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Dedication

To my family Especially my big brother Mourad who being in my back every time I needed ,to my friend and my brother Ammar who share with misery and joy for years

Thanks

For every one help me to make this worke reel start with Mr.Debih to Mrs seghouani and Mr Reffas ,to Ms .benzagouta and Mrs .bouchelouch

thank you so much for every thing

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Introduction

Natural gas is the most energy efficient fossil fuel , offers important energy saving benefits when it is used instead of oil or coal. Although the primary use of natural gas is as a fuel, it is also a source of hydrocarbons for petrochemical feedstock and a major source of elemental sulfur, an important industrial chemical. Its popularity as an energy source is expected to grow substantially in the future because natural gas can help achieve two important energy goals for the twenty-first century [1].

However, Shale oil and gas may have permanently altered the energy landscape. They burst upon the fossil energy scene with a suddenness that initially defied prediction. Much of the uncertainty was due to the fact that the type of reservoir being exploited was dramatically different from the conventional one. The term “unconventional reservoir” was ascribedto this rock. The relatively new techniques of horizontal drilling and hydraulic fracturing were essential. Both of these techniques, but especially the latter, had some environmental baggage, this paper addresses the analytical methods and associated science necessary to permit efficient exploitation while simultaneously protecting the environment [2].

And its content three chapters :

Chapter one: this chapter gives the reader an introduction to natural gas by describing the origin and composition of natural gas, gas sources, phase behavior and properties.

Chapter tow speaks about fracturing fluids and the chemical additives that used in hydraulic fracturing

Chapter three menschen the Problems associated with hydraulic fracturing and his Environmental and Health impact.

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Chapter I:

Natural Gas Fundamentals

1 Chapter I: Natural Gas Fundamentals

1.1 Natural gas origin and sources

There are different theories as to the origins of fossil fuels. The most widely accepted theory of the origin of natural gas assumes that natural gas hydrocarbons come from organic matter (the remains of land and aquatic plants, animals and microorganisms) that was trapped within sediments as they were deposited and transformed over long periods of time into their present form. Two main mechanisms, namely, biogenic and thermogenic are responsible for the degradation of fossil organic material in sediments [3]. Biogenic gas is formed at shallow depths and low temperatures due to the action of bacteria on the organic debris accumulating in the sediments. In contrast, thermogenic gas is formed at deeper depths by degradation of organic matter, called kerogen, accumulated in fine-grained sediments, especially clays and shales. This degradation occurs through the combined effects of temperature and pressure. Thermogenic gas is believed to be produced by two mechanisms, namely, direct thermal cracking of sedimentary organic matter and secondary thermal cracking of oil that is formed in the first stage. The former is called the primary thermogenic gas that coexists with oil, while the latter is called secondary thermogenic gas that coexists with insoluble solid matter, called pyrobitumen. Both mechanisms involve thermal cracking with some degree of sustained pressure, mainly through the weight of the sedimentary formation. Little information is available on the time required to generate thermogenic gas other than the general assumption that it is a long time.

Natural gas comes from both “conventional” (easier to produce) and “unconventional” (more difficult to produce) geological formations. Conventional gas is typically “free gas” trapped in multiple, relatively small, porous zones in various naturally occurring rock formations such as carbonates, sandstones, and siltstones. Conventional natural gas generally occurs in deep reservoirs, either associated with crude oil (associated gas) or in reservoirs that contain little or no crude oil (nonassociated gas). Natural gas from coal (also known as coal-bed methane), tight gas sands, gas shales, geopressurized aquifers, and gas hydrates are often referred to as unconventional gas resources. The common characteristic of the different types of unconventional gas resources is that they contain large quantities of natural gas, but it is usually more difficult to produce this gas as compared to conventional reservoir rocks. New technologies are continually being developed to allow more accurate estimations of the amount of gas in these unconventional reservoirs and to stimulate these rocks to produce the gas. [4]

1.2 Natural gas composition and classification

Natural gas is a complex mixture of hydrocarbon and nonhydrocarbon constituents and exists as a gas under atmospheric conditions. Virtually hundreds of different compounds may be present in natural gas in varying amounts. Even two wells producing from the same reservoir may produce gases of different composition as the reservoir is depleted.

While natural gas is formed primarily of methane (CH_4), it can also include significant quantities of ethane (C_2H_6), propane (C_3H_8), butane (C_4H_{10}), pentane (C_5H_{12}), as well as traces of hexane (C_6H_{14}) and heavier hydrocarbons. Many natural gases often contain nitrogen (N_2), carbon dioxide (CO_2), hydrogen sulfide (H_2S), and other sulfur components such as mercaptans (R-SH), carbonyl sulfide (COS), and carbon disulfide (CS_2). Trace quantities of argon, hydrogen, and helium may also be present. Trace quantities of metallic substances are known to exist in natural gases including arsenic, selenium, mercury, and uranium.

According to the proportion of hydrocarbons heavier than methane, different types of natural gas (dry, wet, and condensate) can be considered. Natural gas is considered “dry” when it is almost pure methane, having had most of the other commonly associated hydrocarbons removed. When other hydrocarbons are present, the natural gas is “wet,” where it forms a liquid phase during production at surface conditions. “Condensate” gases have a high content of hydrocarbon liquids and form a liquid phase in the reservoir during production, during the depletion process.

Natural gases are commonly classified according to their liquid content as either lean or rich and according to their sulfur content as either sweet or sour.

The lean and rich terms refer to the amount of potentially recoverable liquids.
The term usually applies to ethane and heavier components but sometimes applies

instead to propane and heavier components (if ethane is not regarded as a valuable liquid component). To quantify the liquids content of a natural gas mixture, the industry uses GPM, or gallons of liquids recoverable per 1000 standard cubic feet (Mscf) of gas. Lean natural gas has liquid content less than 2 GPM. Moderately rich natural gas has between 2 and 5 GPM, and very rich natural gas has greater than 5 GPM [1].

The sweet and sour terms refer to the H_2S content. Strictly speaking, “sweet” and “sour” refer to both acid gases (H2S and CO2) but are usually applied to H_2S alone. A sweet gas contains negligible amounts of H_2S , whereas a sour gas has unacceptable quantities of H_2S . The terms are relative, but generally, sweet means the gas contains less than 4 ppmv of H_2S . Carbon dioxide can be tolerated to much higher levels, say 3–4 mol%, as long as the heating value of the sales gas is satisfactory.

1.3 Natural gas phase behavior

Natural gas is a naturally occurring hydrocarbon mixture that is found underground and at elevated conditions of pressure and temperature. Therefore, there is an essential need to know a priori how the gas fluid will behave under a wide range of pressure and temperature conditions, particularly in terms of its volumetric and thermophysical properties that are required in simulating reservoirs, evaluating reserves, forecasting production, designing production facilities, and designing gathering and transportation systems. In fact, an accurate knowledge of hydrocarbon fluid phase behavior is crucial in designing and operating the gas- engineering processes efficiently and optimally. This means, having advanced predictive tools for the characterization of hydrocarbon phase behavior with the highest accuracy possible is the key to mastering the economics of natural gas systems.

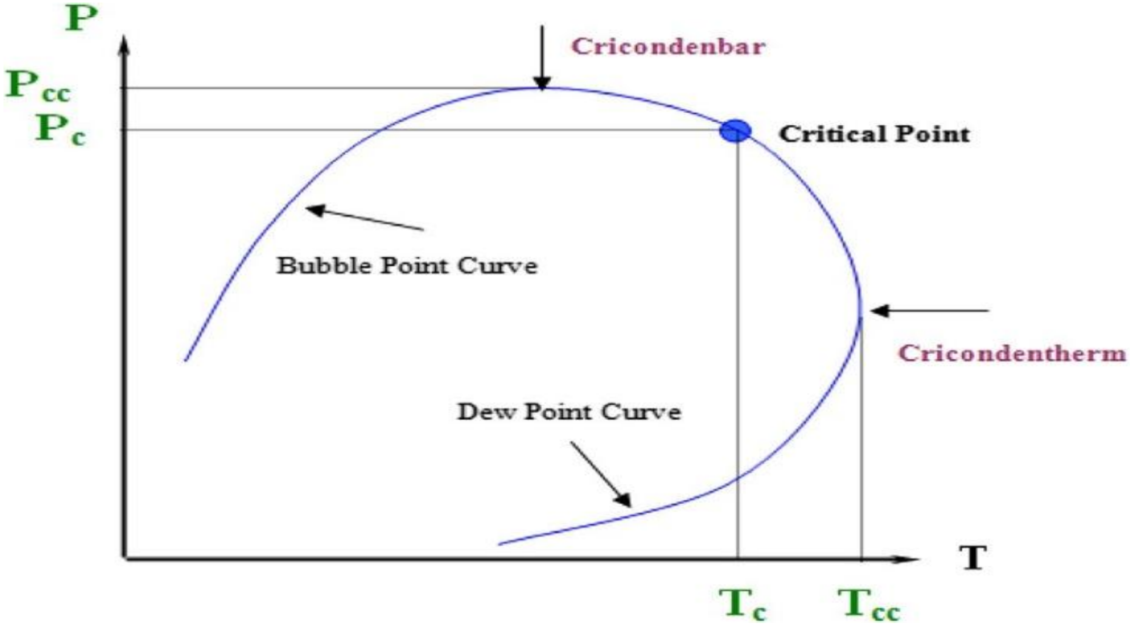

Figure 1:Pressure–Temperature diagram for a typical natural gas mixture.

The natural gas phase behavior is a plot of pressure versus temperature that determines whether the natural gas stream at a given pressure and temperature consists of a single gas phase or two phases, gas and liquid. The phase behavior for natural gas with a given composition is typically displayed on a phase diagram, an example of which is shown in Figure 1-1. The left-hand side of the curve is the bubble point line and divides the single-phase liquid region from the two- phase gas–liquid region. The right-hand side of the curve is the dew point line and divides the two-phase gas–liquid region and the single-phase gas region. The bubble point and dew point lines intersect at the critical point, where the distinction between gas and liquid properties disappears. The maximum pressure at which liquids can form is called the cricondenbar (P_{CC}), and the maximum temperature at which liquids can form is called the cricondentherm (T_{CC}). However, there is something very interesting going on within the region $T_C < T < T_{CC}$, where we will be moving from a 0% liquid to another 0% liquid condition (both on the dew point curve) in an isothermal compression. This different behavior of a vapor under compression is called retrograde (contrary to expectation) condensation. It is also important to see that a similar behavior is to be expected within the region $P_C < P < P_{CC}$. In this case, we talk about retrograde vaporization since we will be moving from a 100% liquid to another 100% liquid condition (both on the bubble point curve) in an isobaric heating.

The natural gas phase behavior is a function of the composition of the gas mixture and is strongly influenced by the concentration of the heavier hydro- carbons, especially hexane plus. The presence of heavier hydrocarbons will increase the phase envelope, and failure to include them in a phase calculation will underpredict the phase envelope. There is also an essential need for proper characterizing the heavy-ends. In fact, although some different fluid descriptions match to some extent the behavior of the reservoir fluids at reservoir conditions, they exhibit larger variations once surface simulators are used and the fluids are subjected to process conditions. [4]

1.4 Natural gas properties

1.4.1 Chemical and physical properties

Natural gas is colorless, odorless, tasteless, shapeless, and lighter than air (see Table 1-1). The natural gas after appropriate treatment for acid gas reduction, and moisture and hydrocarbon dew point adjustment, would then be sold within prescribed limits of pressure, heating value and possibly Wobbe Index (often referred to as the Wobbe Number).

One of the principals uses of natural gas is as a fuel, and consequently, pipeline gas is normally bought and sold on the basis of its heating value that can be produced by burning the gas. The heating value of natural gas is variable and depends on its accumulations which are influenced by the amount and types of gases they contain. The gas industry always uses the gross heating value (frequently called higher heating value) in custody transfer. Obviously, the numerical difference between the two net and gross heating values is the heat of condensation of water at the specified conditions. Heating values for custody transfer are determined either by direct measurement, in which calorimetry is used, or by computation of the value on the basis of gas analysis [2].

The heating value of natural gas is measured in British thermal unit (Btu). A British thermal unit is the energy required to raise the temperature of 1 pound of water by 1 ^{o}F. For larger industrial customers, the abbreviations MBtu (1000 Btu) or MMBtu (1 million Btu) are more commonly used. Since meters measure volume and not energy content, a conversion factor of 1000 Btu/ft^3 is commonly used by gas companies to convert the volume of gas used to its heat equivalent, and thus calculate the actual energy use.

Table 1:Properties of Natural Gas

Properties	Value
Relative molar mass	17e20
Carbon content, weight %	73.3
Hydrogen content, weight %	23.9
Oxygen content, weight %	0.4
Hydrogen/carbon atomic ratio	3.0e4.0
Relative density, 15 ^{O}C	0.72e0.81
Boiling point, ^{O}C	-162
Autoignition temperature, ^{O}C	540e560
Octane number	120e130
Methane number	69e99
Stoichiometric air/fuel ratio, weight	17.2
Vapor flammability limits, volume %	5e15
Flammability limits	0.7e2.1
Lower heating/calorific value, MJ/kg	38e50
Stoichiometric lower heating value, MJ/kg	2.75
Méthane concentration, volume %	80e99
Ethane concentration, volume %	2.7e4.6
Nitrogen concentration, volume %	0.1e15
Carbon dioxide concentration, volume %	1e5
Sulfur concentration, weight % ppm	<5

The Wobbe Index (defined as the gross heating value of the gas divided by the square root of the specific gravity) gives a measure of the heat input to an appliance through a given aperture at a given gas pressure. Using this as a vertical coordinate and the flame speed factor as the horizontal coordinate, a combustion diagram can be constructed for an appliance, or a whole range of appliances, with the aid of appropriate test gases. This diagram shows the area within which variations in the Wobbe Index and flame speed factor of gases may occur for the given range of appliances without resulting in either incomplete combustion, flame lift, or the lighting back of preaerated flames. This method of prediction of combustion characteristics is not sufficiently accurate to eliminate entirely the need for the practical testing of new gase Since natural gas as delivered to pipelines has practically no odor, the addition of an odorant is required by most regulations in order that the presence of the gas can be detected readily in case of accidents and leaks. This odorization is provided by the addition of trace amounts of some organic sulfur compounds to the gas before it reaches the consumer. The sulfur compound, a chemical odorant (a mercaptan also called a thiol with the general formula R-SH and the odor of rotten eggs) is added to natural gas so that it can be smelled if there is a gas leak. The standard requirement is that a user will be able to detect the presence of the gas by odor when the concentration reaches 1% of gas in air. Since the lower limit of flammability of natural gas is approximately 5%, this requirement is equivalent to one-fifth the lower limit of flammability. The combustion of these trace amounts of odorant does not create any serious problems of sulfur content or toxicity.

In the following section, we discuss important gas properties including specific gravity, compressibility factor, formation volume factor, density, isothermal compressibility, and viscosity. [4]

1.5 Gas types

1.5.1 Conventional gas

1.5.1.1 Exploration

Gas is contained in porous rocks at different depths in different locations. So, the first step is to locate where the gas is likely be found. This involves the two disciplines of geophysics and geology.

A seismic survey (geophysics) is conducted to determine the layering of the different rock strata. This helps determine where an accumulation of gas (or oil) may occur, and the potential extent of this accumulation. A seismic survey consists of a wave generator (an explosive device or a vibrator) and a series of geophones, all located at the surface. The geophones detect reflections of the wave from the various layers. The geophysicist interprets the seismic data to generate a 2-D or 3-D picture of the layers in the Earth (see Figure 1-2).

The seismic survey only defines the structure of the rock layers. It does not identify what is contained within the rock. However, it indicates where the highs and lows of the structure are, or if there are any faults. Because of buoyancy effects, the hydrocarbons are more likely to be found in the highs of the structure. In combination with the geoscientist, who brings regional experience and knowledge of the hydrocarbon-bearing potential of these layers, a potential drilling location is determined. The chances of success vary significantly, depending on the degree of oil and gas development in the region. Where there is little knowledge (wildcat exploration) the chances of a successful well are 15–30%, but where there has already been a lot of successful drilling (development wells), the chance of success increases to 75–100%.

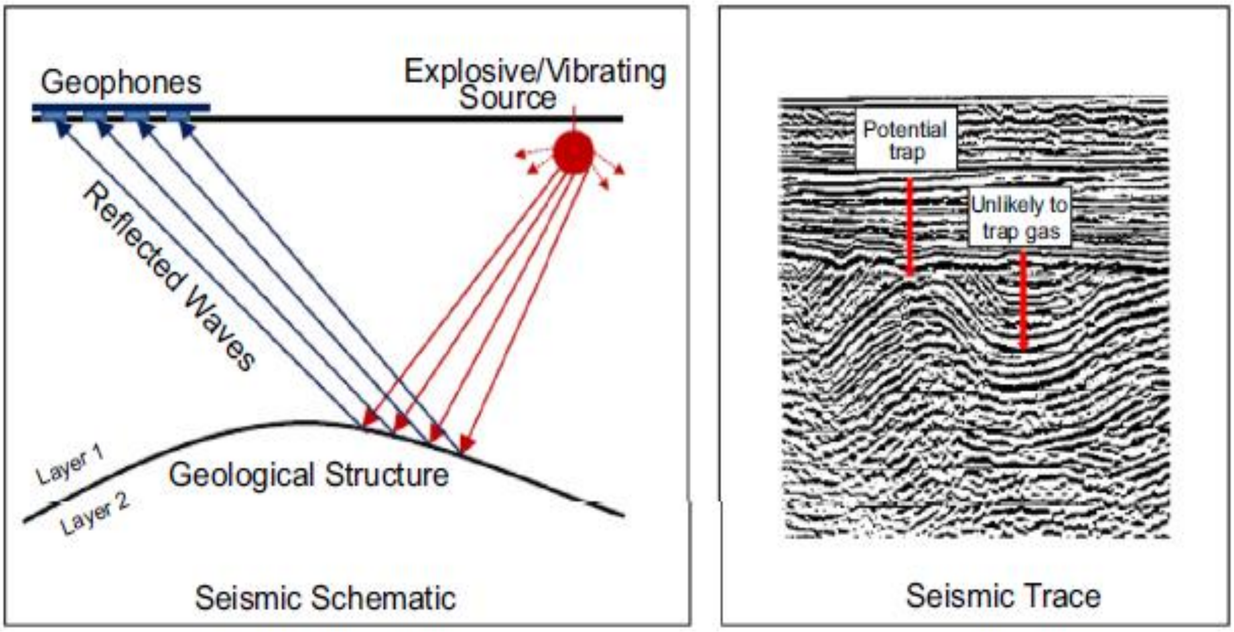

Figure 2:Seismic survey used in exploration.

1.5.1.2 Drilling

The mechanics of drilling are complex, and are significantly more so for an offshore well than for one on land. The well depth can vary from 1000 to 20,000 ft. The well may encounter several layers of gas-, oil-, or water-bearing rocks, but usually, there is one particular layer that is the primary target of interest. While drilling, the wellbore is filled with drilling mud. The hydrostatic pressure of the mud counterbalances the reservoir's pressure, and avoids blowouts during drilling.

Once the intended depth is reached, a suite of electric logs is run from the bottom to the top of the well, to determine the porosity, shale content, fluid saturations, and thickness of the rock layers. If a potential gas-bearing reservoir is found, flow tests can be performed to estimate the permeability of the reservoir. If no productive reservoirs are found, the well is abandoned. If one or more productive layers are found, a steel pipe (casing) is placed in the wellbore and cemented. A "wellhead," which is an assembly of control valves, is placed on top of the well to control the flow from the well.

1.5.1.3 Completion

The casing is perforated where the gas reservoir is known to exist. The perforations penetrate both the steel casing and the surrounding cement sheath, thus creating a flow path, allowing the gas to flow from the reservoir into the well (Figure 1-3).

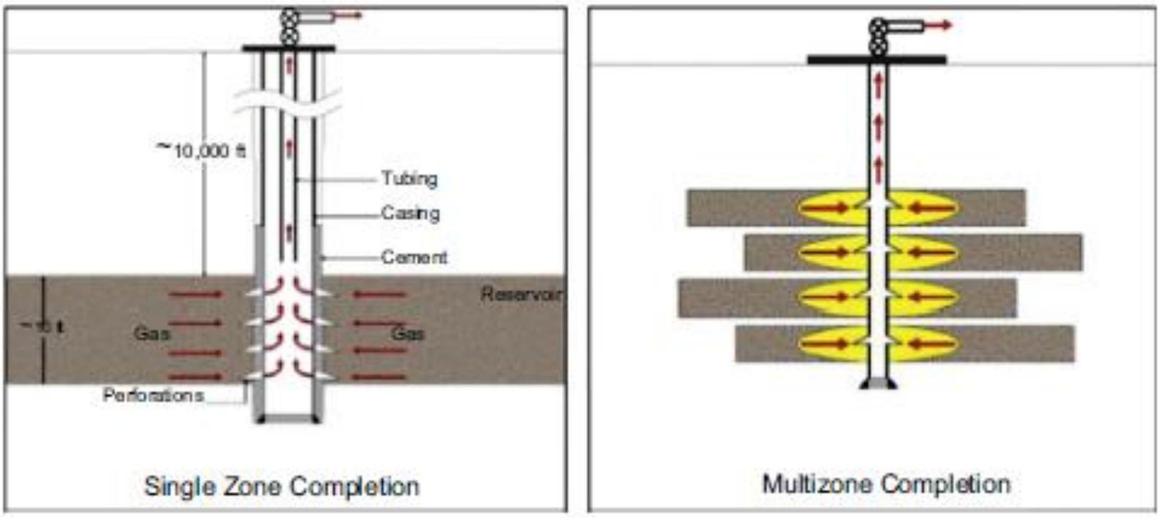

Figure 3:Differentwell completions

When the reservoir rock has a low permeability, the deliverability of the well can be improved significantly by acidizing or hydraulic fracturing. Acidizing increases the permeability in the vicinity of the well. Fracturing in- creases the contact area between the well and the reservoir. To fracture a well, a liquid (usually gelled water with a proppant) is injected at high rates and pressures until the rock cracks. After the completion treatment, flow and shut-in tests are conducted to determine the deliverability potential of the well and to estimate the permeability of the reservoir and the effectiveness of the completion. [4]

1.5.2 Unconventional gas

1.5.2.1 Exploration

Unlike conventional gas, the location of unconventional resources is generally known, often as an indirect result of conventional mining or oil field activity. These unconventional gas resources are generally laterally extensive, and therefore, less exploration is required to locate them.

1.5.2.2 Drilling

Whereas most conventional gas wells are vertical, unconventional gas wells are either horizontal wells or multiple-well pads (Figure 1-4). There are two principal reasons for this:

1. The productivity of the vertical well is too low which is improved by using a horizontal well (single or multilateral).
2. The area of the reservoir that is drained by a vertical well is so small that it would require a large number of wells to effectively drain the whole reservoir. This could be very intrusive on the surface land activity and is resolved by drilling multiple directional wells from a single pad, which significantly minimizes the surface footprint.

1.5.2.3 Completion

Typically, the permeability of unconventional gas reservoirs is extremely small. As a consequence, with conventional completions, the deliverability per well can be uneconomic, in spite of the known presence of large quantities of gas. The best way to improve productivity per well is to increase the area of contact between the well and the reservoir. This is what underlies the success of unconventional gas completions. The single most significant contribution to the commercialization of “shale” gas and “tight” gas has been the multistage hydraulic fracturing of horizontal wells to create this increased contact area (Figure 1-5).

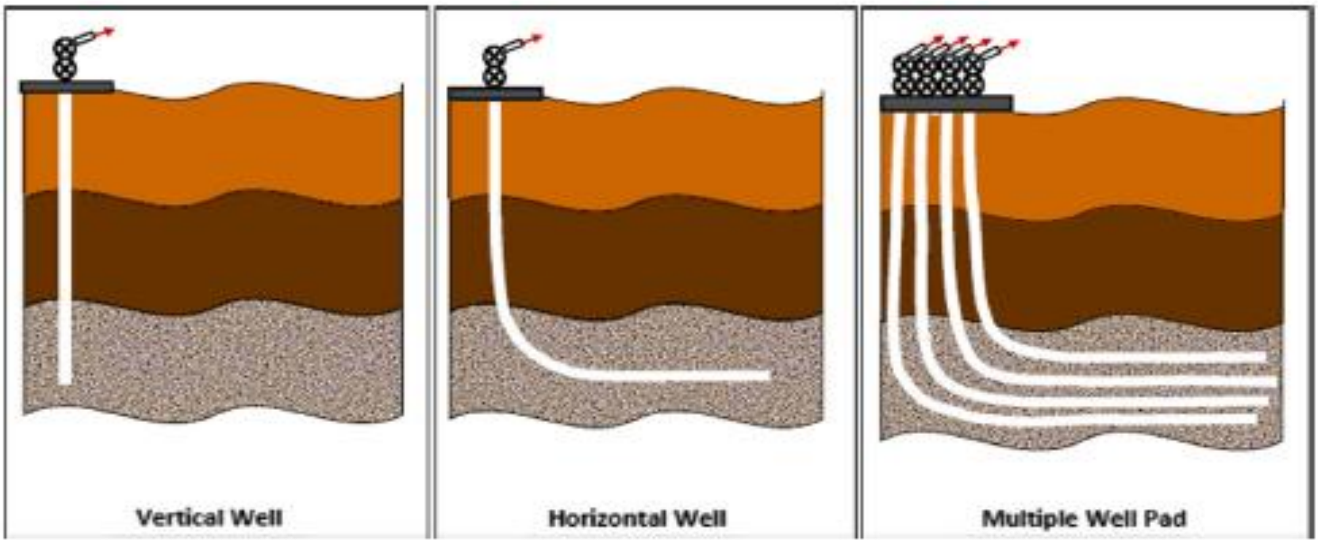

Figure 4:Different drilling patterns

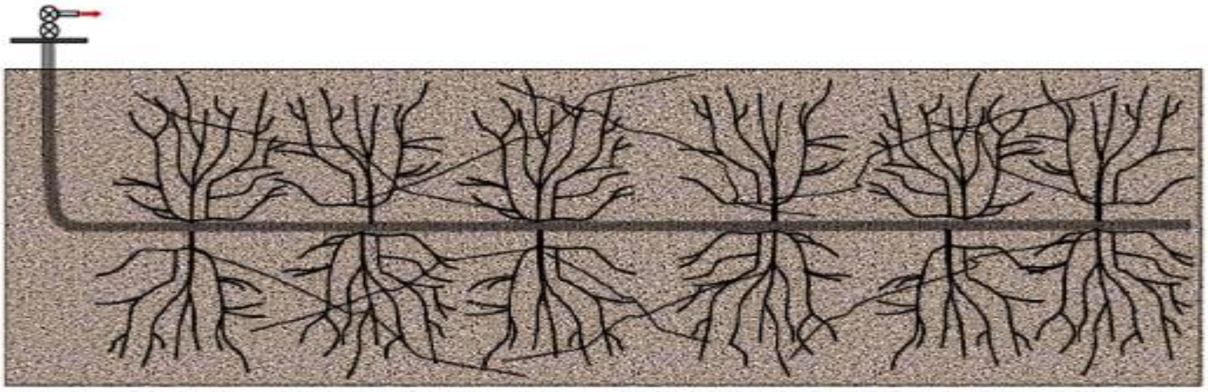

Figure 5:Very large contact area caused by multistage hydraulic fracturing.

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Chapter Ц:

Fracturing Fluids

2 .Chapter Ц: Fracturing Fluids

2.1 Introduction

Hydraulic fracturing as a method for recovering unconventional natural gas from shale formations (tight gas) has been around for several decades. Lately, the recovery of unconventional crude oil from shale formations and from tight formations (tight oil), which would have been otherwise inaccessible, has also been explored and developed.

Hydraulic fracturing is carried out using two broad classes of fracturing materials: fracturing fluid and proppants. The term *fracturing fluid* is a generic term that includes both the base fluid and additives (Tables 2.1 and 2.2). The additives are a wide range of chemicals (Table 2.3) that are used to influence the overall properties of the fracturing fluid. Since the default position of the fractures is the closed position, *propping agents* (*proppants*) are used to stop the fracture from closing after the fracture treatment to enable recovery of crude oil and natural gas, the most common proppant is fine sand.

In the process, the fracturing fluids are injected into the subsurface at a rate and pressure that are too high for the targeted formation to accommodate, and as the resistance to the injected fluids increases, the pressure in the injecting well increases to a level that exceeds the breakdown pressure of the rocks in the targeted formation. In this way, the hydraulic fracturing process fractures the targeted formation and, on occasion, other geologic strata within or around the targeted formation. This process sometimes does create new fractures, and most often the process enlarges existing fractures thereby increasing the connections of the natural fracture networks in the targeted formation. The pressure-induced fracturing serves to connect the network of fractures in the formation to the hydraulic fracturing well (which subsequently will serve as the crude oil and/or natural gas production well).

The fracturing fluids pumped into the subsurface under high pressure also deliver and emplace the proppant, which, under pressure, is forced into the natural and/or enlarged fractures and acts to prop open the fractures even after the fracturing pressure is reduced. The increased permeability due to fracturing and proppant emplacement facilitates the flow and extraction of petroleum and gas from the fractured formation.

Table2 :Different Fluids Used for Hydraulic Fracturing

Fluid	Fluid Type	Main Composition
Water based	Slick water	Water + sand (+chemical additives)
Linear fluids		Gelled water
Cross-linked fluid		Cross-linking agent
Viscoelastic fluids		Electrolyte + surfactant
Surfactant gel fluids		
Foam based	Water-based foam	Water and foamer + N2 or CO2
Acid-based foam		Acid and foamer + N2
Alcohol-based foam		Methanol and foamer + N2
Oil based	Linear fluids	Oil, gelled oil
Cross-linked fluid		Phosphate ester gels
Water emulsion		Water + oil + emulsifiers
Acid based	Linear Cross-linked Oil emulsion	
Alcohol based	Methanol/water mixes or 100% methanol	Methanol + water
Emulsion based	Water–oil emulsions	Water + oil
CO2-methanol		CO2 + water + methanol
Other fluids	Liquid CO2	CO2
Liquid nitrogen		N2
Liquid helium		He
Liquid natural gas		LPG (butane and/or propane)

The advancement in hydraulic fracturing has occurred predominantly over the past two-to-three decades largely due to the development of more advanced drilling technology that allows for horizontal drilling deep under the ground. In the directional drilling process, after drilling downward from the point of entry, the drill turns roughly ninety degrees once deep underground, thereafter traveling parallel to the surface. While the downward drilling proceeds for a considerable distance, after the drill is turned to a horizontal position and moves into the target formation, it provides greater accessibility to the target formation. Thus, the technique (directional drilling) has rendered the method far more productive. However, hydraulic fracturing operations have evolved from using a range of 20,000 to 80,000 gallons of water per well to using up to 8 million gallons of water and 75,000–320,000 pounds of sand (proppant) per well, which can have serious environmental consequences [14][25][27].

A wide variety of chemicals (Table 2.3) is used to perform specific actions, such as the addition of friction reducers, which allows a fracturing fluid and proppant to be pumped to the target zone at a higher rate and reduced pressure than by using water alone. In addition to friction reducers, other additives include biocides to prevent microorganism growth and reduce biofouling of fractures.

Oxygen scavengers and other stabilizers, which prevent corrosion of metal pipes, and acids, which are used to remove drilling mud damage within the area near the wellbore, are also common either in fracturing fluids or as part of the fracture treatment.

The first fracture treatments were performed with gelled crude oil. Later, gelled kerosene was used. By the latter part of 1952, a large portion of fracturing treatments was performed with refined and crude oils. These fluids were inexpensive, readily available, and a permitted use of greater volumes at lower cost. The lower viscosity of such fluids exhibited less friction than the original viscous gel. Thus, injection rates could be obtained at lower treating pressures. To transport the sand, however, higher rates were necessary to offset the lower viscosity of the fluid. With the advent in 1953 of water as a fracturing fluid, a number of gelling agents were developed. Surfactants were added to minimize emulsions with the formation fluid, and potassium chloride was added to minimize the effect on clays and other water sensitive formation constituents. Other clay-stabilizing agents were developed that enhanced the potassium chloride, permitting the use of water in a greater number of formations.

More recent innovations, such as the use of foams and the addition of alcohol, have also enhanced the use of water in more formations (Table 2.1). In the early 1970s, a major innovation in fracturing fluids was the use of metal-based cross- linking agents to enhance the viscosity of gelled water-based fracturing fluids for higher-temperature wells. As more fracturing treatments involved high-temperature wells, gel stabilizers were developed, the first of which was the use of approximately 5% methanol. Later, chemical stabilizers were developed that could be used alone or with the methanol. Aqueous fluids such as acid, water, and brines are currently used as the base fluid in approximately 96% of all fracturing treatments employing a propping agent.

Table 3:Fracturing Fluid Additives

Type	Compound	Comment
Acid	Hydrochloric acid (also called *muriatic acid*)	For the fracturing of shale formations, acids are used to clean cement from casing perforations and drilling mud clogging natural formation porosity, if any prior to fracturing fluid injection (dilute acid concentrations are typically on the order of 15% v/v acid)
Biocide	Glutaraldehyde	Fracture fluids typically contain gels that are organic and can therefore provide a medium for bacterial growth. Bacteria can break down the gelling agent reducing its viscosity and ability to carry proppant. Biocides are added to the mixing tanks with the gelling agents to kill these bacteria
Breaker	Sodium chloride	Chemicals that are typically introduced toward the later sequences of a fracturing project to break down the viscosity of the gelling agent to better release the proppant from the fluid as well as enhance the recovery or "flowback" of the fracturing fluid
Corrosion inhibitor	*N*,*N*-Dimethyl formamide	Used in fracture fluids that contain acids; inhibits the corrosion of steel tubing, well casings, tools, and tanks
Cross-linking agent	Borate salts	There are two basic types of gels that are used in fracturing fluids; linear and cross-linked gels. Cross-linked gels have the advantage of higher viscosities that do not break down quickly
Friction reducer	Petroleum distillate (also called *mineral oil*	Minimizes friction allowing fracture fluids to be injected at optimum rates and pressures
Gel	Guar gum (hydroxyethyl cellulose)	Gels are used in fracturing fluids to increase fluid viscosity allowing it to carry more proppant than a straight water solution. In general, gelling agents are biodegradable

Improvements in cross-linking agents and gelling agents have resulted in systems that permit the fluid to reach the bottom of the hole in high-temperature wells prior to cross-linking, thus minimizing the effects of high shear in the tubing. Ultraclean gelling agents based on surfactant-association chemistry and encapsulated breaker systems that activate when the fracture closes have been developed to minimize fracture conductivity damage.

Table 4:chemical additives

Chemical	Use
Acetic acid	pH Buffer
Acrylic copolymer	Lubricant
Ammonium persulfate	Breaker used to reduce viscosity
Boric acid	Cross-linking agent to increase viscosity
Boric oxide	Cross-linking agent to increase viscosity
2-Butoxyethanol	Reduction of surface tension to aid gas flow
Carbonic acid	Cross-linking agent to increase viscosity
Carboxymethyl hydroxypropyl guar	Gelling agent (thickens fluid)
Crystalline silica (cristobalite)	Proppant (holds open fractures)
Crystalline silica (quartz)	Proppant (holds open fractures)
Citric acid	Iron control or for cleaning wellbores
Diammonium peroxydisulfate	Breaker used to reduce viscosity
Disodium octaborate tetrahydrate	Gelling agent/cross-linking agent to increase viscosity
Gas oils (petroleum), hydrotreated	Guar liquefier
Fumaric acid	pH Buffer
Gelatin	Corrosion inhibitor or gelling agent
Guar gum	Gelling agent
Hemicellulase enzyme	Breaker used to reduce viscosity
Hydrochloric acid	Cleaning of the wellbore prior to fracking
Hydroxyethyl cellulose	Gelling agent
Hydroxypropyl guar	Gelling agent
Magnesium silicate hydrate	Gelling agent
Methanol	Gelling agent
Monoethanolamine	Reduction of surface tension to aid gas flow
Ethylene glycol monobutyl ether	Gelling agent
Muriatic acid	Mutual solvent
Noncrystalline silica	Proppant
Poly(oxy-1,2-ethanediyl)	Proppant
Polydimethyldiallylammonium chloride	Clay control
Potassium carbonate	pH Buffer
Potassium chloride	Clay inhibitor
1-Propanol	Complexing agent
Quaternary polyamines	Clay control
Sodium acetate	pH Buffer
Sodium borate	pH Buffer

Sodium bicarbonate	pH Buffer
Sodium carbonate (soda ash)	pH Buffer
Sodium chloride	Viscosity reducer
Sodium hypochlorite	Bactericide
Sodium persulfate	Viscosity reducer
Terpenes	Reduction of surface tension to aid gas flow
Tetramethyl ammonium chloride	Clay control
Zirconium complex	Cross-linking agent to increase viscosity

Current practices for hydraulic fracturing of shale reservoirs involve a series of sequenced events that require thousands of barrels of water-based fracturing fluids mixed with proppant materials pumped in a controlled and Hydraulic fracturing fluids are predominantly water, pumped at high pressure, with lesser amounts of sand, along with very dilute concentrations of certain additives and chemicals (Table 2.3) designed to stimulate the formation, enhance the return or flowback of the slick water solution following well stimulation, and increase the production of gas from the reservoir. The particular chemistry of the fracturing fluid may vary from site to site. Each fracture interval in a horizontal well may require up to 500,000 to 1 million gallons of water. Vertical wells use the same solutions but typically require two to three times the volume of a single horizontal fracture interval. Collectively, the total volume of fracturing fluid needed for a horizontal well will be significantly higher than that needed for a vertical well.

General properties that should be possessed by a fracturing fluid include low leak- off rate, the capacity to transport a propping agent, and low pumping friction loss. Low leak-off rate allows the fluid to create the fracture and influences the extent of the fracture area [15]. To achieve low leak-off rate, fluid-loss additives are used. Capacity for proppant transport is influenced by density, viscosity, and velocity of fluid flow. The viscosity is the most critical parameter in proppant transport—additives referred to as *viscofiers* are used to enhance viscosity.

The choice of a fracturing fluid is based on site-specific characteristics including formation geology, field production characteristics, and economics. Hydraulic fracturing operations vary widely in the types of fracturing fluids used, the volumes of fluid required, and the pump rates at which they are injected. Water or nitrogen foam frequently constitutes the solute in fracturing fluids used for coalbed methane recovery. Other components of fracturing fluids used to stimulate crude oil and/or natural gas production may contain only benign ingredients, but in some cases, they have included constituents such as diesel fuel that can be hazardous in the undiluted form. Fracturing fluids are significantly diluted prior to injection.

The composition of fluid used for hydraulic fracturing varies widely, depending primarily on the geology of the area being fracked. However, these fluids generally consist of a variety of chemicals and high levels of dissolved solids. The solutions are classed as *clean* prior to introduction into the drill holes, but the post use solutions contain many more components, including high levels of dissolved organics. In addition, and because of the variability of the fluids used from hydraulic fracturing, there are no certified reference materials available. As a result, analysis of the fluids is a major challenge, and because of the complexity of the fluids, it is important to determine the composition (particularly the metal content) of hydraulic fracturing fluids both before use and after use. Such analyses can be used to evaluate how often the fluids can be reused and the measures that must be taken for safe disposal.

Water with a simple sand proppant may be adequate to achieve a desired fracture at some sites, but in many cases, the water must be thickened to achieve higher prop- pant transport capabilities. Thickening can be achieved by using linear or cross- linked gelling agents. Cross-linking agents are costly additives compared to simple linear gels but markedly increase the efficiency of the fracturing fluid. Foam fracturing fluids can be used to considerably reduce the amount of injected fluid required since the reduced water volume requirement translates into reduced volumes of flow- back water requiring disposal.

The use of diesel fuel in fracturing fluids poses a significant environmental threat to because the benzene, toluene, ethylbenzene, and xylene (BTEX) constituents in diesel fuel exceed the maximum concentration limit at the point of injection. In situations when diesel fuel is used in fracturing fluids, a number of factors would decrease the concentration and/or availability of BTEX. These factors include fluid recovery during flowback, adsorption, dilution, dispersion, and potentially biodegradation of constituents. Furthermore, in many cases, approximately one-third of fracturing fluid that is injected is expected to remain in the formation.

The composition and properties of fracturing fluids vary significantly, from simple water and sand to complex polymeric substances with a multitude of additives (Tables 2.1, 2.2, and 2.3). Each type of fracturing fluid has unique characteristics, and each possesses its own positive and negative performance traits. For ideal performance, the necessary qualities that a fracturing fluid should possess are as follows: (i) sufficiently creates a fracture of adequate width, (ii) maximizes fluid travel distance to extend fracture length, (iii) has the ability to transport large amounts of proppant into the fracture, and (iv) requires minimal gelling agent to allow for easier degradation or breaking.

The effectiveness of a hydraulic fracturing operation is controlled by several variables, but only a few are easily controlled, and these are the fracturing fluid properties, the injection rate, and the quality of propping agents [21]. The fracture fluid design is an essential part of the hydraulic fracturing stimulation treatment. Fracture fluids can be classified into four main divisions based on their fluid bases: (i) water-based fluids, (ii) foam-based fluids, (iii) acid-based fluids, (iv) alcohol-based fluids, and (v) emulsion-based fluids (Table2.1) [28][14][25][27]. For decades, oil-based fluids were used preferentially since it was believed that the use of water- based fluids in water-sensitive formations (oil reservoirs) would obstruct oil flow. However, the success of water-based fluid led to their eventual common use with the majority of wells now being fractured with water-based fluids [14] [15] [25] [27]. In fact, water-based fluids have considerable advantage over other bases, including (i) non- inflammability; (ii) higher specific gravity, which translates to lower hydraulic horse power requirements for treatment; (iii) low viscosity, which means that the fluid is easier to pump, as well as the ease of availability and the lower cost.

In general, a fracturing fluid (Tables 2.1, 2.2, and 2.3) can be considered to be the sum of three main components:

Fracturing fluid = Base fluid + Additives + Proppant

A fracturing fluid can be made to be more efficient by the addition of compressed gas (typically carbon dioxide or nitrogen), which provides a substantial portion of the energy required to recover the fluid and places much less water in water-sensitive formations. The disadvantage of the method is that it reduces the amount of proppant that is possible to deposit in the fracture.

Typically, water-based fluids are the simplest and most cost-effective solution to fracture a rock formation. However, alternatives to water-based fluids have significantly outperformed water treatments in many shale reservoirs. For instance, foam- based fluids have been used extensively in depleted conventional reservoirs in which water fractures were not effective. More recently, the development of the unconventional reservoirs (tight formations, shale formations, coal seams) has prompted the reconsideration of *waterless* fracturing treatments as viable alternatives to water-based fracturing fluids. There are several reasons to consider fluids that contain little or no water, namely,

(i) water sensitivity of the formation,
(ii) water blocking,
(iii) proppant placement,
(iv) water availability and cost.

However, the interactions between the rock formation and the fracturing fluids may be detrimental to hydrocarbon production [22].

In terms of *water sensitivity of the formation*, the base mineral composition of a reservoir formation can impact the recovery process of water, gas, and oil. For example, oil-based fluids, liquefied petroleum gas (LPG), carbon dioxide, and foam- based fluids are recommended in water-sensitive formations to prevent migration of fines and also to prevent clay swelling. In many shale formations, proppant conductivity drops considerably in the presence of water because the rock–fluid interactions soften the rock leading to proppant embedment.

Water blocking is essential in undersaturated gas formations where the invasion of water from the fracturing fluid can be very detrimental to gas productivity as any additional water remains trapped because of capillary retention. The increase in water saturation (referred to as water blocking or water trapping) significantly reduces the relative permeability to gas, sometimes by orders of magnitude [20].

In terms of *proppant placement*, foams and other gelled nonaqueous fluids can transport proppant much more effectively than slick water fluids. At high foam qualities (gas volume fraction typically >0.5), the interactions between gas bubbles cause a large energy dissipation that results in a high effective viscosity. At low foam qualities (<0.5) the interactions between bubbles are minimal, so the fluid viscosity resembles that of the base fluid (which is typically gelled).

Water availability and cost can limit the operations to a considerable extent. Either (i) freshwater can be difficult to obtain in areas prone to drought or (ii) local legislation may limit water use, which has prompted the use of waterless fracturing treatments. Alternatively, the supply and the cost of LPG, carbon dioxide, and nitrogen are strongly site specific.

Fracturing with gaseous nitrogen is also a viable technique for formations that are potentially sensitive to aqueous-based fracture fluid systems. In this method, nitrogen is pumped as a cryogenic liquid and then heated to form a gas prior to being injected into the well. Fracturing mechanics occur as in any other hydraulic fracturing technique, the only difference being that the fracturing fluid is a gas. Unfortunately, pumping nitrogen as a gas normally eliminates the possibility of transporting proppants, and as such, nitrogen fracturing can be classified as a proppantless, nonreactive stimulation technique. As with fracturing with liquid carbon dioxide, the principal benefit of fracturing with gaseous nitrogen is the nonaqueous, nondamaging nature of it, particularly in water-sensitive formations. The principal difference between fracturing with liquid carbon dioxide and other fluid systems is in the blending requirements. Proppants and carbon dioxide must be mixed in a purpose- built pressurized blending system, and because of the need to mix the liquid carbon dioxide and proppant under pressurized conditions, the proppant must also be stored and transferred to the blending tub under pressure. This places a practical limit on the amount of proppant that can be used with this system, which is based on the capacity of the pressurized proppant storage bin on the blender.

The ideal fracturing fluid (in addition to being cost-effective) should (i) be able to transport the propping agent in the fracture, (ii) be compatible with the formation rock and fluid, (iii) generate enough pressure drop along the fracture to create a wide fracture, (iv) minimize friction pressure losses during injection, (v) be formulated using chemical additives that are approved by the local environmental regulations, and (vi) exhibit controlled break to a low-viscosity fluid for cleanup after the treatment.

The *viscosity* of the fracturing fluid is an important point of differentiation in both the execution and in the expected fracture geometry. Many current practices, generally referred to as *slick water treatments*, use low-viscosity fluids pumped at high rates to generate narrow, complex fractures with low concentrations of propping agent. In order to minimize risk of premature screen-out, pumping rates must be sufficiently high to transport proppant over long distances (often along horizontal wellbores) before entering the fracture. By comparison, for conventional wide bi-wing fractures, the carrier fluid must be sufficiently viscous to transport higher proppant concentrations.

These treatments are often pumped at lower pump rates and may create wider fractures. The *density* of the carrier fluid is also important and affects the surface injection pressure and the ability of the fluid to flow back after the treatment. Water-based fluids generally have densities near 8.4

pounds per gallon, while the density of an oil-based fluid density will be 70–80% of the density of a water-based fluid. However, the density of foam-based fluids can be substantially less than the density of water- based fluids. In low-pressure reservoirs, low-density fluids, like foam, can be used to assist in the fluid cleanup. Conversely, in certain deep reservoirs (including offshore hydraulic fracturing applications), there is a need for higher-density fracturing fluids, typically, those with a density up to or even higher than 12 pounds per gallon.

A fundamental principle of the process is that the fracture volume should be equal to the total volume of fluid injected minus the volume of fluid that leaks off into the reservoir. The fluid efficiency is the percentage of fluid that is still in the fracture at any point in time, when compared with the total volume injected at the same point in time. If too much fluid leaks off, the fluid has a low efficiency (10–20%), and the created fracture volume will be only a small fraction of the total volume injected. However, if the fluid efficiency is too high (80–90%), the fracture will not close rap- idly after the treatment. In a near-ideal situation, a fluid efficiency of 40–60% will provide an optimum balance between creating the fracture and having the fracture close down after the treatment.

In most low-permeability reservoirs, fracture fluid loss and efficiency are con- trolled by the formation permeability. In high-permeability formations a fluid-loss additive is often added to the fracture fluid to reduce leak-off and improve fluid efficiency. In naturally fractured or highly cleated formations, the leak-off can be extremely high, thereby reducing the efficiency to a range on the order of 10–20% or less. To apply hydraulic fracturing to naturally fractured formations, the fracturing fluid (containing fluid-loss additives) must be pumped at high injection rates.

In summary, the fracturing fluid is varied to meet the specific needs of each location; however, evaluating the widely reported percentage volumes of the fracturing fluid components reveals the relatively small volume of additives that are present. Overall, the concentration of additives in most fracturing fluids is a relatively consistent 0.5–2% v/v with water and proppants making up the remaining 98–99.5% v.v. However, a typical fracturing project uses upward of 5 million gallons of fracturing fluid, so a small percentage amount may actually result in a great deal of chemical usage, no matter how diluted it may be. The overall composition of fracturing fluids varies among companies and the drilling location. However, as a pretty good base- line, fracturing fluids typically contain (i) approximately 90% water, (ii) approximately 9.5% proppant materials, and (iii) approximately 0.5% chemicals, this percentage varies but is typically between 0.5 and 1.0% w/w of total fluid.

2.2 Types of Fluids

Hydraulic fracturing is carried out using two broad classes of fracturing materials: fracturing fluid and proppants. Fracturing fluid is a generic term that involves both the base fluid (water, oil, acid, etc.) and additives (Tables 2.1, 2.2, and 2.3). Additives are chemicals added to influence the overall properties of the fracturing fluid, and propping agents (*proppants*) are materials used to stop the fracture from collapsing and closing after treatment, the proppants effectively hold the fracture open (prop open) to enable hydrocarbon recovery. The comprehensive design and selection of these fracturing materials is essential for successful achievement of the desired fracturing objectives. In fact, an essential element of fracturing technology, not only from the technical aspects but also from the environmental aspects, is the type of fluid used to perform the fracturing of the formation. The choice of the fracturing fluid dictates the type of required chemical additives as well as the need for flowback treatment.

The use of water-based fluids has found application with gas prospecting, as the fluids currently being used for hydraulic fracture treatments in the Marcellus shale are water-based or mixed slick water fracturing fluids [3]. Slick water fracturing fluids consist mainly of water mixed with friction-reducing additives like potassium chloride. High-rate slick water fracturing can induce tensile fractures as well as shear existing fractures in the brittle shale formation with low horizontal stress anisotropy [17]. Furthermore, the use of slick water fluids for fracturing has become the norm in Barnett and Marcellus shale plays, but the disadvantage of slick water fracturing fluids is that due to the low viscosity, such fluids are not efficient carriers of proppants. Hence, though successful in several US shale developments, it has not been suitable for all cases [17]. In cases where the use of slick water fluids is inadequate, hybrid fracturing technologies have been proposed. A hybrid fracture is a combination of slick water (to create the fractures) and another more viscous fracturing fluid (solely for proppant transport) [18].

Careful selection of fluids and proppants (sand constituents) is necessary based on the reservoir properties of the specific shale formation. For most reservoirs, water-based fluids with appropriate additives are most suitable, due to the historic ease with which large volumes of mix-water can be acquired. In some cases, foam generated with nitrogen or carbon dioxide can be used to stimulate shallow, low-pressure zones successfully. When water is used as the base fluid, the water should be tested for quality due to some sensitivity of certain fluids to the mix-water composition.

2.2.1 Water-Based Fluids

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 slick water). Many other water-based fluids are used, broadly speaking, linear fluids, cross-linked fluids, and viscoelastic surfactant fluids.

Slick water fracturing is probably the most basic and most common form of well stimulation in unconventional gas [7]. The fracturing fluid is com- posed primarily of water and sand (>98%). Additional chemicals are added to reduce friction, corrosion, and bacterial growth and provide other benefits during the stimulation process. Low-viscosity slick water fluids generate fractures of lesser width and therefore greater fracture length, theoretically increasing the complexity of the created fracture network for better reservoir-to-wellbore connectivity.

A common practice in the hydraulic fracturing of reservoirs is the use of nonviscous slick water fluids pumped at high rates (>60 bpm) to generate narrow fractures with low concentrations of proppant. In the recent years, these treatments have become a standard technique in fracture stimulation of several shale formations of the United States, including the Barnett, Marcellus, and Haynesville, and yield economically viable production. The low proppant concentration, high fluid efficiency, and high pump rates in slick water treatments yield highly complex fractures. Additionally, compared to a traditional bi-wing fracture, slick water fractures often find the primary fracture connected to multiple orthogonal (secondary) and parallel (tertiary) fracture. Coupled with multistage fracture completions and multiple wells collocated on a pad, complex fracture networks yield a high degree of reservoir contact.

The most critical chemical additive for slick water-fracture execution is the friction reducer. The high pump rates for slick water treatments (often 60–100 bbl/min) necessitate the action of friction reducer additives to reduce friction pressure up to 70%; this effect helps to moderate the pumping pressure to a manageable level during proppant injection. Common chemicals used for friction reduction include poly- acrylamide derivatives and copolymers added to water at low concentrations. Additional additives for slick water fluids may include biocide, surfactant (wettability modification), scale inhibitor, and others. The performance (friction reduction) of slick water fluids is generally less sensitive to mix-water quality, a large advantage over many conventional gelled fracturing fluids. However, in high-salinity mix-water, many friction reducer additives may see a loss in achievable friction reduction. Other advantages and disadvantages of slick water fluids and execution (compared to that of gelled fracturing fluids) are (i) high retained conductivity, due to no filter cake present, (ii) reduced sensitivity to salinity and contaminants in mix-water, and (iii) reduced number of fluid additives required for slick water fracturing fluid.

However there are disadvantages that include (i) larger volumes of water often required for fracture design (compared to gelled fracturing fluids); (ii) larger horsepower requirement (to maintain high pump rates, 60–110 bpm); (iii) limited fracture width, due to low maximum concentration proppant in low viscosity; (iv) reduced %-flowback-water recovery due to loss of the fracturing fluid in complex fracture network far from wellbore; and (v) limitation to fine-mesh propping agents, due to reduced ability of nonviscous fluids in the transport of large proppants.

Since the anticipated proppant-suspension capacity of slick water fluids is quite low; a complementary solution is the use of linear (noncross-linked) gels. These fluids, based on noncross-linked solutions of polysaccharides (i.e., guar, derivatized guar, hydroxyethyl cellulose (HEC), xanthan), have viscosities of up to 100 cP at 100/s at surface temperature, which depend on polymer concentration. As this viscosity is several orders of magnitude higher than slick water, linear gels have improved proppant suspension. When noncross-linked gels are used in late-slurry stages of a fracturing treatment (where the pad and early-slurry stages used slickwater), these are often referred to as hybrid fracturing treatments.

In summary, slick water fluid is an inherently poor proppant carrier, necessitating high pump rates to achieve a sufficiently high flow velocity to overcome the tendency of the proppant to settle. Proppant settling within surface equipment or long horizontal laterals can result in premature termination of the fracturing process and/or poor productivity. Linear gel and cross-linked systems can be used to mitigate the proppant- settling phenomenon (resulting in poor placement of the proppant in the fractures), but the high viscosity that accomplishes this objective can significantly influence the process by reducing the desired fracture complexity. Also, the long fracture closure times and the lack of efficient gel delayed breakers make the proppant placement advantage of gel systems very limited since the proppant can settle while gel is breaking and the fracture has not yet closed. The most important benefits of slick water fracturing are

(i) reduced gel damage,

(ii) higher stimulated reservoir volume,

(iii) better fracture containment.

But there are concerns such as poor proppant trans- port, excessive usage of water, and narrower fracture widths [7].

Some fracturing treatments require a higher-viscosity fluid, such as linear fracturing fluids, which are produced by adding a wide array of different polymers to water. Such polymers are dry powders that swell when mixed with an aqueous solution and form a viscous gel. The gel-like fluid is then more able to transport the prop- pant than would a normal low-viscous (slick water) fluid. Common polymer sources used with the linear gels are guar, hydroxypropyl guar (HPG), HEC, carboxymethyl hydroxypropyl guar (CMHPG), and carboxymethyl hydroxyethyl cellulose (CMHEC) [15], [7].

In low-permeability formations, linear gels control fluid loss very well, whereas in higher-permeability formations fluid loss can be excessive. Linear gels tend to form thick filter cakes on the face of lower-permeability formations, which can adversely affect fracture conductivity. The performance of linear gels in higher-permeability formations is just the opposite, since it forms no filter cake on the formation wall. Much higher volumes of fluid are lost due to viscous invasion of the gel into the formation with environmental consequences.

Cross-linked fluids were developed in order to improve the performance of gelling polymers without increasing their concentration. Borate cross-linked gel fracturing fluids utilize borate ions to cross-link the hydrated polymers and provide increased viscosity. The polymers most often used in these fluids are guar and HPG. The cross- link obtained by using borate is reversible and is triggered by altering the pH of the fluid system. The reversible characteristic of the cross-link in borate fluids helps them clean up more effectively, resulting in good regained permeability and conductivity.

Cross-linked guar gum is an example of a common fracture fluid used for environ- mental application [15][4]. The most widely used form is the continuous mix grade of gum, referred to as such because it hydrates rapidly and reaches a usable level of viscosity fast enough that it can be used continuously. Because of the characteristic high viscosity, guar gum is capable of transporting coarse-grained silica sand or other granular material (proppants), as a slurry, into the fracture. Pumps specifically designed for high-viscosity; high-solid fluid handling should be selected to inject the slurry at the required pressures.

Chemical modification of water-based polymers obtained from guar has produced a wide range of derivatives with useful properties, such as HPG and CMHPG. HEC and CMHEC are derivatives from cellulose, another natural source. These derivatives provide viscosity for fracturing wells with formation temperatures from 18 to approximately 205 °C (60 to ~400 °F). To prevent loss of viscosity due to decomposition of these derivatives at high temperatures (>107 °C; >225 °F), chemical stabilizers such as methanol or thiosulfate are added. For lower temperature regimes (<65 °C;<150 °F), aqueous solutions of these derivatives (base gels) are used [12]. When high viscosity is required, cross-linking a polymer is normally done using transition metal cations; this method is more efficient (and more cost-effective) than merely increasing the concentration of the polymer solution.

Borate cross-linked fluids have proved to be highly effective in formation with both low permeability and also with high permeability. These fluids offer (i) efficient proppant transport, (ii) stable fluid rheology at temperatures as high as 150 °C (300 °F), (iii) low fluid loss, and (iv) good cleanup properties [7]. Organometallic cross-linked fluids are also a very popular class of fracturing fluids. Primary fluids that are widely used are the zirconate and titanate complexes of guar, HPG and CMHPG. Organometallic cross-linked fluids are routinely used to trans- port the proppant for treatments in tight gas sand formations that require extended fracture lengths. These fluids provide advantages in terms of stability at high temperatures and proppant transport capabilities and offer more predictable rheological properties.

Viscoelastic surfactant (VES) *gel fluids* have been described in the patent literature for friction reduction and as well treatment fluids since the early 1980s, but their use as fracturing fluids is relatively a new phenomenon. Principally, these fluids use surfactants in combination with inorganic salts to create ordered structures, which result in increased viscosity and elasticity. These fluids have very high zero-shear viscosity and can transport proppant with lower loading and without the comparable viscosity requirements of conventional fluids. The technology of VES gel fluid systems can be broken down into several categories based on the structure the system creates: worm-like micelles, lamellar structures, or vesicles. As the concentration of surfactant increases in water, micelles start to form and interact with each other—the interactions are based on ionic forces and can be amplified by adding electrolytes (salts) or ionic surfactants.

These fluids do not require any biocides because they do not contain any biopolymers. Furthermore, they do not require additional flowback surfactants because they have inherently low surface and interfacial tension, and additional clay control additives are not necessary.

2.2.2 Foam-Based Fluids

For water-sensitive formations and environments where water is scarce, foam-based fluids have long been considered as one of the best fracturing fluids (Table 2.1) [9] [7]. In particular, foam-based fluids are believed to be an appropriate means for fracturing shale gas reservoirs. These fluids require lower (or no) water consumption and cause less damage in water-sensitive formations, and there is less liquid to recover and handle after the fracturing process. Expansion of the gas phase after the treatment also helps recover the liquid phase introduced into the formation with the foamy fluid [6]. Foams are very unique and versatile because of low-density and high-viscosity characteristics—foam viscosity strongly depends on foam quality (the gas fraction in the total gas and liquid mixture) and foam texture (the number of bubbles in unit mixture volume) [23], [6].

Thus, it is not surprising that foams are being used in a number of petroleum industry applications that exploit their high-viscosity and low liquid content [7]. In the mid-1970s, nitrogen-based foams became popular for both hydraulic fracturing and fracture acidizing stimulation treatments. More recently, carbon dioxide-based foams have been found to exhibit their usefulness in hydraulic fracturing stimulation. The liquid carbon dioxide-based fluid consists of foam of nitrogen gas in liquid carbon dioxide as the external phase stabilized by a special foaming agent that is soluble in liquid or supercritical carbon dioxide [8]. The main advantage of this fluid is the additional viscosity gained by the foam over liquid carbon dioxide.

2.2.3 Oil-Based Fluids

Oil-based fracturing fluids were the first high-viscosity fluids used in hydraulic fracturing operations, an advantage to this type of fluid is the compatibility with almost any formation type. Disadvantages (compared to the use of most water-based fluids) are associated with concerns regarding personnel safety and environmental impact. LPG has been used as stimulation fluid for 50 years and was developed for conventional reservoirs before being adapted to unconventional reservoirs. For instance, it was used to stimulate (or restimulate) oil wells and has also been used to stimulate tight sands because of recovery improvements in reservoirs exhibiting high capillary pressures by eliminating phase trapping [7].

When gelled, LPG provides a consistent viscosity and does not require the costly use of carbon dioxide or nitrogen nor does it require any special cool down or venting of equipment. LPG is an abundant by-product of the natural gas industry and is stored at ambient temperature, and using LPG also reduces the need to flare production to clean up the traditional fracturing fluids, reducing emissions of carbon dioxide. Because propane liquid is half the specific gravity of water, there is reduced trucking to the site and no trucking to transport poststimulation—which can reduce truck traffic by up to 90%. However, a disadvantage is the manipulation of large amounts of flammable propane (and the associated risks/safety hazards).

Many shale formations are water sensitive, and using LPG could avoid this problem. The gel properties include

(i) low surface tension,
(ii) low viscosity,
(iii) low density, and
(iv) solubility within naturally occurring reservoir hydrocarbons.

These properties are believed to promote more effective fracture lengths that are created and thus enable higher production of the well. Another reported advantage is the ability to evenly distribute proppant. The fracturing fluids are totally recovered within days of stimulation, creating economic and environmental advantages by reducing cleanup, waste disposal, and post project truck traffic [7].

2.2.4 Acid-Based Fluids

The main difference between acid fracturing and proppant fracturing is the manner by which fracture conductivity is created. In proppant fracturing, a propping agent is used to prop open the fracture after the treatment is completed, but in the acid fracturing process, acid is used to create channels in the reservoir rock that comprise the walls of the fracture. However, the reservoir rock (e.g., calcium carbonate ($CaCO_3$) must be partially soluble in acid so that channels can be etched in the fracture walls. In shale formations, although many have a significant amount of dissolvable carbonate and limestone, the content of the carbonates in the formation rock is not always a continuous phase. Hence, it is difficult to use acid-based fluids even in the few high carbonate reservoirs such as the Eagle Ford formation. Without a continuous carbonate/limestone phase, it is very difficult to create the required continuous channel. In addition, flowback needs to manage the disposal of significant calcium carbonate/limestone volumes that become dissolved in the acid and come to the surface with the spent acid. Thus, it is appropriate that the application of acid fracturing is confined to carbonate reservoirs and is not applied to stimulate tight sandstone formations, shale formation, or coal-seam reservoirs.

2.2.5 Alcohol-Based Fluids

In the 1990s methanol was first used as a base fluid in fracturing applications in Canada and Argentina, and the fractured formations either had (i) low permeability with high clay content, (ii) low bottom-hole pressure, and/or (iii) minimal load fluid recovery. However, concerns about safety of using methanol (not the least of which is flammability) have led to a movement away from methanol as a base fluid, and there has been a tendency to limit methanol use to that of an additive.

However, in formations with severe liquid (aqueous and hydrocarbon) trapping problems, nonaqueous methanol fluids may be a solution to poor recovery. Nevertheless, the advantages of using alcohol-based fluids have been identified and include

(i) low freezing point,
(ii) low surface tension,
(iii) high solubility in water,
(iv) high vapor pressure,
(v) compatibility with the formation.

In fact, methanol has become the fluid of choice for formations with irreducible water and/or hydro- carbon saturation [15] [5].

Alcohol-based fluids should be selectively used with special safety considerations due to the flammability of methanol. The flash point (i.e., the lowest temperature at which it can vaporize to form an ignitable mixture in air) of methanol is 53 °F (11.6 °C), and the density is greater than that of air, which presents a safety hazard to field personnel. Oxygen contact must be avoided and therefore a blanket of carbon dioxide vapor is used to separate methanol vapor from any oxygen source.

Certain formations have potential to retain even the small amounts of water contained in foams. These fluids may damage these sensitive formations because of irreducible water saturation and liquid trapping. In these formations, replacing 40% of the water phase used in conventional carbon dioxide-based foams with methanol can minimize the amount of water required for fracturing [11].

Another group of commonly used additives in a water-based fracturing fluid is known as surface active agents or surfactants. These include (i) reducing the interfacial tension and hence capillary pressure, (ii) providing a foam stabilizing action, and(iii) reducing the compatibility problems between fracturing fluids and reservoir fluids. Decreasing the capillary pressure is useful in low-permeability formations to reduce the pressure needed in causing flowback of fracturing fluid since less fluid will be retained in the pore spaces of the reservoir. In fracturing fluid recovery, the addition of gases such as nitrogen and carbon dioxide are also claimed to be useful [12].

The foam stabilizing action is effective in gas wells.

2.3 Emulsion-Based Fluids

There are many different emulsion-based fluids that have been developed and used as fracturing fluids. Many of such fluids use emulsions of oil and water and could therefore be classified under the oil-based fluids. Generally, emulsion-based fluids reduce or completely eliminate the use of water. From the 1980s to the present, the use of emulsion-based fluids has been successful, particularly in low-pressure, tight gas applications. The use of emulsion-based fluids has the same advantages as the use of conventional high-quality carbon dioxide-based foams, with the added advantage of minimizing the amount of water introduced into the well [11].

2.4 Cryogenic Fluids

Liquid (or supercritical) carbon dioxide can be used instead of water as the fracturing fluid. The family of these fluids consists of pure liquid carbon dioxide and a binary fluid consisting of a mixture of liquid carbon dioxide and nitrogen to reduce costs [7]. In these systems, the proppant is placed in the formation without causing damage of any kind and without adding any other carrier fluid, viscosity modifier, or other chemicals.

Liquid carbon dioxide has been used in fracture operation since the early 1960s— initially the liquid carbon dioxide was used as an additive to hydraulic fracturing fluids and to acid fracturing in order to improve recovery of treating fluid [19]. The physical properties of liquid carbon dioxide make it a unique fluid. Carbon dioxide is relatively inert compound that, depending on the temperature and pressure, exists as a solid, liquid, gas, or supercritical fluid. After the addition of proppants, high pressure pumps increase the pressure, and as the fluid enters the formation, the temperature increases toward bottom-hole temperature. During flow- back, the pressure decreases and carbon dioxide comes to the surface as a gas.

The use of supercritical carbon dioxide (a fluid state of carbon dioxide where it is held at or above the critical temperature and critical pressure) has been suggested for use as a fracturing fluid [10] ,[1]. Supercritical carbon dioxide is a fluid state where carbon dioxide is held at or above its critical temperature (31.1 °C) and critical pressure (1070 psi). Owing to the unique physical and chemical properties, supercritical carbon dioxide can obtain a higher penetration rate in shale formations and has the potential to cause little or no damage to the reservoir.

2.5 Additives

Additives are chemicals added to the fracturing fluid to achieve specific target properties of the fracturing fluid (Tables 2.2 and 2.3) and constitute between 0.1 and 0.5% v/v of the total fracture fluid [3], [14], [25], [27]. Since each reservoir and each well (even wells in the same reservoir) are sufficiently different for other reservoirs and wells, there is no generally applicable formula for how much of each additive is to be used in a given fracturing fluid, typically between 3 and 12 additives are employed depending on the conditions of the specific well to be fractured and characteristic of the surrounding formations. Additives utilized in hydraulic fracturing operations are intended to serve specifically engineered uses such as biocides to control microorganism/bacterial growth, corrosion inhibitor to prevent corrosion of pipe, viscosity agents to carry proppant, gelling agents to improve proppant placement, friction reduction to decrease pump friction and reduce treating pressure, oxygen scavengers to also aid in corrosion prevention in metal pipes, and acids to help remove drilling mud buildup damage (Table 2.2).

Chemical additives are applied to (i) tailor the injected material to the specific geological makeup of the reservoir, (ii) protect the well, and (iii) improve the operation, which will vary based on the type of well. Since change is the only constant, the composition of the injected fluid may need to be changed as the fracturing project proceeds. Often, acid is initially used to scour the perforations and clean up the near-wellbore area, and afterward, high-pressure fracture fluid is injected into the wellbore, with the pressure above the fracture gradient of the rock. This fracture fluid contains water-soluble gelling agents (such as guar gum), which increase the viscosity of the fluid and deliver the proppant (without settling) into the formation. As the fracturing process proceeds, viscosity-reducing agents such as oxidizer and enzyme breakers (Table 2.3) may be added to the fracturing fluid to deactivate the gelling agents and encourage flowback.

At the end of the project the well is commonly flushed with water (sometimes blended with a friction-reducing chemical) under pressure. The injected fluid is partially recovered and is managed by several methods, such as underground injection control, treatment and discharge, recycling, or temporary storage in pits or containers, while new technology is continually being developed and improved to handle the wastewater and improve reusability. Although the concentrations of the chemical additives are very low, the recovered fluid may be environmentally harmful (and may even be a health hazard) due in part to minerals that are extracted from the formation. The type of additive used also depends on the base fracturing fluid. For example, water-based fluids (more than other base fracturing fluids) require surfactants to reduce interfacial tension and resistance to return flow after treatment. Conversely, additives for friction-loss reduction in fracturing are less needed for water-based fluids since it naturally has a friction-reducing advantage. The same considerations apply to other base fluids, with additives chosen to supplement any inherent limitations in fluid performance. Generally, additives serve the following uses: (i) enhance fracture creation and (ii) reduce formation damage. Additives that enhance fracture creation include viscofiers, temperature stabilizers, pH control agents, and fluid-loss control materials. Those additives that reduce formation damage are gel breakers, biocides, surfactants, clay stabilizers, and gases [12].

Other additives commonly used in the hydraulic fracturing fluid include (Tables 2.2 and 2.3): (i) a *biocide or disinfectant*, used to prevent the growth of bacteria in the well that may interfere with the fracturing operation; biocides typically consist of bromine-based solutions or glutaraldehyde; (ii) a *scale inhibitor*, such as ethylene glycol, used to control the precipitation of certain carbonate and sulfate minerals;(iii) *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; and (iv) *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 (a common food additive), may also 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 fracturing 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.

Finally, nitrogen-based fracturing fluids are also occasionally used to stimulate shale gas plays. These foam fracturing project typically require only 25% v/v of the water demand needed for a slick water fracturing project. However, these nitrogen-based foam fracturing liquids are effective only in formations that reside at relatively shallow depths. At greater depths, the increased formation pressure limits the ability of foam-based fracturing liquids to effectively fracture the formation and deliver the proppant. As a result, water-based fracturing solutions are more common in deep formations.

Common classes or subcategories of additives include (i) fluid-loss additives,(ii) clay stabilizers, (iii) gel breakers, (iv) bactericides and/or biocides, and (v) pH control chemicals.

2.5.1 Fluid-Loss Additives

Fluid-loss additives are used to restrict leak-off of the fracturing fluid into the exposed rock at the fracture face, which leads to prevention of excessive leak-off, thereby maintaining fracturing fluid effectiveness. Fluid-loss additives of the past and pre- sent include bridging materials such as 100 mesh sand, 100 mesh soluble resin, or plastering materials such as starch blends, talc, silica flour (finely powdered silica), and a variety of appropriate clay minerals.

Fluid-loss control in fracturing operations cannot be overemphasized. Thus, fluid- loss additives are added to the base fracturing fluid to prevent the fluid from leaving the fracture, hence, to prevent the fluid from leaking from the fracture into the rock matrix. Loss of fluid through uncontrolled leak-off will cause an increase in proppant concentration around the wellbore, which if allowed can create a proppant bridge and completely stop fracture propagation [12]. Low fluid loss (low leak-off rate) would mean larger and deeper fractures for a given volume of fracturing fluid and injection rate.

In the process [13], the fluid-loss additive, which is largely insoluble, disperses into micron-sized (µm-sized) particles when added to the fracturing fluid. As fracturing takes place, some fluid is lost immediately to the formation, called spurt loss, and after spurt loss the fluid-loss additive deposits a thin film (sometimes called a filter cake) on the face (interior walls) of the newly created fracture, hence preventing further fluid loss to the formation. This process continues as the fracture propagates and new fracture area is exposed. The thin film (filter cake) remains in place, as long as there is pressure in the fracture.

When flowback begins, the filter cake redisperses and flows out through the spaces between propping agents. Briefly, spurt loss is the fluid loss per area, before the formation of a filter cake, and is very significant in naturally fractured reservoirs [16]. It is directly proportional to reservoir permeability and is an important part of the fracturing operation, and an efficient fluid-loss additive would not only coat the fracture face but also prevent excessive spurt loss from occurring.

2.5.2 Clay Stabilizers

Clay minerals pose challenges since they are well known for swelling in the presence of water. Within the crystalline layers, clay minerals contain cations (typically sodium and potassium) that occupy base-exchange positions or sites. Upon contact with water, these cations are solubilized resulting in clay instability that may be manifested in swelling. When clay swells, the ability of the clay-containing formation to permit the passage of liquids and drilling or fracturing fluids as well as hydrocarbons, is diminished and can seriously impede crude oil and/or natural gas production.

Clay stabilizers reduce clay swelling and function through ion exchange, where the clay stabilizer provides a cation to replace the native, solubilized clay cation such as sodium. Potassium chloride (KCl) is commonly used to reduce clay swelling, where the potassium ion is effective at preventing swelling. It presents certain challenges. Potassium chloride is often used at high levels (2–4% w/w) and requires handling at the site to prepare a solution. In addition, potassium chloride can be incompatible with other materials, negatively impacting other aspects of fracturing fluids such as gelation.

In terms of hydraulic fracturing, clay stabilizers are additives that are used to improve the compatibility between the formation and fracturing fluid. Most formations contain clay minerals that are susceptible to swelling and migration, and clay damage is extremely important in low-permeability, low-pressure reservoirs as it affects capillary pressures [2]. Fracturing fluids must provide a high electrovalent strength so that clays contacted would not experience *ionic shock*. Clay stabilizers like inorganic salts such as potassium chloride (KCl), sodium chloride (NaCl), ammonium chloride (NH_4Cl), or calcium chloride ($CaCl_2$) are used to prevent shocking the clays. Other stabilizers such as polymeric clay stabilizers can attach anions to the clay surface in order to control migration of fines, hampering placement of the proppant [12].

2.5.3 Gel Breakers

Hydraulic fracturing fluid must have the capability to decrease in viscosity following proppant placement. This decrease is necessary to (i) minimize return of proppant and (ii) maximize return of fracturing fluid to the surface. This decrease is achieved using chemicals referred to as *gel breakers* (*gelling agent breakers*). Thus, gel breakers are used to degrade the fracturing fluid viscosity, which helps to enhance post fracturing fluid recovery or flowback. The gel breakers can be mixed with the fracturing fluid during pumping, or they can be introduced later as an independent fluid. There are a variety of breaker types including time-release and temperature- dependent types. Most breakers are typically acids, oxidizers, or enzymes. However, gel breakers may contain hazardous constituents, including ammonium persulfate, ammonium sulfate, copper compounds, ethylene glycol, and glycol ethers.

Breakers are added to the fracturing fluid to reduce the molecular weight of the various polymers used. This reduces the viscosity and facilitates the blowback of residual polymer, which allows for cleanup of the proppant pack. The inappropriate use or ineffective breakers can cause significant damage in the proppant pack and a reduced PI. Ideally these materials would be totally inactive during the treatment and then instantly act when pumping stops, rapidly breaking the fluid back to a low viscosity preparing the fracture and formation for flow. This is very difficult to achieve as the breaker activity is very dependent on fluid temperature, which varies with time.

These additives are useful for flowback and cleanup after the fracturing operation. It is important to ensure good fracture conductivity. Gel breakers oxidize the back- bone of the polymer molecules, allowing the polymer to be produced out of the fracture. Enzyme breakers such as hemicellulase are used at temperatures below 50 °C (122 °F) with a pH less than 8.5. Other oxidizing breakers such as ammonium persulfate and sodium persulfate are used at higher temperatures, 66 °C (150 °F), or at lower temperatures with an activator [16].

The three general types of breakers are (i) oxidizers, (ii) acids, and (iii) enzymes.

2.5.4 Bactericides/Biocides

One hydraulic fracturing design problem that arises when using organic polymers in fracturing fluids is the incidence of bacterial growth within the fluids. Biocides are additives for controlling bacterial growth and are often a necessity for water-based fluids. Due to the presence of organic constituents, the fracturing fluids provide a medium for bacterial growth. As the bacteria grow, they secrete enzymes that break down the gelling agent, which reduces the viscosity of the fracturing fluid. Reduced viscosity translates into poor proppant placement and poor fracturing performance. To alleviate this degradation in performance, biocides, bactericides, or microbicides are added to the mixing tanks with the polymeric gelling agents to kill any existing microorganisms (e.g., sulfate-reducing bacteria, slime-forming bacteria, algae) and to inhibit bacterial growth and deleterious enzyme production.

Pumping untreated water into a reservoir can trigger bacterial growth [15]. Aerobic bacteria can destroy the viscosity of a fracturing fluid within a few hours. If anaerobic bacteria are introduced by a fracturing fluid, it can produce hydrogen sulfide (H_2S) within the reservoir. Biocides used to control both types of bacteria include quaternary amines, amide-type chemicals, and chlorinated phenols [15].

2.5.5 pH Control

Fluid pH affects various properties of the fracturing fluid. These include initial polymer gelation rate, cross-linking characteristics, gel break properties, bacteria control, viscosity stability, and other properties. The typical pH range for fracturing fluid is from

3 to 10 (virtually the entire pH range). Buffers made from mixing weak acids with weak bases are used to maintain the desired pH [12]. The selection criteria for fracturing fluid are the following: (i) safety and environ- mental compatibility, (ii) compatibility with formation and additives, (iii) simple preparation and quality control, (iv) low pumping pressure, (v) appropriate viscosity, (vi) low fluid loss, (vii) flowback and cleanup (for high conductivity), and (viii) economics.

2.5.6 Friction Reducers

To optimize the fracturing process, water-based fluids must be pumped at maximum rates, and fluids must be injected at maximum pressures. Increasing flow velocities and pressures in this manner can lead to undesirable levels of friction within the injection well and the fracture itself. In order to minimize friction, friction reducers are added to water-based fracturing fluids. The friction reducers are typically latex polymers or co-polymers of acrylamides. They are added to slick water treatments (water with solvent) at concentrations of 0.25–2.0 pounds per 1000 gallons. Some examples of friction reducers are oil-soluble anionic liquid, cationic polyacrylate liquid, and cationic friction reducer.

2.5.7 Acid Corrosion Inhibitors

Corrosion inhibitors are required in acid fluid mixtures because acids will corrode steel tubing, well casings, tools, and tanks. The solvent acetone is a common additive in corrosion inhibitors.

These products can affect the liver, kidney, heart, central nervous system, and lungs. They are quite hazardous in their undiluted form. These products are diluted to a concentration of 1 gallon per 1000 gallons of makeup water and acid mixture. Acids and acid corrosion inhibitors are used in very small quantities in coalbed methane fracturing operations (500–2000 gallons per treatment).

2.5.8 Viscosity Stabilizers

Viscosity stabilizers are added to the fracturing fluids to reduce the loss of viscosity at high reservoir temperatures [26]. The two most common stabilizers are methanol (used at 5–10% v/v) and sodium thiosulfate. These materials will extend the temperature range of guar-based fluids to over 180 °C (350 °F). Thiosulfate is the more effective of the two and is less hazardous to handle. These materials act as free radical scavengers that are present in the base water. Without the stabilizers these free radicals can naturally oxidize the polymer as described in the breakers section. However, since viscosity breakers are free radical generators and these materials are free radical scavengers, they should not be run at the same time.

2.5.9 Acidizing

The acidizing technique involves pumping acid (typically hydrochloric acid) into a wellbore and thence into the geologic formation that is capable of producing oil and/ or gas. The purpose of any acidizing is to improve the productivity or injectivity of a well and the formation.

Acidizing predates all other well stimulation techniques, including hydraulic fracturing, which was not developed until the late 1940s. However, until the early 1930s, the use of the acidizing technique was limited by the lack of effective corrosion inhibitors to protect the steel tubular segments in the wells from the acid. With the development of effective corrosion inhibitors [24], the use and further development of acid treatment (acidizing) of oil and gas wells proliferated, leading to the establishment of the well stimulation services industry. Currently, acidizing is one of the most widely used and effective means available for crude oil and natural gas production that would improve the productivity (stimulation) of well and reservoirs. Acidizing is commonly performed on new wells to maximize their initial productivity and is also applied to aging wells and partially depleted reservoirs to restore productivity and maximize the recovery of the energy resources. Generally, there are three general categories of acid treatments: (i) acid washing, (ii) matrix acidizing, and (iii) fracture acidizing. Matrix acidizing and fracture acidizing are both formation treatments.

In acid washing, the objective is simply tubular and wellbore cleaning. Treatment of the formation is not intended. Acid washing is most commonly performed with hydrochloric acid (HCl) mixtures to clean out scale (such as calcium carbonate (CaCO_3), rust (iron oxide), and other debris that restricts fluid flow from the reservoir and fluid flow in the well. In matrix acidizing, the acid treatment is injected below the fracturing pressure of the formation, whereas in fracture acidizing, acid is pumped into the system above the fracturing pressure of the formation. “The purpose of matrix or fracture acidizing is to restore or improve an oil or gas well’s productivity by dissolving material in the productive formation that is restricting flow or to dissolve formation rock itself to enhance existing or to create new flow paths to the wellbore.”

Two key factors dominate the treatment selection and design process when planning an acid treatment operation: (i) formation type, which can be composed of carbonate minerals, sandstone deposits, or shale deposits, and (ii) formation permeability, which is the ability of fluid to flow through the formation in its natural state.

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Chapter 3:

Problems Associatevd With Hydraulic Fracturing

3 Problems Associated with Hydraulic Fracturing

The one thing that a person is probably most likely to think about when considering the possible problems associated with hydraulic fracturing is water:

- The 4.4 million gallons of water needed to frack the average oil or gas well [15];
- The alternative residential, commercial, industrial, and other uses to which that water could otherwise be put;
- The complications involved in transporting that water from its source to the fracking site;
- The chemicals that must be added to that water to maximize its efficiency in the process of fracking;
- The disturbance that water creates in rock structures into which it is injected, disturbance that may result in earthquakes and other seismic events;
- The production of additional amounts of water originally stored underground, but released by the fracking process;
- The contamination of the fracking water by the fracking process itself;
- The ultimate fate of the original fracking water along with the newly released water, especially upon its return to the surface; along with the myriad effects on human health and the natural environment caused by the water used in the fracking process and all of the other by- products of that technology. What, then, can be said about these common problems often associated with the fracking of oil and gas wells? Here are some of the most common answers to that question.

3.1 Water Use

Critics of fracking often point out that the technology wastes enormous amounts of water. The primary objection is not that fracking uses a lot of water—many industrial operations do so—but that the water used for that purpose is essentially lost for other possible uses. A nuclear power plant, for example, uses very large quantities of water to cool the reactor core. But that water is stored for a period of time in cooling ponds and then returned to lakes and rivers, from which it can then be extracted for other purposes. But water used for fracking can generally not be recycled in the same way. It may remain buried underground; it may be pumped into empty wells as permanent storage sites; it may be recycled in the fracking of other wells; or it may be treated in wastewater plants and then returned to rivers and streams. The water is very unlikely to end up in a drinking water reservoir, in a farmer's irrigation ditch, or on its way to an industrial plant [6].

A number of studies have attempted to obtain more specific information about the fate of water used in fracking operations, often with only limited success. In one such study of water uses in fracking operations in Pennsylvania and West Virginia, for example, researchers noted that one challenge they encountered was that state reporting requirements were such that only very limited conclusions could be drawn about the way in which fracking water was used and then disposed of [13]. These researchers were, nonetheless, able to reach some qualified conclusions:

- An average of 4.3–5 million gallons of water is used in the fracking of wells in the region.
- About 80 percent of the water used for fracking is taken directly from rivers and streams.
- Between 6 and 8 percent of the water used in fracking is recovered; the balance remains underground, unavailable for future use of any kind.
- More than half of the wastewater from Pennsylvania wells is treated and returned to the environment, while essentially none of the West Virginia wastewater goes through this process [13].

Regardless of the numerous studies that have been conducted, a number of ordinary citizens and the organizations to which they belong are worried about the massive use of water for fracking. That concern is only made more serious if and when drought conditions develop in a region where fracking is occurring or is planned. In late 2012, for example, citizens of Carroll County, Ohio, expressed their growing concerns that the water be withdrawn from the region's water table would result in a deficiency of water for residential, industrial, commercial, and other applications. Even though some of those citizens were accepting payment for water being withdrawn from their own ponds, the consensus view seemed to be that better controls were needed to make sure that the county did not run out of water as oil and gas companies continued to drain the country's natural sources of water [16].

The oil and gas industry's primary response to the concern about water use in the fracking process is that critics should keep the issue in perspective. Every form of energy generation requires the use of water—usually very large amounts of water—and fracking is no exception. The major difference, they say, is that fracking requires *much less* water use than do most other forms of energy generation. In a presentation made to the Ground Water Protection Council in 2009, for example, Chesapeake Energy displayed a table showing the amount of water used for a variety of energy generation technologies, in gallons of water used per million Btu of energy. The table showed that the extraction of shale natural gas requires anywhere from 0.60 to 1.80 gallons per million Btu (gal/ MMBtu), compared to 1 to 3 gal/MMBtu for conventional

natural gas, 2 to 32 gal/MMBtu for coal (depending on method of transport), 8 to 14 gal/MMBtu for nuclear power, 8 to 20 gal/MMBtu for conventional oil, 22 to 26 gal/MMBtu for shale oil, 2,519 to 29,100 gal/MMBtu for ethanol fuel, and 14,000 to 75,000 gal/MMBtu for biodiesel from irrigated soy [11].

3.2 Water Contamination

At first glance, one might expect the drilling and/or fracking of an oil or gas well might inevitably result in some contamination of groundwater in the area around the well. A variety of chemicals is typically added to the drilling fluid used in producing the well, and it would seem reasonable for some drilling line to release at least a minimal amount of those chemicals into groundwater. In fact, such a scenario should occur very rarely. The reason for this expectation is that the oil or gas well is drilled many hundreds or (much more commonly) thousands of feet into the underground rock, while the water table that contains essentially all groundwater in an area lies only a few hundred feet below the surface at the most [10]. The loss of chemicals in a drilling fluid into the water table would, therefore, seem to be a very unlikely unoccurrence.

Yet complaints for residents in the area around oil and gas wells have long been common, arising even before the process of fracking was first used on such wells, but having become much more common since about 2005. These complaints focus on a number of troubling phenomena, the most dramatic of which may well be the case of “burning water.” Some residents have reported that they have been able to set first to the water released from their household taps, presumably because of the methane present from natural gas trapped in the water.

Although this complaint about fracking has received substantial attention and is certainly one of the most dramatic charges brought against the practice, it is unclear to what extent burning water and fracking are closely connected. A number of studies have shown, in fact, that flaming water is anything but an uncommon event in areas where oil and gas are produced. The apparent cause for the phenomenon is the presence of natural gas in shallow layers of earth around oil and gas wells, *whether they have been fracked or not*. Thus, while a legitimate complaint about fracking, it is not clear to what extent flaming water can be used as a major objection to the practice of fracking [5].

One question that might be asked about the contamination of water as a result of fracking is precisely what people mean by the term contamination. According to at least one study, most people are talking about the presence of methane in the water supply when they are talking about “contamination,” and not about the dozens or hundreds of chemicals used in the fracking process [12]. But both the systems by which states keep track of such complaints and the way in which complainants describe their experiences mask the precise meaning individuals ascribe to the term.

From a strictly scientific standpoint, the term *contamination* usually refers to the presence in water of substances normally not present in water and/or having the potential to cause harm to plants, animals (including humans), and other aspects of the environment. But reports of contamination by individuals and organizations often suggest a broader and somewhat more ambiguous experience. For example, the Pennsylvania Alliance for Clean Water and Air maintains a website listing specific complaints registered by individuals and communities that claim their water has been contaminated by fracking. As of late 2014, the website listed nearly 7,000 complaints, many of which came from groups of individuals, rather than single persons. Some of the experiences that complainants registered were the following: stomach pain; nausea; rashes on legs while showering; fatigue; mouth ulcers;

sick and/or dead goats, dogs, cows, horses, and other farm animals; difficulty in breathing; elevated heart rate; lightheadedness; spitting up blood; farm and domestic animals refusing food and water; multiple myeloma; human mortality; air loss; increased sensitivity to chemicals; previously unidentified viruses; paralysis of legs; lesions on spinal cord; stress; shock; mental distress; and "constant fear of developing cancer" [24].

Defenders of fracking suggest that complaints such as those listed here must be assessed carefully. In the first place, many complaints have come from regions where conventional drilling has been practiced for many years. Any health problems that occur may be the result of these operations, rather than of fracking itself. Also, the wide range of problems that have been reported suggest that at least some individuals may be imagining or exaggerating health issues that are not really as severe as they may seem. The constant barrage of criticisms about fracking, supporters of the procedure say, may cause people to fantasize ailments that do not exist in reality.

Intimately associated with the issue of water contamination as a result of fracking is the question as to what chemicals are used in the process.

At least 600 different chemicals are commercially available for achieving one or another of these objectives in the fracking process.

The problem is that oil and gas companies have historically been reluctant to release to the general public (or even to regulatory agencies) the precise composition of chemicals used in any one field. The companies claim that such information is proprietary and can result in financial loss to the company if it becomes generally known.

Some companies, however, have begun to change their views and their policies about disclosing the names of the chemicals used in the fracking of their wells. They have come to realize that the success of their business depends to at least some extent on the trust that their consumers and the general public have in their products. If they can reduce public suspicions about the

substances they are using in their operations, some companies believe, they may be able to avoid lawsuits, additional state and local regulations, and general bad feelings toward the company. One company that has led the way in providing full disclosure about their products is the Baker Hughes company, a supplier for the oil and gas drilling industry. In 2014, the company announced that it would make available on its website a complete listing of all chemicals used in its fracking products [17].

Once the chemicals used in a fracking operation are identified, a person can learn a great deal about the potential health threats posed by each chemical from a variety of sources. For example, TOXNET (Toxicology Data Network) is a ser- vice of the U.S. National Library of Medicine that provides access to 16 databases of hazardous chemicals. By simply enter- ing the name of a chemical, one gains access to a host of information about its chemical and physical properties, along with its potential carcinogenic, mutagenic, teratogenic, and other health hazards to humans. Two other useful sources of information about the health effects of chemicals are the International Chemical Safety Cards (ICSC), produced by the International Labour Organization and the NIOSH Pocket Guide to Chemical Hazards, published by the National Institute for Occupational Safety and Health.

3.3 Air Pollution

Critics of fracking often point to the risks posed to air quality by the procedure. They say that in some cases contamination of air can be as bad as, or even worse than, contamination of water, resulting in its own set of health issues for humans and other animals. The culprit most commonly named in contamination of the air is methane, the primary constituent of natural gas. Methane escapes from oil and gas wells at a number of points in the process of exploration, extraction, processing, and transportation. By far the greatest source of methane leaks at oil and gas wells is intentional venting of the gas to the atmosphere. Recall that oil and gas companies have traditionally allowed natural gas to escape from many wells simply because it is easier and less expensive to do so than to capture and store the gas. According to some studies, about 83 percent of all the methane that escapes from gas and oil production processes is released intentionally, with the remaining 17 percent escaping from leaks and accidental releases [18].

But how serious is the problem of methane linkage from oil and gas wells? How much methane in actual amounts escapes from an oil or gas field during extraction? Surprisingly, little was known about the answer to that question until fairly recently. For many years, experts relied on a report published in 1996 by the Environmental Protection Agency (EPA) estimating that somewhere between 1 and 2 percent of all the methane produced in the United States escaped into the atmosphere [20]. By the second decade of the twenty-first century, however, a number of new studies began appearing suggesting that the EPA estimate was too low, perhaps much too low.

A study of wells in the Denver–Julesburg Basin of the Rocky Mountains by researchers from the National Oceanic and Atmospheric Administration (NOAA) and the University of Colorado, found that about 4 percent of the methane produced from oil and gas wells was escaping into the atmosphere, about twice that of the 1996 EPA report.

In the years following the NOAA–Colorado study, additional research found even more striking data about the loss of methane from oil and gas wells. These data showed loss rates of as high as 14 and 17 percent in some cases, approaching 10 times the 1996 EPA estimates. Then, in late 2013, researchers at the University of California at San Diego published their review of data from a variety of sources about methane emissions in the United States. They concluded that those emissions could be anywhere from 2.3 to 7.5 times greater than the "official" estimates of the highly respected Emissions Database for Global Atmospheric Research [21].

Data suggesting high levels of methane linkage are not accepted uncritically by all observers. Representatives of the oil and gas industry in particular tend to find errors in the conduct of studies leading to these conclusions and/or are able to cite other research that shows very different trends. For example, a writer for the Internet site Energy in Depth has called attention to studies that found methane linkages in the range of 1.5 percent "or less than that," comparable to the 1996 EPA study. The writer concludes his review of the study with the observation that:

> The activist fear-mongering about methane emissions has been exposed as fraudulent by the most comprehensive research on the subject to date, including data that incorporates the first-ever direct measurements of methane emissions from various segments of the production process. Perhaps now we can all come together, take a deep breath, and recognize the clear economic and environmental benefits of natural gas from shale [9].

One of the interesting trends in research on air contamination resulting from fracking operations has been the increasing evidence of air pollutants other than methane itself as potential sources of human health problems.

In 2012, for example, researchers at The Endocrine Disruption Exchange in Paonia, Colorado, reported on their study of compounds known collectively as *non-methane hydrocarbons* (NMHCs) in the effluent from fracked oil and gas wells. NMHCs are hydrocarbons that occur in natural gas at a much lower concentration than does methane itself: ethane, propane, butane, ethene (ethylene), propene (propylene), and ethyne (acetylene), for example. Little attention was paid to the presence, concentration, and health effects of these compounds until 2012. But they appear to pose their own significant and identifiable human health issues. As just one example, researchers found methylene chloride, which causes damage to the nervous system, present almost three quarters of the time in their sampling. They concluded that NMHCs "should be examined further given that the natural gas industry is now operating in close proximity to human residences and public lands" [2]. Many of the chemical compounds found in polluted air in general are also found in areas where fracking is occurring. These compounds include sulfur dioxide, oxides of nitrogen, carbon monoxide, polyaromatic hydrocarbons (PAHs), volatile organic compounds (VOCs), and PM10 and PM2.5 (particulate matter less than 10 and 2.5 micrometers in diameter, respectively). In its annual National Emissions Inventory for 2012, for example, the EPA reported that the oil and gas industry was responsible for the release of more than 1.688 billion tons of VOCs during production, more than seven times as much as the next largest polluter, the storage and transfer industry, and more than a thousand times that of the rest of the mining industry. VOCs have been associated with a wide variety of medical conditions (at least partly because the category includes so many different organic compounds), such as eye, nose, and throat irritation; head- aches; loss of coordination; nausea; damage to liver, kidney, and central nervous system; conjunctival irritation; nose and throat discomfort; headache; allergic skin reaction; dyspnea; declines in serum cholinesterase levels ;and fatigue. Some components of VOCs have also been implicated in the development of cancers in experimental animals.

Finely divided particulate matter (PM) has also been shown to have a number of health problems. Such pollutants have a tendency to become lodged in the respiratory system, causing health concerns such as decreased lung function, in general; irregular heartbeat; nonfatal heart attacks; premature death in people with heart or lung disease; and aggravated asthma [23].

One recent study by the Center for Public Integrity, Inside Climate News, and The Weather Channel, produced a number of troubling findings about air pollution resulting from fracking in the Eagle Ford Play of Texas. Among those findings were the following:

- The state of Texas maintains only five permanent air monitoring systems in the 20,000-square-mile Eagle Ford Play, a number clearly inadequate to obtain the necessary raw data about possible air contamination in the region.
- The state allows oil and gas companies to self-monitor their operations, resulting in the fact that it does not even know how many fracking operations are being conducted in the states, where they are located, or what environmental effects they are having on residents of the region.
- Companies that do violate state regulations are rarely fined, with only two penalties having been assessed in the 164 documented violations found by the investigating team in the period of the study. The largest fine assessed for the violations was $14,250.
- The Texas legislature reduced the budget for the Texas Commission on Environmental Quality (TCEQ) by a third during its 2014 session.
- The release of toxic air pollutants increased by 100 percent between 2009 and 2014.
- Air quality monitoring systems are unequally distributed in Texas with urban areas such as Dallas receiving many more such systems per resident than areas close to fracking operations, such as those in the Eagle Ford Play [22].

3.4 Earthquakes

The question as to the relationship between the extraction of gas and oil and seismic events (earthquakes), if any, has

interested researchers for at least the last half century. During the 1960s, that question arose in a somewhat different context, the use of injection wells for the disposal of radioactive wastes. At the time, scientists were exploring systems for burying or otherwise disposing of the waste materials produced by research on atomic weapons and at nuclear power plants. One proposal was to force those (liquid) wastes into deep wells that had previously been used for other purposes, such as the collection of water for human use. Soon after this method of disposal was begun, the number of seismic events (earthquakes) in the region surrounding the injection wells begin to increase significantly. Researchers came to the conclusion that the liquid wastes were acting as a lubricant on rocks deep underground, causing them to slip and fracture, thus producing the earth- quakes [8].

The effect of oil and gas drilling operations on earth movements has also been a matter of some interest to researchers, although much more so in the past decade than in previous history. From a simple-minded point of view, one would expect at least some effects of drilling on seismic events since oil and gas are often found along unstable rock formations deep under- ground, and the act of drilling itself might be expected to cause some shifts in the rock. In fact, research has shown that conventional oil and gas wells appear to have little or no effect on observable instability of rock formations in surrounding regions. Some evidence suggests that hydraulic fracturing *may* be the cause of some seismic events, but the data for such conclusions is typically uncertain and ambiguous [14].

Evidence for the involvement of injection wells used during fracking operations with seismic events is much more compelling. Recall that very large quantities of water are used in fracking operations and that one common method of disposing of the wastewater produced during fracking is emptying into deep wells. The issue of the relationship between fracking injection wells and seismic events is, thus, similar to that of radioactive waste disposal and seismic events.

For some observers, especially those associated with the oil and gas industry, the connection between earthquakes and deep well injection of fracking wastes is unproved or questionable, at best. In one commentary on this issue, an anonymous writer points out that there are more than 144,000 injection wells in the United States that have been used safely by a variety of industries for decades. The writer quotes the EPA as saying that injection wells are "a safe and inexpensive option for the disposal of unwanted wastes," and that the reports of individual seismic events associated with the use of injection wells by the oil and gas industry are few and far between. The writer suggests that the issue is not one that people should worry about because the “minute vibrations” that occur during such events “may not even be detectable to humans” [4].

The preponderance of scientific evidence at this point in time, however, seems to point to some connection between the use of injection wells for the disposal of fracking wastewater and seismic events. This evidence has been coming in from oil and gas extraction sites across the United States. One of the most extensively studied series of seismic events has been those taking place in central Oklahoma beginning in January 2009. Between that date and the end of 2013, more than 200 seismic events of intensity greater than 3.0 on the Richter scale were recorded, including the largest earthquake ever recorded in the state, which struck near Prague, Oklahoma, on November 5, 2011. That quake registered 5.6 on the Richter scale. The increase in seismic events was striking because the state had experienced an average of fewer than three 3.0 magnitude earthquakes between 1975 and 2008, a number that rose to 40 per year in the period between 2009 and 2013 [19].

A similar pattern was observed in another state without a history of earthquakes: Ohio. Between January 2011 and February 2012, more than 100 seismic events with magnitude between 0.4 and 3.9 were recorded in the Youngstown area, a region with no known history of earthquakes. According to a report by geologist Won-Young Kim, of Columbia University, the probable explanation for the seismic events was the disposal of wastewater into injection wells along a fault line underlying the area.

As of late 2014, the U.S. Geological Survey was still unwilling to express a definite determination between the injection of wastewater from fracking operations into wells and seismic events. Their position at the time was that, based on evidence that had been obtained thus far, further research was needed about this relationship.

As of 2014, the potential hazards posed by injection well disposal of fracking wastewater appear to be increasingly significant. At the annual meeting of the Seismological Society of America, a number of papers were presented that suggested that seismic events associated with deep well disposal were more common, more severe, and more difficult to predict than researchers had previously thought. Some evidence was also presented suggesting that the range of such seismic events from injection wells can be considerably greater than previously listed [18].

The debate over fracking wastewater disposal and seismic events is likely to continue, but at least some governmental agencies have decided to act on the information that is currently available. For example, the state of Colorado decided in June 2014 to issue a temporary ban on the disposal of fracking wastewater at one well near which a number of seismic events had been recorded [1].

3.5 Aesthetic and Related Disturbances

Another large category of objections to fracking operations can be classified as *nuisance* complaints. Legally, the term *nuisance* refers to any action that is harmful or annoying to an individual person or discrete group of individuals (a *private nuisance*) or to a larger community of individuals (a *public nuisance*). Consider some of the actions that are commonly associated with a fracking operation at an oil or gas field. In many cases, roads may have to be built to the fracking site. Land may have to be cleared and private property may have to be condemned by the state or county to gain rights of drilling and access to land. In these processes, aesthetically appealing areas on which people-built homes for their solitude, views, access to nature, or other purposes may be destroyed.

Traffic in a region where fracking is occurring may also increase significantly. Truck traffic may increase in order to bring in the equipment and material used in fracking and to remove the wastewater produced by the operation. This truck traffic may necessitate expensive repairs of city and county roads, an expense that must usually be paid by residents, not the fracking company. These harms to the land may cause

property values to decrease and can increase the difficulties in obtaining normal homeowners insurance and reasonable mort- gage rates. The presence of fracking operations may also have an effect on the economy of a region, such as discouraging the creation of new businesses, driving away customers for existing businesses, reduce the appeal of recreational opportunities, and result in deferred maintenance of existing structures in the region. [3]

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Conclusion

The oil and gas process known as hydraulic fracturing has been known for more than a century. But its widespread use in the industry is no more than about a decade old. During that time, fracturing has been responsible for the explosive growth in oil and gas production from shale and other rock formations, bringing enormous profits to the industry, a dramatic increase in jobs. But the process is also responsible for a number of potentially harmful effects on human health and the natural environment. Concerns about these effects are serious enough that a number of states, cities, and other governmental bodies have banned the use of fracking within their territories or, at the least, imposed significant restriction s on the conditions under which fracking can be used. But it is still early days for fracking in the oil and gas industry, and no one can yet say with any certainty how this technologically important process will contribute to the future energy equation of the world [2] .

> Debate continues over the risks that hydraulic fracturing operations may pose to underground sources of drinking water, and Congress has directed Environmental Protection Agency (EPA) to study this matter. The results of this and other studies could provide a better assessment of potential risks, and particular circumstances that may be associated with such risks, and may help inform the need for additional regulation [1].

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ملخص

تطرقنا في دراستنا هذه إلى الغاز الصخري حيث بينا انه غاز غير تقليدي يستخرج عن طريق عملية تدعي الحفر الأفقي ,هذه العملية تستهلك كميات كبيرة جدا من الماء كما تستخدم مواد كيمياءية مختلفة وقد قمنا بنا بذكرها بالتفصيل ,كما عرضنا المشاكل والأضرار الصحية والبيئية المصاحبة لعملية الحفر الأفقي وأهما تلوث المياه الجوفية ,تلوث الهواء ,وامكانية حدوث هزات أرضية .

Summary

in this paper we study shale gas which is unconventional gas producing by the hydraulic fracturing, these presses waste enormous amounts of water and it use a chemical additive we menschen it in details, we menschen also the problems associated with hydraulic fracturing like water contamination and air pollution and earthquakes.

Résumé

Dans cette étude, nous étudions le gaz de schiste, gaz non conventionnel issu de la fracturation hydraulique, ces presses gaspillent d’énormes quantités d’eau et utilisent un additif chimique. Nous la traitons en détail, nous traitons également des problèmes liés à la fracturation hydraulique, tels que la contamination de l’eau, la pollution de l’air et les tremblements de terre.