There are several functions that must be served by the fracking fluids. The fluids should flow with a minimum of frictional resistance through the long lengths of pipe. Added polyacrylamide helps minimize this friction. The fine sand or ceramic beads should be thoroughly suspended and dispersed throughout the gel-like fracking fluid. Following fracking, the gel structure is broken up and the fracking fluid is withdrawn back up the well, leaving behind only the fine grains of sand separating the layers of shale. Chemicals in the fluid remove oxygen that can form rust in the pipe. Other chemicals act as biocides to kill bacteria that can produce corrosive by-products. Emulsions of shale oil and water are prevented by chemical additives.

It is the chemicals used in these fluids that are controversial for two reasons: (1) For those residing near the fracking wells, a primary concern is the potential toxicity of these chemicals and their possible contamination of the air and water sources near the well. (2) For the well drillers, maximizing the yields of extracted natural gas is the bottom economic line. Fracking is both an art and a science. Each geological formation containing extractable natural gas is apparently different in the pore size and flow characteristics of the natural gas through the resident rocks. Thus, the composition of the chemicals used in the fracking fluid needs to be adjusted to the geology of each drilling site. Fracking is a competitive business and exact recipes developed through extensive research and experience are closely held secrets. After much pressure from nearby residents, the primary ingredients of most fracking fluids have been published at many well sites. Table 9-1 illustrates a generic list of fracking chemical additives taken from a natural gas trade publication. There is pressure to legally require publication of all chemicals used at each well site, so that the identity of water well contaminants can be matched against those contained in fracking and drilling fluids.

The main fracking acid used to dissolve rock and clear up drilling mud is HCl. For example, for limestone rock, the chemical equation would be:

$$CaCO_3\,(solid) + 2HCl\,(aq) \rightarrow Ca^{2+}(aq) + 2Cl^{-}(aq) + H_2CO_3\,(aq) \qquad (9\text{-}4)$$

$$H_2CO_3 \rightarrow H_2O + CO_2\,(gas) \qquad (9\text{-}5)$$

Thus the net result for solid limestone ($CaCO_3$) is a liquid containing soluble $CaCl_2$ salt and two gases, CO_2 and liberated natural gas. The acid is also used to interact with any remaining drilling mud which can interfere with the liberation of the gas during the fracking process.

One fracking component that has raised considerable concern is diesel fuel, which has been used in the past for use in extraction of natural gas from coal beds. Because diesel fuel contains BTEX compounds (benzene, toluene, ethylbenzene and xylenes), all regulated compounds under the Safe Water Drinking Act because they are

either harmful to humans or are a carcinogen, in the case of benzene. Memoranda of Understanding between the EPA and companies representing 95% of the companies engaged in coal bed methane extraction have agreed not to use diesel fuel in fracking fluids for coal bed exploration. Are BTEX compounds in shale fracking fluids? This remains to be seen. Table 9-1 indicates petroleum distillates, which could include BTEX compounds.

After the fracking operation, the fracking fluid is allowed to flow back up to the surface. Greater than 50 % of this fluid is generally recovered and is reused, injected deep into deep geologic sites, or treated to remove objectionable chemicals and released into natural water resources. Each of these options has drawbacks. The flowback fluid contains salts and dissolved minerals and presents treatment and purifications problems. These dissolved minerals also alter the fracking efficiencies if the flowback water is reused. Injected wastewater can migrate in unknown ways through geologic formations. Conventional sewage treatment plants often cannot handle the dissolved chemicals and minerals contained in flowback fracking fluid.

Flowback fluids are often stored temporarily in open pits constructed with plastic liners, which are prone to leakage, causing groundwater contamination. If there are volatile chemicals, there can be air pollution problems. The trend is to store these liquids in closed tanks and to recycle the fracking fluids.

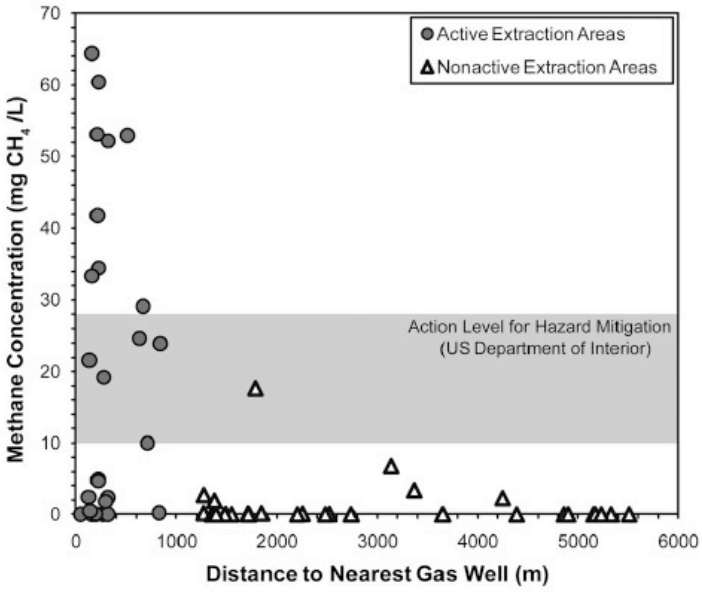

Fig. 9-7 Studies of post-drilling methane concentration in well water samples near drilling sites in Pennsylvania.

A recent peer-reviewed, independent study of Pennsylvania well water at various distances from an active shale natural gas extraction area found methane concentrations went up significantly when the well was less than 1 kilometer (see Fig. 9-7). In some cases the methane concentration in the water was well above the EPA action level for explosion hazard mitigation. Isotopic studies showed that the methane came from a source that was very old, probably from a very deep shale deposit. The same study found no contamination from either drilling or fracking fluids. There was no explanation available for these results, but the authors of the paper called for further study that included well-sampling before and after drilling. The authors

warned that it was entirely possible that drilling locations selected for maximum shale gas could also have had very high pre-drilling well water methane contamination.

Compound*	Purpose	Common application
Acids	Helps dissolve minerals and initiate fissure in rock (pre-fracture)	Swimming pool cleaner
Glutaraldehyde	Eliminates bacteria in the water	Disinfectant; Sterilizer for medical and dental equipment
Sodium Chloride	Allows a delayed break down of the gel polymer chains	Table Salt
N, n-Dimethyl formamide	Prevents the corrosion of the pipe	Used in pharmaceuticals, acrylic fibers and plastics
Borate salts	Maintains fluid viscosity as temperature increases	Used in laundry detergents, hand soaps and cosmetics
Polyacrylamide	Minimizes friction between fluid and pipe	Water treatment, soil conditioner
Petroleum distillates	"Slicks" the water to minimize friction	Make-up remover, laxatives, and candy
Guar gum	Thickens the water to suspend the sand	Thickener used in cosmetics, baked goods, ice cream, tooth-paste, sauces, and salad dressing
Citric Acid	Prevents precipitation of metal oxides	Food additive; food and beverages; lemon juice
Potassium chloride	Creates a brine carrier fluid	Low sodium table salt substitute
Ammonium bisulfite	Removes oxygen from the water to protect the pipe from corrosion	Cosmetics, food and beverage processing, water treatment
Sodium or potassium carbonate	Maintains the effectiveness of other components, such as crosslinkers	Washing soda, detergents, soap, water softener, glass and ceramics
Proppant	Allows the fissures to remain open so the gas can escape	Drinking water filtration, play sand
Ethylene glycol	Prevents scale deposits in the pipe	Automotive antifreeze, household cleansers, deicing, and caulk
Isopropanol	Used to increase the viscosity of the fracture fluid	Glass cleaner, antiperspirant, and hair color

Table 9-1 Some of the common chemicals used in the fracking process for natural gas exploration