DESALINATION AND WATER TREATMENT RESEARCH AT SANDIA NATIONAL LABORATORIES

Mark J. Rigali, James E. Miller, Susan J. Altman, Laura Biedermann, Patrick V Brady, M. Michael Hightower, Stephanie P. Kuzio, Tina M. Nenoff, Susan Rempe

Prepared by
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Albuquerque, New Mexico  87185-0747

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Desalination and Water Treatment Research at Sandia National Laboratories

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ABSTRACT

Water is the backbone of our economy – safe and adequate supplies of water are vital for agriculture, industry, recreation, and human consumption. While our supply of water today is largely safe and adequate, we as a nation face increasing water supply challenges in the form of extended droughts, demand growth due to population increase, more stringent health-based regulation, and competing demands from a variety of users. To meet these challenges in the coming decades, water treatment technologies, including desalination, will contribute substantially to ensuring a safe, sustainable, affordable, and adequate water supply for the United States. This overview documents Sandia National Laboratories’ (SNL, or Sandia) Water Treatment Program which focused on the development and demonstration of advanced water purification technologies as part of the larger Sandia Water Initiative. Projects under the Water Treatment Program include: (1) the development of desalination research roadmaps (2) our efforts to accelerate the commercialization of new desalination and water treatment technologies (known as the ‘Jump-Start Program’), (3) long range (high risk, early stage) desalination research (known as the ‘Long Range Research Program’), (4) treatment research projects under the Joint Water Reuse & Desalination Task Force, (5) the Arsenic Water Technology Partnership Program, (6) water treatment projects funded under the New Mexico Small Business Administration, (7) water treatment projects for the National Energy Technology Laboratory (NETL) and the National Renewable Energy Laboratory (NREL), (8) Sandia-developed contaminant-selective treatment technologies, and finally (9) current Laboratory Directed Research and Development (LDRD) funded desalination projects.
ACKNOWLEDGMENTS

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<tr>
<td>ABCWUA</td>
<td>Albuquerque Bernalillo County Water Utility Authority</td>
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<tr>
<td>AWTP</td>
<td>Arsenic Water Technology Partnership</td>
</tr>
<tr>
<td>AwwARF</td>
<td>American Water Works Association Research Foundation</td>
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<tr>
<td>BGNDRF</td>
<td>Brackish Groundwater National Desalination Research Facility</td>
</tr>
<tr>
<td>BoR</td>
<td>Bureau of Reclamation</td>
</tr>
<tr>
<td>BV</td>
<td>Bed Volume</td>
</tr>
<tr>
<td>CBNG</td>
<td>Coal-Bed Natural Gas</td>
</tr>
<tr>
<td>C-H</td>
<td>Carbon-Hydrogen</td>
</tr>
<tr>
<td>CD</td>
<td>Capacitive Deionization</td>
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<tr>
<td>CHIWAWA</td>
<td>Consortium for Hi-Technology Investigations in Water and Wastewater</td>
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<tr>
<td>CRADA</td>
<td>Cooperative Research and Development Agreement</td>
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<tr>
<td>DOE</td>
<td>Department of Energy</td>
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<tr>
<td>DOE EM</td>
<td>Department of Energy Environmental Management</td>
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<td>DWR</td>
<td>Department of Water Resources</td>
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<tr>
<td>ED</td>
<td>Electrodialysis</td>
</tr>
<tr>
<td>EM</td>
<td>Electrodialysis Metathesis</td>
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<tr>
<td>EPA</td>
<td>Environmental Protection Agency</td>
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<tr>
<td>EPRI</td>
<td>Electric Power Research Institute</td>
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<tr>
<td>EPS</td>
<td>Extracellular Polymeric Substances</td>
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<tr>
<td>EUWP</td>
<td>Expeditionary Unit Water Purification</td>
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<tr>
<td>GFH</td>
<td>Granular Ferric Hydroxide</td>
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<tr>
<td>JWR&amp;DTF</td>
<td>Joint Water Reuse &amp; Desalination Task Force</td>
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<td>LANL</td>
<td>Los Alamos National Laboratory</td>
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<tr>
<td>LDRD</td>
<td>Laboratory Directed Research and Development</td>
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<tr>
<td>LED</td>
<td>Light Emitting Diode</td>
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<tr>
<td>MBR</td>
<td>Membrane Bioreactor</td>
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<tr>
<td>MCL</td>
<td>Maximum Contaminant Level</td>
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<tr>
<td>MD</td>
<td>Membrane Distillation</td>
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<td>MRS</td>
<td>Materials Research Society</td>
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<tr>
<td>NF</td>
<td>Nanofiltration</td>
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<td>NMSBA</td>
<td>New Mexico Small Business Assistance</td>
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<td>NMSU</td>
<td>New Mexico State University</td>
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<td>NMT</td>
<td>New Mexico Institute of Mining and Technology</td>
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<td>NREL</td>
<td>National Renewable Energy Laboratory</td>
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<tr>
<td>ppm</td>
<td>parts per million</td>
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<tr>
<td>PS</td>
<td>Polysulfone</td>
</tr>
<tr>
<td>PV</td>
<td>Photovoltaic</td>
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<tr>
<td>QA</td>
<td>Quaternary Ammonium</td>
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<tr>
<td>RO</td>
<td>Reverse Osmosis</td>
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<tr>
<td>RSSCT</td>
<td>Rapid Small Scale Column Testing</td>
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<tr>
<td>SANS</td>
<td>Specific Anion Nanoengineered Sorbents</td>
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<tr>
<td>SNL, or Sandia</td>
<td>Sandia National Laboratories</td>
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<tr>
<td>TDS</td>
<td>Total Dissolved Solid</td>
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<td>Abbreviation</td>
<td>Full Name</td>
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<tr>
<td>UMPTRA</td>
<td>Uranium Mill Tailings Remedial Action</td>
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<tr>
<td>UNM</td>
<td>University of New Mexico</td>
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<td>US</td>
<td>United States</td>
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<tr>
<td>USC</td>
<td>University of South Carolina</td>
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<td>UTEP</td>
<td>University of Texas at El Paso</td>
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<tr>
<td>UV</td>
<td>Ultraviolet</td>
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<td>WE</td>
<td>Western Environmental</td>
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<td>WEN</td>
<td>Water Energy Nexus</td>
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<td>Waste Management Education and Research Consortium</td>
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<td>WRF</td>
<td>WaterReuse Foundation</td>
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<td>ZDD</td>
<td>Zero Discharge Desalination</td>
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**PRINCIPAL INVESTIGATORS AND PROJECTS**
Here we list the principal investigators, project titles and institutions for the individual projects undertaken on the desalination and water treatment program.

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<td>2015-Present</td>
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<td>Brian Dwyer</td>
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<td>Assessment of a Hydroxyapatite Permeable Reactive Barrier to Remediate Uranium at the Old Rifle Site, Colorado</td>
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INTRODUCTION

The Water Treatment Program at Sandia National Laboratories (SNL, or Sandia) was officially founded in 2003 although several desalination and water treatment projects under the program (e.g. arsenic treatment program) began as early as 2000. It should be noted that his effort was part of a larger program known as the Sandia Water Initiative that included efforts in Water Management and Modeling, the Energy-Water Nexus, Water Monitoring and Water Security in addition to the Water Treatment Program.

Elements of the Water Treatment Program include: (1) desalination road mapping activities, (2) projects focused on accelerating the commercialization of new desalination and water treatment technologies (known as the ‘Jump-Start Program’), (3) long range (high risk, early stage) desalination research (known as the ‘Long Range Research Program’), (4) research projects under the Joint Water Reuse & Desalination Task Force (JWR&DTF), (5) the Arsenic Water Technology Partnership Program (AWTP), (6) several projects funded under the New Mexico Small Business Administration (NMSBA), (7) water treatment projects funded by agencies other than the United States Department of Energy (US DOE) or through commercial partnerships. (8) SNL-developed contaminant-selective treatment technologies, and finally (9) the current portfolio of desalination projects.

The “Desalination and Water Purification Technology Roadmap” was mandated by Congress in 2003 to map out a long-term research strategy for desalination and other water purification technologies. SNL, the US Bureau of Reclamation (US BoR), American Water Works Association Research Foundation (AwwARF) and the WateReuse Foundation (WRF) led a team of experts from industry, academia, government, and water utilities to develop the roadmap. A series of workshops were held to identify high-impact research needs to hasten the rate for the development and implementation of new desalination technologies to meet our nation’s growing water needs (US BoR and SNL, 2003). In 2004, a decision was made to implement the findings and provisions of the Roadmap with the goal of describing the needed research in greater detail. SNL, the American Water Works Association Research Foundation (AwwARF) and the WateReuse Foundation (WRF) teamed to meet this goal. Once again, the team relied upon the contributions of dozens of experts from industry, academia, government, and water utilities who were brought together in a series of workshops. This effort resulted in the creation of a second document entitled the “Implementation of the Desalination and Water Purification Technology Roadmap (SNL, 2006).”

The Jump-Start Program which began in 2003 was a multi-year program funded by congressional appropriation through DOE Environmental Management (EM). The program focused on identifying cutting edge water treatment technologies and providing them with support with the goal of advancing their technological maturation through the pilot testing stage towards commercialization. It sought to take advantage of the Brackish Groundwater National Desalination Research Facility in Alamogordo, New Mexico. At least 15 individual projects have been identified under the ‘Jump-Start Program’. Activities range from bench-scale and beta-testing of desalination technologies to field or pilot testing of desalination and water treatment systems.

The ‘Long-Range Research Program’ also began in 2003 with a focus on investing in next-generation or evolutionary projects in desalination research and development. This program also received funding by congressional appropriation through DOE EM although a number of the
projects were internally through funded Sandia’s Laboratory Directed Research and Development (LDRD) Program. In addition, a portion of the EM funds were used to fund several university and industry led projects via subcontract. Overall, projects under the Long-Range Research Program resulted in numerous presentations, at least 57 publications, and at least 8 patents.

The Long-Range Research Program also provided funding to the JWR&DTF, which comprised SNL, AwwARF, WRF, and the BoR. Each invested $250K for a total of one million dollars to fund projects identified in the Desalination and Water Purification Technology Roadmap that are critical to California water needs. This was matched by California Prop 50 Desalination Funds for a total leveraged investment of two million dollars. JWR&DTF funded a total of 14 desalination research projects over a four-year time span from 2007 to 2010.

The AWTP was a multi-year program funded by a congressional appropriation through DOE EM in response to the US Environmental Protection Agency’s decision to lower the maximum contaminant level of arsenic from 50 parts per billion (ppb) to 10 ppb in 2006. The goal of the AWTP was to develop and test innovative technologies that have the potential to reduce the costs of arsenic removal from drinking water. The AWTP members included SNL, the AwwARF and the Waste Management Education and Research Consortium (WERC), a consortium for environmental education and technology development. The program was designed to move technologies from bench-scale tests to field demonstrations. The AwwARF managed bench-scale research programs, SNL conducted the pilot demonstration program, and WERC evaluated the economic feasibility of the technologies investigated and conducted technology transfer activities. In addition, SNL made LDRD investments that led to the development and patenting of eleven novel arsenic treatment technologies.

At the same time SNL was running the Advanced Concepts Desalination Program, three New Mexico small businesses requested support on desalination and water treatment projects through SNL’s NMSBA Program. These projects are summarized in the section entitled ‘NMSBA Water Treatment Projects.’ And are focused on piloting water treatment technologies in the field for treating oil field and coal bed methane produced water.

Other entities within DOE including the National Energy Technology Laboratory (NETL) and the National Renewable Energy Laboratory (NREL) have also funded desalination and water treatment projects at SNL. This work is described in a section entitled ‘Other Water Treatment Projects.’ For NETL, these projects focused primarily on developing methods for treating power plant cooling water while the NREL project focused on using waste heat to treat non-traditional sources of cooling water for power plant cooling.

A short summary of SNL work on the development of technologies for selective contaminant removal is presented in the ‘Other Water Treatment Projects’ section. This includes the development of permeable reactive barriers and contaminant sorbents. The work was primarily focused on developing technologies for radionuclide remediation, but several of these technologies show considerable promise for heavy metal separation as well. Seven patents in this research area have been identified, and three of these technologies have moved to commercial deployment.

Sandia’s current portfolio of work is presented in a section entitled ‘Current Portfolio of Desalination/Water Treatment Research.’ A total of three projects are active and include two
internally funded LDRD projects and one project funded by the Electric Power Research Institute.

Finally, the impact and legacy of the Sandia Water Initiative is described in the ‘Summary’ section of this document.
1 OVERVIEW OF ADVANCED CONCEPTS DESALINATION PROGRAM

Water is the backbone of our economy – safe and adequate supplies of water are vital for agriculture, industry, recreation, and human consumption. While our supply of water today is largely safe and adequate, we as a nation face increasing water supply challenges in the form of extended droughts, demand growth due to population increase, more stringent health-based regulation, and competing demands from a variety of users. To meet these challenges in the coming decades, water purification technologies, including desalination, will contribute substantially to ensuring a safe, sustainable, affordable, and adequate water supply for the United States (US).

The Advanced Concepts Desalination Program established in 2003 at Sandia National Laboratories (SNL, or Sandia) has the goal of developing cost effective technological ‘tools’ that can be used to help solve the nation’s water supply challenges. Sandia’s goal is to hasten the implementation of desalination technologies by: a) reducing the capital and operating cost of existing and future technologies; b) increasing operational efficiency; and c) expanding contaminant removal capabilities. To carry out this program we established three tasks: 1) developing and implementing the Desalination and Water Purification Technology Roadmap (US BoR and SNL, 2003) on a national scale in collaboration with the US Bureau of Reclamation (US BoR); 2) pilot-testing to accelerate the commercialization of new technologies (the ‘Jump Start’ Program); and 3) performing and directing a Long-Range Research Program at SNL and elsewhere to develop next-generation technologies.

1.1 Desalination Roadmaps

Recognizing that our nation is faced with significant challenges in meeting our future needs for water, Congress requested a desalination technology and implementation plan in the spring of 2002. “…The Committee recognizes that effective desalination cost reduction is the key to wider use of desalination for improving the quality of life in water scarce regions. The Secretary of the Interior shall consult with the Secretary of Energy and the Director of SNL in the development of the technology and implementation plan.” [2002 Energy and Water Development Appropriation Bill]

The Desalination and Water Purification Technology Roadmap (Figure 1-1) was created in 2003 to map out a long-term research strategy for desalination and other water purification technologies (US BoR and SNL, 2003). Together with the US BoR, American Water Works Association Research Foundation (AwwARF) and the WateReuse Foundation (WRF), SNL led a team of dozens of experts from industry, academia, government, and the water utilities. They conducted a series of workshops to identify high-impact and non-replicative research needs to hasten the rate for the development and implementation of new desalination technologies. The resulting Roadmap charts a series of research and development activities that will result in cost-effective, efficient revolutionary desalination and water purification technologies that can meet the nation’s future needs (USBoR and SNL, 2003). The Roadmap’s secondary goal was to define and describe the development activities that are needed to accelerate the rate of improvement of current-generation desalination and water purification technologies, thus allowing these technologies to better meet the near-term needs of the nation.
Five broad technology areas were determined to encompass the spectrum of desalination and water purification technologies: These Technology Areas include

1. Membrane Technologies (technologies that desalinate and purify water by selectively passing it through a semi-permeable membrane),
2. Alternative Technologies (non-traditional methods of desalination),
3. Thermal Technologies (technologies that rely on thermally driven phase changes, evaporation or freezing water, to separate purified water from contaminants),
4. Concentrate Management Technologies (technologies which address the disposal, volumetric reduction, and beneficial use of the primary byproduct of desalination), and
5. Reuse/Recycling Technologies (membrane or alternative technologies for treating post-consumer water, likely with increased or source-specific contaminant loads).

In 2004, SNL began a collaboration with AwwARF and the WateReuse Foundation (WRF) to guide the implementation of the findings and provisions of the Roadmap by describing needed research in greater detail. Funded by congressional appropriation through DOE EM, the team again relied upon the contributions of dozens of experts from industry, academia, government, and water utilities brought together in a series of workshops. This effort resulted in the creation of a second document entitled Implementation of the Desalination and Water Purification Technology Roadmap (SNL, 2006). The document complements the Desalination and Water Purification Technologies Roadmap but differs from it by identifying specific research projects critical to the growth of desalination.

The Implementation of the Desalination and Water Purification Technology Roadmap had two objectives. The first objective is to hasten the rate of technological advance. The second objective is to reduce the cost of desalination technologies. These objectives will be accomplished by cultivating and coordinating multiple research efforts at a national level with the goal of meeting current and projected “real-world,” user-generated needs. The technology areas identified in the original roadmap were reorganized in the implementation roadmap. The Thermal Technology area was combined with Alternative Technologies, and the Recycling/Reuse Technology area was incorporated into both the Membrane and Alternative
Technology areas. A new technology area focused on Institutional Issues in desalination, and water purification was added. The resulting research focus areas are:

1. Membrane Technologies (technologies that desalinate and purify water by selectively passing it through a semi-permeable membrane),
2. Alternative Technologies including Thermal Technologies (non-traditional methods of desalination),
3. Concentrate Management Technologies (technologies which address the disposal, volumetric reduction, and beneficial use of the primary byproduct of desalination), and
4. Institutional Issues in Desalination and Water Purification (to address non-technical barriers to the implementation of desalination).

Reports/Publications/Patents (and other deliverables):


Impact: The roadmaps brought together experts from across the country to develop and provide a strategy for prioritizing the desalination research efforts of multiple funding agencies as well as identifying specific research initiatives that will have the greatest impact on hastening the rate of technical advance in desalination technologies.
2 ADVANCED CONCEPTS DESALINATION: JUMP-START PROGRAM

The ‘Jump-Start Program’ was established in 2003 with congressional appropriation and was funded through DOE EM. It sought to identify cutting edge water treatment technologies to support with the goal of advancing their technological maturation through pilot testing and towards commercialization. While it sought to take advantage of the Brackish Groundwater National Desalination Research Facility (BGNDRF) in Alamogordo, New Mexico projects were performed at several sites around New Mexico.

2.1 Brackish Groundwater National Desalination Research Facility (BGNDRF)

The conceptual design for BGNDRF was funded in 2002. SNL coordinated the development of this design together with a consortium of water utilities, state and federal water agencies, and water research groups. SNL and the USBoR provided a report to Congress in September 2002 outlining the suggested site in Alamogordo NM, the facility attributes and layout needed for researching inland desalination, and an operational and management plan and structure. Construction of the facility began in 2004, followed by a ribbon cutting in August 2007, commissioning in 2008 and research starting in 2009.

BGNDRF (Figure 2-1) is a state-of-the-art research facility designed to address the cost, performance, energy-use, and environmental issues associated with the desalination and beneficial use of brackish groundwater and oil- and gas-produced water in inland areas. The research center has several unique capabilities, including the ability to conduct pilot and commercial-scale desalination technology testing, concentrate management evaluations, and renewable energy desalination testing. Other unique features of the 40-acre facility include multiple water supply wells that provide three different qualities of brackish water for desalination testing and research. The facility houses six enclosed desalination research bays, a water laboratory, offices for on-site and visiting researchers, three large outdoor desalination research pads, evaporation and concentrate management research areas, and an area for evaluating renewable energy applications for desalination.

Figure 2-1. The Brackish Groundwater National Desalination Research Facility, Alamogordo New Mexico.

Reports/Publications/Patents (and other deliverables):


Impact: BGNDRF is a unique research facility operated by USBoR for the desalination and treatment of impaired waters including brines, brackish water and produced water. SNL
coordinated the development of the conceptual design for the facility together with a consortium of water utilities, state and federal water agencies, and water research groups. For nearly a decade, the facility has been utilized by numerous companies (including General Electric, Water Standard Company, Veolia, Evoqua and Voltea) and universities (MIT, 2015 Desalination Prize Winner), Arizona, Texas Tech, Nevada Reno and UTEP for the piloting of novel desalination and water treatment technologies (www.usbr.gov/research/AWT/BGNDRF).

2.2 Zero Liquid Discharge

A major portion of the cost of inland desalination is the disposal of concentrate. This concentrate is an environmental and regulatory concern and is a prime factor in locating and fielding appropriate desalination technologies in the arid west as well as the inland areas near the gulf coast. The Jump Start Program funded a project with the University of South Carolina (USC) and ZDD, Inc., to investigate the use of a zero liquid discharge process for brackish water desalination (Figure 2-2). The USC technology is designed to separate and purify saleable resources including calcium sulfate from the concentrate stream. The technology involves a combination of RO and electrodialysis (ED) to achieve high water recovery from inland waters. The process of ED (Figure 2-2) involves the transport of salt ions from one solution across ion exchange membranes to another solution under the influence of an applied electric field.

![Figure 2-2. A process diagram for mineral recovery with an enhanced reverse osmosis (RO) electrodialysis (ED) process including a separate precipitation reactor.](Figure 2-2)

A high water recovery was demonstrated for the system in bench-scale testing. A pilot system was then designed and built into a trailer to enable field studies. Sandia and USC set the pilot system up for demonstration at the grand opening of the BGNDRF facility.

**Roadmap Technology Area:** Membrane Technologies and Concentrate Management.

**Impact:** Sandia testing and optimization of a hybrid RO/ED system at the BGNDRF facility resulted in very high water recoveries of >96% (Malynda Cappelle, personal communication, 2016). This led directly to an exclusive licensing agreement between Veolia and ZDD. At the end of the effort, SNL donated the pilot testing trailer to UTEP to enable further testing, evaluation and development of the ZDD RO/ED technology for future commercialization.
2.3 Controlled Precipitation and Beneficial Use of Concentrate for Increased Recovery

Sandia funded the University of New Mexico (UNM) to explore increasing the water recovery from traditional RO. Water recovery from RO is impeded by mineral precipitation on the membrane surface (Ahuja and Howe, 2008). Calcium sulfate in particular has low solubility and is not easily removed by traditional softening approaches. This project investigated the degree of supersaturation that can be tolerated before fouling occurs and also the removal of calcium sulfate from a reverse osmosis process by using an off-line seeded precipitation reactor (desupersaturator).

In the first focus area, the extent of supersaturation that could be accommodated in a laboratory-scale RO system (Figure 2-3) without adverse impacts to the RO system was investigated using calcium sulfate (Ahuja and Howe, 2008). Results demonstrated that it was possible to maintain low levels of supersaturation for up to one week without membrane fouling (the duration of the experiments). However, membrane selection was important. When operating under similar conditions, fouling occurred with an Osmonics RO membrane but not with an Osmonics nanofiltration (NF) membrane. Operating conditions that minimized concentration polarization (higher velocity, smaller channel spacer height) also led to less fouling; salt rejection was also affected by the level of supersaturation. For the second focus, precipitating the salts from the supersaturated synthetic solutions onto seed crystal media in a precipitation column, and monitoring the ability of the precipitation columns to continually do so over a period of one week was investigated. The study found that upflow worked better than downflow and that reagent grade calcium sulfate worked better than the other types of media tested, but overall it was difficult to operate for extended periods because the precipitates tended to solidify in the column and obstruct the flow of water.

An analysis demonstrated over 90 percent of the mass of the mineral content in desalination concentrate, i.e. calcium sulfate, calcium carbonate, sodium chloride, and sodium sulfate, could be put to beneficial use (Ahuja and Howe, 2008). Opportunities exist to use the sodium chloride directly in a brine form, for example in the chloro-alkali industry, but the presence of other ions as contaminants would have to be closely monitored. Calcium sulfate and calcium carbonate would likely have to be precipitated and used in solid form to enable beneficial use. However, other industries (primarily the power generation industry) have been recovering and beneficially using calcium sulfate from their waste streams, suggesting that it may be possible for the desalination industry to use a similar approach. Finally, opportunities for beneficial use of the sodium sulfate appear limited because of the high solubility of this material and the lack of markets for the salt.
Figure 2-3. A process diagram for calcium sulfate precipitation from RO feedwater using a desupersaturator.

Roadmap Technology Area: Concentrate Management.

Reports/Publications/Patents (and other deliverables):

Impact: The project demonstrated that it is possible to successfully recover calcium sulfate and other minerals from the combined RO/desupersaturator process and to increase water recovery (Ahuja, N. and K.J. Howe, 2007). The combined RO/desupersaturator process needs to be investigated at the pilot scale to obtain more information on its overall efficiency and scalability to industrial scale water desalination

2.4 Optimization of the Membrane Bioreactor-RO Process for Treatment and Reuse of Municipal Wastewater: Field Studies

Sandia also funded UNM to explore the use of integrated membrane systems to enable water reuse. The reuse of waste water is a cost-effective method to produce new water (Thompson et al., 2008). While water is low in dissolved salts in comparison to other brackish resources, it does require significant treatment to be reclaimed. An attractive water reuse scheme is to apply integrated membrane systems involving membrane bioreactor (MBR) (Figure 2-4) and RO membranes to achieve superior water quality.

Figure 2-4. MBR membrane cassette.
RO fouling, when treating effluent from three different wastewater treatment processes, was investigated: 1) the MBR variation of the activated sludge process, 2) the conventional complete mix activated sludge process, and 3) the aerated lagoon wastewater treatment process (Thompson et al., 2008). The project consisted of a sequence of field tests using a small full scale RO treatment unit. Testing was conducted at the Rio del Oro MBR plant operated by New Mexico Service Company, the Metropolitan Detention Center aerated lagoon plant operated by the Albuquerque Bernalillo County Water Utility Authority (ABCWUA) and the Southside Water Reclamation Plant also operated by the ABCWUA.

Roadmap Technology Area: Concentrate Management.

Reports/Publications/Patents (and other deliverables):

Thomson, B., et al., 2008, Optimization of the MBR-RO Process for Treatment and Reuse of Municipal Wastewater: Field Studies, The University of New Mexico, Albuquerque, New Mexico, 137 p. (Summarized above.)

Impact: At the time that this project was initiated, few investigations had been done on the nature and rate of organic fouling of RO membranes used to treat effluent from the MBR process (Thompson et al., 2008). It was established that if RO processes are used to treat wastewater, the user must assume that microbial growth will occur and should consider how it will affect process performance as well as instrumentation and control equipment. For solids removal, high quality pretreatment is critical to assuring the RO membranes perform effectively. Based on the experience of this study, it can be concluded that feed water sources and the required every treatment process will be different from site to site. This will result in different causes of RO membrane fouling, the fouling will occur at different rates, and prevention of the fouling and membrane cleaning protocols must be tailored for the feed water chemistry.

2.5 Novel Inexpensive Rotary-Boiler Desalinator

Sandia contracted a two-year program to Innovative Sciences Corporation, who then became B&W Global Tech LLC in late 2006, to investigate an advanced thermal desalination process referred to as vapor compression centrifugation. The technology was partially developed by the National Aeronautics and Space Administration (NASA) for a mission to Mars for water recovery from human and other wastes. B&W Global Tech LLC developed a new version of this technology as a small portable commercial grade desalinator (Figure 2-5). The desalinator uses thin film boiling and drop-wise condensation of purified water with highly efficient spinning shells to develop a thin evaporating water film on the boiling surface and dropwise condensation on the reverse side of a spinning heat exchanger. The goal was to produce an advanced prototype capable of serving as a beta test unit for high purity water production. The desalinator has the following characteristics:

- Small (1 liter-bottle size), portable, rugged, and inexpensive to fabricate
- Made of molded ABS plastic & acrylic (except for boiler-condenser)
- Easily disassembles like a thermos bottle for rapid and easy cleaning
- Boiler-Condenser made from disposable (easily replaceable) aluminum cans
- Vapor compression technology
• Designed to produce between 10 and 20 GPD from seawater
• Personal or village size desalinator can be easily powered by portable photovoltaic (PV) source

![Figure 2-5. Innovative Sciences Corporation prototype desalinator.](image)

Testing of the B&W Global Tech LLC prototype desalinator using artificial seawater showed nearly complete salt removal (desalination). All cations and anions were removed from the input water at greater than 99.5% resulting in a high purity water output. Next, a series of tests were conducted at Cedars-Sinai Hospital in Los Angeles, to determine if the prototype desalinator could effectively remove radiological and biological wastes in hospital waste streams. The testing results showed the output water had complete removal of $^{32}$P (a radioactive isotope), as well as complete removal of all E-Coli bacteria. Based on this series of tests, it is expected that other radionuclides and bacteria/protozoa will be completely absent from the freshwater product. However, it was determined that further testing needs to be performed to verify these conclusions.

**Roadmap Technology Area**: Alternative Technologies.

**Reports/Publications/Patents (and other deliverables):**


B&W Global Tech LLC, 2008, Summary of Purity Testing at Sandia National Laboratories and Cedars-Sinai Hospital, 12p. (Summarized above.)

**Impact**: The funding successfully helped to advance the prototype rotary-boiler desalinator through beta-testing at Cedars-Sinai (B&W Global Tech LLC, 2008).

### 2.6 Downhole Brine Compatibility Study

Sandia funded Los Alamos National Laboratory to examine the potential impacts of the injection of RO concentrate into New Mexico Aquifers (Figure 2-6). The study provided a high-level screening tool to evaluate the potential impact of RO concentrate injection on receiving aquifer permeability (Keating and Fabryka-Martin, 2006). The tool enables the user to evaluate the extent to which the operational lifetime of an injection well might be limited due to chemical
incompatibilities between an injected RO concentrate and the native saline groundwater in a receiving aquifer. Chemical incompatibility results in net precipitation of common scaling minerals such as calcite and gypsum. The framework was applied to water chemistry data for 239 samples of brackish and saline waters, the large majority of which were collected from New Mexico aquifers. Of these, 209 were treated as potential feed waters and 31 were considered to be potential receiving formations for testing the framework.

Batch geochemical modeling determined whether mixing of concentrate and receiving formation waters would produce scale and, if so, what volume of scale per liter of mixed water would be produced (Keating and Fabryka-Martin, 2006). Scale-producing mixtures were classified as “incompatible.” Incompatibility was predicted for a large proportion of the tested combinations of waters. Using several methods, the length of time it might take to significantly reduce porosity in the receiving formation was estimated. Initial calculations assumed the volume of scale expected to result from mixing would be deposited within a stationary “mixing zone” within a given radius of the injection well. For a medium sized RO plant, predicted times were quite short (less than one year). However, previous field studies and reactive transport modeling suggests that often the location and size of the mixing zone will be neither stagnant nor near the injection well. To investigate this possibility, reactive transport models were developed. It was determined that if anti-scalants were effective indefinitely, the zone of scale deposition will move with the leading edge of the injected water plume and scale will not accumulate indefinitely in any given location. In contrast, if anti-scalants become ineffective in the subsurface within a finite period of time after injection, a zone of scale accumulation will build near the injection well. The resulting porosity reduction could become significant within a fairly short period of time. However, these results also show that a large benefit that could be gained—in terms of enhanced sustainability of the injection well—by relatively small increases in the longevity of anti-scalants in the subsurface.

**Roadmap Technology Area:** Concentrate Management.

**Reports/Publications/Patents (and other deliverables):**
Keating E., and J. Fabryka-Martin, 2006, Assessment of the Potential to Inject RO Concentrate into New Mexico Saline Aquifers: Focus on Chemical Compatibility, Los Alamos National Laboratories, Los Alamos, New Mexico. 23p. (Summarized above.)

Impact: The high-level screening tool developed by LANL on this project enables the evaluation of the potential impacts of RO concentrate injection into basin aquifers in concentrate management for inland desalination.

2.7 Self-Sealing Evaporation Pond Liner

Concentrate disposal is a critical step that must be overcome for desalination to be widely pursued in areas that have no easy access to coastlines. Presently, desalination residuals – typically calcium sulfate/bicarbonate-rich brine is disposed of down sewers, into other freshwater bodies, into deep well disposal zones, or into evaporation ponds. Disposal of desalination concentrates in arid areas where land is often inexpensive is done using evaporation ponds. The primary expense of the ponds is the synthetic liner that must be emplaced to prevent seepage of brines to underlying soils and aquifers. Because many salt lakes in New Mexico and elsewhere apparently seal themselves, there is the potential that evaporation ponds might be chemically configured to do likewise – thus avoiding the expense of the liner. At the same time, an evaporation point that would “self-seal” by continually growing new minerals (Figure 2-7) should be more likely to prevent brine seepage in the face of settling and compaction, events that might tear a synthetic liner. SNL collaborated with NMSU, the Texas Water Development Board, and the Texas Bureau of Economic Geology at the University of Texas in Austin to understand the chemical controls over clay formation in RO concentrate brines to develop a recipe that mimics natural clay formation in the sealing of brine lakes.

Figure 2-7. A photomicrograph of sepiolite—a clay mineral that forms from evaporite brines.
Source: http://www.minersoc.org/pages/gallery/claypix/sepiolite/sepiolite_sep4_2med.jpg

Roadmap Technology Area: Concentrate Management.

Reports/Publications/Patents (and other deliverables):


Impact: This simple and innovative project aimed to reduce the costs for the disposal of desalination residuals by creating self-sealing evaporation ponds and thereby eliminating the need for expensive pond liners (Nicot, J.P., 2009). Efforts at growing clays in situ using Tularosa soil and a model soil indicate that permeability can be lowered by silicate and magnesium (common clay components) additions, but not enough to replace the synthetic liners.

2.8 Silica Removal from Desalination Concentrates

Most inland brines contain dozens of parts per million (ppm) of dissolved silica (Figure 2-8). Reverse osmosis raises silica levels further until scales form – typically when dissolved levels exceed roughly 100 ppm. Subsequent silica scale formation on the RO membranes limits water recovery and considerably increases the amount of waste brine requiring disposal. One way to increase RO recovery and limit concentrate disposal volumes is to develop new means for removing silica from saturated solutions. In a two-year project co-funded by SNL and El Paso Water Utilities, SNL worked with UTEP researchers of the Consortium for Hi-Technology Investigations in Water and Wastewater (CHIWAWA) to specifically examine sorption and polymerization of dissolved silica on high-surface-area sorptive materials. The goal was to identify and develop a low-cost material that can lower levels from 100 ppm to 50 ppm of dissolved silica in a short period of time (minutes) and thereby allow the concentrate to go through an additional RO step without scaling.

Figure 2-8. Silica structure. (from http://www.osha.gov/SLTC/etools/silica/silicosis/silica.gif)

Roadmap Technology Area: Concentrate Management.

Impact: Concentration management is a critical concern for inland desalination where ocean discharge is impractical.

2.9 Synergistic Behavior between Silica and Alginate: Novel Approach for Removing Silica Scale from RO Membranes

A series of experiments run on a lab-scale RO membrane system examined the fouling of membranes when the feed water was spiked with organic and inorganic foulants (Higgin et al., 2010). Alginic acid (Figure 2-9) was used as the biofoulant and silica was used as the inorganic foulant. Studies involving interactions of these two foulants have not previously been reported in literature. Experiments were run with each foulant individually to characterize fouling at different velocities and pressures. Experiments were then run using both foulants together to
characterize the synergistic effects on membrane fouling. One set of experiments with both foulants demonstrated that alginic acid inhibits silica fouling on RO membranes. Further experiments indicated that alginic acid added after silica fouling had already occurred was able to remove silica scale from the membrane and restore permeate flux.

**Roadmap Technology Area:** Membrane Technologies.

**Reports/Publications/Patents (and other deliverables):**

Higgin, R., 2007, Investigating the Synergistic Effects of Biofouling and Silica Scaling on Reverse Osmosis Membranes, Master’s Thesis. The University of New Mexico, Albuquerque New Mexico. 89 p.

Higgin, R., et al., 2010, Synergistic behavior between silica and alginate: Novel approach for removing silica scale from RO membranes, Desalination 250, 76–81. (Summarized above.)

**Impact:** The formation of mineral scale deposits on membranes is pervasive and expensive problem for the water treatment industry (Higgin, et al., 2010). In this project, experiments demonstrated that alginic acid inhibits silica fouling on RO membranes. In addition, some experiments indicated that alginic acid added after silica fouling had already occurred was able to remove silica scale from the membrane and restore permeate flux.

### 2.10 High Performance Reverse Osmosis Membrane Element Design

The fluid dynamics of water flow in the membrane module has a large impact on mixing, the build-up of salts near the membrane surface (concentration polarization), and attachment of foulants to the membrane. All of these affect membrane performance. MIOX Corp. demonstrated that replacing the usual membrane spacer with a dimpled membrane allows a much thinner feed channel for water flowing over the membrane (Figure 2-10), which increases water flow velocity, enhances mixing, reduces salt buildup, and potentially reduces fouling. As a result, they have demonstrated up to two times greater pure water production compared to conventional module designs. This means less energy expenditure, less membrane area needed, and smaller plant design for a given capacity system.

![Figure 2-10. A dimpled feed spacer design allows smaller feed channel dimensions in membrane modules, resulting in higher flow velocity, better mixing, and higher membrane throughput.](image)

**Roadmap Technology Area:** Membrane Technologies.

**Impact:** Improving performance by minimizing salt and foulant buildup on membrane surfaces has a significant impact on reducing energy consumption. In collaboration with MIOX, SNL
modeled the fluid dynamics of membrane modules to optimize MIOX’s design, as well as to provide the basis for advanced membrane modules using new higher performance membranes.

2.11 Capacitive Deionization for Coal-Bed Natural Gas Produced Water Treatment

Site operators face increasing environmental problems and expense in hauling and disposing produced water ($1 to < $4/barrel in the San Juan Basin at the time of the project) and disposal issues could severely restrict natural gas production. Efficient water treatment methods are of major importance in remote areas, where the costs and maintenance issues with RO systems pose significant problems.

Desalination of coal bed natural gas (CBNG) produced water creates a new source of water that can be used beneficially. For example, the treated produced water can be used for rangeland enhancement, jump-starting grass seedlings and nurturing native grasses.

Capacitive deionization (CD) is a promising innovative desalination technology that uses high surface area and high capacitance electrodes to remove salt ions from water. The potential advantage of the technology is that it can be ‘tuned’ to treat brackish waters to a target salinity level, significantly reducing the energy requirements over more common technologies such as RO. For applications where the treated water does not need to be of high quality, such as irrigation, stock watering, or rangeland rehabilitation, the technology may provide a much more cost effective and robust water treatment approach.

Laboratory testing of a prototype commercial system (Figure 2-11) showed the CD bench top unit appears to remove all ions in similar quantities regardless of valence or mobility. This indicates that CD technology appears to be applicable to the treatment of produced water, especially CBNG produced water, where the slightly brackish water can be easily treated to a level that would enable its use for irrigation of rangeland.

![Figure 2-11. A lab-scale configuration for performance testing of Capacitive Deionization technology.](image)

Roadmap Technology Area: Alternative Technologies.

Reports/Publications/Patents (and other deliverables):
Donahue, R. and E. Wright, 2005, Capacitive Deionization Desalination Technology for Coal Bed Methane Produced Water Treatment and Rangeland Rehabilitation. SAND 2005-6164c. (Conference Presentation.)
**Impact:** The potential advantage of CD is that it can treat impaired waters to a target salinity level and thereby reduce the energy requirements over more common technologies such as RO (Michael Hightower, personal communication, 2016). Laboratory testing of the CD technology indicated considerable promise for treat-to-need application including rangeland rehabilitation but further pilot testing is required.

### 2.12 CHIWAWA – SANDIA Partnership

The Consortium for Hi-Technology Investigations in Water and Wastewater (CHIWAWA) was formed in 2005 institutions in New Mexico and Texas, the El Paso Water Utilities Board, City of Alamogordo, University of Texas at El Paso, Texas A&M University, New Mexico State University, and SNL to provide opportunities to create sustainable urban and rural water supplies and to protect environmental quality by conducting innovative, collaborative research, education, and training programs in inland desalination technology, concentrate disposal, and water resources management. The combination of skills of each of the partner would be applied to help facilitate the development of new desalination concepts and the testing and commercialization of these new concepts in a large utility environment (the El Paso Water Utility).

**Roadmap Technology Area:** Membrane Technologies, Concentrate Management, Institutional Issues

**Impact:** The CHIWAWA consortium is/was long-lived institution that found a physical home at the Kay Bailey Hutchison Desalination Plant in El Paso, Texas. CHIWAWA was envisioned as being the driver behind a variety of important activities in the region, including: (1) the organization of conferences, training programs, short courses and meetings on issues related to water treatment, conservation, water resource management, and desalination; (2) joint research in desalination technologies, brine management, and assessment of brackish water supplies and (3) working together to inform and assist all stakeholders in the region’s water supply. Relationships developed between individuals at Sandia and member institutions are enduring. The TecH2O Center associated with CHIWAWA is an educational and training center located adjacent to the desalination building that is open to the public and frequently visited by students in grades 5th and up to learn about the importance of water conservation.

### 2.13 Affordable Desalination Coalition

Formed in 2004, the Affordable Desalination Collaboration (ADC) was a California non-profit organization composed of a group of leading U.S. companies and agencies in the field of desalination that agreed to pool their resources and share their expertise in the mission to make desalination affordable and cost-competitive to conventional water supply alternatives in water limited regions of the United States. Richard Kottenstette served as Sandia’s interface with the coalition. The ADC constructed a 200-300 m$^3$/day seawater reverse osmosis treatment plant with the objective of demonstrating an energy efficient combination of commercially available RO technologies and equipment including pumps, membranes and energy recovery systems. Isobaric energy recovery, i.e. Pressure exchange (PX) was of particular interest. The stated goal was to “improve seawater desalination treatment technologies in terms of cost, energy use, and environmental impacts and to use the estimated costs generated as a result of this work to further refine the paradigm for engineers, planners, OEMs, membrane manufacturers, and policy makers related to the costs of seawater desalination.” It was reported in November 2009 [IDA World Congress, Dubai, UAE, November 7-12, 2009, REF: IDAWC/DB09-154] that members and participants in a demonstration included.
Roadmap Technology Area: Membrane Technologies

Reports/Publications/Patents (and other deliverables):


Impact: The treatment system operated continuously for at least three years at the Navy’s Seawater Desalination Test Facility in Port Hueneme, California. Various operating configurations and parameters were evaluated. The above referenced report the ADC claims it had demonstrated total energy consumption for seawater desalination at 11.28 kWh/kgal (2.98 kWh/m³) at a projected total cost of $3.00/kgal ($0.79/m³). They further stated that results demonstrate that the cost and energy consumption is comparable to more conventional options for Southern California, and therefore an affordable drought-proofing option for the region.

2.14 Desalination Decision Aid

Sandia funded Robert Wessley, Systems Engineering Consultant, to develop a web-based interactive desalination decision support tool to walk city managers and interested stakeholders through the financial, water quality, and waste disposal considerations that are involved in implementing desalination at the community level. The decision aid model was intended to provide the user with a basic understanding of the processes, issues and trade-offs associated with desalinating a supply of brackish water.

Roadmap Technology Area: Institutional Issues.

Reports/Publications/Patents (and other deliverables):
A Windows-based tool, Desalination Decision Aid (DDA Version 0.3) was delivered to Sandia.

**Impact:** As with any general purpose model, the tool provides coarse approximations for the user and is a useful starting point for managers and stakeholders as they embark on more detailed engineering analyses.
3 DESALINATION: LONG-RANGE RESEARCH PROGRAM

3.1 Sweeping Gas Membrane Desalination Using Commercial Hydrophobic Hollow Fiber Membranes

Membrane distillation (MD) is an emerging technology for separations that are usually accomplished by conventional distillation or RO (Miller and Evans, 2002). Membrane distillation involves the transport of water vapor from a saline solution through the pores of a hydrophobic membrane. In sweeping gas MD (Figure 3-1), a flowing gas stream is used to flush the water vapor from the permeate side of the membrane, thereby maintaining the vapor pressure gradient necessary for mass transfer. Liquid does not penetrate the hydrophobic membrane hence dissolved ions are completely rejected by the membrane. Membrane distillation has a number of potential advantages over conventional desalination including low temperature and pressure operation, reduced membrane strength requirements, compact size, and 100% rejection of non-volatiles. This work evaluated the suitability of commercially available technology for sweeping gas membrane desalination. Evaluations were conducted with Celgard Liqui-Cel® Extra-Flow 2.5X8 membrane contactors with X-30 and X-40 hydrophobic hollow fiber membranes. The results demonstrate that sweeping gas membrane desalination systems using low grade heat are capable of producing low total dissolved solids (TDS) water, typically 10 ppm or less, from seawater.

![Figure 3-1. Schematic Diagram of a hollow fiber membrane cartridge with counter current sweeping gas flow.](image)

Reports/Publications/Patents (and other deliverables):


Impact: This distillation technology has considerable promise for desalination applications. However, there are several barriers that currently prevent it from being a viable as a desalination technology (Miller and Evans, 2002). The main problem is that large air flows are required to achieve significant water yields, and the costs associated with transporting this air are prohibitive. To overcome this barrier, at least two improvements are required. First, new and different contactor geometries are necessary to achieve efficient contact with an extremely low pressure drop. Second, the temperature limits of the membranes must be increased. In the absence of these improvements, sweeping gas MD will not be economically competitive for water treatment. However, it is possible that the membranes may find use in hybrid desalination systems.
3.2 Review of Water Resources and Desalination Technologies

Desalination has now been practiced on a large scale for more than 50 years (Miller, 2003). Over this timeframe continual improvements have been made, and the major technologies are now efficient, reliable, and inexpensive. For many years, thermal technologies were the only viable option, and multi-stage flash was established as the baseline technology. Multi-effect evaporation is now the state-of-the-art thermal technology, but has not been widely implemented. With the growth of membrane science, RO overtook multi-state flash as the leading desalination technology, and should be considered the baseline technology. At the time the report was written, RO of seawater could be accomplished with an energy expenditure in the range of 11-60 kJ/kg at a cost of $2 to $4 per 1000 gallons. The theoretical minimum energy expenditure is 3-7 kJ/kg.

It was concluded that since RO is a fairly mature technology, further improvements are likely to be incremental in nature, unless design improvements allow major savings in capital costs (Figure 3-2). Therefore, the best hope to dramatically decrease desalination costs is to develop “out of the box” technologies. These “out of the box” approaches must offer a significant advantage over RO (or multi-effect evaporation, if waste heat is available) if they are to be viable.

![Figure 3-2. The trade-off between capital costs and energy consumption for practical desalination systems.](image)

Roadmap Technology Area: Membrane, Thermal, and Alternative Technologies.

Reports/Publications/Patents (and other deliverables):


Impact: This review of current and state-of-the-art desalination technologies has been sited over 180 times; impressive for a SAND report (James Miller, personal communication, 2016). It has helped to establish benchmarks for future work and identified opportunities for reducing capital costs and energy demand of desalination by developing out-of-the-box, revolutionary technologies (Miller, J.E., 2003).
3.3 Biomimetic Membranes

This project focused on developing desalination membranes through the emulation of biological water channels such as those in human cell walls (Rempe et al., 2010). With molecular modeling, three key mechanisms used by nature for selecting specific ions for transport across a cell membrane were identified. Each mechanism of selective ion binding shared a common structural feature: binding sites. It was determined that binding sites composed of dipolar functional groups with specific architectural characteristics can stabilize specific ions for permeation across natural membranes. In addition, the properties of a binding site can be ‘tuned’ without changing its structure simply by modulating the charge-response properties of the surrounding environment. Comparison with the crystal structure of biological water-selective channels showed a distinct absence of ion binding sites in the water permeation pathway. Natural water channels contain a collection of dipoles, alternating in direction, and mixed with hydrophobic groups that line the channel walls (Figure 3-3).

Efforts to turn nature’s structural design features into robust synthetic porous membranes produced five models of biomimetic pores, which were fabricated using self-assembly and novel atomic-layer deposition strategies (Rempe et al., 2010). Experimental and theoretical platforms allowed successive modification of pore size and surface chemistry and charge, followed by measurements of pore structure and selective transport function to deduce structure/transport property relationships in the inorganic nanopores. It was found that purely hydrophobic pores, as achieved with trimethylsilane coverage, fully inhibited water transport. As in the natural water-selective channel proteins, partially hydrophilic pore surfaces are required to provide ‘binding sites’ that stabilize water molecules, increase diffusion, and increase water flux across the membrane. Furthermore, narrow pores with diameters in the nanometer length scale or smaller are required for ion rejection functionality because large pores stabilize ions by permitting counterions and water molecules to permeate with the ions.

In the final fabrication of organic modified nanopores by self-assembly and plasma-assisted atomic layer deposition (ALD), nanopores were synthesized with multiple organic surface derivatizations to mimic more closely the structure of water-selective protein channels in cell membranes (Rempe et al., 2010). In these channels, a polymer network composed of opposing dipoles from carbonyl and amine groups, with hydrophobic groups in between, stretch across the nanopores. The pores notably lack well-defined ion binding sites characteristic of ion-selective...
biological channels. Gas permeance measurements confirmed the presence of a nanoporous structure. In a side-by-side comparison of performance between SNL’s ALD polypeptide membranes and DOW commercial membranes, the ALD membranes maintained high enough salt rejection to produce drinking water, yet significantly outperformed the commercial membranes in terms of water permeability.

Roadmap Technology Area: Membrane Technologies.

Reports/Publications/Patents (and other deliverables):

Rempe et al., 2010, Computational and Experimental Platform for Understanding and Optimizing Water Flux and Salt Rejection in Nanoporous Membranes. SAND2010-6735 (summarized above).


Asthagiri, D. et al., 2004, Hydration structure and free energy of biomolecularily specific aqueous dication s, including Zn$^{2+}$ and first transition row metals. J. Am. Chem. Soc. 126:344-351.


Jiang, Y.-B., et al., 2006, Nanometer-thick conformal pore sealing of self-assembled mesoporous silica by plasma-assisted atomic layer deposition. Journal of the American Chemical Society, 128(34), 11018-11019.

Jiang, Y.-B., et al., 2007, Sub-10 nm thick microporous membranes made by plasma-defined atomic layer deposition of a bridged silsesquioxane precursor. Journal of the American Chemical Society, 129(50), 15446-15447.


US patent application (pending).

**Impact:** Advances in biotechnology including biomimetic membranes hold considerable promise for increasing water production while reducing energy demand (Rempe et al., 2010).
Bench scale testing has shown that the advantages of SNL’s nanoporous biomimetic membrane design include: 1) an order-of-magnitude improvement in membrane permeability, which reflects a reduction in membrane resistance to flow; 2) high salt rejection that is maintained independently of driving pressure; and 3) purification of water with nearly four times the water flux as compared to commercial membranes (DOW FILMTEC SW30HR) (Rempe et al., 2011). Based on testing results the projected reduction in excess energy cost due to membrane resistance to flow is 88%, a savings of $1.45 M/yr for a 100 ML/day desalination plant. This project generated 30 publications focused on fundamental research in membrane science. Further, the technology has received international recognition via R&D 100 Award (2011), research highlighted by US Department of Energy (DOE) Secretary Chu (2011), and a Federal Laboratories Consortium Notable Technology Development Award (2012) (Susan Rempe, personal communication, 2016). The project also established a foundation for new bio-inspired membranes that SNL is developing for gas separations (e.g., CO₂).

3.4 High Efficiency Electrodialysis Membranes

This project was primarily focused on the development of fuel cell membranes however the investigators made an effort to develop electrodialysis membranes for water treatment. Electrodialysis is an electrochemical process that removes salt from water using electric current and specialized ion-exchange membranes. This process is particularly attractive for desalination of brackish water, and separation of salts in the waste stream to yield economically valuable products. The efficiency of ED depends on the membranes being able to conduct electric current through transporting salt ions with high efficiency and selectivity. In this project SNL developed advanced ion exchange membranes using nanometer-scale self-assembly techniques, to achieve significantly higher efficiency than current membranes. These advanced membranes enable ordered ‘block’ transport of salts as opposed to the less efficient random transport allowed by conventional ED membranes (Figure 3-4). In addition, the membranes will lower electrical energy consumption and result in decreased cost for desalinated water, and higher ion selectivity could facilitate recovery of marketable salts and minimize waste.

Figure 3-4. Illustration of block and random transport of ions through an ED membrane.

Roadmap Technology Area: Membrane Technologies.

Reports/Publications/Patents (and other deliverables):
**Impact:** Sandia created and patented a new class of ion exchange membranes using advanced polymer synthesis techniques (Michael Hibbs, personal communication, 2016). While the primary function of the membranes is for fuel cell applications, bench top testing of these membranes in an ED water treatment system indicated superior performance with lower energy consumption as compared to commercially available membranes. Further testing and evaluation moving to pilot scale testing in ED systems is required before considering the commercial potential of these membrane materials for desalination.

### 3.5 Mitigation of Biofouling in Membrane Processes

Biofilms arise from a wide variety of naturally occurring organisms and form complex colonies of bacteria and extracellular polymeric substances (EPS) that are excreted by the organisms to form a matrix for support and protection of the colony. The EPS contains a variety of proteins, lipids, polysaccharides, and nucleic acids. Fouling of membranes because of the growth of biofilms is one of the major operational problems associated with membrane water treatment technologies, leading to high operational and maintenance costs, increased energy use because of reduced membrane efficiency, reduced membrane life, and high replacement costs. Biofilm formation and mitigation are poorly understood, and biofilms are notoriously resistant to common cleaning and disinfectant treatments.

Homogeneous biofilms were grown using drip-flow reactors under nutrient-limiting conditions. Degradative enzymes such as proteinase K, lysozyme, DNase, and those found as contaminants in the antibiotic Bacitracin, were applied to the biofilms to evaluate their effectiveness of biofilm removal. Application of crude Bacitracin to biofilms of *Pseudomonas fluorescens* showed a very significant effect. After the addition of Bacitracin, the mucus-like biofilms were rapidly degraded into fragmented, non-viscous remnants. Confocal Laser Scanning Microscopy (CLSM), Environmental Scanning Electron Microscopy (ESEM), and Scanning Electron Microscopy (SEM) were utilized to better understand the distribution of macromolecules in biofilms and the effect of enzyme treatment on the biofilm structures (Figure 3-5). A bench-scale reverse osmosis system was used to simulate membrane biofouling (natural, heterogeneous biofilms) with produced water from gas-producing wells in the Farmington area as the feed. These biofilms were used to validate the findings of pure-culture biofilms.

![Figure 3-5. Scanning electron microscope images showing bacteria and associated extracellular polymeric substances (EPS).](image-url)
Roadmap Technology Area: Membrane Technologies.

Reports/Publications/Patents (and other deliverables):


Impact:

NMT developed a biofilm treatment strategy that uses broad-spectrum degradative enzymes to degrade the extracellular polymeric substance (EPS) that is excreted by organisms to serve as a substrate and protective matrix for the biofilm. Enzyme screening studies have shown that enzymes associated with the common antibiotic Bacitracin are remarkably effective at degrading EPS for a variety of biofilm-forming organisms. The membrane treatment procedure is expected to prevent biofilm formation and remove established biofilms, without harming the membrane itself or creating environmental hazards in the waste stream.

3.6 Mitigating Membrane Biofouling

This project involved three closely related efforts to mitigate desalination membrane biofouling. Biofouling, the unwanted growth of biofilms on the surface of water-treatment membranes has a negative economic impact in desalination and water treatment (Altman, et al., 2009). With biofouling there is a decrease in permeate production and an increase in energy expenditure due to increased cross-flow pressure needed. Micromixers (Figure 3-6) that promote chaotic mixing were fabricated on reverse-osmosis membrane surfaces and evaluated using computational models and laboratory experiments to determine their effectiveness in reducing biofouling. In addition, a new concept for the modification of RO membranes by coating the surface with a hydrophilic biocidal polymer was also investigated. The synthesis of a series of poly(sulfone)s with attached quaternary ammonium (QA) groups was achieved along with a method for spraying alcoholic solutions of the QA polymers to form water-permeable coatings.

Figure 3-6. Micromixers printed on the surface of a RO membrane.

Roadmap Technology Area: Membrane Technologies.
Reports/Publications/Patents (and other deliverables):

Altman, S.J., et al., 2008, Use of Ceragenins to Create Novel Biofouling Resistant Water-Treatment Membranes. SAND2008-7895. (Summarized above.)

Altman, S.J. et al., 2009, Analysis of Micromixers and Biocidal Coatings on Water-Treatment Membranes to Minimize Biofouling. SAND2009-8316 (Summarized above).


Impact: Membrane fouling is one of the most important factors impacting energy demand in RO desalination (Altman et al., 2008). Minimizing or preventing biofouling on RO membranes has the effect of significantly reducing energy demand for desalination. This project generated an impressive number of patents and publications on two novel methods, one physical and one chemical, to mitigate membrane biofouling. Both methods show considerable promise but both require further investigation and development before being considered for commercial application.

3.7 Clathrate Desalination

Freezing water to form ice naturally excludes salt, and desalination processes based on freezing are possible. In a similar fashion, many molecules (e.g. methane, ethylene, propane, CO₂) will form a solid ‘clathrate hydrate’ (Figure 3-7) at high pressure and low temperature, containing large amounts of water, and excluding salt from the surrounding salt water (Bradshaw, 2006). Separating the solid hydrate from the salt water allows recovery of the fresh water, forming the basis of a thermally efficient desalination process. This process has failed in previous attempts at commercialization because of poor understanding and control of the clathrate formation and growth process and inefficient separation the solid hydrate from the salt water. This program employs a unique process for clathrate formation and separation of the solid hydrate and salt
water. The aim is to improve the thermal efficiency and separation process to make this approach economically competitive with other desalination processes.

The LDRD project began by using R141b (1,1-Dichloro-1-fluoroethane), a refrigerant that has been studied previously for desalination, and then expanded to include hydrofluorocarbons, such as HFC-32 (difluoromethane), that have been identified as promising candidates in the literature. Experiments were conducted to determine the impacts that these hydrate formers have on the nucleation environment and the extent to which this environment can be tailored to produce hydrates with the desired morphological characteristics (i.e. no dendritic growth and entrapped salt). The possible utilization of additives to inhibit dendritic hydrate growth and thus minimize interstitial salt entrapment was also investigated. Fundamental studies into the rate of nucleation and crystallization of these hydrates at a variety of experimental conditions were conducted (e.g. pressure, temperature, flow rate) to develop an extensive knowledge base from which to operate. Directly coupled with this effort was the first-principles computational modeling of these systems and their corresponding nucleation kinetics. Molecular modeling of the stability of the various clathrate hydrates was performed in support of the experimental work to determine the relative stabilities of candidate gas clathrates using energy optimization and molecular dynamics methods. The latter method allows determination of the pressure-temperature phase limits for each of the clathrates and helps constrain the experimental conditions of the water treatment process, especially for clathrates for which limited literature data are available.

Roadmap Technology Area: Alternative Technologies.

Reports/Publications/Patents (and other deliverables):


Impact: This project focused on developing new hydrate formers and separation processes for clathrate desalination (Bradshaw, et al., 2007). Sandia advanced the state-of-knowledge of
clathrate desalination and developed and patented a technology that utilizes clathrate technology to separate water from salts.

3.8 Nanoscience Review- Prop 50: SAND Report

Nanomaterials and nanotechnology methods have been an integral part of international research over the past decade (Mayer et al., 2011). Because many traditional water treatment technologies (e.g. membrane filtration, biofouling, scale inhibition, etc.) depend on nanoscale processes, it is reasonable to expect one outcome of nanotechnology research to be better, nano-engineered water treatment approaches. The most immediate, and possibly greatest, impact of nanotechnology on desalination methods will likely be the development of membranes engineered at the near-molecular level. Aquaporin proteins that channel water across cell membranes with very low energy inputs point to the potential for dramatically improved performance. Aquaporin-laced polymer membranes and aquaporin-mimicking carbon nanotubes (Figure 3-8) and metal oxide membranes developed in the lab support this. A critical limitation to widespread use of nano-engineered desalination membranes will be their scalability to industrial fabrication processes. Subsequent, long-term improvements in nano-engineered membranes may result in self-healing membranes that ideally are 1) more resistant to biofouling, 2) have biocidal properties, and/or 3) selectively target trace contaminants.

Figure 3-8. Schematic of methane moving through carbon nanotubes. Similar carbon nanotubes might be used for desalination.


Roadmap Technology Area: Alternative Technologies.

Reports/Publications/Patents (and other deliverables):


Impact: To dramatically increase membrane performance new materials and technologies must be examined (Mayer, T., et al., 2011). This report identified active state-of-the-art research as well as new research opportunities for the development of nanoengineered membranes for desalination.

3.9 Desalination: Joint Water Reuse & Desalination Task Force

To hasten the development of the technology needs identified in the Desalination and Water Purification Roadmap, the task force identified critical projects for investment. SNL, AwwARF,
WRF and the BoR each invested 250K for a total of 1 million dollars (Figure 3-9). This was matched by California Prop 50 Desalination Funds to fund projects identified in the Desalination and Water Purification Technology Implementation Roadmap that are critical to California water needs. A total of 14 projects were funded from 2007 to 2010. The projects include:

- **State of the Science Review of Membrane Fouling: Organic, Inorganic and Biological** (WRRF-06-010A) - HDR Engineering, Inc., was the contractor.

- **Feasibility study of Offshore Desalination Plants** (WRRF-06-010B) - HDR Engineering, Inc., was the contractor.

- **Consideration for the Co-Siting of Desalination Facilities with Municipal and Industrial Facilities** (WRRF-06-010D) - Kennedy/Jenks Consultants was the contractor.

- **Development of Selective Recovery Methods for Desalination Concentrate Salts** (WRRF-06-010E) - The University of New Mexico (UNM) was the contractor.


- **IM&E Reduction Guidance Document for Existing Seawater Intakes** (WRRF-10-04) - The Alden Research Laboratory, Inc., was the contractor.

- **Seawater Intake Systems for Desalination Plants** (WRF 4080) - Carollo Engineers was the contractor.

- **Post Treatment Stabilization of Desalinated Water** (WRF 4079) - The University of Central Florida was the contractor.

- **Guidelines for Implementation of Seawater and Brackish Water Desalination Facilities** (WRF 4078) - The Stratus Consulting Group was the contractor.

- **Investigation of Vibratory RO to achieve >99% Water Recovery of Treat RO Brines** (WRF 4148) - The University of Washington was the contractor.

- **A Novel Hybrid Forward Osmosis Process for Drinking Water Augmentation Using Impaired Water and Saline Water Sources** (WRF 4150) - The Colorado School of Mines was the contractor.

- **Method of Producing Commercially Viable Ceramic Bipolar Bi-Layer Membranes** (WRF 4151) - The University of Wisconsin, Madison was the contractor.

- Membrane Fouling by Marine Algae in Seawater Desalination (WRF 4201) – The University of Illinois was the contractor.

- **Opportunities for Nanotechnology Applications in Membrane Water Treatment, A State-of-the-Science Review** - Thomas M. Mayer was the principal investigator.
Roadmap Technology Area: Membrane Technologies, Alternative Technologies, Concentrate Management and Institutional Issues

Reports/Publications/Patents (and other deliverables):


Impact: California Department of Water Resources (DWR), AwwRF, SNL, and the WRF jointly sponsored 14 research and development projects which addressed issues related to seawater and brackish water desalination. Upon the conclusion of the research projects, the project contractors provided meaningful results to aid in the future decision making regarding desalination. New techniques were tested such as clay flocculation and vibratory shear-enhanced processing; existing practices were evaluated including the coupling of forward osmosis and RO; and the state of the science was reviewed.

3.10 Interfacial Water

Water confined between surfaces, within channels, or in pores (Figure 3-10) is ubiquitous in technology and nature (Cygan et al. 2008). Its physical and chemical properties in such environments are unpredictably different from bulk water, however. As a result, advances in water desalination and purification technologies have been slow, and—more importantly—inefficient to meet the anticipated international demand for safe, potable water. The research accomplished through this Laboratory Directed Research and Development (LDRD) project have addressed three key areas: (1) identify those properties of interfacial water whose better scientific understanding could lead to new desalination/purification technology opportunities; (2) define the new experimental, theoretical, and simulation approaches to predictive understanding of these key properties; and (3) provide a plan that links research successes in these areas to market-based technology opportunities. Sandia’s expertise in surface science and chemistry, theory and simulation, in situ characterization, and the synthesis of well-defined porous materials and fluidic architectures has provided an opportunity to succeed in a science-based approach to engineering improved desalination membranes, urgently needed to alleviate the worldwide potable water supply crisis.
Figure 3-10. Massively parallel Sandia computing enables large-scale classical/quantum molecular simulation for transport of water through nonpores.

Roadmap Technology Area: Membrane Technologies and Alternative Technologies

Reports/Publications/Patents (and other deliverables):

Cygan et al., 2008, Exploiting Interfacial Water Properties for Desalination and Purification Applications. SAND2008-5729. (Summarized above.)


Feibelman, P.J., 2007, Comment on "Free energy of solvation of simple ions: Molecular dynamics study of solvation of Cl- and Na+ in the ice/water interface". Journal of Chemical Physics, 126, 237101.


Ockwig, N.W. et al., 2008 Molecular dynamics studies of nanoconfined water in clinoptilolite and heulandite zeolites. Physical Chemistry Chemical Physics, 10, 800-807.


**Impact:** Developing a fundamental understanding of water-membrane-contaminant interactions at the membrane-water interface holds the promise for developing revolutionary desalination and water treatment technologies (Cygan et al., 2008). This SNL-funded LDRD project represents a significant contribution to the field of surface science particularly in water-contaminant-membrane interactions at the nano- to molecular-scale.

### 3.11 Desalination of Brackish Ground Waters and Produced Waters Using In-situ Precipitation

Brackish water can be viewed as a collection of various solvated anions and cations (Pless J., et al., 2004). We have achieved the ability on this LDRD to use low cost oxides that have a preference to select the anions and cations commonly found in brackish water (Figure 3-11). This is done with minimal extra energy due to the high selectivity of the ion exchange materials. Because the ion exchangers are comprised of durable inorganic oxides they are very stable over a wide range of pH. Overall, the favorable kinetics of ion exchange enables rapid and easily implemented desalination of brackish water, to produce potable water. The anionic getter developed is Hydrotalcite (HTC) \([\text{Mg}_6\text{Al}_2(\text{OH})_{16}]^{2+}[\text{A}]^{-2}n\text{H}_2\text{O}\) where A = Cl\(^-\), Br\(^-\), I\(^-\), NO\(_3^-\), CO\(_3^{2-}\) and SO\(_4^{2-}\). The hydrotalcites synthesized provide significant anionic sequestration from brackish waters. The cationic getter developed is an amorphous silica, which provides significant cationic sequestration from brackish waters. It is similar to an aluminosilicate named Permutite, with general formula Si\(_3\)AlO\(_9\). The synthesis of these getter materials is based on inexpensive starting chemicals, which react at room temperature and precipitate relatively rapidly. The process achieves the desalination of brackish water to potable or disposable (permit-free) water by providing a process that uses a flow-through, column or settling tank systems similar to those found in municipal treatment plants. The preferred method of water treatment is first to flow the brackish water through a column containing an anion remover such as hydrotalcite, which removes monovalent ions such as chloride and nitrate, as well as divalent anions such as sulfate, and replaces them with hydroxide ion (OH\(^-\)). The water is then introduced into a column containing a cation exchanger, such as permutite that has been pretreated with acid. This column removes cations such as sodium, calcium, and magnesium, and replaces them with hydrogen (H\(^+\)) ions. The resultant water is potable, with a TDS concentration of less than 100 ppm and a pH of 5-8. Energy and cost savings result from (1) the use of our getters with current city water treatment plants, with modifications; (2) the elimination of costly RO pumping and membranes replacement/upkeep; (3) no brine product pumping/storage; (4) the ability to sell/use crystallized precipitates (building materials or infill); (5) the application inland to brine/brackish groundwater; (6) pre-treatment process for RO; (7) low capital requirements; (8) is field deployable in remote areas; and (9) can be efficiently operated at low plant capacities (< 1000 gal/day).
Roadmap Technology Area: Alternative Technologies.

Reports/Publications/Patents (and other deliverables):

Pless J., et al., 2004, Desalination of Brackish Ground Waters and Produced Waters Using In-situ Precipitation. SAND2004-3908. (Summarized above.)


Pless, J.D. et al., 2005, Structure-Property Relationship of Permutite-like Amorphous Silicates, \( \text{Na}_{x+y} \text{M}^{3+} \text{Si}_{1-x} \text{O}_{2+y} \) (\( \text{M}^{3+} = \text{Al}, \text{Mn}, \text{Fe}, \text{Y} \)), for Ion-Exchange Reactions, Chem. Mater. 2005, 17, 5101-5108.

Impact: Alternative technologies hold the promise of leapfrogging the performance of conventional RO technologies. This project demonstrated a novel technology for inland desalination of brackish waters that avoids conventional RO methods and their concomitant energy demands (Pless J., et al., 2004). It also has the potential to desalinate some of these impaired waters at cost competitive prices as compared to RO treatment (see below).

3.12 Initial Cost Analysis of a Desalination Process Utilizing Hydrotalcite and Permutite for Ion Sequestration

An LDRD focused on an initial cost analysis of the proposed of the In situ Precipitation desalination process (developed by Nenoff (as described above)) was performed (Evans and Miller 2004). The proposed process (Figure 3-12) utilizes tailored inorganic ion exchangers, hydrotalcite and permutite, to sequester anions and cations from a brackish water solution. Three different process scenarios were considered: 1) disposal of the spent exchangers as dry waste 2) conventional chemical regeneration, and 3) acid regeneration of permutite coupled with thermal (550 °C) regeneration of hydrotalcite. Disposal of the resin and conventional regeneration are not viable options from an economic standpoint. Applying limited data and optimistic assumptions to the third scenario yielded an estimate of $2.34/kgal of product water. Published values for applying conventional RO to similar water streams range from $0.70 to $2.65/kgal. Consistent with these baseline values, the Water Treatment Estimation Routine, WaTER, developed by the US Department of the Interior, BoR produced a cost estimate of $1.16/kgal for brackish water RO.
Figure 3-12. Basic flow process considered in the cost analysis of in situ precipitation desalination.

**Roadmap Technology Area:** Alternative Technologies.

**Reports/Publications/Patents (and other deliverables):**


**Impact:** This economic analysis indicates that the in-situ precipitation desalination process developed is cost competitive and in some cases less expensive than conventional RO desalination processes (Evans, L.R. and J.E. Miller, 2004).

### 3.13 Forward Osmosis: A New Approach to Water Purification and Desalination

Forward (or direct) osmosis (FO) is an emerging process for dewatering aqueous streams that might help resolve this problem (Miller and Evans, 2006). In FO, water from one solution selectively passes through a membrane to a second solution based solely on the difference in the chemical potential (concentration) of the two solutions (Figure 3-13). The process is spontaneous, and can be accomplished with very little energy expenditure. Thus, FO can be used, in effect, to exchange one solute for a different solute, specifically chosen for its chemical or physical properties. For desalination applications, the salts in the feed stream could be exchanged for an osmotic agent specifically chosen for its ease of removal, e.g. by precipitation.
Figure 3-13. Forward osmosis, the spontaneous flow of a contaminant across a membrane.

A number of approaches to osmotic agents were identified on this LDRD, several of which were explored in basic laboratory evaluations using RO membrane’s, FO specific membranes, and porous hydrophobic membranes. The approaches include agents with retrograde solubility (thermal agents), and agents that can be chemically precipitate through a small pH swing, e.g. through the addition of CO$_2$. Initial system designs were evaluated, and the data was used to develop cost estimates for using FO as a pretreatment technology (Miller and Evans, 2006). Improvements in membranes and osmotic agents are required. At its current state of development, FO will not replace RO as the most favored desalination technology, particularly for routine waters. However, a future role for FO is not out of the question. The ability to treat waters with high solids content or fouling potential is particularly attractive. Although our analysis indicates that FO is not cost effective as a pretreatment for conventional BWRO, water scarcity will likely drive societies to recover potable water from increasingly marginal resources, for example gray water and then sewage. In this context, FO may be an attractive pretreatment alternative.

**Roadmap Technology Area**: Alternative Technologies.

**Reports/Publications/Patents (and other deliverables):**


**Impact**: This technology review concluded that in current state of development, FO will not replace RO as the most favored desalination technology (Miller J.E. and L.R. Evans, 2006). To move the technology forward, continued improvement and optimization of membranes is recommended. The identification of optimal osmotic agents for different applications is also recommended as it is clear that the space of potential agents and recovery processes has not been fully explored.
3.14 UV Ultraviolet Water Purification Systems for Rural Environments and Mobile Applications

The focus of this one-year LDRD project was to explore UV water purification systems concepts that would take advantage of the cost, size, robustness, and energy saving potential of this emerging solid-state deep UV light emitting diode LED technology (Crawford et al., 2005). This LDRD project had three major tasks. The first task was to perform an assessment of rural and international UV water purification systems including design considerations for an LED based system. The second task was to perform an assessment of mobile, point-of-use UV purification systems, once again including designs considerations for an LED-based system. The third task was to perform UV inactivation studies of E. coli contaminated water samples using SNL-developed deep UV LEDs. This task required the additional parallel efforts of optimizing the deep UV LED performance for water purification as well as developing an optical system for delivering relatively uniform UV light to the water sample. Recognizing the relatively low output powers of deep UV LEDs at this early stage of development, the purpose in this task was to perform proof-of-concept experiments (Figure 3-14) to evaluate the effectiveness of UV LEDs in E. coli inactivation, and to reveal the distinctive benefits and challenges in the application of solid-state LEDs to water purification. The ultimate goal of this project is to combine the results of applications assessments and experimental studies to provide a recommended technical path for potential follow-on programs that would seek to realize an LED-based water purification system.

Figure 3-14. SNL developed experimental test apparatus to assess UV LED performance for water purification.

The research identified several potential advantages of employing LEDs over lamp based systems, including potential for longer lifetimes of the UV sources (LEDs) before replacement and the ability to include more frequent on-off cycles in the overall design (Crawford et al., 2005). These benefits are related to lower life-cycle costs, more reliable designs and overall sustainability of the complete water purification solution (purifier + energy source). We further evaluated systems design issues for compact, PV-powered water purification systems for mobile and/or military environments. Increased durability when used with intermittent power sources such as PV, integratability, and mechanical robustness were identified as beneficial attributes of LEDs over lamps. We further estimated that achieving a wallplug efficiency of approximately 10% for 265 nm LEDs would be a reasonable performance goal to impact mobile/military water purification applications.
Given the clear potential benefits that were identified for LED-based water purification systems, a remaining task was to evaluate what state-of-the-art deep UV LEDs are capable of at this early stage of development (Crawford et al., 2005). Work in this area consisted of development efforts to specifically optimize LED performance for water purification. Toward that end, a significant increase (~8X) in output power of 270 nm LEDs; a wavelength that can provide ~95% germicidal effectiveness was demonstrated. Some of the optical challenges of collecting and uniformly distributing UV light from small area LED arrays, and designed a beam collimation set up for improving the spatial uniformity of light from a multi-element LED array were identified. We applied this collimation set up to the demonstration of E. coli inactivation using 270-295 nm LEDs. While it was demonstrated that between 99.0 and 99.9999% E. coli inactivation from SNL-developed deep UV LEDs could be achieved, the required exposure times on the order of 10 minutes revealed that single pass exposures from small LED arrays are not practical for the majority of water purification scenarios.

**Roadmap Technology Area:** Alternative Technologies.

**Reports/Publications/Patents (and other deliverables):**


**Impact:** This project, identified the potential benefits for the use of deep UV LED-based water purification systems for E. coli inactivation (Crawford M., et al., 2005). However, the long exposure times required make our small led arrays impractical for most water purification systems. This SAND report is well cited having received 35 citations.

### 3.15 Optimized Coagulant Chemistry for Water Treatment

This project focused on optimizing water treatment coagulants (Figure 3-15) for contaminant removal, especially pathogens (Nyman et al., 2008). The first portion of the project, focused on making hybrid precipitates composed of anionic inorganic clusters-cationic amphiphiles or cationic inorganic clusters-anionic amphiphiles. These are hydrophobic precipitates that are very effective in enmeshing contaminants upon precipitation; and their efficacy is related to the size of colloid formed in solution, as well as their insolubility. The second half of this project was focused on understanding the efficacy of aluminum-based coagulants and optimizing them for field-based conditions. The substitution of 7.6% of the aluminum on a per-mol basis with gallium resulted in improved water treatment performance, and substitution of 7.6% of the aluminum with germanium resulted in decreased performance. These results enable a mechanism for contaminant removal via coagulation to be determined. Furthermore, we have discovered an optimized aluminum coagulant that performs optimally for water clarification tests including dissolved organic contaminant removal, residual aluminum content, and removal of bacteria and viruses.
Figure 3-15. Chemical structure of gallium-substituted alumina keggin ion coagulant developed by Sandia for contaminant removal.

Roadmap Technology Area: Membrane Technologies.

Reports/Publications/Patents (and other deliverables):

Nyman M.D. et al., 2008, Optimized Coagulant Chemistry for Water Treatment. SAND2008-6230. (Summarized above.)

Stewart, T. et al., 2009 Enhanced Water Purification: A Single Atom Makes a Difference, Environmental Science and Technology, 43, 5416-5422


Impact: On this project, a next-generation coagulant for the removal of removal of bacteria and viruses was developed and patented (Nyman, M.D, and T.A. Stewart, 2012). This was accomplished through the chemical optimization of traditional aluminum-based coagulants. Continued testing and piloting of the coagulant is warranted as is a cost analysis and performance comparison of Ga-based coagulants to traditional aluminum-based coagulants.

3.16 Membranes and Surfaces Nano-engineered for Pathogen Capture and Destruction

This project focused on the fundamentals of capturing water-borne pathogens on a surface (Figure 3-16) followed by their destruction by photocatalytic processes (Nyman and Stewart, 2011). Microbiological pathogens, viruses and bacteria in particular, are of great concern in municipal and at-the-source water supplies. Filtration remains a common method of choice for water treatment for both municipal plants and at the source or home treatment, given the ease of use, rapid treatment rate, and re-usability filter media (thus reduced cost). However, size-exclusion filtration is challenging for small pathogens such as viruses. Therefore, filtration by chemical affinity is an attractive option. Furthermore, self-cleaning membranes or surfaces are particularly attractive for water treatment technologies, in that biofouling is a considerable challenge. Finally, the ability to clean filtration media extends its use and lifetime.

Three general themes were explored on this project: 1) Screening chemical surface modifiers for pathogen capture, 2) Developing photocatalysts and 3) Combining both on surfaces to demonstrate capture followed by photocatalytic destruction (Nyman and Stewart, 2011). Pathogen capture was done most effectively by inorganic polycations, similar to active ingredients in coagulation reagents for water treatment. Furthermore, they offered photodegradation resistance, which is problematic for comparably effective organic functional groups. We identified delaminated titanates as effective photocatalysts that could be readily
attached to surfaces. Furthermore, we developed a cheap and time-effective method of synthesizing delaminated titanates. Combined on a surface, these showed synergistic functionality of capturing bacteriophage, followed by photocatalytic destruction.

This study showed that we can functionalize ideal surfaces with 1) chemical species that bind microorganisms and 2) photocatalysts that are of ideal geometry (flat) and chemistry (anionic) for compatibility with the binding chemical species (Nyman and Stewart, 2011). We determined that a high cationic charge is important for adsorbing the microorganisms by chemical affinity (rather than settling or some other physical mechanism). Hydrophobicity is also potentially important, but it can degrade under UV-irradiation for photocatalysis. Future work in this thrust may involve functionalizing membranes for water filtration, to improve filtration beyond size exclusion, into the chemical affinity realm. In addition, the titanate layers alone may also be useful for antifouling; which is one of the biggest challenges of water treatment by filtration.

![Image](Figure 3-16. Illustration depicting chemical modification of a membrane surface for pathogen capture.)

**Roadmap Technology Area:** Membrane Technologies.

**Reports/Publications/Patents (and other deliverables):**


Stewart, T. et al., 2011, Delaminated titanate and peroxotitanate photocatalysts, Applied Catalysis B: Environmental, 105, 69-76.

**Impact:** This project studied the fundamentals of capturing water-borne pathogens on a surface, and enabling their destruction by photocatalytic processes (Nyman, M.D. and T. Stewart, 2011). Future work should involve research focused on functionalizing membranes for water filtration to enable pathogen destruction.
4 ARSENIC

4.1 Arsenic Water Technology Partnership

In January of 2006, the US Environmental Protection Agency (EPA) lowered the maximum contaminant level (MCL) of arsenic from 50 parts per billion (ppb) to 10 ppb. The Arsenic Water Technology Partnership (AWTP) (Figure 4-1) led a multi-year program funded by a congressional appropriation through the DOE EM to develop and test innovative technologies that have the potential to reduce the costs of arsenic removal from drinking water. The AWTP members included SNL, the American Water Works Association Research Foundation (AwwARF) and Waste Management Education and Research Consortium (WERC). The program was designed to move technologies from bench-scale tests to field demonstrations. The AwwARF managed bench-scale research programs; SNL conducted the pilot demonstration program and WERC evaluated the economic feasibility of the technologies investigated and conduct technology transfer activities.

![Figure 4-1. The Arsenic Water Technology Partnership.](image)

Arsenic Treatment Technology Vendors Forum

From 2004 to 2006 SNL sponsored the Arsenic Water Treatment Technology Vendors Forum and Theme Session as part of the annual New Mexico Environmental Health Conference (Everett, et al., 2006). The Forum has attracted standing-room-only audiences by providing attendees the opportunity to hear presentations describing cutting-edge, commercially available, or soon-to-be-available technologies given by representatives from large water treatment companies, smaller research and development firms, and universities.

Sandia assembled Technical Evaluation Teams comprised of recognized experts in water treatment technology that were drawn from the commercial, regulatory, and academic sectors (Everett et al., 2006). At a closed session after the open Forum, the commercial technologies were evaluated for possible use in pilot demonstrations conducted by SNL at community sites. The technologies were evaluated in six categories: (1) performance, (2) level of maturity and viability of the company, (3) costs, (4) implementability (i.e., regulatory acceptance), (5) effects on the user community, and (6) degree of innovation. Of the 27 vendors that have participated in the Forums, 10 became involved in Sandia Pilot demonstration studies as part of the AWTP.
Reports/Publications/Patents (and other deliverables):


**Impact:** The AWTP Vendors Forum and its summary report described the results of the technology evaluations provide information useful to these communities and also establish an objective and defensible basis for selection of technologies for pilot testing by SNL in the AWTP (Everett, R.L., et al., 2006). The Forum provided small research and development firms exposure to a larger audience that they normally would not encounter, along with the opportunity to demonstrate their technology in a program with a national scope.

### 4.2 Comprehensive Arsenic Tool (CoAsT)

Implementation of the Arsenic Rule will cost some communities a great deal. Choosing the wrong technology could cost more. WERC developed an online tool to help to narrow options for community representatives to choose from.

The Comprehensive Arsenic Tool (CoAsT) was a free, user-friendly, web-based interactive tool that integrates “arsenic decision tools.” The CoAsT is geared toward small communities, decision-makers and design engineers, and uses decision trees, cost models, a rate-setting tool and living documentation to answer the following questions:

- What is the optimal arsenic removal technology, and how will this technology perform compared to other technologies?
- How much does the technology cost?
- How do we pay for it?
- Where can I get support information?

According to WERC News, March 2006 issue 3/4, the ‘Living Document/State-of-Science’ includes general information about arsenic in drinking water, arsenic chemistry, health effects, federal and state(s) regulatory information, etc. The decision trees address mitigation strategies or treatment minimization, pre-oxidation processes, enhancement of existing treatment processes and the addition of new treatment technologies. The user inputs utility-specific data and preferences, and then applies the trees iteratively. Three cost models were included: the American Water Works Association Research Foundation (AwwaRF) model, the ARCE (EPA Cost) model and, the U.S. EPA Multiple Technologies model. Once an appropriate technology has been identified using the decision trees and evaluated using one of more of the cost models, the rate tool, a converted Excel-based spreadsheet used by the Rural Community Assistance Corporation (RCAC), can be applied to estimate a cost per user connection.

**Roadmap Technology Area:** Institutional Issues

**Key Deliverables:** CoAsT was an online tool that was made available: [http://www.arsenicpartners.org](http://www.arsenicpartners.org). It should be noted that this website no longer hosts the tool.

**Impact:** CoAsT is an enabling tool to allow water resource managers to better allocate and conserve water. It also serves as a resource to walk city managers and interested stakeholders
through the financial, water quality, and waste disposal considerations that are involved in implementing desalination at the community level.

### 4.3 Rapid Small Scale Column Testing

The ability to rapidly evaluate As adsorbent media is necessary to evaluate the effect of water quality and design parameters on media performance. The rapid small scale column testing (RSSCT) procedure (Figure 4-2) is a quick and low-cost method to efficiently determine As sorption characteristics of large-scale fixed-bed adsorbers using small column experiments. The method uses adsorption theory and mass transfer models to develop scaling relationships that allow the correlation of small column tests at accelerated flow rates to assess full-scale column performance. In other words, the small scale tests are based on scaling factors that maintain the similitude between a bench-scale column test and a full-scale treatment column. Thus, these short duration bench tests effectively simulate the performance of full-scale fixed-bed adsorbers in treatment facilities.

![Figure 4-2. Rapid small-scale column testing for arsenic removal using iron-oxide based adsorption media.](image)

**Reports/Publications/Patents (and other deliverables):**

No reports, publications or patents have been located for this project.

**Impact:** The RSSCT testing adopted by SNL enabled rapid and low cost assessments of the performance As sorption media (Patrick Brady, personal communication, 2016). Another advantage of RSSCT is that the results can be used to predict the performance of media in full-scale systems. Results from media testing guided the selection of media for the As field demonstration pilots described below.

### 4.4 Sandia Arsenic Pilot Demonstration Program

Sandia conducted pilot scale evaluations of the performance and cost of innovative drinking water treatment technologies aimed at meeting the new arsenic MCL of 10 μg/L. A total of 5 pilot evaluations were conducted at the following sites: Anthony, New Mexico; Jemez Pueblo, NM; Rio Rancho, NM; Socorro Springs, NM; and Weatherford, Oklahoma.

**Impact:** The results of these pilots (described below) defined both a cost and performance envelope for the various treatment options available to communities faced with implementing As treatment technologies to meet the new drinking water standard.

#### 4.4.1 Sandia Arsenic Pilot Test Demonstration Program – Anthony, New Mexico

As part of the AWTP program, a pilot demonstration project was conducted in Anthony, New Mexico between August 2005 and December 2006 at Desert Sands Mutual Domestic Water Consumers Association (Desert Sands) Well #3 (Figure 4-3). The site was chosen for its difficult
water chemistry and because it is the site of a full-scale Environment Protection Agency pilot demonstration. The arsenic in this water is almost all arsenic (III), which is difficult to remove if it’s not first oxidized to arsenic (V). Other challenging characteristics in this water source include its high TDS and iron.

The pilot was completed in 4 phases with a comparison of a total 13 commercially available media in the ambient pH water at the Desert Sands site. In addition, Sandia developed Specific Anion Nanoengineered Sorbents (SANS) was evaluated along with the commercial media. The goal is to provide the Desert Sands community with information that will help them select a new treatment material because the system installed during the EPA pilot has not proved to be a reliable or cost-effective means for arsenic removal. With an estimated media life of 56,000-66,000 bed volumes (BV) of water treated to 10 ppb, AdEdge E33, a granular ferric oxide material, outperforms all other media. SANS was the fourth best performer in terms of volumetric capacity with an estimated media life of 34,000 BVs of water treated to 10 ppb.

Figure 4-3. Sandia engineer Malynda Aragon is shown training student sampler Pedro Gutierrez at the Desert Sands Demonstration for arsenic treatment.

Reports/Publications/Patents (and other deliverables):

Aragon, M., et al., 2007 Arsenic Pilot Plant Operation and Results- Anthony, New Mexico SAND2007-6059. (Summarized above.)

4.4.2 Sandia Arsenic Pilot Test Demonstration Program – Jemez Pueblo, New Mexico

As part of the AWTP program, a pilot demonstration project was conducted at the Jemez Pueblo, New Mexico. Sandia tested four separate coagulation-assisted direct filtration systems (Blue Water Technology, Hungerford & Terry, Kinetico, and Orca) and compared to performance of full scale system. All four pilot units removed As below the MCL of 10 ppb and also removed Fe below the MCL of 0.3 ppm.

4.4.3 Sandia Arsenic Pilot Test Demonstration Program – Rio Rancho, New Mexico

As a member of the AWTP, SNL carried out Phase 1 pilot demonstration activities at Rio Rancho, New Mexico (Cappelle et al., 2007). Rio Rancho Well #21 was chosen for its water quality characteristics of high pH and vanadium, both of which can impact arsenic removal media effectiveness.
In Phase I, six different arsenic adsorption media were tested side-by-side in the same chlorinated feedwater. These media included two iron oxyhydroxides (Adedge E-33 and Kemiron CFH-10), two resins with active metal oxide surfaces or nanoparticles (Purolite AresnX and Resin Tech ASM-10HP), one zirconium oxide (MEI Isolux 302M), and one titanium oxide (Dow Adsorbia GTO). The Adedge E-33 outperformed all other materials tested.

In Phase II, nine arsenic adsorption media were tested side-by-side. In addition to the media tested in Phase I, a modified silicate (ADA Am. Si.), a bone char (Brimac Bone Char) and a SNL-developed granular iron/copper oxide (SANS) were added to the pilot. Again Adedge E-33 outperformed all other materials tested while SNL’s SANS was the third best performer in terms of number of BVs to 10 ppb.

**Reports/Publications/Patents (and other deliverables):**

Cappelle, M.J. et al., 2007, Arsenic Pilot Plant Operation and Results- Rio Rancho, New Mexico. SAND2007-2452. (Summarized above.)

4.4.4 Sandia Arsenic Pilot Test Demonstration Program – Socorro Springs, New Mexico

As part of the AWTP program, SNL completed a phase I pilot demonstration project (Figure and initiated a phase II pilot at Socorro, New Mexico (Figure 4-4) (Aragon et al., 2007). The Sedillo and Socorro Springs, which are the sources of water for the Socorro pilot demonstration, have been flowing at 500 gallons per minute for many years. This is a very inexpensive source of water for the city of Socorro. The springs have an average As concentration of 42 ppb. Cost-effective arsenic removal strategies will allow for continued use of this resource. In addition to its As content, the Socorro Springs site was chosen for its high temperature water, which is also high in silica and pH, all of which can significantly impact arsenic removal efficiency. Cost-effective arsenic removal strategies will allow for continued use of this resource.

In Phase 1, five different media were tested in the ambient pH water at the Socorro Springs site. The media tested included: 1) Granular Ferric Oxide Adedge E-33, 2) Granular Ferric Oxide Englehard Corporation ARM 200, 3) Granular Titanium Oxide Hydrglobe Metsorb, 4) Nanoparticle Zirconium Oxide MEI Isolux 302M, 5) Iron Impregnated Resin Purolite ArsenXnp. For the pilot tests, the values of BVs and capacity at 10 ppb (10 μg/L) arsenic show a fairly consistent relationship between the media: Adedge E33 >Isolux 302M ~ > Metsorb > ARM 200.

In Phase 2, the same five media were tested in pH-adjusted water and in ambient pH water to focus on the effect of lowered pH. In previous work (Phase I) lower pH was shown to increase the capacity of arsenic-removal media in Phase. In addition to the five commercial media, SNL developed SANS, was also pilot-tested in this phase. Preliminary results indicated that, as expected, all the media performed significantly better in the pH adjusted water with Isolux 302M, Metasorb and ArsenXnp showing the highest capacity.
4.4.5 Sandia Arsenic Pilot Test Demonstration Program – Weatherford, Oklahoma

As part of the AWTP program, a pilot evaluation was conducted at Well #30 of the City of Weatherford, Oklahoma, which supplies drinking water to a population of more than 10,400 (Ahora et al., 2007). Well water contained arsenic in the range of 16 to 29 ppb during the study. Four commercially available adsorption media were evaluated side-by-side for a period of three months. The selected adsorption media included ADSORBSIA TM GTO TM manufactured by DOW Chemical, npRio by SolmeteX, Kemira CFH0818 by Kemira Water Solutions and E33 by AdEdge. For the coagulation/filtration study, ferric chloride was used as the coagulant and anthracite media was used for filtration.

Both adsorption and coagulation/filtration effectively reduced arsenic from Well #30. Based on BVs treated corresponding to an effluent arsenic concentration of 10 ppb, AdEdge E33 performed the best, followed by ADSORBSIA TM GTO TM, Kemira CFH0818 and npRio. A preliminary economic analysis indicated that adsorption using an iron oxide media (E33) was more cost effective than the coagulation/ filtration technology.

Reports/Publications/Patents (and other deliverables):

Ahora, H., et al., 2007, Arsenic Pilot Plant Operation and Results-Weatherford, Oklahoma, SAND2007-2540. (Summarized above.)

4.4.6 Kirtland Field Trial Studies

This field trial program was carried out at Well #15 located at Kirtland Air Force Base, Albuquerque, New Mexico, to evaluate the performance of two relatively new arsenic removal media, ALCAN-AASF50 (ferric coated activated alumina) and granular ferric hydroxide (US Filter-GFH) (Kahndaker et al., 2005). This program showed that both media were able to remove arsenate and meet the new total arsenic MCL in drinking water of 10 µg/L.
The arsenate removal capacity was defined at a breakthrough effluent concentration of 5 µg/L arsenic which is 50% of the arsenic MCL of 10 µg/L (Kahndaker et al., 2005). At an influent pH of 8.1 ±0.4, the arsenate removal capacity of AASF50 was 33.5 mg As(V)/L of dry media (29.9 µg As(V)/g of media on a dry basis). At an influent pH of 7.2 ±0.3, the arsenate removal capacity of GFH was 155 mg As(V)/L of wet media (286 µg As(V)/g of media on a dry basis). Silicate, fluoride, and bicarbonate ions are removed by ALCAN AASF50. Chloride, nitrate, and sulfate ions were not removed by AASF50. The GFH media also removed silicate and bicarbonate ions; however, it did not remove fluoride, chloride, nitrate, and sulfate ions. Differences in the media performance partly reflect the variations in the feed-water pH between the 2 tests. Both the exhausted AASF50 and GFH media passed the Toxicity Characteristic Leaching Procedure test with respect to arsenic and therefore could be disposed as nonhazardous waste.

Reports/Publications/Patents (and other deliverables):

Khandaker, N. et al., 2005, Performance Evaluation of ALCAN-AASF50-Ferric Coated Activated Alumina and Granular Ferric Hydroxide (GFH) for Arsenic Removal in the Presence of Competitive Ions in an Active Well: Kirtland Field Trial–Initial Studies SAND2005-7693. (Summarized above.)

4.5 Rural Arsenic Outreach Program

Because of the reduction in the As MCL, many water systems in New Mexico faced a decision regarding how to reduce the arsenic level in their drinking water (Krumhansl, et al., 2006). To assist these systems, there are a wide range of programs available that include technical assistance, funding, and research. The technical assistance efforts include SNL’s Rural Arsenic Outreach Program, funded by the DOE, includes the Environmental Finance Center at New Mexico Tech, and UNM. This program was set up to address the specific needs of smaller communities who will have the greatest difficulties in complying with the standard. There are a variety of funding sources for arsenic treatment. Research is being conducted by EPA, SNL and others to develop more effective solutions and to test existing technologies under New Mexico-specific conditions.

A document was developed to assist systems in continuing to address their needs past the end of the program. The document provides a summary of resources that target the particular needs of the smallest water systems impacted by the new arsenic regulations (generally less than 500 connections). The document emphasizes treatment systems and technologies that are currently commercially available and could be purchased (or designed for) immediately.

In addition, a publication entitled ARSENIC REMOVAL FROM DRINKING WATER: A HANDBOOK FOR COMMUNITIES was compiled (Khandaker et al., 2009). This handbook (Figure 4-5) provides critical review the important features of arsenic removal technologies; where technologies work, and where they won’t. In addition, the handbook outlines arsenic chemistry and the sampling procedures that are critical to successful arsenic removal strategies.
4.6 Development of Novel Arsenic Treatment Approaches

The lowering of the As drinking water standard has prompted a search for cheaper, more effective As removal approaches. On this project a series of As removal technologies were developed from a comprehensive analysis of the chemical controls over As uptake by solids and are collectively referred to as Specific Anionic Nanoengineered Sorbent (SANS) (Figure 4-6). Specifically, Cu and Zn additives to Fe hydroxide were found to substantially enhance its performance and led to the development of SANS materials. The product can be manufactured in four different forms: (1) Granular SANS which is a new filter media possessing higher uptake capacity for As than industry standards; (2) the addition of Cu and Zn enhances lime softening leading to effective coagulation removal of As; and (3) In Situ-SANS which is a new approach for lowering As levels in situ in an aquifer; and (4) Coagulation SANS which entails the addition of Cu and Zn to an Fe-oxide flocculant to enhance coagulation removal of As. The uses for SANS include the treatment of drinking water, industrial waste water, and groundwater. In addition, SANS can also be used for sludge stabilization.
Figure 4-6. Molecular simulation of arsenate sorbing to Sandia’s novel sorbent media known as Specific Anionic Nanoengineered Sorbent (SANS).

Reports/Publications/Patents (and other deliverables):


Impact: The technologies developed and patented on this project focused on low cost As removal media and in situ treatment strategies as well as inexpensive easy-to-deploy treatment systems to meet the needs of small rural communities nationwide.

4.7 Novel Approaches for Arsenic Removal from Water

Magnesium hydroxide (Mg(0H)₂) is a very strong sorbent (Figure 4-7) for arsenic in both the +3 and +5 oxidation states (Moore et al., 2002). However, one problem with using Mg(0H)₂ in water treatment is its reaction with carbonate in water to form MgCO₃ which does not sorb arsenic. This problem has been eliminated by stabilizing the Mg(OH)₂ as a Sorrel’s cement. Sorrel’s cements are composed of MgCl₂ with Mg(OH)* in a polymerized form. Additionally, a new sorbent based on zirconium has been developed for arsenic sorption. Zirconium is an environmentally benign material found in many common products such as toothpaste. It is currently used in water treatment and is very inexpensive. In this work, zirconium has been bonded to activated carbon, zeolites, sand and montmorillonite. Because of its high charge in ionic form (+6), zirconium is a strong sorbent for many anions including arsenic.
Figure 4-7. Sorption of arsenic (V) as a function of time showing rapid uptake of arsenic by magnesium hydroxide.

Reports/Publications/Patents (and other deliverables):

Moore R.C. et al., 2002, Sorption of Arsenic from Drinking Water to Mg(OH)₂, Sorrels cements and Zirconium Doped Materials. SAND2002-3641. (Summarized above.)


Impact: The technologies developed and patented on this project resulted in low cost materials for As remediation.

4.8 Investigation of Potential Applications of Self-Assembled Nanostructured Materials in Nuclear Waste Management

Successful waste and environmental management requires technology innovation to address challenging technical problems (Wang et al., 2003). One element of this technology innovation effort is the development of functional materials (Figure 4-8) that can be used for effective waste treatment, separation, containment, and monitoring of anionic contaminants. For example, there is increasing concern with pertechnetate (TcO₄⁻) in radioactive wastes and arsenate (AsO₄³⁻) contamination in groundwater. The objectives of this project were to (1) provide a mechanistic understanding of the control of nanometer-scale structures on the ion sorption capability of materials and (2) develop engineering approaches to improving material properties based on such an understanding. The project has been focused on developing and evaluating two types of nanostructured materials: self-assembled mesoporous materials (Figure 4-8) and layered double hydroxides.
While the primary focus was on the development of getters for radionuclides that speciate as oxyanions, e.g. TcO$_4^-$, the effectiveness of the self-assembled mesoporous materials and layered double hydroxides to getter arsenate was also assessed. Both materials demonstrated a high affinity for arsenate. However, double hydroxides have showed the most promise for the removal of anionic contaminants.

**Reports/Publications/Patents (and other deliverables):**

Wang, Y. et al., 2003, Potential Applications of Nanostructured Materials in Nuclear Waste Management. SAND2003-3313. (Summarized above.)


**Impact:** The technologies developed and patented on this project focused low cost materials for the treatment of radionuclides that speciate as oxyanions (Wang, Y. et al., 2003). In addition, they show considerable promise for As remediation.
5 NMSBA WATER TREATMENT PROJECTS

This section summarizes three water treatment projects performed at the behest of New Mexico small businesses through the New Mexico Small Business Assistance (NMSBA) Program.

5.1 Enhanced Water Treatment to Remove Hydrogen Sulfide from Oil Field Produced Water

A significant amount of water is produced from oil wells in the United States. Typically, these wells are older wells that produce approximately 8-10 barrels of water for every barrel of oil. Produced water is typically disposed of by deep aquifer injection or via an evaporation pond. Both solutions are expensive and result in the loss of water that can be otherwise be reclaimed for use industrially, agriculturally, or domestically. Treated produced water is potentially a new source of water and enhanced treatment systems will enable greater access to this new source of water.

Frequently, produced water from oil and gas wells contains a significant amount of hydrocarbons and in some cases a high amount of dissolved hydrogen sulfide gas (H$_2$S). This project was aimed at increasing water recovery from oil and gas produced water treatment membrane systems by removing H$_2$S and hydrocarbons to enhance water production and improve the life expectancy of membranes used in this very aggressive environment (Figure 5-1). By enhancing water recovery from oil and gas operations, new water is produced, and expensive disposal requirements are avoided.

![Figure 5-1. Schematic diagram of an improved produced water treatment system to remove H2S.](image)

Sandia worked with Western Environmental (WE) a small New Mexico engineering firm that has actively been testing a well-head desalination pilot plant. Sandia funded the project jointly with the State of New Mexico to address membrane fouling by sulfide. Tests were conducted by SNL and WE at an operating desalination pilot plant for produced water at a natural gas well in Eddy County near Carlsbad, New Mexico. This pilot plant consisted of a novel hydrophilic ultrafiltration (UF) unit that removes hydrocarbons that are entrained in the gas-well produced water. This is a major step forward, but it leaves other membrane fouling chemicals in the water after the UF step. Hydrogen sulfide (H$_2$S) and low molecular weight hydrocarbons like benzene and toluene pass through the UF unit and cause fouling of the subsequent NF membranes. Sandia collaborated with WE to develop a hydrocarbon/H$_2$S stripping process to reduce fouling on the NF membranes in order to enhance the recovery of fresh water from the gas-well water.
Roadmap Technology Area: Membrane Technologies

Reports/Publications/Patents (and other deliverables):
No reports, papers or patents have been located on this project.

Impact: Treated produced water is potentially a new source of water and enhanced treatment systems will enable greater access to this new source of water. This project focused on treating produced water to enable fresh water recovery. The combination of NF with H₂S tripping process was very effective at removing salts, hydrocarbons and H₂S to produce fresh water. However, an analysis determined that the process was not economic and therefore was never commercialized by WE (Scott Bierle, WE, personal communication, 2016).

5.2 Produced Water Desalination Pilot San Juan Basin, New Mexico,

The extraction of natural gas from coal-seam beds, results in the co-production of a considerable amount of brackish water (water quality can range up to 60,000 mg/L TDS or higher) (Cappelle et al., 2008a). This produced water can create environmental problems if untreated and is typically disposed of via injection wells or other disposal methods. The cost for hauling and disposing of produced water can be significant and could restrict the production of natural gas from coal beds. Partnering with ConocoPhillips, Biosphere Environmental, NMSU, and the US Department of Agriculture, SNL performed pilot desalination studies at a CBNG site (Figure 5-2) in the Four Corners Area near Navajo Dam, NM. In this project, the produced water from the CBNG wells was desalinated to less than 1,000 mg/L TDS. Over three field seasons, both treated and untreated produced water were then applied (spot irrigation) to the existing rangeland grasses at two adjacent plots on the well/pad site. A third plot received natural rainfall and was compared to the plots receiving treated and untreated produced water.

The CBNG produced water desalination pilot operation in the fall of 2007 and 2008 effectively demonstrated a proof of concept for low energy RO treatment of the water. The influent water quality (TOC, turbidity, and iron levels) varied throughout the pilot operation. However, using RO membranes in sub-optimal conditions (high fouling-tendency, single membrane), good quality water was produced for the rangeland/riparian improvement study. In 2009, the primary goal was to evaluate the potential of NF as a desalination technique. A treatment system with granulated activated carbon (GAC) and ultrafiltration (UF) cartridges was used in front of a NF membrane and as a result excellent NF permeate quality was obtained. In fact, results showed a water quality close to RO permeate with significantly lower pressures (lower energy).
The three plots of land were compared: (1) natural rainfall only no additional water added, (2) untreated produced water, and (3) treated produced water. A comparison of the three plots demonstrated: 1) the untreated water didn’t harm growth substantially and 2) the treated water allowed for some increased growth (as compared to the natural rainfall control). An area that was inadvertently exposed to a mixture of treated and untreated water appeared to have the best results suggesting a mixture of the two waters may be optimal for plant life at this well pad.

**Roadmap Technology Area:** Membrane Technologies.

**Reports/Publications/Patents (and other deliverables):**

Cappelle, M.J. et al., 2008a, Coal Bed Natural Gas Produced Water Preliminary Pilot Plant Operation and Results. SAND2008-4824. (Summarized above.)


**Impact:** Treat-to-need approaches can reduce the energy demand and cost for desalination and water treatment of produced water (Cappelle, M.J. et al., 2008a). Using a lower energy desalination approach with NF membranes as opposed to conventional RO membranes, the team successfully demonstrated that treated produced water could be used for watering rangeland vegetation at a cost that is competitive with conventional produced water disposal methods.

### 5.3 Membrane Distillation Project for Water Energy Nexus (WEN) Engineering Co.

In 2013 the New Mexico Small Business Association asked SNL to help WEN Engineering Co. to develop a physics model for utilizing a membrane distillation process to treat power plant cooling water (Figure 5-3). A major disadvantage of MD is in its propensity to lose heat needed to drive the distillation process across very thin membranes. WEN’s premise is that this disadvantage of a membrane distillation process could be turned into an advantage by inserting the MD process into a power plant’s cooling water loop. Since a cooling water loop needs to lose heat as well as create makeup water for cooling towers, a cooling process incorporating membranes might work to everyone’s advantage.
Figure 5-3. Conceptualization for using waste heat to drive membrane distillation water treatment.

Roadmap Technology Area: Alternative Technologies.

Reports/Publications/Patents (and other deliverables):

One patent application is pending.

Impact: The NMSBA was successful by demonstrating the feasibility of inserting the MD process into a power plant’s cooling water loop. WEN is pursuing a proposed pilot at the Red Hawk coal fired power plant in Arizona to demonstrate the concept (personal communication, Charles Morrow, 2016).
6 OTHER WATER TREATMENT PROJECTS

The following is a summary of water treatment projects funded by customers after the earmark funds were exhausted. These projects took place in the 2011-2012 timeframe.

6.1 Silica Removal for NETL

Better silica control methods are needed to treat impaired waters and enable their use for power plant cooling, steam production, and drinking water (Brady, et al., 2011). Many impaired waters, (e.g. saline ground waters and waste waters) contain high dissolved silica levels and can form silica scale if concentrated. Once formed, silica scale is resistant to most forms of chemical attack (e.g. acid washing) and far harder to remove from towers, boilers, and membranes than other mineral scales.

Lowering the pH of impaired waters using power plant flue gas CO$_2$ slows the polymerization of silica and formation of silica scale (Figure 6-1) (Brady et al., 2011). Experimental studies show that lowering the pH of solutions containing 200 ppm silica prevents scale formation for over 300 h. While silica scale forms most quickly near a pH of 8, solutions with pH in the range of 3.6–3.7 can maintain silica levels of 1,000–3,000 ppm for roughly 90 h. Membrane testing showed that silica scale formation lag times of approximately 72 h were achievable after lowering the pH to 4.5–4.7. This has the potential to allow the flushing of silica-laden solutions through flow reversal before scale formation occurs during water treatment.

Roadmap Technology Area: Concentrate Management.

Reports/Publications/Patents (and other deliverables):

Brady, P.V. et al., 2011, Flue Gas Injection Control of Silica in Cooling Towers. SAND2011-2859. (Summarized above.)

Brady, P.V. et al., 2013, pH modification for silica control, Desalination and Water Treatment, 51, DOI:10.1080/19443994.2013.76690 [SAND2012-9464 P]


Impact: Power plant cooling towers typically concentrate dissolved solids 3 to 10-fold from feedwater, but in theory might achieve greater water reuse and lower blowdown disposal outlays with
more extensive silica scale prevention (Brady et al, 2011). This project demonstrated that lowering solution pH using power plant flue gas CO\textsubscript{2} slows the polymerization of silica and formation of silica scale and enables increased water use efficiency.

6.2 Coagulation Chemistries for Silica Removal from Cooling Tower Water for NETL

The formation of silica scale is a problem for thermoelectric power generating facilities. This study investigated the potential for removal of silica by means of chemical coagulation from source water before it is subjected to mineral concentration in cooling towers (Stewart et al., 2011). In the first phase of this study, a screening of many typical (as well as novel) coagulants was carried out using concentrated cooling tower water (Figure 6-2), with and without flocculation aids, at concentrations typical for water purification with limited results. Next, it was decided that treatment of source or make-up water was more appropriate and that higher dosing with coagulants delivered promising results. In fact, the less exotic coagulants proved to be more efficacious for reasons not yet fully determined. Some analysis was made of the molecular nature of the precipitated floc, which may aid in process improvements. In the third phase of this study, the process conditions for aluminum chloride coagulation were evaluated. Lime-soda water softening and the precipitation of magnesium hydroxide were shown to be too limited in terms of effectiveness, speed, and energy consumption to be considered further for the present application. In Phase IV of this study, sodium aluminate emerged as an effective coagulant for silica, and the most attractive of those tested to date because of its availability, ease of use, and low requirement for additional chemicals. Some process optimization was performed for coagulant concentration and operational pH. It was concluded that silica coagulation with simple aluminum-based agents is effective, simple, and compatible with other industrial processes.

Figure 6-2. Flocculation by polyaluminum coagulant in flasks, immediately after (left) and 20 minutes after (right) the end of stirring, showing rapid settling of the floc and water clarity.
Roadmap Technology Area: Concentrate management.

Reports/Publications/Patents (and other deliverables):

Stewart T., et al., 2011 Coagulation Chemistries for Silica Removal from Cooling Tower Water. SAND2011-0800. (Summarized above.)

Impact: This project demonstrated that silica coagulation with low cost aluminum-based agents is effective, simple, and compatible with other industrial processes (Stewart T., et al., 2011).

6.3 Membrane Treatment of Side-Stream Cooling Tower Water for Reduction of Water Usage

Large volumes of water are needed to support thermoelectric power generation (Altman et al., 2012). For example, thermoelectric generation was responsible for 49% of freshwater withdrawals in the US in 2005 and 3% of freshwater consumption. The latter represents the amount of water withdrawal that is not returned to the source. This means that approximately 10 million m$^3$ per day (or ~3 billion gallons per day) of freshwater is consumed by thermoelectric power generation. In the future there is likely to be increased competition and cost for freshwater usage as freshwater supplies become scarcer. Therefore, it is to the power generation industries' benefit to develop methods to minimize water consumption and maximize water usage efficiency. This may allow power plants to expand operations while minimizing new water supply and water disposal costs.

Altman et al., 2012 conducted a pilot study (Figure 6-3) to determine whether membrane treatment on a side stream of recirculating cooling-tower water could reduce overall water usage and discharge. Treated permeate was returned to the cooling tower while the concentrate was discharged to the sanitary sewer. Flow rates, pressures and water chemistry were monitored. The pilot demonstrated potential substantial water savings showing maximum make-up water and discharge reduction at 16% and 49%, respectively. To maximize water conservation, a high permeate recovery is needed. However, silica scaling on the membranes limited water savings in this pilot. It was determined that the development of membranes with a solute-rejection capacity less than the 92% average of the membranes used in the pilot would assist in optimizing water savings. Finally, while decreased water outlays compensated for the additional energy used by membrane treatment it was determined that scaling control is critical for economic operation.

Figure 6-3. Flow diagram of a cooling water system with a nanofiltration water treatment loop (left) and a photograph of the nanofiltration system used for pilot testing (right).
Roadmap Technology Area: Membrane Treatment and Concentrate Management.

Reports/Publications/Patents (and other deliverables):

Altman, S. J., et al., 2012, Membrane Treatment of Side-Stream Cooling Tower Water for Reduction of Water Usage, Desalination, 285, 177-183. (Summarized above.)

Impact: This study demonstrated that membrane treatment on a side stream of recirculating cooling-tower water could reduce overall water usage and discharge (Altman, S. J., et al., 2012). However, silica scaling on the membranes limited the water savings for this pilot.

6.4 Water Recovery Using Waste Heat from Coal Fired Power Plants for NREL

With funding from NREL, SNL evaluated the potential of treating non-traditional water sources using power plant waste heat in conjunction with MD (Morrow et al., 2011). Researchers and power plant designers continue to search for ways to use that waste heat from Rankine cycle power plants to recover water thereby reducing water net water consumption. Unfortunately, waste heat from a power plant is of poor quality. However, MD systems may be a technology that can use this poor quality heat i.e. low temperature waste heat (<100 °F) to treat water because they operate at low temperature and usually low pressure.

A thermodynamics based membrane distillation model (Figure 6-5) was developed to integrate into a power plant model in order to determine the amount of water produced using the different energy sources listed above (Morrow et al., 2011). The three different energy streams evaluated for driving MD include: 1) the boiler blow down, 2) the steam diverted from bleed streams, and 3) the cooling water system. The cooling water system (option 3) appears to be the best source of energy for MD. The model used to assess this option added a loop, referred to as the brackish water loop, between the steam condenser loop and the cooling water loop. Brackish water from an external source is treated in this loop and the distillate added to the cooling tower system as make up water. Modeling suggests that this option produces 370 lb/s (3,670 gpm) of treated water for a 1-2 GW power plant. However, significant modifications must be made to the power plant in order for the MD operations to work.

![Figure 6-5. Control volume diagram for membrane distillation unit model.](image)

Roadmap Technology Area: Alternative Technologies.
Reports/Publications/Patents (and other deliverables):


**Impact:** Sandia demonstrated that power plant waste heat can be a source of energy for treating power plant cooling water using MD. Modifying existing plants will require significant effort but the concept has potential to be included in the design of future plants (Morrow, C.W., et al., 2011).
7 CONTAMINANT SELECTIVE TECHNOLOGIES FOR WATER TREATMENT

For more than two decades SNL has been developing contaminant selective materials for water treatment. The focus has been on radionuclide contaminants including Cs, Sr, U, Pu, Tc etc. but significant work has also focused on heavy metals including As (described above) and Se. Sandia has developed and patented a number of materials for selective contaminant remediation. Several notable materials have been patented and two high impact success stories associated with these materials are described below.

1. Crystalline Silico-titanates (CSTs) – Currently in use at Fukushima, Japan for radioactive Sr remediation (see below);
2. Monosodium Titanates (MSTs) – In use for radioactive Sr removal from Savannah River liquid waste streams;
3. Modified Monosodium Titanates (mMSTs) – Currently being considered for use at Savannah River for Sr removal from liquid tank waste;
4. Sandia Octahedral Molecular Sieves (SOMS) – A sorbent engineered to remove Sr and other 2+ cations from solution.
5. Apatites and modified Apatites – A versatile sorbent capable of remediating Sr, U, Tc, Se and many other heavy metals. Currently in use at the Hanford site for Sr remediation and under evaluation in Rifle CO for uranium remediation (see below);

7.1 CSTs for Radioactive Cesium Remediation

CSTs (Figure 7-1) were originally developed by Bob Dosch (SNL) together with Ray Anthony and C.V. Philip (Texas A&M) and patented for Cs remediation by SNL in the mid-1990’s (Miller and Brown, 1997). UOP licensed the technology and entered into a CRADA with SNL to develop it into a commercial product for Cs remediation (IONSIV IE-910, and IE-911). The commercial product was primarily intended to be used for Cs remediation at Hanford and other DOE sites. CSTs have seen significant testing and evaluation at Hanford, Savannah River, Oak Ridge and INEL as well as other sites. They were successfully used to treat >30,000 gallons of supernate solution from Melton Valley Storage Tanks at Oak Ridge in a demonstration in 1997 (Walker et al., 1998). A total of ca. 1,142 Ci of $^{137}$Cs was loaded onto CST during the demonstration.
Following the earthquake and tsunami that damaged the Fukushima Daiichi nuclear power plant in Japan on March 11, 2011, seawater was pumped into the plant in order to cool the reactors. This resulted in seawater contaminated with radioactive Cs that could not be released back into the ocean. Quick action by SNL and UOP researchers in the Spring of 2011 to verified that the CSTs would perform effectively in removing the cesium from the contaminated seawater and would outperform commercially available zeolites. The positive test results led to rapid licensing and deployment of the technology in Japan, where it continues to be used to clean up cesium-contaminated water at the Fukushima power plant.

**Reports/Publications/Patents (and other deliverables):**


**Impact:** The IONSIV IE-910 and IE-911 products are an R&D 100 award winner in 1995. To date, >30,000 gallons (1,142 Ci) of highly radioactive Melton Valley waste (Walker et al., 1998), and more than 160 million gallons of contaminated seawater have been treated at Fukushima using the CST product (Dean Runde, personal communication, 2014).

### 7.2 In situ Apatite Permeable Reactive Barrier to Remediate Radioactive Strontium in Hanford Groundwater

Apatite is very effective at binding and immobilizing radionuclides and heavy metals (Moore et al., 2002). It can be used as a sorbent in traditional pump and treat remediation operations as well as a permeable reactive barrier (PRB) in contaminated soils and sediments. Sandia has developed and patented (Moore 2002; Moore, 2003) a unique process for the in situ deployment of apatite as a permeable reactive barrier. To begin, an aqueous mixture containing chelated calcium citrate and sodium phosphate is prepared. Next, the resulting solution is pumped (or gravity fed) through a well or series of wells into the subsurface. As the solution disperses in the subsurface, soil and sediment micro-organisms process the citrate and release the calcium which then reacts
rapidly with sodium phosphate to form apatite. The in situ formed apatite coats and lines pores and fractures in the sediment and then can sorb and/or incorporate contaminants including plutonium, uranium strontium, lead, and several heavy metals. To demonstrate its efficacy as a PRB, an experimental apatite barrier was deployed in the subsurface in 2005 (Figure 7-2) along a 300-foot-long section of Columbia River shoreline to prevent radioactive strontium from reaching the river. The barrier was then field-tested by Pacific Northwest National Laboratories (PNNL) and Fluor Hanford Inc. After six years, (2005-2011) monitoring of wells drilled between the barrier and the Columbia River demonstrated that the barrier sequestered an average of 95 percent of the strontium before it could reach the river (Vermuel et al., 2014).

![Figure 7-2. Installation of the Sandia developed in situ apatite barrier at the Hanford Site.](image)

**Reports/Publications/Patents (and other deliverables):**


**Impact:** Traditional pump-and-treat remediation technologies are costly and energy intensive. This in situ treatment technology eliminates the need for pump-and-treat by removing contaminants in place through the use of a permeable reactive barrier. The initial barrier deployment was so successful that CH2M HILL Plateau Remediation Company has begun an expansion of the barrier to protect a total 2,500 feet of Columbia River shoreline (Vincent Vermuel, personal communication, 2016).
8 CURRENT PORTFOLIO OF DESALINATION WATER TREATMENT RESEARCH

Through its LDRD program, SNL is currently making investments in the development of high impact desalination and water treatment technology in order to address research needs identified in the Desalination and Water Purification Roadmaps. In addition, SNL has a CRADA and two DOE funded projects to develop low energy water treatment technologies.

8.1 Water Treatment System for Resilient Energy Production

The objective of this project is to enable resilient water production by developing novel membranes that decrease the energy intensity of desalination. Reducing the water demands of energy production by recycling produced water and thermal power plant cooling water requires high-flux, high-recovery, chemically robust desalination membranes. Revolutionary water treatment systems for energy production would operate at energy intensities <2 kWh/m³ and have high chemical tolerance. Laminar GO structures (Figure 8-1) are promising desalination membranes since their intrinsic membrane structure drives low-friction flow of water and energetically prohibits solvated ion permeation. GO/polymer membranes comprise a laminar GO layer covalently bound to a porous polymer support.

Figure 8-1. Illustration of water molecules transported through a graphene oxide membrane.

Roadmap Technology Area: Membrane Technologies.

Reports/Publications/Patents (and other deliverables):

None completed to date.

Impact: Membrane technologies are the dominant technology for desalination and water treatment. Improving their performance with low energy consumption, <2 kWh/m³, that approaches the energy minimum for membrane technologies and high chemical tolerance will revolutionize RO desalination. To date, this project has demonstrated chlorine tolerance as high as 1-3 ppm (Laura Biedermann, personal communication, 2016). At this level of chlorine tolerance, biofouling is minimized and gray water recycling is enabled without expensive chlorine removal steps.

8.2 Waste Water for Power Generation via Energy Efficient Selective Silica Separations

Existing anti-scalant technology can already prevent calcite buildup. However, there is no low energy method for preventing silica scaling, thereby limiting the amount of impaired water recycling in power plants that can be achieved. Dissolved silica is ubiquitous in impaired waters,
resistant to existing anti-scalants, and difficult to remove from power plant feed waters. This LDRD is focused on developing silica getter materials that will be tested at the field and pilot scale. Our project is both an innovative approach for developing high silica capacity and selectivity solid sorbent materials, and is cutting edge for collaboratively (1) developing novel materials and their processes for silica removal, with the use of (2) techno-economic modeling and analysis to aid in real-world implementation. We will build upon our unique experiences in low energy desalination and silica removal screening tests (TRL 1-2) to ensure success in this TRL 3-4 development LDRD.

**Roadmap Technology Area:** Alternative Technologies.

**Reports/Publications/Patents (and other deliverables):**

1 TA submitted for US Patent, 1 publication submitted (Env. Sci & Tech 2016), 3 national and international presentations (Tina Nenoff, personal communication, 2016).

**Impact:** Replacement of the freshwater used for power plant cooling with purified oilfield produced waters, municipal or agricultural wastewaters, and subsurface brines is possible only if dissolved silica and calcite are prevented from forming mineral scales during the power generation process.

### 8.3 Extended Permeation Testing of Thermal Power Plant Cooling Water SNL-EPRI CRADA

In this project, SNL will conduct cross-flow permeation tests with a few real cooling water samples from thermoelectric power plants to understand the conditions leading to scaling and the impact on membrane performance. Such tests will be conducted with a cross-flow membrane cell and a GO/polymer membrane (Figure 8-2) having an effective membrane area of 42 cm² and a maximum pressure of 1000 psi. Ion rejection will be monitored via real-time conductivity measurements as well as selected ion chromatography analysis of the permeate and feed. Scalant structure and chemistry will be determined via scanning electron microscopy/energy dispersive x-ray spectroscopy and x-ray fluorescence. The pH of the feed water chemistry will be adjusted to minimize scaling.

![Figure 8-2. Sandia developed graphene oxide (GO)/polymer membrane.](image)

**Reports/Publications/Patents (and other deliverables):**
None completed to date.

**Impact:** Initial tests of GO/polymer membranes show that the pristine GO/polymer membranes have a phenomenal energy intensity of only 0.1-0.5 kWh/m$^3$ for desalination of brackish water (2000 ppm MgSO4) and a flux of up to 3.1 LMH at a driving pressure of 2.9 bar for the same brackish water solution (e.g., 1.6 GFD at 52 psi). The flux increases with driving pressure (e.g., 25 LMH at 14 bar). Much of our prior work has investigated the low-pressure filtration limits. Additionally, we have shown that these membranes are tolerant to extended exposure to 1 ppm free chlorine (Laura Biedermann, personal communication, 2016).

### 8.4 Membrane Distillation Using Geothermal DOE

This project involves National Renewable Energy Lab, Colorado School of Mines, SNL, University of California Riverside, Ormat Technologies, and General Electric. The goal is to demonstrate at a pilot plant level that use of waste heat from geothermal sources with MD can generate economically attractive purified water. Membrane distillation is a water treatment alternative to RO or progressive distillation that produces pure, distilled water. The process uses low-grade waste heat – usually temperatures on the order of 150 °C. Sandia’s role is to provide a physics model of the distillation process (Figure 8-3).

![Figure 8-3. Control volume diagram for membrane distillation unit model.](image)

**Roadmap Technology Area:** Alternative Technologies.

**Reports/Publications/Patents (and other deliverables):**

A SAND report and computer model are in preparation.

**Impact:** This project is focused on enabling low cost treatment and reuse of power plant cooling water by using waste heat to power MD. To date SNL has upgraded the closed loop model first developed for WEN engineering (see above) to work with plate and frame heat exchangers and to be compatible with vacuum-driven membrane distillation systems (Charles Morrow, personal communication, 2016).

### 8.5 Assessment of a Hydroxyapatite Permeable Reactive Barrier to Remediate Uranium at the Old Rifle Site, Colorado

Sandia and PNNL performed an initial evaluation and testing program to assess the effectiveness of a hydroxyapatite permeable reactive barrier and source area treatment to decrease uranium mobility at the DOE former Old Rifle uranium mill processing site (Figure 8-4) in Rifle, western Colorado (Moore and Rigali, 2015). Uranium ore was processed at the site from the 1940’s to the 1970s. The mill facilities at the site as well as the uranium mill tailings previously stored there...
have all been removed. Groundwater in the alluvial aquifer beneath the site still contains elevated concentrations of uranium and is currently used for field tests to study uranium behavior in groundwater and investigate potential uranium remediation technologies. The technology investigated in this work is based on SNL’s in situ formation of apatite in sediment to create a subsurface apatite PRB and also for source area treatment. Phase I of this multi-phase project was completed in March of 2016 and involved column testing of the apatite barrier on rifle sediments to test its effectiveness. Initial column testing with Old Rifle sediments indicates that Ca-citrate-phosphate treatment showed good effectiveness as a source area treatment to stabilize uranium in sediments and decrease leaching, and good effectiveness as a permeable reactive barrier at low groundwater velocities. We anticipate moving to field studies of the apatite barrier performance in the summer of 2016.

![Figure 8-4. Old Rifle uranium mill processing site.](image)

**Roadmap Technology Area:** Alternative Technologies.

**Reports/Publications/Patents (and other deliverables):**


**Impact:** Traditional pump-and-treat remediation technologies are costly and energy intensive. This in situ treatment technology eliminates the need for pump-and-treat by removing contaminants in place through the use of a permeable reactive barrier. The apatite PRB has the potential to preventing 99% or more of the uranium contamination from migrating to the Colorado River. It may find broad use for remediating uranium at Uranium Mill Tailings Remedial Action (UMTRA) sites across the US (Moore and Rigali, 2015).
9 SUMMARY

In collaboration with government agencies, industry and universities Sandia National Laboratories (SNL) charted the course for the future of desalination by summarizing the water supply challenges facing the United States (US) and identifying future areas of research and development that can lead to technical solutions to these challenges. Further, this same team identified specific research and development projects to hasten the rate of advancement of these technical solutions to reduce both the cost and energy demand of desalination. The resulting effort was captured in the Desalination Roadmap (USBoR and SNL, 2003) and its companion document, the Implementation Roadmap (SNL, 2006). These documents are enduring and still very much relevant to US desalination and water treatment challenges even though they are now a decade old.

Funded by DOE EM in 2002, SNL and the USBoR coordinated the development of the conceptual design for the Brackish Groundwater National Desalination Research Facility (BGNDRF) together with a consortium of water utilities, state and federal water agencies, and water research groups. SNL and the BoR provided a report to Congress in September 2002 outlining the suggested site (located in Alamogordo, New Mexico), facility attributes and layout needed for inland desalination research issues, and an operational and management plan and structure. Construction of the facility began in 2004, followed by a ribbon cutting in August 2007, commissioning in 2008 and research starting in 2009. Today, the facility actively supports desalination research for a number of private industry and university clients. Past and current clients include General Electric, the Water Standard Company, Veolia, Evoqua, Voltea, Massachusetts Institute of Technology (2015 Desalination Prize Winner), Arizona, Texas Tech, Nevada Reno and the University of Texas in El Paso.

Sandia’s jump start program, funded by DOE EM, identified and supported cutting edge water treatment technologies with the goal of advancing their technological maturation through bench- and pilot-scale testing and towards commercialization. While it sought to take advantage of the BGNDRF in Alamogordo, New Mexico, projects were performed at several sites around New Mexico. One of the noteworthy successes in this program involved a project with the University of South Carolina (USC) and Zero Discharge Desalination (ZDD) Inc., to investigate the use of a zero liquid discharge process for brackish water desalination. Sandia testing and optimization of the novel USC-ZDD hybrid RO/EM pilot system at the BGNDRF facility resulted in very high water recoveries of >96% with minimal liquid discharge. The success of the pilot testing caught the attention of an industry leader in water treatment, Veolia, and led to an exclusive license agreement and CRADA between ZDD and Veolia to develop the hybrid RO/EM system for commercialization.

Sandia has made numerous contributions to fundamental science through its long-range research program in water treatment and desalination. For example, the interfacial water Laboratory Directed Research and Development project focused on developing a fundamental understanding of water-membrane-contaminant-interactions at the atomistic to molecular scale and resulted in 16 peer-reviewed journal articles. When Peter Agre won the Nobel prize in 2004 for the discovery of aquaporins, proteins that move water molecules through cell membranes, SNL recognized the potential to develop and engineer a next desalination membrane based on these materials. Our aquaporin inspired biomimetic membranes achieve an order-of-magnitude improvement in membrane permeability to water flow compared to commercial membranes and
still maintain high salt rejection ratios. The technology has received significant national recognition via R&D 100 Award in 2011 (https://www.youtube.com/watch?v=11RQ3N9uH1w), it was highlighted by DOE Secretary Chu (2011), and a Federal Laboratories Consortium Notable Technology Development Award (2012).

When the Environmental Protection Agency lowered the MCL of arsenic from 50 parts per billion (ppb) to 10 ppb (January 2006), SNL initiated the Arsenic Water Technology Partnership (AWTP) program to provide assistance to the numerous communities across the US faced with implementing new and costly treatment systems to meet the new standard. AWTP was a multi-year program funded by a congressional appropriation through the DOE EM to develop and test innovative technologies that have the potential to reduce the costs of arsenic removal from drinking water. AWTP members included SNL, the American Water Works Association Research Foundation and Waste Management Education and Research Consortium (A Consortium for Environmental Education and Technology Development). Sandia ran laboratory and field testing of arsenic removal technologies. We established RSSCT laboratory testing protocol to enable rapid and low cost assessments of the performance As sorption media as well as to predict the performance of media in full-scale systems. Our As field pilots defined both a cost and performance envelope for the various As treatment options available to communities faced with implementing treatment technologies to meet the new drinking water standard. Finally, the rural outreach project was set up to help address the specific needs of smaller communities who are having the greatest difficulty in complying with the standard.

The arid State of New Mexico is faced with considerable water supply challenges. Through the Sandia New Mexico Small Business Assistance program, we worked with several small businesses across the state to find innovative ways to increase water supply as well as to find beneficial uses brackish and produced water. Using a lower energy desalination approach with NF membranes, as opposed to conventional RO membranes, we worked with the Biosphere Environmental Company to successfully demonstrate that treated produced water could be used for watering rangeland vegetation at a cost that is competitive with traditional produced water disposal methods. In addition, we successfully demonstrated the feasibility of using a membrane distillation process in a power plant cooling water loop to enable water reuse in plant cooling for Water Energy Nexus (WEN) Engineering. WEN is currently pursuing a proposed pilot at the Red Hawk coal fired power plant to demonstrate the concept. Because thermoelectric power generation is the largest user of freshwater in the US, at ~500 billion gallons a day, technologies that enable power plant water reuse have the potential to significantly reduce fresh water usage in New Mexico and across the US.

As described above large volumes of water are needed to support thermoelectric power generation across the US and the majority of this water is used for cooling. Thermoelectric generation is responsible for ~50% of freshwater withdrawals in the United States and ~3% of freshwater consumption. Should the EPA mandate that power plants switch from once through cooling to evaporative cooling, fresh water consumption would rise considerably. Sandia is developing novel technologies to enable water reuse with a focus on treating silica scale. Dissolved silica is ubiquitous, resistant to existing anti-scalants, and difficult to remove from power plant feed waters. Success in preventing silica scaling has the potential to reduce power plant water consumption considerably and thereby increase freshwater availability for other uses.

In an effort that parallels the water initiative, SNL has been developing contaminant selective materials for water treatment more than two decades. The focus has been on capturing
radionuclide contaminants including Cs, Sr, U, Pu, Tc etc. from water to enable clean up at contaminated DOE sites across the US including Hanford and Savannah River. Significant work has also focused on heavy metals including Pb, Hg, As and Se. Sandia has developed and patented a number of materials for selective contaminant remediation. Several of these materials have moved to commercial products and have found use at radioactively contaminated sites. Sandia’s crystalline silicotitanates were developed into a selective sorbent for the removal of Cs from water and licensed and developed into a commercial product by Honeywell UOP under a CRADA agreement. The product was used to sequester ca. 1,140 Ci of radioactive cesium from waste at Oak Ridge National Laboratory. Deployed to Japan following the Fukushima disaster, the material had treatment more than 160 million gallons of contaminated seawater. At Hanford, the SNL developed apatite permeable reactive barrier has been deployed to prevent 1 Ci of radioactive strontium from reaching the Columbia River. At Savannah River, SNL developed monosodium titanates are being used to remove radioactive strontium from liquid tank waste.

In 2016, nearly a decade and a half after initiating the water initiative, SNL continues to develop next generation desalination and water treatment technologies through its LDRD program. Sandia has an investment in the development graphene oxide materials for membrane desalination. These graphene oxide membranes have the potential to significantly reduce (15-50%) the energy demand and cost of desalination of sea water and brackish water. In addition, we continue to develop novel technologies for preventing silica scaling to enable water reuse for power plant cooling.
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