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WATER HAZARD A holding pond for a hydraulically fractured gas well in Waynesburg, Pa.

CLEANER FRACKING

Unconventional oil and gas drilling brings a flood of business for **WATER TREATMENT** firms

MELODY M. BOMGARDNER, C&EN NORTHEAST NEWS BUREAU

ACCORDING TO the most recent estimate by the U.S. Energy Information Administration, the Marcellus Shale formation of the Appalachian Basin contains more than 140 trillion cu ft of natural gas that is recoverable but as yet almost wholly unexplored. To get to the gas, energy companies will use a drilling process known as hydraulic fracturing. It's a process that involves a great deal of water.

Much of the public concern about this process, also known as fracking, has focused on the mixture of water and chemicals that is injected into the ground to fracture open rock and unlock the gas. But experts point out that the most critical risk of pollution from fracking lies in how operators handle the water that comes back out of the ground.

This wastewater, a combination of the injected fracking fluid and groundwater, is so saline that it is highly toxic to plants and aquatic life. What's more, its high dissolved solids content can easily overwhelm municipal treatment facilities and contaminate drinking water supplies.

Handling all that water is a problem not just in the Marcellus region. In the coming years, oil and gas recovered throughout North America will primarily come from unconventional sources, including shale formations, enhanced recovery from older wells, and oil sands. All of these sources create a great deal more wastewater per unit of oil or gas than conventional sources.

This is bad news for the oil and gas industry but good news for the water treatment industry. Well operators are increasingly likely to treat wastewater with a combination of chemicals, biocides, filters, and membranes along with more expensive equipment such as evaporators and concentrators.

But the quality of wastewater varies widely from site to site, and different service providers promote different technologies depending on their own expertise or the equipment they've invested in, experts say. As a result, whether the oil or gas comes from Wyoming or Pennsylvania, the business of treating the wastewater is like the Wild West. "It's a great industry for a water treatment chemist and for a consultant—everyone is still figuring things out," says Tom Pankratz, a desalination expert at Global Water Intelligence, a consulting firm.

The companies that supply the fracking industry with chemicals, equipment, and services are looking to grab a piece of a

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large and growing market. Treating water from North American oil and gas wells was a $2.5 billion industry in 2010, according to GWI. Another $2.5 billion was spent on reinjection, minimization, and off-site disposal of water. The $5.0 billion combined market will double by 2025, GWI predicts. And water treatment is expected to be the faster growing of the two segments, with an annual growth rate of between 10 and 20%.

THERE'S A LOT of water to treat. Hydraulic fracturing requires between 3 million and 5 million gal of water per gas well. The water is combined with fracturing chemicals and a sand or ceramic proppant and then pumped into the horizontal branches of the well. The proppant props open fractures in the shale, allowing gas that has been trapped for eons to flow out. After fracking, roughly 35% of the water returns to the surface as flowback in the first weeks. Additional liquid known as produced water—a mix of fracking fluid and groundwater—comes up with the gas for most of the life of the well.

Hydraulic fracturing got its start in western states, where oil and gas drillers pump untreated wastewater into nearby wells driven deep into porous rock. For decades, deep-well injection has been the first choice for disposal because of its low cost. But the Marcellus areas of Pennsylvania and West Virginia have a geology that is not suited to deep-well injection.

To dispose of the water off-site would require around 40 truck trips every day for weeks or months. That is costly, and energy companies can literally wear out their welcome when using local roads.

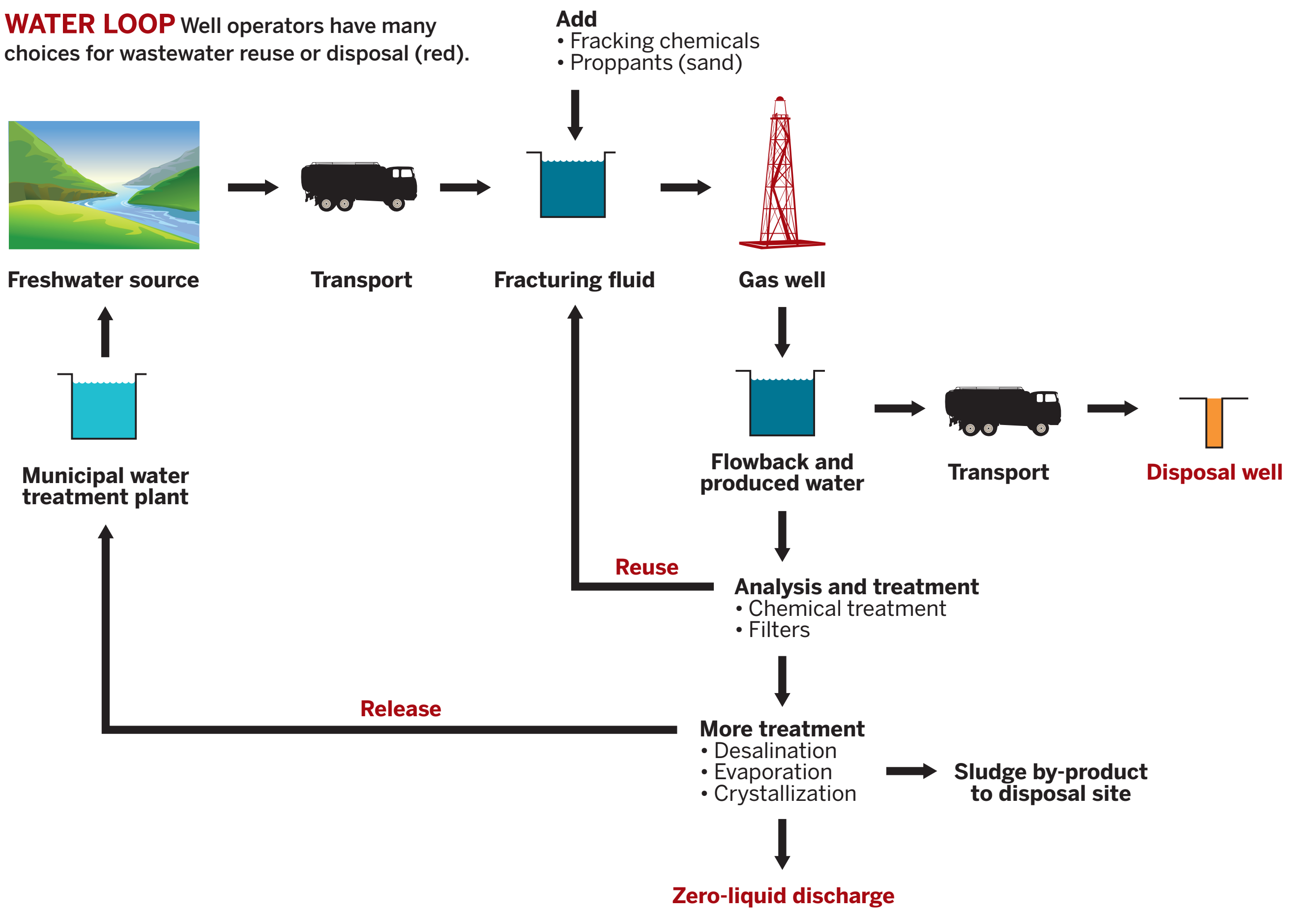
In contrast, the goals of wastewater treatment are to reuse, recycle, or reduce the water that comes out of the well. Chemical firms that specialize in water treatment such as Kemira and Ecolab's Nalco unit; equipment makers including GE and Siemens; and service providers, both large and small, customize their offerings depending on the water's contents and where it is destined to go. The main consideration in selecting technologies, all agree, is cost.

With prices for natural gas at a historic low of less than $3.00 per thousand cu ft, energy firms are compelled to select the cheapest legal alternative. "My biggest competitor is a hole in the ground," says Mark Wilson, marketing director for unconventional gas at GE Power & Water. "We are looking for more energy efficiency and lower capital costs."

Gas drillers that use hydraulic fracturing treat wastewater with the intention of reusing it at the next well. Reuse requires keeping a close eye on water chemistry. Because the water will go back down into a well, operators must ensure that it does not produce scale or cause an explosion in bacterial growth when it gets into the shale formation. Either type of gunk can slow the flow of gas. In addition, reused water must not interfere with the ability of the fracking chemicals to do their job of placing a load of proppant into the shale fractures.

To keep water quality high, water services firm Kroff monitors the water flowing out of a well in real time. Produced water is high

WATER LOOP Well operators have many choices for wastewater reuse or disposal (red).



SHUTTERSTOCK/C&EN

FRACKING RECIPE

Example of fracturing fluid composition from a gas well in Beaver, Pa.

INGREDIENT FUNCTION	CHEMICAL	MAXIMUM INGREDIENT CONCENTRATION, % BY MASS
Carrier/base fluid	Freshwater	85.47795%
Proppant	Crystalline silica	12.66106%
Acid	Hydrochloric acid in water	1.29737%
Gelling agent	Petroleum distillate blend	0.14437%
	Polysaccharide blend	0.14437%
Cross-linker	Methanol	0.04811%
	Boric acid	0.01069%
Breaker	Sodium chloride	0.04252%
Friction reducer	Petroleum distillate, hydrotreated light	0.01499%
pH-adjusting agent	Potassium hydroxide	0.01268%
Scale inhibitor	Ethylene glycol	0.00540%
	Diethylene glycol	0.00077%
Iron control agent	Citric acid	0.00360%
Antibacterial agent	Glutaraldehyde	0.00200%
	Dimethyl benzyl ammonium chloride	0.00067%
Corrosion inhibitor	Methanol	0.00142%
	Propargyl alcohol	0.00010%

NOTE: Additional proprietary ingredients not listed in material safety data sheet: acid, alcohol, biocide, copolymer, disinfectant, enzyme, polymer, silica, solvent, surfactant, and weak acid. **SOURCE:** FracFocus

in dissolved solids. Kroff uses the analytical data to design a treatment scheme for the water so it can be mixed with additional freshwater and fracturing chemicals and used in the next well. The treatment itself happens on the well site with mobile units.

Dave Grottenthaler, Kroff's general manager, says his firm focuses on removing barium, calcium, iron, sulfate, and bacteria from produced water. "The biggest fear is barium," he says. "When it forms barium sulfate, the scale is almost irreversible." Kroff relies mostly on off-the-shelf treatment chemicals such as soda ash, caustic soda, acids, and flocculants. The insoluble contaminants are removed via flocculation, sedimentation, and filtration.

THE RESULTING WATER is quite salty but useful in fracking. "Although much of the flowback and production brines have high chlorides, we can reuse the water effectively up to 100,000 mg/L. Clean salt water outperforms freshwater for the hydrofracturing process," Grottenthaler claims. Recently, the company designed and built a core flow analyzer that tests shale rock from a drill cutting and measures the effect of treated water on the formation's permeability.

Companies developing fracking fluid ingredients must also be mindful of the quality of produced water at their customers' wells. That's the case for the water treatment chemical maker Kemira, which formulates polymeric friction reducers that help ease proppants into tiny fractures. "We receive the data, and we provide feedback on product of choice for these conditions," says Daniel Detter, Kemira's marketing manager for oil and mining.

Kemira has learned that an ingredient that works in a fracking fluid made with freshwater won't necessarily work in one based on produced water. "Polymer friction reducers are quite good but are not tolerant of high brine concentrations," Detter says. Kemira is working on new versions of its polymers that are more brine tolerant. Depending on the condition of the produced water, for example, a customer may require a nonionic or cationic friction reducer, rather than the more typical anionic variety.

At Nalco, meanwhile, water experts are focused on improving the biocides that reduce populations of microbes growing in flowback water. Joel Pastore, the firm's marketing manager for unconventional resources and water management, says Nalco is designing a biocide that does not interfere with other fracturing chemicals. It also breaks down into more environmentally friendly by-products. And as a bonus feature, "it oxidizes iron and precipitates iron out of the solution, which would otherwise interfere with the friction reducer," Pastore says.

Chemical treatment is just one approach

to treating produced water. The technology options lie along a continuum, with chemical-dependent processes on one end and more muscular—and expensive—evaporation and concentration methods on the other. With treatment offerings all along the spectrum, GE Power & Water says it is prepared for any problem a customer brings it.

"Many philosophies exist about how much you have to clean up the water to reuse it," GE's Wilson says. "Some customers worry about the salt content or just the divalent ions, while others want to take it to a more pristine state. We have technology that can take it to whatever end state the producer wants it to be in, to virtually distilled water."

REUSING PRODUCED water in fracking is common for now in the Marcellus region, but with additional treatment to remove salts, well operators have other options. In Pennsylvania, for example, water recovered from a mobile evaporator is more than clean enough—at less than 100 mg of total dissolved solids per liter of water—to be discharged to a municipal treatment plant and returned to surface water. The concentrated brine that is left—about 40% of the original volume—can then be trucked to a crystallizer to recover salt for use as road deicer.

In western states such as Wyoming or Colorado, most produced water is not as saline as in the Marcellus area, and reverse-osmosis membranes are sufficient for removing ions, Wilson explains. Well operators in the West generally use deep-well injection for disposal. But in the future, especially in dry regions, Wilson says, treated water may have value in agriculture or other applications that would more than compensate for the cost of purification.

As another benefit, Wilson notes, specialized membranes can reduce the amount of fracturing chemicals needed, especially biocides. GE's mobile water fleet can pretreat freshwater, filtering out bacteria before the water is sent down the well. Biocides are generally the most toxic additive used in fracturing fluids and limit the uses of recovered water.

GE is working to further adapt its treatment equipment for the oil and gas market. It is developing specialized fluoropolymer-coated membranes that remove suspended solids and bacteria and are tolerant of the contaminants in produced water. It is even testing new engines that can power equipment with gas obtained at the well site.

GWI's Pankratz says that instead of having to choose between chemical and physical water treatment processes, the best possible solution is to have all options available nearby. But most operators are dealing with companies trying to promote their own technology niche, he says. "The problem is when you get a company that tries to fit its round peg in a square hole." A chemical-only approach may not achieve the optimal output, whereas evaporation and concentration come with high energy costs, Pankratz warns.

As the unconventional oil and gas industry grows, new technologies will enter the game that may help minimize trade-offs or change strategies entirely. Industrial gas firm Linde, for example, is testing a fracking process in which a foam of CO_2 and water, with a thickness similar to shaving cream, carries proppant into the fractures. According to the company, the method requires less water and fewer chemicals.

John T. Lucey Jr., executive vice president of business development at Heckmann, a large and fast-growing water services company, says he is technology agnostic and watches new developments closely. One technology that has drawn his interest is electrocoagulation, a treatment that applies electric current across metal plates to remove emulsified oil, heavy metals, and suspended solids.

As for removing dissolved salts cheaply, Lucey allows for a little wishful thinking. "There is an opportunity to end up with innovative technology to help bend the laws of physics or osmotic pressure," he says.

Pankratz is more of a realist. "I don't think there is any step-change technology that is waiting to be unveiled," he says. The biggest opportunity lies in successfully integrating the technologies that already exist while compensating for changes in produced water quality and quantity over time. To do that requires a clearheaded understanding of each technology's limitations, he says. "No one has done that yet." ■

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SALTY STUFF

The mix of fracking fluid and groundwater known as produced water contains wide variations in water chemistry

	SHALE FORMATION		
CONTENT (MG/L)	BARNETT (TEXAS)	HAYNESVILLE (ARK., LA., TEXAS)	MARCELLUS (N.Y., PA., W.VA.)
TDS	40,000–185,000	40,000–205,000	45,000–185,000
Cl^-	25,000–110,000	20,000–105,000	25,000–105,000
Na^+	10,000–47,000	15,000–55,000	10,000–45,000
Ca^{2+}	2,200–20,000	3,100–34,000	5,000–25,000
Sr^{2+}	350–3,000	100–3,000	500–3,000
Mg^{2+}	200–3,000	600–5,200	500–3,000
Ba^{2+}	30–500	100–2,200	50–6,000
Fe^{2+}/Fe^{3+}	22–100	80–350	20–200
SO_4^{2-}	15–200	100–400	10–400

TDS = total dissolved solids. **SOURCE:** GE Power & Water

GE POWER & WATER

ROAD WARRIOR This GE mobile evaporator unit travels to well sites.