

The Basics of Wells – Chemicals used in Wells

Chemicals Used in Fracturing

The identities of chemicals incorporated in fracturing fluids were probably the first thing sensationalized about fracturing. The movie “Gasland” created quite a stir with the statement that a “cocktail” of several hundred toxic chemicals were “potentially” used in fracturing. The grain of truth was that there are many chemicals in additives sold for incorporation in fracturing; however, the fact is that most fracs use only a dozen or so major chemicals, some of which are food-grade additives and many are in parts per million concentration. About half of fracturing jobs are “slick water” fracturing fluid that often use low concentrations of two to five chemicals. Many claims of chemical usage also include trace amounts of chemicals at the edge of detection and most well below the EPA’s strictest limits. Analysis of drinking water, for comparison, has shown arsenic, lead, chromium, solvents, gasoline, pesticides, prescription drugs, and a myriad of household products as the most common contaminants – none from fracturing. The upside to this commentary is that public concerns have moved chemical manufacturers to make and operators to use safer chemicals and less overall chemicals. Many companies have moved toward biocides with less residual activity, mechanical biocides such as ultraviolet light and the use of chemicals on the US EPA’s Safer Choice chemicals (formerly Designed For Environment or DfE) or UK North Sea’s OCNS Hazard rating of Gold Band (lowest possible hazard quotient). These listed materials meet requirements of rapid biodegradation and minimum harm to environments.

Friction reducer, the largest volume chemical in slick water fracs, is polyacrylate, a polymer whose main use is in baby diaper absorbent and as a drinking water purifier that adsorbs heavy metals. A cross section of chemicals used in fracturing, the volumes used and some alternate uses helps explain oil field fracturing chemical usage. Chemicals such as diesel, benzene and proven carcinogens, mutagens and endocrine disruptors are not used in modern safe fracturing fluids. The CAS number identifies exact identity (no “trade secret” identities).

Common Fracture Additives for Slickwater Fracture Treatment				
Common Frac Additive	Composition	CAS Number (Chemical Abstracting Service – exact identifier)	~Total amount used in a single 500,000 gallon fracture treatment	Alternate Use
Friction Reducer	Polyacrylate	9003-05-8	2000 gallons	Absorbent in diapers, flocculent for drinking water
Biocide	Glutaraldehyde	111-30-9	100 gallons	Medical disinfectant
Scale inhibitor (not frequently used)	Phosphonate	6419-30-0 (one example)	25 gallons	Detergents

One of the most impactful problems from fracturing in Pennsylvania was the use of local water treating plants to treat water produced from oil and gas wells before disposal into Pennsylvania rivers. The

practice was evidently instituted in Pennsylvania decades prior to the shale drilling boom in the Marcellus when volumes of water flowed from conventional wells was very small and natural salt contents were low. Dilution of locally severe acid mine drainage in some creeks by the produced water was expected to be beneficial; however; large volumes of produced water from fracturing in the shales with high salinity and ions such as bromine and barium proved too problematic for such a disposal method. This practice, although allowed by law in Pennsylvania until about 2010, has been forbidden by law in nearly all western states since the 1950's.

Chemicals Used in Production Operations

Producing oil and gas with the associated salt water from hydrocarbon bearing formations creates corrosion potential, flow restriction deposits such as mineral scales of calcium or barium and challenges in separating oil from water. Corrosion remains one of the biggest deterioration problems in the oil industry (a large problem in other industries as well). Scales may precipitate in tubulars until they restrict flow. Paraffins (wax) are longer carbon chain components of oil and can deposit anywhere in the well as temperatures cool and pressure declines. Mixing of salt water, oil, gas and a small amount of solids such as sand, rust or even ice can produce emulsions, froths and foams that must be separated before the oil and gas can be sold and the salt water can be recycled or properly re-injected into the hydrocarbon producing formation. A wide variety of specialty chemicals, often at part per million (ppm) concentration, can be used, but only a handful of products are typically selected after laboratory testing. Using minimum amounts of the best additives reduces cost and risk in transport or storage.

Production Problem	Chemical Requirement	Example Chemical Type
Corrosion control	Inhibitor technology to slow corrosion attack.	Quaternary amine, organic phosphonates
Hydrate Control	Prevent hydrate blockage of flow lines.	Methyl alcohol, polymers
Paraffin/Asphaltene precipitation	Prevents precipitation or deposition of wax or asphaltenes.	Solvents, lemon oil, surfactants, resins
Emulsions, foams, froths	Breaks emulsions and speeds separation of water and oil.	Silicone de-foamers, surfactants, mechanical methods (non-chemical)
Scale formation	Prevent calcium carbonate, calcium sulfate and barium sulfate.	Phosphate Esters, polymers, phosphonates
Bacterial damage control	Biocide	Glutaraldehyde

Any chemical usage may be frightening to some people and there are definitely chemicals that should not be used, particularly where contamination or airborne emissions are possible. By using chemicals proven safe for specific uses, all elements of potential pollution are reduced. Even when the chemicals will never be disposed of in the environment outside of oilfield containment, the safe chemical route minimizes impact in the event of a spill or leak.

Note: BTX (Benzene, Toluene, Xylene) content in many additives is steadily declining but some operators have not phased the products out completely. Many companies are reviewing product offerings for the BTX or other troublesome materials and choosing alternatives. Although BTX is often reported in wells as if they were part of a chemical additive, the most likely source is in the produced oil. BTX and diesel range oil components are a natural part of many produced oils.

Disclosure: George E. King is a Texas Registered Professional Engineer with over 44 years oilfield experience. His technical background includes fracturing, workovers, chemicals, acidizing, well integrity and horizontal wells.