What About Those Gas Well Stimulation Chemicals Anyway?

What are they ;Where and How much is they used; Why & When are they used; Will they affect area water, or cause negative environmental impact ? Is “GREEN” chemistry possible?

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Typical Well Stimulation Chemicals in Piceance; There are No Secrets just MSDS FORMS; Provided by all service companies on request !

- Friction Reducers: Polyacrylamide (not green) emulsions made with " greener" mineral oil or paraffin based hydrocarbon slurry ; not diesel. green citrus and plant based oils to replace even the greener mineral and paraffin based oils.

- "Greener" polymers; soy based and ester based are becoming available now to replace polyacrylamides.

Typical Chemicals cont'd.:

- Biocides: Some Gluteraldehydes, Sodium hypochlorite (bleach), or Chlorine dioxide used but they are not "Green";
- Newer Electrochemically Activated salt water available which IS green and has been used, & is available.
- Also a new "greener" biocide based on the antimicrobial chloroxylenol or PCMX is coming onto the scene (EPA reports: "NO harmful dermal, ocular, inhalation or ingestion affects to humans or animals as well as NO toxicological endpoints of concern for acute, short term or chronic exposure to PCMX through residential or occupational exposure have been identified except for mild eye irritation.

Typical Stimulation Chemicals in Piceance, Cont'd.

- Surfactants (Not green) and/or Interfacial tension Reducing agents as Micro-emulsion additives (Green) are used for reservoir fluid compatibility and treatment flow-back improvement.
- Scale inhibitors (not green) Phosphonates, & polyacrylates used to prevent scaling of tubulars

Potentially the Most Dangerous Chemical on Piceance Basin Locations: H_2O (water) !

- Dirty water sources, that is, used for drilling, completion and stimulation!
- Produced water from gas reservoirs; flow-back water from previous treatments are biomass and bacteria laden and threaten to produce toxic iron complexes and H_2S (sour gas) Poison Gas! Iron sulfide already being detected.
- Water quality monitoring, storage, handling,re-use versus disposal, and pre-treatment issues are paramount priorities of many operators in Piceance Basin.

Water production, & Usage/ Re-use issues for oil & gas operations

- Water quality monitoring; storage on location or central ponds; handling and transportation; re-use versus disposal; and pre-treatment issues are paramount priorities of many operators in Piceance Basin.
- These can be addressed positively for "ALL" cases.

Critical Water Issue in Storage and Production Facilities

- Water containing 0.25 to 1.0 % condensate as droplets so small (< 2 microns) that they almost cannot be seen, but can be smelled!
- These droplets are stabilized by colloidal iron (also < 2 micron particle size) at between 0.1 1nd 0.2 % by weight.
- These may contribute to “black water” , bacteria and often render many bacteria control agents useless or less effective.

What happens to Water Injected Down-hole during Fracturing Treatments

- Water with pressure from pumps (yes they are diesel powered just like over -the -road trucks hydraulically cracks the earth and proppant (sand) is carried by the water to fill-up or prop open the cracks (fractures) so that gas may be produced faster and more efficiently. Much of the water is produced back with the gas and naturally occurring produced water.

What happens to the chemicals used in the water fracs?

- Friction Reducers (polyacrylamides) are run at < or = to 0.1% or 1 gallon per 1000 gallons of water and are diluted to less than 0.001% upon being pumped with the large volumes of frac water. Most of that is adsorbed onto the producing formation or is degraded with temperature and time to extremely short chain polymers that become bio-degradable in most cases. Could they be reduced even further? Yes, but they are diluted to lower levels than similar polymers used for separating solids in many drinking water systems.

What happens to the biocides?

- Even the less than green biocides such as gluteraldehydes, et.al. are consumed by the reaction with even more harmful bacteria (some of which are sulfate reducing and can and do produce poisonous H2S gas)
- New PCMX or ECA biocides are now available to reduce residual potentials to even lesser levels that will less harmful than the salinity of the brines that are produced and must be haled away and disposed of at a cost of $6 -$12 per barrel in some cases! They are used at lower concentrations than the disinfectant sprays that may often be used in the home to kill germs in the air and are breathed.

What happens to the surfactants?

- These additives are similar to the same products that you use at home to wash dishes, and many are available and are used that utilize plant based solvents and surfactants so as to improve fluid recovery, reduce formation damage, and degrade at the very low levels used (<0.1 %) within the very hydrocarbons being produced (gas and condensate). They also adsorb onto the proppants and formations and thus stay in the formation from which gas and water are produced.

What happens to the Scale Inhibitors?

- These are products which chemically “tie up” scaling ions such as Calcium and Magnesium in order to keep them from accumulating on tubulars and production equipment and restricting or choking flow of produced fluids.
- Many of these chemicals are also used in hot tubs, evaporative coolers, and swimming pools to control the development of harmful and unsightly scales on surfaces.
- They too are combined with the scaling ions down-hole and produced in the produced water at dilute levels which can be disposed of in approved disposal wells into deep unproductive reservoirs away from any populated areas.

Twelve Principles of Green Chemistry

- **1. Prevent waste:** Design chemical syntheses to prevent waste, leaving no waste to treat or clean up.
- **2. Design safer chemicals and products:** Design chemical products to be fully effective, yet have little or no toxicity.
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- **3. Design less hazardous chemical syntheses:** Design syntheses to use and generate substances with little or no toxicity to humans and the environment.
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- **4. Use renewable feedstock's:** Use raw materials and feedstock's that are renewable rather than depleting. Renewable feedstock's are often made from agricultural products or are the wastes of other processes; depleting feedstock's are made from fossil fuels (petroleum, natural gas, or coal) or are mined.
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- **5. Use catalysts, not stoichiometric reagents:** Minimize waste by using catalytic reactions. Catalysts are used in small amounts and can carry out a single reaction many times. They are preferable to stoichiometric reagents, which are used in excess and work only once.
- **6. Avoid chemical derivatives:** Avoid using blocking or protecting groups or any temporary modifications if possible. Derivatives use additional reagents and generate waste.

Twelve Principles of Green Chemistry, Contd.

- **7. Maximize atom economy:** Design syntheses so that the final product contains the maximum proportion of the starting materials. There should be few, if any, wasted atoms.
- **8. Use safer solvents and reaction conditions:** Avoid using solvents, separation agents, or other auxiliary chemicals. If these chemicals are necessary, use innocuous chemicals.
- **9. Increase energy efficiency:** Run chemical reactions at ambient temperature and pressure whenever possible.
- **10. Design chemicals and products to degrade after use:** Design chemical products to break down to innocuous substances after use so that they do not accumulate in the environment.
- **11.Analyze in real time to prevent pollution:** Include in-process real-time monitoring and control during syntheses to minimize or eliminate the formation of byproducts.
- **12. Minimize the potential for accidents:** Design chemicals and their forms (solid, liquid, or gas) to minimize the potential for chemical accidents including explosions, fires, and releases to the environment.
- Originally published by Paul Anastas and John Warner in **Green Chemistry: Theory and Practice** (Oxford University Press: New York, 1998).

Summary

- Stimulation, as well as drilling and completion chemicals can be derived from “natural” or green (er) sources and used economically to facilitate effective stimulation treatments.
- Availability of these additives is not as great as “less-green” chemistries that have been used for years.

Summary cont'd.

- Stimulation chemicals have been used since 1947 and very few incidents related to health or environmental damage have been documented. It doesn't mean there haven't been those that have gone unnoticed; just as many household chemical effects have over the same time frame.
- Point: Most versions are getting greener!

Conclusions

- Well stimulation additives can and are being improved.
- Economics are factors and previously “greener” products meant higher costs or less effectiveness. That is no longer true now! Operators and service companies must be proactive together to introduce “greener” chemistry into treatment programs , and educate the public that such improvements are in fact possible and being made!

Conclusions

- Finally, all activities in industry and private sector alike are usually condensed to the following criteria as postulated by the 3M company in the late ’70’s:
- Everyone wants services and products to be three things: Good (quality); Fast

(expedient & efficient) and Cheap (Cost effective). The challenge is that all three are desired, but only two are often realized! Try it!

Reference

- David L. Holcomb, Ph.D.
- Director of Research and Development
- FracTech Services, Ltd.
- 1137 S. Huron Street
- Denver, Colorado 80403
- Experience in well stimulation: 39 years

FracTech Stimulation Job Execution

FracTech Job Set-up 360 degrees

Chemical Addition for 180K gal. Frac

Chem-Add unit: Biocide, Surfactant, Friction Reducer; Scale Inhibitor

Frac Pumps Tied into Frac Manifold