhesion and flow of fluids on surfaces possessing structure or compositional heterogeneity on length scales at or below the capillary length (typically sub-centimeter), particularly when the interfacial morphology or chemistry changes dynamically. Figure 2.3.2 [3] shows examples of interfacial heterogeneity relevant to wetting within rock systems.

There are also opportunities to rationally design interfacial morphology to manipulate wetting properties in manufactured systems. Factors such as the shape of nanoscale topographic features can have a dramatic impact on the manner in which water and aqueous fluids interact with the surface. Characterizing the structure at the fluid-solid interface is critical to ultimately achieving the foundational knowledge needed for predictive design of desired functionality into interfaces (Figure 2.3.3 [4]).
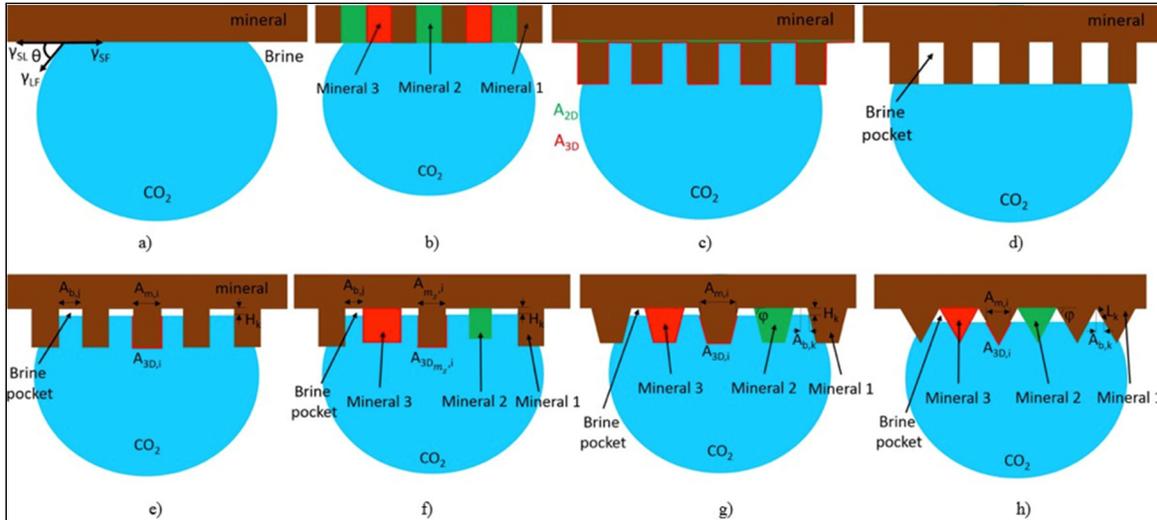
Figure 2.3.2. The wetting of mineral surfaces by immiscible fluids is strongly affected by structural, compositional, and surface chemical heterogeneity.
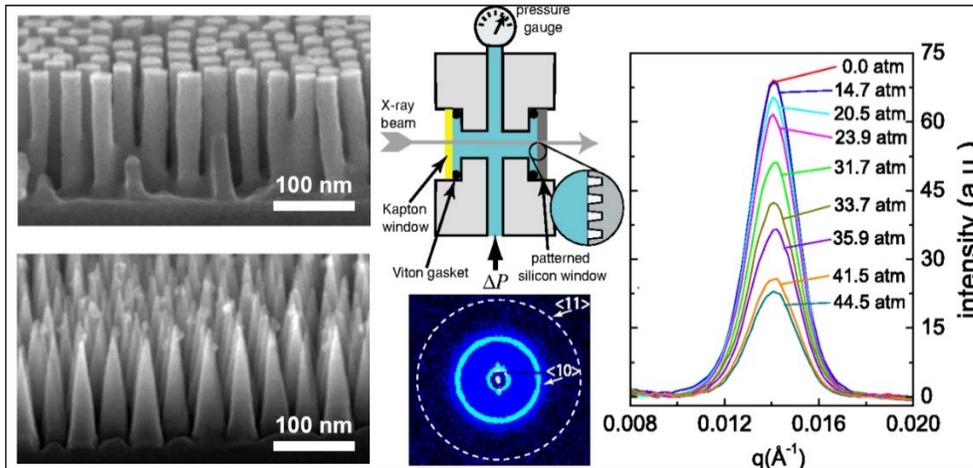
Figure 2.3.3. Small-angle x-ray scattering (SAXS) characterization of water infiltration. The study of new materials for the energy-water issues requires the development and leveraging of techniques to study buried and hydrated interfaces in realistic conditions at relevant time and concentration levels.

Thrust 3b: Designing Solid Materials

Integrating advances in materials synthesis — including nanostructured, porous materials or hybrid materials with materials characterization, catalyst development, ligand design, electrochemistry, photochemical processes, and analytical chemistry — presents opportunities to develop new concepts for novel multi-functional materials that could lead to selective and efficient water treatment technologies. Designing solid materials encompasses fundamental advances in catalysts, membranes, sorbents and coatings. Materials design based on knowledge of interactions and processes at the atomic scale could lead to molecularly crafted specificity, highly efficient transport, customized chemical conversions, and active pumping mechanisms to transport against concentration gradients. The design of materials with specific, active, and selective interactions with solutes and water leverages new and scalable materials chemistry approaches, including self-assembled, nanopatterned and bio-inspired materials; selective receptors that target specific, low-concentration contaminants; and other new synthetic approaches.

The knowledge-based design of functional materials for processes in energy-water systems encompasses a range of basic science questions and approaches. The fundamental science of materials chemistry, for instance, is needed to understand the chemical control of structure and collective properties while research into membrane chemistry could

provide insights into how to use, or what one might learn from, naturally occurring pore-forming proteins in cell membranes. It is clear that this knowledge-based material design will involve mastering fundamental complexities that extend far beyond our current capabilities. These materials systems are often compositionally and structurally heterogeneous, comprised of multiple components and phases spanning multiple length scales. As an example, a large number of anti-fouling studies that seemingly address how surface chemistry and morphology of membranes affect the extent of fouling have resulted in a confusing array of conclusions. This lack of consensus on which property to target and what metrics to design for in large part stems from the fact that the performance of energy-water materials systems hinges on interactions with, and the properties of, the fluids with which they are in direct contact; these fluids, in turn, are also multi-component and multi-phase in nature. Articulating metrics and establishing methods and facilities that allow for uniform characterization will go a long way in developing the ability to specify a priori, and design accordingly, functional materials and materials systems for processes in energy-water systems.

A core challenge for water remediation chemistry lies in the need to address a diverse array of soluble and particulate pollutants. These range from biological and anthropogenic organic and halogenated hydrocarbons to 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 have limitations as sustainable, full-cycle water remediation technologies. **Advancing the fundamental science of oxidative [5–7] and reductive [8,9] catalytic processes** provides opportunities to develop sustainable remediation methods that couple degradation of wastewater pollutants with energy and resource recovery [10]. Such catalytic electrochemical and photochemical redox processes provide a complement to separation and sequestration-based methodologies. They 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. Methods in which catalytic activity can be accelerated, for example, through application of electrical potential or illumination, merit fundamental investigation.

The creation of new materials that combine chemical catalytic activity with physical molecular separation activity is an important science goal. A number of advances are being made in designing, controlling, and developing nanoscale, porous, or other materials (including inorganic, organic, and hybrid systems) for adsorbents and membranes for selective separations for water purification. Inducing reactions within the pores, channels, or surfaces of these systems by incorporating catalysts into structural motifs would lead to new concepts for selective reactive separations of specifically targeted species. Photochemically or catalytically active materials could be deposited onto nano- or meso-porous systems using solution or gas phase processes. For example, atomic layer deposition (ALD) and/or sequential infiltration synthesis (SIS) could provide uniform coatings of photoactive semiconductors on structured nanostructured membranes, fibers, and layered materials.

Important research areas include the de novo design and synthesis of multi-functional materials. For example, the design of new nanostructures and or building blocks for multi-functional systems stemming from self-assembly or other hierarchical approaches are enabled by advanced theory and advanced structural and spectroscopic tools, as well as molecular modeling and synthesis. The design and development of multi-electron redox catalysts, including a priori design of new catalytic sites is another important opportunity. The design rules that predict binding of specific molecules near the catalytic site for multi-electron, multi-proton, bond-breaking reactions are not well described.

Understanding and controlling elementary processes for binding, reactivity, transport, and energetics of interactions of contaminants at surfaces and interfaces, as well as within nanoconfined environments, is required to design new systems. Understanding matrix effects in complex reaction media (e.g., high salt concentrations, various organic contaminant, multi-phase, or heterogeneous) on catalyst performance (and design) is also critical. Reaction pathways for the destruction of organic contaminants involve complex, multi-step reactions involving a number of redox reactions, thus elucidating reaction pathways and mechanisms is critical for the design of catalytic systems.

An opportunity with electrocatalysis is the use of the signal coming from an electrocatalytic signaling layer as a means of identifying the need for turning on catalytic anti-fouling functionality. An example implementation would be a porous electrocatalyst layer coated over a membrane, serving as a protective layer to interact and bind with organic foulants, although other realizations are also possible. Regeneration of the membrane would be achieved by applying

a positive potential to the catalyst layer to initiate the oxygen evolution reaction by splitting H_2O to various forms of hydroxide, peroxide, and oxygen radicals. Such species could subsequently oxygenate the adsorbed organic foulants at their binding sites, thereby weakening their interaction with the support and rendering them soluble by the solution. Integrating conductive materials within separation membranes offers opportunities for actively monitoring and controlling a range of membrane fouling, adhesion, and transport problems. Biomaterial adhesion can be detected by the appearance of excess impedance to solution electrochemistry, at which point the catalytic function could be initiated. Developing new photocatalysts is another research direction, including using a broader than UV spectrum of illumination. (Figure 2.3.4 [11]).
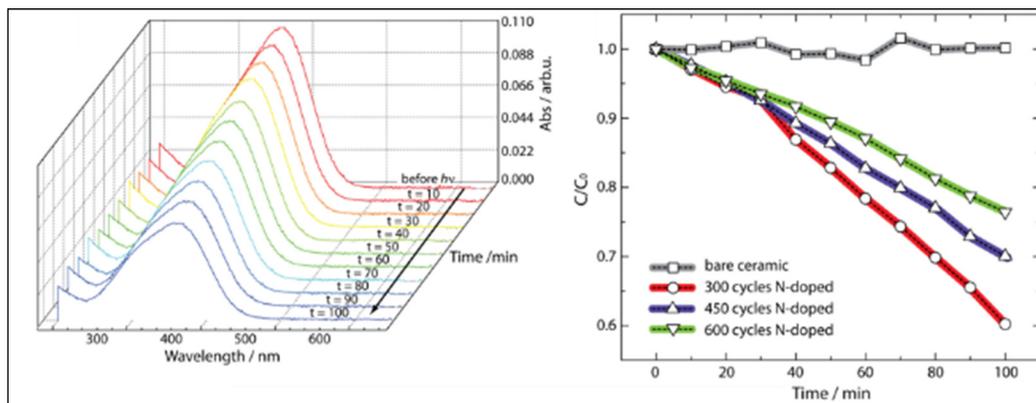

Figure 2.3.4. Visible-light photocatalytic degradation of organic molecules using novel doped semiconductor coatings.

Development of robust and affordable sorbents capable of targeted removal of contaminants from water has the potential to greatly enhance the scope of water decontamination. Adsorption-based processes are already widely used in contaminant removal; however, the existence of a wide range of contaminants means that many opportunities exist for advances in this area. Common adsorbents include zeolites [21], activated carbon [22], silica gel [23], and polymers [24]. Zeolites are most often polar, crystalline aluminosilicates, although non-polar siliceous zeolites also exist. Fundamental research is needed on mesoporous molecular sieves, sol–gel-derived metal oxide xerogels and aerogels, MOF, π-complexation and composite adsorbents, new carbonaceous materials (carbon nanotubes, carbon fibers, and super-activated carbons), high-temperature ceramic sorbents, and strong chemical sorbent materials. Although these new sorbent materials have demonstrated promising sorption properties for many existing and new applications, systematic studies on synthesis methods and characterization of these new materials are necessary to fully explore and realize their potential as practical sorbents. Stages of the decontamination process, including capture of target analytes, disposal of spent materials or concentrated brines, and mechanisms for regeneration of the sorbent should be considered in design of next-generation materials.

Research challenges in this topic include the use of computational and other high-throughput methods to select or design adsorbents with appropriate binding motifs for targeted species. Interference of binding sites with species present at a much higher concentration than the targeted species is a ubiquitous challenge; laboratory techniques suitable for characterizing these effects in complex mixtures are needed. Fundamental insight into the mechanisms of chemical degradation (or conversely, chemical stability) in adsorbent materials exposed to complex aqueous environments is greatly needed.

Biomimetic approaches are likely to be valuable in seeking adsorbents providing a step change in selectivity for trace contaminants. Adapting knowledge from enzymes that are capable of capturing radioactive ions with extraordinary specificity, for example, has great potential. Opportunities to exploit this kind of biological function could either involve direct efforts to immobilize enzymatic species in usable configurations for water treatment, or more indirect use of the structural and mechanistic aspects of these systems to further the design of other materials.

The design of new materials based upon knowledge of specific material-fluid interactions will enable step-change improvements in membrane for water purification.

Among the most important materials for energy-water issues — and among those for which innovations are most needed — are membranes. Semi-permeable membranes — structures made of hard or soft matter that allow some chemical species to pass through, but not others — are essential for many energy-water problems. An obvious example is the challenge of water purification [12,13], including desalination [14,15], decontamination, and disinfection of seawater, freshwater, groundwater, and wastewater. In this case, the goal is to remove unwanted constituents such as ions, solutes, pathogens, or particles. Improved semi-permeable membranes that allow water to pass through, but not the undesirable species, are needed. These purification processes often consume energy (e.g., salt water must be pressurized in RO desalination), and therefore are prime examples of energy-water issues.

Effective membranes have certain performance requirements: they must exhibit mechanical, chemical, and thermal robustness; they must have high water (or proton) flux; and they should demonstrate high solute rejection. In addition, they should be non-fouling, or at least easy to clean. Few membranes satisfy all of these factors [18]. In order to design membranes with tailored properties, a number of basic science issues must be fully understood. They include: How do ions (including protons) and solutes interact with water? In particular, can one understand, tune, and access the full range of hydrophilic and hydrophobic interactions? What is the hydration structure and dynamics of water around ions and solutes? What are the transport properties of ions, solutes, and water itself? One of the salient features of membranes is that water, ions, and solutes are confined in pores, so it is essential to understand how material interactions and confinement change the structure and dynamics — even hydrodynamics — of these species.

The ability to predictively design materials with desired functionality could lead to molecularly crafted specificity, highly efficient transport, and active pumping mechanisms. The design of materials with specific, active, and selective interactions with solutes and water leverages many new and scalable materials chemistry approaches, including self-assembled and nanopatterned materials, the design of selective receptors to target specific, low-concentration contaminants, and other new synthetic approaches. For example, as illustrated in Figure 2.3.5 [19], these design motifs could originate from careful tuning of water-surface interactions and hierarchical structures that are prevalent in natural systems such as aquaporin, which transport water at rates thousands of times faster than conventional pores or from geometric constraints introduced by materials structure such as nanotubes with similar water flow enhancements. New size-exclusion membranes with aligned pores and highly tuned pore sizes may be based on self-assembled materials, such as block copolymers and programmed small molecules or combinations of these strategies. Controlling transport via interfacial design is likely to enable custom chemical structure-based selectivity and active pumping through membranes, which represent new modes of separation that are not driven by chemical potential gradients.
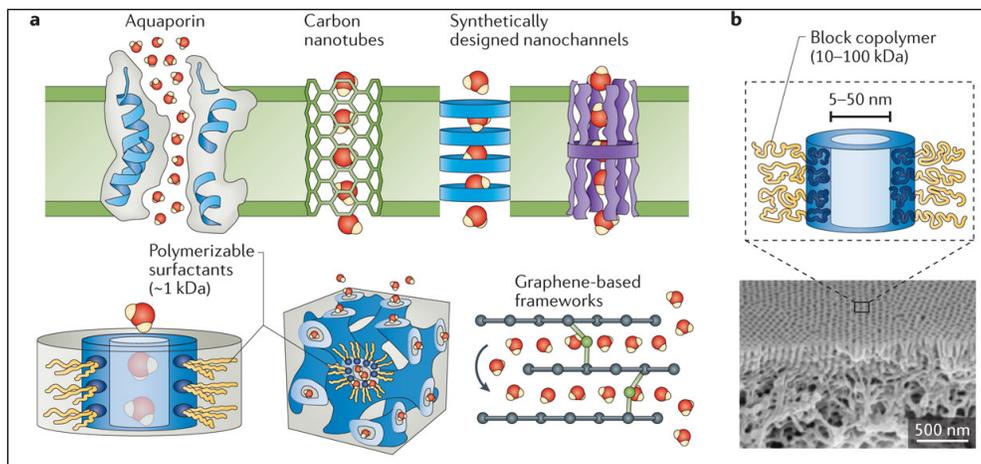
Figure 2.3.5. Molecular design of selective membranes through the insertion of various types of amphiphilic molecules pore-forming structures.

Similarly, harnessing insights into the role of confinement on water could lead to new physical phenomena and enhanced or selective transport of water and solutes. For example, small carbon nanotube pores (<1 nm) demonstrate a 10× enhancement in proton conductivity compared to bulk water [20]. Controlling transport via interfacial design is likely to enable custom chemical structure-based selectivity and active pumping through membranes, which represent new modes of separation that are not driven by chemical potential gradients.

Another opportunity in the area of materials development involves increasing the multi-functionality of water purification materials systems. How do we design membranes that simultaneously filter and disinfect through the introduction of photocatalysts? One approach to address this challenge successfully is to develop methods to embed photocatalysts in membrane materials while retaining functionality. What new approaches will increase flux through membranes while retaining selectivity through the introduction of carbon nanotubes? This requires mastery of precision placement of and access to carbon nanotubes in materials. How do biological systems control ion transport through channels and how can we incorporate those principles in the design of materials targeted at specific contaminants? Further, can these ion channels be used to concentrate valuable contaminants to produce value from byproduct streams? This requires fundamental research into how ion channels operate and whether they, or synthetic mimics yet to be created, can retain interesting and useful properties in designed membranes systems. How does the introduction of 2D materials, like graphene, graphene oxide, or MoS_2, influence surface properties like hydrophilicity? TiO_2 membranes are particularly interesting because they are photocatalytic [16] and can be used as effective disinfectants. Another recently developed inorganic photocatalyst for disinfection is MoS_2 [17]. How does material structure change when hydrated, and can this be leveraged in the design of both the material and the fluid with which it is interacting on a dynamic basis?

An overarching challenge for development of improved materials for water purification is the need for enhancing fouling resistance and creating regeneration mechanisms. Fouling of materials in energy-water processes occurs by a staggering array of contaminants, including organics, inorganics, colloids, and biologicals, as illustrated in Figure 2.3.6. The design of fouling-resistant materials requires a detailed, molecular understanding of the interactions among the foulant, surface, and surrounding fluid. Further, while significant work on interfaces has already occurred, energy-water processes generally include flowing fluids and other external forces. Designs for fouling resistance are likely to exploit the dynamic properties of both the material and fluid. For example, it is not necessary that a foulant be completely repelled from the surface as long as it is easily sloughed off either under the shear stresses present in normal operation or during standard cleaning

Figure 2.3.6. Fouling can occur from a wide array of organics, inorganics, biologicals, and colloids. New designs for fouling-resistant, robust, and easily cleaned materials must be based on molecular-scale strategies to prevent attachment and promote release.

procedures. New materials designs will need to utilize cooperative effects to result in a surface chemistry and morphology that are simultaneously fouling-resistant and/or self-cleaning and robust.

The goal of simply avoiding fouling during water purification is overly simplistic; research is needed to control and improve the ability of water purification materials in their capacity for regeneration. Oxidative treatment is widely used to mitigate fouling, and the stability of membrane materials with respect to this treatment can be a strong limiting factor on overall performance. Improved understanding of the molecular-scale mechanisms of materials degradation during these and similar treatments would have great value. Similarly, advances in materials that either have improved resistance or have the potential to self-heal after degradation can make important contributions to this area.

Recently, the extended family of 2D materials, spearheaded by graphene, has captured attention for their potential in water treatment. The origin of much of this interest is their extremely high surface area, offering large sorption capacity for materials such as oils and common solvents that are attracted to the basal planes of graphene and related materials [27–29]. These 2D 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 since it can

dramatically reduce the life-cycle cost and sustainability for 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 as oil and organic solvent sorbents [30], particularly for use in water bodies where fluid selectivity is important. Once oil has been extracted from the water 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 (Figure 2.3.7 [31]).

Among the most challenging goals in sorption research is the ability to tailor surface properties for solute-specific adsorption. Achieving this goal would enable not only effective capture of difficult water contaminants such as nitrate [32], phosphate [33], and heavy metals, including hexavalent chromium, lead, and mercury [34], but it 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 substantially greater, however, if true ion-specific sorption were possible. What if one could capture calcium separately from magnesium? Such sorbents would allow for unprecedented resource recovery from waste streams

Figure 2.3.7. Advanced regenerable oil sorbents. A repeatable sequence of a simulated oil spill (top: blue-dyed silicone oil, bottom: crude oil), followed by sorption into a surface-treated polymeric sorbent, squeezing the oil out of the sorbent, and a second sorption cycle. This can be done repeatedly with the same piece of sorbent material and with recovery of the oil.

and from contaminated water sources, thereby revolutionizing the economics of many water operations. Another powerful example would be the ability to sequester bioactive molecules such as endocrine disruptors from wastewater treatment plants, while allowing nonhazardous organic materials to pass through.
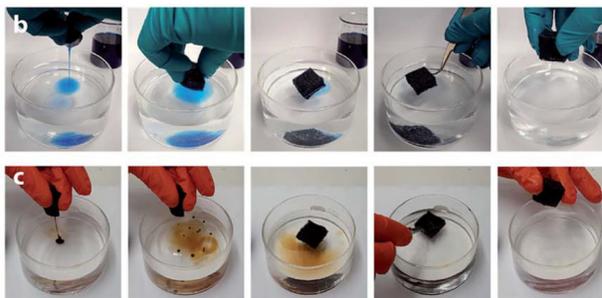
The development of broadly fouling-resistant materials will likely require the design of new, orthogonally functional materials that combine many different fouling-resistant strategies while maintaining other functionalities (specificity, geometry). This specific example highlights the general need to understand the complex multi-body interactions between fluid constituents and with interfaces, so that proper specifications can be spelled out ahead of the design of materials and materials systems for energy-water processes. This challenge also presents an opportunity to address designer fluids of appropriate constituents and compositions for subsurface resource recovery processes squarely within the intersection of energy and water issues.

Materials developed for energy-water issues require extreme functional dimensionality. Effective separations are likely to require a combination of the interactions discussed above. For example, one could envision selective molecular receptors displayed on the pore walls of a designed nanoporous size exclusion membrane that also incorporates fouling-resistant features, or the design of membrane materials that simultaneously filter and disinfect. This multi-dimensional design presents new and distinct computational challenges bridging atomistic through macroscopic length scales and an equally broad range of timescales. Similar challenges exist in the materials synthesis of carefully controlled hierarchical materials with orthogonal functionalities and in their characterization.

All of the above materials design challenges rely on the development and leveraging of new scattering, spectroscopy, and imaging methods that probe hydrated, porous, and confined interfaces, including 3D and internal morphology, heterogeneity in real time, and environmental conditions. The design of this broad class of functional materials for energy-water issues requires careful characterization of complex, hierarchical materials in complex geometries. Leveraging the development of new scattering, reflectivity, spectroscopy, and imaging methods that probe hydrated, porous, and confined interfaces, including 3D and internal morphology, heterogeneity in real time, and environmental conditions, is necessary. Viewing the internal structures of pores is a particular challenge, principally in cases where one would like to understand the dynamics of water and extremely dilute solute transport within these pores. Frequently the concentrations that are important for energy-water systems are much lower than those at which our analytic techniques for studying diffusion (e.g., NMR and quasi-elastic neutron scattering) operate.

2.3.3 Impacts

Basic science advances for the design of complex fluids and materials will have a major impact on the creation of more effective energy-water systems. New paradigms and approaches for materials design and synthesis are needed to revolutionize membrane, sorbent, ion exchange, and catalyst performance. New ideas for multi-purpose materials are needed that combine several functions — selectivity, precise size exclusion, reactivity, fast transport/active pumping, self-cleaning, and repair. Design of new complex fluids and materials based on molecular-level understanding of interactions and processes is an important underlying science for both energy-efficient water purification and the concentration of valuable byproduct streams. Materials with robust new surface treatments exhibiting anti-fouling and anti-corrosion properties will extend the lifespan of countless components of infrastructure within energy-water systems, ranging from pipe networks to separations media. Subsurface resource recovery will benefit from new fluids capable of more efficient transport and more effective interactions with minerals, as well as from increased robustness of materials integrated into well bore hardware.

Understanding water/solute/material interactions and how to leverage these in design motifs is likely to result in breakthroughs in materials for other energy-relevant applications, including electrochemical materials (e.g., batteries, fuel cells, and artificial photosynthesis), nuclear separations, environmental management, separations, and remediation applications. Pollution mitigation efforts can leverage advances in membrane and sorbent technologies, offering the prospect of targeted, efficient separations to pull specific pollutants out of complex mixtures.

This work will also result in the development of a broad suite of forefront techniques focused on structure and dynamics at buried interfaces and confined spaces. National user facilities offer a fertile arena for the development of powerful new methods for probing transport and reactivity in both model and realistic systems, with ramifications extending far beyond energy-water issues.

2.4 **PRD 4** — ADVANCE SCIENCE TO HARNESS THE SUBSURFACE FOR A TRANSFORMATIONAL IMPACT ON WATER

Reactive natural and engineered subsurface materials offer tremendous potential for water storage and treatment. Realizing this potential will require revolutionary advances in approaches to quantify, image, and predict coupled, multi-scale physical, chemical, mechanical, and biological processes occurring in complex subsurface systems.

2.4.1 Scientific Challenges

To harness the potential of the subsurface for a transformational impact on water, new approaches must consider the complex fluids, interfacial reactions, and materials- and fluids-by-design challenges described by the previous PRDs *in the context of heterogeneous subsurface geological materials and dynamic hydrological and geochemical gradients*. Significant basic science challenges exist to understand and predict dynamic subsurface process coupling occurring at native scales and their influence on integrated subsurface system behavior. Advances in basic subsurface science hold significant potential to underpin new strategies leading to game-changing water benefits.

The rapidly changing landscape for water supply, paired with increasing water demand and a variety of societal needs, presents an unprecedented opportunity for basic science to revolutionize a transition to a radically different water future. Current U.S. water storage and treatment approaches were largely designed for 20th-century populations, energy systems, and environmental conditions, often using trial-and-error approaches [1]. Examples include the use of dams to store water and the use of ex situ approaches to treat contaminated groundwater. While several water technology advances have occurred over the past decades, lacking are fundamental understandings of multi-scale, multi-phase chemical, physical, and biological processes that could underpin a radically different future water paradigm. Foundational scientific advances could lead to a range of science-based subsurface strategies that ensure water can easily be stored, treated, and retrieved for specific purposes. This vision requires the discovery and integration of complex subsurface system behavior with new materials, catalysts, models, and sensors to enable a future where water supply and demand are in perpetual, sustainable balance.

Several significant basic science challenges must be tackled to realize this ambitious vision. Developing a predictive understanding of subsurface system behavior is hindered by the multi-scale complexity of the subsurface (Figure 2.4.1) — a dynamic system that includes heterogeneities and reactivity across approximately 12 orders of magnitude in length scale. The dynamic and non-ideal subsurface environment encompasses the vadose (unsaturated) and saturated zones, which are actively linked to surface waters, the biosphere, and the atmosphere. Minerals, fluids, dissolved constituents, and microbes interact within and across these in complex ways — over length scales of nanometers to kilometers, across interfaces ranging from pore-mineral to saturated-unsaturated compartments, and from timescales ranging from picoseconds to millennia and longer.

Overarching challenges that motivate the basic science subsurface research include identification of molecular through pore scale processes that drive larger-scale system behavior; quantification of how these processes will evolve with intense precipitation, prolonged droughts, and artificial recharge; determination of how hydrological, geochemical, and biological processes occurring at native scales couple and aggregate to lead to cumulative macro-system behaviors; and development of predictive and in situ strategies to control subsurface systems to enhance the reactivity and storage capacity for game-changing performance. Although work has been done to advance strategies such as water banking (e.g., [2,3]) and engineered infiltration (e.g., [4, 5]), significant opportunities exist for advancing fundamental understanding that will enable predictive control of adsorption, permeation, or reactivity associated with
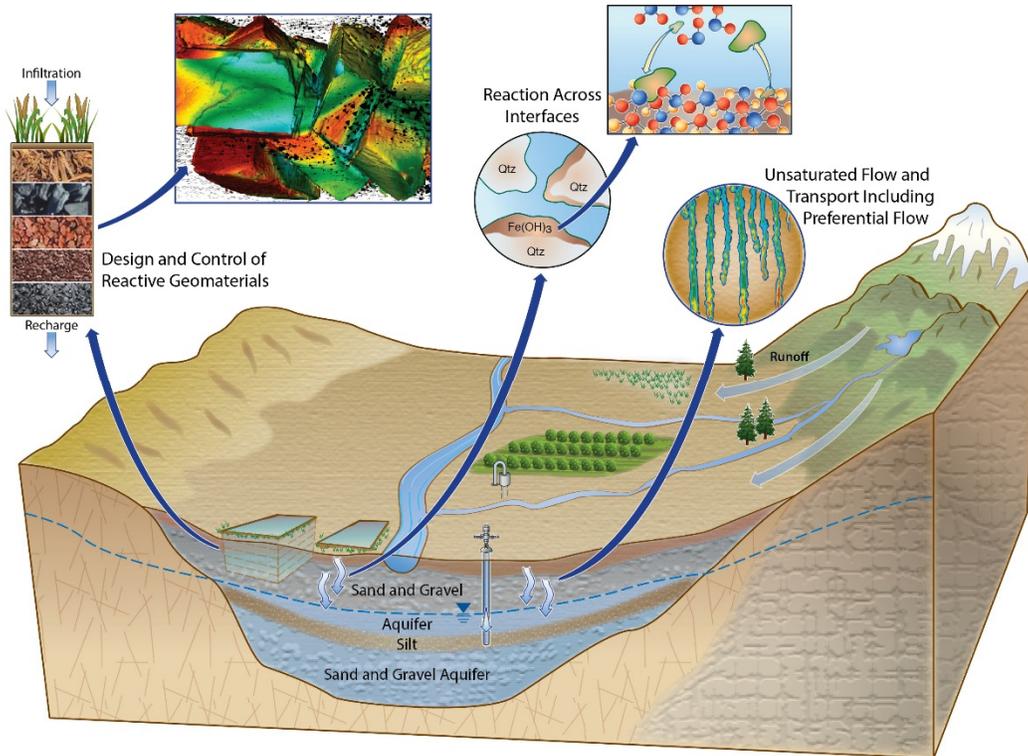
Figure 2.4.1. Advancing predictive control of the subsurface for in situ water storage and treatment requires quantification of complex fluid behavior, control of reactions across interfaces, and design of material-fluid interactions — all of the PRD challenges described above — as well as their manifestation in the context of natural heterogeneity and large-scale hydrological and geochemical gradients and transients. Quantifying and predicting coupled geochemical, hydrological, geomechanical, and biological processes that occur at native scales, their cumulative influence on the behavior of natural aquifer systems, and the design of in situ approaches that can lead to game-changing water treatment or storage benefits are grand challenges. (Courtesy of Susan Hubbard, Lawrence Berkeley National Laboratory.)

subsurface recharge, evapotranspiration, and geochemical reactions in subsurface systems. In essence, design of in situ manipulation strategies for transformational water benefits requires quantification of complex fluid behavior, reactions across interfaces, and design for select material-fluid interactions — all of the scientific challenges described above — with the additional complexity that these processes occur within a heterogeneous geologic material and in the presence of significant hydrological and geochemical gradients and transients (Figure 2.4.1).

The identification of basic science research directions must also consider several constructs important for effective future water strategies. "Fit for purpose" is an important concept, where approaches are developed to specifically treat water to a quality appropriate for a specific use, such as for thermoelectric cooling, hydraulic fracturing, irrigation, or drinking water. Important in this regard is understanding which and to what extent molecular through pore scale processes of degraded source water and its interactions with minerals can be transformed to meet needs for other applications. To address the various water demands, it will be imperative to consider the molecular properties and processes associated with a range of unconventional fluids and their interactions with the natural environment, including brackish groundwater, produced water, seawater, municipal reclaimed water and industrial wastewater. Another important construct is the interoperable utilization of natural and manufactured geosystems. Conventionally, the former typically refers to natural aquifer processes and the latter to control of ex situ water treatments. However, opportunities exist to manipulate natural aquifers, to create altogether new geomaterials targeted for specific water treatment functionality, and to co-utilize these previously distinct systems for greatly enhanced selective adsorption, permeation, or reactivity. Recognition of expected future extremes in rainfall, temperature, and other environmental factors must also be a key consideration in the design of future water strategies. For example, hydrological perturbations that greatly alter water content, salinity, and pH in subsurface systems can irreversibly alter the physical properties of aquifers and perturb the geochemical status, significantly influencing the sorption or desorption of contaminants from mineral surfaces and the kinetics of oxidation-reduction

reactions. Fundamental understanding of how fluid-mineral interactions change in response to transients is needed to transition from approaches that rely on seasonally repeatable precipitation and temperature trends to strategies that can take advantage of significant environmental perturbations where and when they occur. Examples include the use of the immense subsurface pore volume and natural hydrological and geochemical subsurface gradients to store or "bank" excess surface or previously treated water, which can be subsequently extracted when needed (see Section 3.2.2.1, Panel 2).This concept is referred to as water banking, managed aquifer recharge, or aquifer storage and recovery [2].

A hypothetical example is provided to illustrate the potential of a future, fit-for-purpose water vision underpinned by fundamental science. Through a greatly enhanced predictive understanding of non-linear unsaturated zone flow and subsurface mineral-fluid-gas-organic interactions, the infiltration of excess storm runoff or treated wastewater into the subsurface would be controlled while minimal evaporative losses and enhancing beneficial subsurface geochemical reactions would be realized. Beneficial geochemical reactions will be controllable through several mechanisms designed to target specific water quality goals, including manipulating reactants, controlling the rate of infiltration into the natural aquifer, or routing specific water streams through geomaterials specifically designed to greatly enhance the removal or degradation of unwanted constituents. Treated water streams will be used for specific energy, industry, agricultural, or urban uses. Ultimately, aquifers will serve as a significant bank for storing infiltrated water "at scale," allowing for below ground water storage at a volume equivalent to all conventional dams currently in the United States, but with far more flexibility and lower cost. Banked water of predictable water quality will be withdrawn and used when and where needed across the "water grid." Intermittent renewable energy or waste heat will be used to drive water pumping and treatment processes. Networked sensing systems will allow for precision tracking of water and its constituents, vertically from the ground surface through deep groundwater and across water basins using a range of autonomous capabilities. Assimilation of hydrological and geochemical measurements into mechanistic models will allow the development of feedback control schemes capable of accounting for dynamic changes in local operational environments (e.g., feedwater quality, production demand, and evolution of energy strategy mix), while maintaining optimal system operation (e.g., with respect to production level and efficiency, as well as energy production or consumption).

With a pressing need for future water in a changing world, and with advanced imaging, analytical, and computational capabilities, an unprecedented potential exists to use basic science to understand, quantify, and predict coupled hydrological, geochemical, physical, and microbiological processes needed to harness the tremendous potential of natural environments for transformational water benefits.

2.4.2 Research Thrusts

Building on the three PRDs described earlier, which are all important for advancing subsurface science, three additional scientific thrusts are identified. The first focuses on developing fundamental understanding of fluid flow and reactions in complex natural systems, with particular focus on variably saturated regions and associated coupled chemical, mechanical, and hydrological properties. The second thrust focuses on the control of reactive aquifers as well as designed geomaterials for in situ subsurface use. The third thrust focuses on development of 4D networked monitoring systems, and the assimilation of new water, materials, and geochemical datasets into mechanistic models to predict function and response of subsurface environments and design new approaches to utilize the subsurface for water benefits.

Thrust 4a: Fundamental Understanding of Fluid Flow and Reactions in Complex Subsurface Systems

The shallow subsurface environment contains a variety of complex physical and molecular machinery that operates in tandem to perform different functions. This system is incredibly important for all life on earth: it provides water, supports agriculture and biodiversity, sequesters CO_2, can naturally clean water, and can serve as a repository for waste. The many beneficial interactions that occur in this environment among fluids, minerals, microbes, and dissolved constituents, and that provide these significant benefits, have evolved naturally over time. Substantial advances in our understanding of subsurface flow and reactions in environmental systems are urgently needed to sustain current beneficial interactions in the presence of external forcings (e.g., droughts and floods), and enhance natural and design synthetic environments for robust, fit-for-purpose water storage or treatment. Three critical

scientific gaps are identified that, if addressed, could provide a significant foundation for new water-energy strategies: unsaturated reactive transport, interactions across natural system interfaces, and coupled aquifer geomechanical-geochemical-hydrological processes.

Unsaturated reactive transport. The physics of unsaturated flow and reactivity is particularly ripe for advancing a new generation of experimental and modeling approaches that combine real-time imaging with cutting-edge computational tools [6,7]. Quantifying water, particle, and gas transport and reactivity in the unsaturated (or vadose) zone is a basic science challenge critical to energy-water issues. While significant research has focused on improving understanding and prediction of fully saturated groundwater systems, the ability to predict reactive infiltration through the variably unsaturated subsurface, including reactions occurring between infiltrating fluids and minerals, is extremely limited. Current research tends to focus on two extremes of the scale continuum — pore scale and catchment/landscape scales; efforts are needed to understand and predict how small-scale phenomena influence larger-scale reactive infiltration into and through the subsurface.

Preferential flow through the vadose zone (Figure 2.4.2 [6,8,9]) results from significant spatial variations in water velocities due to heterogeneities in soil properties at both pore and continuum (or Darcy) scales. While the underlying causes of preferential flow may differ, flow commonly converges toward preferential pathways and non-equilibrium states driven by water pressures and solute concentrations. Given the challenging nature of transport processes, quantifying reactive processes — including chemical reactions occurring at mineral surfaces or due to mixing of fluids and gases — remains an outstanding challenge. The transport of nanoparticles (i.e., colloids) through unsaturated systems is especially difficult to understand and predict, partially due to the complex effects of, for example, particle size, surface charge and chemistry, ionic strength, and pH [10]. The development of new imaging approaches and predictive models for nanoparticle transport behavior also offers an opportunity for basic science to underpin entirely new approaches in passive treatment, for instance, using engineered nanoparticles, as discussed further below.
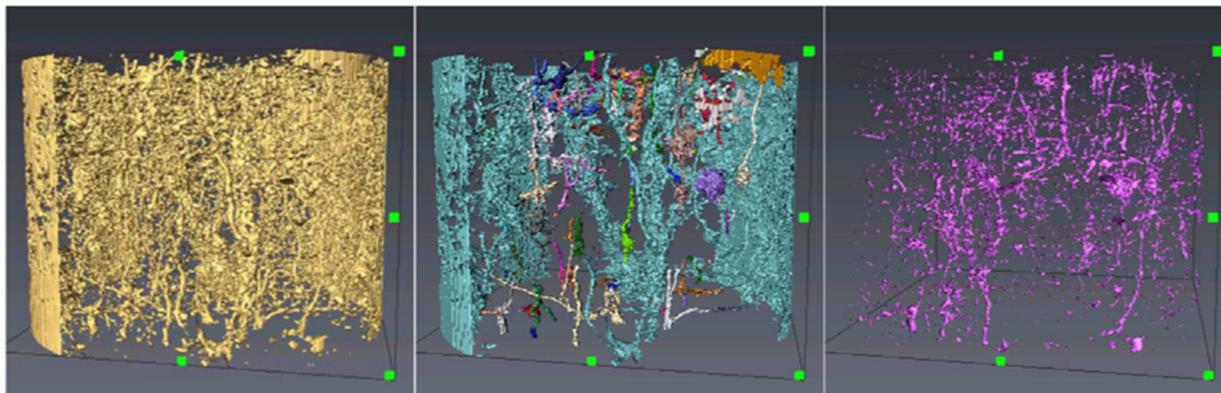

Figure 2.4.2. Interfaces (liquid [water and air] and solid) controlling flow and transport through the unsaturated zone. A 3D representation of the entire structure (left) compared to the active macropore network with color coding indicating an isolated macropore network (middle) and the complement of their intersection (right) [9]. The structures of the active network are substantially different from the overall pore structure. The images are derived from x-ray scanning of a soil core (diameter of 135 mm) exposed to frequent wetting events. Heterogeneity at various scales drives contrasts in porosity, texture, hydrophobicity, and reactivity that can lead to non-equilibrium states of water content and pressure in different regions.

Interactions across natural system interfaces. In an extension of the "Interface" theme of PRD2, basic research is needed to quantify hydrological, geochemical, and microbiological interactions occurring across a range of hydrogeological interfaces, particularly in response to transient perturbations. Although decades of studies have focused on fundamental pore fluid–mineral interactions, a significant gap exists in understanding how these interactions change in the presence of transients and other natural interfaces. Within aquifer systems, several types of interfaces are host to poorly understood interfacial interactions, where rapid reactions often occur in response to fluid mixing. For example, interfaces between geologic units (such as a sandy and a clay-rich unit) and between different hydrologic units (such as between the unsaturated zone, the capillary fringe, and the water table) embody a range of reactions that unfold over molecular- to meter-scale interfaces.

Although sorption of ions and molecules at interfaces has received much attention, most studied systems have been fairly simple. Many questions exist in naturally complex systems, such as understanding the influence of nanoporous biofilms and variably crystalline metal oxide coatings on sorption and mineral dissolution-precipitation. Of perhaps greater importance to water quality are the oxidation-reduction reactions that occur in the subsurface. Some of these are catalyzed or promoted by naturally occurring minerals (Figure 2.4.3), including Fe-(oxyhydr)oxides such as magnetite [11,12], Fe-sulfides such as pyrite [13], and Fe-bearing clays [14,15,16]; other reactions occur entirely in solution or are mediated by microbial communities [2]. The kinetics of abiotic reactions can be quite rapid due to mixing, while the chemical gradients that develop in response can encourage a range of microbial metabolisms. Both abiotic and biotic reactions can result in "fouling" or unwanted reductions in permeability [5], which poses a significant problem for a wide range of water production and treatment strategies and where conventional treatments are costly and only partially effective.

Coupled mechanical-geochemical aquifer behavior.
Sinking of an area of land, known as land subsidence, is a global problem and, in the United States, more than 17,000 square miles — an area roughly the size of New Hampshire and Vermont combined — have been directly affected by subsidence. In some regions, subsidence is significant — with land sinking on the order of several meters. More than 80% of the identified subsidence in the United States is a consequence of human impact on subsurface water, such as groundwater overdraft by pumping. Land subsidence can be extremely detrimental to energy infrastructure, including energy and water system wells and pipes.

Figure 2.4.3. Role of naturally occurring surfaces in mediating contaminant transformations. Top: Conceptual model for reduction of hexavalent uranium (U(VI)) by Fe(II)-bearing minerals [11]. Bottom: Clay-mediated formation of polychlorodibenzo-p-dioxins and dibenzofurans (PCDD/Fs) can occur via electron transfer to Fe(III)-montmorillonite clay [15]. The schematic shows the potential reaction pathway for formation of the direct precursors ("predioxins") of the most toxic PCDD congeners [16].

Withdrawal-related subsidence has been linked to increased groundwater contamination due to the migration of toxic elements from the clay layers [17]. This phenomenon is often called the "dirty sponge effect," and the concentrations of expelled contaminants can vary by many orders of magnitude, both temporally and spatially. For example, arsenic (As) occurs naturally in sediments (termed "geogenic" contaminants). Geogenic contaminants are present in many aquifers throughout the world. In the aquifers of South and Southeast Asia, their release to groundwater is recognized to be through the reductive dissolution of Fe(III)(hydr)oxides [18] (see Groundwater Contamination Sidebar). However, the fundamental chemical-mechanical controls on As releases with depth and changes in aquifer stress are not well understood.

The conceptual model for compaction-induced groundwater contamination is that deep groundwater extraction causes interceded clay layers to compact and expel water containing dissolved As to deep aquifers (bottom panel of the following sidebar [19]). The expansion and compaction of clays during wetting and drying cycles can have cascading yet unpredictable consequences on aquifer hydrology and geochemistry. Such activities could irreversibly alter storage capacity and lead to the expulsion of undesirable ions, including not only As, but also uranium (U) and chromium (Cr).
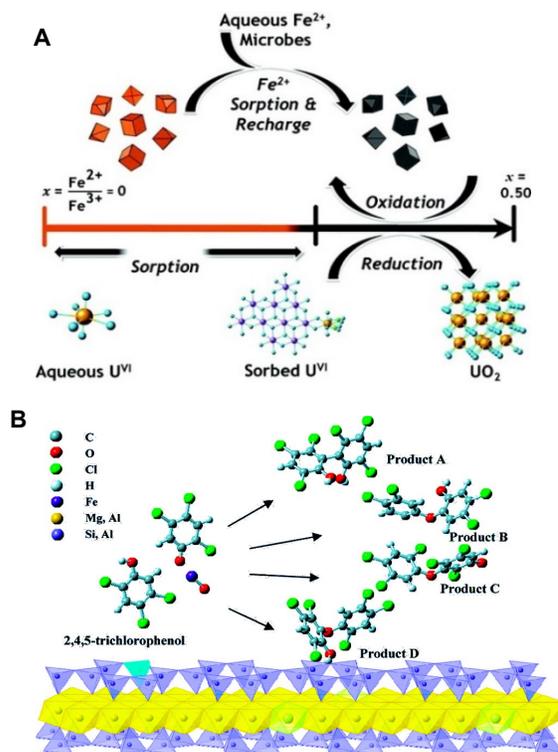
GROUNDWATER CONTAMINATION

While changes in water infiltration and pumping may lead to changes in redox and compaction that, in turn, can detrimentally impact water quality, a mechanistic understanding of mechanical-geochemical process coupling is lacking. This figure highlights the presence of naturally occurring "geogenic" arsenic in groundwater. Arsenic is a potent carcinogen that poses a massive and growing human health threat, especially throughout South and Southeast Asia, where as many as 100 million people are chronically exposed (left panel [19]).
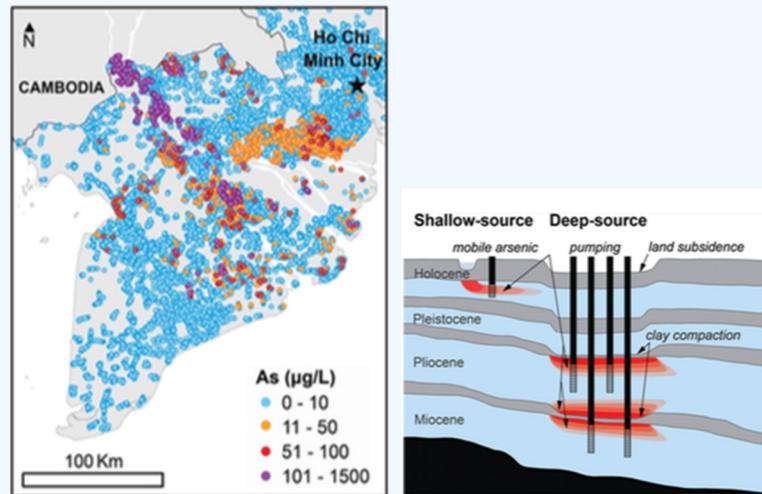
In spite of the increasing pervasiveness of subsidence-related subsurface stress and its potential to detrimentally influence water quality, an understanding of the coupling between geomechanical and geochemical processes is severely lacking. Significant science challenges are associated with the quantification of molecular- to pore-scale fluid-mineral interactions, as well as their manifestation at larger scales.

Thrust 4b: Understanding Reactive Geosystems

Classes of contaminants encountered in water and energy systems that require specific treatment include complex surfactants from energy (oil, gas, and coal) extraction; metallic (chelated) and organic contaminants from mining, manufacturing, and thermoelectric power plant cooling; and agricultural wastes (e.g., nitrate, pesticide). Bromide and iodide at high concentrations commonly associated with produced waters can also pose a problem if introduced to drinking water sources via formation of unwanted disinfection byproducts. As noted above, groundwater degradation can occur during groundwater pumping, leading to compaction of the geologic unit and the release of natural and anthropogenic contaminants from fine-grained layers [17].

While multiple technologies exist for improving nontraditional water quality for fit-for-use water benefits, many of the existing approaches are costly or energy intensive, or have other challenges, including management of highly variable compositions, large but distributed volumes, and intense transient discharges. Examples of existing approaches include gravity-based separations, membrane-based separations, thermal evaporation, biological treatment, and a myriad of chemical treatments. Some existing approaches are performed in situ and some are performed ex situ.

This thrust focuses on exploring a new class of reactive geosystems that could be designed to selectively enhance infiltration as well as sorption and reactivity in both natural and engineered systems. The concept builds upon the recognition that engineered subsurface systems used to manage urban storm water often utilize some form of engineered infiltration or subsurface filtration to reduce the volume of runoff leaving a developed site [5], and that experience with managed aquifer recovery suggests water quality can improve after passage of water through natural geological materials [2]. Although analog approaches have potentially very unique benefits for water storage and the capacity to remove contaminants, the promise of these engineered subsurface systems is only just now being recognized [19]. The inset of Figure 2.4.1 shows an example of the use of geomaterials within a subsurface engineered system for removal of a variety of compounds. The success of engineered infiltration for contaminant removal rests on developing a fundamental understanding of the interactions between reactive pore fluids and reactive subsurface engineered materials in the context of hydrological gradients.

Contaminants are removed during passage through an infiltration or an aquifer system in three main ways: (1) filtration, (2) sorption, and (3) transformation (including inactivation and biodegradation). Metals, hydrophobic organics, and pathogens can exist as both dissolved species (or freely suspended in the case of pathogens) and in association with colloids. Even if filtration and sorption are successful, contaminants may be later released to the dissolved phase. For many aqueous contaminants, controlled oxidation-reduction reactions are a critical pathway, but long-term stability remains an important question. An improved understanding of electron transfer and the means by which it controls pore fluid-mineral reaction kinetics could lead to game-changing new approaches to use the subsurface to treat urban storm water, produced water, or other large-volume flows. Enhancing the passive use of natural aquifers could also improve water infiltration/storage, as well as water quality, thus eliminating the need for more energy-intensive approaches.

An understanding of the chemical reactions between a range of infiltrating contaminated fluids and natural or engineered materials has the potential to dramatically influence the field of environmental remediation. Several amendment materials have been explored for remediation of subsurface contaminants, many of which were developed through trial-and-error approaches. This approach is inefficient and leads to inadequate results, often due to the site-to-site variability in processes that largely impact treatment efficacy. Examples of materials that are being explored include biochar [20] and aqueous oxidants or reductants (which can lead to unintended consequences due to production of undesirable species). Figure 2.4.4 [21] illustrates an example of pyrite as a candidate natural material for removing contaminants. For more challenging waste streams, such as produced waters or industrial contamination, more aggressive subsurface treatment strategies, including electrochemistry, have been proposed [22]. Given the complexity of reactions and the potential for complex redox cycling, predictive understanding of electron transfer in natural and manufactured geomaterials and their control on reaction kinetics is critically needed, particularly for reactions associated with fluid mixing and interfaces. To target fit-for-purpose outcomes, both field and model system experiments (using the new generation of time-resolved spectroscopy) and theoretical ab initio methods could allow for the enhancement of cheap and readily available natural materials and the development of engineered systems optimized for a range of influent fluids.
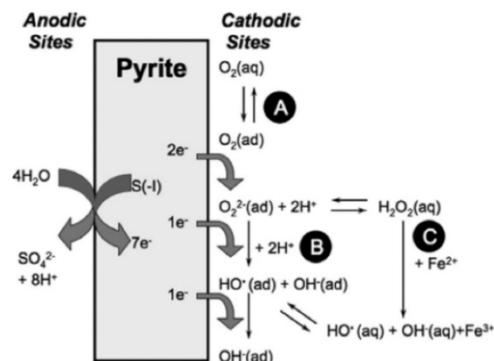

Figure 2.4.4. Mineral-induced reactive oxygen species (ROS) formation: Pyrite is an example of a mineral that can be useful for water treatment. Pyrite spontaneously produces hydrogen peroxide and hydroxyl radical ROS when dispersed in water through a series of stepwise reactions involving dissolved oxygen. The formation of ROS can be leveraged in strategies to kill waterborne pathogens and to degrade persistent organic pollutants. Other natural materials known to spontaneously produce ROS include specific clays, olivine, and magnetite. The figure illustrates the stepwise reduction pathway.

Thrust 4c: Fundamental Advances in Multi-Scale Imaging and Simulation

Multi-scale sensing and computational advances are required to quantify and design new in situ water solutions. Several characteristics of these approaches are desirable, including their ability to quantify and predict key system parameters across a range of subsurface domains (including deep energy reservoirs, groundwater, and surface waters) and their interactions with built system components (e.g., power generation plants and water treatment/desalination systems); consider processes playing out over a wide range of time and space scales — from nanometers to kilometers and from femtoseconds to decades; provide information about physical, geochemical, and microbiological properties; and integrate sensing, modeling, and analytical capabilities to rapidly synthesize information toward adaptive control of in situ subsurface systems for water benefits.

Imaging of natural systems has a wide charter, as it is necessary to monitor key aspects of the water cycle associated with all relevant Earth system compartments: from vegetation to surface waters (lakes, rivers, and wetlands) to subsurface (agricultural soil, aquifers, and reservoirs). It is also necessary to monitor water extractions, such as those related to agriculture, energy water purification, and urban water use. Sensors can be used to measure chemical content and composition or to measure water flow and volume. Each of these types can span a diverse target range of applications. Temperature, pressure, and flow sensors, for instance, are of value for urban applications, such as city water leak detection, and for the measurement of vadose zone infiltration rates. The

measurement of chemical content, for another example, can apply to measuring nitrogen dissolved in the water contained in aquifers or corrosion of water or energy infrastructure. Measurement of volume applies in the characterization of changes in water bodies over time (e.g., lakes and reservoirs) and of the levels of groundwater. There are also varied demands upon the cost, performance, size, and detection levels of sensing technologies.

Techniques for water sensing generally fall into two general categories: (1) remote techniques, based on electromagnetic, seismic, gravity and dielectric responses, which can be acquired from satellites, aircraft, unmanned aerial systems (UASs), or ground-surface geophysical methods; and (2) point measurements, which are reliant on contact-based measurements or proxies, and are typically collected at a single point in space. While direct approaches offer the benefit of providing measurements of the property of interest, they are often sparse due to the inaccessibility of the system. Remote sensing can provide greater spatial coverage and higher resolution than direct approaches, but typically provide only proxy information about the property of interest. In the first category, satellite hyperspectral imagery is increasingly popular, and data are obtainable 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 to measure 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. Example point measurements include real-time data on flow rates, temperature, pressure, turbidity, salinity, and concentration of target species water composition. The diverse measurements span a range of temporal and spatial scales.

An important research frontier is the development of indirect approaches to characterize and monitor inaccessible water-energy reactive subsurface systems. Many new sensing approaches offer promise, including surface geophysical, fiber-optic acoustic and chemical imaging systems, unmanned aerial vehicle (UAV)-based approaches, injectable tracers that can be imaged remotely, and energy-harvesting microchip sensors that can be distributed in the environment to autonomously sample geochemical and biological properties (or some proxy thereof), or to perturb the local environment and measure the response. New characterization approaches will enable understanding of processes across scales as well as the coupling of these processes. Examples are multi-sensor systems that simultaneously monitor key processes in different relevant Earth system compartments, as well as quantify the relationship between the indirect (proxy) signature and the property of interest, which may require theoretical-, numerical-, and laboratory-based investigations.

While the interpretation of hydrologic, mechanical, biological, physical, or geochemical property distributions based on proxy measurements is generally non-unique, time-lapse acquisition model-based data assimilation can constrain interpretations and reduce the non-uniqueness. Developing the science for effective integration (or assimilation) of sensor data with computational models will allow the development of new monitoring systems that can guide adaptive feedback control schemes, which account for dynamic changes in local operational environments (e.g., feedwater quality, production demand, and renewable energy availability) while maintaining optimal system operation. A significant opportunity also exists to take advantage of the "Internet of Things" to connect direct and proxy sensor networks, leading to smart, autonomous, and networked monitoring systems. Such sensor networks could enable the validation of deterministic models of system behavior while also providing a basis for constructing data-driven models that can be updated via self-learning.

The multi-scale complexity of the subsurface (Figure 2.4.1) requires the development and use of new modeling approaches to incorporate understanding of multi-scale process interactions, their aggregation to effective system behavior, and the design of new approaches for transformational water benefits. In addition to the key process-based and characterization challenges described above, computational advances are needed to accurately simulate bi-directional coupling between processes across highly disparate spatial and temporal scales. Characteristics of current subsurface fate and transport prediction capabilities underscore the need for new computational advances. Single-scale process models now are well developed across a range of scales from atomistic to global; direct connections among models at diverse scales are currently limited by computational demands. Diverse datasets are now becoming available as described above, but few capabilities exist to rapidly assimilate heterogeneous information into models for improved "real-time" predictions. Due to structural and parameter uncertainties, models

currently cannot be used to decipher how (and under what conditions) coupled microscale processes are manifested in system-scale behavior. With impending exascale capabilities, a significant opportunity now exists to develop "scale-adaptive" simulation and assimilation approaches that can lead to vastly improved predictions of subsurface system behaviour and its interaction with wellbores and energy systems. Across molecular, pore, continuum, and subsurface system scales, adaptive mesh refinement and big data approaches (data analytics, deep learning, and signature discovery) hold potential for data-driven discovery and prediction of complex, multi-scale subsurface systems.

2.4.3 Impacts

Improving our ability to quantify, image, and predict interactions among fundamental chemical, mechanical, hydrological, and biological properties in natural and engineered subsurface systems has the potential to lead to transformational water benefits. Fundamental scientific research will provide the foundation for advances in the ability to image and manipulate subsurface flow; such capabilities, in turn, have the potential to lead to new geotechnical approaches for designing critical energy and water infrastructure that takes advantage of natural system properties and hydrogeochemical gradients. Increased fundamental knowledge and the ability to predict multi-phase flow and reaction, especially across pore-mineral and geological unit interfaces, are expected to be extensible to many subsurface energy challenges, including those associated with oil and gas and CO_2 storage strategies. Likewise, new understandings about chemical-mechanical interactions associated with aquifer subsidence may also shed light on how such processes play out in subsurface energy reservoirs, which are also subject to a variety of stresses from pumping, fluid and material injection, and stimulation of various sorts, including fracturing.

The scientific impact expected from new multi-scale subsurface imaging and computational advances has the potential to be significant and broad, with applications to water resources, agriculture, subsurface energy production, geotechnical engineering, geological carbon sequestration, nuclear waste storage, and ecosystem restoration. For example, basic science advances in understanding of the reactivity of vadose zone flow will provide the critical foundation needed to finesse the delivery of irrigation water and nutrients to agriculture sites. The development of sensor suites that can jointly and remotely monitor mechanical, chemical, physical, and/or biological properties — in situ and at process-relevant scales — could greatly influence many applications associated with dynamic natural or engineered complex systems. Development of novel data-driven discovery methods for subsurface datasets (data analytics, uncertainty quantification, deep learning, and signature discovery) and the integration of multi-model data and model outputs across a wide range of scales could lead to rapid identification of critical indicators of emergent integrated system responses to small-scale behaviours. This represents an overarching challenge in subsurface science that could have enormous impact. New scale-adaptive modeling methods could be used to identify and ameliorate sources of model error in subsurface simulations, toward greatly improved predictability. In particular, the potential impacts of exascale modeling for underpinning water benefits are clear. Advanced predictions will lead to vastly improved models that properly represent emergent effects of fundamental microscale mechanisms on larger scale system behavior. Models that can accurately predict flow and reactive transport across the approximately 12 orders of magnitude in length scale over which water phenomena occur in natural systems are expected to underpin new classes of in situ cost- and energy-efficient water storage and treatment strategies.

3. Basic Research in Energy-Water Systems

The Basic Research Needs Workshop for Energy and Water was structured around four panels:

Basic Science Challenges to Improve Water Use for Industrial Applications and Electricity Generation (Section 3.1, Panel 1)

Basic Science Challenges to Reduce Water Use in Energy and Fuel Production (Section 3.2, Panel 2)

Basic Science Challenges to Increase Fit-for-Purpose Water Availability (Section 3.3, Panel 3)

Crosscutting Basic Science in Energy-Water Systems (Section 3.4, Panel 4)

Each panel produced a report on the status of the field, specifically identifying (a) current status and recent advances, (b) scientific challenges and opportunities, and (c) the potential for energy-relevant technologies. These reports (Sections 3.1 through 3.4 of this chapter) provided the basis for identifying the four Priority Research Directions, which are described in Chapter 2.

3.1 BASIC SCIENCE CHALLENGES TO IMPROVE WATER USE FOR INDUSTRIAL APPLICATIONS AND ELECTRICITY GENERATION

3.1.1 Introduction

As noted in the Introduction (Section 1), water is arguably the most important substance on earth. Industrial activity represents a small fraction of overall water use (roughly 5%); however, this activity would be impossible were it not for low-cost 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, energy supply, or direct incorporation of water in the product. Some industrial consumers rely on public supply, but many large consumers are self-supplied to lower costs and control water quality to meet their individual needs.

The need to reduce the coupling of energy and water is a significant goal that needs to be addressed and has been discussed earlier in specific technological contexts, for example, coal-fired steam electricity plants [1] (Figure 3.1.1 [2]). To reduce this coupling, we need to reduce water intake and minimize output by reusing and recycling water at every process step, both in energy generation and in other industrial applications, whenever practical. Specific high-impact targets include:

1. Reducing residuals, such as salts and organics, from manufacturing and treatment processes and seeking to approach ZLD;

2. Reducing freshwater usage from both surface and aquifer sources;

3. Increasing water reuse; and

4. Minimizing the energy/economic footprint affiliated with water (capital expenditure and lifecycle cost).

Enhancing the efficiency of water use requires basic science research on issues from solvation to sorption, to separations to sensing. Understanding solute-specific factors, such as size, charge, and hydration spheres, is important in many aspects of water use and reuse. Solubility of organics in water, while generally low, is highly variable and must be understood for controlled chemistry and separations. Chemical reactions in water, including catalysis and biocatalysis, as well as water splitting and photochemistry, must be better understood so that water can be used more effectively in energy-intensive processes and can be reused with the most economical levels and methods of treatment. Different means of separation appropriate for different sources of water, such as inland brackish water and industrial or municipal wastewater, should be considered.
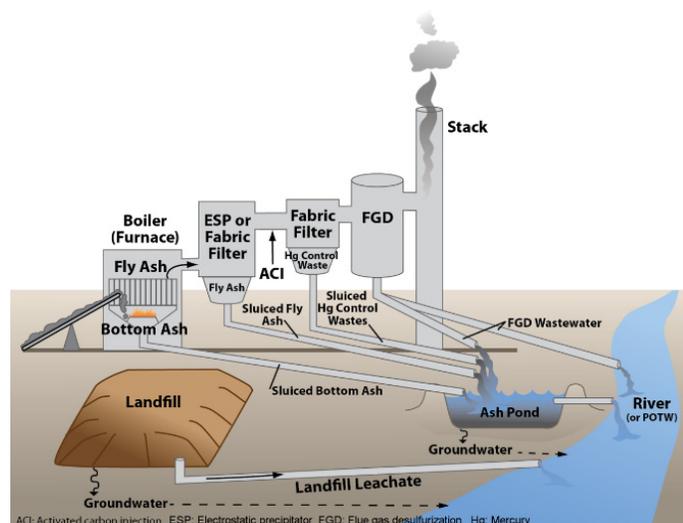

Figure 3.1.1. Key waste streams in coal-fired steam electric power plants.

Some questions relevant to water use in electricity production are not about water directly. An important example is the need to improve or eliminate some of the uses of cooling water, such as with air, thermoelectrics, more efficient cooling processes, or more efficient water reuse. Sensing and sensors are important to acquire and communicate data on moisture, nutrients, metals, pathogens and pollutants in soil, geological formations, and bodies of surface and subsurface water. Biological research is needed at multiple scales — e.g., from molecular understanding of redox reactions to more complex mesoscale interactions — to understand nitrogen fixation in natural and biomimetic systems, to minimize fertilizer use, and to reduce water contamination due to fertilizer runoff. A better understanding of the fate of nutrients introduced into water is needed. Sensing of levels of soil moisture, nutrients, heavy metals, and other micro-pollutants, as well as pathogens, is crucial. Robust pipes for water distribution are needed, with reduced toxicity, greater resistance to corrosion and fouling, lighter weight, greater strength, and ability to withstand extreme conditions.

This panel examined and reported on many basic science questions related to enhancing the efficiency of water use in industry and electricity, including possibilities for reuse. Limitations of current methodologies were analyzed. Consideration was given to the use of instrumental tools and facilities to facilitate these improvements.

Panel 1's discussion pointed out needs in:

1. Materials (membranes, adsorbents, and catalysts) for water purification that meet high-throughput high-selectivity performance targets as set by specific process needs, while considering cost constraints and large-scale manufacturing requirements;

2. Thermophysical data and their use in developing predictive models to describe complex aqueous mixture behavior (e.g., mixtures with high solids concentration);

3. Effects of corrosion and degradation; and

4. Larger-scale process models that, in part, rely on sensors and machine learning approaches.

Each of these areas will now be addressed individually.

3.1.2 Challenges and Research Opportunities

3.1.2.1 Membranes, Sorbents, and Catalysts

Membranes

Semi-permeable membranes are structures made of hard or soft matter that allow some chemical species to pass through, but not others (Figures 3.1.2 [3,4] and 3.1.3 [5–7]). Such membranes are essential for many problems in energy-water systems. An obvious example is the water purification problem [8,9], different manifestations of which are desalination [10,11], decontamination, and disinfection of seawater, freshwater, groundwater, and wastewater. Effective membranes have diverse performance requirements: they must exhibit mechanical, chemical, and thermal robustness; have high water (or proton) flux; and demonstrate high solute rejection [3–7; 12,13]. In addition, they should be non-fouling, or at least easy to clean. Ultimately, they must also be cheap enough to fabricate on the large scales needed in many end-use applications. Few current membranes satisfy all of these factors.

Membranes can be categorized in terms of the size of chemical species that are excluded (see Figure 2.2.8 in PRD 2). RO membranes used in the desalination process have pores small enough, and with the appropriate electrostatic properties, to exclude monatomic sodium and chloride ions. Nanofiltration (NF) membranes have pores that are slightly larger, on the order of a few nanometers, which filter out organic molecules. Ultrafiltration (UF) membranes
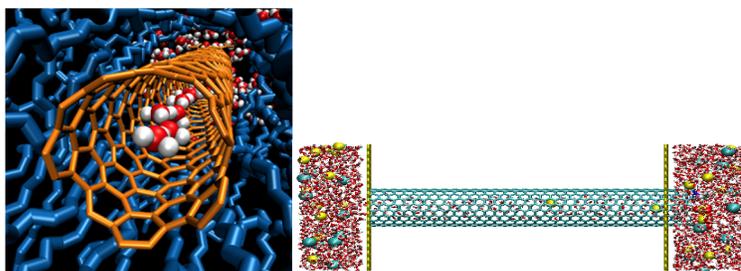

Figure 3.1.2. Active and facilitated transport in carbon nanotubes. (Courtesy of Bruce Hinds.)
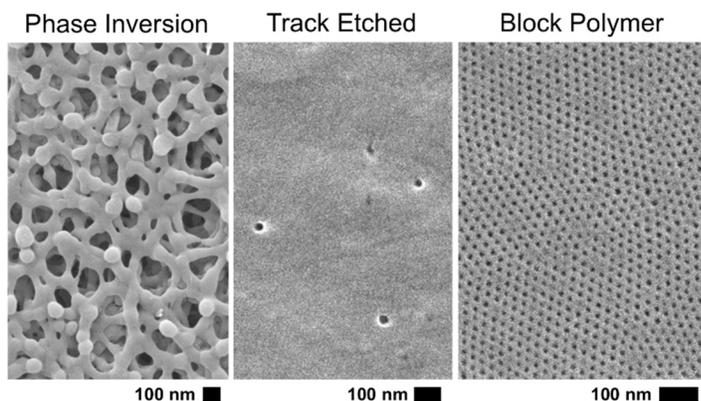
Figure 3.1.3. Meso- to nano-porous membrane structures with tunable pore entries and walls. (Courtesy of William Phillip.)

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 like 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 their constituents. Inorganic membranes are typically composed of nanocrystalline ceramics, like TiO_2 or SiO_2, or mixtures thereof. Many current MF, UF, and NF membranes are made from organic polymers, like cellulose acetate and polyvinylidene fluoride. RO and proton-exchange membranes are also polymeric: cross-linked polyamides in the former and sulfonated fluoropolyethylenes in the latter. 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 like carbon nanotubes and graphene (and graphene oxide) to make interesting membranes, surfactants to make soft-matter membranes, and even incorporate proteins like aquaporin into membranes.

An essential step in the development of new membranes is their characterization. We need tools for quantitative measurement of microstructure and transport. One class of tools involves 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; the latter have a unique capability to derive contrast in aqueous systems via deuteration. Vibrational spectroscopy (infrared 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 [14]. Another advantage of vibrational spectroscopy is that new ultrafast time-domain versions are useful for probing dynamics. Two-dimensional infrared spectroscopy (2D-IR) has proven to be a useful technique for measuring dynamics in bulk systems, while 2D-SFG is fast becoming the widely used technique for dynamics at surfaces. Another essential step in the development of new membranes, related to both their design and characterization, involves theory and computation. Direct simulation of condensed-matter systems can be performed on many levels, involving a wide range of time and length scales.

To address some of the basic science issues outlined above, it is essential to study model systems. Such systems allow researchers to focus on specific scientific questions, which help to elucidate specific design principles. They also provide a venue for direct comparison between experiment and theory/simulation. This comparison is important in the validation of both experimental and computational methods and plays a central role in the overarching challenges going forward.

Some of the basic science questions in this area have to do with the structure and dynamics of water near soft and hard interfaces. Other basic science questions have to do with the effect of confinement. Confinement by soft-matter interfaces can be researched systematically. One can first study "zero-dimensional water," or "dots" by considering small water pools in surfactant reverse micelles [15], as shown in Figure 3.1.4.
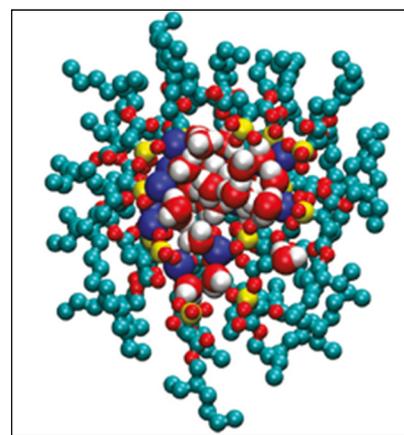

Figure 3.1.4. Simulation of water confined within a surfactant reverse micelle.

52

Still other basic science questions involve biological water, in water channels formed by proteins in cell membranes, such as aquaporin; in ion channels, such as the famous potassium KcsA channel or similar potassium channels in nerve cells; or in proton channels, such as the M2 channel in influenza A. The overarching goal of research in this area is to develop new, robust, and inexpensive membranes that can be tailored for specific uses. Basic science on model systems drives this development, in that we need to be able to understand how chemistry, charge, microstructure and morphology, and confinement affect water structure and dynamics. This knowledge will allow us to design membranes with desired properties. The next steps are synthesis and characterization. Finally, the membranes need to be validated; that is, we need to determine how well they perform for the desired tasks. Of course, this entire process needs to be iterated, in that validation outcomes suggest new basic science studies.

Sorbents

Sorbents are materials that absorb or adsorb other materials, either by physically trapping them or by 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 onto 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 [16–19] (Figure 3.1.5), activated carbon [20], silica gel [21], and polymers [22]. 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 selectively interact with specific ions or molecules (Figure 3.1.6 [17,18,19]). A widely used (and low-

Figure 3.1.5. Atomic model of prototypical zeolite structure.

cost) adsorbent is activated carbon. Heating carbon sources in an oxygen-free environment under exposure to an oxidizing agent (e.g., steam or CO_2) drives reactions that form 3D 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 [23]. 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.

Figure 3.1.6. Model predictions and comparison with experimental data for ethanol adsorption in zeolites from an aqueous solution. (Courtesy of Ilja Siepmann.)

In water treatment, ion exchange is an important subcategory of adsorption. This process involves swapping of ions between an electrolyte solution and a surface. This surface can use a porous or gel polymer as an ion-exchange resin (Figure 3.1.7); a zeolite; or a natural material, such as clay or soil humus. These materials can function as cation exchangers, anion exchangers, or amphoteric exchangers, which can process ions of both charges at the same time. (The same goal can be achieved by combining anion and cation exchangers.)

Common applications for ion exchange include water softening, purification, and decontamination. Softening is achieved by exchanging multi-valent 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.

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 metal–organic frameworks (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 [24], but there may also be opportunities to explore their use in the capture of materials from water.

Figure 3.1.7. Ion-exchange resin beads.

Recently, the extended family of 2D materials 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 [25–27]. Other 2D porous materials, like 2D- zeolites [28] and 2D-MOFs, could also be explored for membrane- and adsorption-based water purification.

In summary, among the most challenging goals in membrane and sorption research is the ability to tailor surface properties for solute-specific adsorption. Achieving this goal would not only enable effective capture of difficult water contaminants, such as nitrate [29], phosphate [30], and heavy metals, including hexavalent chromium, lead, and mercury [31], 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 substantially greater if selective ion-specific sorption were possible, for example, selectively capturing calcium in the presence of magnesium. Such sorbents would allow unprecedented resource recovery from waste streams and from contaminated water sources, revolutionizing the economics of many water operations. Another powerful example would be the ability to sequester bioactive molecules, such as endocrine disruptors, from wastewater treatment plants while allowing nonhazardous organic materials to pass through.

Catalysts

A core challenge for water remediation chemistry lies in the need to address a diverse array of soluble and particulate pollutants. These pollutants 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 Section 3.1.2.1, 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 [32–34] and reductive [35,36] catalytic processes offers opportunities to develop sustainable, full-cycle remediation technologies that couple degradation of wastewater pollutants with energy and resource recovery (Figure 3.1.8) [37]. 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.
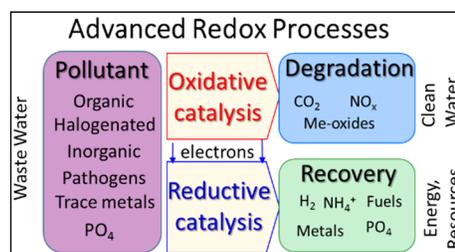
Figure 3.1.8. Advanced redox process for wastewater remediation that integrates oxidative and reductive catalysis to achieve combined pollutant degradation with energy and chemical resource recoveries.

3.1.2.2 Corrosion and Degradation of Materials

Material components in energy and water systems can be seriously degraded by corrosion, by the precipitation of deposits on surfaces, or by other degradation mechanisms. 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 oil and gas (O&G) and geothermal infrastructure and reservoirs. Predicting corrosion and precipitation requires a quantitative understanding of the interfacial aqueous chemical and materials processes at play [38–40]. Reducing corrosion can be aided by improved separation of impurities from process fluids, by selection of bulk and surface materials properties for the relevant conditions, and sometimes by the addition of surface treatments. Specific areas of interest for predictive modeling include corrosion of steam turbines, nuclear waste containers [38], and pipes, solution nucleation, and scale formation and its prevention.

The great importance of corrosion-related processes can be seen in the following examples. 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. The precipitation of silica from cooling high-temperature fluids is a significant cause of steam turbine degradation and scale formation in geothermal systems. The speciation of silica in water and precipitation pathways is 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. 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 [41]. 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 timescales. The recent public health tragedy in Flint, Michigan, was initiated when a change in drinking water chemistry provoked an onset of lead pipe corrosion in residential water pipes [42].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 [43]. Predicting the extent and timing of scale formation is often not possible; analyses rely instead on post hoc rationalizations (e.g., [44]).

3.1.2.3 Thermophysical Data and Modeling of Energy-Water Systems

Modeling at multiple levels of fidelity and length scales is critical to improving water use in many venues. At microscopic levels, thermophysical data are required to develop predictive models to describe complex aqueous mixture behavior (e.g., mixtures with high solids concentration).There are many fundamental needs to define appropriate descriptions of these challenging systems, as well as to provide carefully validated data for model systems of sufficient complexity.

Software systems go through a series of passages that account for their inception, initial development, productive operation, upkeep, and retirement from one generation to another. Larger-scale process models have been developed with today's large-scale computational capabilities. In addition to the ongoing interest, debate, and assessment of process-centered or process-driven software engineering environments that rely on process models to configure or control their operation [45,46], a number of promising avenues have opened for further R&D with software process models. It is clear that contemporary model development must account for interrelationships between software products and production processes, as well as for the roles played by tools, people, and their workplaces. Modeling these patterns can utilize features of traditional software lifecycle models, as well as those of automatable software process models. Nonetheless, we must also recognize that the death of the traditional system lifecycle model may be at hand. New approaches for model development are enabled by the Internet, group facilitation and distant coordination within open-source software communities, and shifting business imperatives in response to these conditions, and they are giving rise to a new generation of process models. These new models provide a view of software development and evolution that is incremental, iterative, ongoing, interactive, and sensitive to social and organizational circumstances. At the same time, such models are increasingly amenable to automated support, facilitation, and collaboration over large distances of space and time.

3.1.3 Conclusion

Panel 1's discussions recommended research in several interconnected topics. A common theme in these topics is the strong need to make progress on challenging fundamental science problems to enable long-term impact on the daunting issues that exist in practical settings. Key areas for research recommended by the Panel include multi-scale modeling in tight coordination with experimental characterization and validation; intensive study of the fundamental properties of high-performance membrane and sorbent materials with tailorable properties; the study of fundamental mechanisms (and prospects for mitigation of) corrosion, aging, and degradation of materials in complex aqueous environments; and instrumental and data-driven advances to allow real-time sensing of temperature, particle size, the presence of ion, metals, or organics and other physical characteristics of water processes on large length scales and in complex environments.

3.2 BASIC SCIENCE CHALLENGES TO REDUCE WATER USE IN ENERGY AND FUEL PRODUCTION

3.2.1 Introduction

Energy and fuel production are frequently water-intensive processes [1,2]. This panel reviewed areas in which advances in fundamental understanding could significantly reduce the water use requirements for hydraulic fracturing, enhanced recovery of hydrocarbons and geothermal energy, the production of biofuels, and other applications. The opportunities and benefits include the following:

- Reduced impacts of O&G production and coal mining and combustion byproducts on the quantity and quality of freshwater resources,

- Improved unconventional O&G production with more hydrocarbon production for less drilling and lower volumes of produced waters,

- Increased security and efficiency of geologic carbon sequestration,

- Improved integrity of wellbore seals,

- Recovery of valuable resources (e.g., rare earth elements) from solid byproducts and produced waters,

- Improvement in sustained enhanced geothermal energy (EGS) heat mining, and

- Less water-intensive bioenergy feedstocks with the potential for sequestration to achieve net negative CO_2 emissions.

3.2.1.1 Overview of Subsurface Systems for Energy and Fuels

Subsurface systems provide critical resources for obtaining energy and fuels and will continue to do so for the foreseeable future. In recent years, there have been significant changes in the uses of subsurface systems for hydrocarbon extraction and geothermal energy extraction, and an associated increase in the disposal of waste brines. An important recent trend is the transition from conventional to non-conventional sources of fossil fuel [3] and geothermal energy [4]. These rapidly developing technologies involve the injection of fluids — almost exclusively aqueous fluids — into subsurface rock formations. There are acknowledged unsolved problems for the optimization of these approaches that directly affect their productivity for energy, their water intensity, and their potential to adversely affect freshwater resources.

3.2.1.2 Hydrocarbon Extraction

Enhanced oil recovery (EOR) mobilizes residual hydrocarbons from depleted reservoirs through several mechanisms, such as the injection of gas (e.g., CO_2) that both reduces viscosity and can dissolve some hydrocarbons. 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). The complex aqueous mixtures used in hydraulic fracturing display features of non-Newtonian fluids [5]. Non-aqueous fluids, particularly CO_2, have been used for enhanced oil extraction and are being considered for hydraulic fracturing [6].

3.2.1.3 Geothermal Energy Extraction

A combination of deep drilling, water injection, and hydraulic fracturing of hot dry rocks could allow access to new EGS energy resources. Progress in both fundamental understanding and technical capabilities is required for creating a suitable fracture network, monitoring (e.g., imaging) changes in permeability, and managing the flow of fluid and heat to optimize electricity generation, minimize water use, and maximize lifetime [4,7]. EGS has extreme materials challenges due to the high temperatures and potential for corrosion and scaling.

3.2.1.4 Disposal of Brines

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. Although hydraulic fracturing fluids can be recycled, the produced and flowback waters must either be disposed of by injection into a deep saline aquifer or treated for beneficial reuse, such as irrigation. Treatment is highly challenging because production waters typically have salt concentrations similar to or far exceeding seawater levels and contain diverse inorganic and organic contaminants [8]. There are tens of thousands of active disposal wells in the United States, but wastewater injection carries risks of groundwater contamination [9] (typically associated with aboveground operations) and of induced seismicity (see Induced Seismicity and Water-Energy Systems sidebar [10,11]). 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 U.S. O&G opportunities and similarly add burdens to any new application, including geologic carbon sequestration, which may produce subsurface brines.

The injection of supercritical CO_2 into a subsurface aquifer causes a pore pressure increase that subsides when injection ceases due to flow and dissolution. Extraction of brine during the injection of CO_2 from a well that is located elsewhere in the aquifer is a strategy for pressure control. The extracted brines typically have a salinity significantly higher than seawater (100,000 mg/L or higher), with a chemical composition depending 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.

3.2.2 Challenges and Research Opportunities

3.2.2.1 Nucleation, Growth, and Ion Incorporation

In subsurface energy technologies, the introduction and withdrawal of fluids from the subsurface creates chemical disequilibria that may lead to mineral precipitation or dissolution that can change rock permeability and alter the stability of stressed fractures. A widespread problem associated with mineral precipitation is scale formation in pipes, wells, or in hydrocarbon and geothermal reservoirs [12]. Scales are typically poorly soluble salts, such as calcium and magnesium carbonates, or metal sulphates or phosphates including barite. Scale inhibits fluid flow, increases the energy cost for fluid transport in pipes and creates inefficiencies in energy extraction [13].

Scale is initiated by surface (heterogeneous) nucleation. Classical models solely consider that a substrate increases mineral formation rates by reducing the free energy barrier for the formation of a particle relative to solution. The molecular structures, reaction mechanisms, and interactions determining the interfacial tension, however, are not completely understood, even for the nucleation of water ice on a mineral surface [14]. Moreover, a long record of study of structure, dynamics, and reactivity at mineral-water interfaces supports additional roles for the substrate phase beyond surface tension. These might include altering interfacial water structure and pKa [15], ion exclusion in porous media [16], and by recruiting precursor species to the near-surface region through adsorption. It is also becoming clear that bulk fluid thermodynamics and chemical kinetics may not be accurate for predicting solute speciation and mineral reaction in nanopores due to geometric and chemical confinement [17,18].

INDUCED SEISMICITY AND WATER-ENERGY SYSTEMS

- Induced seismicity has become a serious concern in many historically low-seismicity regions of the United States [11,19]. The increased frequency of induced earthquakes has been largely driven by a rapid growth in wastewater disposal volumes since approximately 2005 associated with unconventional hydrocarbon production. Other subsurface activities, such as O&G production, geologic carbon storage, and geothermal energy systems, may also induce seismic events [20].

- Improved methods and stimulation fluids that reduce water production in O&G extraction, as well as advanced brine treatment methods enabling fit-for-purpose water reuse, have the potential to reduce the total volume of disposed fluids and help mitigate this hazard.

- At the same time, new technologies and practices will take time to be deployed at scale and will never be able to eliminate the need for subsurface disposal [21,22]. Induced seismicity is likely to remain an enduring challenge for energy and fuel production.

- Techniques for managing seismic risk have been largely empirical to date, suggesting a need and an opportunity for obtaining and applying improved understanding of the causes of seismic events [23].

- Improved understanding of the coupling between fluid transport and subsurface stress has the potential to significantly reduce unwanted seismic activity associated with geologic water–energy activities [20].
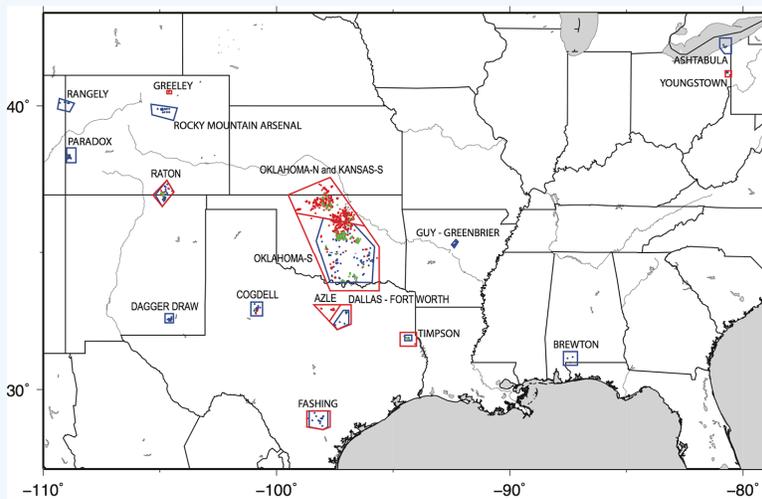
The U.S. Geological Survey identified 17 areas of potential induced seismicity for inclusion in an update to the National Seismic Hazard Model. This update is necessary to account for the growing impact of energy-related activities on earthquake hazard in many regions of the United States. Reproduced from [24].

Contaminant Sequestration in Solid Solutions

Mineral precipitation can be beneficial if it leads to incorporation and immobilization of hazardous trace elements, including heavy metals, radionuclides, and other toxic ions. Examples of cation incorporation include the co-precipitation of radium in barite as the solid solution $(Ba,Ra)SO_4$ (Figure 3.2.1) and co-precipitation of cadmium in carbonate as the solid solution $(Ca,Cd)CO_3$ [25]. Examples of anion incorporation include the co-precipitation of arsenate with barite by anionic substitution $Ba(SO_4,HAsO_4.H_2O)$ and co-precipitation of chromate with barite by anionic substitution $Ba(SO_4,CrO_4)$ solid solution. Opportunities for sequestering contaminants from subsurface brines remain to be fully explored due to several gaps. Thermodynamic models of solid solutions are inadequate due to limited data. Observations at the nanoscale have shown complex behavior not predicted by current models, including kinetically limited zonation.

Coupled Feedback among Water-Rock Reactions and Permeability in Complex Heterogeneous Systems

Highly nonlinear interactions can result from the interplay of transport and reaction due to the emergence of positive feedback between fluid flow and mineral reaction. These interactions manifest at large spatial scales (field scale), but depend on processes operative at the molecular and nanoscale. There is a need for high-resolution observation and imaging techniques that reveal how coupled processes interact to govern observed system properties. Advances in

x-ray and neutron imaging have made it possible to observe porous media as intact 3D systems [26–28], which will provide unrivalled views of rock-fluid reactions under relevant conditions, but significant challenges remain [29].

First, there is much to be learned about how 3D rock texture and pore structure affects transport and reaction. We lack good tools to classify 3D structures that incorporate all the length scales and compositional heterogeneity of real rocks. There are likely valuable roles for machine learning methods in which the very large imaging datasets are used to link rock texture to mechanical and chemical properties [30]. Possible predictive parameters include mineral phase composition, mineral grain size distributions and relative distributions, and pore-fluid accessible surface area.

Second, we lack the ability to transfer insights across all relevant length and timescales. An important concept for predicting flow and reaction is the representative elementary volume (REV),

Figure 3.2.1. Top Left: Molecular dynamics simulation of barite (BaSO$_4$)-water interface [31]. Top Right: Element map of arsenic (blue) incorporated in solid solution within a growing barite platelet. Data from the Hard X-ray Nanoprobe beamline at NSLS2 and courtesy of J. Fitts, Princeton University. Bottom: X-ray computed tomography (XCT) image of barite nucleation and precipitation in a porous medium [32]

which homogenizes a multi-component system into a continuum description of properties such as permeability and elastic moduli. For different rock systems, REVs may be in the range of 1 to 100 cm. There are currently few established approaches to predict macroscopic properties when they are affected by nonlinear coupled processes, especially involving interfacial reactions.

3.2.2.2 Interfacial Reactivity and Characterization of Non-crystalline Solid Phases

There are several non-crystalline phases that can influence solid-water reactions in systems that will impact energy-water systems. Because of their poorly crystalline nature and variable compositions, there is presently insufficient information on their stability and reaction kinetics to enable predictions of their impacts on energy-water systems.

One particularly important non-crystalline solid material is the product of the combustion of coal (fly ash) (Figure 3.2.2 [4]). The diverse solid phases generated include the non-combustible and condensable organic and inorganic compounds of the original source coal. The phase composition within fly ash particles includes major amounts of amorphous

Figure 3.2.2. Distribution of coal ash ponds in the United States.

materials (glasses). Elements of interest to energy-water systems are toxic trace elements that can leach out and diminish freshwater resources and valuable elements (e.g., rare earth elements) that could be recovered from the ashes [33]. Because the behavior of these elements is not governed by their overall content in the solid phases but rather by their chemical speciation and physical distribution within fly ash particles, new information on the properties that govern the solid-water interactions with fly ash particles is needed. Detailed characterization is required to understand the nature of the amorphous solids, especially nanoparticles, in rocks and coal fly ash. For example, it has recently been discovered that coal fly ash contains oxygen-deficient TiO_2 nanoparticles that show rapid reaction with biological systems [34].

A second important class of non-crystalline solid phase is the glassy inclusions in igneous rocks that react with fluids during enhanced geothermal energy recovery and carbon sequestration. For example, the basalts for which carbon minerals have been observed following carbon injection in Wallula, Washington, and at the CarbFix site in Iceland have extensive amounts of glasses that react with water-wet CO_2 and CO_2 saturated brines. Unlike the crystalline phases present in these basalts, these non-crystalline phases do not have established equilibrium solubility parameters or dissolution rate parameters. Without such information, it is difficult to integrate the necessary chemical reactions into the larger-scale simulations required to manage the sequestration of CO_2 in such systems.

3.2.2.3 Complex Fluids

Complex Aqueous Fluids

The aqueous fluids pertinent to the main challenges in water–energy systems include very high ionic strength brines and aqueous solutions containing organic chelators and surfactants, as well as colloidal particles. The chemistry and thermodynamics of brines remain challenging to predict [35], while models and equations of state for high-salinity systems also containing soluble surfactants as a function of temperature and pressure wait to be developed. Mechanisms of solvation, hydration, and chemical reactions are thus not modeled in a way that has been fully tested experimentally or theoretically.

Solutions with high solute concentrations present a particular challenge to experiment and theory. In such systems, solvent sharing and contact ion pairing likely prevail, strongly influencing solute availability and transport. Yet, molecular-scale depictions of solute association structures, and their effects on chemical processes, remain poorly understood. An important goal is the extension of current technology and computational methods for these high-concentration regimes. X-ray and neutron scattering and spectroscopy, and surface-sensitive optical spectroscopies, coupled with molecular simulation, are increasingly providing insights into molecular structure in bulk fluids and at interfaces [36,37,38]. The extension to longer-range associations and more complex fluids will be important for many fluids in energy-water systems. Elucidating the interfacial and bulk solvent and solute dynamics, structure, and interactions will inform reactivity, flow, reaction mechanisms, solvation mechanisms, aggregation kinetics, and dissolution mechanistic behaviors.

Low-Water-Activity Fluids

One example is the recent discovery of the remarkable reactivity of water-wet CO_2 with the most common rock-forming minerals on earth [39]. We presently cannot write down the stoichiometry or the rate equations for reactions that occur in the very thin water films that form on minerals in water–CO_2 systems. Although supercritical CO_2 is already known to be an effective solvent for nonpolar organic molecules, our understanding of how water-wet supercritical CO_2 affects the reactivity of ions and other inorganic species is very limited. Major challenges are the inability to predict and understand fundamental reactions like protonation/deprotonation and electron transfer in such low-water-content fluids.

Understanding and predicting the reactions of water-wet CO_2 could prove key for ensuring the safety of geologic storage of CO_2. For geologic carbon sequestration, the fluids with which minerals are in contact over a significant period can be dominated by water-wet supercritical CO_2 and not aqueous brines saturated with dissolved CO_2 [40]. An illustration of this remarkable reactivity is the formation of carbonate minerals on basalts reacted with supercritical CO_2 with a low water content (thousands of ppm) (Figure 3.2.3). While it was well known that the silicate minerals would dissolve and that the cations released could precipitate as carbonates from reaction with the dissolved carbon

present in CO_2-saturated aqueous solutions, our previous paradigm would have anticipated that a CO_2-dominated fluid would be inert with respect to reactions with the minerals present in a basalt.

The reactivity of water-wet non-aqueous fluids will provide challenges and opportunities in many other energy and subsurface systems, including those for reducing water use in unconventional O&G production and managing the lifetime of gas transport and storage infrastructure. Enhanced oil recovery operations often involve alternating water-flooding and CO_2-flooding stages. We envision that it will be possible to control the reactivity of wet-CO_2 stages to alter the surface wettability and hydrocarbon release from depleted reservoirs [41]. The water content of CO_2 streams will also strongly influence the fluid's corrosivity, which is relevant to our infrastructure for CO_2 transport in stainless-steel pipes for any application. Moreover, in addition to systems involving water-wet CO_2, these issues are relevant to other low-water-content fluids, such as compressed air involved in compressed air energy storage.

Figure 3.2.3. Surface of a 100-µm-wide fracture of a Columbia River flood basalt before and after reaction in water-saturated supercritical CO_2 at 100 C and 100 bar. The top of the fracture was open to the wet CO_2, and the bottom of the fracture was sealed. Upon reaction with the wet CO_2, iron(II) in silicate minerals was oxidized to form red iron oxide products and calcium carbonate (aragonite shown in the electron micrograph) precipitated from reaction of the wet CO_2 with calcium released from the basalt. Data from W. Xiong, 2017, Ph.D. thesis, Washington University in St. Louis.

Rheology of Non-aqueous Fluids

Fracking fluids are highly complex [5]. The current status quo composition for fracking fluids is dominated by water, which typically constitutes more than 90% of this fluid. Upon injection of the primarily aqueous solution into the shale beds, dissolution and release of minerals and organic constituents make their way into the fracking fluid [42]. A significant amount of the aqueous solution is left behind in the shale cavities, but it is typically unknown how the fluid is trapped or lost.

Opportunities exist to design and develop low-water-content fracking fluids that have a low environmental impact, provided we develop new capabilities to independently control critical chemical and physical parameters of non-aqueous fluids [6]. In particular, fluid viscosity and compressibilities are critical parameters to reduce the energy required for flow in microscopic fractures and to transmit pressure and create new fracture networks. There are many unknowns in the microscopic details of the interactions of the fluids (the solvent and solutes) within the shale pores and fracture surfaces that are not understood. Innovative designer fluids could be conceived of that selectively solvate ions and molecules, wet distinct constituents of complex subsurface reservoirs, and stabilize existing nano- to micro-porous regions and preserve the structural integrity of existing or engineered flow pathways. Current technologies exist in spectroscopy within academic and national laboratories for the research opportunities mentioned above. Areas of molecular design to optimize additive-plus-water viscosity and to develop highly tuned macromolecular assemblies to facilitate micro-solvation while retaining shale integrity are critical to the success of moving to low-water-content working fluids. This then will provide new low-water extraction technologies for shale gas extraction. Spectroscopic investigation geared at elucidating molecular information at buried interfaces must be coupled with nanofabrication to build experimental models for rock and membrane structures such that spectroscopic investigation can ensue. Successful experiments will require the marriage of several spectroscopic methods with the development of a model film system for access to the buried interface model system.

3.2.2.4 Controlling Water Dynamics of Bioenergy Feedstock Crops

The use of biomass for production of fuels and chemicals continues to be an expanding area of science as well as in the bioeconomy. Bioenergy crops are used to produce liquid transportation fuels compatible with heavy vehicles, aircraft, and ship engines; can generate societal benefits for rural economic development; and could enable carbon negative footprints if used for power generation in conjunction with carbon capture and sequestration. The use of
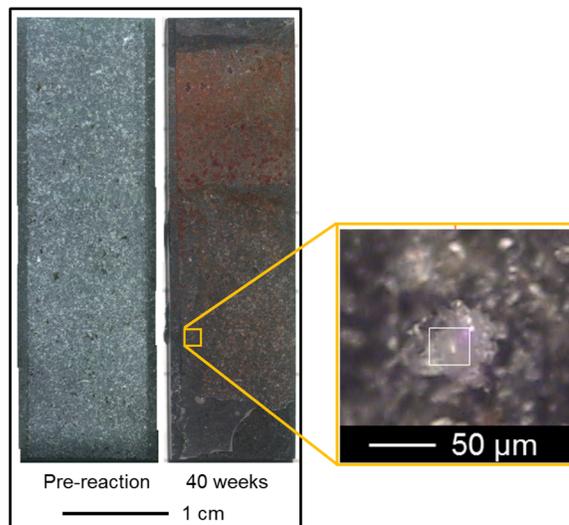
biomass resources presents many challenges for both water quantity and quality, from growth of the crop plants to conversion of the resulting biomass components to products [43]. From atomic- to meso-scale, a fundamental mechanistic understanding of water use and function in biomass production; in chemical catalytic, pyrolytic, or enzymatic conversion processes; and in separations of desired products is critical to devising strategies that maximize water use efficiencies.

Water for crop irrigation, including bioenergy crops, represents the second largest sector of water use and comprises about one-third of water withdrawals. New sensor technologies can improve irrigation efficiency and reduce water withdrawals for agriculture. Nondestructive, noninvasive, portable, ultrasonic sensors have recently been developed that can accurately and rapidly measure in vivo water content and turgor pressure, thereby fine-tuning irrigation timing or delivery rates to minimize water consumption [44]. The development, improvement, and use of such sensors builds on basic scientific knowledge such as understanding mechanisms of water use in plants and the identification and characterization of new materials and material properties.

One area of research that can affect both water quantity and quality is crop yield improvement. Improvements can be envisaged in at least three dimensions — in the biorefinery as product yield per unit of biomass, in the field as biomass per acre, and in the agricultural landscape as maximized acres on which biomass can be grown. The value of multidisciplinary research and insights is reflected in two examples of yield improvement — a generation of new plant varieties and development of new technologies for more effective water use. New capabilities in gene and genome editing [45] are being exploited to understand and develop traits in plants and, in turn, grow bioenergy crops with minimal water inputs. For example, genetic engineering of Arabidopsis plants to express the transcription factor CEB1 transforms the leaves of this common weed into thick succulent leaves like those of a cactus [46]; the resulting plants demonstrated increased tolerance to drought and salt stress. Such basic research to understand water stress, uptake, and loss in plants incorporates a range of scientific disciplines, from genetics and breeding to biochemistry and physiology, to understand the fundamental scientific mechanisms underlying those traits.

Processes used for deconstruction and conversion of biomass also entail significant water use, presenting several opportunities for improvements in water use efficiencies. Lignocellulosic biomass is composed of a range of polysaccharide and aromatic substrates that can be reduced for components of liquid hydrocarbon fuels or even oxidized in pathways to chemicals [47,48]. Various deconstruction technologies are used to fractionate biomass into sugar and aromatic streams prior to their conversion into fuels and chemicals. Basic research in plants and microbes is providing new insights and approaches to improve biomass deconstruction and conversion processes and thus help maximize water use efficiency. For instance, studies of nature's catalysts, enzymes, can present new strategies for the development of chemical catalysts with improved efficiency and selectivity — and potentially with the capability for regeneration. Such improvements could reduce the amount of water and energy needed for the various catalytic steps in the biomass conversion process.

A looming challenge is the large energy and water costs associated with separation of sugars and aromatics and their desired reaction products from aqueous and other complex mixtures. Ten to 15% of U.S. energy consumption is dedicated to separation processes such as distillation. Again, nature can provide insights into possible innovation in separations. Biological membranes demonstrate highly selective transport of ions, metabolites, and compounds; understanding how these membranes effectively separate various molecular species — and how they self-repair — could provide strategies for new synthetic membranes that are more efficient and thus require less water [49]. Another approach is to combine new modified feedstocks with improved downstream conversion and separations technologies to enable more sustainable use of water in biorefineries. For example, transgenic poplar trees have been engineered to make either syringyl or guaiacyl lignins rather than the combination of the two found in native poplar. The transgenic trees produce isoeugenol or dihydro-eugenol, respectively, when treated with a chemical catalyst that depolymerizes lignin, thus eliminating the problem of separating one desired product from the other.

3.2.3 Conclusion

The opportunities for improving water use in energy strategies that rely on Earth systems are significant, but require advances in fundamental research. Examples of fundamental science gaps associated with strategies that involve injection or withdrawal of subsurface fluids include the properties and behavior of complex fluids; interfacial reactions, nucleation, growth, and incorporation of ions into solid phases; and characterization of non-crystalline solid phases such as fly ash. Significant advances in these topics could have broad impacts for energy extraction as well as for nuclear waste storage and contaminant remediation. Fundamental studies in biological systems — understanding how water interacts in plant cells and cell walls, how enzymes work under ambient conditions, how biological membranes are controlled — can provide new ways to look at and address challenging problems, and thus help foster the discovery and development of new catalysts, chemical analyses, sensors, separations membranes, and other materials that can enable advances at the intersection of water and bioenergy.

3.3 BASIC SCIENCE CHALLENGES TO INCREASE FIT-FOR-PURPOSE WATER AVAILABILITY

3.3.1 Introduction

Water-stressed regions are increasingly reliant on unconventional water sources, including brackish groundwater, seawater, municipal reclaimed water, industrial wastewater, storm water, and other nontraditional waters [1] to meet the demands of the agriculture, industry, energy production, fossil fuel extraction, mining, and residential sectors, particularly during periods of prolonged drought. Concurrently, extraction of brackish to saline waters during unconventional gas and oil extraction brings large quantities of water to the surface, where it has the potential to supplement existing water resources. Intensive land use also has the potential to impair existing freshwater resources because of, for example, nutrient loading or increases in naturally derived but toxic contaminants (e.g., As, Se, and U).

The rapidly changing landscape for water supply and demand presents an unprecedented opportunity for basic science to contribute toward the critical fundamental understanding needed to transition to a radically different "water infrastructure" that allows for precision tracking of water and its constituents from contact with the ground surface to groundwater wells or surface waters through treatment schemes that improve the water to match specific human needs. Many different types of contaminants are encountered in water and energy applications, including surfactants, metals, organic contaminants, and agricultural nutrient waste. Contaminant concentrations can vary by many orders of magnitude, both temporally and spatially. Multiple technologies exist for improving nontraditional water quality, and both efficacy and energy costs of accessing, treating, and redistributing alternative water sources vary considerably. Basic-science advances are necessary to underpin the development of a flexible, distributed, and finely tuned "fit-for-purpose" water system, where the quality of reclaimed water is treated only to the level appropriate for the intended use. Innovation for efficient, selective water treatment technologies can promote water reuse and increase access to water from marginal and nontraditional sources. Basic research is needed to guide the development and deployment of clean water technologies that can improve the efficient use of existing water supplies, and lower the cost, electricity use, and carbon emissions of technologies that would act to increase our overall supply of fresh water.

Fit-for-purpose water requires connecting traditionally distinct sectors of water systems (i.e., ex situ water treatment and in situ water storage) in fundamentally new ways, as illustrated in Figure 3.3.1. For example, we would like to capture excess surface water (unclaimed surface water discharge to storm runoff) and use it to recharge groundwater, requiring specific water-quality metrics and optimized subsurface properties to allow for maximal recharge and minimal evaporative losses, while providing sufficient time and conditions for beneficial geochemical reactions to occur. As new water infiltrates and interacts with the natural surfaces and pore spaces and mixes with native fluids, opportunities for a host of interfacial and homogeneous reactions arise. Such reactions need to be understood at a level such that the
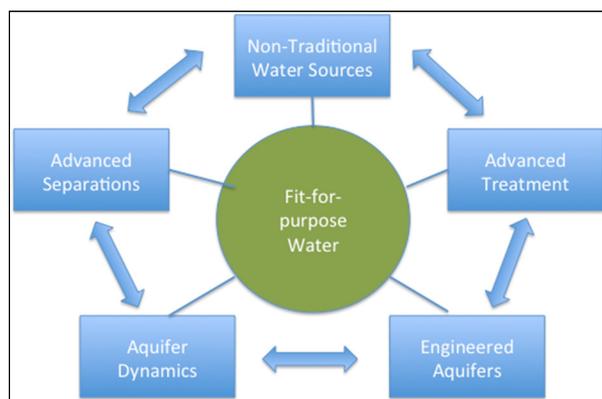

Figure 3.3.1. Achieving fit-for-purpose water systems requires basic research associated with five key categories.

addition, removal, or conversions of dissolved solids are entirely predictable — a capability that is limited by existing knowledge of mineral-fluid-gas-organic interactions and fundamental knowledge gaps in our understanding of the non-linear physical processes by which fluids move through variably saturated porous media. Design of materials and chemicals that allow for passive treatment of large quantities of water through surface spreading and managed recharge would allow us to harness the immense storage space that exists below our feet while reducing energy costs, and possibly allowing for passive treatment of traditionally challenging water streams (brackish, saline, and high-particulate). "Process control" of reaction chemistry and physical processes in engineered natural reservoirs could lead to scalable, low-cost, nonhazardous, passive, in situ water treatment and enable getting more surface water, such as storm water, underground as soon as possible. Major concerns surrounding intensification of recharge involve the longevity of such systems when exposed to entirely new and likely variable water streams, and the geomechanical consequences of water extraction (compaction and expansion) and the so-called "dirty sponge effect" wherein ions — often undesirable ones such as, U, and Cr — are expelled to the aquifer, requiring additional treatment.

Innovation can reduce the costs and energy consumption of new water treatment technologies, thereby increasing water sustainability and reuse [2]. Fundamental scientific understanding of the movement of water through the subsurface, including across pore-mineral as well as aquifer interfaces, is needed, as are innovative materials and new chemical approaches to treat water in systems ranging from passive systems to a new generation of active treatment systems that take advantage of the subsurface. Fundamental advances can enable dynamic and selective treatment of diverse and complex primary and waste streams as well as provide for flexible storage and recovery. Creating fit-for-purpose water requires treatment systems that can be tailored to meet a range of treatment goals, depending on the specific application. The ability to use intermittent renewable energy or waste heat to drive treatment and separation processes provides new opportunities to render energy-water interactions more efficient.

### 3.3.2 Challenges and Research Opportunities

Fundamental science is needed to understand, control, and manage both subsurface and aboveground water, as well as to develop novel in situ and ex situ treatment concepts. Basic science is required to understand the operation of aquifer machinery in order to use groundwater systems more effectively as part of a fit-for-purpose scheme. The central theme is "*How do aquifers respond to rapidly changing boundary conditions (land cover/land use, water extraction, or water inputs) that perturb them away from equilibrium?*" In addition to understanding natural reservoirs, response to the growing freshwater crisis requires understanding of chemical reactions in perturbed systems, particularly redox reactions in the unsaturated zone and capillary fringe, i.e., *"How can we harness natural material properties to address large-scale water challenges?"* Other questions center on coupling natural and engineered systems. Basic science is also needed to understand how to create structure and functionality for selective adsorption, permeation, or reactivity to develop novel concepts for efficient and effective water treatment. Key questions include how to remove salts or other contaminants as well as how to analyze composition and define treatment goals. Fundamental understanding and new materials can lead to innovative, efficient, and selective treatment and separation processes.

3.3.2.1 Understanding Integrated Aquifer System Dynamics

Aquifer dynamics are governed by complex physical and molecular machinery that operates in tandem to perform different functions. This machinery can be quite sensitive to changes in external forcing in ways that are difficult to predict. Although aquifer systems are perhaps as important to human civilizations as the aboveground biosphere, we know much less about how they operate. For example, we lack robust estimates of the amount of groundwater and its properties, including the residence time (age) of the water and what chemical (organic and inorganic) components it contains. Knowledge of how much water is present in the subsurface, the chemical composition of that water, and how it flows belowground is foundational to energy-water issues. A crosscutting challenge is thus to improve our understanding of fluid transport and chemical reactions to allow for precise predictions of aquifer dynamics and their response to changing boundary conditions. Only then can we store, treat, and allocate water in such a way as to achieve the water security and energy savings that a distributed fit-for-purpose water system requires. For example, successful banking and retrieval of subsurface water requires advances in fundamental knowledge in the areas of multi-phase flow and transport, aquifer geomechanics, and the kinetics and thermodynamics of geochemical

reactions that may release or attenuate contaminants — all of which occur within aquifers having different gross geochemical and hydrological characteristics.

SUBSURFACE WATER STORAGE
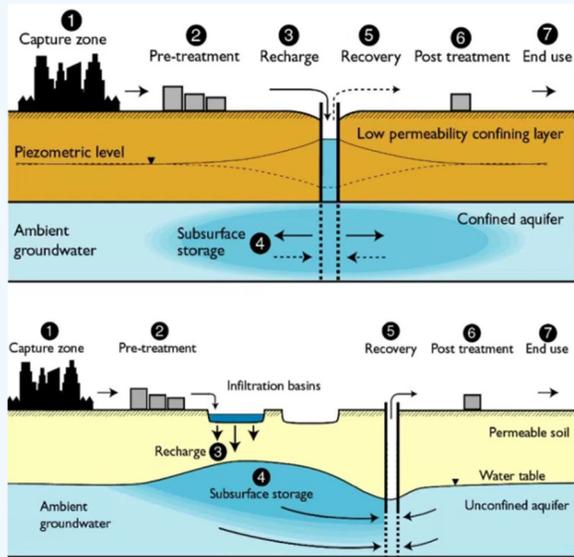
The schematic at left shows the gross geometry and characteristics of aquifers that drive contrasts in porosity, texture, hydrophobicity, and reactivity, which in turn influence molecular-to-pore-scale processes (such as gas bubble migration and entrapment, illustrated by Figure 3.3.2). This schematic illustrates different ways to store water in the subsurface, depending on the geometry of the aquifer system.

While we can use airborne measurement devices (such as GRACE, the Gravity Recovery and Climate Experiment Satellites) or surface-based measurements to estimate changes in aquifer volume, we know little about the overall volume. In a fit-for-purpose context, it becomes necessary to discover and map new resources, both for water and for storage. Although some research focuses on the estimation of subsurface water volumes, the estimates tend to be static and focused more on fresh water than on the important fit-for-purpose brackish and saline reserves. Thus, a basic science question centers on how to translate signals (satellite-based, airborne, geophysical, etc.) into physically and geochemically meaningful estimates of the quantity and quality of subsurface water bodies (e.g., see Figure 3.3.3). The aquifer machinery is also characterized by vertical structures that act as compartments, each with slightly different functions, whereas faults and other structures can separate the compartments laterally. Hence, we need approaches that are sensitive to this internal structure.
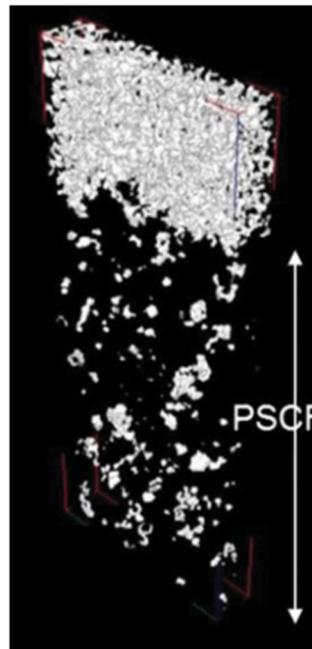
Figure 3.3.2. Illustration of the important role of capillary trapping of gas bubbles within water-saturated porous media and the associated dynamics and mobilization of upward-moving gas bubbles. In the "capillary fringe" of aquifers, located between the unsaturated zone and groundwater (see Subsurface Water Storage sidebar), entrapment and dissolution of bubbles control the dissolved-oxygen levels and the resulting redox potential [3]. The gas phase typically consists of isolated trapped gas phases or gas clusters and the interphase mass transfer is hindered by slow water diffusion. X-ray tomography can be used to study the gas-water interface during artificial water table rise, as indicated by the height of the arrow [3]. The column is 30 cm in length.

Figure 3.3.3. A surface geophysical method, electrical resistivity tomography (ERT), is used to image seawater intrusion along the coast of Monterey Bay, California. Imaging reveals a complex distribution of subsurface fresh and saltwater, influenced by geology, groundwater pumping, recharge, and land use.

Once we discover and quantify groundwater volumes, its movement and quality must be tracked with precision. However, our descriptions of both the h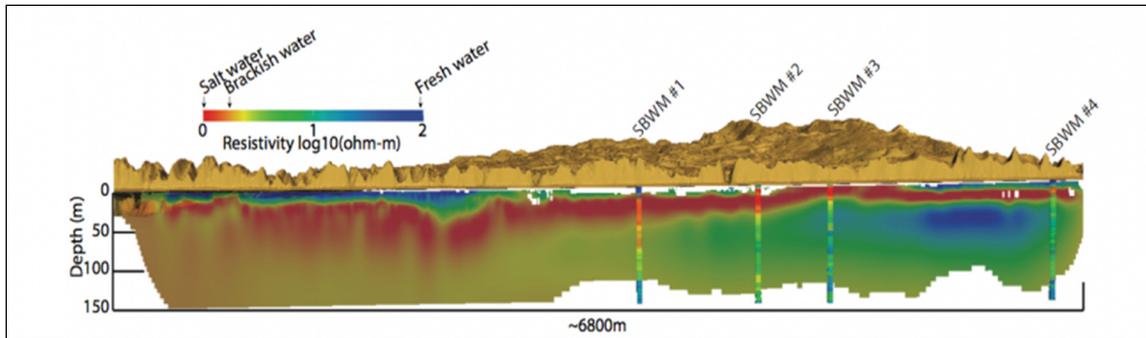ighly nonlinear flow and transport processes and the myriad chemical transformations are incomplete. Often, the chemical and physical processes are strongly linked; thus, understanding of water flow is particularly important when considering chemical reactions occurring at mineral surfaces or during the mixing of fluids. Groundwater flow equations can be thought of as a simplified (volume-averaged) form of the Navier-Stokes equations with clear connections between Darcy's Law and Stokes flow through a porous medium. Although it is not necessary to solve the Navier-Stokes equations to predict groundwater flow, there are cases and scales where the assumptions in Darcy's Law do not hold and momentum terms and dispersion due to pore-scale velocity distributions must be directly considered. These conditions often occur at interfaces (such as between unsaturated and saturated zones (see Subsurface Water Storage sidebar) and the hyporheic zone, which exists between riverbed and subsurface systems) and are exacerbated by extreme conditions that may typify highly managed water systems. Thus, a central basic-science challenge is to improve our understanding of (1) water, gas, and particle movement in the unsaturated zone; (2) zones of fluid mixing; and (3) connections among the unsaturated zone, groundwater, and surface waters under highly transient conditions.

Significant basic-science challenges are associated with quantifying water and gas transport in the unsaturated zone, the cascade of chemical reactions they drive, and their impact on water treatment strategies. For example, excess surface waters or storm waters need to infiltrate from the ground surface to the subsurface as quickly as possible to avoid evaporative losses and damage to surface infrastructure and crops. Predicting how water moves from the unsaturated zone to the capillary fringe under extremely dynamic conditions and moisture regimes remains a challenge because the transport occurs largely at interfaces, via thin films at mineral surfaces, as water vapor or gas bubbles (Figure 3.3.2), and through finger or preferential flow (Figure 2.4.2).

There are many gaps in our understanding of how various hydrological fluxes drive reactions in the unsaturated zone. For example, trapped gases can also stimulate a host of currently unpredictable chemical reactions. The transport of nanoparticles (i.e., colloids) through the unsaturated zone is poorly understood, owing to the complex effects of particle size, surface charge and chemistry, ionic strength, pH, etc. [4]. Given the rapid increase in industrial nanoparticles in the environment, the development of predictive models for nanoparticle transport behavior is another research opportunity where basic understanding may allow for entirely new approaches to passive treatment using engineered nanoparticles.

Another critical basic-science knowledge gap is in our understanding of the geomechanics of aquifers, and in particular, the impacts of subsidence due to groundwater withdrawals. Subsidence has been linked to increased groundwater contamination due to migration of elements such as As from the clay layers (see Groundwater Contamination sidebar in Section 2.4.2 [5]). The expansion and compaction of clays during wetting and drying, as well as the consequences for hydraulic conductivity and porosity, have not been examined. Are such changes reversible? Can we develop energy-efficient approaches to treat the degraded water quality associated with subsidence? Are we irreversibly losing key pieces of aquifer machinery through extensive overdrafts?

3.3.2.2 Creating and Controlling Reactive Aquifers

As mentioned above, a host of complex reactions can occur in subsurface systems (see Figure 2.4.1), including across key interfaces. Although decades of studies have focused on mineral-fluid interfacial interactions of "homogeneous" systems, aquifer systems possess two interfaces that are poorly understood and where rapid reactions tend to occur, largely in response to fluid mixing. These interfaces are (1) the unsaturated zone and capillary fringe (i.e., the dynamic intersection with the water table) and (2) the hyporheic zone, where groundwater mixes with oxygenated river water. Both pose multi-scale problems driven by processes that unfold over molecular- to meter-scale interfaces. Although sorption of ions and molecules at interfaces has received much attention, most systems studied have been fairly simple, and research is needed on naturally complex earth materials.

A significant gap exists in our understanding of redox reactions in and across hydrogeological interfaces. Some of these reactions are catalyzed or promoted by naturally occurring minerals, including Fe (oxhydr)oxides such as magnetite [6, 7], Fe sulfides such as pyrite [8] (see Figure 2.4.4]), and Fe-bearing clays [9,10]. In some cases, reactions occur entirely in solution or are mediated by microbial communities. Even the kinetics of abiotic reactions can be quite rapid because of fluid mixing, while the chemical gradients that develop in response can encourage a range of microbial metabolisms. Both abiotic and biotic reactions can result in "fouling" or unwanted reductions in permeability, which is a common and costly challenge for many water treatment strategies, as well as deeper subsurface energy strategies.

Given the complexity of the reactions and the potential for complex redox cycling, predictive understanding of electron transfer and the means by which it controls the reaction kinetics is critical for many water issues, as well as energy systems (including unconventional hydrocarbon reservoirs where oxygenated fluids are introduced into highly reducing environments). Thus, a basic science need is to develop an understanding of naturally occurring redox reactions associated with fluid (and gas) mixing. Both field and model-system experiments using the new generation of time-resolved spectroscopy and other methods combined with theoretical approaches using ab initio methods and/or expansion of existing theories, especially those involving electron transfer at interfaces [6–11], could allow for the development of engineered systems that enhance the natural transport and reactivity properties, and bolster predictions regarding the consequences of large-scale fluid mixing associated with managed recharge and other aquifer management problems.

A related problem is the growing recognition of groundwater contamination from naturally occurring processes that appear to be accelerated by land-use/water-management practices. This contamination includes toxic and/or carcinogenic elements, such as chromium [Cr(VI)], uranium [U(VI)], As, and Se (see [11,12]). A well-known example of natural contamination is the correlation between U(VI) and nitrate in wells within agricultural areas (Figure 3.3.4). This correlation is also observed for Cr(VI) in California groundwater used for drinking water [13]. Although nitrate may indirectly or directly mobilize and oxidize U, the link between Cr(VI) and nitrate is currently unknown. Increasing fluxes through the unsaturated zone, as well as changes in pH and alkalinity due to land use, may also play a role in the release of natural contaminants.

Extensive groundwater withdrawals have also led to water-quality problems due to compaction and release of elements from fine-grained layers, often called the "dirty sponge effect" [3]. Releases of As to groundwater at managed recharge sites where treated water has been injected have also occurred [14], emphasizing the need to understand the basic geochemical reactions that occur as new fluids interact with existing surfaces decorated with an array of ions. Bromine and iodide at high concentrations, as are typical of produced waters, can also pose a problem if introduced to drinking-water sources, owing to formation of unwanted disinfection byproducts. The presence of any element of concern (EOC) in groundwater used for drinking water presents a special treatment problem and thus creates links between the belowground processes and ex situ treatment. It also requires that we know about not only the major components of groundwaters, but also the dynamics of the trace constituents, often present at levels of µg/L.
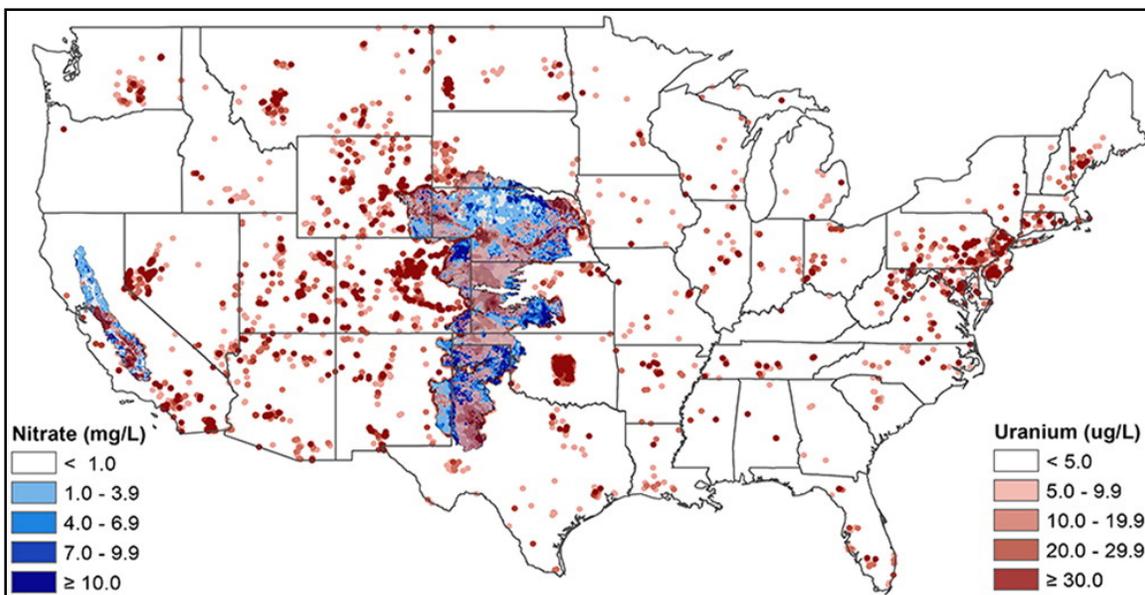
Figure 3.3.4. Map of uranium (red) and nitrate (blue) from Nolan and Weber [11] measured in groundwater wells across the United States with emphasis on the High Plains and Central Valley aquifers, which provide water to about 6 million people and irrigation water for 1/6 of U.S. agricultural revenue. Ten percent of the wells were above the maximum contaminant level (MCL) for U (30 μg/L), and 21% were above the MCL for nitrate (10 mg/L). A basic-research challenge is the quantification of electron transfer processes that drive redox reactions in subsurface materials, and their influence on water quality.

Fundamental understanding of the dominant physical and chemical processes underpinning the machinery of aquifers is required to design and control these processes to serve as passive water treatment systems, allowing for reuse of treated water but also providing a way to bypass some more energy-intensive approaches.

Can we perform process design to control aquifer behavior? Although the science challenges outlined above extend to this application, it also presents new basic-science opportunities, including the design of materials and chemicals that can be used to enhance natural treatment or to control EOCs [15]. For example, biochar is widely used in many treatment strategies, but it is a poorly understood material, particularly with regard to the functional groups, such that it is largely created through trial and error [16]. Research to modify natural nano-geomaterials, aimed at synthesis that enhances their ability to remove pollutants and their selectivity for specific types of contaminants, is underway (e.g., [17]). Groundwater treatment using aqueous oxidants or reductants is also performed at severely contaminated sites, although approaches remain poorly understood and often result in unintended consequences. Thus, new materials and chemicals developed for passive treatment may dramatically influence remediation strategies both across the DOE complex and within the vast number of other contaminated groundwater systems in the United States. Other areas for design could include in situ geomaterials that allow for control of permeability and reactivity, finely tailored to water source characteristics and fit-for-purpose water treatment objectives (Figure 3.3.5). The potential benefit of such passive systems for treatment of brackish or saline waters is significant.
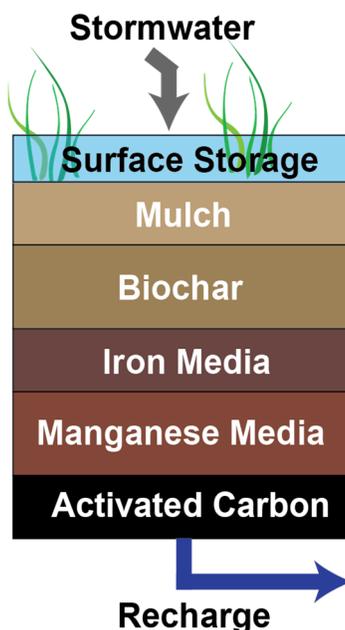
Figure 3.3.5. Example of engineered in situ geomaterial strategy for treating urban storm water (modified from [18]). Existing systems typically rely on infiltration through native soil or sand/soil mixtures. Large variations in moisture content and the need to control the timescales of infiltration relative to the timescales of the chemical reactions pose challenges for treatment. Significant opportunities exist to develop new materials for in situ water treatment that are finely tuned on the basis of fundamental understanding of infiltration and reaction processes and their timescales.

3.3.2.3 Next-Generation Redox-Driven Water Purification

A wide range of technologies have been developed and employed to treat water for a wide range of purposes. They typically involve a combination of physical, chemical, and biological processes, often in series to attain desired treatment targets. Sedimentation and membrane filtration can remove many impurities, whereas many organic contaminants can be destroyed by advanced oxidation processes (AOPs). AOPs involve the generation of highly reactive, non-selective agents (e.g., reactive oxygen species, such as hydroxyl radicals [•OH⁻]) by chemical (e.g., Fe/H_2O_2), photochemical (e.g., irradiated semiconductors), or electrochemical pathways. While these technologies can separate or destroy a wide range of contaminants to levels that are acceptable for many applications, treatment to remove specific contaminants often requires removal or destruction of all or most of the contaminants in water streams, resulting in high usage of energy, chemicals, and materials.

Fundamental R&D is needed to develop concepts that can enable water treatment with enhanced specificity and lower cost and energy demand. Future water treatment technologies must be capable of efficiently dealing with spatially and temporally diverse arrays of pollutants over wide ranges of concentrations. Unfortunately, the molecular transformation pathways and the energetics of many redox processes in complex aqueous media are poorly understood. Fundamental science challenges include developing mechanistic understanding of catalysis for contaminant degradation, designing materials for specific binding of contaminants, and discovering concepts for selective reactivity in chemically harsh and complex environments. Understanding and control of biological and enzymatic pathways are needed to enable more efficient biotreatment processes or hybrid chemical/biological concepts. The selective design, synthesis, and application of nanomaterials holds promise for advancing adsorption, chemical oxidation and reduction reactions, and liquid-based and membrane-based separations. Major advancements in the design, control, and synthesis of nanoscale and mesoscale materials, as well as advanced theory, modeling, and simulation coupled with advanced characterization methods including state-of-the-art structural tools, will drive research in this area.

Novel functional materials can be designed for selective and efficient removal or destruction of contaminants, leading to advances in nanostructured, porous, or organic/inorganic hybrid materials. Understanding molecular interactions in ligands, surfaces, or structured materials to induce molecular recognition in complex aqueous media could lead to new concepts for the selective binding or separation of inorganic or organic contaminants. Design principles for ligands, polymers, or sorbents can be based on size, shape, polarity, or chemical binding (see Little Molecules with Big Impacts on the Production of Energy sidebar). Molecular recognition in water, particularly concentrated aqueous

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LITTLE MOLECULES WITH BIG IMPACTS ON THE PRODUCTION OF ENERGY [19]
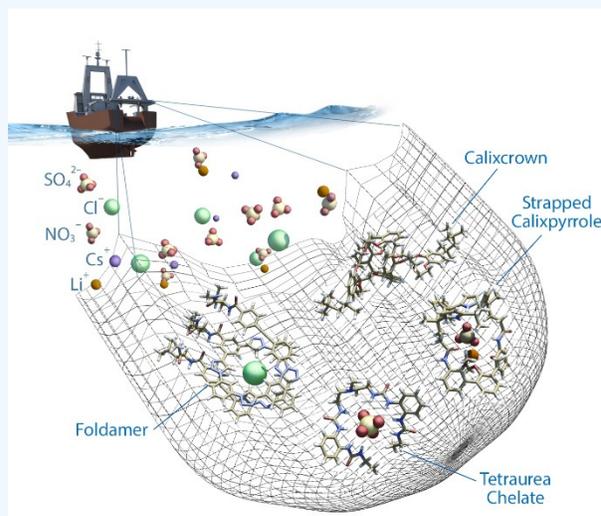
Specific ions can be captured using designed molecular chelators ranging from foldamers for chloride to tetraurea chelates for sulfate, strapped calixpyrroles for lithium nitrate, and calixcrowns for cesium.

Chemists have developed various classes of chelators that can selectively capture specific ions using a combination of chemical bonding, attractions between opposite charges, and/or wrapping of the ions in complementary binding pockets [20–24]. Strategically designed ion chelators will have a highly positive impact on the safe production of energy from nuclear sources and may also find application in the purification of water and sequestration of other elements, such as lithium, that are key to sustained energy independence. Chelators act on the molecular scale to capture and selectively separate specific ions from concentrated mixtures of other ions. In mixed aqueous solutions, chelates containing several urea groups can wrap around sulfate, an ion that is extremely detrimental to the reprocessing and storage of nuclear waste. Chelates with two different binding sites can ultimately be used for binding both anions and metal ions. Foldamers collect ions in one location and release them in another location, using sunlight as a trigger.

solutions with complex matrix effects, is not understood well. State-of-the-art characterization techniques, including in situ methods, can be used to probe molecular interactions under realistic conditions encountered in complex waste streams, including understanding the effects of high salt concentrations or heterogeneous mixtures. Metal-organic frameworks and other hierarchical approaches, e.g., "foldamers" (chelators that can fold up around ions) or polymers, could be designed to operate in aqueous solutions. Recently, it has been shown that cross-linked β-cyclodextrins within rigid polymers can provide a high-surface-area, mesoporous system for binding of organic contaminants [25]. Ligands have also been developed for selective binding of ions, showing the promise of new design concepts.

Binding efficiencies (formation constants) could also potentially be greatly increased by control of pore size, inclusion of functional groups, or nanostructuring of surfaces for porous materials or supports. Theory and computation could guide materials discovery. Biomimetic approaches, including selective anion binding in proteins or selective transport in membranes, could inspire the development of new materials. Developing principles and mechanisms to regenerate or recover specific ligands or sorbents is another important area for research. Research in this area could also lead to new concepts for specific recovery of valuable contaminants such as precious (or "strategic" or "critical') metals.

AOPs are well established but can require significant amounts of energy or chemicals. They can involve complex reaction pathways comprising many elementary steps. Furthermore, they may fail to fully degrade all contaminants to benign products (e.g., CO_2), leading to degradation byproducts. Understanding, designing, and controlling new multi-electron redox catalysts could lead to more efficient energy and chemical usage. The design of new catalytic systems for contaminant degradation requires a more complete understanding of oxidative or reductive degradation pathways as well as reaction orders, intermediates, and energetics. The

Figure 3.3.6. Advanced technologies for solar energy disinfection.

development of analytical and spectroscopic methods is critical to exploring reaction mechanisms and to understanding the presence and formation of potentially hazardous degradation byproducts, as well as setting overall treatment objectives. New catalysts also need to be developed for the destruction of recalcitrant organic contaminants, such as hydrodechlorination of chlorinated hydrocarbons. New catalysts and concepts that use solar energy can be developed (Figure 3.3.6 [26]). Characterizing, understanding, and controlling interfacial and even interphase phenomena, including charge transfer, substrate/solute/contaminant interactions, and chemical reactivity, are critical. Advances in this area could build on new understanding and design of interfaces for photoelectrochemical water splitting.

To achieve fit-for-purpose water with minimum energy input requires multiple, responsive target-specific treatments, including oxidation and reduction processes. Catalysts currently in use do not possess sufficient specificity or efficiency in complex aqueous media; a more fundamental understanding of catalytic, electrocatalytic, and photocatalytic processes is needed. Rationally designed materials and catalytic processes could lead to disruptive changes in water treatment, providing for a tailored approach to contaminant removal, while simultaneously accelerating the evolution of distributed water purification systems. Research is needed to create tailored next-generation redox-driven contaminant degradation processes that are species-specific yet provide for highly energetic oxidation or reduction reactions, leading to complete degradation of the targeted contaminants to benign products (e.g., CO_2). We can envision the creation of new selective reaction environments by integrating selective binding or adsorption with catalytic reactions. We currently do not understand how to couple catalytic sites to host materials for selective molecular or ion adsorption. Designing new advanced water-treatment platforms will require theoretical descriptions and modeling of solute and solvent interactions, binding energetics of catalytic host materials, bound-solute interactions and reactivity, catalytic active site generation, solvent-solute-surface-catalyst interactions, and reaction pathways. Creating the targeted levels of specificity in a reactive environment could be accomplished by binding whole classes of molecules, or specific ions or molecules, to robust catalytic sites, for interaction with potent oxidants or reductants. Research efforts could focus on coupling catalytic sites to new nanostructured materials

(hosts) that would provide systems to chemically, electrochemically, or photochemically generate potent redox agents within nanoscale confined environments.

Design rules need to be developed for binding specific molecules near catalytic sites. Potentially important research avenues could include adding catalytic chemistry to structural motifs by

- Incorporating selectivity via shape, size, polarity, binding, or other molecular recognition attributes into electrochemical electrode or photochemical electrode materials via chemical or physical modification of surfaces or the incorporation of nanostructured pores or channels.

- Incorporating catalytic sites into selective separation materials, sorbents, or membranes by inducing degradation reactions within pores or channels, creating redox active sites in frameworks of mesoporous systems, or depositing (via atomic layer deposition or other controllable processing methods) catalytically or photochemically active materials onto nanostructures or porous materials.

- Integrating theoretical understanding, synthesis, and characterization to design new multi-functional materials based on self-assembly of new building blocks or other hierarchical approaches to create hybrid materials for selective binding/reaction that have sufficiently chemically (e.g., oxidatively) stable ligands or polymer systems.

- Using advanced theory and computation to model reactions in nanoscale confined environments, including transport, homogeneous, and heterogeneous reactions.

For example, one could envision new nanoporous membranes with photocatalysts as well as nanoporous catalyst supports with specific functionality for selective binding. Combining catalytic concepts with membrane separation could lead to new concepts for preventing scaling or fouling of membranes.

3.3.2.4 Harnessing Charged Interfaces for Separations and Reactions

Water-stressed regions are increasingly supplementing conventional water sources with marginal sources of water such as brackish water or seawater, or through water reuse from municipal reclaimed water, storm water, or other sources. Desalination offers an opportunity to convert previously unusable saline water to fresh water. A wide range of separation technologies have been developed and employed for water treatment: bulk and surface adsorption; partitioning into membrane materials; ion exchange; reverse and forward osmosis; membrane distillation; and micro-to nano-filtration. Many of these processes are membrane-based, and there is significant opportunity for the design of new materials with enhanced properties and performance (also see Section 3.4, Crosscutting Basic Science in Energy-Water Systems). Electro-mediated separation processes such as capacitive deionization or other capacitive desalination concepts are being advanced. These methods are not based on membranes but use electrically charged electrodes for ion capture and separation. Electro-capacitive separation concepts have the potential to utilize less energy than membrane-based reverse osmosis technologies, particularly for brackish water or water with lower concentrations of salts (see Figure 2.2.12).

Despite their potential, these methods are often hampered by slow processes, diffusion limitations, and inefficient reductions in salt concentrations. Understanding and mitigating biofouling of electrode materials are also critical. There is a significant opportunity for fundamental science to provide important understanding of interfacial processes across multiple scales to aid in the discovery and development of new electrode materials that could potentially overcome these limitations. New materials and processes can enhance energy efficiency, potentially enable the selective removal of specific ions, and even allow for the potential absorption/recovery of valuable contaminants for reuse to develop revenue streams from contaminant purification. For example, high-surface-area porous electrodes could lead to more energy-efficient processes. Scientific challenges include understanding and modeling (1) the structure, dynamics, and energetics of water and solutes at surfaces; (2) the effects of nanoconfinement on properties and transport; and (3) the structure and space charge of double layers. Theoretical and experimental methods can be applied to describe or even predict the structure, dynamics, and processes at charged electrode interfaces, particularly in complex and/or concentrated media.

We need to go beyond empirical models to develop computational tools to bridge the atomistic to mesoscopic scale and continuum levels of water/material interactions in order to understand and predict fundamental interactions, ion transport at continuum and atomistic levels, and ion sorption and diffusion, particularly at complex surfaces or in complex media. As described in Section 3.1 (Basic Science Challenge to Improve Water Use for Industrial Applications and Electricity Generation), we have a poor understanding of the structure of water in nanoconfined environments (e.g., at surfaces and in pores or channels), which is further exacerbated by the presence of ions. We also do not understand these phenomena at electrified interfaces or at the water/air interface; for example, are they acidic/basic? How do they change in the presence of ions and neutral molecules? High-resolution characterization methods across multiple length scales can be used to probe the structure and dynamics of surfaces, interfaces, and nanopores. Understanding the molecular origins of the electric double layer will make it possible to quantitatively describe local diffusivities, solvent rearrangements, and ion sorption processes. It is also important to understand ionic conductivity and mobility in complex solutions over a wide range of concentrations.

To create selective separation concepts based on unique, designable, controllable surface structure and properties, we need to understand structure/function relationships for selective adsorption, transport, and permeation. Probing pore/water interfaces can help identify what kinds of interactions (e.g., hydrophobic or hydrophilic) are most beneficial for selectivity. This information is critical for predictive approaches using nanoporous electrode materials, colloidal transport through porous media, and salt dissolution/precipitation rates and mechanisms.

A key research area is the design, synthesis, and characterization of new multi-functional materials for charge and ion storage and transfer. New approaches to materials design, synthesis, and characterization could advance a number of electro-mediated separation concepts. Advancing the science of charged fluid-solid interfaces will enable the community to predict, design, and control systems. New materials with higher ion loading capacity and better conductivity would increase the productivity of the technologies. The development of new high-surface-area electrode materials and other concepts can particularly benefit from advances in nanoscience and nanoscale materials.

Developing the science for selective removal of species from water is a key challenge. Materials designed for adsorption/desorption of targeted species could be used to tailor water treatment processes. For example, one could imagine hybrid approaches that incorporate ionic membranes or organic polymers that could be selective for critical anions (e.g., NO_3^-, F^-, and AsO_3^-) relative to chloride. Advances in the fundamental theory, modeling, and characterization of charged interfaces in complex aqueous environments could facilitate materials-by-design approaches. Selective electrodes with functionalization, channels or nanostructuring for binding, or concentration gradients could be developed.

Electro-capacitive devices also have the potential to integrate energy recovery or energy storage with water purification. Concentrated salt solutions could be employed as chemical batteries and enable reversible processes that could more closely approach thermodynamic limits.

3.4 CROSSCUTTING BASIC SCIENCE IN ENERGY-WATER SYSTEMS

3.4.1 Introduction

This section is organized around four broad topics relevant to energy-water systems:

- New materials and their properties;
- Critical processes;
- Analytical, characterization, and data management strategies; and
- Basic science that cuts across other panel topics.

3.4.2 New Materials and Materials Properties

3.4.2.1 Introduction

Key components in energy-water system processes (including membranes for water and wastewater treatment and reuse, catalysts and sorbents to remove contaminants, and other technologies) rely on materials with specific chemical, physical, mechanical, and surface interactions to create selectivity for separations and reactions. Most components in the water-energy pathways are manufactured from a handful of materials, initially developed decades ago. Owing to the limited knowledge available at the time, these materials were typically identified through Edisonian and heuristic approaches. These materials have been tuned, modified, and optimized extensively since their initial discovery. This optimization has led to efficient materials for specific, well-established applications related to energy-water systems. However, these incremental advances do not deliver the range of selectivity and specificity necessary to deliver tunable, dynamic, and selective purifications and transformations. This outcome is of particular importance given the inherently complex, multi-component, heterogeneous nature of the fluids involved in energy-water systems, which must then interact with necessarily multi-functional materials.

For example, the limited range of materials available also limits the types of separations available today. Many current membranes rely on pore flow, separating through a size-sieving mechanism. Wide pore size distributions lead to limited separation capabilities and restrict the application of membranes in a broader range of separations relevant to energy-water systems. Reverse osmosis and nanofiltration membranes, designed to retain ions but pass water, suffer from similar limitations that arise from structural heterogeneities. Separations of yet more complex mixtures that are prevalent in an expanding set of water-energy processes (e.g., removal of small organic molecules and uncharged micropollutants, as well as selective removal and concentration of specific ions and metals) are also not well-addressed by membranes, owing to material limitations. The ability to separate and isolate this ever-expanding list of constituents will enable many processes, including but not limited to water and wastewater treatment, concentrate management, and water reuse in resource extraction. The molecular design of materials leveraging self-assembled and nanopatterned materials, selective receptors, and other new synthetic approaches could provide a paradigm shift in terms of tunability and specificity in separations. Similarly, design of materials with improved fouling and corrosion resistance relies on empirical heuristics, with much fundamental knowledge — about the influence of foulant chemistry, charge, and size; membrane pore size and size distribution; and membrane chemistry, topology, pore structure, and operating conditions on fouling — remaining obscure. Sorbents remove contaminants by selectively adsorbing or binding to them, or by trapping them in functional nanopores. Activated carbon is an inexpensive, widely used sorbent employed in water treatment as it adsorbs most organics and non-polar compounds

effectively. Zeolites, metal-organic frameworks, silica, and polymer particles all could provide more selectivity on a designer basis. Similar cases can be made for energy-water process components, ranging from catalysts to coatings, in which the design of materials to selectively control transport and transformation could be applied to create entirely new and necessary properties (including active, autonomous pumping, corrosion and fouling resistance, self-cleaning and healing, and robust surfaces).

3.4.2.2 Challenges and Research Opportunities

The design of next-generation materials for tunable, dynamic, and selective purifications and transformations relies on a much-expanded understanding of the hierarchy and taxonomy of water and solute interactions with structured interfaces. This knowledge will enable the design of materials to tune transport and harness inherently complex multi-component fluids and necessarily multi-functional materials to control overall properties and performance. Figure 3.4.1 [1] is an example of multi-component block-copolymer materials that readily organize into potentially functional architectures, a fruitful area for future fundamental research.
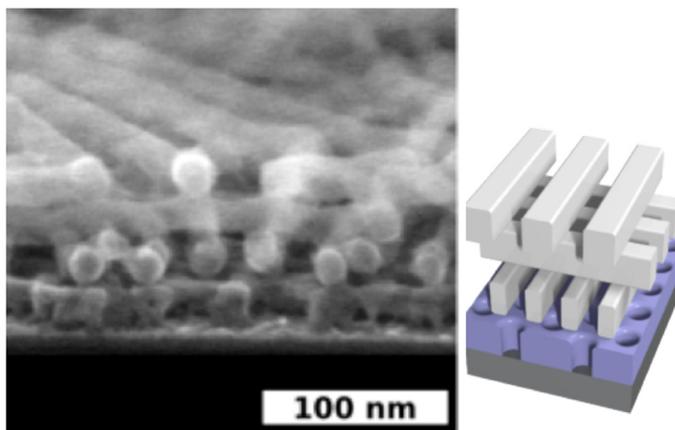

Figure 3.4.1. Three-dimensional block-copolymer morphologies that may be leveraged for the development of multi-functional membranes.

The rational design of the next generation of functional materials that make use of specific material/fluid/solute interactions will leverage the advances enabled by the Materials Genome Initiative (MGI). For example, the design from first principles (theory) and synthesis of molecular cages that interact specifically with nitrates and borates directly leverage MGI approaches, as do the design and synthesis of nanoscopic filters based on self-assembly with functionalized pores for absorption of micropollutants. Rational design of functional materials for energy-water processes will, however, involve complexities that extend far beyond the advances of MGI. These materials and materials systems are often compositionally and structurally heterogeneous, as they comprise multiple components and phases spanning multiple length scales. Complications beyond those addressed by MGI also arise from the lack of taxonomy or metrics to guide rational design (i.e., what are we designing for?). As an example, a large number of anti-fouling studies that seemingly address how surface chemistry and morphology of membranes affect the extent of fouling have resulted in a confusing array of conclusions. This lack of consensus on which property to target and what metrics to design for stems, in large part, from the fact that the performance of materials and materials systems in energy-water applications hinges on their interactions with and the properties of the fluid they are in direct contact with, which is also multi-component and multi-phase in nature. Articulating metrics and establishing methods and facilities that allow for uniform characterization will go a long way in moving the community toward the ability to specify a priori, and design accordingly, functional materials and materials systems for energy-water processes. It also follows that rational materials design for components used in energy-water processes will need to account for the multi-body interactions between the solid and the fluid. An opportunity thus exists for the synergistic design of material-fluid pairs by, for example, taking into account both molecular and nanoscopic size exclusion and absorption effects, as well as surface and structural features of the material and its specific interactions with the constituents of the multi-phase and multi-component fluid, to significantly enhance fouling resistance while simultaneously improving surface wettability of the said fluid. Similarly, atomistic-scale experiments and theory to understand water structure and physics at hard and soft interfaces should be leveraged to design materials that take advantage of water confinement effects to control the transport of fluid within pores.

Titanium dioxide is the predominant photocatalyst that is used to treat/disinfect water today. An opportunity exists to explore new materials for such applications. Can naturally occurring, earth abundant minerals, for example, facilitate disinfection, sorption, and degradation of organics? Along the same lines, the phase space for catalytic materials candidates is large. Different polymorphs and different crystalline facets can result in drastically different catalytic

activity. It is thus important to elucidate the structure-function relationships of these material candidates in search of new and more effective catalysts. The evaluation of photocatalytic activity has traditionally emphasized how the said catalyst decomposes organics and microbes. Equally important but seemingly ignored are the byproducts that form during photocatalytic disinfection. Rational design of new catalysts should take a holistic perspective of the system to preclude the formation of unintended byproducts.

An opportunity in the area of materials development involves increasing the functional dimensionality of these materials and materials systems. Design challenges include (a) combining separation with catalysis or antimicrobial activity; (b) increasing flux while retaining selectivity with new materials; and (c) taking inspiration from ion channels in biological systems to target specific contaminants. All of these materials design challenges rely on the development and leveraging of new scattering, spectroscopy, and imaging methods that probe the characteristics of hydrated, porous, and confined interfaces, including 3D and internal morphology, heterogeneity in real time, and environmental conditions.

3.4.3 Processes Critical to Energy-Water Systems

3.4.3.1 Introduction

Energy-water processes span a wide range of pressures and temperatures, as well as length and time scales, and involve complex fluids interacting with natural media (e.g., rocks and soils) or engineered media (e.g., membranes). The separation, injection, or treatment of fluids often leads to non-equilibrium conditions, which induce changes in both the fluid and the media (e.g., fouling of membranes and loss of porosity of rocks). As a result, the efficiency of these energy-water processes evolves over time. Predicting the evolution of energy-water processes and design of active (reverse osmosis, ultrafiltration, etc.) and passive (aquifers) treatment systems must build on detailed understanding of a wide range of physical, chemical, and biological processes, such as the following:

- Heat transport/transfer,
- Multi-phase flow through porous media,
- Formation and stability of water complexes,
- Mineral dissolution and precipitation,
- Chemical transformations,
- Clathrate nucleation and growth,
- Fouling of surfaces,
- Microbial growth on surfaces, and
- Electron transfer processes.

The complexity of fluids and media combined with the physicochemical conditions of energy-water processes is far from well characterized. Model systems that form the basis for our knowledge are limited. The interfacial interaction between water and solutes (e.g., ions, organic solutes, and biomolecules) and other materials (e.g., membranes, pipes, and rocks) also needs better understanding to address challenges in these critical processes. Our knowledge of energy-water processes is further challenged by our limited ability to make in situ observations in the field at time and length scales relevant to energy-water processes. For example, injection of supercritical CO_2 into deep saline formations leads to acidity in the formation waters that in turn can drive reactions with minerals that proceed over timescales of years to millennia.

3.4.3.2 Challenges and Research Opportunities

Fundamental research is needed to expand our knowledge of physical, chemical, and biological processes relevant to the conditions encountered in energy-water processes. The following challenges illustrate this need.

Understanding Mineral Stability and Reactivity

A major challenge is to understand how fast minerals dissolve or precipitate in high-ionic-strength aqueous systems. For example, injection of supercritical CO_2 into deep saline formations leads to highly saline acid solutions that react with the rock matrix. Experimental data relevant to these conditions are limited. Hence, there is little insight on how reaction mechanisms are affected by high-ionic-strength conditions, which is necessary for developing predictive capability. Similarly, there is a lack of understanding of how water at low activity — for example, water dissolved in supercritical CO_2 (e.g., wet supercritical CO_2) — reacts with the mineral surface. Complicating matters is the fact that such surface reactions further alter the composition, salinity, and pH of the fluid. This evolution of both the mineral surface and the fluid sets up complexities that need to be understood to be able to accurately model/predict/control relevant energy-water processes.
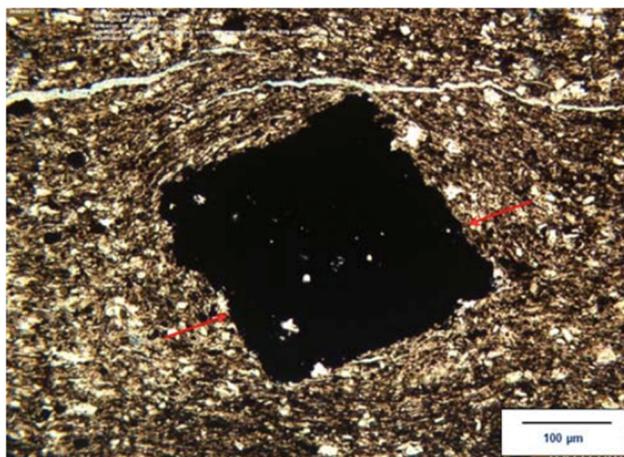
Nucleation and Growth of Clathrates

The formation of clathrates during transport of gas-rich aqueous fluids in the exploitation of hydrocarbon leads to clogging of pipes. The incomplete understanding of nucleation and growth of clathrates and the role of the fluid composition and interaction with surfaces inhibits the development of preventive measures. An unexplored opportunity remains to assess these clathrates as separating agents. Under what conditions can we unlock the cages of clathrates to release trapped hydrocarbons? A better understanding of the conditions under which, and the mechanisms with which, clathrates form and dissolve will allow us to suppress clathrate formation in pipes and/or leverage clathrate formation for separation purposes.

Molecular-Level Understanding of Degradation of Surfaces Critical in Energy-Water Systems

The efficiency of energy-water systems and processes, such as cooling, catalytic water treatment, separation through membrane filtration, or reverse osmosis, can be severely compromised by organic fouling, biofouling, and scaling and/or corrosion of surfaces. Organic fouling and biofouling are common problems in reverse osmosis and filtration installations used to treat water. Preventive measures or remediation techniques based on a sound understanding of the processes that trigger the growth of microbes, accumulation of extracellular polymeric substances and other organic molecules (e.g., oil), or deposition of biogenic minerals can increase efficiency and reduce cost. Equally important is understanding the conditions/circumstances under which the initial adsorption of organics and/or microorganisms can be reversed. Mineral deposition in pipes, valves, and heat exchangers as a result of changes in pressure and/or temperature can ultimately require either harsh chemical treatment to dissolve mineral deposits or replacement of infrastructure. A molecular understanding of the onset of scaling (heterogeneous nucleation and growth of minerals on energy-water system-relevant surfaces) could open the way for new strategies to prevent or inhibit scaling. Exposure of energy-water critical infrastructure systems to corrosive solutions can lead to infrastructure failures, leaks, and high dissolved-metal content in drinking water. Understanding corrosion processes at the fundamental level will provide new avenues for preventive or remediation measures as well as improved predictive models to facilitate retardation of such surface processes.

Understanding surfaces is critical to separation technologies, friction and tribology, and catalysis of water treatment. For example, there is a need to be able to better understand and control the wettability of engineered surfaces (e.g., sorbents or membranes) and mineral surfaces (e.g., for applications in enhanced oil recovery). For example, when the bandgap of nitrogen-doped titania to be used as a photocatalyst is altered, this modification of the bulk, in turn, alters the electrostatics at the surface. The resulting photocatalyst is far more hydrophilic compared to its undoped counterpart. This example highlights the complexities that underpin energy-water materials systems and processes. A fundamental and comprehensive understanding will shed light on the unintended consequences that result from such seemingly straightforward modifications to energy-water materials systems and processes.

3.4.4 Enabling Fundamental Science

3.4.4.1 Introduction

Most energy-water processes are a complex network of chemical, physical, and biological processes that interact through (nonlinear) feedbacks. To gain insight into this complexity, one needs a firm understanding of the underpinning processes and properties of media and fluids under energy-water system-relevant conditions. For example, the flow of an aqueous fluid through porous media in an engineered energy-water system may evolve as biological and chemical processes (e.g., biofouling of a membrane) alter the fluid and/or media. An understanding of fluid dynamics, solvent-solute properties, solute-interface interactions, and chemical reactivity, as well as microbial metabolism and enhanced oil recovery, is necessary to start resolving this complexity.

3.4.4.2 Challenges and Research Opportunities

The ability to accurately model and capture the properties of aqueous solutions and dispersions remains a challenge. This barrier has, in turn, limited our ability to predict the behavior and properties of solutions and dispersions prior to experimentation. A critical enabler of the ability to model solution and dispersion properties is the development of new methods and improved force fields that capture the complex solute-solute and solute-water interactions. This will require close coupling of experimental research and computational modeling of energy-water processes, including geochemical processes.

Given the complexities and heterogeneities that are present in the fluids and media involved in energy-water processes, understanding transport of water and solutes through structurally and compositionally heterogeneous media is critical. This understanding is complicated by complex interactions between solutes and with water, as well as those with the walls of the media. Attention should also be paid to the possible structural and compositional evolution of the media as a consequence of fluid transport. In response to this challenge, there need to be better laboratory models that allow the accurate capture of fluid transport through heterogeneous media. Such models should accurately capture the effects of pore size distribution and pore connectivity on fluid transport.

A fundamental understanding of chemical and physical processes that take place at functional interfaces of energy-water processes is critical. Chemical degradation, including scaling and corrosion, as well as physical adsorption resulting in fouling, critically affect the long-term performance of energy-water processes. Understanding the evolution of media and fluid and the interface between them over appropriate length and timescales will lead to fundamental insights that can form the basis for new preventive strategies or improved skill in predicting these complex energy-water processes.

3.4.5 Enabling Analytical, Characterization, and Data Management Strategies

3.4.5.1 Introduction

Advancing our understanding of energy-water system processes as well as the fundamental chemical, physical, and biological processes that underpin them requires the integration of observations in the field, experimental studies, computational models, and theoretical advances. Over the last decade, new sensors (e.g., fiber optical techniques) have been developed that can be deployed in the field and integrated into distributed sensing networks to sense or control energy-water infrastructure and make observations in natural systems. In parallel, significant advances have

been made in our ability to study processes under more realistic conditions in real time and at high-resolution spatial and/or temporal scales to provide new insights into the dynamics of energy-water processes by effectively creating 4D (x, y, z, and t) datasets. The advances in both sensing and characterization tools generate large datasets that need to be processed, analyzed, and visualized. The community should leverage advances in high-performance computing and new machine learning techniques to manage and analyze the large amounts of imaging and sensing data that are acquired with the new analytical, characterization, and data management tools (e.g., Figure 3.4.2).

3.4.5.2 Challenges and Research Opportunities

Energy-water system processes span a large range of conditions (pressure and temperature) and unfold over timescales that range from seconds to days to thousands of years and operate over length scales from nanometers to kilometers (Figure 3.4.3). The broad physicochemical conditions within energy-water processes present several basic science challenges, including the following:

Develop new sensors and actuators that can be deployed reliably under relevant energy-water system conditions to detect and control, respectively, energy-water infrastructure and processes in natural or large-scale geo-engineered systems. For example, networks of nano-robots might be developed that can be deployed to monitor infrastructure for pressure drops to speed up the response to the development of leaks.

Develop new characterization tools and methods to study energy-water processes under realistic or possibly operando conditions. The availability of state-of-the-art synchrotron-based imaging/scattering/spectroscopy techniques, neutron scattering, environmental transmission electron microscopy, and other nondestructive analytical tools provides the opportunity to study and characterize buried interfaces, capture changes in media exposed to fluids, spatially and temporally resolve changes in oxidation state, determine the structure of media and fluids at interfaces, and follow self-assembly processes in real time. One of the frontiers is to study processes using multiple techniques so that complementary information can be obtained to build a more complete picture of the evolutionary processes. One challenge is to develop environmental/operando cells that can be utilized with multiple techniques. A second challenge is to develop precise fiducial markers and software that allow the registry, fusion, and quantitative analysis of data obtained from two or more techniques. A third challenge, particularly for techniques involving x-rays and electrons, is to understand and prevent irradiation-induced damage to the sample.

Develop methods to study energy-water processes in which the timescale of the processes of interest often exceed the time frame during which experiments can be realistically conducted. This challenge calls for strategies that accelerate energy-water processes without losing relevance. Examples in this context are corrosion of infrastructure components, degradation of cement supports used in fracking infrastructure, and evolution of pore size distribution and pore connectivity in a wide range of media (e.g., membranes, sorbents, and rocks) while exposed to fluids. The development of specialized experimental reaction cells allows for small representative steel coupons or thin sections of cement to be studied over the course of days under realistic conditions, avoiding the slow process of advection of reactants and removal of product. Further studies are needed to validate this approach and its expansion to other energy-water-relevant processes that proceed slowly.

Figure 3.4.2. Development of high-performance liquid chromatography on a chip. (Courtesy of C. Stafford, NIST.)
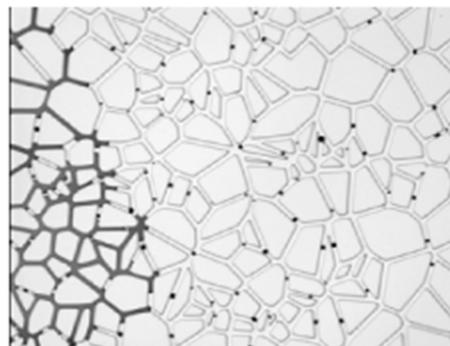
Figure 3.4.3. Microfluidic porous media models for pore size of 4–8 μm.

Develop laboratory-scale systems to improve our understanding of physical or chemical processes underpinning energy-water systems. For example, displacement of saline fluids with supercritical CO_2 in the subsurface is poorly understood, but insight can be gained through the study of fluid displacement in small-scale microfluid or 3D-printed model systems and its comparison with model calculations. While comparisons thus far have shown the efficacy of such models in capturing certain macroscopic properties, these laboratory models do not completely capture the phenomena under study. This discrepancy points to the importance of structural heterogeneities in impacting energy-water processes. An opportunity thus exists to conduct experiments with next-generation laboratory models that capture such structural heterogeneities, including pore size distribution and pore connectivity, to better understand the physical and chemical processes that underpin processes in energy-water systems.

4. Conclusion

Energy-water systems represent one of the largest potential growth areas in energy science, as suggested by the recognized and pervasive interconnection between these two sectors. The focus, to date, has been largely on engineering processes as well as on data, modeling, and analysis. The figure below, from the 2014 DOE report *The Water-Energy Nexus: Challenges and Opportunities* [1], lays out five technological areas related to energy-water systems. This figure further illustrates that many areas of science underpinning these areas are only indirectly about water; many are related to other aspects of chemistry and materials. This BRN workshop assessed those basic-science bottlenecks and gaps in our understanding of issues related to the energy-water connection.
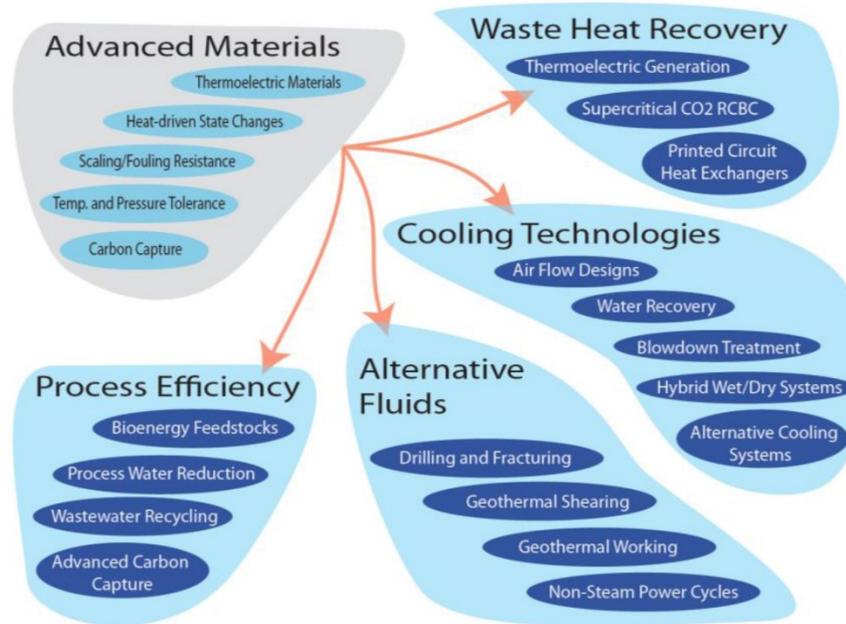
There is an enormous need and opportunity for basic energy science research on water and its relationship to energy. This research spans a range of scientific disciplines and can make exciting new uses of user facilities. The as-yet unexploited opportunities for BES-supported science to drive innovative new research aimed at energy-water systems are tremendous. It is clear the understanding of energy-water systems will benefit from the convergence of the powerful combination of BES programs in chemical, physical, biochemical, geological, and materials sciences coupled, as needed, with BES facilities. The aims of the workshop and report are to define the new insights and innovations needed from these basic research areas to enable scientific and technological advances for energy-water systems.

Chemical, geo- and bio-sciences in energy-water systems. Fundamental research in chemistry, geology, and biochemistry, including efforts not directly focused on water, will provide new insights to enable scientific and technological advances in energy-water systems. This research involves a range of topics: organic chemical transformations (synthesis, degradation) in water, including chemical, bio- and photo-catalysis; nucleation

phenomena in water; hydrogen bonding and its effects on solvation of molecules and electrons; interfacial science of water in contact with solids and air, including confined water; hydration of ions and its role in ionic conductivity; movement of ions in biological and synthetic membranes and via molecular transporters; natural and artificial photosynthesis, for instance, water splitting in energy conversion and storage (i.e., production of chemicals and fuels). A special issue of the *Journal of Chemical Physics* in December 2014 used these words: "Chemical physics research on the fundamental properties of liquid water and aqueous solutions has gone hand-in-hand with studies of the biological properties of water. The result is a deeper understanding of water in living systems." Research across these three scientific disciplines can reveal a wealth of new knowledge impacting improved water use efficiency and recovery from energy generation and industrial processes, enhanced environmental and hydrological applications in the subsurface; development of new methods such as atom-trapping/isotope dating or tracers for tracking groundwater; and enhanced water use for bioenergy, for example, in the chemical catalytic conversion of biomass to fuels.

Materials sciences in energy-water systems. Beyond the obvious, but important, goal of designing and synthesizing new water purification membrane/sorbent materials and catalysts, many basic materials sciences research directions affect energy-water systems without being directly concentrated on water. New thermoelectric materials could successfully cool processes, reducing cooling water withdrawals and generating useful power, in some cases. Surface treatments to reduce scaling and fouling would improve efficiency of many water-intensive processes. As with chemistry, new developments in materials sciences benefit efforts related to catalytic processes such as artificial photosynthesis, potentially revealing new insights into processes relevant to water and energy. Other efforts involve the discovery, design, and synthesis of biomimetic and bioinspired functional materials and complex structures based on principles and concepts of biology. Research in this area can underpin development of new materials to control transport across membranes and make separations and purification processes more efficient. Finally, in the realm of membrane materials, effective water purification demands numerous different kinds of membranes, as well as new understanding of ion exchange and transport, from desalination, to micro-, ultra-, and nanofiltration, to specialized membranes and processes for treating produced water and water used in hydraulic fracturing. There is tremendous scope for basic materials research related to water and energy.

Facilities for research in energy-water systems. Upgraded facilities for x-ray and neutron scattering coming online in the next decade have tremendous potential to provide unprecedented new information on water structure relevant to energy sciences matters. For example, anomalous and resonant x-ray scattering near absorption edges of various ions will provide new information on ion distributions and transport in water-permeated materials, with relevance in energy storage, water purification, and bioenergy applications. Neutron scattering, in both total scattering intensity and various dynamic and inelastic modes, has unique power to reveal new local structural information about water, via deuterium substitution. Further, developments of x-ray photon correlation spectroscopy will allow the determination of real water equilibrium dynamics on timescales ranging from tenths of femtoseconds to minutes, and length scales from nearest-neighbor distances to several nanometers. Nanoscience centers provide a wealth of capabilities to synthesize and interrogate materials relevant to energy-water systems. High-performance computing facilities will be central in implementing models and simulations to gain insights into the thermodynamics and reactivity of complex fluids, the design of novel materials, and the nuances of transport phenomena in natural and manufactured systems.

APPENDIX A: WORKSHOP PARTICIPANTS

Chair: Matthew Tirrell, University of Chicago/Argonne National Laboratory
Associate Chairs: Susan Hubbard, Lawrence Berkeley National Laboratory
David Sholl, Georgia Institute of Technology

Co-chairs: Dan Giammar, Washington University in St. Louis
Ben Gilbert, Lawrence Berkeley National Laboratory
Lynn Loo, Princeton University
Kate Maher, Stanford University
Eric Peterson, Idaho National Laboratory
Martin Schoonen, Brookhaven National Laboratory
Michael Tsapatsis, University of Minnesota
William Tumas, National Renewable Energy Laboratory

Report and Factual Document Assistance: Seth Darling, Argonne National Laboratory

Basic Energy Sciences Team:

Harriet Kung, Bruce Garrett, Linda Horton, Gail McLean
Katie Runkles (Administrative)

Panel 1: Basic Science Challenges to Improve Water Use for Industrial Applications and Electricity Generation

Leads: Eric Peterson, Idaho National Laboratory
Michael Tsapatsis, University of Minnesota

*Yoram Cohen, University of California—Los Angeles
Benny Freeman, University of Texas—Austin
Michael Hickner, The Pennsylvania State University
Bruce Hines, University of Washington
Kristen Jenkins, Southern Research
Branko Kerkes, University of Michigan
Megan Mauter, Carnegie Mellon University
Daniel Miller, Lawrence Berkeley National Laboratory (LBNL)
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William Philip, University of Notre Dame
Patrick Pinhero, University of Missouri
Dan Shantz, Tulane University
Ilja Siepmann, University of Minnesota
Fotis Sotiropoulos, Stony Brook University
Daniel Stepan, Energy & Environmental Research Center
Vincent Tidwell, Sandia National Laboratories (SNL)
Aaron Wilson, Idaho National Laboratory (INL)

Panel 2: Basic Science Challenges to Reduce Water Use in Energy and Fuel Production

Leads: Daniel Giammar, Washington University in St. Louis
                Benjamin Gilbert, Lawrence Berkeley National Laboratory

Heather Allen, Ohio State University
*Susan Brantley, The Pennsylvania State University
Sean Bushart, Electric Power Research Institute
Susan Carroll, LLNL
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Heileen Hsu-Kim, Duke University
Maureen McCann, Purdue University
B. Pete McGrail, Pacific Northwest National Laboratory (PNNL)
Robin Newmark, National Renewable Energy Laboratory (NREL)
Catherine Peters, Princeton University
Masa Prodanovic, University of Texas—Austin
Agathe Robisson, Schlumberger
Andrew Stack, Oak Ridge National Laboratory (ORNL)
John Weare, University of California-San Diego
Adam Weber, LBNL
*Charles Werth, University of Texas—Austin

Panel 3: Basic Science Challenges to Increase Fit-for-Purpose Water Availability

Leads: Kate Maher, Stanford University
                William Tumas, National Renewable Energy Laboratory

Neal Armstrong, University of Arizona
Gregory Characklis, University of North Carolina—Chapel Hill
Laura Condon, Syracuse University
John Crittenden, Georgia Tech
Sheng Dai, ORNL
Amar Flood, Indiana University
Shemin Ge, University of Colorado
Jeri Sullivan Graham, University of New Mexico
*Jaehong Kim, Yale University
Harold Kung, Northwestern University
Richard Magee, New Jersey Corp for Advanced Technology
Claudia Mora, Los Alamos National Laboratory (LANL)
Peter Nico, LBNL
Kenneth Chul Park, Northwestern University
Sue Richardson, University of South Carolina
*David Sedlak, University of California—Berkeley
Rachel Segalman, University of California—Santa Barbara
Seth Snyder, Argonne National Laboratory (Argonne)

Panel 4: Crosscutting Basic Science in Energy-Water Systems

Leads: Yueh-Lin (Lynn) Loo, Princeton University
              Martin Schoonen, Brookhaven National Laboratory

Ayse Asatekin, Tufts University
Chuck Black, Brookhaven National Laboratory (BNL)
*Seth Darling, Argonne
Ron Faibish, Argonne
Carolyn Koh, Colorado School of Mines
Brent Lindquist, Texas Tech University
Lisa Miller, BNL
Kirk Nordstrom, U.S. Geological Survey
Kevin Rosso, PNNL
Miquel Salmeron, LBNL
Vincent Shen, National Institute of Standards and Technology (NIST)
Jim Skinner, University of Chicago
Xiaolong Yin, Colorado School of Mines
Wenlu Zhu, University of Maryland

*Indicates the plenary speakers.

Basic Research Needs Workshop for Energy and Water
Invited Participants (alphabetical)

Heather Allen, Ohio State University
Neal Armstrong, University of Arizona
Ayse Asatekin, Tufts University
Chuck Black, Brookhaven National Laboratory
Susan Brantley, Pennsylvania State University
Sean Bushart, Electric Power Research Institute
Susan Carroll, Lawrence Livermore National Laboratory
Gregory Characklis, University of North Carolina—Chapel Hill
Yoram Cohen, University of California—Los Angeles
Laura Condon, Syracuse University
John Cushman, University of Nevada
Sheng Dai, Oak Ridge National Laboratory
Seth Darling, Argonne National Laboratory
Ron Faibish, Argonne National Laboratory
Amar Flood, Indiana University
Benny Freeman, University of Texas—Austin
Shemin Ge, University of Colorado
Daniel Giammar, Washington University in St. Louis
Benjamin Gilbert, Lawrence Berkeley National Laboratory
Jeri Sullivan Graham, University of New Mexico
Michael Hickner, Pennsylvania State University
Bruce Hinds, University of Washington
Susan Hubbard, Lawrence Berkeley National Laboratory
Heileen Hsu-Kim, Duke University
Kristen Jenkins, Southern Research
Jaehong Kim, Yale University
Carolyn Koh, Colorado School of Mines
Harold Kung, Northwestern University

Brent Lindquist, Texas Tech University
Yueh-Lin (Lynn) Loo, Princeton University
Richard Magee, New Jersey Corp for Advanced Technology
Kate Maher, Stanford University
Megan Mauter, Carnegie Mellon University
Maureen McCann, Purdue University
B. Pete McGrail, Pacific Northwest National Laboratory
Daniel Miller, Lawrence Berkeley National Laboratory
Lisa Miller, Brookhaven National Laboratory
Claudia Mora, Los Alamos National Laboratory
Robin Newmark, National Renewable Energy Laboratory
Peter Nico, Lawrence Berkeley National Laboratory
Kirk Nordstrom, U.S. Geological Survey
Aleksandr Noy, Lawrence Livermore National Laboratory
Kenneth Park, Northwestern University
Catherine Peters, Princeton University
Eric Peterson, Idaho National Laboratory
William Philip, University of Notre Dame
Patrick Pinhero, University of Missouri
Masa Prodanovic, University of Texas—Austin
Sue Richardson, University of South Carolina
Geri Richmond, University of Oregon
Agathe Robisson, Schlumberger
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David Sedlak, University of California—Berkeley
Rachel Segalman, University of California—Santa Barbara
Dan Shantz, Tulane University
David Sholl, Georgia Tech University
Ilja Siepmann, University of Minnesota
Jim Skinner, University of Chicago
Seth Snyder, Argonne National Laboratory
Fotis Sotiropoulos, Stony Brook University
Andrew Stack, Oak Ridge National Laboratory
Christopher Stafford, National Institute of Standards and Technology
Daniel Stepan, Energy & Environmental Research Center
Vincent Tidwell, Sandia National Laboratory
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Michael Tsapatsis, University of Minnesota
William Tumas, National Renewable Energy Laboratory
John Weare, University of California-San Diego
Charles Werth, University of Texas—Austin
Aaron Wilson, Idaho National Laboratory
Xiaolong Yin, Colorado School of Mines
Wenlu Zhu, University of Maryland

APPENDIX B: WORKSHOP AGENDA

BASIC RESEARCH NEEDS WORKSHOP FOR ENERGY AND WATER

Bethesda North Marriott Hotel and Conference Center January 4–6, 2017

Chair:	Matt Tirrell, University of Chicago/Argonne National Laboratory
Associate Chairs:	Susan Hubbard, Lawrence Berkeley National Laboratory
	David Sholl, Georgia Institute of Technology
Co-chairs:	Dan Giammar, Washington University in St. Louis
	Ben Gilbert, Lawrence Berkeley National Laboratory
	Lynn Loo, Princeton University
	Kate Maher, Stanford University
	Eric Peterson, Idaho National Laboratory
	Martin Schoonen, Brookhaven National Laboratory
	Michael Tsapatsis, University of Minnesota
	William Tumas, National Renewable Energy Laboratory

WEDNESDAY, JANUARY 4, 2017

7:00–8:00 AM	Registration/Breakfast
Opening Plenary Session *(Salon A-C)*	
8:00–8:15 AM	**Welcome and Workshop Charge** Steven Binkley, Deputy Director for Science Programs, Office of Science Harriet Kung, Associate Director of Science for Basic Energy Sciences
8:15–8:30 AM	**Chair Welcome and Workshop Structure** Matthew Tirrell, Argonne National Laboratory/University of Chicago
8:30–9:00 AM	**The Energy-Water Nexus at DOE** Diana Bauer, Office of Energy Systems Analysis and Integration, Water-Energy Tech Team
9:00–9:30 AM	**Complex Aqueous Interfaces: Fundamental Discoveries, Opportunities and Challenges for the Energy-Water Nexus** Geraldine Richmond, University of Oregon
9:30–10:00 AM	**Advanced Water Treatment Materials and Technologies at the Water-Energy Nexus** Jaehong Kim, Yale University
10:00–10:30 AM	*Break*
10:30–11:00 AM	**The Next Frontier: Integration of Engineered and Natural Water Treatment Systems** David Sedlak, University of California-Berkeley
11:00–11:30 AM	**Fundamental Science Issues Related to Porosity and Surface Area of Subsurface Rocks** Susan Brantley, Penn State University
11:30–12:00 PM	**Basic Science toward Enabling Use of Non-traditional Water Sources** Seth Darling, Argonne
12:00–1:00 PM	*Working Lunch*

1:00–1:30 PM	**Panel Introductions — Workshop Co-Chairs**
1:30–5:30 PM	**Parallel Panel Sessions** *(Refreshments available from 3:00–4:00 PM)*
	Panel 1 — *Basic Science Challenges to Improve Water Use for Industrial Applications and Electricity Generation* (Forest Glen) Eric Peterson, Idaho National Laboratory Michael Tsapatsis, University of Minnesota
	Panel 2 — Basic Science Challenges to Reduce Water Use in Energy and Fuel Production *(Glen Echo)* Daniel Giammar, Washington University in St. Louis Benjamin Gilbert, Lawrence Berkeley National Laboratory
	Panel 3 — Basic Science Challenges to Increase Fit-for-Purpose Water Availability *(Brookside A/B)* Kate Maher, Stanford University William Tumas, National Renewable Energy Laboratory
	Panel 4 — Crosscutting Basic Science in Energy-Water Systems *(Linden Oak)* Yueh-Lin (Lynn) Loo, Princeton University Martin Schoonen, Brookhaven National Laboratory
5:30–7:00 PM	*Break for Dinner (on own)*
7:00–10:00 PM	Parallel Panel Discussions (continued)

THURSDAY, JANUARY 5, 2017

7:00–8:00 AM	Breakfast

Plenary Session *(Salon A-C)*

8:00–8:30 AM	**Energy-Water Nexus Challenges for Subsurface Resource Extraction and Storage** Charles Werth, University of Texas-Austin
8:30–9:00 AM	**Smart Distributed Water Treatment Systems — Advances and Research Needs** Yoram Cohen, University of California — Los Angeles
9:00–9:30 AM	*Break and move to panel sessions*
9:30–10:30 AM	Parallel Panel Sessions for discussion/preparation of preliminary reports
10:30–10:40 AM	*Break and move to plenary room for panel reports*
10:40–11:00 AM	**Report from Panel 1 — Basic Science Challenges to Improve Water Use for Industrial Applications and Electricity Generation**
11:00–11:20 AM	**Report from Panel 2 — Basic Science Challenges to Reduce Water Use in Energy and Fuel Production**
11:20–11:40 AM	**Report from Panel 3 — Basic Science Challenges to Increase Fit-for-Purpose Water Availability**
11:40–12:00 AM	**Report from Panel 4 — Crosscutting Basic Science in Energy-Water Systems**
12:00–1:30 PM	*Working Lunch*
1:30–5:30 PM	Panel Discussions (continued) *(Refreshments available from 3:00–4:00 PM)*
5:30–7:00 PM	*Break for Dinner (on own)*
7:00–10:00PM	Panel Discussions (continued) & Preparation for final panel reports

FRIDAY, JANUARY 6, 2017

7:00–8:00 AM	Breakfast
8:00–8:30 AM	**Report from Panel 1 — Basic Science Challenges to Improve Water Use for Industrial Applications and Electricity Generation**
8:30–9:00 AM	**Report from Panel 2 — Basic Science Challenges to Reduce Water Use in Energy and Fuel Production**
9:00–9:30 AM	**Report from Panel 3 — Basic Science Challenges to Increase Fit-for-Purpose Water Availability**

9:30–9:45 AM	*Break*
9:45–10:15 AM	**Report from Panel 4 — Crosscutting Basic Science in Energy-Water Systems**
10:15–11:00 AM	Discussion
11:00–11:30 AM	**Closing Remarks** Matthew Tirrell, Argonne National Laboratory/University of Chicago
11:30 AM	**Workshop Adjourned**
Noon–5:00 PM	**Working Lunch/writing (only chairs, panel leads and designated writers)**

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4 Conclusion
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Sidebar

*Little Molecules with Big Impacts on the Production of
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Figure 3.3.6

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Panel 4

Figure 3.4.1

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Sidebar

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