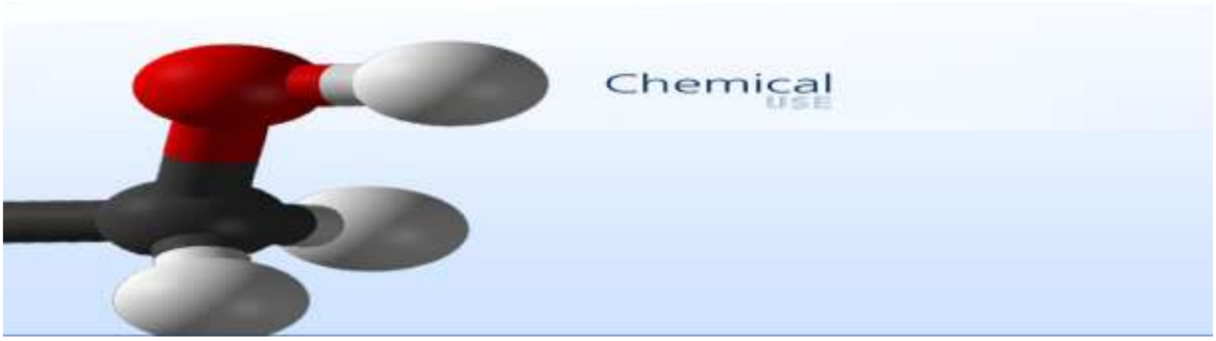
What Chemicals Are Used



As previously noted, chemicals perform many functions in a hydraulic fracturing job. Although there are dozens to hundreds of chemicals which could be used as additives, there are a limited number which are routinely used in hydraulic fracturing. The following is a list of the chemicals used most often. This chart is sorted alphabetically by the Product Function to make it easier for you to compare to the fracturing records .

Chemical Name	**CAS**	**Chemical Purpose**	**Product Function**
Hydrochloric Acid	007647-01-0	Helps dissolve minerals and initiate cracks in the rock	Acid
Glutaraldehyde	000111-30-8	Eliminates bacteria in the water that produces corrosive by-products	Biocide
Quaternary Ammonium Chloride	012125-02-9	Eliminates bacteria in the water that produces corrosive by-products	Biocide
Quaternary Ammonium Chloride	061789-71-1	Eliminates bacteria in the water that produces corrosive by-products	Biocide
Tetrakis Hydroxymethyl-Phosphonium Sulfate	055566-30-8	Eliminates bacteria in the water that produces corrosive by-products	Biocide
Ammonium Persulfate	007727-54-0	Allows a delayed break down of the gel	Breaker
Sodium Chloride	007647-14-5	Product Stabilizer	Breaker
Magnesium Peroxide	014452-57-4	Allows a delayed break down the gel	Breaker
Magnesium Oxide	001309-48-4	Allows a delayed break down the gel	Breaker
Calcium Chloride	010043-52-4	Product Stabilizer	Breaker

Choline Chloride	000067-48-1	Prevents clays from swelling or shifting	Clay Stabilizer
Tetramethyl ammonium chloride	000075-57-0	Prevents clays from swelling or shifting	Clay Stabilizer
Sodium Chloride	007647-14-5	Prevents clays from swelling or shifting	Clay Stabilizer
Isopropanol	000067-63-0	Product stabilizer and / or winterizing agent	Corrosion Inhibitor
Methanol	000067-56-1	Product stabilizer and / or winterizing agent	Corrosion Inhibitor
Formic Acid	000064-18-6	Prevents the corrosion of the pipe	Corrosion Inhibitor
Acetaldehyde	000075-07-0	Prevents the corrosion of the pipe	Corrosion Inhibitor
Petroleum Distillate	064741-85-1	Carrier fluid for borate or zirconate crosslinker	Crosslinker
Hydrotreated Light Petroleum Distillate	064742-47-8	Carrier fluid for borate or zirconate crosslinker	Crosslinker
Potassium Metaborate	013709-94-9	Maintains fluid viscosity as temperature increases	Crosslinker
Triethanolamine Zirconate	101033-44-7	Maintains fluid viscosity as temperature increases	Crosslinker
Sodium Tetraborate	001303-96-4	Maintains fluid viscosity as temperature increases	Crosslinker
Boric Acid	001333-73-9	Maintains fluid viscosity as temperature increases	Crosslinker
Zirconium Complex	113184-20-6	Maintains fluid viscosity as temperature increases	Crosslinker
Borate Salts	N/A	Maintains fluid viscosity as temperature increases	Crosslinker
Ethylene Glycol	000107-21-1	Product stabilizer and / or winterizing agent.	Crosslinker
Methanol	000067-56-1	Product stabilizer and / or winterizing agent.	Crosslinker
Polyacrylamide	009003-05-8	“Slicks” the water to minimize friction	Friction Reducer
Petroleum Distillate	064741-85-1	Carrier fluid for polyacrylamide friction reducer	Friction Reducer
Hydrotreated Light Petroleum Distillate	064742-47-8	Carrier fluid for polyacrylamide friction reducer	Friction Reducer
Methanol	000067-56-1	Product stabilizer and / or winterizing agent.	Friction Reducer
Ethylene Glycol	000107-21-1	Product stabilizer and / or winterizing agent.	Friction Reducer
Guar Gum	009000-30-	Thickens the water in order to suspend the	Gelling Agent

	0	sand	
Petroleum Distillate	064741-85-1	Carrier fluid for guar gum in liquid gels	Gelling Agent
Hydrotreated Light Petroleum Distillate	064742-47-8	Carrier fluid for guar gum in liquid gels	Gelling Agent
Methanol	000067-56-1	Product stabilizer and / or winterizing agent.	Gelling Agent
Polysaccharide Blend	068130-15-4	Thickens the water in order to suspend the sand	Gelling Agent
Ethylene Glycol	000107-21-1	Product stabilizer and / or winterizing agent.	Gelling Agent
Citric Acid	000077-92-9	Prevents precipitation of metal oxides	Iron Control
Acetic Acid	000064-19-7	Prevents precipitation of metal oxides	Iron Control
Thioglycolic Acid	000068-11-1	Prevents precipitation of metal oxides	Iron Control
Sodium Erythorbate	006381-77-7	Prevents precipitation of metal oxides	Iron Control
Lauryl Sulfate	000151-21-3	Used to prevent the formation of emulsions in the fracture fluid	Non-Emulsifier
Isopropanol	000067-63-0	Product stabilizer and / or winterizing agent.	Non-Emulsifier
Ethylene Glycol	000107-21-1	Product stabilizer and / or winterizing agent.	Non-Emulsifier
Sodium Hydroxide	001310-73-2	Adjusts the pH of fluid to maintains the effectiveness of other components, such as crosslinkers	pH Adjusting Agent
Potassium Hydroxide	001310-58-3	Adjusts the pH of fluid to maintains the effectiveness of other components, such as crosslinkers	pH Adjusting Agent
Acetic Acid	000064-19-7	Adjusts the pH of fluid to maintains the effectiveness of other components, such as crosslinkers	pH Adjusting Agent
Sodium Carbonate	000497-19-8	Adjusts the pH of fluid to maintains the effectiveness of other components, such as crosslinkers	pH Adjusting Agent
Potassium Carbonate	000584-08-7	Adjusts the pH of fluid to maintains the effectiveness of other components, such as crosslinkers	pH Adjusting Agent
Copolymer of Acrylamide and Sodium Acrylate	025987-30-8	Prevents scale deposits in the pipe	Scale Inhibitor
Sodium Polycarboxylate	N/A	Prevents scale deposits in the pipe	Scale Inhibitor
Phosphonic Acid Salt	N/A	Prevents scale deposits in the pipe	Scale Inhibitor

Lauryl Sulfate	000151-21-3	Used to increase the viscosity of the fracture fluid	Surfactant
Ethanol	000064-17-5	Product stabilizer and / or winterizing agent.	Surfactant
Naphthalene	000091-20-3	Carrier fluid for the active surfactant ingredients	Surfactant
Methanol	000067-56-1	Product stabilizer and / or winterizing agent.	Surfactant
Isopropyl Alcohol	000067-63-0	Product stabilizer and / or winterizing agent.	Surfactant
2-Butoxyethanol	000111-76-2	Product stabilizer	Surfactant

One of the problems associated with identifying chemicals is that some chemicals have multiple names. For example Ethylene Glycol (Antifreeze) is also known by the names Ethylene alcohol; Glycol; Glycol alcohol; Lutrol 9; Macrogol 400 BPC; Monoethylene glycol; Ramp; Tescol; 1,2-Dihydroxyethane; 2-Hydroxyethanol; HOCH2CH2OH; Dihydroxyethane; Ethanediol; Ethylene gycol; Glygen; Athylenglykol; Ethane-1,2-diol; Fridex; M.e.g.; 1,2-Ethandiol; Ucar 17; Dowtherm SR 1; Norkool; Zerex; Aliphatic diol; Ilexan E; Ethane-1,2-diol 1,2-Ethanedio.

This multiplicity of names can make a search for chemicals somewhat difficult and frustrating. However, if you search for a chemical by the CAS number it will return the correct chemical even if the name on the fracturing record does not match. For example if the fracturing record listed the chemical Hydrogen chloride and you searched for it by name using a chemical search site you may not get a result. But if you search for CAS # 007647-01-0 it might return Hydrochloric acid which is another name of Hydrogen chloride. Therefore, by using the CAS number you can avoid the issue of multiple names for the same chemical.

Multiple names for the same chemical can also leave you with the impression that there are more chemicals than actually exist. If you search the National Institute of Standards and Technology (NIST) ‡ website the alternate names of chemicals are listed. This may help you identify the precise chemical you are looking for. The NIST site also contains the CAS numbers for chemicals. NIST is only one of many websites you can use to locate additional information about chemicals. You can also search the following websites using the chemical name or CAS number:

OSHA/EPA Occupational Chemical Database ‡

The Chemical Database ‡

EPA Chemical Fact Sheets ‡

Hydraulic Fracturing: The Process

What Is Hydraulic Fracturing?

Contrary to many media reports, hydraulic fracturing is not a “drilling process.” Hydraulic fracturing is used after the drilled hole is completed. Put simply, hydraulic fracturing is the use of fluid and material to create or restore small fractures in a formation in order to stimulate production from new and existing oil and gas wells. This creates paths that increase the rate at which fluids can be produced from the reservoir formations, in some cases by many hundreds of percent.

The process includes steps to protect water supplies. To ensure that neither the fluid that will eventually be pumped through the well, nor the oil or gas that will eventually be collected, enters the water supply, steel surface or intermediate casings are inserted into the well to depths of between 1,000 and 4,000 feet. The space between these casing “strings” and the drilled hole (wellbore), called the annulus, is filled with cement. Once the cement has set, then the drilling continues from the bottom of the surface or intermediate cemented steel casing to the next depth. This process is repeated, using smaller steel casing each time, until the oil and gas-bearing reservoir is reached (generally 6,000 to 10,000 ft). A more detailed look at casing and its role in groundwater protection is available HERE.

With these and other precautions taken, high volumes of fracturing fluids are pumped deep into the well at pressures sufficient to create or restore the small fractures in the reservoir rock needed to make production possible.

What's in Hydraulic Fracturing Fluid?

Water and sand make up 98 to 99.5 percent of the fluid used in hydraulic fracturing. In addition, chemical additives are used. The exact formulation varies depending on the well. To view a chart of the chemicals most commonly used in hydraulic fracturing and for a more detailed discussion of this question, click HERE.

Why is Hydraulic Fracturing Used?

Experts believe 60 to 80 percent of all wells drilled in the United States in the next ten years will require hydraulic fracturing to remain operating. Fracturing allows for extended production in older oil and natural gas fields. It also allows for the recovery of oil and natural gas from formations that geologists once believed were impossible to produce, such as tight shale formations in the areas shown on the map below. Hydraulic fracturing is also used to extend the life of older wells in mature oil and gas fields.

Source: Modern Shale Gas Development in the United States, US Department of Energy

How is Hydraulic Fracturing Done?*

The placement of hydraulic fracturing treatments underground is sequenced to meet the particular needs of the formation. The sequence noted below from a Marcellus Shale in Pennsylvania is just one example. Each oil and gas zone is different and requires a hydraulic fracturing design tailored to the particular conditions of the formation. Therefore, while the process remains essentially the same, the sequence may change depending upon unique local conditions. It is important to note that not all of the additives are used in every hydraulically fractured well; the exact “blend” and proportions of additives will vary based on the site-specific depth, thickness and other characteristics of the target formation.

1. An acid stage, consisting of several thousand gallons of water mixed with a dilute acid such as hydrochloric or muriatic acid: This serves to clear cement debris in the wellbore and provide an open conduit for other frac fluids by dissolving carbonate minerals and opening fractures near the wellbore.

2. A pad stage, consisting of approximately 100,000 gallons of slickwater without proppant material: The slickwater pad stage fills the wellbore with the slickwater solution (described below), opens the formation and helps to facilitate the flow and placement of proppant material.

3. A prop sequence stage, which may consist of several substages of water combined with proppant material (consisting of a fine mesh sand or ceramic material, intended to keep open, or “prop” the fractures created and/or enhanced during the fracturing operation after the pressure is reduced): This stage may collectively use several hundred thousand gallons of water. Proppant material may vary from a finer particle size to a coarser particle size throughout this sequence.

4. A flushing stage, consisting of a volume of fresh water sufficient to flush the excess proppant from the wellbore.

Other additives commonly used in the fracturing solution employed in Marcellus wells include:

• A dilute acid solution, as described in the first stage, used during the initial fracturing sequence. This cleans out cement and debris around the perforations to facilitate the subsequent slickwater solutions employed in fracturing the formation.

• A biocide or disinfectant, used to prevent the growth of bacteria in the well that may interfere with the fracturingoperation: Biocides typically consist of bromine-based solutions or glutaraldehyde.

• A scale inhibitor, such as ethylene glycol, used to control the precipitation of certain carbonate and sulfate minerals

• Iron control/stabilizing agents such as citric acid or hydrochloric acid, used to inhibit precipitation of iron compounds by keeping them in a soluble form

• Friction reducing agents, also described above, such as potassium chloride or polyacrylamide-based compounds, used to reduce tubular friction and subsequently reduce the pressure needed to pump fluid into the wellbore: The additives may reduce tubular friction by 50 to 60%. These friction-reducing compounds represent the “slickwater” component of the fracing solution.

• Corrosion inhibitors, such as N,n-dimethyl formamide, and oxygen scavengers, such as ammonium bisulfite, are used to prevent degradation of the steel well casing.

• Gelling agents, such as guar gum, may be used in small amounts to thicken the water-based solution to help transport the proppant material.

• Occasionally, a cross-linking agent will be used to enhance the characteristics and ability of the gelling agent to transport the proppant material. These compounds may contain boric acid or ethylene glycol. When cross-linking additives are added, a breaker solution is commonly added later in the frac stage to cause the enhanced gelling agent to break down into a simpler fluid so it can be readily removed from the wellbore without carrying back the sand/ proppant material.

Fractures: Their orientation and length

Certain predictable characteristics or physical properties regarding the path of least resistance have been recognized since hydraulic fracturing was first conducted in the oilfield in 1947. These properties are discussed below:

Fracture orientation

Hydraulic fractures are formed in the direction perpendicular to the least stress. Based on experience, horizontal fractures will occur at depths less than approximately 2000 ft. because the Earth’s overburden at these depths provides the least principal stress. If pressure is applied to the center of a formation under these relatively shallow conditions, the fracture is most likely to occur in the horizontal plane, because it will be easier to part the rock in this direction than in any other. In general, therefore, these fractures are parallel to the bedding plane of the formation.

As depth increases beyond approximately 2000 ft., overburden stress increases by approximately 1 psi/ft., making the overburden stress the dominant stress This means the horizontal confining stress is now the least principal stress. Since hydraulically induced fractures are formed in the direction perpendicular to the least stress, the resulting fracture at depths greater than approximately 2000 ft. will be oriented in the vertical direction.

In the case where a fracture might cross over a boundary where the principal stress direction changes, the fracture would attempt to reorient itself perpendicular to the direction of least stress. Therefore, if a fracture propagated from deeper to shallower formations it would reorient itself from a vertical to a horizontal pathway and spread sideways along the bedding planes of the rock strata.

Fracture length/ height

The extent that a created fracture will propagate is controlled by the upper confining zone or formation, and the volume, rate, and pressure of the fluid that is pumped. The confining zone will limit the vertical growth of a fracture because it either possesses sufficient strength or elasticity to contain the pressure of the injected fluids or an insufficient volume of fluid has been pumped.. This is important because the greater the distance between the fractured formation and the USDW, the more likely it will be that multiple formations possessing the qualities necessary to impede the fracture will occur. However, while it should be noted that the length of a fracture can also be influenced by natural fractures or faults as shown in a study that included microseismic analysis ‡ of fracture jobs conducted on three wells in Texas, natural attenuation of the fracture will occur over relatively short distances due to the limited volume of fluid being pumped and dispersion of the pumping pressure regardless of intersecting migratory pathways.

The following text and graphs are excerpts from an article written by Kevin Fisher of Pinnacle, a Halliburton Company for the July 2010 edition of the American Oil and Gas Reporter.

“The concerns around groundwater contamination raised by Congress are primarily centered on one fundamental question: Are the created fractures contained within the target formation so that they do not contact underground sources of drinking water? In response to that key concern, this article presents the first look at actual field data based on direct measurements acquired while fracture mapping more than 15,000 frac jobs during the past decade.

Extensive mapping of hydraulic fracture geometry has been performed in unconventional North American shale reservoirs since 2001. The microseismic and tiltmeter technologies used to monitor the treatments are well established, and are also widely used for nonoil field (*sic*) applications such as earthquake monitoring, volcano monitoring, civil engineering applications, carbon capture and waste disposal. Figures 1 and 2 are plots of data collected on thousands of hydraulic fracturing treatments in the Barnett Shale in the Fort Worth Basin in Texas and in the Marcellus Shale in the Appalachian Basin.

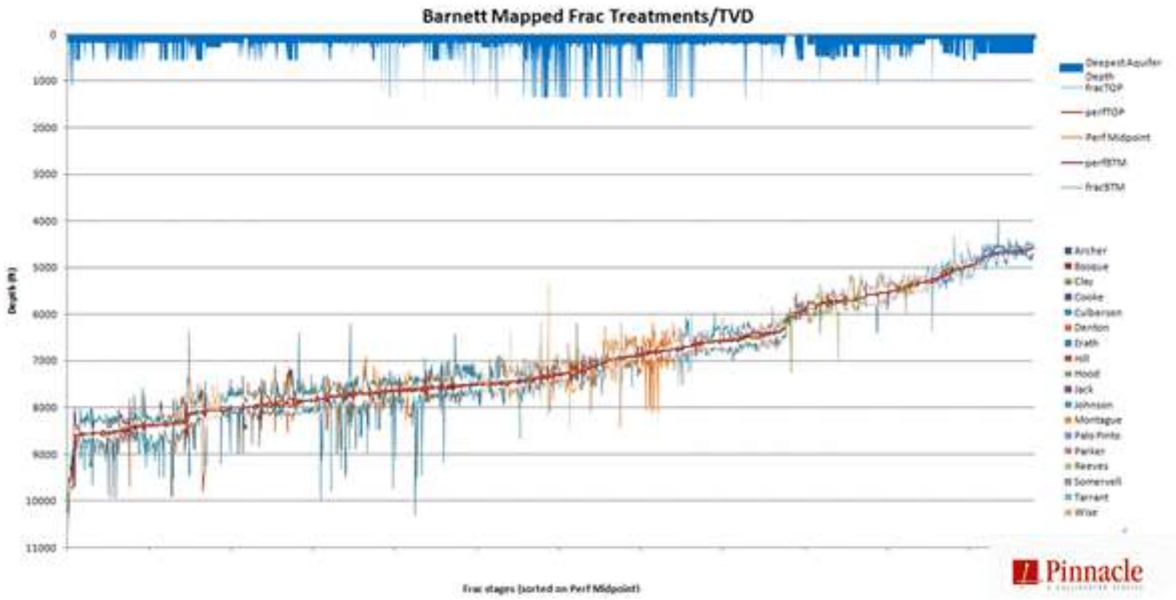


Figure 1. Barnett Shale

More fracs have been mapped in the Barnett than any other reservoir. The graph illustrates the fracture top and bottom for all mapped treatments performed in the Barnett since 2001. The depths are in true vertical depth. Perforation depths are illustrated by the red-colored band for each stage, with the mapped fracture tops and bottoms illustrated by colored curves corresponding to the counties where they took place.

The deepest water wells in each of the counties where Barnett Shale fracs have been mapped, according to United States Geological Survey (http://nwis.waterdata.usgs.gov/nwis ‡), are illustrated by the dark blue shaded bars at the top of Figure 1. As can be seen, the largest directly measured upward growth of all of these mapped fractures still places the fracture tops several thousands of feet below the deepest known aquifer level in each county.

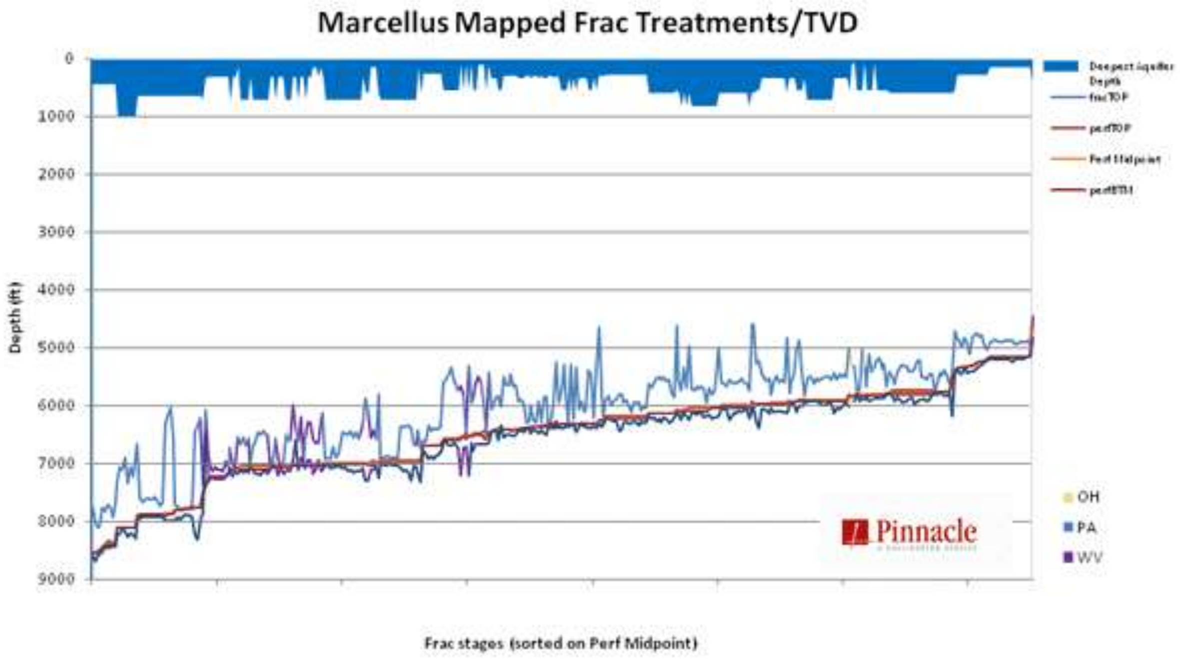


Figure 2 Marcellus Shale

The Marcellus data show a similarly large distance between the top of the tallest frac and the location of the deepest drinking water aquifers as reported in USGS data (dark blue shaded bars at the top of Figure 2). Because it is a newer play with fewer mapped frac stages at this point and encompasses several states, the data set is not as comprehensive as that from the Barnett. However, it is no less compelling in providing evidence of a very good physical separation between hydraulic fracture tops and water aquifers.

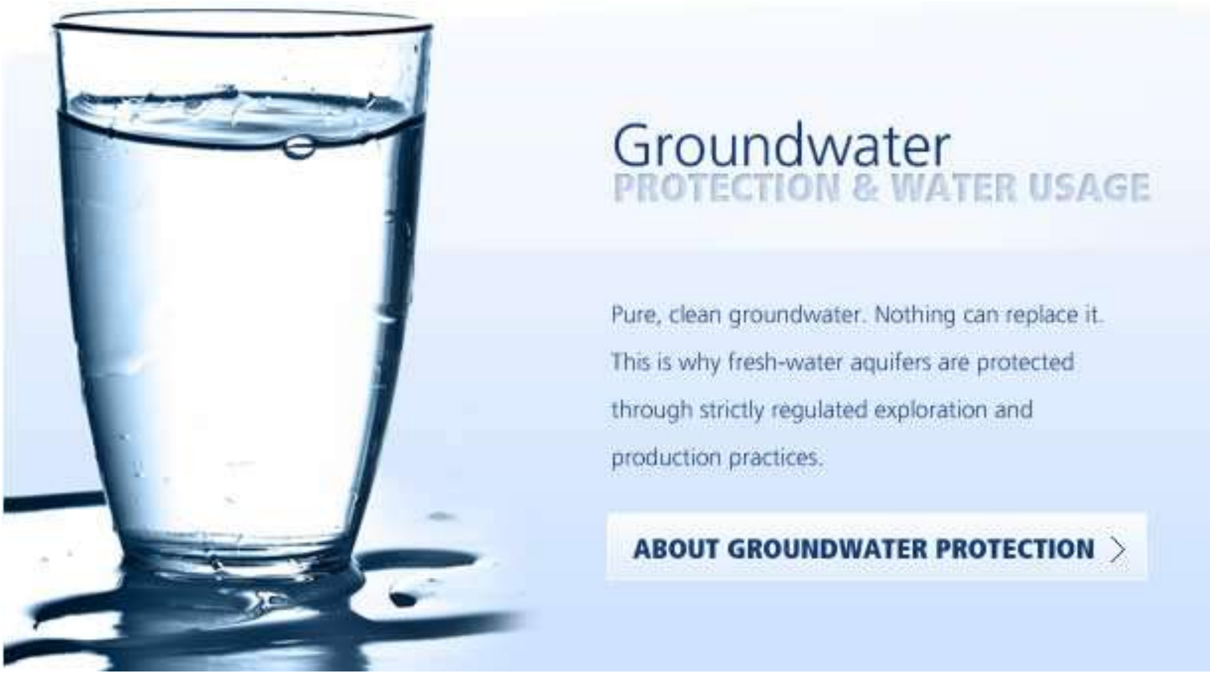
Almost 400 separate frac stages are shown, color coded by state. As can be seen, the fractures do grow upward quite a bit taller than in the Barnett, but the shallowest fracture tops are still ±4,500 feet, almost one mile below the surface and thousands of feet below the aquifers in those counties.

The results from our extensive fracture mapping database show that hydraulic fractures are better confined vertically (and are also longer and narrower) than conventional wisdom or models predict. Even in areas with the largest measured vertical fracture growth, such as the Marcellus, the tops of the hydraulic fractures are still thousands of feet below the deepest aquifers suitable for drinking water. The data from these two shale reservoirs clearly show the huge distances separating the fracs from the nearest aquifers at their closest points of approach, conclusively demonstrating that hydraulic fractures are not growing into groundwater supplies, and therefore, cannot contaminate them."

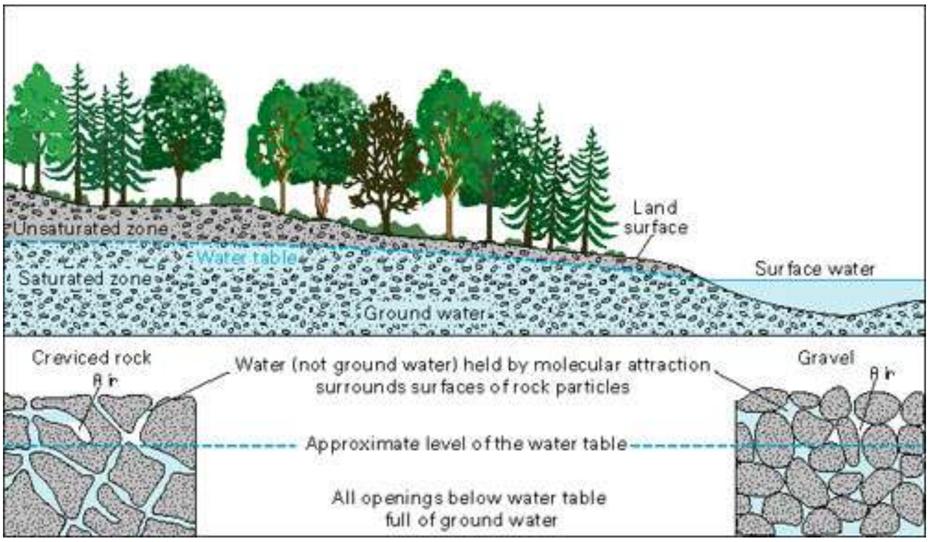
* Pennsylvania Department of Environmental Protection
"Hydraulic Fracturing Overview." 07/20/2010.
http://www.dep.state.pa.us/dep/deputate/minres/oilgas/new_forms/marcellus/Reports/DEP%20Fracing%20overview.pdf ‡ (4/11/2011).

‡ - When you click links marked with the ‡ symbol, you will leave the FracFocus website and go to websites that are not controlled by or affiliated with this site.

Groundwater & Aquifers



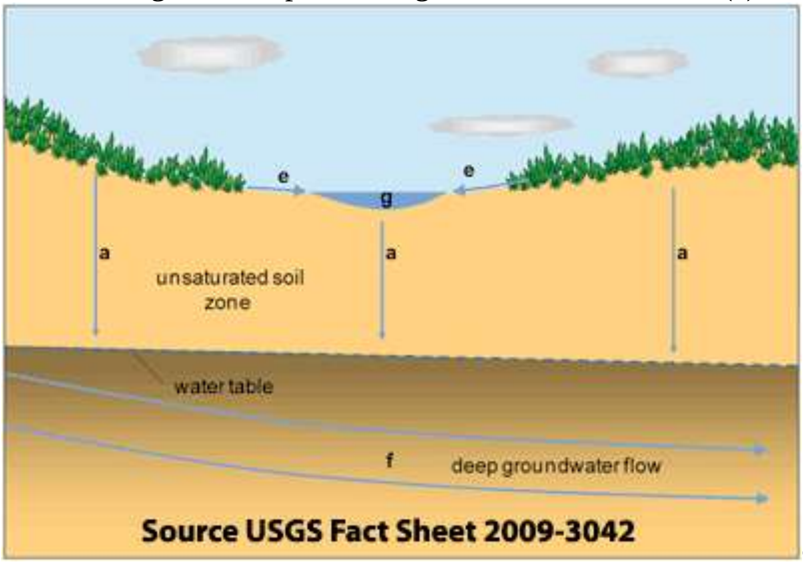
Nearly half of the U.S. population relies on groundwater as their primary source of drinking water. In rural areas, this figure approaches 95%. It is easy to see from these figures that groundwater is an importance source of water that should be protected. But what exactly is groundwater?



Groundwater is the water that is held within the interconnected openings of saturated rock beneath the land surface in much the same way as water would be held in a bowl full of marbles. Although the marbles would fill the bowl, there would be spaces between the marbles. These spaces can hold fluid. As shown in the diagram above, this is how water exists in the subsurface.

On the graphic below, the hydrologic cycle ‡ shows that when rain falls to the ground, some water flows along the land surface to streams or lakes (e) and (g), some water evaporates into the atmosphere, some is taken up by plants, and some seeps into the ground.

As water begins to seep into the ground, it enters a zone (a) that



contains both water and air, referred to as the unsaturated zone or vadose zone ‡. The upper part of this zone, known as the root zone or soil zone, supports plant growth and is crisscrossed by living roots, holes left by decayed roots, and animal and worm burrows.

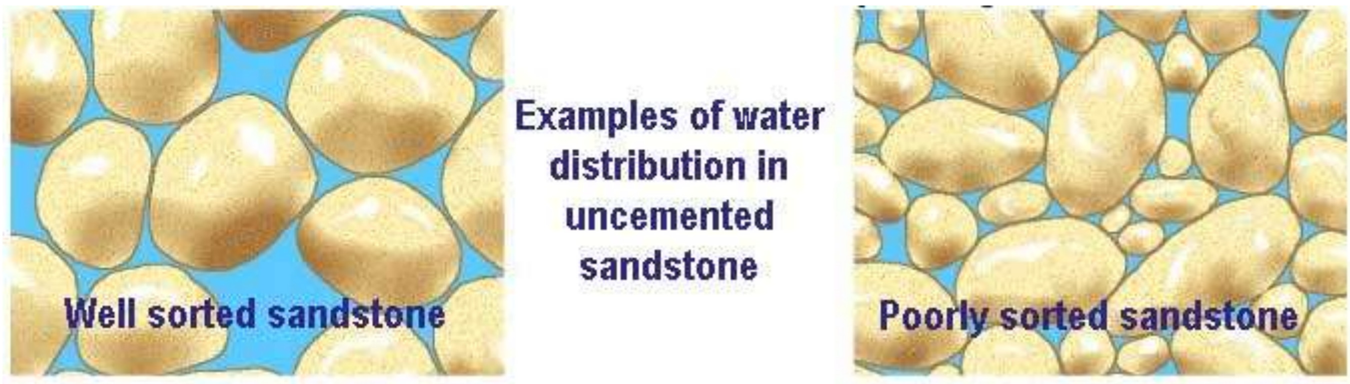
Below the root zone lies a capillary fringe ‡ which results from the attraction between water and rocks. As a result of this attraction, water clings as a film on the surface of rock particles.

Water moves through the unsaturated zone into the saturated zone ‡ (f), where all the interconnected openings between rock particles are filled with water. It is within this saturated zone that the term "groundwater" is correctly applied. Groundwater is held in aquifers which are discussed in the following sections.

Groundwater myths:

- Groundwater moves rapidly.
- Groundwater migrates thousands of miles.
- There is no relationship between groundwater and surface water.
- Groundwater removed from the earth is never returned.
- Groundwater is mysterious and occult.
- Groundwater is not a significant source of water supply.

The diagram below shows how groundwater is held in the spaces between rock particles.



The Miriam Webster dictionary defines an aquifer as a “water-bearing stratum of permeable rock, sand, or gravel.” Aquifers may contain fresh, brackish or salty water in volumes ranging from minor to large enough to serve a public water system.

Aquifers that provide sustainable fresh groundwater to urban areas and for agriculture are usually located at depths of less than a few hundred feet below the ground surface.

Gravity is the dominant driving force in groundwater movement in aquifers that are not bounded above and below by impermeable rock. This is called an unconfined aquifer. Under natural conditions, groundwater moves "downhill" until it reaches the land surface at a spring such as the one shown below or through a seep in the side or bottom of a river bed, lake, wetland, or other surface water body.

Groundwater can also leave the aquifer via the pumping of a well. The process of groundwater outflowing into a surface water body or leaving the aquifer through pumping is called discharge.

Many rivers, lakes, and wetlands rely heavily on groundwater discharge as a source of water. During times of low precipitation, these bodies of water would not contain any water at all if it were not for groundwater discharge. It is important to note that because of discharge, contaminants in groundwater can flow into surface water bodies. This process can make the removal of contamination very complex.

Confined aquifers are bounded above and below by impermeable rock. The driving force of groundwater movement in confined aquifers is pressure, rather than gravity.

When the intersection between the aquifer and the land's surface is natural, the pathway is called a spring. A typical spring is shown at left. If discharge occurs through a well, that well is a flowing or artesian well. To read more about the movement of groundwater go to the National Ground Water Association website. There you will find an excellent discussion about groundwater hydrology ‡.

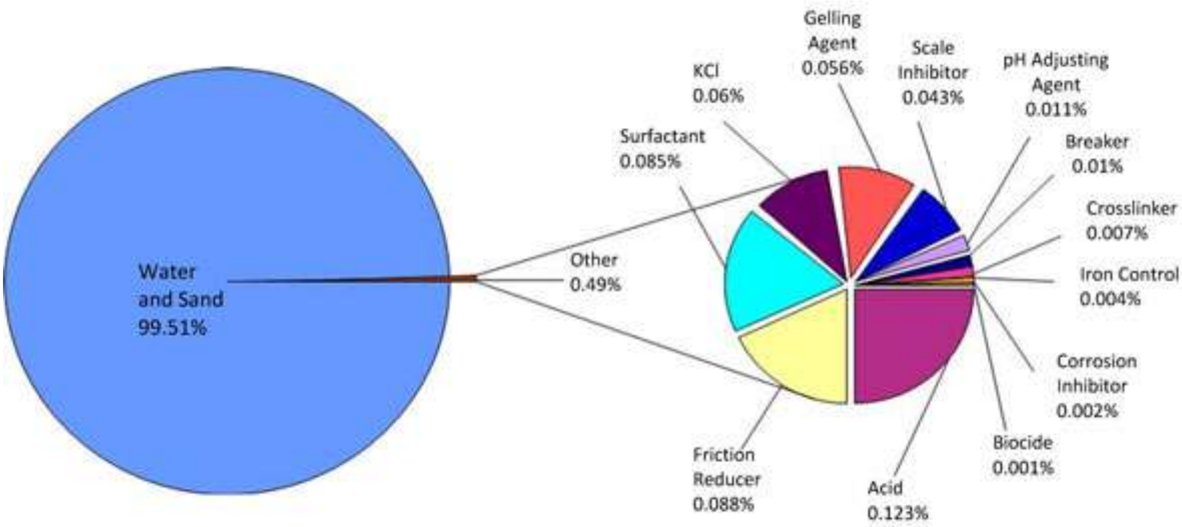
You can also get more information about aquifers on the U.S. Geological Survey website. ‡

Chemical Use In Hydraulic Fracturing

Chemicals serve many functions in hydraulic fracturing. From limiting the growth of bacteria to preventing corrosion of the well casing, chemicals are needed to insure that the fracturing job is effective and efficient.

The number of chemical additives used in a typical fracture treatment depends on the conditions of the specific well being fractured. A typical fracture treatment will use very low concentrations of between 3 and 12 additive chemicals, depending on the characteristics of the water and the shale formation being fractured. Each component serves a specific, engineered purpose. For example, the predominant fluids currently being used for fracture treatments in the gas shale plays are water-based fracturing fluids mixed with friction-reducing additives (called slickwater). The addition of friction reducers allows fracturing fluids and sand, or other solid materials called proppants, to be pumped to the target zone at a higher rate and reduced pressure than if water alone were used. In addition to friction reducers, other additives include: biocides to prevent microorganism growth and to reduce biofouling of the fractures; oxygen scavengers and other stabilizers to prevent corrosion of metal pipes; and acids that are used to remove drilling mud damage within the near-wellbore area.

Fluids are used to create the fractures in the formation and to carry a propping agent (typically silica sand) which is deposited in the induced fractures to keep them from closing up. The chart below taken from [Modern Shale Gas Development in the United States: A Primer] demonstrates the volumetric percentages of additives that were used for a nine-stage hydraulic fracturing treatment of a Fayetteville Shale horizontal well.



The make-up of fracturing fluid varies from one geologic basin or formation to another.

Evaluating the relative volumes of the components of a fracturing fluid reveals the relatively small volume of additives that are present. The additives depicted on the right side of the pie chart represent less than 0.5% of the total fluid volume. Overall the concentration of additives in most slickwater fracturing fluids is a relatively consistent 0.5% to 2% with water making up 98% to 99.5%.

Because the make-up of each fracturing fluid varies to meet the specific needs of each area, there is no one-size-fits-all formula for the volumes for each additive. In classifying fracturing fluids and their additives it is important to realize that service companies that provide these additives have developed a number of compounds with similar functional properties to be used for the same purpose in different well environments. The difference between additive formulations may be as small as a change in concentration of a specific compound.

Although the hydraulic fracturing industry may have a number of compounds that can be used in a hydraulic fracturing fluid, any single fracturing job would only use a few of the available additives. For example, the chart shown above, represents 12 additives used, covering the range of possible functions that could be built into a fracturing fluid.