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 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 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.

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.

Chemicals Commonly Used in Shale Fracturing

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 and corrosion in pipe.
Corrosion Inhibitor	Used in 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?	Concentration
Acid (15% HCl)	Yes	2000 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 derivative)	In some hybrid fracs	varies
KCl (potassium Chloride)	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 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%

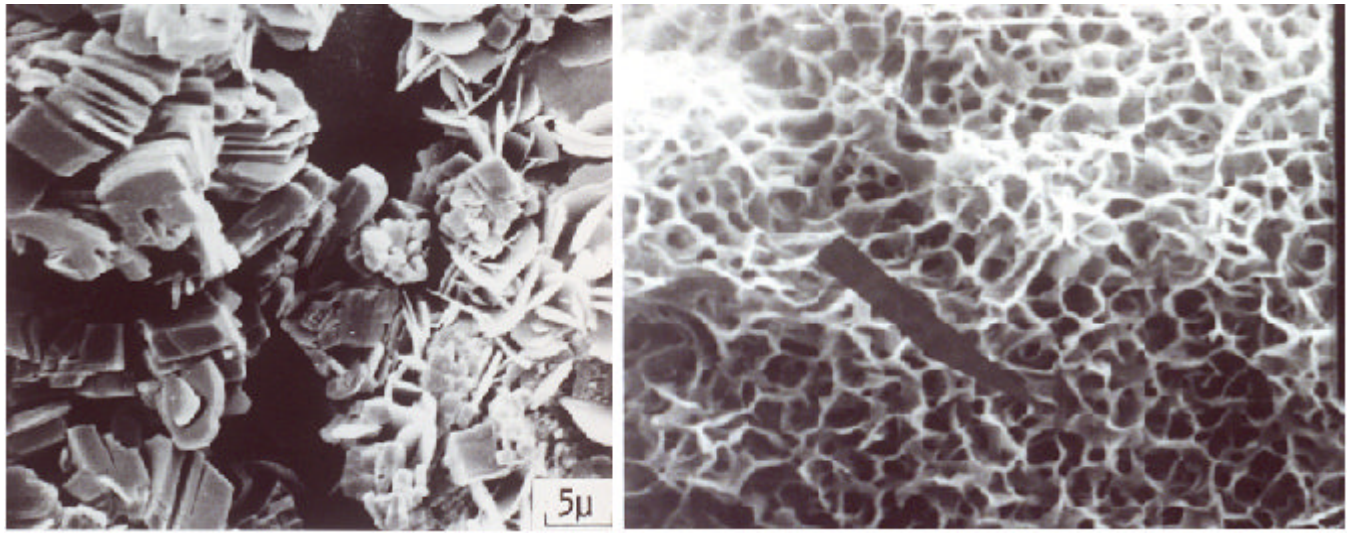
Chemical Risks and Green Alternatives for Common Shale Frac Additives

Chemical	Composition	Common Use	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?

Most 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 bleed back very slowly, usually in the concentration of 5 to 10 parts per million of water.

Right: clays (kaolinite, chlorite and smectite) that offer surface area adsorption sites 10^6 times larger than 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.
- 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 very economic.

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?