SANDIA REPORT
SAND2005-6220
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Printed October 2005

Frontiers of Interfacial Water Research: Workshop Report

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Abstract

Water is the critical natural resource of the new century. Significant improvements in traditional water treatment processes require novel approaches based on a fundamental understanding of nanoscale and atomic interactions at interfaces between aqueous solution and materials. To better understand these critical issues and to promote an open dialog among leading international experts in water-related specialties, Sandia National Laboratories sponsored a workshop on April 24-26, 2005 in Santa Fe, New Mexico. The "Frontiers of Interfacial Water Research Workshop" provided attendees with a critical review of water technologies and emphasized the new advances in surface and interfacial microscopy, spectroscopy, diffraction, and computer simulation needed for the development of new materials for water treatment.

Acknowledgements

The authors would like to acknowledge the following individuals at Sandia National Laboratories for their contributions and support in compiling this workshop summary: Jeffrey Brinker, Self-Assembled Materials Department, Bruce Bunker, Biomolecular Materials and Interfaces Department, Wendy Cieslak, Physical, Chemical, and Nano Sciences Center, Peter Feibelman, Surface and Interface Sciences Department, John Merson, Geoscience and Environment Center, Tina Nenoff, Chemical and Biological Systems Department, and Neal Shinn, Center for Integrated Nano Technologies. Michael Hickner and Louise Criscenti kindly volunteered to help with scribe duties during the breakout sessions. Their computer-based notes helped immensely with bringing the workshop discussions back to life. We are thankful for the workshop chair duties provided by Paul Fenter of Argonne National Laboratory, James Rustad of University of California at Davis, and John Pellegrino of University of Colorado. Christopher Cornelius, Peter Feibelman, and Nancy Missert represented Sandia National Laboratories as co-chairs. These individuals did a fantastic job in "herding cats" and keeping discussions on track and on time. Finally, Goldie Piatt and, especially, Sandhya Rajan provided exceptional support in making the interfacial water workshop a success. The workshop and the writing of this report were sponsored by the Water Nanoscience project of the Laboratory Directed Research and Development Program at Sandia National Laboratories. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under Contract DE-AC04-94AL85000.

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Group photo of participants at Frontiers of Interfacial Water Research Workshop held April 24-26, 2005 at La Posada de Santa Fe in Santa Fe, New Mexico.

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1. Introduction

Water is the critical natural resource of the new century. Inadequate supplies of potable water plague half the world's population, causing death, disease, and international political tension. Understanding water behavior, especially in porous materials, has a profound impact on water supply, decontamination, and desalination technologies. Significant improvements in traditional water treatment processes require novel approaches based on a fundamental understanding of nanoscale and atomic interactions at interfaces between aqueous solution and materials. To understand these critical issues better and to promote an open dialog among leading international experts in water-related specialties, Sandia National Laboratories sponsored a workshop on April 24-26, 2005 in Santa Fe, New Mexico. The "Frontiers of Interfacial Water Research Workshop" provided attendees with a critical review of water technologies and emphasized the new advances in surface and interfacial microscopy, spectroscopy, diffraction, and computer simulation needed for the development of new materials for water treatment.

The workshop organizers identified six critical scientific questions to guide the discussions:

- What are the structures and transport mechanisms of water confined in porous solids?
- How can a material or membrane surface be optimized for ion-exchange and or facile transport?
- How is a material or membrane tuned for the efficient separation of salts?
- What structural, morphological, and chemical aspects of a membrane surface lead to the interfacial layer of pure water and aqueous species in reverse osmosis materials?
- What properties of highly-efficient biological water and ion channels can be adapted for use in synthetic membranes for water treatment?
- How can we ensure stability and avoid membrane fouling in water treatment?

To grasp and understand these technical concerns, the workshop was divided into three critical research themes: 1) Structure, 2) Chemistry, and 3) Transport. The workshop comprised six plenary lectures, three breakout sessions based on these topics, and several general discussion sessions. The formal agenda for the workshop is provided below.

Forty-five researchers attended the workshop including fifteen from universities, twenty-nine from national laboratories (Argonne National Laboratory, Los Alamos National Laboratory, Pacific Northwest National Laboratory, and Sandia National Laboratories), and a representative from the National Science Foundation. A listing of the workshop attendees, specializations, and affiliations is provided in the appendix at the end of the report. The workshop was held in the conference facilities at La Posada de Santa Fe located in historic Santa Fe. Additional information and workshop summaries are published on the internet at www.sandia.gov/water/waterworkshop.

2. Workshop Agenda

Sandia National Laboratories
Frontiers of Interfacial Water Research Workshop

La Posada de Santa Fe
Santa Fe, New Mexico, U.S.A.

Sunday April 24, 2005

6:00 PM to 9:00 PM Welcoming reception
Salon

Monday April 25, 2005

8:00 AM Continental breakfast
Montaña Ballroom A

9:00 AM Welcome and introductions
Montaña Ballroom A

9:10 AM Water Nanoscience at Sandia: The Bigger Picture
Neal Shinn, Sandia National Laboratories

9:30 AM Interfacial Water—Puzzles and Opportunities
Steve Granick, University of Illinois at Urbana-Champaign

10:15 AM Break
Montaña Ballroom Lobby

10:30 AM Experimental and Computational Study of Aqueous Interfaces: Current Research and Future Outlook
James Kirkpatrick, University of Illinois at Urbana-Champaign

11:15 AM Multiscale Analysis of Water and Ion Transport in Nanochannels
Narayan Aluru, University of Illinois at Urbana-Champaign

12:00 PM Introduction to breakout sessions

12:05 PM Buffet lunch
Fuego Viga

1:30 PM Breakout sessions
Chemistry: Montaña Ballroom A
Transport: Montaña Ballroom B
Structure: Canyon Meeting Room

4:00 PM Break
Montaña Ballroom Lobby

4:15 PM Structures of Mineral-Water Interfaces as Revealed by Synchrotron Radiation
Neil Sturchio, University of Illinois at Chicago
Montaña Ballroom A

6:30 PM Banquet
Santacafé
231 Washington Avenue (two blocks north of Plaza)

Tuesday April 26, 2005

7:30 AM Continental breakfast
Montaña Ballroom A

8:30 AM Ion Removal Using Zeolite Membranes
Michael Tsapatsis, University of Minnesota
Montaña Ballroom A

9:15 AM Unresolved Problems at Aqueous-Crystal Interfaces
Tony Haymet, CSIRO Marine Research

10:00 AM Break
Montaña Ballroom Lobby

10:15 AM Breakout sessions
Chemistry: Montaña Ballroom A
Transport: Montaña Ballroom B
Structure: Canyon Meeting Room

12:15 PM Buffet lunch
Fuego Viga

1:30 PM Summary reports from breakout sessions
Montaña Ballroom A

2:15 PM General discussion

3:15 PM Adjournment

3. Background

A synopsis of the plenary presentations and breakout summary reports are provided in the following sections. Approximately fifteen attendees participated in each of the breakout sessions during the workshop. The breakout reports are not intended to represent a review of waste treatment science and technology, but to provide a snapshot of expert opinions of what the state-of-the-art is for interfacial water research and what critical technical gaps exist. While the workshop participants avoided any pretense of forecasting future waste treatment technologies, several promising materials and processing methods are indicated in the following discussion summaries. It will perhaps be up to individual researchers to develop these and other new ideas into reality to improve water treatment methods. One thing is almost certain: new water treatment technologies will only evolve from a fundamental understanding of the solid-water interface.

Although no specific references are presented in the breakout summary reports, the interested reader may want to consult the following review articles, which include additional background information on interfacial water properties, structure, and energetics, and which have extensive reference materials.

Fenter, P. and Sturchio, N. C. (2004) Mineral-water interfacial structures revealed by synchrotron X-ray scattering. *Progress in Surface Science*, 77, 171-258.

Guillot, B. (2002) A reappraisal of what we have learnt during three decades of computer simulations on water. *Journal of Molecular Liquids*, 101, 219-260.

Head-Gordon, T. and Hura, G. (2002) Water structure from scattering experiments and simulation. *Chemical Reviews*, 102, 2651-1670.

Henderson, M. A. (2002) The interaction of water with solid surfaces: Fundamental aspects revisited. *Surface Science Reports*, 46, 5-308.

Netz, R. R. (2004) Water and ions at interfaces. *Current Opinions in Colloid and Interface Science*, 9, 192-197.

Richmond, G. L. (2001) Structure and bonding of molecules at aqueous surfaces. *Annual Review of Physical Chemistry*, 52, 357-389.

Richmond, G. L. (2002) Molecular bonding and interactions at aqueous surfaces as probed by vibrational sum frequency spectroscopy. *Chemical Reviews*, 102, 2693-2724.

4. Plenary Presentations

Six plenary lectures were presented during the course of the workshop to provide general topical reviews and to stimulate discussion for the breakout sessions. Researchers at the University of Illinois at Urbana-Champaign presented the first set of plenary lectures. In the opening lecture, Steve Granick provided a summary of the physics and chemistry of interfacial water with an emphasis on the "puzzles and opportunities" in spectroscopic measurements. Granick highlighted experimental measurements of the disorder state, fluidity, transport, and shear forces associated with surface and confined water. Among the analytical methods, Granick highlighted results obtained from atomic force microscopy, surface force apparatus, surface enhanced Raman spectroscopy, ellipsometry, X-ray reflectivity, and fluorescence resonance energy transfer. Jim Kirkpatrick presented the results from several environmental science projects that combine spectroscopy with molecular simulation to provide detailed atomic descriptions of the structure, energy, and transport of water on complex oxide surfaces. Sum frequency vibrational spectroscopy and magic-angle spinning NMR spectroscopy were incorporated in these efforts. Classical molecular simulation methods were used to obtain equilibrated models that describe the hydrogen bonding networks and unique behavior of the water layers as a function of distance from the interface. Narayan Aluru completed the first session with his presentation on the multiscale analysis of water and ion transport in nanochannels. Aluru used classical molecular dynamics and a modified Poisson-Boltzmann method to model density profiles for water and electrolytes within various-sized channels at different charge distributions. Embedded methods that combine molecular dynamics with a continuum approach were also used to help bridge spatial scales. Aluru emphasized the usefulness of these theoretical methods to model complex processes associated with membranes having multiple asymmetric channels, and biomimetic and hybrid channels.

Neal Sturchio of the University of Illinois at Chicago reviewed the use of several synchrotron-radiation methods to investigate the structure of interfacial water for various oxide and mineral systems. Sturchio demonstrated the effectiveness of high-resolution X-ray scattering techniques such as grazing-incidence X-ray reflectivity, surface and thin-film diffraction, crystal truncation rods, and X-ray standing waves methods. Results from synchrotron experiments involving interfacial water and quartz, rutile, muscovite, orthoclase, alumina, hematite, and other materials surfaces were presented. The plenary presentation by Michael Tsapatsis of the University of Minnesota reviewed the application of zeolite materials for water treatment. Tsapatsis reviewed the various structures and compositions of crystalline molecular sieve materials, and emphasized their utility in chemical separation, catalysis, chemical sensors, and as nanostructured hosts. The synthesis and characterization methods for these materials were discussed, and selected materials specifically for water treatment were highlighted. The final plenary presentation was given by Tony Haymet of CSIRO Marine Research in Hobart, Tasmania. Haymet emphasized the lack of understanding associated with solutes at interfaces, particularly for processes occurring at hydrophobic surfaces. Haymet reviewed several models of the ice-water interface and compared the thermodynamics of ion solvation in water and in ice. Haymet discussed experiments measuring the Workman-Reynolds effect, which is the electrical potential of liquid relative to ice generated during the freezing of dilute aqueous systems. Several biological applications involving water-ice issues were presented. These included the analysis of antifreeze proteins,

associated with some fish species, simulations of the lipid bilayer, and the preservation of sheep cells upon freezing.

Additional presentations were given by Neal Shinn of Sandia National Laboratories and by Mark Shannon of the University of Illinois at Urbana-Champaign. Shinn provided a general review of the role of water research at Sandia, with particular emphasis on nanoscience issues and the recent development of the Center for Integrated Nanotechnologies, which is a DOE National User Facility. Shannon introduced the workshop participants to WaterCAMPWS, Center of Advanced Materials for Purification of Water with Systems. WaterCAMPWS is sponsored by the National Science Foundation, and is a research and education center for increasing water supplies for human use through enhanced treatment technologies.

5. Breakout Sessions

5.1 Structure

5.1.1 Participants

Co-Chair: Paul Fenter, Argonne National Laboratory
Co-Chair: Peter Feibelman, Sandia National Laboratories
Secretary: Jeffery Greathouse, Sandia National Laboratories

Bruce Bunker, Sandia National Laboratories
Randall Cygan, Sandia National Laboratories
Daval Doshi, Los Alamos National Laboratory
Steve Granick, University of Illinois
Jack Houston, Sandia National Laboratories
Andrey Kalinichev, University of Illinois
John Merson, Sandia National Laboratories
Mark Shannon, University of Illinois
Ilja Siepmann, University of Minnesota
Konrad Thuermer, Sandia National Laboratories
Frank Van Swol, Sandia National Laboratories
Sotiris Xantheas, Pacific Northwest National Laboratory

5.1.2 Range of Expertise

Participants in the Structure breakout session represent a wide variety of skill sets. On the experimental side, participants indicated expertise in 1) X-ray reflectivity techniques to probe solution-solid interfaces; 2) nanofluidic structures; 3) neutron reflectivity of hydrophobic surfaces; 4) scanning tunneling microscopy; 5) interfacial force microscopy of superhydrophobic surfaces and self-assembled monolayers; and 6) dielectric behavior and biofouling of water purification membranes. On the theoretical/computational side, expertise included 1) *ab initio* calculations of bulk water and water dissociation on idealized metal surfaces; 2) classical simulations (Monte Carlo and molecular dynamics) of bulk water, aqueous solutions and solution-mineral interfaces; and 3) classical density functional theory of water and wetting phenomena.

5.1.3 Purpose

The group considered four key areas pertaining to the structure of interfacial water: 1) bulk water; 2) water at a solid surface; 3) nature of the solid surface; and 4) water in pores. The discussion was originally divided into gaps of our current understanding and state-of-the-art techniques.

5.1.4 Bulk Water

The structure of bulk water is not completely understood. The traditional model of hydrogen-bonding in water, in which each water molecule participates in up to four bonds of equal energy, has recently been challenged. Sum frequency generation spectroscopy, as well as computational results, have led to the recognition of “strong” and “weak” hydrogen bonds, which depend both on energetic and orientational criteria. Additionally, we have an incomplete understanding of the

structure and thermodynamics of water around dissolved species, particularly ions. Numerous force field-based models are currently used for classical simulations of water and related media. In general, these models do a reasonable job, which is why their widespread use continues in the scientific community. The simulated bulk properties of water, nonetheless, such as dielectric constant or density, are very much model-dependent. One model may produce the correct hydrogen-bonding network for bulk water but requires a very large applied pressure to achieve the experimental density. Some models are based on experimental data of water structure, while others are derived from *ab initio* calculations of water clusters. Another shortcoming of current water models is their poor transferability from a bulk homogeneous environment to a heterogeneous environment such as an interface. A water model that works well for bulk solutions may yield poor results for two-dimensional (surfaces) or one-dimensional (pores) situations. Finally, the question remains as to whether it matters if a particular water model demonstrates poor bulk properties but adequately describes interfaces. A water model may be useful for some situations and not for others.

5.1.5 Water at a Solid Surface

Numerous gaps were identified for this area. Current experimental techniques such as X-ray scattering and neutron diffraction have helped to identify a solid-water interface region of approximately 1-nm thickness. A primary concern is an accurate description of water behavior at a surface, including 1) the initial dissociation of water molecules at the surface; 2) the formation of two-dimensional water clusters (wetting) and eventual formation of a water monolayer; 3) the subsequent formation of a second layer of water; and 4) the structure of water normal to the surface (vertical) and parallel to the surface (lateral). Experimentally, pH effects remain an essential issue, particularly the dependence of surface charge on solution pH for surfaces with amphoteric sites such as hydroxyl groups. The adsorption of water and dissolved species are processes that require additional study. Specifically, both experimental and modeling efforts should be directed at better understanding the thermodynamics of adsorption. Kinetics experiments that can elucidate the lifetime of surface water states are also a missing piece of the puzzle.

5.1.6 Nature of the Interface

The behavior of interfacial water depends a great deal on the atomistic details of the surface itself. Water adsorption onto a pure material (e.g., single crystal surface) has not been compared with corresponding process on natural minerals. Another gap involves the effect of surface roughness (steps, edges, kinks) on interfacial behavior. There is a need to connect water viscosity with surface structure through simultaneous measurement of water transport properties and surface structure. Experimentally, some progress has been made with the use of the surface force apparatus, which can provide surface tilt angle effects. Additionally, new simulation techniques have been used to accurately describe water attachment to sliding silicon surfaces.

5.1.7 Water in Pores

Solid surfaces buried beneath the bulk present a new challenge to our understanding of interfacial water. The concept of an “internal interface” without the usual surface periodicity becomes relevant. The issue of surface defects and buried interfaces must be overcome to understand water behavior in pores. Another gap in this area involves determining the effect of water flow on water structure. Finally, the need exists for a quantitative description of

hydrophobic and hydrophilic pores. The difference in water structure at these disparate interfaces can be compared by contact angle measurements and the extent of hydrogen bonding. The solution/vapor interface is a subset of this category, if one considers air as a hydrophobic surface in contact with water. The disruption of the water hydrogen bonding network has been measured by spectroscopic experiments, particularly sum frequency generation spectroscopy. This interface has not been addressed to great extent by the theoretical community.

5.1.8 A New Language

Participants in this breakout group identified a challenge common to all four technical area discussed above: macroscopic vs. microscopic scales. One major roadblock to progress in this area centers on the scientific terminology that we incorrectly use to describe interfacial phenomena. Descriptive terms that are appropriate for bulk properties (dielectric constant, viscosity, and thermal conductivity) are usually inappropriate for interfacial properties. The call was made for a new set of molecular terms to describe similar events at the nanometer dimension of interfacial water. Three examples serve to illustrate the concept: 1. Adsorption in the macroscopic scale is described in terms of thermodynamics (adsorption energies) and contact angles. The molecular detail of adsorption involves terms such as surface structure, surface roughness, geometry (surface or pore), solute hydration at surfaces and in solution, and hydrogen bonding. 2. Transport is often considered a bulk property quantified by viscosity measurements. The disruption of interfacial hydrogen bonding networks, both lateral and vertical as defined above, provides a microscopic explanation for transport properties. The dissipation of molecular clusters and networks also influences macroscopic viscosity. Combining these microscopic terms, viscosity could be considered as a drag on a large cluster of water molecules, accompanied by breaking and forming of hydrogen bonds. 3. Wetting of a surface is usually described with contact angles, with the surface classified as either hydrophobic or hydrophilic. Key microscopic descriptors include the vertical and lateral ordering of water, the second layer of water, dissociation, flow, and surface speciation of dissolved solute. One outcome of this clarification is that a thorough description on an idealized interface will then be used to better understand water structure in pores.

5.2 Chemistry

5.2.1 Participants

Co-Chair: James Rustad, University of California at Davis
Co-Chair: Nancy Missert, Sandia National Laboratories
Secretary: Louise Criscenti, Sandia National Laboratories

Patrick Brady, Sandia National Laboratories
Wendy Cieslak, Sandia National Laboratories
Steven Garofalini, Rutgers University
Tony Haymet, Commonwealth Scientific and Industrial Research Organization
James Kirkpatrick, University of Illinois
Kevin Leung, Sandia National Laboratories
Tina Nenoff, Sandia National Laboratories
Susan Rempe, Sandia National Laboratories
Neil Sturchio, University of Illinois at Chicago
Richard Sustich, University of Illinois
Renee van Ginhoven, Sandia National Laboratories
Yifeng Wang, Sandia National Laboratories

5.2.2 Range of Expertise

Participants in the Chemistry breakout session included those with expertise in fundamental chemistry, physics, environmental studies, earth sciences, and materials science. Both experimentalists and theorists contributed to the discussions.

5.2.3 Purpose

The discussions associated with the Chemistry breakout sessions concentrated on defining the state-of-the-art for chemistry issues as related to three basic water treatment tasks: desalination, decontamination, and disinfection. Although various chemistry topics were reviewed and discussed, discussions were directed towards answering and clarifying the critical technical questions in each of these three applications. As expected, the Chemistry group topics included several issues common to the other two breakout sessions. Typically, these overlapping concerns focused on the technical gaps associated with understanding the atomistic behavior of water molecules at the solid-solution interface.

5.2.4 Basic Tasks

Understanding the chemistry of the aqueous solution-solid interface is fundamental to the development of new technologies for the treatment of contaminated water. Improvements in the desalination of seawater and brackish inland waters will require the analysis of a large number of aqueous ions and other chemical species. This entails a better analysis of complex multicomponent aqueous systems that may include both inorganic and organic species that have neutral or multiple charges. Interactions with membranes and other complex surfaces will add significant levels of complexity to this analysis. Decontamination of aqueous systems will necessitate the selective removal of specific ions that occur at relatively low concentrations. And disinfection of waters requires an understanding of biological contaminants and their complex surface interactions with membrane materials and aqueous species. Specific treatment tasks will

evolve on fairly short time scales and will depend on the nature of the chemical systems. We need to know how to make rational responses quickly. This ability depends on understanding interfacial reactivity at a fundamental level. Homeland security and other political issues may force such water treatment decisions to an extraordinarily compressed response time.

5.2.5 Chemistry 101

Group participants emphasized the general need to maintain an integration of the fundamental aspects of aqueous solution chemistry. Acid-base behavior, ligand exchange, and electron transfer processes are critical in the bulk solution phase, and are all coupled processes. Thermodynamics and kinetics play significant and complementary roles in aqueous systems. Ligand exchange rates of aqueous ions are strongly pH dependent, while electron transfer rates depend on the hydrolysis state. For example, $Fe(OH)^{2+}$ is more difficult to reduce than Fe^{3+}. Our ability to design interfaces for specific waste treatment purposes depends on extending our understanding of these basis concepts to interfacial environments. This extension requires a significant improvement in our understanding of how surfaces and substrates modify solution chemistry. The dissociation of water at the interface (or pore) will modify the surface structure and influence the behavior of the nearby aqueous region. What determines the acidities of the various functional groups at the interface, and what is the pH of the interfacial water? What does the sign of the activation volume mean at an interface: association, dissociation, and interchange? What is the interfacial dielectric constant—if it can be defined—and how do we assess proton-coupled electron transfer at the interface? Modifications to Marcus theory for electron transfer reactions will be needed to accommodate these surface-modified processes.

5.2.6 Experimental Challenges

There are several critical challenges associated with experimental studies of the chemistry of interfacial water. In contrast to bulk materials (liquid, aqueous, gas, solid, mixtures, etc.), there are no compilations or databases for surface data. Crystal structure databases, such as the ICSD (Inorganic Crystal Structure Database), are maintained to ensure a comprehensive and uniform set of structural data for crystalline materials. But due to the complex nature of surfaces and interfaces, and the difficulty of their characterization, there are no similar resources yet available for aqueous surfaces (several data sets for vacuum-terminated surfaces exist). Attempts have therefore been made to utilize model materials in testing theory and simulation. Surface structures must be accurately known for at least a few ideal and common materials to make any significant progress in understanding the surface chemistry. To date, there is no consensus for such a standard. Participants suggested various phases and categories of materials that may help in this effort: phyllosilicate basal planes (mica), TiO_2 (rutile), polynuclear ionic structures (Al-based Keggin ions), and crystalline hydrates. These materials occur with clearly-defined surfaces or have unique internal water structures. It is important that the model materials also be amenable to molecular simulation and have computationally tractable solutions. Experimental efforts on such model materials or other phases must include surface structure determinations with the presence of water. It was widely agreed that vacuum-based or and non-aqueous experimental configurations would not necessarily represent the true surface when water is present. Surface composition, as opposed to bulk analysis, surface charge as a function of pH to help evaluate surface protonation states, and coherence lengths for the statistical understanding of complex surfaces were all considered to be necessary surface properties to be assessed.

5.2.7 When is a Model Good Enough?

Discussions of molecular simulations and theoretical issues emphasized the limitations of available models for water, particularly as applied to water on surfaces. There is agreement among the participants that an accurate water model involving interfacial phenomena would necessarily include proton transfer mechanisms and surface protonation. Although this issue has been a concern for many years, most classical-based molecular simulations to date either ignore the issue completely or develop a crude reactive force field approach. Multiscaling efforts may help resolve proton transfer issues where explicit treatment of hydrogen between solution and surface is treated at a particular scale as needed. Quantum chemistry and electronic structure methods would be capable of providing this detail. Often it is hard to identify the active hydrogen sites (acid-base reactions) at an interface and therefore the simulation incorporates a brute force approach by including all sites. Timescale problems will also exist and necessitate a better understanding of reactive flux, transition path sampling, and other processes that may not be assessable using any single simulation method. Better integration among the interfacial researchers and the theorists is needed to resolve these issues. So when is a water model good enough, especially one to simulate the water-solid interface? Several key points were noted in the discussion group: 1) structure and thermodynamics are equally important; 2) benchmark efforts must be defined and readily accessible; 3) models must have complete transferability from system to system (problem to problem) and may need additional physics incorporated; and 4) "Don't let the perfect be the enemy of the good".

5.2.8 Practical Chemistry

The participants recommended several standard materials to provide a baseline understanding of interfacial water processes for water treatment. Silicates (and silica), polyamides, iron oxides and iron oxyhydroxides, and amorphous carbon were suggested. It is important to include both environmental phases (silicates and iron oxides) and synthetic materials (organic membranes and activated carbon) in such chemical research. An evaluation of minerals providing a natural attenuation of contaminants would be just as beneficial to a comprehensive understanding of interfacial water for waste treatment as the analysis of organic polymer membranes typically used in reverse osmosis methods. Development of new materials such as biomimetic phases and the functionalization of surfaces, including novel TiO_2 and carbon nanotubes, was considered to be a promising approach to improved waste treatment materials. The design of such new materials would probably rely on computational methods to define new pathways. Additionally, treatment methods involving composite membranes would include new materials with multifunctionality to reduce complex treatment and multiple waste streams.

5.2.9 Parting Thoughts

The Chemistry breakout participants agreed that the era of waste treatment empiricism should be considered over. A more fundamental approach is needed. We should first better understand the chemistry of standard materials and solution interfaces before designing new water treatment membranes.

5.3 Transport

5.3.1 Participants

Co-Chair: John Pellegrino, University of Colorado
Co-Chair: Christopher Cornelius, Sandia National Laboratories
Secretary: Michael Hickner, Sandia National Laboratories

Narayana Aluru, University of Illinois
Jeffrey Brinker, Sandia National Laboratories
Paul Crozier, Sandia National Laboratories
Thomas Davis, University of South Carolina
John Georgiadis, University of Illinois
Thomas Mayer, Sandia National Laboratories
James McGrath, Virginia Tech
Bryan Pivovar, Los Alamos National Laboratory
Phillip Pohl, Sandia National Laboratory
Geoffrey Prentice, National Science Foundation
Michael Tsapatsis, University of Minnesota

5.3.2 Range of Expertise

Expertise in the Transport breakout session ranged from fundamental science to water treatment and large-scale application.

5.3.3 Purpose

The discussion group concentrated on the identification of known and unknown aspects of solute and solvent transport in primarily aqueous systems. Categorization of transport topics into system engineering, transport, and physical chemistry issues provided an opportunity to bridge the fundamental science with the water treatment application. Of course, there are several issues in the transport topic that overlap with the other two breakout discussion groups. It was determined that the identification of technological gaps associated with transport phenomena would provide a convenient basis for the discussions.

5.3.4 The Known

Systems engineering issues associated with the transport of solute and solvents in aqueous systems are fairly well defined and understood. Manufacturing and sales of commercial water treatment units are mature after many years of tested and proven technologies. In particular, membrane processes involving reverse osmosis, nanofiltration, and ultrafiltration methods have been successfully designed and commercialized. Macroscopic engineering and modeling of these membrane systems have progressed, and have proven successful in meeting required flux and production targets for optimal drinking water. Transport phenomena including diffusion rates for bulk water and solutes in aqueous systems have been experimentally measured, and are in agreement with values predicted from atomistic and phenomenological theories. Similarly, properties of membranes are known and membrane characteristics provide an effective description of transport of solution through the membrane materials. The relationship between membrane structure and transport behavior is well known and understood.

As most water treatment methods using membrane technology rely on organic polymers, much research has been devoted to evaluation and optimization of water within the polymer systems. Bound water within the polymer and plasticizing material, which leads to a reduction in the glass transition temperature for the polymer, will impact the mechanical properties of the membrane. This effect will necessarily be important in the design of new systems and materials. Biological channels such as the renal protein aquaporin have been structurally characterized to better understand the physical chemistry of transport and solute selectivity. Aquaporin has both high flux and high selectivity suggesting that the protein can provide a unique basis for development of new synthetic membranes. Transport on the scale of a single pore as in a biochannel provides an excellent case study. In general, the physical chemistry of organic-water interactions is fairly well understood, as are the physics and thermodynamics of water, ions, and electrolyte solutions. However, the incorporation of limiting current density concepts in electrodialysis methods of water treatment may not necessarily be correct and can affect the prediction of transport rates. The physical chemistry and transport of associated water shells with the electrolyte ion is poorly understood.

5.3.5 At the Edge of the Unknown

Several surface chemistry and systems engineering issues relating to water and solute transport are poorly understood and require significant investments in research. Fundamental chemistry of water structure and interfacial adhesion processes are critical to improving important commercial water treatment systems. Biofouling of membranes, especially those made of organic materials prone to degradation, is probably the least understood process and ultimately new research can lead to the most significant improvements in commercial water treatment. The role of various contaminants on transport behavior, especially the effect of multicomponent and complex mixtures, is poorly understood. Contaminants would include the addition of solvated organic molecules and ions to the electrolyte solution. The stability, lifetime, and the physical aging of polymers are general problems that influence the performance of membranes in water treatment. At a more applied level, we understand little about how simple modifications to a water treatment system will impact the integrated system. For example, little is known on how cleaning, types of waste streams, materials properties, or pretreatment processes will ultimately impact the efficiency of a particular water treatment. How are the materials impacted and how is the lifetime of the water processing affected?

5.3.6 Structure-Property Relationships

The fine structure of nanoporous membranes has significant impact on the water treatment process. Pore size and pore distribution will impact transport and selectivity but little is known on how and why these relations occur. What methods can be used to characterize pores and free volumes of the membranes properly? This may be less an issue with inorganic membrane material where bulk crystal structures can be ascertained through X-ray diffraction methods, but analysis of polymer-based membranes is problematic as would be defect characterization. Perm-porosimetry, microscopy, single fluorescent probes, and other visualization methods may lead to better membrane characterization. In general, though, the structures of polymer-based membranes are not known at the necessary level of detail. To overcome such difficulties in membrane characterization, it may be helpful to identify model systems such as PEBAX and phase-separated polymers for characterization. It may be helpful to incorporate single channel techniques from biological systems to characterize transport in these membranes. Current pulses

and other stochastic patterns of flux would help to determine transport rates and to validate predictive models. It is also important to discriminate between the fixed pore spaces and the fluctuating free volume of the membrane to better characterize the transport domain. Knowledge of the macroscopic pores including the effects of tortuosity and pore size distribution are critical in evaluating the bulk transport properties and rates. Accurate diffusion and pore flow models would help to facilitate system design.

5.3.7 Models and Theory

Models and simulations of transport processes in aqueous systems have evolved over the last few decades but still lack the robustness to predict transport in complex membranes accurately. It would be helpful to improve our understanding of fast transport of water in confined spaces and in hydrophilic media. Multiscale integration of transport length scales and an improved coordination of theory with experiment are desired. For example, there are cases where a hundred-fold disagreement exists between transport rates derived from micro and macro experiments. There is also a fundamental difference between diffusion rates involving self-diffusion (no concentration gradient) and those driven by concentration gradients. It is also desirable to simulate water in non-equilibrium settings and energy dissipative systems where steady state behavior may conflict with equilibrium situations.

The breakout participants recognized that a rigorous thermodynamic approach is required to describe water behavior better, with and without fixed pores. The local thermodynamic state of water in response to pore walls and chemical effects in a confined volume are needed. Similarly, a standard method is needed for the measurement of the microscale transport of water and solutes, especially one wherein single pore models can be validated. It was suggested that perhaps NMR relaxation methods and dielectric and impedance spectroscopies can help in these efforts.

5.3.8 The Advantage of Interfacial Transport

The discussion group agreed that little is known on how nanoscale processes can best be used to improve waste water treatment. An improved understanding of interfacial transport processes and the partitioning of chemical species at a surface can ultimately lead to enhanced separation technologies. Several specific research areas were identified to support this effort: transport behavior into a single pore, surface diffusion processes, shedding of solvation spheres, enhanced selectivity by modifying local water structure, understanding minimum water association for ion transport, streaming potentials at various interfaces, and suitability of ionizable and non-ionizable functional groups. Ultimately, these issues will affect any optimization of the water treatment method where there is a tradeoff between selectivity and permeability.

5.3.9 Nature as Your Guide

Several breakout participants supported the use of natural processes and biological materials in providing guidance for development of water treatment materials. Can selectivity mechanisms from nature be mimicked in polymer and porous membranes? Is it possible for us to duplicate natural features of aquaporin in synthetic channels and create other systems with desired boundary conditions that will lead to a new and effective treatment? In this effort, it would be important to understand the causality of functionalizations in biochannels; how they work and what are the driving forces.

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