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Natural Gas Plays in the Marcellus Shale: Challenges and Potential Opportunities

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Tapping the lucrative Marcellus Shale natural gas deposits may have a host of environmental concerns.

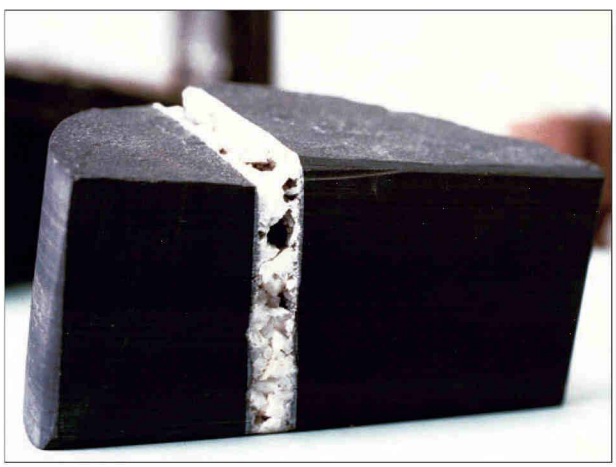

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Figure 1 features locations of shale basins across the U.S. that bear natural gas. There are many reasons to pursue the development of natural gas. First, the supply of natural gas in the U.S. is very reliable, and the delivery system is less subject to interruption compared to imported fossil fuel. Second, the high energy content of natural gas (about 30 kJ/m^3 [1000 Btu/ft^3]) and a well-developed infrastructure make it easy to use natural gas in a number of applications. Finally, natural gas is efficient and clean burning, emitting approximately half the CO_2 when compared with burning coal along with lower levels of sulfur dioxide (SOx), nitrogen oxide (NOx), carbon monoxide (CO), and mercury (Hg). In the trend toward a sustainable green economy, this potentially vast energy resource, with lower carbon emissions than coal or oil, is already a bridge fuel as the U.S. develops more sustainable and renewable fuel options.

The U.S. has abundant natural gas resources within the Barnett Shale, Haynesville/Bossier Shale, Antrim Shale, Fayetteville Shale, New Albany Shale, and Marcellus Shale. Technically recoverable natural gas from these shales is more than 1,744 trillion cubic feet (Tcf) (50 km^3), which includes 211 Tcf of proven reserves (*1*). At the annual production rate of about 19.3 Tcf, there is enough natural gas to supply the U.S. for the next 90 years with some estimates extending the supply to 116 years. The total number of natural gas and condensate wells in the U.S. rose 5.7% in 2008 to a record 478,562 with some of the produced natural gas lost via flaring (*2*). However, available data on flaring of natural gas is incomplete and inconsistent.

This article is focused on the Marcellus Shale because it is the most expansive shale gas in play in the U.S. The Marcellus Shale, which is Devonian age (416−359.2 My), belongs to a group of black, organic-rich shales that are common constituents of sedimentary deposits. In shale deposition, the clay-sized grains tend to lie flat as the sediments accumulate. Pressurized compaction results in flat sheet-like deposits with thin laminar bedding that lithifies into thinly layered shale rock. Natural gas is formed as the organic materials in these deposits degrade anaerobically. The Marcellus Shale gas is mostly thermogenic, with enough heat and pressure to produce primarily dry natural gas. Covering an area of 240,000 km^2 (95,000 mi^2), it underlies a large portion of Pennsylvania, east of West Virginia, and parts of New York, Ohio, and Maryland (Figure 1). Recent production data suggest that recoverable reserves from Marcellus Shale could be as large as 489 Tcf (*3*, *4*).

Natural gas extraction in the Marcellus Shale is currently an expensive endeavor. A typical horizontal drilled well, using multistage fracturing techniques, costs roughly $3−5 million to complete. The large amount of water used, and management of the wastewater are also very costly factors. Nevertheless, Marcellus Shale extraction is expected to usher jobs creation and other economic opportunities. A large demand for laborers at the gas fields and support businesses, such as drilling contractors, hydraulic fracturing companies, and

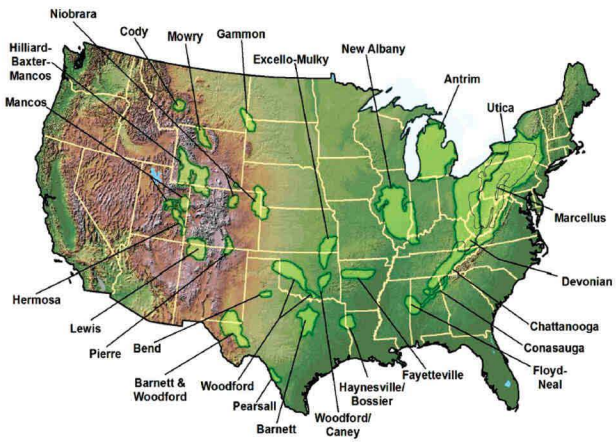

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FIGURE 1. Shale basins in the lower 48 states.

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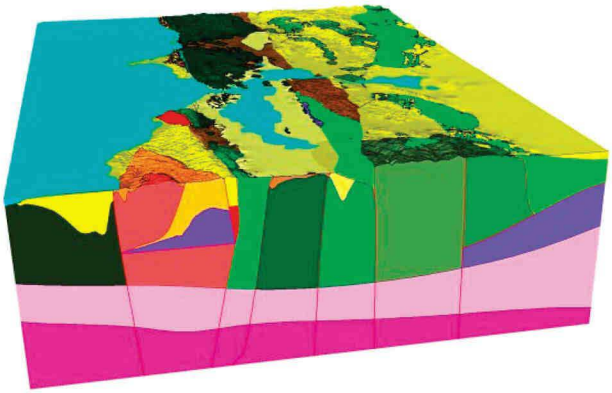

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FIGURE 2. 3-D geologic and seismic velocity model of the San Francisco Bay Region showing subsurface features (*7*).

trucking companies is also expected. In Pennsylvania alone, 2008 estimates show the creation of more than 29,000 jobs and revenues of $2.3 billion (*5*). Tax revenues for state and local governments, generated from indirect business taxes, including excise taxes, property taxes, and sales taxes increased by more than $238 million from the previous year (*5*). There are new marketing opportunities for businesses with innovative wastewater treatment technologies. Many land owners are expected to benefit financially. Thousands of leases have been signed with prices ranging from hundreds of dollars to $5,000/acre ($2024/ha), paying 12−20% royalties, and offering hopes of economic prosperity (*6*). Some companies however, only pay royalties on their net, after expenses.

There are numerous regulatory challenges related to gas extraction from the Marcellus Shale. The Safe Drinking Water Act excludes the regulation of hydraulic fracturing by the U.S. Environmental Protection Agency (EPA). This exemption has allowed the hydrofracture fluid formulas to be kept confidential, complicating treatment efforts by wastewater plants of hydrofracture fluids.

This article is focused on the technical challenges and potential opportunities related to natural gas production in the Marcellus Shale region. The authors firmly believe that understanding these challenges and opportunities is key to developing effective policies, adequately reviewing the thousands of current and future permit applications, and cost effectively producing natural gas in an environmentally sound manner.

Challenges

Throughout most of its spatial extent, the Marcellus Shale is nearly a 1.6 km (1 mi) or more below the surface (*1*). Natural gas generated is captured mainly within pores of the shale. The pore spaces are tiny, very poorly connected, and have very limited permeability on the order of 10^{-2}−10^{-5} mdarcies (1 darcy = 0.987×10^{-12} m^2). Sustainable and environmentally sound production of natural gas from Marcellus Shale requires overcoming challenges related to exploration and drilling, water resources, hydraulic fracturing, wastewater management, and radioactivity.

Exploration and Drilling. Seismic surveys have been used to produce 3-D images of the subsurface (Figure 2) including images of very productive natural shale gas reservoirs. The results of the seismic survey are used to identify a suitable drill site.

Following the decision to drill, a well pad is prepared, the area for the well is leveled off, gravel roads are constructed, and pipelines installed. The protection of sensitive ecosystems or habitat for flora and fauna that may be destroyed during site preparation is a major challenge. Generally, as the column of drill pipe extends deeper into the earth, drilling challenges including time and their associated costs increase. In addition, the increase in rock hardness and abrasiveness with depth leads to a decrease in rate of penetration with resulting shorter drill bit life. The control of well bore trajectory and placement of casing become increasingly difficult with depth, as does the efficient removal of drill cuttings. At the Marcellus Shale, temperatures of 35−51 °C (120−150 °F) can be encountered at depth and formation fluid pressures can reach 410 bar (6000 psi) (*8*). This can accelerate the impact of saturated brines and acid gases on drilling at greater depths. In addition, the effect of higher temperature on cement setting behavior, poor mud displacement and lost circulation with depth makes cementing the deep exploration and production wells in the Marcellus Shale quite challenging. For example following a recent report by residents of Dimock, PA, of natural gas in their water supplies, inspectors from the Pennsylvania Department of Environment Protection (PADEP) discovered that the casings on some gas wells drilled by Cabot Oil & Gas were improperly cemented, potentially allowing contamination to occur (*9*). As much as 50% of the total drilling cost is consumed by drilling the last 10% of the hole. To penetrate a maximum number of vertical rock fractures and a maximum distance of gas-bearing pore spaces, the vertical well is deviated horizontally. Graphic representation of a horizontal well completion is provided as Supporting Information (SI). During drilling into the tight Marcellus Shale, there is a slight risk of hitting permeable gas reservoirs at all levels. This may cause shallow gas blowouts and underground blowouts between subsurface intervals. Other geo-hazards that may pose challenges to drillers in the Marcellus Shale include: (1) disruption and alteration of subsurface hydrological conditions including the disturbance and destruction of aquifers, (2) severe ground subsidence because of extraction, drilling, and unexpected subterranean conditions, and (3) triggering of small scale earthquakes.

The environmentally sound management of drilling mud and drill cuttings may pose some challenges as well. Drill cuttings are typically comprised of shale, sand, and clays that are often coated with, or contain, residual contaminants from the drilling mud or from the borehole. At the surface, the drill cuttings are separated from the drilling mud, which is stored for reuse, while the drill cuttings are solidified and disposed of off-site (*10*).

Hydraulic Fracturing. Once drilling and casing are completed, a perforation gun shoots holes through the casing and cement at predetermined locations. To generate a hydraulic fracture, the applied pressure must exceed the rock's tensile strength and any additional tectonic forces that may be present. Hydraulic fracturing is commonly performed in stages where operators (1) perforate the casing and cement, (2) pump water-based fracturing fluids (hydrofracture fluids) through the perforation clusters, (3) set a plug, and (4) move up the wellbore. This process is then repeated at each fracturing location, of which there may be up to 15 in a given well. The result is a highly fractured reservoir that is 984 m (3000 ft) or more long in each direction from the wellbore. Fracturing materials include a proppant to keep fractures from closing completely after the hydrofracturing pressure is released and the effective geostatic pressure at this location returns. In addition, a fluid that initiates and propagates the fracture by transmitting hydraulic pressure to the formation and transporting the proppant into the created fracture is introduced into the target formation. Although nonaqueous systems have been used, water-based fracturing fluids are the most common. Quartz sand or ceramic material are usually the least expensive proppants. Gels are added to increase the hydrofracture fluid viscosity and reduce fluid loss from the fracture. Additional additives may include the following: acids to remove drilling mud near the wellbore,

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biocides to prevent microbial growth that produce gases (e.g., H_2S) that may contaminate the methane gas (CH_4), scale inhibitors to control the precipitation of carbonates and sulfates, and surfactants to increase the recovery of injected fluid into the well by reducing the interfacial tension between the fluid and formation materials (*11*).

After completion of the hydraulic fracturing process, the viscosity of the hydrofracture fluids is expected to break down quickly, so the fluids can be easily removed from the ground and the gas extracted. It does not always work that way. Gels sometimes do not completely break, and there is always a residue in the flow back water following partial gel decomposition. Sometimes the nature of the reservoir is such that the fracturing liquids can become trapped, remaining in the reservoir and impeding the flow of the gas. As much as 80% of injected fluids may not be recovered prior to placing the well in production. In addition, not all proppants make it to the fractures. The proppants that pushed into the fractures can quickly settle out of the water, allowing much of the fractures to close after the hydrofracturing pressure is released. A challenge is to develop environmentally friendly fluids that suspend the proppant for very long times. Perhaps the most difficult challenge in hydraulic fracturing is to complete the greatest number of fracturing stages as economically as possible. This is currently an active area of shale gas research.

Large hydrofracture treatments often require moving large amounts of supplies, equipment, and vehicles to remote drill sites. This could potentially lead to erosion and sediment overload that could threaten local small watersheds. There is also the risk of spills and leaks.

Water Resources. Drilling requires large amounts of water to create a circulating mud that cools the bit and carries the rock cutting out of the borehole. Depending on the depth and permeability of the formation, from 7.7−38 ML (2−10 million gal) of water, mixed with various additives, is required to complete the fracturing of each horizontal deep well (*12*). Because of huge transportation costs of trucking water from great distances, drillers usually extract on-site water from nearby streams or underground water supplies. Concerns about the ecological impacts to aquatic resources resulting from huge water withdrawals have been raised throughout the Marcellus Shale region. This is particularly an issue under drought conditions, low seasonal flow, locations with already stressed water supplies, or locations with waters that have sensitive aquatic communities that depend on clean, cool waters. For example, about 36% (12,639 km^2 ((4937 mi^2)) of the Delaware River Basin (DRB), which is home to 5 million people, are headwaters and underlain by the Marcellus Shale. Water withdrawal for hydraulic fracturing is a major water resources concern in the DRB.

Health and Environmental. The chemical formulations of the hydrofracture fluid are highly researched and closely guarded. The fluid is usually in close contact with the host rock during the course of the hydrofracture process. It is therefore expected to contain both formation chemicals and introduced chemicals. Formation chemicals may include toxic metals, salts, and radionuclides. Introduced chemicals in the hydrofracturing fluid may include a variety of toxic and nontoxic chemicals. For example, some fluids may contain hydrochloric or muriatic acid, hydroxyethyl cellulose as gel, glutaraldehyde as biocide, petroleum distillate (or diesel) as friction reducer, ammonium bisulfate as oxygen scavenger, 2-hydroxy-1,2,3-propanetricaboxylic acid for iron control, *N,n*-dimethyl formamide as corrosion inhibitor, ethylene glycol (or 2-butoxyethanol) as scale inhibitor, and methanol-based surfactants (*11*). Fluorocarbons, naphthalene, butanol, and formaldehyde have also been reported to be present in the introduced fluids. Many of these chemicals are either carcinogenic or associated with numerous health problems affecting the eyes, skin, lungs, intestines, liver, brain, and nervous system. In New York, records show that formaldehyde, pesticides, acids, and numerous other hazardous materials are added to the hydrofracture fluids (*13*). In a recent article published in InsideEPA.com (*14*), results of water well sampling in Pavillion, WY, showed natural gas drilling-related chemicals in several of the wells tested.

Management of the hydrofracture wastewater varies from state to state. Open pits for storage of freshwater and wastewater and for evaporation of the wastewater are common. The solids that remain following evaporation are disposed of as dry waste. (See SI for additional discusion.) One common disposal method required by some states is processing the wastewater in wastewater treatment plants (WWTP). A significant challenge to this method is the observation that contaminants and total dissolved solids (TDS) in the water may complicate wastewater treatment (*15*). For example, the discharge of inadequately treated natural gas drilling wastewater with high TDS and other chemicals was suspected to be a source for the elevated TDS in Monongahela River (*16*). Other potential suspected sources include the presence of already high TDS in the river when the water entered Pennsylvania from West Virginia, low water conditions that could lead to a high concentration of the TDS, TDS from abandoned mine drainage, and high TDS wastewater from all kinds of resource extractions being delivered to treatment plants. The TDS problem led the PADEP to issue a water-quality-advisory for 325,000 customers to use bottled water. Although the hydrofracture fluid systems are 90−95% water, the TDS in the wastewaters can rise to over 200,000 mg/L, precluding many standard water treatment technologies from processing and cleaning hydrofracture wastewater. The development of treatment infrastructure currently lags far behind the fast-paced exploration and extraction of Marcellus shale gas activities.

Another challenge in drilling the Marcellus Shale is the occurrence of potentially elevated concentrations of radionculides. Field and sample surveys on composited Marcellus rock cuttings and cores indicate background levels of radioactivity that are of low exposure concern for workers or the general public associated with Marcellus cuttings (*13*). However, in a recent article (*17*), New York's Department of Environmental Conservation (NYDEC) reported that thirteen samples of wastewater from Marcellus Shale gas extraction contained levels of radium-226 (226Ra) as high as 267 times the safe disposal limit and thousands of times the limit safe for people to drink. The New York Department of Health (NYDOH) analyzed three Marcellus Shale production brine samples and found elevated gross alpha (α), gross beta (β), and 226Ra in the production brine (*18*). Devonian-age shales contain naturally occurring radioactive material (NORM), such as uranium (U) and thorium (Th) and their daughter products, 226Ra and 228Ra (*19*). The Marcellus Shale is considered to have elevated levels of NORMs (*20*). NORMs that have been concentrated or exposed to the accessible environment as a result of human activities, such as mineral extraction, are defined by the EPA as technologically enhanced NORM (TENORM) (*19*). TENORM may be concentrated because of (1) temperature and pressure changes during oil and gas production, (2) 226Ra and 228Ra in produced waters reacting with barium sulfate ($BaSO_4$) to form a scale in well tubulars and surface equipment, (3) 226Ra and 228Ra occurring in sludge that accumulates in pits and tanks, and (4) NORM occurring as radon (Rn) gas in the natural gas stream (*21*).

Air pollution is also a major challenge. In the gas-producing areas of Texas, Wyoming, and Colorado, the release of CH_4, CO_2, and other volatile organic chemicals (VOCs) from processing plants and diesel exhaust trucks has been

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blamed for ozone (O_3) and other air quality problems. These problems could also emerge as major air pollution challenges in a Marcellus Shale boom.

Potential Opportunities

Drilling. The oil and gas industry has advanced the art of drilling and fracturing with potential opportunities to make the process cost-effective. Some companies are already taking advantage of multilateral drilling, which is known to be more effective than horizontal drilling as it enables drainage of multiple target zones, enlarges recoverable reserves, and increases productivity. An expanded use of multilateral drilling in the Marcellus Shale is expected.

Many operators have recently abandoned the use of diesel in favor of more environmentally acceptable fluids, such as high paraffinic fluids (*22*). Paraffinic fluids possess reduced toxicity and reasonable biodegradability characteristics. A simple replacement of diesel fuel by natural gas can result in 85% less VOCs spewing into the air. The industry is also curbing methane emissions by employing IR cameras or gas detectors and airborne laser-based gas analysis systems to locate and seal leaking wells and pipelines. To eliminate the thousands of truck delivery trips and the diesel exhaust that comes with these trips, the industry has been building a network of pipes to transport its fluids. This practice may be expanded in the Marcellus Shale drilling region especially in areas where the topography is conducive to such installations.

Alternatives to Hydraulic Fracturing. Intensified concerns by the public have prompted some companies to search for alternatives to hydrofracturing and, in some cases, to develop more environmentally friendly hydrofracture fluids. For example, diesel is being replaced by mineral oil, and some companies are experimenting with plant-based oils, such as palm oil and soy (*23*). EnCana reports that it stopped using 2-butoxyethanol, a solvent that has caused reproductive problems in animals. BJ Services are reported to have discontinued the use of fluorocarbons that are persistent environmental pollutants. While this may be good news, replacements for the discontinued chemicals are yet to be identified.

One of the most effective methods of reducing exposure to contaminated wastewater is to implement processes that do not generate wastewater. GASFRAC Energy Services is testing the use of liquefied petroleum gas (LPG), a fracturing agent that also transports the proppants into the fractures. First introduced in Marcellus Shale drilling in September 2009, LPG is derived from natural gas processing and consists mainly of propane in gel form (*24*). The process generates no wastewater since all of the LPG is recaptured back up the well.

One technique already being used successfully, particularly in Canada, is Dry Frac (*25, 26*). The technology has been tested extensively in more than 1,200 successful simulations and has performed better than other fracturing fluids during several U.S. DOE sponsored demonstration projects in the U.S. (*25*). Dry Frac uses liquid CO_2 [$CO_{2(l)}$] as the carrier fluid without water or any additional treatment additives. A pressurized CO_2 blender mixes the proppant into the [$CO_{2(l)}$] stream, thus eliminating the need for traditional carrier fluids to transport the sand. Universal Well Services performed 19 CO_2/sand simulations on 8 Devonian shale wells in eastern Kentucky and 3 Devonian sandstone gas storage wells in western Pennsylvania. Results indicate that average cumulative gas production is as much as five times greater than production from conventional hydrofracture treatments. However, ice formation in wells resulting from the use of [$CO_{2(l)}$] is a real possibility. Consequently, the process has been optimized with the addition of nitrogen (N_2) gas, which not only reduces the formation of ice but also reduces the overall treatment costs (*27*). A major challenge to the potential opportunity of using inexpensive N_2/CO_2 fracturing liquids is the lack of an infrastructure to transport $N_{2(l)}$ and $CO_{2(l)}$ from the production sites to application sites in the Marcellus Shale region. Natural gas producers from the Marcellus Shale region may want to seriously consider using this innovative technology.

Water Resources. One solution to the management of hydrofracture fluid wastewater is the reuse of the wastewater as hydrofracture fluid (or flowback water). This has the potential to solve both water supply and environmental problems. However, the major problem with use of flowback water for makeup of frac water is the very high concentration of scale forming constituents including barium, calcium, iron, magnesium, manganese, and strontium (Ba, Ca, Fe, Mg, Mn, and Sr) (*28*). These constituents readily form precipitates which rapidly block the fractures in gas bearing formations required for economic gas production. According to Halliburton, a major supplier of hydrofracture water chemicals, flow back water should have a maximum total hardness of 2,500 mg/L measured as $CaCO_3$.

The use of treated acid mine drainage (AMD) water may solve both water quantity and quality problems. In many Marcellus Shale areas of Pennsylvania, AMD from past coal mining activities is present in large amounts, and its use could alleviate a major water quality problem. Recently, about 12 ML (3 million gal) of treated AMD was obtained from the Blue Valley Fish Culture Station and used in a Marcellus completion hydrofracture process (*29*).

The development of best management practices (BMPs) for water conservation must be encouraged and practiced by natural gas developers in the Marcellus Shale region. The goal should be to keep the pace of drilling and production activities within the bounds of sustainable water use. For example in Texas, a consortium of Barnett Shale drilling companies developed BMPs for water conservation. Similar steps need to be taken for the Marcellus Shale gas production areas.

Health and Environmental. To reduce exposure of wastewater to the environment, enclosed fluid capture systems have been used by some companies. One common disposal practice in the Barnett Shale production area of Texas that has been utilized for some Marcellus wells drilled in West Virginia involves re-injecting the wastewater fluids back into the ground at a shallower depth (*30*). However, the possible contamination of drinking water supply aquifers has limited the practice of re-injecting hydrofracture fluids. Injecting the wastewater fluid into deeper formations below the Marcellus Shale that are not used as aquifers (such as the Oriskany or Potsdam Sandstones) is an option that has recently been considered. These formations may also be good candidates for CO_2 capture and sequestration.

When water has to be used to fracture Marcellus Shale wells, one viable option is to treat the wastewater on-site. ProChemTech is reported to have invented a sequential precipitation process for treatment of hydrofracture wastewater (*31*). There is however, no documented case of the use of this technology in field applications. Alternatively, an advanced GE Thermal Evaporation process has been developed by STW Resources for recycling of hydrofracture wastewater (*32*). However, the viability of this technology is yet to be proven on a larger scale. In some instances, distillation-crystallization has been proposed, but it is very expensive (*33*).

Core technologies currently in use for the removal and concentration of dissolved solids vary and depend on the concentration of the TDS. For example, ion exchange is used in low-TDS waters and for the removal of sodium (Na^+) in high bicarbonate/carbonate (HCO_3^-/CO_3^{2-}) water. For TDS concentrations of up to 20,000 mg/L, reverse osmosis has been the preferred method. Thermal distillation and evaporation is used

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for waters with TDS concentrations of 40,000−100,000 mg/L. New and cost-effective technologies that treat wastewaters with TDS exceeding 200,000 mg/L are needed.

Potential disposal options for wastewater and other wastes containing radioactivity are currently unclear. Given the limited data available, opportunities exist in further evaluating the potential impact of Marcellus Shale drilling on the release of TENORM. If elevated TENORM is encountered during natural gas extraction, then development of a site health and safety plan that includes the measurement and identification of risk pathways for TENORM in production waters, flowback waters, and drill cuttings may be needed. One approach proposed by the NYDEC is for the Marcellus Shale drilling companies to survey all wastewater for radioactivity before it is allowed to leave the well site. In this scenario, waste handlers will need to be licensed, and their workers tested for radioactive exposure. This would reduce the potential risk of exposure from waters, cuttings solids, wastes, and contamination of equipment. Design of storage pits, ponds, and TENORM residual solids disposal may become a major issue for risk managers to address. In summary, the Marcellus Shale boom, while economically desirous, would come with a potentially significant environmental impact. The issues noted herein need to be risk assessed and accounted in the impact calculus.

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Supporting Information Available

Additional information on horizontal well completions in the Marcellus Shale, as well as challenges and current efforts to regulate the extraction of natural gas from Marcellus Shale. This information is available free of charge via the Internet at http://pubs.acs.org/.

Literature Cited

(1) U.S. Department of Energy. *Modern Shale Gas Development in the United States: A Primer*; DE-FG26-04NT15455; U.S. DOE: Washington, DC, 2009.
(2) U.S. Department of Energy. *U.S. Natural Gas Annual Report*; EIA-0131(08); U.S. DOE: Washington, DC. 2008.
(3) Engelder, T.; Lash, G. Unconventional natural gas reservoir could boost U.S. supply. *Penn State Live* [Online] **2008**, http://live.psu.edu/story/28116.
(4) Engelder, T. Marcellus 2008: Report card on the breakout year for gas production in the Appalachian Basin. *Fort Worth Basin Oil and Gas Magazine*, 2009, 20.
(5) Considine, T.; Watson, R.; Entler, R.; Sparks, J. An emerging giant: prospects and economic impacts for developing Marcellus Shale. Penn State University, 2009.
(6) Collier, C. R. Potential Impact of Marcellus Shale Drilling on Water Resources in the Delaware, Presentations of American Water Resources Association, Philadelphia Metropolitan Area, 2009.
(7) U.S. Geological Survey. 3-D Geologic and Seismic Velocity Models of the San Francisco Bay Region, 2010, http://earthquake.usgs.gov/regional/nca/3Dgeologic/otherviews.php.
(8) Driscoll, F. G. *Groundwater and Wells*; Johnson Filtration Inc.: St Paul, MN, 1986.
(9) Mufson, S. Drilling right into a heated environmental debate. *Washington Post*, 2009, http://www.washingtonpost.com/wp-dyn/content/article/2009/12/02/AR2009120203984.html?nav=emailpage
(10) McNabb, A. Drill mud or industrial liquid waste? 2009, http://www.ttmag.com/index/webapp-stories-action?id=984.
(11) Arthur, J. D.; Bohm, B.; Layne, M. Hydraulic fracturing considerations for natural gas wells of the Marcellus Shale. Ground Water Protection Council Annual Forum, 2008.
(12) ProChemTech Int. Innovations in water management, 2009, http://prochemtech.com/Literature/TAB/TAB_Marcellus_Hydrofracture_Disposal_0509.pdf.
(13) New York State Department of Environmental Conservation. *Draft Supplemental Generic Environmental Impact Statement on the Oil, Gas and Solution Mining Regulatory Program*; New York State Department of Environmental Conservation: New York, 2009.
(14) Discovery of "fracking" chemical in water wells may guide EPA review. InsideEPA.com, 2009, http://insideepa.com/secure/docnum.asp?docnum=POLICYALERT-26-17-21&f=epa_2001.ask.
(15) Soeder, D. J.; Kappel, W. M. Water resources and natural gas production from the Marcellus Shale. *USGS Fact Sheet*; 2009-3032; U.S. Geologic Survey: 2009.
(16) Pennsylvania Department of Environmental Protection. PADEP investigates elevated TDS in the Monongahela River, 2009, http://www.wwdmag.com/Pennsylvania-DEP-Investigates-Elevated-TDS-in-Monongahela-River-newsPiece16950.
(17) Lustgarten, A. Is New York's Marcellus Shale too hot to handle? *ProPublica* [Online] **2009**, http://www.propublica.org/feature/is-the-marcellus-shale-too-hot-to-handle-1109.
(18) New York State Department of Health. Marcellus shale potential public health concerns, 2009, http://s3.amazonaws.com/propublica/assets/natural_gas/nysdoh_marcellus_concerns_090721.pdf.
(19) U.S. Environmental Protection Agency. *Technologically Enhanced Naturally Occurring Radioactive Materials From Uranium Mining*; EPA 402-R-08-005; U.S. EPA/ORIA: Washington, DC, 2008.
(20) Hill, D. G.; Lombardi, T. E.; Martin, J. P. Fractured shale gas potential in New York. *Northeastern Geol. Environ. Sci.* **2004**, *26*, 8.
(21) Railroad Commission of Texas. NORM—Naturally Occurring Radioactive Material, 2009, http://www.rrc.state.tx.us/divisions/og/keyprograms/norm.html.
(22) Fefer, M. *the Benefits of Very High Paraffin Drill Mud Fluids and Their Advantages for Cuttings Disposal*; SPE Annual Technical Conference and Exhibition, Denver, CO; Society of Petroleum Engineers: Richardson, TX, 2003; Paper 84586-MS.
(23) Lustgarten, A. Underused drilling practices could avoid pollution. *ProPublica* [Online] **2009**, http://www.propublica.org/feature/underused-drilling-practices-could-avoid-pollution-1214.
(24) Smith, M. Frac Forward: Startup cracks propane fracture puzzle, provides 'Green' solution. *New Technol, Mag.* [Online], **2008**, http://www.ntm.nickles.com/issues/printer.aspx?aid=1000225211.
(25) Wright, T. R. Frac technique minimizes formation damage—Dry Frac. *World Oil* [Online] **1998**, http://findarticles.com/p/articles/mi_m3159/is_n1_v219/ai_20387355/.
(26) Mazza, R. L. Liquid-free stimulations—CO_2\Sand Dry-Frac, Conference Proceedings of Natural Gas, Conference of Emerging Technologies for Natural Gas Industry, 1997.
(27) Gupta, D. V. S.; Bobier, D. M. *The History and Success of Liquid CO_2 and CO_2/N_2 Fracturing System*; SPE, Canadian Fracmaster Ltd., SPE Gas Technology Symposium, 15−18 March 1998, Calgary, Alberta, Canada; Society of Petroleum Engineers: Richardson, TX, 1998.
(28) Keister, T. Marcellus gas well water supply and wastewater disposal, treatment, and recycle technology, 2009, http://www.prochemtech.com/Literature/TAB/PDF_TAB_Marcellus_Gas_Well_Water_Recycle.pdf.

DIM0186217 DIM0186221

(29) ProChemTech International, Inc. Treatment of abandoned mine drainage for use as Marcellus gas well hydrofracture makeup water, 2009, http://www.prochemtech.com/Literature/TAB/PDF_TAB_Marcellus_Hydrofracture_Water_Supply_%20From_AMD_1009.pdf.
(30) Kasey, P. New drilling efforts raise questions: Charleston, WV. *The State Journal* [Online] **2008**, http://statejournal.com/story.cfm?func=viewstory&storyid=42542.
(31) ProChemTech International, Inc. Process for treatment of gas well completion, fracture, and production wastewaters for recycle, discharge, and resource recovery. USPTO Patent Application 61/199,588, Novemeber 19, 2008.
(32) Green Car Congress. GE and STW resources collaborate to recover up to 70% of hydraulic fracturing wastewater, 2007, http://www.greencarcongress.com/2008/07/ge-and-stw-reso.html.
(33) Swistock, B. Treatment/disposal options for wastewaters from shale gas drilling, 2009, Penn State University, http://downloads.cas.psu.edu/naturalgas/pdf/updated%20wastewater%20webinar%20oct%202009.pdf.

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DIM0186217 DIM0186222