I want a product line that is EPA DfE listed by CAS Registry Number, there is quite an extensive list to choose from.”

As the chair of the Green Chemistry Institute’s recently established Hydraulic Fracturing Roundtable, Durham will have the opportunity to share his expertise and gain new insights from others in the industry. GCI is a division of the American Chemical Society, which publishes C&EN.

The roundtable will examine the current slate of chemicals used in hydraulic fracturing, including solvents, microbiocides, and corrosion inhibitors, and work to develop more sustainable alternatives. According to Durham, the main concern is the risk of surface spills; chemicals in the ground water may require new additives such as cross-linkers, Hill says. Cross-linkers—traditionally used in drilling applications, including solvents, microbiocides, and corrosion inhibitors, and work to develop more sustainable alternatives. According to Durham, the main concern is the risk of surface spills; chemicals in the well generally break down during the life of the well’s operation, which can be years.

Spills do happen, though they appear to be rare. Colorado is home to more than 53,000 active oil and gas wells, many of them along the front range of the Rocky Mountains, a corridor that is also home to the residents of Denver, Boulder, and Fort Collins. In 2013, 600 spills at well sites were reported to the Colorado Oil & Gas Conservation Commission, up from 399 in 2012. The volume of water spilled was a mere 0.004% of the total produced water from all wells.

According to the commission, leading causes of spills at oil and gas wells are equipment failure and human error. Of the 399 spills reported in 2012, 63 impacted groundwater and 22 impacted surface water. The commission does not track spills that happen during the transportation of chemicals or produced water.

**ONE ENVIRONMENTAL STRATEGY** that the industry has taken up over the past two years is to reuse the water produced by one well in a nearby well, according to A. Daniel Hill, professor of petroleum engineering at Texas A&M University. But the salts and minerals in produced water require changes to the chemical routine.

For example, chemicals used to thicken fracturing fluids so they can carry proppants far distances underground might not gel properly in salty water. And the poor-quality water may require new additives such as cross-linkers, Hill says. Cross-linkers—traditionally borate salts and zirconium complexes—are used to firm the gel formed from guar gum and other thickeners.

What’s more, after the proppants are set up in the fractures, operators require that the viscous mixture reliquefy so the oil and gas can flow out. So they add special time-release breakers to make the gel fall apart. To ensure this happens in salty water, Texas A&M researchers are investigating ways to encapsulate breakers, including nano-entrapped structures, Hill reports.

At Dow, researchers are looking for ways to make oil and gas wells more productive even as the down-hole environment becomes more extreme. Salinity and high temperatures and pressures are all increasingly common, Byrne says. Thus, Dow’s scientists work in labs where they can simulate being 2 or 3 miles below the earth or several thousand feet below the ocean. “Part of what we offer today are rheology modifiers, such as cellulosic ones, and products able to withstand high temperatures,” Byrne explains. Rheology modifiers let operators tune the viscosity of the water-chemical mixture that moves prop-

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**BIOCIDE BLAST** Sophisticated microbial control is required at all stages of the oil- and gas-drilling process.

### FRACKING WATER IS PRETREATED

Water used in drilling applications, whether fresh or recycled, contains naturally occurring microorganisms that can multiply once down-hole. Pretreatment helps prevent this.

- ClO₂, oxidizers
- Quaternary ammonium%/TTPC
- DBNPA
- TTPC

### BIOCIDES ARE ADDED TO CHEMICAL MIXTURE

Microbes that thrive underground can be particularly difficult to control. Sulfate-reducing bacteria, for example, emit hydrogen sulfide, a corrosive gas. To prevent corrosion, biocides are added to fracturing chemicals.

- Glutaraldehyde
- Acrolein
- Glutaraldehyde + quaternary ammonium
- THPS
- Bronopol
- Glutaraldehyde

### LONG-LASTING BIOCIDES ENHANCE PRODUCTION

After hydraulic fracturing is complete, microbe populations can rebound, creating slime that prevents oil and gas from flowing freely from the fractures. Biocides that survive high heat and salinity help to prevent “souring” of the well.

- CTAC
- Dazomet
- DMO
- THM

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**Sources**: Dow Chemical, C&EN

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