Chemistry and Engineering of Shale Gas and Tight Oil Resources Development: Workshop in Brief

DETAILS

16 pages | 8 1/2 x 11 |
ISBN 978-0-309-38939-6 | DOI: 10.17226/21882

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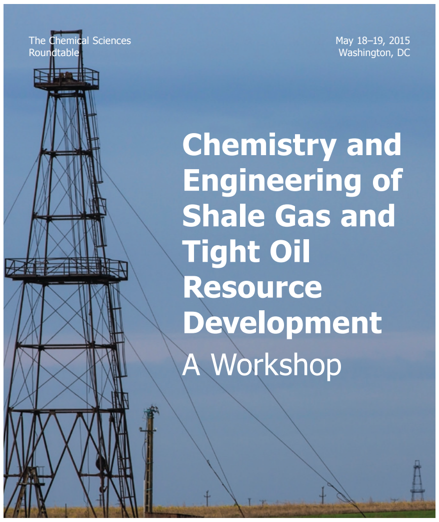
WORKSHOP IN BRIEF
Board on Chemical Sciences and Technology
Division on Earth and Life Studies
November 2015

Chemistry and Engineering of Shale Gas and Tight Oil Resource Development

A Workshop for the Chemical Sciences Roundtable



The Chemical Sciences Roundtable
May 18–19, 2015
Washington, DC

Chemistry and Engineering of Shale Gas and Tight Oil Resource Development
A Workshop

Oil and gas exploration in the United States has expanded with the increased use of horizontal, or directional, drilling to facilitate the recovery of shale gas and tight oil resources. The U.S. Environmental Protection Agency (U.S. EPA) estimates that 25,000 to 30,000 new hydraulic fracturing wells were drilled each year between 2011 to 2014 (U.S. EPA, 2015) , and the impact of those wells and the use of hydraulic fracturing has been a topic of public and policy discussion in recent years. Though chemistry and chemical engineering are used extensively in the hydraulic fracturing process, their roles are not well understood outside of the oil and gas industries. In a workshop held May 18–19, 2015 in Washington, DC by the Chemical Sciences Roundtable, practitioners and experts in these fields came together to discuss shale gas and tight oil resource development.

In order to be successful, each step of the hydraulic fracturing process relies on a combination of chemistry and chemical engineering, from the formulation of the chemical used to the development of methods to enhance resource recovery to the treatment of water emerging from the well. At the workshop, audience members representing industry, academia, regulatory agencies, NGOs, and the general public participated in the plenary sessions and in a series of focused breakout sessions. Topics included industry drivers for resource development, some social and economic impacts of the development, recent advances in technology and future research needs, and environmental concerns and impacts.

This workshop was designed to achieve two goals:

1. Inform scientists, engineers, policy makers, federal and state managers, and other interested parties about the chemistry and chemical engineering of shale gas and tight oil resource development.
2. Inform chemical scientists, engineers, and researchers in other relevant fields in industry and academia about research that is under way and potential areas for further research.

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[1] Assessment of the Potential Impacts of Hydraulic Fracturing for Oil and Gas on Drinking Water Resources, EPA, June 2015

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ECONOMIC DRIVERS OF SHALE GAS AND TIGHT OIL RESOURCE DEVELOPMENT

Key points made by presenter Alan Krupnick:

- The growth of hydraulic fracturing has national and sometimes regional impacts on gas and oil prices, and local and regional effects on regulation and infrastructure.
- Most forecasts predict a modest increase in natural gas prices; a natural gas will likely be one of a mix of energy sources commonly used in the future.

Although the technology of hydraulic fracturing was invented in the late 1940s, it was not until the early 2000s

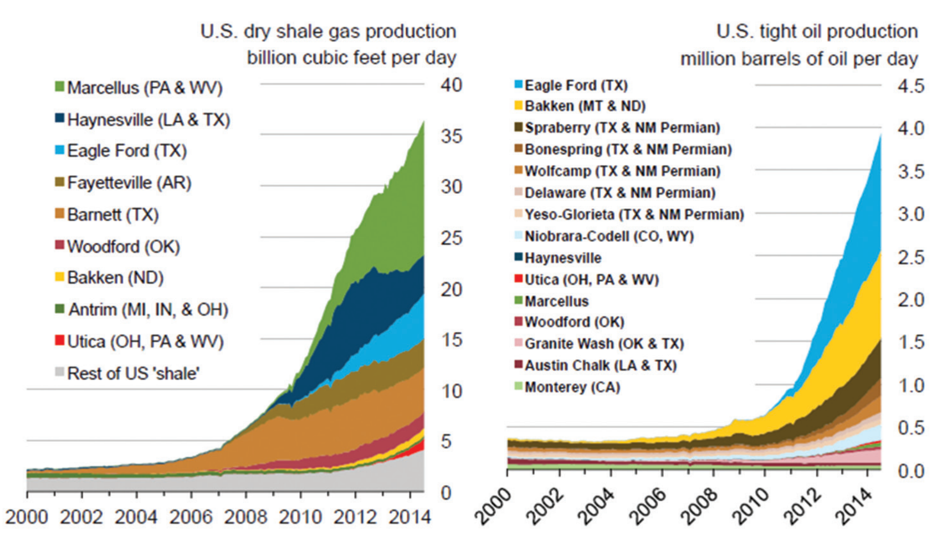

Figure 1. *Advances in horizontal drilling and fracturing technologies in the early 2000s drove a rapid expansion of shale gas and tight oil development throughout the United States across multiple shale rock formations. SOURCE: EIA, 2014. EIA derived from state administrative data collected by DrillingInfo Inc. Data are through July 2014 and represent EIA's official tight oil & shale gas estimates, but are not survey data. State abbreviations indicate primary state(s).*

A Short Description of Hydraulic Fracturing

Oil and gas rich shale reservoirs are typically found at least one mile or more below Earth's surface. Because shale formation rocks hold oil and gas tightly, conventional drilling is not very effective for extracting those fluids. Instead, a combination of horizontal drilling and hydraulic fracturing (often called "fracking") is used. As illustrated in the figure, a borehole is drilled vertically into the rock formation, just above the target shale formation, and is then curved horizontally into the shale formation for up to two miles or more. After the well has been drilled to a depth below any fresh water aquifers at the site, the hole is encased with cement and steel to prevent contamination of groundwater before any additional drilling occurs. This process is repeated after the total depth of the well has been achieved. This cementing prevents unintended migration of liquids and gases between rock layers. Once the well has been prepared, a mixture of fluids (0.5–1% by volume) and water is pumped under high pressure into the shale formation in order to fracture the rock. One well may use several million gallons of water.

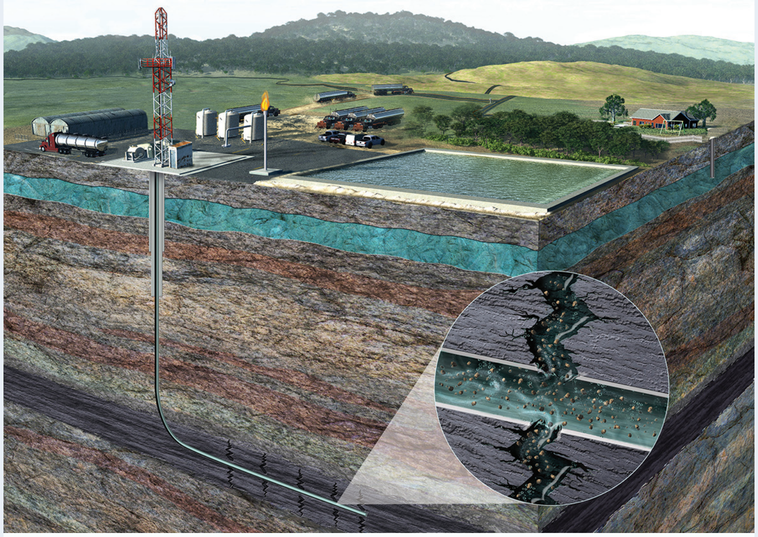

Illustration of the hydraulic fracturing process above and below ground. Reproduced with permission from Nicolle Fuller, Sayo-Art, LLC.

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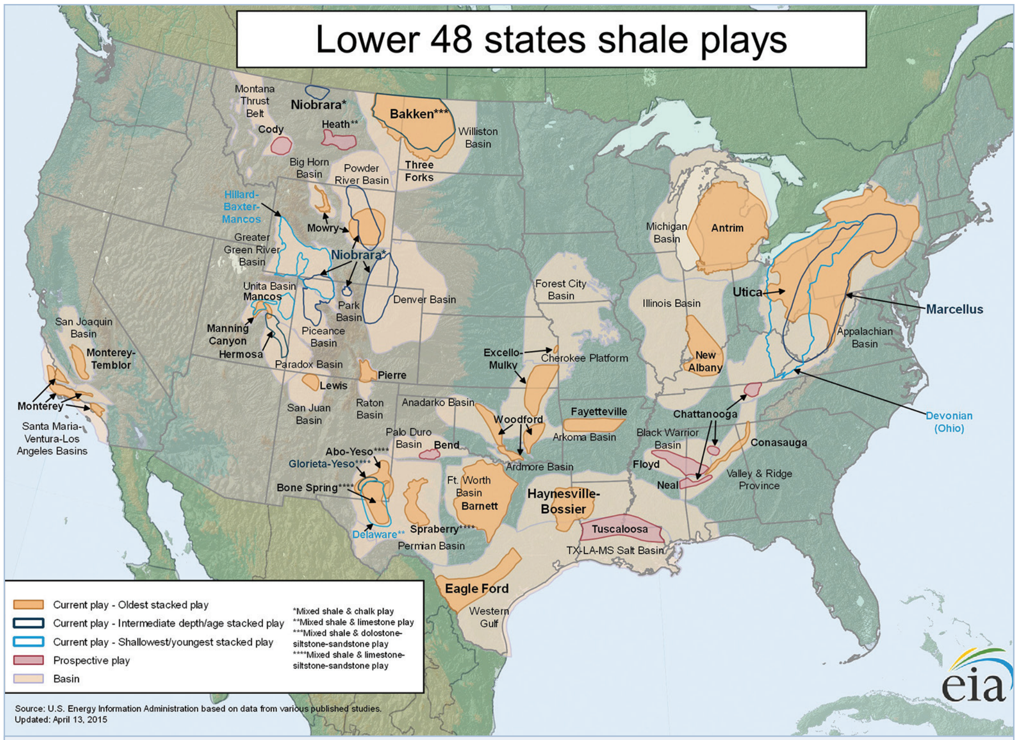
that horizontal drilling and fracturing technology was extensively used to extract natural gas (2000s) and oil (after 2010) from shale reservoirs. The subsequent expansion of oil and gas production in the United States has been dubbed a revolution. (See Figures 1 and 2.)

The workshop opened with a plenary talk about the economic present and future of shale gas and tight oil resource development from Alan Krupnick, Co-Director of Resources for the Future's (RFF) Center for Energy and Climate Economics. He opened by describing



Source: U.S. Energy Information Administration based on data from various published studies.
Updated: April 13, 2015

Figure 2. *Map indicating shale rock formations in the contiguous United States. EIA, 2015. Accessed 10/20/2015. http://www.eia.gov/oil_gas/rpd/shale_gas.pdf*

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The fluids are injected over a short period of time, usually within a week. Sand or other inert solids, such as ceramic beads, are injected into the formation to provide a support, or "proppant", which prevents the fractures from closing once the well pressure is released. In addition to proppant, other chemicals are added to the injected hydraulic fracturing fluids, typically blended at the wellhead during, or immediately before injection. The chemicals involved in the process, which make up a small percentage of the total volume of fluids introduced into the formation, may include the following:

- gelling and foaming agents to help to create desired fluid rheology, to create fracture volume and area, and to transport the proppant material;
- friction reducers to reduce the pressured needed to pump fluid into the wellbore;
- surfactants to optimize hydrocarbon removal by minimizing water oil-wetting of the rock surface;
- crosslinkers to enhance the ability of the gelling agent to transport the proppant material;
- breakers to force the gelling agent to break down into a less viscous fluid to aid fluid recovery later in the process;
- pH buffers to maintain the fracturing fluid in the correct pH range for optimum rheology;
- biocides to prevent the growth of bacteria in the well;
- corrosion inhibitors to prevent degradation of the steel well casing;
- scale inhibitors to control the precipitation of certain carbonate and sulfate materials;
- iron control chemicals to inhibit precipitation of iron compounds by keeping them in a soluble form; and
- clay protection chemicals to minimize clay damage to the formation from clay swelling or migration of fine particles.

The pressure in the well results in recovery of the desired oil and shale gas, in addition to fracturing fluids, called "flowback", and water from the formation, called "produced water". These waters are collected and may be treated and reused or disposed of, often in disposal wells.

some of the economics of the natural gas revolution in the plenary session. An increase in natural gas prices in the mid-2000s powered a boom, he said, but high levels of production and a drop in oil prices have since driven natural gas prices back down, where, according to Krupnick, they have mostly stabilized. Though its use for electricity generation has increased, Krupnick said the use of natural gas as a feedstock for chemical fertilizers and plastics has driven a kind of "renaissance" in the petrochemical industry. A movement to use natural gas in long-distance trucking and for short-haul fleets of commercial and municipal trucks and buses and some other transportation uses could drive additional demand, Krupnick said. On the resource recovery side, productivity per rig is increasing, though the number of rigs overall has decreased.

Krupnick conveyed a number of issues that could affect the economics of natural gas, including what he calls "social contract" issues. He highlighted the local economic effects of hydraulic fracturing operations. Many local governments, he said, are seeing revenues that either the state is sharing or that the local governments are earning from various taxes on the oil industry. In contrast, some towns have seen negative economic effects. For example, the city of Dickinson, ND in the Bakken shale field witnessed a 4-fold increase in tax revenues during the boom, but their debt went from $2.7 to 65 million as they paid for improvements to sewer systems, drinking water systems, and roads. In response to this problem, the North Dakota legislature just passed the SURGE bill, which provides to boom towns $500 million for road reconstruction, another $500 million to help with local financial difficulties.

Krupnick's group also looked at effects on local property values, which he said is a great aggregator of both perceived and real risks at the local level as it represents the "balance between the local negative impacts and the local economic positive impacts of development." For example, in an RFF study in Washington County, PA, they found that within 1.5 km of an active well, a home that is sitting on groundwater supplies was selling for markedly less than a comparable home further from the well. The findings indicated that proximity to the well was more important than intensity of activity at the well. Krupnick's team is also examining local effects on areas where shale gas development is occurring, for example, the potential of drilling-related truck traffic to affect accident rates in Pennsylvania.

Regulation is another issue that could affect the industry, Krupnick said. Government at the federal and state levels have tightened regulations throughout the entire development period, but Krupnick does not think those regulations have imposed significant costs on the industry. For example, increases in the number of states requiring pre-drilling water testing or other similar regulations could result in additional costs.

Another critical issue, Krupnick explained, is the question of how much methane is escaping into the atmosphere from shale gas and tight oil production. Because methane is a powerful greenhouse gas, it does not take much natural gas escaping to make it a greater contributor to greenhouse effects than coal for electricity generation. "For natural gas to really make gains and get the environmental community off of its back," said Krupnick, it needs to clearly have less of an environmental impact than energy produced from coal. Participants in the meeting noted that organizations and academic researchers are engaged in studying methane leaks from hydraulic fracturing wells, and more information will be available in the coming years.

Looking to the future, there will be no bust, Krupnick said. Physically and geologically, there are still many productive shales, and all forecasts project increases in natural gas prices over time. In terms of consumption, Krupnick said that the growth in electricity demand will be primarily met with natural gas and renewables. New work from RFF looks at how the fuel mix might change as a result of the Clean Power Plan, which is a federal policy to reduce greenhouse gas emissions from the electricity sector. The mix, he said, would depend primarily on how states implement the plan. "Nobody knows which [scenario will] play out," Krupnick said, "but in the best case for natural gas there is an increase of 22 percent in the demand for the electricity sector."

HYDRAULIC FRACTURING: PROCESS AND CHALLENGES

Key points made by presenter Randy LaFollette:

- Rock formations are not equal. No one approach to hydraulic fracturing applies in all cases.
- Current computational models do not take into account the full 3D physics of the shale reservoir and 3D seismic data is limited.

Randy LaFollette, a chemical engineer at Baker Hughes, provided an overview of the potential benefits of hydraulic fracturing and the many variables that affect production results. A main point, he said, is that the physical, chemical and mechanical properties of rock formations vary widely. Any drilling of this type will require passing through multiple layers of different types of rock, which can vary in depth from millimeters to tens of feet or more. Each layer will have its own characteristics, including porosity and strength, and the interfaces between these layers can be complex. In addition, contained within each layer there may be natural fractures that can affect the performance of the drilling and of the recovery.

The ease with which shale gas or tight oil can be recovered is affected by the reservoir's "mobility," (described as μ in Figure 3, where k is the permeability of the formation, and μ is the viscosity of the oil or gas). Mobility refers to how easily fluid flows through a particular rock pore network. All else being equal, the lower the natural permeability of a given well, the greater the need for effective hydraulic fracturing to achieve recovery. LaFollette said that the U.S. reservoirs with the highest mobility, where oil and gas came up out of the ground without fracturing, were mostly depleted by the end of World War II, producing about 7 billion barrels of oil. The industry moved on to lower permeability reservoirs that needed some stimulation to produce oil. Today, LaFollette said, we are dealing mostly with the lowest mobility reservoirs, which are rock formations that have been under high pressure (0.7–0.9 psi per foot below the surface) for geologic time. Those formations are the most abundant by volume, and are actually the source rocks for the higher mobility wells.

In lower quality reservoir rock, fracture surface area is critical for good recovery: a lot of surface area is necessary for a reservoir to provide a pathway for the oil or gas. This relationship between the system permeability, whether natural or enhanced by fracturing, and production is described mathematically by the Fundamental Rate Relationship (see Sidebar, next page), and an operator will use this law along with an assessment of the unique physical properties of the formation to determine the best approach for recovery for a given well. Essentially, the lower the mobility within a formation, the greater the fracture length required for a productive well. LaFollette noted that fracture spacing is important too: "If your spacing is too far apart, you'll leave a lot of oil and gas trapped in the shale formation."

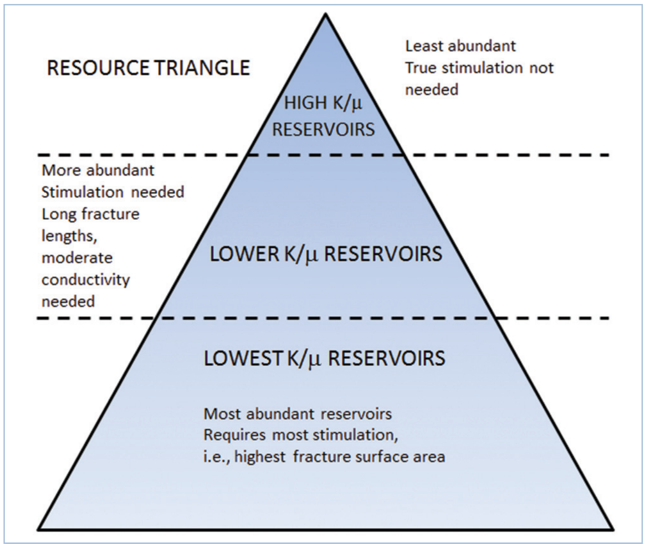

Figure 3. *Hydraulic fracturing is used to extract tightly held oil and gas from shale rocks, which are the "lowest mobility reservoirs" for oil and gas. The highest mobility reservoirs, where oil and gas rose naturally from the ground, were mostly depleted by the end of World War II and reservoirs that required more stimulation (lower mobility reservoirs) have been heavily drilled for many decades. SOURCE: LaFollette, R. Modified after Gray, 1977 in Masters, 1979.*

WHAT DRIVES INDUSTRY CHOICES IN HYDRAULIC FRACTURING FLUIDS AND CHEMICALS?

Key points made by presenters Javad Paktinat and Bruce McKay:

- With increased economic and regulatory pressures in recent years, standard practices are being fundamentally re-examined to improve hydraulic fracturing production, while reducing cost and environmental impacts.
- Translating knowledge gained in the laboratory to a functioning well is often challenging because the range of temperatures and pressures present in a borehole sometimes greatly exceed what is currently feasible to create in the laboratory.

Economically efficient production of oil and gas from unconventional shale resources requires a very large volume of hydraulic fracturing fluids, which today are highly engineered to enhance production. The number of chemical additives and the specific mixtures used in a typical fracture treatment depends on the properties of the reservoir rock, more specifically the rock permeability and brittleness.

Javad Paktinat of the Anadarko Petroleum Corporation discussed his ongoing work to improve hydraulic fracturing production, while reducing cost and environmental impacts. He presented these advances in the context of emerging challenges, including recent restrictions on the use of fresh water, growing environmental concerns of reusing flowback and produced water, and lower prices for natural gas.

Paktinat said the elements that engineers can alter to optimize hydraulic fracturing are: (1) the water source (freshwater, flowback or produced water, or reclaimed or waste waters); (2) the fracturing fluid system (guar gel system, cross-linked gel system, or slickwater, see Box 1); and (3) the major fracturing fluid chemicals for friction reduction, bacteria control, clay stabilizer, and scale inhibitors. He illustrated in several areas how experimentation and case studies have provided new ways to achieve multiple goals.

Paktinat said that the source water is a major factor driving the choice of hydraulic fracturing fluid. Increased use of high salinity waters, such as those found in produced water, can adversely impact fracturing fluid performance. Thus designing systems and disposal systems that work well with high salinity waters is a priority, Paktinat noted, because using such waters can both conserves fresh water and help eliminate trucking traffic needed to bring in fresh water and dispose of produced waters.

Box 1. Characteristics of Fracturing Fluid Systems

- **Guar gel system**
  - Made from guar bean
  - Advantage of being a cross-linked fluid to better carry sand (proppant) into the well
  - Resistant to high total dissolved salt (TDS) brines
- **Cross-linked (CMC) gel system**
  - Made from cellulosic material
  - More sensitive to high TDS brines
  - A polymer required to achieve same viscosity as guar
- **Slickwater (SW), one type of friction reducer)**
  - Polyacrylamide
  - Most common fluid used
  - High molecular weight, low cost

Paktinat said that bacteria control is the second most important element that engineers and formulators must consider when designing the fluids. Bacteria produce hydrogen sulfide, which can sour a well very quickly. Bacteria control must be compatible with the fracturing fluid, quickly kill bacteria and

Fundamental Rate Relationship for Hydraulically-fractured Wells

The production rate (q) of a hydraulically-fractured well is dependent on its mobility (k/μ) as determined by the "fundamental rate relationship" where k is the permeability of the rock, h is the thickness of the producing layer, Pres is the reservoir static pressure and Pwf is the wellbore flowing pressure, μ is the viscosity of the reservoir fluid in situ (the lower the μm, the greater the ease at which hydrocarbons can flow in that pore system), re is the drainage radius of the well, rw is the well radius, and S is the skin factor for the well.

$$q \approx \frac{2\Pi kh(P_{res} - P_{wf})}{\mu[\ln(r_e / r_w) + S]}$$

LaFollette described several challenges his company and others in industry are examining and trying to solve, including:

- Uncertainty in "height growth" barriers of the fracture, which can affect how far apart fractures can be placed and must account for vertical stress in the rock, subseismic defects, and other factors. LaFollette said that a big part of this issue is that the current computational models do not take into account the full 3D physics of the reservoir and 3D seismic data is limited. For example, subseismic defects (natural fractures) are mostly unknown.
- Fracture propagation is not 100% efficient—there is "leakoff." That is, some of the injected fluid moves into the pore system in the rock formation adjacent to the fracture walls, including open natural fractures. The extra fluid gets sucked in and stays put, LaFollette said.
- Some fracturing proppants (sand or other material to keep the wells open) are not stable in harsh environments. Long-term immersion in high salinity brine and shale at high temperature results in strength loss and also scaling.

keep it down, meet environmental standards, and be cost-effective. There are standard approaches to controlling these bacteria, but other approaches, chemical and physical are also being investigated.

Regarding fracturing fluid systems, Paktinat discussed innovations and modifications being used in an endeavor to increase return and to tailor systems to specific wells. For example, he highlighted the use of hybrid systems composed of two or three fracturing fluids, to maximize their distinct advantages. Typically, a fracture is opened with slickwater, which is a low friction system, and then cross-linked gels are used toward the end of each stage to better carry sand and proppants into the fracture.

With increased economic pressures in recent years, Paktinat said, all of the standard practices are being fundamentally re-examined. For example, he was involved with an experiment to determine the value of using clay stabilizer. The results showed that in that in one case there was no adverse effect when it was removed, the formulation was modified accordingly. Similarly, with regard to scaling of the well due to salts and minerals, Paktinat said the industry is now carrying out rigorous water monitoring to learn more about what is driving scaling and how best to treat it with available methods. Industry is also running predictive models to calculate the optimal amount of scaling inhibitor so as to eliminate most of the scaling without wasting the inhibitor, which is costly.

Paktinat also spoke of advances made by using polyacrylamide friction reducers—both cationic and anionic—which can be optimized depending on the water used. Notably, cationic friction reducers perform well in higher salinity produced waters, permit the use of a wider range of biocides, and exhibit some clay stabilizing properties. Anionic friction reducers perform well in fresh and mid salinity waters, and allow the use of a wide range of scale inhibitors. Increasing the understanding of the role and chemistry behind each of the elements of the fracturing fluids may result in additional tools operators can use to reduce water and material usage at the wells.

Bruce McKay, a chemical engineer at Schlumberger, discussed the engineering objectives that drive industry decisions in the design and development of fracturing fluids. The ideal goal of the oil and gas industry, said McKay, to provide society with access to energy sources and with feedstocks for the petrochemical industry as efficiently and responsibly as possible. This requires that a number of operators must first decide where to drill by evaluating the rock formations and determining the size and mobility of the reservoirs. The next step, which is McKay's job, is to design an efficient and economical completion system—defined as "the establishment of the intimate contact between the well as it is drilled, cased, and cemented—and the reservoir, as a living, breathing, producing thing through which hydrocarbons can be accessed." McKay said his most important message is that, although every rational decision should be connected to a piece of information, engineers almost never have access to all the information that they would like to have.

Hydraulic fracturing engineering jobs are as complicated as the space shuttle, McKay said, because the shale formations really do not want to give up their oil and gas. Industry is always on the lookout for new methods. "Operators all want to be the *second* to try a new method of stimulating a well," he quipped. "They have no tolerance for operational or safety risks, they all want to minimize costs and, if the last two are satisfied, they might be able to improve production."

McKay said there are three roles for the hydraulic fracturing fluid: (1) propagate a fracture; (2) transport proppant; and (3) degrade or otherwise not interfere with recovery pathways. McKay works on permeability—the ease of fluid flow through a given rock system. To keep the fluid flowing, you have to add proppant to "prop up" the fracture to keep the fluid flowing through it, or the permeability may decline, said McKay, as a result of the residue from active drilling.

He talked about advances in hydraulic fluids being used to enhance production. The industry today is widely using a gel called borate cross-linked guar, McKay said. Guar is a biopolymer grown from beans. The guar gel has a viscosity comparable to olive oil, except it is much better at suspending proppant. The magic, McKay said, is in creating a cross-link by "stapling the polymer together" with borate. It displays a property known as shear recovery, making it possible to pump a thick gooey gel at 50 barrels per minute and pass it through holes about "the size of a pinky" and then through newly exposed fractured rock. The fluid is not degraded by all those high shear events and maintains its viscosity. It works well at temperatures below 300 degrees Fahrenheit, which is representative of the temperatures in many wells, but at higher temperatures other strategies arerequired, such as some of those described by Javad Paktinat.

McKay described another new development, slickwater gels, which are used primarily for gas and dry gas production. Slickwaters overcome friction because they contain a synthetic polymer that “flexes” as it meets eddy currents and dissipates energy before the rock walls can push back with friction. Slickwater moves through a pipeline at high velocity so that turbulent flow moves sand grains, turn corners, and even props open natural fractures. New research is focused on using a hybrid of slickwater and guar gel.

There are other areas ripe for future research because it is very difficult to replicate real-world conditions in the lab, McKay said. Developing the ability to test under real world conditions of pressure and temperature simultaneously may be a fruitful avenue. McKay also noted that improving the conductivity of proppants, controlling emulsions of oil and water, and controlling bacteria, biofilms, and scaling from carbonate and sulfate minerals—which some say create challenges for about 30% of hydraulic fracturing activities on a global scale—would support more efficiency.

ALTERNATIVE WATER SOURCES FOR HYDRAULIC FRACTURING

Key points made by presenters Danny Reible and Radisav Vidic:

- Waste water handling and storage methods around the country vary widely.
- Water availability for hydraulic fracturing may pose a challenge in certain locales. Shipping fresh water to sites where it is not locally available is costly, and reducing the reliance on fresh water is a goal for the industry.
- Water sources used and being considered for use in hydraulic fracturing in the future include wastewater, brackish groundwater, and recycled produced water.
- Efforts are underway to identify ways to use less desirable water sources, such as contaminated water from historic mining operations, for hydraulic fracturing operations.
- There are many options being considered for use of produced water from hydraulic fracturing, but the risks of using these waters for different applications have not yet been fully assessed.

Danny Reible of Texas Tech University explained the challenges and opportunities of using alternative water sources for hydraulic fracturing. Reible began his talk by describing how issues of water availability tend to be local. Nationally there is water enough for hydraulic fracturing, but water scarcity is a local and regional concern, and addressing water usage must take that into account. Total water use for hydraulic fracturing in the United States was expected to peak at 120,000 acre-feet per year, which is not a high number when compared to other water uses, such as agriculture. Nonetheless, both in the U.S. and abroad, Reible said, many shale plays are located in areas that are water stressed, sometime exceeding sustainable rates of water withdrawal (see Figure 4)[2]. “To the extent possible,” Reible said, “we need to minimize the “good water” we pump down the hole.”

He said that most of the technical issues could be overcome, but that most of the challenges lie in issues that are economic, regulatory, historic, and logistic. From an economic perspective, Reible said, we do not value water equally across all uses (e.g., agriculture, municipal, hydraulic fracturing) and water costs/value is a fraction of that of oil. This affects the drivers for creating an infrastructure, such as pipelines, for water distribution to where it is needed. A second challenge in Texas is that disposal of produced water is much cheaper than treating or recycling it. It is the opposite in the Marcellus Shale (e.g. PA and WV) where the high cost of disposal has driven a lot of recycling. Alternative water use

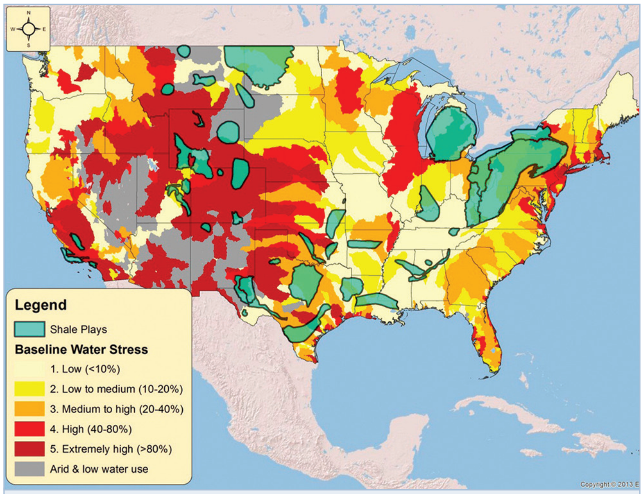

Figure 4. *Several shale plays are located in areas that are moderately to extremely water stress, making it important to assess alternative water sources for hydraulic fracturing.*[2]

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[2] Reprinted with permission from Avner Vengosh, Robert B. Jackson, Nathaniel Warner, Thomas H. Darrah, and Andrew Kondash *Environmental Science & Technology* 2014 48 (15), 8334–8348DOI: 10.1021/es405118y Copyright 2014 American Chemical Society.

in Texas has been driven by the cost of access to water and also the negative perception of growth of hydraulic fracturing during a period of severe drought, Reible said.

Reible examined three types of water that could be used for fracking to address water availability: (1) municipal and other wastewaters; (2) brackish groundwater; and (3) recycled produced water. As always, Reible said, the old real estate adage applies: the extent to which each option can be applied is all about "location, location, location." For each option, availability of the water near the point of use is critical. Regulatory factors can be a problem, for example some places require the return of wastewaters to the environment after use to maintain environmental flows, said Reible For example, the municipal wastewaters cannot be used unless they can be returned to the same watershed, something that is not feasible for flowback or produced water from a hydraulic fracturing process due to contamination and salinity.

Reible explained that many shale reserves are co-located with brackish ground waters that provide a possible alternative water source. The location of those waters is known, because industry needs to avoid them when they drill to get oil and gas, and the chemical characteristics of these waters can vary widely from site to site. One problem in their use in hydraulic fracturing, Reible said, is that an understanding of the chemistry of concentrated brine solutions and reactions that can occur within them is currently lacking. Though there is some understanding of the fundamental chemistry, thermodynamic models and an understanding of the conditions under which they could increase scaling, for example, would be beneficial.

Reible said that he thinks there is a lot of potential for reusing produced water to offset fresh water needs for hydraulic fracturing, but that conditions have to be right. The biggest requirement is a good match of the volume of produced water and the volume of water needed for fracturing, he said. Reible talked about one operator in Texas with the right conditions: they collect produced water from their 165 wells that produce about 30,000 barrels of oil per day and use it toward their ongoing requirement for 30,000–60,000 barrels of water for hydraulic fracturing; they own the water and mineral rights on the land; and they have developed a

Use of Abandoned Mine Drainage as a Water Source for Hydraulic Fracturing

Radisav Vidic of the University of Pittsburgh talked about some of the challenges of reusing produced water in the Marcellus Shale and some potential solutions he is exploring. The desire to reuse water is high in Pennsylvania for two reasons, Vidic said. The first is that water disposal is very expensive, because the produced water has to be trucked to Ohio or West Virginia. Second, truck traffic is the biggest complaint industry gets from members of the community. Shifting from trucking water into an area to pumping it could significantly reduce traffic and, potentially, costs. However, water reuse in the Marcellus Shale is complicated by the fact that the produced water is high in total dissolved solids (TDS) such as Ba^{2+}, Sr^{2+} and Ca^{2+}, which can cause scaling underground, and also very high in naturally occurring radioactive materials (NORM).

Vidic and his team had the idea of using Abandoned Mine Drainage (AMD) as a water source. In Pennsylvania, the Marcellus Shale is just under the state's coal reserve. AMD water, which is full of sulfates, affects 4,000 miles of streams and associated groundwater. The idea was to mix the produced water rich in Ba^{2+}, Sr^{2+} and Ca^{2+} with sulfate-rich AMD water in order to precipitate out solids such as, barite, celestite and gypsum, respectively, and help clear the water. "If you take the AMD from the environment," said Vidic, "the industry is a savior because it's helping to solve legacy environmental problems."

Vidic and his team tested the idea in the lab. They found that barite precipitates out and leaves clear water with very low turbidity (<1 ntu). However, in real world conditions, they found radium was coming out of the water in equal parts with barium, resulting in a radioactive solid. Pennsylvania has allowed industry to dispose of radioactive solids in landfills under what is known as the Allowed Source Term Loading guidelines, but has recently made the guidelines more stringent. Vidic said that his calculations show that, with these new rules, such disposal will be violating the allowable limits by the 2030s.

Vidic has been exploring a new alternative for managing solid radioactive waste by putting it back in the ground as proppant. The only problem, Vidic said, is that the proppant particles were a too small to meet American Petroleum Industry guidelines. Thus, Vidic's team has been working on a method to grow the particle size and is getting good results.

relatively easy treatment method to remove the iron and oil from the produced water and also control the bacteria in it. There are few environmental impacts of the recycling, Reible said, and the operator was proud that they eliminated 80,000 local truck trips to carry water. Barriers for reusing produced water are not as much technical as logistical and regulatory, said Reible. He noted that depending on local restrictions, it may not be allowable to recycle or reuse the water at a nearby site or to transport it to a different location. Some areas are modifying these restrictions to allow for increased movement of water between sites and operators.

ECOLOGICAL AND ENVIRONMENTAL CONSIDERATIONS

Key points made by presenters Briana Mordick, Avner Vengosh, Denis Tuck, and Will Stringfellow:

- Public concern about hydraulic fracturing and its processes has grown along with the expansion of the practice. These concerns relate to water sourcing contamination from waste water and drilling operations, injection of chemicals into the ground, and risks from spills.
- Transparency among companies, governments, and the public regarding chemicals used during the hydraulic fracturing process has increased, but there is room for additional work in this area.
- The number of chemicals and complexity of the mixtures in which they are used, combined with the extreme and variable conditions under which they are handled, is a challenge for understanding their fate and transport as well as toxicity or environmental concerns posed by their use.
- Additional research may help identify appropriate methods for monitoring of wells to identify sources of contamination.

As the utilization of hydraulic fracturing grows, so too does the level of public concern over the practice's impacts on the environment. Concerns include the high consumption of water resources, the generation of large volumes of wastewater, the irreversible injection of chemicals deep underground, and the potential impact on drinking water and surface water resources via potential migration of contaminants from well pads or accidental and operational spills.

Briana Mordick of the Natural Resources Defense Council said that the majority of states that have significant oil and gas production all have some sort of law requiring disclosure of the chemicals used in hydraulic fracturing, but that there are several issues with the quality of what is being disclosed. One issue, she said, is that it can be hard to determine the specific chemicals being used and in what amounts. A recent EPA study found that, on average, disclosure reports had five chemicals that were reported as “confidential business information” (CBI), Mordick said. Disclosures include the total volume of water used and the ingredients are noted as a percent mass of the total fluid. As neither the total volume of fluid used nor the total mass of the fluid used are reported, Mordick noted that this introduces “a bit of opacity” in understanding the total quantity of a given chemical used, though it can be approximated by assuming the majority of the fluid is water. She added that chemicals are often reported by their trade name and by their purpose, which is sometimes straightforward (e.g., corrosion inhibitor) but can be vague (e.g., “additive”).

Another issue, Mordick said, is that there is no disclosure of chemicals that form as hydraulic fracturing fluids interact with the rock formation. This is an issue that is very important for an occupational health researcher, because the person who is most likely to be exposed is the person who is dealing with the produced water from the service company.

It is also important to realize that hydraulic fracturing fluids are only part of the universe of chemicals used in the oil and gas production process, but they are currently the only fluids for which the chemical components are disclosed, Mordick said. Other fluids, such as drilling fluids, enhanced oil recovery fluids, and produced water do not have to be disclosed. The task is made all the more difficult, she said, because produced water has a very wide range of compositions.

Mordick pointed out that while public interest over fracking is driving public policy, it is not necessarily where the greatest environmental or health risk lies. In California, the vast majority of oil and gas production is still conventional, which she said has been mismanaged for decades—more than 2500 wells were permitted to inject wastewater into federally-protected drinking water aquifers. It is extremely important, she said, to get the scientific information to those who are setting policy and make sure that policy focuses on the “right risks” with regard to hydraulic fracturing.

Avner Vengosh of Duke University said the motivation for research his team has conducted is that the U.S. Energy Information Administration (EIA) has shown that, in spite of the price drop, natural gas will be in demand for the foreseeable future (see Figure 5). Thus, understanding the environmental impact, especially on water, is important.

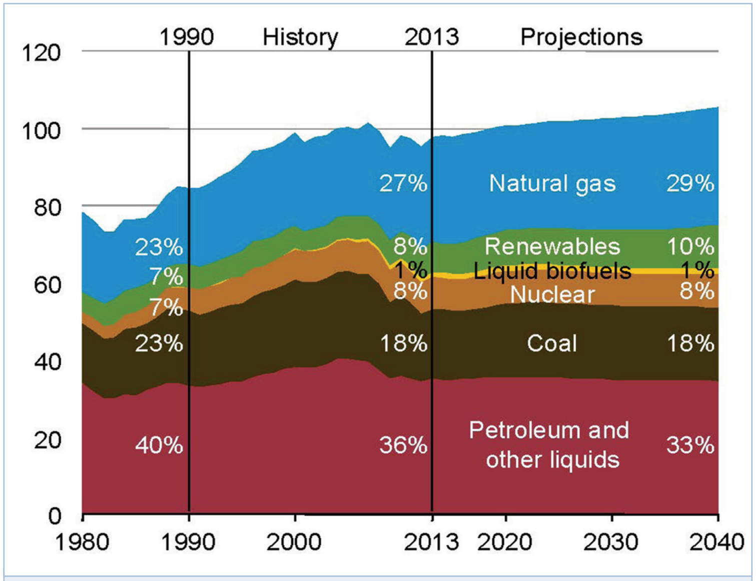

Figure 5. *EIA projections of energy consumption by fuel show that natural will be in demand for the foreseeable future. SOURCE: EIA 2015*

Vengosh and his research team have reviewed the scientific literature and collected samples from several states (see Box 2) in an effort to understand the different processes that occur both upstream and downstream from shale gas development. Specifically the team is looking for evidence of:

1. stray gas contamination of shallow aquifers;
2. contamination of surface water and shallow groundwater from spills, leaks, and disposal of wastewater and hydraulic fracturing fluids;
3. accumulation of toxic and radioactive residues in soil or stream sediments;
4. formation of carcinogenic disinfection byproducts in downstream drinking water utilities from disposal or spill oil and gas wastewater; and
5. over-extraction of water resources that could induce water shortages.

Vengosh said that the naturally occurring chemicals in the brines contained in the produced waters should be added to the list of chemicals that are managed. He referred to a 2009 report by Hayes[3] showing that 25–45% of the total injected water is returned, which means that a lot of injected water is staying underground and that the water coming back is mostly brine that was entrapped within the shale formation. Vengosh also pointed out that the high concentrations of bromide and iodide present produced water, even if diluted as part of disposal procedures, has the potential to result in the creation of unexpected byproducts during drinking water disinfection procedures. He noted that these byproducts should also be monitored.

The need to monitor the dose level of NORM, which were a known concern for hydraulic fracturing back in 1950s, is very important, Vengosh said. The Marcellus Shale formation contains a high concentration of radioactive nuclides compared to other formations in the United States, and some of these nuclides are present in produced water from the wells at concentrations far exceeding those allowable under the federal drinking water standard. The rapid intensification in oil and gas production is increasing the risk of leaks or incorrect disposal that could lead to ground and surface water contamination, and this may affect the ability of downstream water treatment facilities to maintain acceptable levels of radiation in drinking water, he said.

To help determine if contamination in a sample is coming from hydraulic fracturing fluids or if it is coming from other sources of contamination such as acid mine drainage, Vengosh said his team developed a systematic method of looking at chemical isotopes in a sample. Using multiple geochemical and isotopic tracers (carbon isotopes in hydrocarbons, noble gas, strontium, boron, and radium isotopes), they developed an isotopic fingerprint

Box 2. Sampling by Duke University Research Team

- 800+ shallow private wells in PA, NY, WV, AK, NC, TX;
- About 100 produced/flowback waters samples from conventional and unconventional wells in PA, NY, AK, CA;
- 200+ surface waters in PA, CO, WV and river sediments downstream from waste waters disposal sites.

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[3] Hayes (2009), Sampling and Analysis of Water Streams Associated with the Development of Marcellus Shale Gas

Figure 6. Produced water used for irrigation in the Cawelo water district in California. SOURCE: Lauren Summer/KQED Public Media for Northern California.

to distinguish between naturally occurring dissolved gas and salts in water and contamination directly induced from shale gas drilling and hydraulic fracturing operations.

With their method, Vengosh's team was able to help show in a 2013 paper[4] that in Pennsylvania, wastewater being moved to brine treatment facilities was not adequately treated to remove all the inorganic contaminants, some of which were ending up in streams and rivers. Vengosh said other potential pathways into the environment include spills and accidental releases, spraying of salts from operations onto roads for deicing and dust suppression, and leaking from ponds and storage reservoirs.

University of the Pacific and Berkeley National Laboratory, explained the work he has been doing over the past two years to better understand hazards and risks posed by tight oil production in California. He said the studies were prompted by the Bureau of Land Management in response to a public concern and related lawsuits about hydraulic fracturing on federal lands, and also by a group of new laws in California requiring various scientific studies. Stringfellow emphasized the fact that the studies are very California-specific and so would not necessarily apply to other geologies and places where natural gas production is the focus, rather than oil production as it is in California.

Stringfellow said his team has developed inventories of chemicals used, which are heavily reliant on voluntary reports from industry, such as those provided thorough FracFocus, an online registry managed by the Ground Water Protection Council and Interstate Oil and Gas Compact Commission that encourages voluntary reporting by industry of the chemicals they are using. The full list of the databases they consulted is in Box 3. Stringfellow's team identified more than 300 chemicals or chemical mixtures that have been reported as being used in California for hydraulic fracturing. "The problem in trying to respond to public concerns is how to evaluate so many chemicals, because you have to go through the whole list," Stringfellow said.

To get a handle on this problem, Stringfellow's group is developing an environmental profile for each chemical, which is a necessary first step for evaluating the hazards and risks associated with a chemical and for conducting analyses such as how the chemical is transported in groundwater. As the list of chemicals to be profiled is long, chemicals that are used most often and work in the largest quantities and concentrations are being given priority. The profile assigns a level of toxicity (aquatic and mammalian) as well as other hazards, such as flammability and corrosiveness, on the basis of the Globally Harmonized System for the Classification And Labeling of Chemicals (GHS)—a worldwide system now adopted in the United States. Added complications arise, he said, because industrial chemicals often are not pure compounds; they may be mixtures, blends, and include such things as solvents and surfactants. Some companies have developed similar scoring systems for internal use. For example, Denise Tuck of Halliburton describes her company as having a system that takes into account environmental concerns such as bioaccumulation, biodegradation, ozone depletors, volatile organic compounds, hazardous air pollutants, priority water pollutants, and environmental

Box 3. Data Sources for Chemical Inventories in California

- Voluntary industry reports
- FracFocus (Versions 1 & 2)
- Department of Oil Gas & Geothermal regulation (DOGGR)
- Central Valley Regional Water Quality Control Board (CVRWQCB)
- South Coast Air Quality Management District (SCAQMD)

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[4] Warner, N.R. et al. (2013) "Impacts of Shale Gas Wastewater Disposal on Water Quality in Western Pennsylvania" *Environmental Science & Technology* 47 (20), 11849–11857 DOI: 10.1021/es402165b

endocrine disruptors in addition to those captured under GHS.

The studies are just beginning to look at releases of chemicals into the environment, Stringfellow said. A big issue, he continued, is communicating to the public that chemical inventories do not become an environmental hazard until there is a release into the air, water, or soil. His team is looking at the known ways chemicals are released into the environment, including re-injection of produced water for enhanced oil production and use of produced water in dust control and irrigation, a process that is unique to California. According to Stringfellow, some produced water is going into unlined disposal pits in the California Central Valley.

The processes by which chemicals may undergo transformation or be transported in the environment are poorly understood, which makes it hard to determine the environmental risks, said Stringfellow. Determining risks to humans requires the additional step of assessing exposure pathways.

Stringfellow thinks the public is not convinced that hydraulic fracturing is safe, and that there is a need to respond to public concerns. Mandatory disclosures implemented in 2014 are helpful, he said, but he also called for more “modern rules” of operation. “We are doing things like disposing in unlined pits, which was a bit of a shocker to most of the people who have been involved in the hazardous waste industry,” he said. “That just does not appear to be a very good practice.”

CLOSING THOUGHTS

The speakers covered a wide range of topics addressing chemical and chemical engineering challenges at each stage of the hydraulic fracturing process for shale gas and tight oil recovery, from evaluation of a site to disposal of produced waters and other environmental concerns. Given the limitations inherent to a 1.5 day workshop, neither speakers nor participants could provide a comprehensive examination of these issues, but it is hoped that the summary here will provide a useful reference and addition to any engaged in conversations about hydraulic fracturing in their community or country.

Topics Discussed in the Breakout Sessions

Discussions during the breakout sessions were guided by questions suggested by the organizers. Topics discussed were presented by rapporteurs from each session. The comments are not reflective of consensus views of the participants, the CSR members, or the National Academies of Sciences, Engineering, and Medicine. They are provided here to present a complete picture of the workshop's events. The breadth of topics is an indication of the array of perspectives and technical challenges present in this area. Those who wish to seek guidance from this list are advised to obtain additional input from appropriate experts.

Participants discussed technical challenges and information gaps on the following topics:

Chemistry in the Well

- Characterization of the actions of all additives and increase understanding of the modes of action of each (clays, emulsifiers, etc.)
- Characterization of injected materials, including in-well transformation, transport, and degradation pathways and products, both organic and inorganic
- Identification of substitutes or alternative chemicals or methods of achieving the same effect with reduced hazardous effects or undesirable degradation products that interfere with production
- Clarification of the differences in chemistry that can occur with different water sources (brine, recycled produced water, etc.)
- Identification of methods to modify wettability in a formation

Geophysical/Geochemical

- Improvement of the understanding of the origin of the produced water. How is it affected by the heterogeneity of the geological features and the injection water?
- Improved reservoir modeling, mechanical modeling, and 3D modeling of fractured systems
- Increased accuracy of geochemical models to improve predictive capabilities
- Improved understanding of mechanisms of extraction of minerals and metals from the rocks
- Clarification of the reasons for variations in flowback characteristics across formations
- Improvement of the understanding of the origins of source water for recharged wells

Sample and Data Sharing

- Development of systematic methods of collecting and distributing samples from sites
- Creation of a centralized and standardized database or system for sharing files and data related to this research
- Increased sharing of geophysical data to support model development

On-Site Monitoring

- Development of both techniques and strategies for sampling from wells
- Improved aqueous and solid-state tracers for monitoring of flow pathways would aid in monitoring techniques for active and closed wells
- Longitudinal studies of fracturing fields (active and inactive) might assist with understanding the dynamics of the system and long-term integrity of capped well bores

Water Sourcing

- Continued work to support produced water reuse
- Consideration of new strategies for transport of produced waters to multiple sites
- Improved understanding of the variables important for compatibility of water, fluids, and formations.
- Characterization of the kinetics and thermodynamics of concentrated brines

(continued)

Topics Discussed in the Breakout Sessions (continued)

Biology in the Well

- Characterization of bacterial populations in wells
- Development of new methods for controlling bacterial populations to reduce the need for biocides

Management of NORM in Produced Water.

- Development of techniques and materials to support separation, encapsulation, retention in the well, etc.
- Characterization of fate and transport of this material in the subsurface
- Management of environmental and health impacts in case of spills or other release
- Development of systems that reduce the risks of release (reduced number of joints, continuous welds, etc.)

Environmental Concerns

- Increased understanding of potential environmental concerns including silicate/dust exposures, vapors and emissions, acid handling, air toxics, etc.

Other Concerns

Public Engagement

- Creation of spaces to bring together technical experts, social science experts, and stakeholders for shared discussion and learning
- Transparency of the activities occurring related to hydraulic fracturing in communities and in decision-making could support public engagement

Industrial-Academic Collaborations

- Development of a roadmap in collaboration with academic and industrial representatives might aid in directing research, both fundamental and applied
- Consistent funding for industry-academic collaborations can be challenging as its availability is often linked to global economic trends. Could additional mechanisms to support cross-institutional/cross-sector research on targeted areas be identified?
- Cross-industry collaborations could allow for pre-competitive space to address fundamental, cross-cutting technical challenges appropriate for academic and industrial study

Testing and Development

- Academics have stated they have challenges gaining access to sites in use for studies
- Laboratory spaces for testing of fluids under field-representative temperature and pressure conditions are lacking and expensive to develop. A shared, national facility could assist researchers from both industry and academia
- An inventory of high pressure and temperature facilities at national laboratories would be helpful for test and development efforts
- A real world test site, perhaps a well going offline, might serve to facilitate training, testing of sampling and monitoring methods. It could act as intermediate step between high-pressure lab environment and work site.

DISCLAIMER: This Workshop in Brief has been prepared by Nancy Huddleston and Kathryn Hughes as a factual summary of what occurred at the meeting. The committee's role was limited to planning the meeting. The statements made are those of the authors or individual meeting participants and do not necessarily represent the views of all meeting participants, the planning committee, the Chemical Sciences Roundtable, or the National Academies of Sciences, Engineering, and Medicine. The summary was reviewed in draft form by **Mark Barteau,** University of Michigan; **Ken Carlson,** Colorado State University; **Robert L. Kleinberg,** Schlumberger; **Jane Long,** University of California, Berkeley; and **William Stringfellow,** University of the Pacific and Lawrence Berkeley National Laboratory to ensure that it meets institutional standards for quality and objectivity. *The review comments and draft manuscript remain confidential to protect the integrity of the process.*

The organizing committee consisted of **David T. Allen,** University of Texas at Austin; **Michael J. Fuller,** Chevron; **Robert L. Kleinberg,** Schlumberger; **Kenneth G. Moloy,** DuPont; and **Danny D. Reible,** Texas Tech University. The members of the Chemical Sciences Roundtable are **William F. Carroll, Jr.,** Indiana University (*Co-Chair*); **Jennifer Sinclair Curtis,** University of California, Davis (*Co-Chair*); **Tina Bahadori,** U.S. Environmental Protection Agency; **Michael R. Berman,** Air Force Office of Scientific Research; **Carol Bessel,** National Science Foundation; **Carole Bewley,** National Institute of Diabetes and Digestive and Kidney Diseases; **Donna G. Blackmond,** Scripps Research Institute; **Emilio Bunel,** Argonne National Laboratory; **Allison Campbell,** WR Wiley Environmental Molecular Sciences Laboratory; **Richard R. Cavanagh,** National Institute of Standards and Technology; **Julio de Paula,** Lewis & Clark College; **Miles Fabian,** National Institute of General Medical Sciences; **Miguel Garcia-Garibay,** University of California, Los Angeles; **Jack Kaye,** National Aeronautics and Space Administration; **JoAnn Slama Lighty,** National Science Foundation; **Kenneth G. Moloy,** DuPont Central Research and Development; **Tanja Pietrass,** U.S. Department of Energy; **Kathleen J. Stebe,** University of Pennsylvania; **Patricia A. Thiel,** Ames Laboratory and Iowa State University

The Chemical Sciences Roundtable provides a neutral forum to advance understanding of issues in the chemical sciences and technologies that affect government, industry, academic, national laboratory, and nonprofit sectors, and the interactions among them; and to furnish a vehicle for education, exchange of information and discussion of issues and trends that affect the chemical sciences. The Roundtable accomplishes its objectives by holding annual meetings with its members and by organizing workshops on relevant and important topics for which published proceedings are made broadly available throughout the chemical sciences community.

This activity and summary were supported by the U.S. Department of Energy under Grant No. DE-FG02-07ER15872, the National Institutes of Health under Contract No. HHSN26300024, and the National Science Foundation under Grant No. CHE-1546732. Any opinions, findings, conclusions, or recommendations expressed in this publication do not necessarily reflect the views of any organization or agency that provided support for the project.