

WHITEPAPER

Analytical and Measuring Instruments

Hydraulic Fracturing and the Environment



■ Introduction

As powerful nations struggle to maintain power and smaller nations struggle to gain power, one of the major prizes upon which they keep their eye are oil and gas reserves. It is no secret that control of oil and gas reserves plays a major role in the economic and strategic future of any nation. We may not all realize the importance of fossil fuels in the global economy. While the burning of fossil fuel and subsequent release of carbon dioxide and other “greenhouse” gases has been linked to “climate change”, we must realize that fossil fuels, including coal, petroleum, and natural gas, are essentially energy and that our industrialized civilization depends upon the substitution of manual labor for mechanical power. Fossil fuels replace manpower in a variety of ways, from the diesel trucks that transport goods across the nation and the ships powered by fuel oil carrying merchandise across oceans, to the electricity used to cool and heat our houses and the tremendous amount of lubricants that turn our machines.

...we must realize that fossil fuels ... are essentially energy and that our industrialized civilization depends upon the substitution of manual labor for mechanical power

The petroleum industry is one of the largest industries in the world, with very large revenues and very large operating costs; an oil company makes about 6 cents per every dollar. Among the costs of producing oil and gas are exploration, production, refining, distribution, and marketing.¹

Oil companies, often referred to in the media as “big oil”, are not owned by single individuals, but instead are owned almost entirely by IRA’s, industrial investors, individual investors, and pension funds. The oil and gas industry employs nearly one million workers, is a large customer for other support industries, and serves the entire economy with an essential commodity called power.

The oil and gas industry is based upon the utilization of a natural resource, petroleum and related natural gas. Both petroleum and natural gas are distributed widely geographically and geologically, but are confined almost exclusively to clastic sedimentary rocks. Winning oil and gas from these deeply buried deposits is a high-technology geologic and engineering venture.

■ The Geology of Petroleum

Oil and natural gas deposits are found in sedimentary rocks. Clastic sedimentary rocks are formed by weathering and deposited in basins largely during catastrophic storm events that carry a huge amount of sediment and organic material, which eventually settles as a function of grain size, specific gravity, and shape. Gravel falls first, followed by sand, silt, and then finally clay. Chemical sedimentary rocks, such as gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and limestone (CaCO_3) precipitate in shallow seas and lakes.

Once sediment is deposited and buried, it undergoes a process of physical and chemical change, called diagenesis, the degree of which is a function of overburden pressure, the chemistry of the deposit including rock material and interstitial fluids, and heat. As the grains are compacted, the space between the grains decreases and interstitial fluids are squeezed out. As these fluids are squeezed out, dissolved minerals precipitate between the grains decreasing porosity and cementing grains together. Common secondary minerals that cement sedimentary rocks together are calcite (CaCO_3) and hematite (Fe_2O_3).

Clastic sedimentary rocks

Conglomerate is the sedimentary rock formed by compaction and cementation of clastic particles with grain sizes greater than 2 mm. Conglomerates often have sand and clay trapped between the grains. Conglomerates are river deposits found close to existing or prehistoric mountain ranges.

¹ American Petroleum Institute www.api.org/oil-and-natural-gas-overview/industry-economics, accessed May 1, 2014

Sandstone is composed of cemented sand grains (grain sizes between 0.06 mm and 2 mm) and comprises approximately 20 -30% of all sedimentary rocks.² Sandstones usually contain about 60% quartz with the remainder being feldspar and rock fragments. Many of the sandstones of economic importance to oil and gas were deposited along sea coasts as barrier islands isolating large bays where poor circulation favored anaerobic decomposition of organic matter.

Shale is formed from clay minerals and other very fine grained (less than 0.004mm) particles that have been compacted into rock as a result of burial. Shale is often high in organic matter, a result of the decay of microorganisms that were deposited with the clay. This organic matter converts to oil and/or gas during diagenesis and is slowly squeezed out of the clay into overlying rock.

Sandstone and clay are deposited together spatially. Imagine a barrier island system such as Padre Island, Texas, and the large bay (Laguna Madre) that lies between Padre Island and Texas. The barrier island consists of sand particles carried to the Gulf of Mexico by rivers and deposited into the river delta. The long shore currents distribute the sand. Clay particles are so small in grain size they do not settle out near the shoreline but they do settle out in the deeper ocean or the inland bays where there is not much wave action. Further offshore, where there is no sediment, limestone may be deposited, and further inland, if there is a large influx of freshwater, an estuary may form.

During a storm event, such as a hurricane, both sand and clay are carried inland. The barrier island moves with the storm and sand covers the clay deposits of the inland bay. Vertically, the coastline consists of alternating layers of sand and clay. The sand layers represent the movement of the barrier island as it moved seaward, covering ocean clay deposits, or landward covering the bay and estuary deposits. Geologically, these deposits represent a time sequence of alternating layers of sandstone, shale, limestone, and perhaps peat (from the estuary deposit). See Figure 1 for an example of a barrier island deposit.

The clay layers are rich in organic matter, with a very low porosity, while the sand layers are devoid of organic matter but have higher porosity. As the clay is heated during burial, some of the organic matter decays into petroleum and gas. During compaction the interstitial fluid, including seawater, oil, and gas, is squeezed out and travels upwards into the pore space of the overlying sandstone. The fluids travel upwards through the sandstone until they reach an overlying shale layer and are trapped. They have become a traditional oil and gas deposit

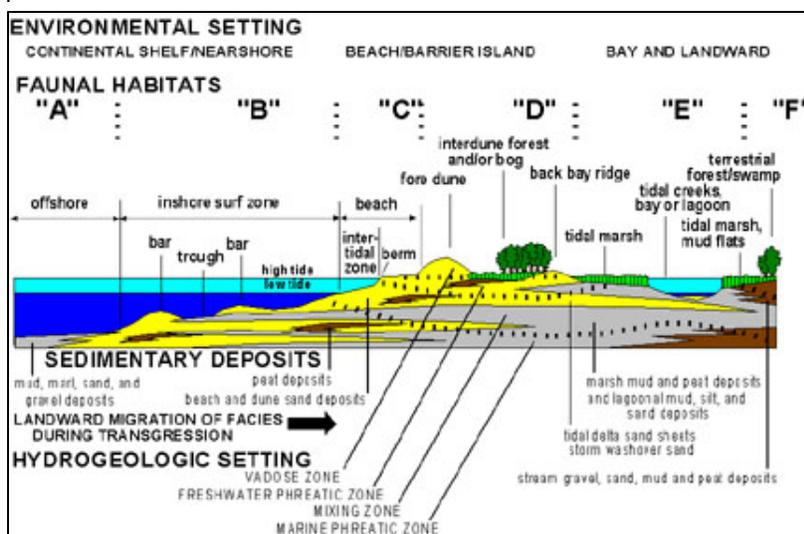


Figure 1: Barrier Island Deposit³

² By F. J. Pettijohn, Sand and Sandstone, Springer-Verlag, 1987

³ <http://3dparks.wr.usgs.gov/nyc/shoreline/beaches.htm>; accessed May 9, 2014

■ Traditional Oil and Gas Exploration and Recovery

In the preceding example, an oil and gas deposit formed as a result of the burial and diagenesis of alternating sand and clay deposits along a pre-historic Texas coast. A geologist familiar with this sequence of events explores exposed rock formations, mapping their occurrence and the geologic dip. He finds alternating layers of marine sandstone and dark shale he believes is high in organic matter. A quick total organic carbon (TOC) test using an analyzer with the capability of measuring TOC in solids (Figure 2) confirms that organics are present and that the shale is a good candidate for a source rock.



Figure 2: Shimadzu TOC Analyzer

He extrapolates the layers underground and looks at faults and folds where hydrocarbons may be trapped in a sandstone reservoir rock against an impervious layer to form a pool. A well is drilled into the potential pool. If oil and/or gas is found (Figure 3) and is estimated to be of sufficient quantity, the well is stimulated for recovery. During well stimulation, water containing various chemicals that assist in recovery, are piped down into the well to apply pressure that fractures the sandstone and dissolves the calcite or hematite cement. This process is sometimes called hydraulic fracturing and is used to increase the porosity of the reservoir and allow the hydrocarbons to flow freely out. The process of “hydraulic fracturing” has been used since the 1940’s to stimulate more than one million oil and gas wells.⁴

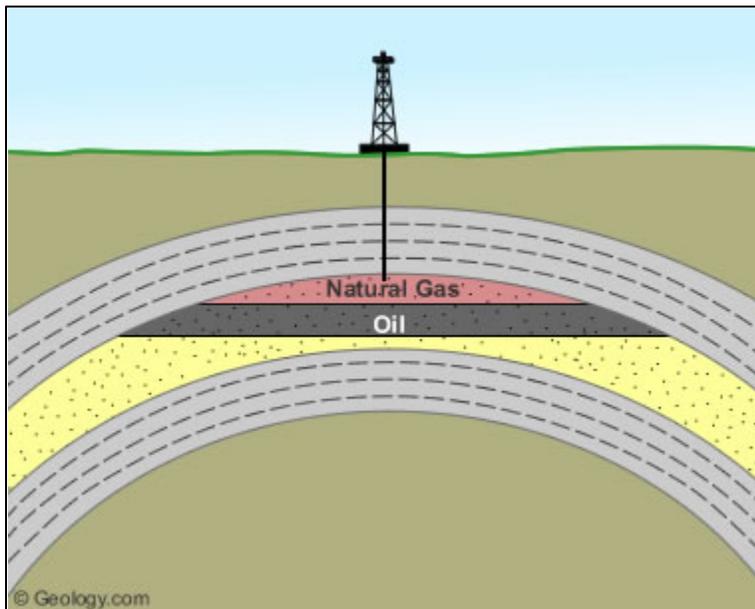


Figure 3: Traditional Oil and Gas Well⁵

■ Untraditional Oil and Gas Exploration and Recovery

A traditional oil and/or gas deposit is one where the petroleum reserves are trapped in a clastic reservoir rock against an impervious cap rock, such as shale or a salt dome. Untraditional wells require new highly energy-intensive production techniques and new processes to deal with their inaccessible placements or unusual compositions.⁶ Coal bed methane (CBM) is an example of an untraditional gas deposit. Coal bed methane is primary coal seam gas collected from unmined coal beds. The coal seams are drilled into, releasing the

⁴ http://cewc.colostate.edu/wp-content/uploads/2012/02/ei_shale_gas_regulation120215.pdf, accessed May 8, 2014

⁵ <http://geology.com/articles/oil-and-gas-investments/>; accessed May 9, 2014

⁶ http://carnegieendowment.org/files/unconventional_oil.pdf; accessed May 9, 2014

associated gas.⁷ Hydraulic fracturing with water and sand is currently the most widely used fracturing technique in the CBM industry.⁸

One of the many benefits of CBM is that the large surface area of the coal is capable of storing about five times more gas than a traditional sandstone reservoir of the same rock volume. Another benefit is that coal seam wells are much closer to the surface than most traditional gas wells, making them easier and less costly to drill into. Some drawbacks are that there must be a network of low-pressure pipelines to receive and transport the gas to a distribution center, and the potentially high cost of dewatering and produced water disposal. In the early stages of production, large volumes of water are pumped into the well. As the water travels through the well, it dissolves trace organic and inorganic compounds. This produced water must be analyzed for contaminants, and disposed of properly.

Another untraditional oil and gas deposit is oil and/or gas shale. Like CBM, the oil/gas shale is both the reservoir and the source rock. Unlike the CBM, the oil/gas is tightly held inside the rock and not easily liberated. While CBM wells may be 1500 – 3000 feet in depth⁹, a typical shale gas well in the Marcellus formation is 5000 – 8000 feet.¹⁰ The Marcellus Shale is organic-rich, black marine shale deposited about 390 million years ago. It has long been considered a source rock for traditional oil and gas reserves and is now being exploited as an untraditional gas reservoir.¹¹

The great depth of the Marcellus Shale, and other similar gas shale deposits, means that very large volumes of gas must be recovered to pay for the drilling costs. A traditional, vertical well cannot recover enough gas from a low porosity source rock such as shale. These wells must employ new horizontal drilling technology (Figure 4) and new well stimulation technology to ensure economic production.

The great depth of the Marcellus Shale, and other similar gas shale deposits, means that very large volumes of gas must be recovered to pay for the drilling costs.

Recoverable natural gas occurs within the pore spaces of the shale; however, shale porosity is very low. A horizontal well begins as a vertical bore which extends from the surface to just above the target formation. Then it turns at an arc to penetrate the formation and then continues horizontally within the formation. Since the gas reservoir rock is longer than it is thick, more reservoir rock is exposed to the well bore surface than would be the case with a vertical well.¹²

⁷ <http://www.clarke-energy.com/gas-type/coal-gas/>; accessed May 9, 2014

⁸ <http://www.epa.gov/cmop/docs/fra-technologies.pdf>; accessed May 9, 2014

⁹ http://www.halliburton.com/public/pe/contents/Books_and_Catalogs/web/CBM/H06263_Chap_01.pdf; Accessed May 9, 2014

¹⁰ <http://www.elibrary.dep.state.pa.us/dsweb/Get/Document-97683/0100-FS-DEP4217.pdf>; accessed May 9, 2014

¹¹ http://www.dcnr.state.pa.us/topogeo/econresource/oilandgas/marcellus/marcellus_faq/marcellus_shale/index.htm; accessed May 9, 2014

¹² http://www.eia.gov/pub/oil_gas/natural_gas/analysis_publications/drilling_sideways_well_technology/pdf/tr0565.pdf accessed May 9, 2014

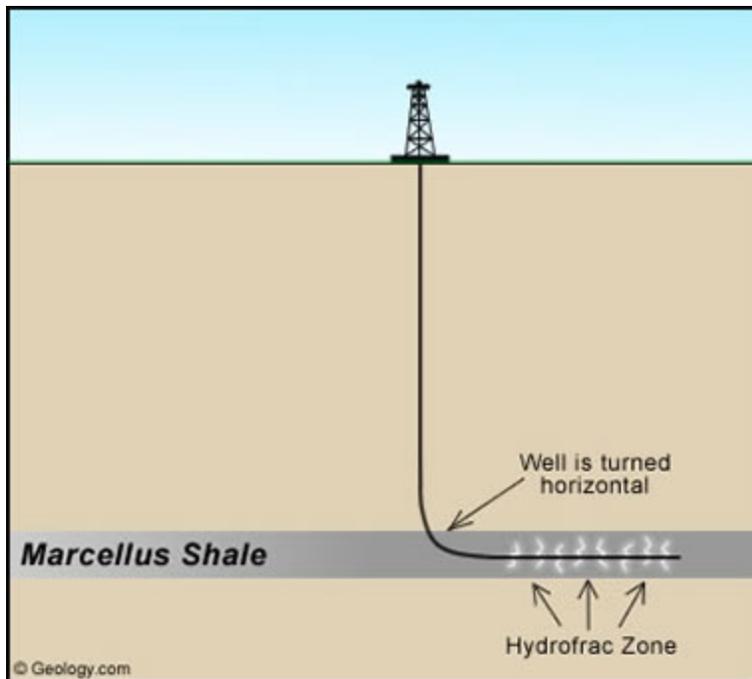


Figure 4: Horizontal Shale Gas Well¹³

The stimulation of a shale gas well requires millions of gallons of water mixed with sand.¹⁴ The sand and water mixture is pumped into the formation with enough pressure to fracture the shale. The sand with water is injected into the shale, and as the shale collapses under pressure, the sand stays behind forming channels of porosity that allows gas to flow out. The “fracking” solution contains various chemicals that are necessary to hold the sand in suspension, reduce friction of the water with the walls of the pipe, minimize corrosion and/or scale, prevent biological growth, and dissolve minerals, such as hematite and calcite, which may be cementing the grains of the shale together. Table 1 gives the volumetric composition of a fracturing fluid used for treatment of a Fayetteville Shale horizontal well.¹⁵

Compound	Percent (%) by Volume
Water and sand	99.51
Surfactant	0.085
KCL	0.06
Gelling Agent	0.056
Scale inhibitor	0.043
pH adjustment	0.011
Breaker	0.01
Cross linker	0.007
Iron Control	0.004
Corrosion Inhibitor	0.002
Biocide	0.001
Acid	0.123
Friction Reducer	0.088

Table 1: Volumetric Composition of a Fracturing Fluid

¹³ <http://geology.com/articles/marcellus-shale.shtml>; accessed May 9, 2014

¹⁴ <http://www.epa.gov/safewater/uic/pdfs/hfresearchstudyfs.pdf>; accessed May 12, 2014

¹⁵ Spellman, Frank R.; Environmental Impacts of Hydraulic Fracturing; CRC Press, September 17, 2012

■ Major Components in “fracturing” Fluids and How to Analyze for Them

Sand

Sand is used to keep the fractures open so that gas can flow through. Sand is defined as a particle size distribution ranging from 60 to about 2000 microns. The best “sands” for use in hydraulic fracturing are perfectly spherical ceramics with a very narrow grain size distribution to maximize porosity. The selection of material and grain size plays a key role in hydraulic fracturing.¹⁶ Instruments, such as the Shimadzu SALD-2300 (Figure 5), can be used to accurately and precisely measure grain size distribution between 0.017 and 2000 microns in samples from very low to high concentrations of suspended particles.



Figure 5: Shimadzu SALD-2300 Particle Size Analyzer

Surfactants

Surfactants are used as a wetting agent that, when used along with other chemicals, can significantly increase the productivity of a well.¹⁷ Unlike many other techniques used to monitor surfactants, the Shimadzu LCMS-8040 (Figure 6) can be used to simultaneously analyze anionic, amphoteric, and non-ionic surfactants in very complex environmental samples.¹⁸ Simpler and less expensive methods, such as Standard Methods 5540¹⁹, determine surfactants as “groups” that can be extracted and measured using a UV-Vis spectrophotometer, such as the Shimadzu UV-1800.



Figure 6: Shimadzu Triple-quad LCMS-8040 Mass Spectrometer

KCL, Guar, and Cross-linkers

Cross linkers are usually boron or zirconium compounds that are used to “link” guar gum molecules together. The guar is a water soluble polymer used to thicken the fracking fluid and hold the sand in suspension as it is carried through the pipe and into the fractures made in the shale. The addition of potassium prevents negatively charged carboxymethyl groups on the polymer from repelling each other, allowing the polymer to occupy less space than it would if potassium had not been added.²⁰ Potassium or Sodium Chloride is also added to the fracking solution to prevent, or minimize, swelling of clay minerals.²¹

¹⁶ Mader, D.; Hydraulic Proppant Fracking and Gravel Packing; Elsevier; 1989

¹⁷ http://bergen.spe.no/publish_files/ODS2010_PG_Cole-Hamilton.pdf; accessed May 12, 2014

¹⁸ Simultaneous analysis of anionic, amphoteric and non-ionic surfactants using ultra-high speed LC-MS/MS; Paper PO-CON1212E;

¹⁹ Rice, E.W., Baird, R.B., Eaton, A.D., and Clesceri, L.S., ;Standard Methods for the Examination of Water and Wastewater 22nd Edition, APHA, AWWA, WEF; 2012

²⁰ <http://omrl.eng.ua.edu/Library/Manuscripts/CrosslinkingPapers/SPE90840/SPE90840-3.pdf>; accessed May 12, 2014

²¹ http://www.halliburton.com/public/cem/contents/Chem_Compliance/web/H02686.pdf; accessed May 12, 2014



Figure 7: Shimadzu ICPE-9000 Inductively Coupled Plasma Emission Spectrometer

Boron, sodium, and potassium along with other trace metals, such as iron, calcium, and magnesium, are readily determined by Inductively Coupled Argon Plasma Atomic Emission Spectroscopy (ICAP-AES) methods, such as USEPA Method 200.7.²² Because the drilling solutions are prepared containing very high salt content, it is important to use an ICP-AES that is capable of aspiration of high salt solutions without clogging the nebulizer or excessive memory effects that may occur. The Shimadzu ICPE-9000 (Figure 7) employs a vertical torch arrangement with a high salt nebulizer and self-draining spray chamber. The ICPE-9000 software and potential for both axial and radial view of the plasma make it possible to analyze both trace and very high concentrations of analyte with very little dilution.

Scale Inhibitor

If the concentration of calcium and/or barium is high enough, and the conditions are right, they can precipitate with carbonate or sulfate to form scale. The formation of scale inside the pipe or within the rock fractures decreases gas production. The addition of phosphonates or ammonium chloride as ingredients of the fracking solution helps to minimize scale. Simple colorimetric tests combined with visible spectrophotometers, such as the Shimadzu UV-1800, can be used for measurement of scale inhibitors.

Acid

Hydrochloric acid and various organic acids, such as citric acid, are used in the fracking solution to dissolve remnants of cement left behind from the drilling process or to dissolve the calcite and hematite cement that binds the individual mineral grains of the shale together. Since hydrochloric acid is composed of the hydrogen and chloride ions, it is impossible, other than by pH or a neutralization titration, to determine the concentration of hydrochloric acid in the fracking solution. A Shimadzu organic acid HPLC system with a UV or conductivity detector can be used to determine concentrations of organic acids.

Friction Reducer

High molecular weight polyacrylamide blended with petroleum distillates is added to the fracking solution to create laminar flow and decrease the total energy (horsepower) required to pump the solution down-hole.²³ The petroleum distillate may contain aromatics hydrocarbons, such as benzene, toluene, ethylbenzene, and xylenes (BTEX). USEPA method 624²⁴ is a gas chromatography coupled with mass spectrometry method capable of accurate determination of BTEX along with multiple other volatile organic compounds in very complex matrices. The Shimadzu GCMS-QP2010 SE coupled with an EST Purge and Trap sample concentrator (Figure 8) can be used for the analysis of volatile organics in fracking water samples.



Figure 8: Shimadzu GCMS-QP2010 SE Gas Chromatograph Mass Spectrometer

²² http://water.epa.gov/scitech/methods/cwa/bioindicators/upload/2007_07_10_methods_method_200_7.pdf

²³ <http://cdn.intechopen.com/pdfs-wm/44660.pdf>, accessed May 12, 2014

²⁴ <http://www.epa.gov/osw/hazard/testmethods/sw846/pdfs/8260b.pdf>

■ Potential Environmental Impact of Fracking on US Water Supplies

Hydraulic fracturing is a well-stimulation process used to improve the recovery and production of oil and natural gas from untraditional petroleum deposits. Coal bed methane and gas shale are examples of untraditional petroleum deposits that require “fracking”. When fracking a well, a large volume of water mixed with sand and chemicals are injected into the formation at pressures high enough to cause the rock to crack. The sand fills the fissures, creating channels that allow the gas to escape into the pipe. Coal bed methane gas deposits do not require as much water as shale gas deposits. Because shale “fracking” requires millions of gallons of water, there is genuine concern that the environment will be adversely impacted.

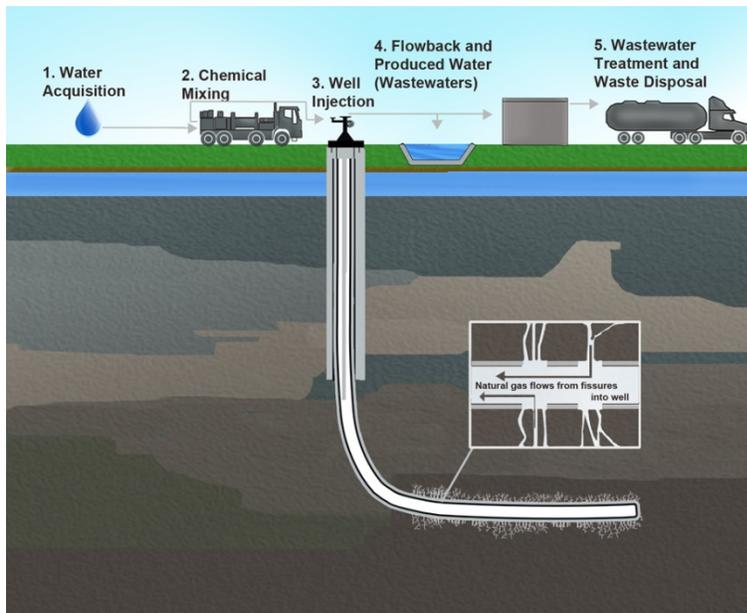


Figure 9: Five Stages of a fracking operation

Figure 9 illustrates the five stages of a fracking operation.²⁵ These are:

1. Acquire enough water needed for the hydraulic fracturing of the well. This could be up to 5,000,000 gallons of water.
2. Mix the chemicals with the water.
3. Inject the water plus chemicals into the well.
4. Recover the flow-back water and production water (hydraulic fracturing wastewater).
5. Treat and dispose of the wastewater.

Step 1 notes that the fracking operation needs to acquire millions of gallons of water. This water may be withdrawn from relatively clean fresh groundwater or surface water supplies and contaminated with fracking chemicals and salts dissolved from the formation. Some petroleum companies are starting to recycle flow-back water, but most of them still dispose of it by deep well injection.

Mixing the chemicals with fresh water could result in spills at the mixing site. If mixing zones are not lined or contained there is the possibility of ground and surface water contamination from a spill.

As the injected water flows through the formation it dissolves existing minerals and carries with it the interstitial water. The fracking solution chemistry differs from the formation water and can dissolve elements,

²⁵ <http://www2.epa.gov/hfstudy/hydraulic-fracturing-water-cycle>; accessed May 12, 2014

such as uranium, that were trapped in the formation.²⁶ When the fracking water returns back to the surface, it carries with it some of the interstitial formation water, and any trace inorganic and/or organic compounds that may have dissolved. As little as 10% to up to 100% of the fracking water returns to the surface as the fracking wastewater.²⁷ This wastewater is collected into pits and disposed of.

It is the flow-back water from the fracking process and the large volumes of produced water that pose the largest risk of environmental contamination.²⁸ Because of the very high salt content of the water, it is difficult to treat by conventional wastewater treatment procedures. Due to these very high salt concentrations, most methods normally used to analyze wastewater may not be applicable for testing fracking wastewater without modification.²⁹ Table 2³⁰ is an example of some typical fracking solution flow-back water analyses.

Table 2: Example of Flow Back Water Analysis

Component	Concentration (mg/L)
pH	6.6 (S.U)
Alkalinity as CaCO ₃	140
Total Dissolved Solids (TDS)	67,300
Total Suspended Solids (TSS)	100
Total Organic Carbon (TOC)	63
Biochemical Oxygen Demand (BOD)	3
Oil & Grease	< 5
Sodium as Na	18,000
Calcium as Ca	4,950
Magnesium as Mg	560
Barium as Ba	690
Iron as Fe	40
Chloride as Cl ⁻	41,850
Bicarbonate as HCO ₃ ⁻	74
Ammonium as NH ₄ ⁺	82
Volatiles	ND – 1 (BTEX and acetone)
Semi-volatile	ND – 1 ppm (PAH)

Other constituents that may be present in flow-back water are surfactants, glycols, methanol, and polyacrylates, which are major ingredients added to the stimulation water mixture. These compounds are not on the “regular” EPA method lists routinely used when screening drinking water, groundwater, or wastewater for environmental compliance. Existing methods, such as EPA SW846 Method 8015 Non Halogenated organics by Gas Chromatography³¹, may not have sufficient sensitivity or selectivity in the complex matrices.

Drinking Water

Drinking water supplies, such as rivers, lakes, or shallow wells, could be contaminated by flow-back and production water in the event of spills, improperly lined storage ponds, or leaking well casings from disposal by underground injection. Since the maximum allowable level for TDS in drinking water is 500 mg/L and chloride has a high solubility and mobility in the environment, drinking water contamination can be quickly detected by a sudden increase in chloride concentration. With the exception of potential contaminants for

²⁶ Impacts of Shale Gas Wastewater Disposal on Water Quality in Western Pennsylvania; *Environ. Sci. Technol.*, 2013, 47 (20), pp 11849–11857

²⁷ <http://blogs.nicholas.duke.edu/thegreengrok/frackingwater/> accessed May 13, 2014

²⁸

[http://www.wef.org/uploadedFiles/Access_Water_Knowledge/Wastewater_Treatment/Fracking%20Factsheet%20Final\(1\).pdf](http://www.wef.org/uploadedFiles/Access_Water_Knowledge/Wastewater_Treatment/Fracking%20Factsheet%20Final(1).pdf) accesses May 13, 2014

²⁹ <http://www2.epa.gov/sites/production/files/documents/hf-report20121214.pdf> accessed May 13, 2014

³⁰ http://www2.epa.gov/sites/production/files/documents/12_Hayes_-_Marcellus_Flowback_Reuse_508.pdf

³¹ <http://www.epa.gov/osw/hazard/testmethods/sw846/pdfs/8015c.pdf>; accessed May 13, 2014

which there are no existing approved drinking water methods, all approved methods are capable of analyzing drinking water supplies. See Table 3 for a listing of Maximum Contaminant Levels (MCL) for primary drinking water contaminants, and Table 4 for a listing of MCLs for secondary contaminants.³²

Table 3: Primary Drinking Water Contaminants and MCLs

Contaminant	MCL (mg/L)
Antimony	0.006
Arsenic	0.010
Barium	2
Beryllium	0.004
Cadmium	0.005
Chromium	0.1
Copper	1.3
Cyanide (free)	0.2
Fluoride	4.0
Lead	0.015
Mercury	0.002
Nitrate	10
Nitrite	1
Selenium	0.05
Thallium	0.002
Acrylamide	Zero
Alachlor	0.002
Atrazine	0.003
Benzene	0.005
Benzo(a)pyrene	0.0002
Carbofuran	0.04
Carbon Tetrachloride	0.005
Chlordane	0.002
Chlorobenzene	0.1
2,4-D	0.07
1,2-Dichloro-3-Dibromopropane	0.0002
o-Dichlorobenzene	0.6
p-Dichlorobenzene	0.075
1,1-Dichloroethane	0.005
1,1-Dichloroethylene	0.007
Cis 1,2-Dichloroethylene	0.07
Trans 1,2-Dichloroethylene	0.1
Dichloromethane	0.005
1,2-Dichloropropane	0.005
Di(2-ethylhexyladipate)	0.4
Di(2-ethylhexylphthalate)	0.006
Dinoseb	0.007
Dioxin	Zero
Diquat	0.02
Endothall	0.1
Endrin	0.002
Epichlorohydrin	Zero
Ethyl Benzene	0.7
Ethylene Dibromide	Zero
Glyphosate	0.7
Heptachlor	0.0004
Heptachlor Epoxide	0.0002

³² <http://water.epa.gov/drink/contaminants/> accessed May 18, 2014

Hexachlorobenzene	0.001
Hexachlorocyclobutadiene	0.05
Lindane	0.0002
Methoxychlor	0.04
Oxamyl	0.2
PCB's	0.0005
Pentachlorophenol	0.001
Pichloram	0.5
Simazine	0.004
Styrene	0.1
Tetrachloroethylene	0.005
Toluene	1
Toxaphene	0.003
2,4,5-TP	0.05
1,2,4-Trichlorobenzene	0.07
1,1,1-Trichloroethane	0.005
Vinyl Chloride	0.002
Xylenes	10
Gross Alpha	15 pCi/L
Gross Beta	4 millirem per year
Radium 226 + Radium 228	5 pCi/L
Uranium	30 ug/L

Table 4: Secondary Drinking Water Contaminants and MCL's

Contaminant	MCL (mg/L)
Aluminum	0.05 – 0.2
Chloride	250
Copper	1
Color	15 CU
Fluoride	2
Foaming Agents (Surfactants)	0.5
Iron	0.3
Manganese	0.05
pH	6.5 – 8.5
Silver	0.1
Sulfate	250
Total Dissolved Solids (TDS)	500
Zinc	5

The contaminants in **bold** are those that have been reported in³³, or are likely to occur in water supplies that have been impacted with production or back-flow water. Most of the contaminants in the USEPA drinking water primary and secondary pollutants list are industrial chemicals, such as chlorinated solvents and pesticides that are not very likely to be detected in oil-field water. Contaminants, such as methane or ethylene glycol, are not on the list, and unless specifically tested for, will not be reported even if they are present. Also, there are no USEPA-approved methods for parameters such as methane or ethylene glycol.

Water systems (and laboratories) must use EPA-approved methods to demonstrate compliance with drinking water regulations. Shimadzu Instruments, such as the GCMS-QP2010 SE (Figure 8) and the ICPE-9000 (Figure 7) are fully capable of analyzing fracking water-impacted drinking water supplies for volatile organics by EPA Methods 524.2, 524.3, and 524.4, and for trace metals by EPA 200.7 and 200.5.

The increase of contaminants, such as chloride and bromide (not routinely monitored for drinking water compliance) could lead to an increase in the formation of disinfection by products during the drinking water treatment process.

³³ <http://www.uta.edu/news/releases/2013/07/Schug-water-well-contaminants-study.php>, accessed May 18, 2014

Wastewater

The potential for pollution of surface water and groundwater comes from improper handling of flow-back water, and accidental spills of production water, flow-back water, or fracturing chemicals.³⁴ Total Dissolved Solids (TDS) have been found in shale gas wastewater at concentrations up to 350,000 mg/L, and chloride at concentrations approaching 200,000 mg/L. TDS and chloride are not significantly removed by conventional POTW (Publically Owned Treatment Works) systems requiring pretreatment of the shale gas wastewater prior to discharge to the POTW. Other constituents in shale gas wastewater may interfere with the POTW treatment process or precipitate in the bio solids. A POTW cannot receive a wastewater that would cause it to violate its NPDES permit.³⁵

In October 2011, the USEPA announced plans to develop effluent guidelines for Section 304(m) of the Clean Water Act for wastewater discharges produced by natural gas extraction from underground coal-bed methane and shale formations.³⁶ In a 2012 Preliminary Effluent Limitation Guidelines (EGL) plan, published August 7, 2013, the EPA announced that it proposes to discontinue revisions requiring regulation of coal-bed methane wastewater discharges, but will continue to develop revisions to provide additional controls on pollutant discharges from untraditional oil and gas wells.

According to the EPA, direct discharges from untraditional oil and gas wells are subject to NPDES permit regulations (40 CFR Part 122- 125) and indirect discharges into POTW's are subject to general pretreatment regulations under 40 CFR Part 435.³⁷ This means that all methods used to monitor pollutants in discharges from untraditional oil and gas wells must be listed at 40 CFR Part 136.³⁸ The problem is that many, if not all, of the currently approved methods have not been validated in matrices with dissolved salt content as high as 350,000 mg/L TDS. Table 5 is an example of some USEPA 40 CFR Part 136 approved methods and their possible limitations in the analysis of produced and flow-back water from untraditional oil and gas wells.

Table 5: 40 CFR Part 136 methods required for analysis of pretreatment samples and potential interferences that could cause difficulty in flow-back and production water analysis

Parameter	EPA approved method	Interferences
Alkalinity	SM 2320	Soap (surfactants), oily matter, suspended solids, or precipitates. Do not filter or dilute sample
Total Dissolved Solids (TDS)	SM 2540 C	Highly mineralized water with considerable calcium, magnesium, chloride and/or sulfate may be hygroscopic and require prolonged drying, proper desiccation, and rapid weighing. Limit residue to 200 mg. (at 200,000 mg/L TDS sample size = 1 milliliter)
Total Organic Carbon (TOC)	SM 5310B	Salts build up in the combustion furnace, shortening its life and causing memory (high blanks) effects.
	SM 5310C	Oxidation is inhibited if the chloride concentration exceeds 500 mg/L; Lower recoveries than 5310B on refractory heterocyclic nitrogen organic compounds
Biochemical Oxygen Demand (BOD)	SM 5210	Trace metals and trace organics may be toxic to micro-organisms, causing results to be low. The test does not oxidize many refractory heterocyclic nitrogen organic compounds or nitriles.
Chemical Oxygen Demand (COD)	SM 5220	The most common interference is the chloride ion, which can complex with the silver catalyst, causing results to be low. However, chloride can also react with dichromate, causing the results to be high. Do not test for COD by this method if chloride exceeds 2000 mg/L.

³⁴ Rao, V.; Shale Gas: The Promise and the Peril; Research Triangle Institute; 2012

³⁵ http://www.epa.gov/npdes/pubs/hydrofracturing_faqs.pdf; accessed May 28, 2014

³⁶ <http://water.epa.gov/scitech/wastetech/guide/304m/factsheet2011.cfm#summary>. Accessed June 12, 2014

³⁷ <http://water.epa.gov/scitech/wastetech/guide/oilandgas/unconv.cfm>. Accessed June 12, 2014

³⁸ <http://water.epa.gov/scitech/methods/cwa/basic.cfm>, accessed June 12, 2014

Oil and Grease	EPA 1664	Any filterable material that is soluble in hexane, such as elemental sulfur, surfactants, organic dyes, etc., will be falsely identified as Oil and Grease. Heavier petroleum and highly polar organic compounds that are not soluble in hexane will not be extracted. Lighter compounds, such as gasoline range organics, are not measured. Non-oil and grease compounds are extracted and measured in samples with a very high dissolved salt content
Anions (F ⁻ , Cl ⁻ , NO ₂ ⁻ , NO ₃ ⁻ , Br ⁻ , PO ₄ ⁻³ , SO ₄ ⁻²)	EPA 300.0, and other ion chromatography methods	Carbonate and small organic acids co-elute with fluoride. The retention times of all anions may shift if organic acids are present. Samples with high chloride concentrations may require dilutions greater than 1000x. These high dilutions prevent other anions from being measured in the same injection. Trace metals and high levels of organics can interfere. ³⁹
Metals (by ICP-AES)	EPA 200.7 and /or 200.5 or equivalent	Spectral interferences are numerous and difficult to solve ⁴⁰ . There are over 50,000 ICP-AES spectral lines reported, making a high-resolution ICP spectrometer necessary if samples will contain high concentrations of various trace metals. Background may be elevated depending upon individual samples requiring sophisticated dynamic background correction. Ionization efficiency differences between standards and samples may require internal standards and ionic strength adjustment. Matrix matching may be necessary to overcome viscosity differences. Some ICP-AES spectrometers can tolerate simple salts up to 30%; however, complex bivalent salts can be problematic. Most likely, samples will require dilution. Dilution raises the minimum detectable concentrations.
Metals (by ICP-MS)	EPA 200.8 or equivalent	Spectral interferences are fewer than for ICP-AES. Use of a collision cell can overcome most polyatomic and isobaric interferences (species that has a mass similar to the analyte). ICP-MS methods recommend against using HCL, H ₂ SO ₄ , or H ₃ PO ₄ ; however, the anions of these acids are major constituents in the flow-back or produced water matrix. Preliminary chromatographic or precipitation techniques may be necessary prior to introduction of the sample into the plasma. Transport and ionization effects caused by differences in the viscosity and total ionic strength of the samples and standards change the efficiency of aerosol production. Matrix matching or the method of standard additions may be required. A TDS of 5000 mg/L should be considered the maximum allowed.
Metals (GFAAS)	EPA 200.9 or equivalent	There can be variable retention of the analyte on the tube depending on the sample. Low dynamic range and single element analysis, but high salt tolerance.
As and Se (Hydride)	SM 3114B	High concentrations of transition metals may decrease the response
Gross Alpha and Gross Beta	EPA 900	The maximum allowed mass is 100 mg for gross alpha and 200 mg for gross beta. At 200,000 mg/L TDS the maximum sample volume for gross alpha is 0.5 milliliters.
Volatile Organics	EPA 624	High concentrations of surfactants cause foaming that can contaminate the entire system. Highly polar organic compounds may suffer decreased purging efficiency with an increase in the salt content of samples. High concentrations of high molecular weight compounds may carry-over from one sample analysis to the next, resulting in "ghost" peaks.
Semi-Volatile Analysis	EPA 625	Surfactants and various other constituents in the samples may cause emulsions preventing organic and aqueous layers from separating and lowering extraction efficiency. The high salt content of samples may increase the extraction of analytes and surrogates compared to the blank and laboratory control sample. Samples high in organics may require dilution, or possibly prevent concentration of the sample to 1 milliliter. A high organic content of the sample may mask surrogate and analyte recovery, or require diluting the surrogate and analytes to below detection. A high organic concentration may prevent accurate identification or quantitation of the analyte.

³⁹http://campuscms26.ucmerced.edu/sites/snri/files/public/documents/Ion%20Chromatography%20in%20Envrionmental%20Analysis_P.%20Jackson_Dionex%20%20Corp.pdf, accessed June 26, 2014

⁴⁰ <http://www.inorganicventures.com/icp-oes-measurement>, accessed June 26, 2014

Ammonia	EPA 350.1 or SM 4500 NH ₃	Distillation can hydrolyze primary amines (caused by temperature and pH) into NH ₃ . Low molecular weight amines, ketones, alcohols, aldehydes are distilled and can interfere. Electrodes are fouled by surfactants, fatty acids, and detect low molecular weight amines. Amines can interfere with the Berthelot reaction.
Total Kjeldahl Nitrogen (TKN)	EPA 351.2 or SM 4500 org	Samples high in salt can raise the boiling point resulting in low recovery. Digestion must be prolonged to improve recovery of refractory organic compounds. Low recovery on many heterocyclic organic nitrogen compounds.

Table 5 listed some examples of 40 CFR Part 136 approved methods and some potential interference that could prevent these methods from obtaining results suitable for compliance reporting. While 40 CFR Part 136.6 allows laboratories some flexibility to modify methods, the laboratory is left with a dilemma of needing to modify methods to obtain satisfactory results and risk violating the permit because they modified the method; you can modify the method to get the right result but the result is out of compliance because you modified the method. If the EPA is going to regulate flow-back and production water as pretreatment, then methods to measure regulated parameters in these matrices need to be validated.

Research and development of new or modified methods capable of accurately determining regulated pollutants in high TDS samples is needed.

■ Conclusion

The recovery of natural gas and oil from untraditional wells is necessary for the economic stability of the United States. Shale gas deposits are deep below the earth's surface and recovery of gas is expensive and requires millions of gallons of water mixed with chemicals, known as "fracking solution". Most fracking solution stays underground or returns to the surface mixed with formation water, also known as production water.

The shale gas recovery operation risks environmental contamination of drinking water and surface water as a result of poorly lined waste ponds, poorly designed wells, or chemical spills. Since the fracking and production water solutions are very high in Total Dissolved Solids and chloride ion, contamination of wells can be rapidly and easily detected. Analysis of the fracking water itself is possible with highly sophisticated instruments, such as those available from Shimadzu.

Currently approved drinking water methods are sufficient to monitor drinking water and source water supplies. One of the problems may be that drinking water target organic analytes are mostly chlorinated solvents and pesticides. These compounds are not used in fracking solutions. Methods for the analysis of methane, alcohols, and glycols should be developed.

The EPA has indicated that it will consider wastewater from shale gas production as part of the pretreatment program of the Clean Water Act. Compliance with pretreatment requires that the wastewater not contain constituents that can pass through a POTW, or contain constituents that can cause a pretreatment sludge to fail its permit. All methods used to monitor discharges from these untraditional oil and gas wells must be listed at 40 CFR Part 136, however, the listed EPA-approved methods have not been validated in the high TDS matrices typical of untraditional shale gas recovery wells. Research and development of new or modified methods capable of accurately determining regulated pollutants in high TDS samples is needed.



First Edition: July 2014

SHIMADZU Corporation
www.shimadzu.com/an/

For Research Use Only. Not for use in diagnostic procedures.
The contents of this publication are provided to you "as is" without warranty of any kind, and are subject to change without notice.
Shimadzu does not assume any responsibility or liability for any damage, whether direct or indirect, relating to the use of this publication.

SHIMADZU SCIENTIFIC INSTRUMENTS
7102 Riverwood Drive, Columbia, MD 21046, USA
Phone: 800-477-1227/410-381-1227, Fax: 410-381-1222
URL: www.ssi.shimadzu.com

© Shimadzu Corporation, 2014