Chemicals in Fracturing

- Basics
  - What needs exist in fracturing that require chemicals?
  - What chemicals are typical in fracturing? – these change with the areas
  - Where do chemicals go in the formation and do they come back?
  - What is the route and risk for frac chemicals to reach a fresh water sand?
  - What is the likely source of chemicals found in fresh water sands?
- What greener chemicals or substitutes methods are available?
- Minimum Expectations, Best Practices and Key Performance Indicators (KPI)

First, Chemicals in Well Operation

- Chemicals are not just used in fracturing.
  - Wells are designed to exceed the producing and stimulation requirements placed on the pipe, cement and seals by the pressure, temperature, earth stresses and fluids within the formation.
  - Formation conditions change during production. Even properly designed wells may require corrosion programs or even redesign to insure that the overall pipe and barrier seals remain within design specifications to prevent failures of the barriers between the well and the formation.
  - Conditions change from field to field and often within a field.
  - Operational changes may require chemicals such as regular corrosion treating to prevent problems.
  - Chemicals in well operation are applied in smaller quantities, at lower pressure and in a regular fashion during a well's life.

Typical Water Frac Needs that Require Chemicals

- Friction Reduction – used in high rate fracturing.
- Bacterial Control – required when using surface waters and when recycling waters – needed to prevent serious problems later on. For fracturing, many greener microbial control products are now available.
- Corrosion Inhibition for the small amount of acid used in formation cleanup.
- Viscosity – needed to build frac width & carry proppant.
- Oxygen scavenger - needed when surface waters are used to prevent aerobic bacteria growth and severe oxygen corrosion. Also – reduces need for corrosion inhibitors.

Chemicals Commonly Used in Shale Fracturing and consequences of not using the chemical

Chemical	Use	Consequences of not using chemical
Acid	Removes near well damage	Higher treating pressure, slightly more engine emissions.
Biocides	Controls bacterial growth	Increased risk of souring the formation (H_2S gas from sulfate reducing bacteria growth) and increasing corrosion.
Corrosion Inhibitor	Used in the acid to prevent corrosion of pipe	Sharply increased risk of pipe corrosion from acid. Well integrity compromised.
Friction Reducers	Decreases pumping friction	Significantly increases surface pressure and frac pump engine emissions .
Gelling Agents	Improves proppant placement	Increased water use. Natural gas recovery may decrease in some cases by 30 to 50% where frac fluids must be gelled (conventional fracs).
Oxygen scavenger	Prevents corrosion of well tubulars by oxygen	Corrosion sharply increased and well integrity (containment) compromised.

How Much Chemical is Used? Examples:

Chemical	Common in a Shale Frac?	Normal Concentration Ranges (actual minimum set by testing)
Acid (15% HCl)	Yes	1500 to 2500 gallons total
Bacteria Control	Yes	0.0 to 0.001%
Friction Reducer	Yes	0.01 to 0.025%
Oxygen Scavenger (ammonium bisulfite)	Yes	0.005%
Corrosion Inhibitor	Yes	0.001% in the frac to 0.2% in acid
Surfactants (multiple products – similar to products in dish washing soaps)	Common, but often over used	0.005 to 0.01%
Gelling Agent (guar gum or cellulose product)	Only in Hybrid fracs	10 to 20 lb/1000 gallons
Cross Linker (borax base is laundry detergent)	In some hybrid fracs	Varies, but very low conc.
KCl (potassium chloride is table salt substitute)	Uncommon in shale	2%
Gel Breaker (ammonium persulfate)	Only with gel	0.01%
pH adjusting agent (sodium carbonate)	Only with gel	0.01%
Scale Inhibitor (5% to 10% active phosphate ester, or polymer or 0.02 to 0.4% ethylene glycol)	Rare	1 to 2 gallons per 1000 gallons
Iron Control (Citric Acid)	Rare	0.001 to 0.004%

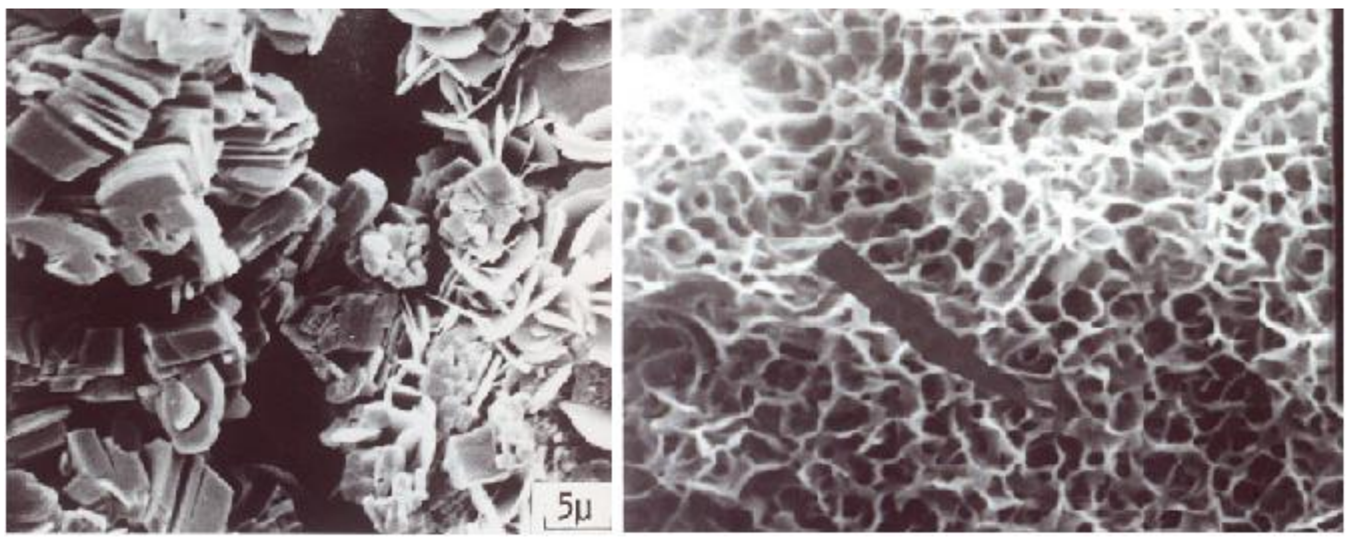
Chemical Risks and Green Alternatives for Common Shale Frac Additives

Chemical	Composition	Common Use	Spends or breaks down to?
Acid (HCl)	15% hydrochloric acid	Swimming Pool Treating	Water and chloride salt.
Biocides	(Sodium hypochlorite ----------- Chlorine dioxide)	Swimming pool treating ----------------- Drinking water treating	Chloride ions and salts ----------------------------------- Chloride ion
Corrosion Inhibitor for acid	Usually not green, but green forms starting to appear	Pharmaceuticals, boilers, plastics	Amines, nitrates and salts. Readily adsorbed in the formation, rarely indicated in backflows.
Friction Reducers	Polyacrylamide	Soil and water treating, cosmetics	Polymer chain, most stays in the formation
Gellants	Guar gum, Cellulose and derivatives.	Food additive, cosmetics	Chain decomposes to short chains in water – eaten by bacteria when aerobic conditions are reached.
Oxygen scavenger	Ammonium bisulfite	Used in food and beverage processing	Forms sodium sulfate, naturally occurring neutral pH salt, returns with water. Unreactive to oxidation or reduction.

Where do the chemicals go in the formation?

Surface active agents (most corrosion inhibitors, scale inhibitors, surfactants, etc.) adsorb onto minerals such as clays in the formation with enormous surface areas and a surface charge that attracts the chemicals. The chemicals may seep back very slowly, usually in the concentration of 5 to 10 parts chemical per million parts of water.

Right: clays (kaolinite, chlorite and smectite) that offer surface area adsorption sites one million times the surface area size of sand grains.



Other materials like acid, spend in the formation and return as salt water.

For those that do not adsorb such as biocides, a much greener approach is needed.

Other Considerations

- Chemical additives are high cost, often adding tens of thousands of dollars to the bottom line cost of the frac.
- Most engineers defer to the service vendor to tell them what chemicals they need.
- In many cases the vendor doesn't have the information needed to optimize chemical usage, thus chemicals are over-used. Better understanding = less chemical used.
- Solution? The producing company should be doing the necessary testing and supplying data to help the vendor optimize the chemical usage, both with greener chemicals and less total chemical volume. Judging from what these additives cost and the number of wells to be treated, the testing would be <u>very</u> economic.

Risk of frac chemicals polluting fresh water sands (1)

- From surface spills? – very low risk. Transport leaks with fresh waters do not contain chemicals. Transport leaks with flowback waters contain traces of chemicals, generally less than 5 to 10% of initial chemical levels, but do contain salt and may contain biocide. Transport of concentrated chemicals (pre-mix) are in shipping vessels regulated by D.O.T. Mixing with frac fluids is generally on the "fly" as the fluids are injected.
- From cement mud channels during fracturing? – extremely low risk. Mud channels in the cement are on the order of 0.5 inch diameter (and often are not continuous), but the friction of flowing fluids up two thousand to eight thousand feet of wellbore annulus limited by these small channels, would create so much friction that rate of fluid movement would be on the order of 50 to 100 gallons of the frac fluid with chemical concentration of 0.001 to 0.05% or perhaps a few ounces total of concentrated chemical. Such a leak would also require the pipe and cement barrier across the water sand to fail.

Risk of frac chemicals polluting fresh water sands (2)

- From a well casing rupture (over-pressure)? – extremely low risk. Actual rupture of pipe during fracturing is most rare and would be picked up by pressure monitoring the annulus between the production casing. An over-pressure of the annulus would cause the frac job to be immediately shut down. (See the module on Well Construction)
- From a hydraulic fracture breaking through all layers to rock from the gas pay zone to the surface water zones? - no risk. Fractures are either limited by natural frac barriers in the rock strata or by leakoff to the rock taking as much fluid as can be injected. The industry has to put several fractures in a thick pay zone because fractures do not grow heights of more than a few hundred feet.
- From connection of a fracture into a fault that extends to the surface waters? Only one case has been documented in about a million fractured wells.

How do chemicals likely get into fresh water zones?

- The highest risk to contamination of fresh water sands with chemicals is from unregulated or poorly constructed (illegal) industrial chemical disposal wells:
  - To place any significant levels of chemicals in a water zone, the time of operational contact is measured in months or years, not the few hours of a fracturing treatment.
  - The cancer-causing and poisonous chemicals that have been measured in the few known instances of ground water contamination are NOT common to hydraulic fracturing use.

Chemical Best Practices

- Minimum of Chemicals Used?
  - Testing core or cuttings and fluids to identify best chemicals and lowest concentrations?
- Greener chemical alternatives identified and considered for chemicals that must be used?
- Risk of pollution from spills and leaks taken into economic considerations?
- Chemical behavior of chemicals over life of project considered?