

Geochemistry at U. S. National Labs: *Sandia National Laboratories*

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Introduction

The pink-colored granite of the Sandia Mountains in central New Mexico provides the backdrop for geochemistry research activities at Sandia National Laboratories in Albuquerque, New Mexico. Sandia National Laboratories is funded primarily by the U. S. Department of Energy and is managed by Lockheed Martin Corporation. Additional research facilities in Livermore, California; Carlsbad, New Mexico; Amarillo, Texas; and Kauai, Hawaii (Yes, Kauai!) combine to make Sandia the leading national security, science, engineering, and energy laboratory in the world. Sandia partners with a variety of other government, industry, and academic institutions to provide “exceptional service in the national interest” for a wide array of applied and basic science concerns. Established in 1948 by President Harry S. Truman, Sandia was originally responsible for designing all of the non-nuclear parts of nuclear weapons. Since those early days of the Cold War, Sandia has expanded its role to address key issues in science and engineering projects that contribute in various ways to national security and critical energy issues. Today, Sandia employs approximately 8,600 people, has an annual budget of \$2.3 billion, and is involved in diverse research ranging from the design of environmental microsensors for homeland security to the development of a noninvasive blood glucose monitoring device for diabetes patients.

Geochemical research at Sandia originally developed in part from corrosion studies of metals and alloys conducted in the mid-1970s, mostly in support of technical efforts to extract alternative energy by drilling into volcanic systems. The expanding need to evaluate materials stability under relatively high temperature and high pressure led to the hiring of several qualified PhD scientists from the ranks of leading experimental petrology laboratories in universities. William Luth, in particular, did much to expand Sandia’s geochemistry staff and laboratory facilities during this early period and into the 1980s. Sandia’s present-day

Geoscience and Environment Center—comprised of Geochemistry, Geophysics, Geomechanics, Geohydrology, and Geotechnology Departments—owes much to Luth’s ability to recognize the essential role of geoscience research in alternative energy, waste management, environmental, material science, and national security issues. Also during the 1970s, Sandia took on a leadership role in the development of the Waste Isolation Pilot Plant (WIPP) for the permanent storage of low-level nuclear waste in bedded salt deposits near Carlsbad, New Mexico. Geophysicists and geochemists from Sandia led continental drilling projects in Hawaii, Oregon, California, and Alaska during this period. With a firmly established reputation in these various arenas, scientists at Sandia were poised to participate in growing research programs in environmental geochemistry, especially as applied to the safe storage and remediation of radionuclides and the cleanup of hazardous chemical wastes, both important concerns to the U. S. Department of Energy and the legacy of the Cold War.

Through the 1990s and to the present day, geochemistry staff at Sandia have continued to lead research programs in environmental chemistry, radionuclide and chemical waste remediation, water quality and potability, waste stream management, materials synthesis and processing, and numerous other research topics. Many of these studies emphasize the fundamental aspects of geochemical processes, often at the atomic- and nano-scale. Yet, technical solutions are often obtained through extension of the laboratory and theoretical studies, leading to development, testing, and ultimate application to the field site. The Geochemistry Department operates several modern wet chemistry laboratories that contain advanced experimental, analytical, spectroscopic, and imaging tools. Along with access to other state-of-the-art analytical and computational facilities throughout the labs, these facilities and the research staff provide an impressive foundation for geochemistry research to continue to flourish at Sandia.



The following sections provide snapshot summaries of several ongoing geochemical research programs at Sandia National Laboratories. Although not meant to be exhaustive and detailed, they provide examples of the range of fairly basic to relatively applied research projects at Sandia. Most of the geochemistry research is performed in Albuquerque at the main laboratory site, although the Carlsbad facility hosts much of the current research related to WIPP. Funding of geochemical research is provided by several sources and includes various U. S. Department of Energy programs: Office of Basic Energy Sciences, Environmental Management Science Program, Environmental Molecular Science Institute, Advanced Simulation and Computing, National Energy Technology Laboratory, Office of Civilian Radioactive Waste Management, and Waste Isolation Pilot Plant. Among the other funding agencies are the U. S. Nuclear Regulatory Commission, U. S. Environmental Protection Agency, Defense Advanced Research Projects Agency, and the Laboratory Directed Research and Development program at Sandia National Laboratories.

Radioactive Waste Disposal

Geochemistry at Sandia is an integral part of nuclear waste repository programs such as the WIPP in Carlsbad and the Yucca Mountain Project (YMP) in Nevada. Geochemical activities related to these programs focus on supporting Performance Assessment (PA) models. These models are used in the predictive evaluation of radionuclide releases from the waste isolation system. The PA model is evaluated within the scope of regulatory requirements in accord with nuclear waste disposal and environmental safety.

The WIPP transuranic radioactive waste repository is situated in southeastern New Mexico, approximately 35 miles from the nearest significant population center (Figure 1). The repository is located 655 m underneath the surface within a Permian bedded salt formation. Given the physical and chemical conditions in this environment, accurate knowledge of actinide solubilities and aqueous complexation in brines is needed to derive appropriate solubility ranges for implementation in the WIPP PA. The basis for the actinide solubility model includes the use of the Pitzer

activity coefficient approach for modeling concentrated electrolyte solutions. Sandia developed the Pitzer thermodynamic database for WIPP solubility calculations. Another aspect of geochemistry applied to the WIPP project includes experimental and modeling activities assessing the efficiency of the backfill material comprised primarily of MgO (periclase). This backfill

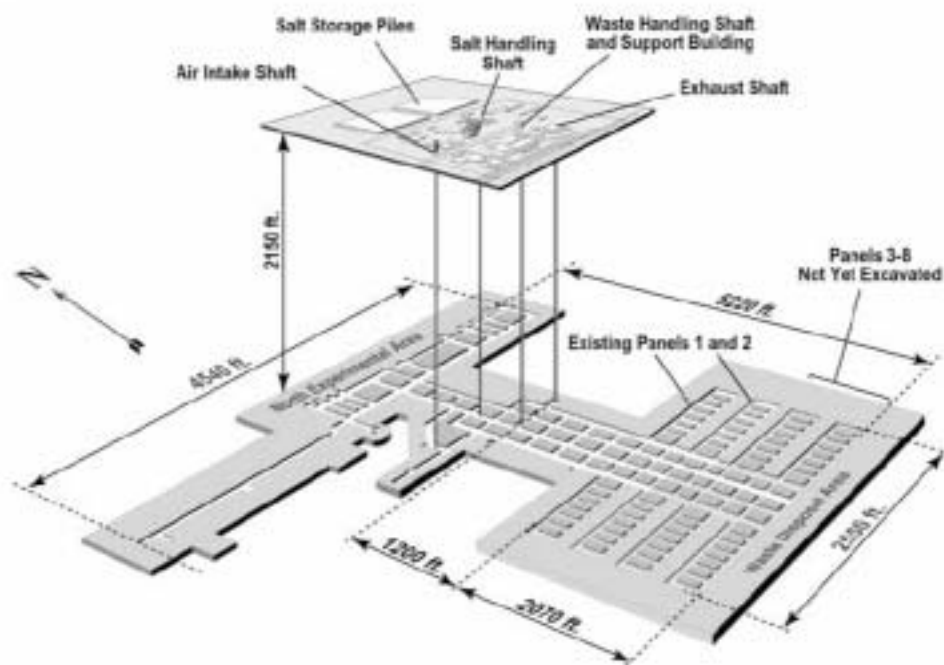


Fig. 1. Schematic depiction of the Waste Isolation Pilot Plant in southeastern New Mexico.

buffers brine chemistry, thereby reducing actinide solubility at the WIPP repository horizon. Reaction of MgO(s) with H₂O and CO₂ produces brucite and magnesite, thereby reducing CO₂ availability and generating mildly alkaline pH conditions where most actinide solubilities are relatively low.

Other geochemistry issues relevant to underground waste repositories include modeling of the chemical evolution of fluids within the waste site as a consequence of evaporation, mixing, thermal transients, variable pH and Eh, and other related processes. Evaluation of chemical changes due to these complex processes is made through the use of equilibrium aqueous speciation and reaction path calculations based on specialized thermodynamic databases. Characterization of the fluid chemistry is important in the assessment of corrosion environments on and within waste packages, and radionuclide solubilities and colloid stability in in-package and in-drift solutions. Other Sandia-based activities include experimental investigations to establish: 1) the likely redox state inside breached waste packages at the repository, 2) the effectiveness of waste package corrosion products in retarding problematic radionuclides, and 3) the development of

effective radionuclide sorbents or “getters” to impede radionuclide mobility in repository areas beyond the waste package.

Geochemical Molecular Modeling

Advances in molecular modeling software and the availability of faster computer workstations over the past decade have provided an opportunity for geochemists to expand their theoretical tools. Today, it is not unusual to combine laboratory and field observations with atomistic-based computer models to better understand geochemical processes. Molecular models, or computer experiments, provide a convenient method for controlling variables in complex mineral and mineral-fluid systems to better evaluate structure, dynamics, thermodynamics, and kinetics. Sandia has been at the forefront of these efforts since the early 1990s with theoretical work relating to understanding the behavior of radionuclide sorption on mineral surfaces.

Classical simulation methods, in which the energies of atomic interactions are described by relatively simple analytical functions, are often used to evaluate large complex systems with the number of atoms ranging from hundreds to perhaps millions. Monte Carlo and molecular dynamics (MD) simulations can now be performed on either a personal computer or workstation. Large-scale simulations, involving many hundreds of thousands of atoms, require computer clusters or massively parallel supercomputers. At Sandia, we have the capability of running MD simulations of a million atoms for a million time steps—one nanosecond based on a femtosecond time step. Similarly, quantum approaches with either Hartree-Fock or density functional methods have allowed the geochemist to perform *ab initio* calculations on much smaller chemical systems (typically under a hundred atoms), but without relying on a parameterized force field. Recent research at Sandia relating to the interaction of water on oxide surfaces has used *ab initio* MD methods in which the Schrodinger’s equation is solved for every dynamics time step, although simulation time is limited on the order of several picoseconds.

Molecular modeling at Sandia has been used to explore numerous geochemical and material science problems over the past years. MD methods have been incorporated to examine the efficacy of various waste treatment approaches. The recent development at Sandia of a generalized energy force field for the simulation of complex hydrated systems has led to several new research efforts for evaluating the binding of various metal cations or organic contaminants on the surface of an oxide or hydroxide, and in the interlayer of complex clay.

One example of the latter

is provided in Figure 2 for the case of uranyl (UO_2^{2+}) sorption from an aqueous solution onto the basal surface of montmorillonite. Large-scale MD calculations were performed for up to a nanosecond of simulation time using the LAMMPS parallel code and a Linux PC cluster. A snapshot from the equilibrated system exhibits the sorption of two different uranyl complexes onto the basal surface. Ultimately, analysis of the simulations and derivation of atomic density profiles provide a unique method for evaluating partition coefficients (K_D) for chemical species between a solid and an aqueous solution. For example, the uranyl-montmorillonite model provides a technical basis for evaluating the wide range of K_D values from experimental and field studies of uranium sorption and groundwater transport, especially for incorporation in PA models.

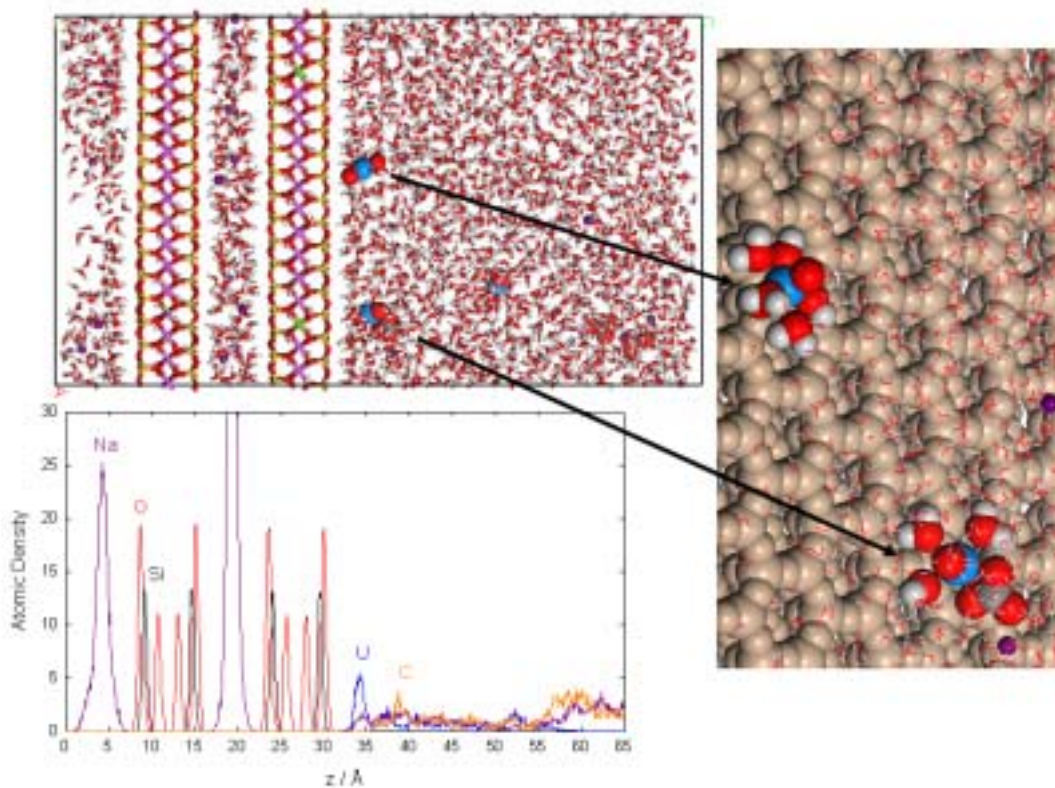


Fig. 2. Results of a large-scale molecular dynamics simulation of the sorption of uranyl groups onto the basal surface of montmorillonite clay. The upper images show views of the sorbed uranyl complexes, one as a uranyl hydrate and the other as a uranyl carbonate hydrate. The lower plot provides the corresponding atomic density profile normal to the clay basal layer. Research is sponsored by the U. S. Nuclear Regulatory Commission.

Advanced Desalination Technologies

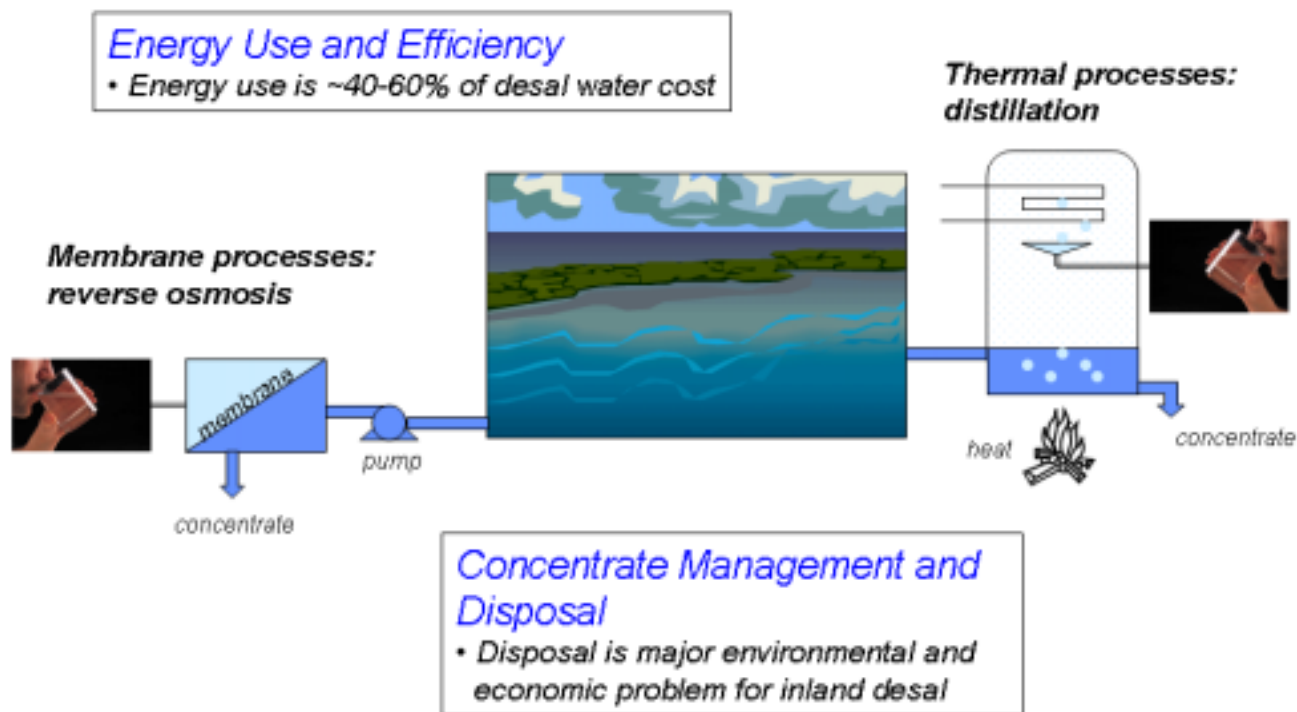


Fig. 3. Major technical pathways for the desalination and the production of potable water. Technical challenges include the energy efficiency and waste stream management.

Related molecular modeling studies in geochemistry at Sandia include the simulation of metal-anion pairing and sorption on oxides and hydroxide surfaces, the structure and dynamics of gas hydrate systems, the behavior of water in various clay phases, the stability of layered double hydroxides (LDH; inverse clays), the intercalation of amino acid anions in LDH, and the sorption of metals onto the cell wall of microbes. Collaborative efforts in materials science have also led to successful molecular modeling projects. Classical and quantum methods have been used to successfully model the structure and behavior of lithium manganese compounds for bulk and thin film battery components. Similarly, molecular modeling efforts have contributed to understanding atmospheric corrosion of metals, especially in evaluating the behavior of water at the metal-water and oxide-water interface. Crystal growth and morphology of zincite have been extensively investigated to support the development of nanostructured oxides for applications as diverse as optical sensors to the controlled separation of proteins.

Desalination and Water Purification

Recurring drought in the western United States, the increasing overallocation of water in much of the rest of the country, and concern about water-borne micropollutants has prompted a national search for technological solutions that can produce “new water”—useable water from brackish groundwater, from seawater,

from agricultural and municipal return flows, or from water previously made unusable by the presence of trace contaminants such as arsenic or perchlorate. Nine orders of magnitude span the contaminant removal levels needed for water purification: from NaCl at parts per thousand (ppt) in seawater, to arsenic and perchlorate at parts per billion (ppb), to NDMA (n-nitrosodimethylamine) and pharmaceuticals at parts per trillion (ppt). Removing a contaminant present at 1 ppt is equivalent to extracting the dissolved mass of a grain of sugar from an Olympic-sized swimming pool. The science of water treatment is obviously being challenged as never before.

The problem might be broken down into two distinct processes: micropollutant removal from water through sorption/oxidation/reduction and removal of water itself from macropollutants (brines). Both tend to be controlled by interfacial processes. Micropollutant removal often relies on inorganic filter media (typically metal oxides). Reverse osmosis through organic membranes is used for desalting (Figure 3). And there is the expectation that engineered biologically-active interfaces will play a larger role in both treatments in the future.

One aspect of the future of water treatment is fairly easy to anticipate: most, if not all, *major technical advances will come from an improved understanding of the microscopic behavior of water and contaminants at engineered interfaces*. Research at Sandia proceeds on this hypothesis by teaming Sandia and outside researchers on a wide variety of research topics that hold in common the linking of fundamental microscopic behavior with macroscopic improvements in the science of water treatment. Sandia represents a unique convergence of technical expertise

in interfacial chemistry, molecular design, and aquatic chemistry—all in a region that is facing several simultaneous train wrecks of water problems including salt accumulation, arsenic contamination, and persistent drought.

Sandia's water treatment work bridges from the theoretical to the applied through several programs: Long range Desalination/Water Purification research, and "jump-start" testing. Arsenic treatment pilot testing is in partnership with the American Water Works Association Research Foundation—AwwaRF—and WERC (see below). The jump-start program seeks to accelerate the implementation and commercialization of new desalination technologies, primarily at the Tularosa Basin National Desalination Research Facility, presently being constructed near Alamogordo, New Mexico. At the same time, Sandia is working with AwwaRF, the WaterReuse Foundation, and the Bureau of Reclamation to develop a national roadmap for desalination/water purification research. Some research areas are listed below to provide a flavor of Sandia's water science research effort:

Fig. 4. Sandia Pilot Arsenic Treatment Pilot System: Each of the three columns and the cartridge on left contains a different adsorbent medium. The three columns on right contain a single medium (granular ferric oxide) with different contact times.



- Molecular design of sorbents for arsenic and perchlorate
- Development of self-sealing evaporation ponds
- Clathrate crystallization desalination
- Optimization of GAC surface chemistry for perchlorate removal
- Electrodialysis for concentrate management of inland brines
- Biomimetic membrane design
- Enzymatic reduction of biofouling

Arsenic and Drinking Water

The Arsenic Water Technology Partnership (AWTP) program is a multi-year program funded by a congressional appropriation through the U. S. Department of Energy to develop and test in-

novative technologies that have the potential to reduce the costs of arsenic removal from drinking water. The AWTP members include Sandia National Laboratories, the American Water Works Association (Awwa) Research Foundation, and WERC (A Consortium for Environmental Education and Technology Development). The program is designed to move technologies from bench-scale tests to field demonstrations. The Awwa Research Foundation is managing bench-scale research programs; Sandia is conducting the pilot demonstration program and WERC will evaluate the economic feasibility of the technologies investigated and conduct technology transfer activities.

The scope for field demonstration testing by Sandia includes 1) selection of sites and identification of technologies for pilot demonstrations, 2) laboratory studies to develop rapid small-scale test methods, and 3) pilot-scale studies at community sites involving side-by-side tests of innovative technologies. The goal of site selection is to identify sites that allow examination of treatment processes and systems under conditions that are relevant to different geochemical settings throughout the country. A num-

ber of candidate sites have been identified through reviews of groundwater quality databases, conference proceedings and discussions with state and local officials. These include sites in New Mexico, Arizona, Colorado, Oklahoma, Michigan, and California.

Most of the treatment technologies being considered for pilots fall into two broad categories: 1) sorption processes that use fixed bed adsorbents and 2) membrane processes including coagulation/filtration with or without electrochemical processes. Several innovations that could lead to lower treatment costs have been proposed for adsorptive media systems. These include: 1) higher capacity and selectivity using mixed oxides composed of iron and other transition metals, titanium and zirconium based

oxides, or mixed resin-metal oxides composite media; 2) improved durability of virgin media and greater chemical stability of the spent media; and 3) use of inexpensive natural or recycled materials with a coating that has a high affinity for arsenic. Improvements to filtration-based treatment systems include: 1) enhanced coagulation using improved iron compounds, polyelectrolytes, and electrical gradient or via electrochemical reactions and 2) improved filtration with nanocomposite materials.

The conceptual treatment process for arsenic adsorption media filters is based on passing arsenic-contaminated feed water through a fixed bed of media that has a strong affinity for arsenic. The removal capacity and effectiveness of the arsenic removal media is dependent on a number of factors, of which surface area and specific chemical affinity of the arsenic for the surface are of primary importance. Other factors that determine the capacity and effectiveness of adsorbent media are accessibility of the pore sites for arsenic ions, time available for arsenic ions to migrate to pore sites, competing ions for pore sites, concentration of arsenic in the feed water, and the pH of the feed water. As water passes down through a filter vessel containing fixed bed media, the arsenic concentration declines until it is no longer detectable. As the upper portion of the media becomes saturated, the treatment region (mass transfer zone) progresses downward until all adsorptive capacity is used and arsenic breakthrough occurs. In the pilot tests, the innovative technologies are evaluated in terms of adsorptive capacity for arsenic; robustness of performance with respect to water quality parameters including pH, TDS, foulants such as Fe, Mn, silica, and organics, and other metals and radionuclides; and potentially deleterious effects on the water system such as pipe corrosion from low pH levels, fluoride removal, and generation of disinfection by-products.

The first pilot test is being conducted on water from a geothermal spring used to supply drinking water to Socorro, New Mexico, a town of about nine thousand residents located eighty miles south of Albuquerque. The objectives of the Socorro Pilot include evaluation of: 1) the treatment performance of five adsorptive media using the same water source, 2) the effects of pH adjustment and contact time on the performance of selected media; and 3) limited assessment of maintenance and operational requirements for all media. The adsorptive media include two granular ferric oxides, a titanium oxide, a zirconium oxyhydrate, and a hybrid anion exchange resin-ferric oxide material (Figure 4). The treatment performance is based on the arsenic removal capacity of all five media under ambient pH conditions (approximately 7.7). Three of the media are also evaluated at an adjusted pH of 6.8 to determine the effect on arsenic removal capacity. The pH is lowered using a CO₂ injection system, which does not require the use of mineral acids. A second parameter, empty bed contact time (EBCT), is varied for one of the granular ferric oxide media to determine the correlation between treatment contact time and arsenic removal capacity. The results of this last test will help design future, potentially shorter, pilot tests.

The new Maximum Contaminant Level (MCL) for arsenic may be one of the most costly health regulations ever promulgated. The projected annual national compliance cost of implementing the new 10 g/L standard ranges from \$165 million, estimated by the U.S. EPA to \$605 million, estimated by AwwaRF. Sandia's program may help to alleviate some of the burdens associated

with the standard by 1) comparing the costs and performance of alternative methods for arsenic treatment in specific community wells in side-by-side pilot tests of several different technologies and 2) by identifying potentially deleterious effects associated with different technologies. As technologies progress from a bench-scale demonstration phase to full-scale commercial production, it is likely that significant cost reductions will be realized. However, at this time, the potential magnitude of cost savings associated with innovative adsorptive media or other treatment processes can not be accurately estimated. Through direct field demonstration and the associated outreach program, the Sandia program can provide independent evaluations of the relative merits of the numerous alternative technologic choices that will be presented to communities throughout the U. S. In addition, although the compliance deadline for the new arsenic standard is January 2006, there will be opportunities for water utilities to apply for exemptions, extensions and variances. These will allow communities the time to gather additional information from this and other programs and make a more informed choice of technology. The information might prevent expensive mistakes from being made by small communities, especially those that have few technical or financial resources to carry out adequate assessments of the claims made by vendors about their products.

Coda

Finally, for those wondering about the origin of the word *Sandia* from which the laboratories has taken its name, you may want to consult your high school Spanish dictionary. *Sandia* is the Spanish word for *watermelon*, and was supposedly used by the sixteenth-century Spanish explorers of the Rio Grande valley to describe the majestic west-facing mountains reflecting the setting sun. The Precambrian Sandia granite is capped by a distinctive white band of Pennsylvanian carbonates to collectively suggest a section of watermelon to the imaginative, and, perhaps, thirsty Spanish explorer. Ultramafic xenoliths associated with the granite might even be interpreted as the watermelon seeds.

Additional information on Sandia National Laboratories and geochemical activities at the labs can be obtained at www.sandia.gov and www.sandia.gov/eeselector/gc/gc/geochem, respectively. Sandia is a multi-program laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE-AC04-94AL85000.

