Water Consulting Services in Support of the Supplemental Generic Environmental Impact Statement for Natural Gas Production

NYSERDA Contract PO Number 10666

WATER-RELATED ISSUES ASSOCIATED WITH GAS PRODUCTION IN THE MARCELLUS SHALE:

Additives Use
Flowback Quality and Quantities
Regulations
On-site Treatment
Green Technologies
Alternate Water Sources
Water Well-Testing

Prepared by

URS

URS Corporation

Fort Washington, PA

May 21, 2010

NOTICE

Table of Contents

List of Figures

List of Tables

1 INTRODUCTION AND SCOPE

1.1 Introduction

The Marcellus Shale formation has been identified as a potentially major source of natural gas, and gas well drilling currently is at the exploratory stage. The core formation extends over an eight state area, including parts of New York State. The formation is exposed at the surface in some locations and at depths greater than 7,000 feet at other locations. In general, drilling activities target areas where the formation is 2,000 feet or more below the surface.

In 1992, the New York State Department of Environmental Conservation (NYSDEC) issued a Generic Environmental Impact Statement (GEIS) that provides a comprehensive review of the potential environmental impacts of oil and gas drilling and production and how they may be mitigated. NYSDEC is now preparing a draft Supplemental GEIS (dSGEIS) to assess issues unique to drilling and high-volume hydraulic fracturing in the Marcellus Shale area. The New York State Energy Research and Development Authority (NYSERDA) is assisting NYSDEC by developing information and data needed for the dSGEIS. NYSERDA has contracted several consultants to research, review, compile, and provide to NYSERDA reports that address different aspects of the final scope for the dSGEIS on the Oil, Gas and Solution Mining Regulatory Program, which was developed by NYSDEC. The SGEIS will be issued by the NYSDEC to establish State Environmental Quality Review (SEQR) thresholds for permitting horizontal drilling and high-volume hydraulic fracturing projects to develop the Marcellus Shale and other low permeability gas reservoirs.

The process of high-volume hydraulic fracturing uses relatively large volumes of water, from about 0.5 to 6 million gallons per well. Water is typically withdrawn from surface water or groundwater sources and stored at each well pad or at centralized facilities until ready to be used. The water is then mixed with proprietary concentrations of proppant and other additives (the mixture is referred to as fracturing fluid), and pumped down into the well at high pressure to fracture the shale. A portion of the fracturing fluid returns to the surface as "flowback" fluid, which requires appropriate treatment and disposal.

This report addresses the following topics related to Marcellus Shale operations:

a. Fracturing fluid additives
b. Flowback fluids
c. Sufficiency of regulations and guidelines
d. On-site flowback fluids treatment or recycling technologies
e. Potential 'green' (environmentally-friendly) hydraulic fracturing technologies
f. Alternate water sources for hydraulic fracturing operations, and
g. Water well sampling needs

The scope of review for each of these topics is briefly described below.

1.2 Report Outline

Section 2 provides a review of fracturing fluid additives used in drilling/fracturing operations; Section 3 provides a review of flowback fluid volumes and composition. Both of these sections draw on publicly available information and from proprietary data from service companies and operators received via NYSDEC under a confidentiality agreement. As such, these two sections present broad classes of inputs or the generic constituents of additives or flowback, but not the chemical suppliers, product names or the product compositions.

Section 4 provides a review of federal and New York State regulations and guidelines related to water that may impact the oil and gas industry. This section compares a preliminary list of parameters found in additives and analytical results for flowback with parameters regulated by the Safe Drinking Water Act (SDWA), pollutants regulated by the State Pollutant Discharge Elimination System (SPDES) program, or which have guidance through the Technical & Operational Guidance Series 1.1.1 (TOGS111).

Section 5 surveys on-site treatment or recycling technologies that may potentially be available for operations in the Marcellus Shale.

Section 6 surveys 'environmentally-friendly' hydraulic fracturing technologies and chemicals, and draws experiences from gas and oil exploration in the North Sea.

Section 7 surveys potential alternate water sources that may be utilized for hydraulic fracturing operations.

Section 8 surveys existing private water well sampling, testing, and monitoring requirements in other states with Marcellus Shale type development activity. This section identifies potential additional requirements that may be applied within New York State for private water well sampling, testing, and monitoring. This section also identifies potential compounds/elements for testing typical private water wells in New York State in baseline and post-drilling modes.

Section 9 summarizes the findings and lists limitations of the study.

Section 10 provides a list of references.

2 FRACTURING FLUID ADDITIVES

2.1 Introduction

Hydraulic fracturing is a process whereby a water, proppant and additives mixture (fracturing fluid) is pumped down a well at high pressure. The force of the injection fractures the underground rock (shale formation) allowing the natural gas to seep through the fractures into the wellbore and up to the surface.

Hydraulic fracturing fluid consists of water, a “proppant” (a permeable material such as sand that keeps the opened fractures from resealing after the fracturing fluid vacates the space), and a relatively small amount (<0.5 percent by volume) of several types of chemical additives. The additives serve a number of purposes listed below. After fracturing the shale, a variable percentage, of the fracturing fluid returns to ground surface as flowback.

2.2 Desirable Properties of Fracturing Fluids

Additives are used in hydraulic fracturing operations to elicit certain properties / characteristics that would aide and enhance the operation. The desired properties / characteristics include [1, 2]:

- Non-reactive
- Non-flammable
- Minimal residuals
- Minimal potential for scale or corrosion.
- Low entrained solids
- Neutral pH (pH 6.5 – 7.5) for maximum polymer hydration
- Limited formation damage
- Appropriately modify properties of water to carry proppant deep into the shale
- Economical to modify fluid properties
- Minimal environmental effects

2.3 Classes of Additives

Table 2-1 lists the types, purposes and examples of additives that have been proposed to date for use in hydraulic fracturing of gas wells in New York State.

Table 2-1 - Types and Purposes of Additives Proposed for Use in New York State

Additive Type	Description of Purpose	Examples of Chemicals[1]
Proppants	"Props" open fractures and allows gas / fluids to flow more freely to the well bore	Sand [Sintered bauxite; zirconium oxide; ceramic beads]
Acid	Cleans up perforation intervals of cement and drilling mud prior to fracturing fluid injection, and provides accessible path to formation	Hydrochloric acid (HCl, 3% to 28%)
Breaker	Reduces the viscosity of the fluid in order to release proppant into fractures and enhance the recovery of the fracturing fluid	Peroxydisulfates
Bactericide / Biocide	Inhibits growth of organisms that could produce gases (particularly hydrogen sulfide) that could contaminate methane gas. Also prevents the growth of bacteria which can reduce the ability of the fluid to carry proppant into the fractures	Gluteraldehyde; 2-Bromo-2-nitro-1,2-propanediol
Clay Stabilizer / Control	Prevents swelling and migration of formation clays which could block pore spaces thereby reducing permeability	Salts (e.g., tetramethyl ammonium chloride) [Potassium chloride (KCl)]
Corrosion Inhibitor	Reduces rust formation on steel tubing, well casings, tools, and tanks (used only in fracturing fluids that contain acid)	Methanol
Crosslinker	The fluid viscosity is increased using phosphate esters combined with metals. The metals are referred to as crosslinking agents. The increased fracturing fluid viscosity allows the fluid to carry more proppant into the fractures.	Potassium hydroxide
Friction Reducer	Allows fracturing fluids to be injected at optimum rates and pressures by minimizing friction	Sodium acrylate-acrylamide copolymer; polyacrylamide (PAM)
Gelling Agent	Increases fracturing fluid viscosity, allowing the fluid to carry more proppant into the fractures	Guar gum
Iron Control	Prevents the precipitation of metal oxides which could plug off the formation	Citric acid; thioglycolic acid
Scale Inhibitor	Prevents the precipitation of carbonates and sulfates (calcium carbonate, calcium sulfate, barium sulfate) which could plug off the formation	Ammonium chloride; ethylene glycol; polyacrylate
Surfactant	Reduces fracturing fluid surface tension thereby aiding fluid recovery	Methanol; isopropanol

[1] Chemicals in brackets [ ] have not been proposed for use in the State of New York to date, but are known to be used in other states or shale formations.

2.4 Composition of Fracturing Fluids

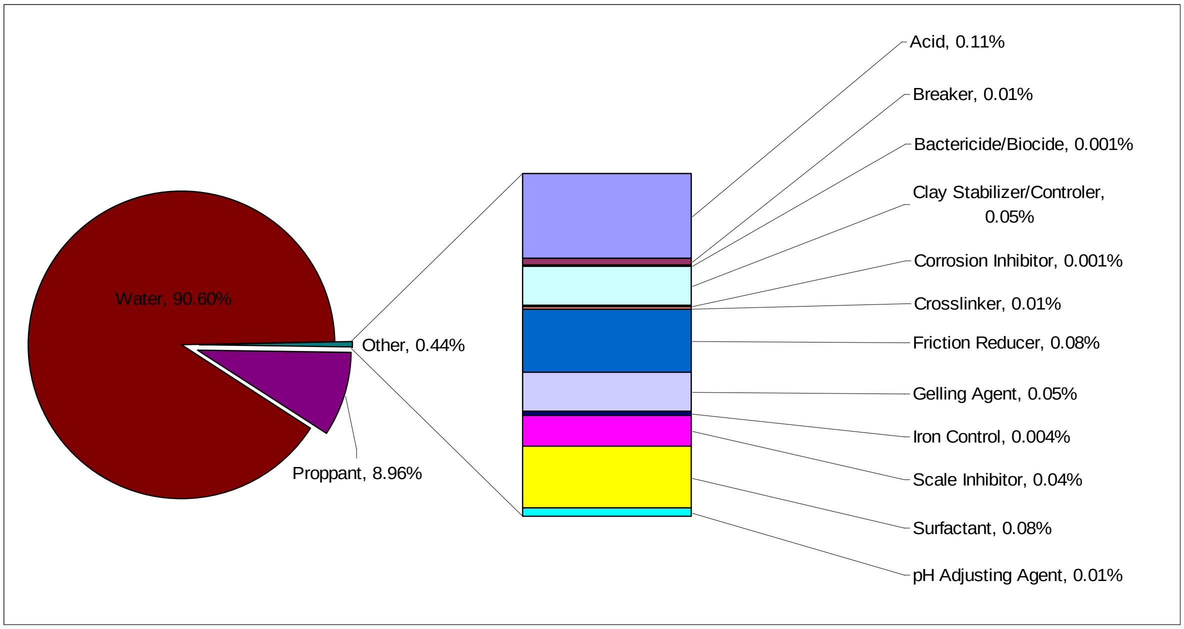
The composition of the fracturing fluid used may vary from one geologic basin/formation to another in order to meet the specific needs of each operation; but the range of additive-types available for potential use remains the same. There are a number of different products for each additive type; however, only one product of each type is typically utilized in any given gas well. The selection may be driven by the formation and potential interactions between additives. Additionally not all additive types will be utilized in every fracturing job.

A sample composition by weight of fracturing fluid is provided in Figure 2-1 [3]; this composition is based on data from the Fayetteville Shale[2]. Based on this data, approximately 90 percent of the fracturing fluid is water; another approximately 9 percent is proppant; the remainder, typically less than 0.5 percent [3] consists of chemical additives listed above.

Barnett Shale is considered to be the first instance of extensive hydraulic fracturing technology use; the technology was later applied in other areas such as the Fayetteville Shale and the Haynesville Shale. Data collected from applications to drill Marcellus Shale wells in New York indicate that the typical fracturing fluid composition for operations in the Marcellus Shale is similar to that provided for the Fayetteville Shale. Even though no horizontal wells have been drilled in the Marcellus Shale in New York, applications filed to date indicate that it is realistic to expect that the composition of fracturing fluids used in the Marcellus Shale would be similar [3].

[2] Similar to the Marcellus Shale, the Fayetteville Shale is a marine shale rich in unoxidized carbon (i.e. a black shale). The two shales are at similar depths, and vertical and horizontal wells have been drilled/fractured at both shales.

Figure 2-1 - Sample Fracturing fluid Composition by Weight [3]



Each product within these twelve classes of additives may be made up of one or more chemical constituents. Table 2-2 is a list of chemical constituents and their CAS numbers, that have been extracted from complete product chemical composition and Material Safety Data Sheets submitted to the NYSDEC for over 200 products used or proposed for use in hydraulic fracturing operations in the Marcellus Shale area of New York. It is important to note that several manufacturers / suppliers provide similar products (i.e. chemicals that would serve the same purpose) for any class of additive. Therefore only a handful of chemicals from Table 2-2 would be utilized in a single well. Table 2-2 represents constituents of all hydraulic-fracturing-related additives submitted to NYSDEC to date for potential use at shale wells in the State.

Data provided to NYSDEC to date indicates similar fracturing fluid compositions for vertically and horizontally drilled wells.

Table 2-2 – Chemical Constituents in Additives/Chemicals[3,4]

CAS Number[5]	Chemical Constituent
2634-33-5	1,2 Benzisothiazolin-2-one / 1,2-benzisothiazolin-3-one
95-63-6	1,2,4 trimethylbenzene
123-91-1	1,4 Dioxane
3452-07-1	1-eicosene
629-73-2	1-hexadecene
112-88-9	1-octadecene
1120-36-1	1-tetradecene
10222-01-2	2,2 Dibromo-3-nitrilopropionamide
27776-21-2	2,2'-azobis-{2-(imidazlin-2-yl)propane}-dihydrochloride
73003-80-2	2,2-Dobromomalonamide
15214-89-8	2-Acrylamido-2-methylpropanesulphonic acid sodium salt polymer
46830-22-2	2-acryloyloxyethyl(benzyl)dimethylammonium chloride
52-51-7	2-Bromo-2-nitro-1,3-propanediol
111-76-2	2-Butoxy ethanol
1113-55-9	2-Dibromo-3-Nitriloprionamide (2-Monobromo-3-nitriilopropionamide)
104-76-7	2-Ethyl Hexanol
67-63-0	2-Propanol / Isopropyl Alcohol / Isopropanol / Propan-2-ol
26062-79-3	2-Propen-1-aminium, N,N-dimethyl-N-2-propenyl-chloride, homopolymer
9003-03-6	2-propenoic acid, homopolymer, ammonium salt
25987-30-8	2-Propenoic acid, polymer with 2 p-propenamide, sodium salt / Copolymer of acrylamide and sodium acrylate
71050-62-9	2-Propenoic acid, polymer with sodium phosphinate (1:1)
66019-18-9	2-propenoic acid, telomer with sodium hydrogen sulfite
107-19-7	2-Propyn-1-ol / Progargyl Alcohol
51229-78-8	3,5,7-Triaza-1-azoniatricyclo[3.3.1.13,7]decane, 1-(3-chloro-2-propenyl)-chloride,
115-19-5	3-methyl-1-butyn-3-ol
127087-87-0	4-Nonylphenol Polyethylene Glycol Ether Branched / Nonylphenol ethoxylated / Oxyalkylated Phenol
64-19-7	Acetic acid
68442-62-6	Acetic acid, hydroxy-, reaction products with triethanolamine
108-24-7	Acetic Anhydride
67-64-1	Acetone
79-06-1	Acrylamide

[3] Table 2-2 is a list of chemical constituents and their CAS numbers that have been extracted from complete chemical compositions and Material Safety Data Sheets submitted to the NYSDEC.

[4] These are the chemical constituents of all chemical additives proposed to be used in New York for hydraulic fracturing operations at shale wells. Only a few chemicals will be used in a single well; the list of chemical constituents used in an individual well will be correspondingly smaller.

[5] Chemical Abstracts Service (CAS) is a division of the American Chemical Society. CAS assigns unique numerical identifiers to every chemical described in the literature. The intention is to make database searches more convenient, as chemicals often have many names. Almost all molecule databases today allow searching by CAS number.

CAS Number[5]	Chemical Constituent
38193-60-1	Acrylamide - sodium 2-acrylamido-2-methylpropane sulfonate copolymer
25085-02-3	Acrylamide - Sodium Acrylate Copolymer or Anionic Polyacrylamide
69418-26-4	Acrylamide polymer with N,N,N-trimethyl-2[1-oxo-2-propenyl]oxy Ethanaminium chloride
15085-02-3	Acrylamide-sodium acrylate copolymer
68551-12-2	Alcohols, C12-C16, Ethoxylated (a.k.a. Ethoxylated alcohol)
64742-47-8	Aliphatic Hydrocarbon / Hydrotreated light distillate / Petroleum Distillates / Isoparaffinic Solvent / Paraffin Solvent / Napthenic Solvent
64743-02-8	Alkenes
68439-57-6	Alkyl (C14-C16) olefin sulfonate, sodium salt
9016-45-9	Alkylphenol ethoxylate surfactants
1327-41-9	Aluminum chloride
73138-27-9	Amines, C12-14-tert-alkyl, ethoxylated
71011-04-6	Amines, Ditallow alkyl, ethoxylated
68551-33-7	Amines, tallow alkyl, ethoxylated, acetates
1336-21-6	Ammonia
631-61-8	Ammonium acetate
68037-05-8	Ammonium Alcohol Ether Sulfate
7783-20-2	Ammonium bisulfate
10192-30-0	Ammonium Bisulphite
12125-02-9	Ammonium Chloride
7632-50-0	Ammonium citrate
37475-88-0	Ammonium Cumene Sulfonate
1341-49-7	Ammonium hydrogen-difluoride
6484-52-2	Ammonium nitrate
7727-54-0	Ammonium Persulfate / Diammonium peroxidisulphate
1762-95-4	Ammonium Thiocyanate
7664-41-7	Aqueous ammonia
121888-68-4	Bentonite, benzyl(hydrogenated tallow alkyl) dimethylammonium stearate complex / organophilic clay
71-43-2	Benzene
119345-04-9	Benzene, 1,1'-oxybis, tetratpropylene derivatives, sulfonated, sodium salts
74153-51-8	Benzenemethanaminium, N,N-dimethyl-N-[2-[(1-oxo-2-propenyl)oxy]ethyl]-, chloride, polymer with 2-propenamide
10043-35-3	Boric acid
1303-86-2	Boric oxide / Boric Anhydride
71-36-3	Butan-1-ol
68002-97-1	C10 - C16 Ethoxylated Alcohol
68131-39-5	C12-15 Alcohol, Ethoxylated
10043-52-4	Calcium chloride
124-38-9	Carbon Dioxide
68130-15-4	Carboxymethylhydroxypropyl guar
9012-54-8	Cellulase / Hemicellulase Enzyme
9004-34-6	Cellulose
10049-04-4	Chlorine Dioxide
77-92-9	Citric Acid

CAS Number[5]	Chemical Constituent
94266-47-4	Citrus Terpenes
61789-40-0	Cocamidopropyl Betaine
68155-09-9	Cocamidopropylamine Oxide
68424-94-2	Coco-betaine
7758-98-7	Copper (II) Sulfate
31726-34-8	Crissanol A-55 (Poly(oxy-1,2-ethanediyl), alpha-hexyl-omega-hydroxy)
14808-60-7	Crystalline Silica (Quartz)
7447-39-4	Cupric chloride dihydrate
1120-24-7	Decyldimethyl Amine
2605-79-0	Decyl-dimethyl Amine Oxide
3252-43-5	Dibromoacetonitrile
25340-17-4	Diethylbenzene
111-46-6	Diethylene Glycol
22042-96-2	Diethylenetriamine penta (methylenephonic acid) sodium salt
28757-00-8	Diisopropyl naphthalenesulfonic acid
68607-28-3	Dimethylcocoamine, bis(chloroethyl) ether, diquaternary ammonium salt
7398-69-8	Dimethyldiallylammonium chloride
25265-71-8	Dipropylene glycol
139-33-3	Disodium Ethylene Diamine Tetra Acetate
5989-27-5	D-Limonene
123-01-3	Dodecylbenzene
27176-87-0	Dodecylbenzene sulfonic acid
42504-46-1	Dodecylbenzenesulfonate isopropanolamine
50-70-4	D-Sorbitol / Sorbitol
37288-54-3	Endo-1,4-beta-mannanase, or Hemicellulase
149879-98-1	Erucic Amidopropyl Dimethyl Betaine
89-65-6	Erythorbic acid, anhydrous
54076-97-0	Ethanaminium, N,N,N-trimethyl-2-[(1-oxo-2-propenyl)oxy]-, chloride, homopolymer
107-21-1	Ethane-1,2-diol / Ethylene Glycol
9002-93-1	Ethoxylated 4-tert-octylphenol
68439-50-9	Ethoxylated alcohol
126950-60-5	Ethoxylated alcohol
67254-71-1	Ethoxylated alcohol (C10-12)
68951-67-7	Ethoxylated alcohol (C14-15)
68439-46-3	Ethoxylated alcohol (C9-11)
66455-15-0	Ethoxylated Alcohols
84133-50-6	Ethoxylated Alcohols (C12-14 Secondary)
68439-51-0	Ethoxylated Alcohols (C12-14)
78330-21-9	Ethoxylated branch alcohol
34398-01-1	Ethoxylated C11 alcohol
61791-12-6	Ethoxylated Castor Oil
61791-29-5	Ethoxylated fatty acid, coco
61791-08-0	Ethoxylated fatty acid, coco, reaction product with ethanolamine
68439-45-2	Ethoxylated hexanol

CAS Number[5]	Chemical Constituent
9036-19-5	Ethoxylated octylphenol
9005-67-8	Ethoxylated Sorbitan Monostearate
9004-70-3	Ethoxylated Sorbitan Trioleate
64-17-5	Ethyl alcohol / ethanol
100-41-4	Ethyl Benzene
97-64-3	Ethyl Lactate
9003-11-6	Ethylene Glycol-Propylene Glycol Copolymer (Oxirane, methyl-, polymer with oxirane)
75-21-8	Ethylene oxide
5877-42-9	Ethyloctynol
68526-86-3	Exxal 13 (Alcohols, C11-14-iso, C13-rich)
61790-12-3	Fatty Acids
68188-40-9	Fatty acids, tall oil reaction products w/ acetophenone, formaldehyde & thiourea
9043-30-5	Fatty alcohol polyglycol ether surfactant
7705-08-0	Ferric chloride
7782-63-0	Ferrous sulfate, heptahydrate
50-00-0	Formaldehyde
29316-47-0	Formaldehyde polymer with 4,1,1-dimethylethyl phenolmethyl oxirane
153795-76-7	Formaldehyde, polymers with branched 4-nonylphenol, ethylene oxide and propylene oxide
75-12-7	Formamide
64-18-6	Formic acid
110-17-8	Fumaric acid
65997-17-3	Glassy calcium magnesium phosphate
111-30-8	Glutaraldehyde
56-81-5	Glycerol / glycerine
9000-30-0	Guar Gum
9000-30-01	Guar Gum
64742-94-5	Heavy aromatic petroleum naphtha
9025-56-3	Hemicellulase
7647-01-0	Hydrochloric Acid / Hydrogen Chloride / muriatic acid
7722-84-1	Hydrogen Peroxide
79-14-1	Hydroxy acetic acid
35249-89-9	Hydroxyacetic acid ammonium salt
9004-62-0	Hydroxyethyl cellulose
5470-11-1	Hydroxylamine hydrochloride
39421-75-5	Hydroxypropyl guar
35674-56-7	Isomeric Aromatic Ammonium Salt
64742-88-7	Isoparaffinic Petroleum Hydrocarbons, Synthetic
64-63-0	Isopropanol
98-82-8	Isopropylbenzene (cumene)
68909-80-8	Isoquinoline, reaction products with benzyl chloride and quinoline
8008-20-6	Kerosene
64742-81-0	Kerosine, hydrodesulfurized
63-42-3	Lactose

CAS Number[5]	Chemical Constituent
64742-95-6	Light aromatic solvent naphtha
1120-21-4	Light Paraffin Oil
14807-96-6	Magnesium Silicate Hydrate (Talc)
1184-78-7	methanamine, N,N-dimethyl-, N-oxide
67-56-1	Methanol
68891-11-2	Methyloxirane polymer with oxirane, mono (nonylphenol) ether, branched
8052-41-3	Mineral spirits / Stoddard Solvent
141-43-5	Monoethanolamine
44992-01-0	N,N,N-trimethyl-2[1-oxo-2-propenyl]oxy Ethanaminium chloride
64742-48-9	Naphtha (petroleum), hydrotreated heavy
91-20-3	Naphthalene
38640-62-9	Naphthalene bis(1-methylethyl)
93-18-5	Naphthalene, 2-ethoxy-
68909-18-2	N-benzyl-alkyl-pyridinium chloride
68139-30-0	N-Cocoamidopropyl-N,N-dimethyl-N-2-hydroxypropylsulfobetaine
7727-37-9	Nitrogen, Liquid form
68412-54-4	Nonylphenol Polyethoxylate
121888-66-2	Organophilic Clays
64742-65-0	Petroleum Base Oil
64741-68-0	Petroleum naphtha
70714-66-8	Phosphonic acid, [[(phosphonomethyl)imino]bis[2,1-ethanediylnitrilobis(methylene)]]tetrakis-, ammonium salt
8000-41-7	Pine Oil
60828-78-6	Poly(oxy-1,2-ethanediyl), a-[3,5-dimethyl-1-(2-methylpropyl)hexyl]-w-hydroxy-
25322-68-3	Poly(oxy-1,2-ethanediyl), a-hydro-w-hydroxy / Polyethylene Glycol
24938-91-8	Poly(oxy-1,2-ethanediyl), α-tridecyl-ω-hydroxy-
51838-31-4	Polyepichlorohydrin, trimethylamine quaternized
56449-46-8	Polyethlene glycol oleate ester
62649-23-4	Polymer with 2-propenoic acid and sodium 2-propenoate
9005-65-6	Polyoxyethylene Sorbitan Monooleate
61791-26-2	Polyoxylated fatty amine salt
127-08-2	Potassium acetate
12712-38-8	Potassium borate
1332-77-0	Potassium borate
20786-60-1	Potassium Borate
584-08-7	Potassium carbonate
7447-40-7	Potassium chloride
590-29-4	Potassium formate
1310-58-3	Potassium Hydroxide
13709-94-9	Potassium metaborate
24634-61-5	Potassium Sorbate
112926-00-8	Precipitated silica / silica gel
57-55-6	Propane-1,2-diol, or Propylene glycol
107-98-2	Propylene glycol monomethyl ether

CAS Number[5]	Chemical Constituent
68953-58-2	Quaternary Ammonium Compounds
62763-89-7	Quinoline,2-methyl-, hydrochloride
15619-48-4	Quinolinium, 1-(phenylmethl),chloride
7631-86-9	Silica, Dissolved
5324-84-5	Sodium 1-octanesulfonate
127-09-3	Sodium acetate
95371-16-7	Sodium Alpha-olefin Sulfonate
532-32-1	Sodium Benzoate
144-55-8	Sodium bicarbonate
7631-90-5	Sodium bisulfate
7647-15-6	Sodium Bromide
497-19-8	Sodium carbonate
7647-14-5	Sodium Chloride
7758-19-2	Sodium chlorite
3926-62-3	Sodium Chloroacetate
68-04-2	Sodium citrate
6381-77-7	Sodium erythorbate / isoascorbic acid, sodium salt
2836-32-0	Sodium Glycolate
1310-73-2	Sodium Hydroxide
7681-52-9	Sodium hypochlorite
7775-19-1	Sodium Metaborate .8H_2O
10486-00-7	Sodium perborate tetrahydrate
7775-27-1	Sodium persulphate
9003-04-7	Sodium polyacrylate
7757-82-6	Sodium sulfate
1303-96-4	Sodium tetraborate decahydrate
7772-98-7	Sodium Thiosulfate
1338-43-8	Sorbitan Monooleate
57-50-1	Sucrose
5329-14-6	Sulfamic acid
112945-52-5	Syntthetic Amorphous / Pyrogenic Silica / Amorphous Silica
68155-20-4	Tall Oil Fatty Acid Diethanolamine
8052-48-0	Tallow fatty acids sodium salt
72480-70-7	Tar bases, quinoline derivs., benzyl chloride-quaternized
68647-72-3	Terpene and terpenoids
68956-56-9	Terpene hydrocarbon byproducts
533-74-4	Tetrahydro-3,5-dimethyl-2H-1,3,5-thiadiazine-2-thione (a.k.a. Dazomet)
55566-30-8	Tetrakis(hydroxymethyl)phosphonium sulfate (THPS)
75-57-0	Tetramethyl ammonium chloride
64-02-8	Tetrasodium Ethylenediaminetetraacetate
68-11-1	Thioglycolic acid
62-56-6	Thiourea
68527-49-1	Thiourea, polymer with formaldehyde and 1-phenylethanone
108-88-3	Toluene
81741-28-8	Tributyl tetradecyl phosphonium chloride

CAS Number[5]	Chemical Constituent
68299-02-5	Triethanolamine hydroxyacetate
112-27-6	Triethylene Glycol
52624-57-4	Trimethylolpropane, Ethoxylated, Propoxylated
150-38-9	Trisodium Ethylenediaminetetraacetate
5064-31-3	Trisodium Nitrilotriacetate
7601-54-9	Trisodium ortho phosphate
57-13-6	Urea
25038-72-6	Vinylidene Chloride/Methylacrylate Copolymer
7732-18-5	Water
1330-20-7	Xylene

Chemical Constituent
Aliphatic acids
Aliphatic alcohol glycol ether
Alkyl Aryl Polyethoxy Ethanol
Alkylaryl Sulfonate
Aromatic hydrocarbons
Aromatic ketones
Oxyalkylated alkylphenol
Petroleum distillate blend
Polyethoxylated alkanol
Polymeric Hydrocarbons
Salt of amine-carbonyl condensate
Salt of fatty acid/polyamine reaction product
Sugar
Surfactant blend

2.5 Selection of Additives

Information available from well operators, service companies, and chemical suppliers indicate that there are a number of breakers, biocides, clay stabilizes, etc. that may be selected from for any hydraulic fracturing operation. The different product options may not be interchangeable because of undesirable chemical reactions that may occur between different classes of chemicals. The actual selection of additives is somewhat driven by the specific operation.

Operators are required to divulge the types of additives, product names, specific chemical constituents, and chemical formulas to be used in a hydraulic fracturing operation before NYSDEC will issue a well permit. The fact that such information is often considered proprietary does not prevent the NYSDEC from requiring full-disclosure of this information. The handling of any information submitted to the NYSDEC and claimed to be a trade secret is governed by the New York State Public Officer’s Law and the Department’s Records Access Regulations.

2.6 Additives Sequence

Several types of additives may be used in a single well; however, they are not used at the same time. The additives are sequenced to elicit a specific fracturing fluid characteristic at different phases of the operation. A typical sequence may include the following:

- Phase 1: Corrosion inhibitors, iron controls and acids are used in the initial stage to reduce rust formation on steel tubing, well casings, tools, and tanks [4]; to prevent precipitation of metal oxides which could plug the shale; and to improve fluid access into the formation, respectively.

- Phase 2: Gelling agent, crosslinker, and other additives are used in the second stage to improve the fracturing fluid's capacity (typically by increasing viscosity) to carry proppant into the fractures. In addition, bactericide/biocide would be used to prevent the growth of bacteria, which can reduce the ability of the fluid to carry proppant into the fractures [5].

- Phase 3: Once the proppant is conveyed to the formation, the proppant needs to be released into the formation. Therefore a breaker is used to reduce the viscosity of the fluid and release the proppant into fractures and to enhance the recovery of the fracturing fluid. Use of friction reducers allows fracturing fluids to be injected at optimum rates. Biocides are also used in this stage to inhibit the growth of organisms that could potentially produce gases such as hydrogen sulfide that could contaminate natural gas. A clay stabilizer may be used to prevent swelling and migration of formation clays which could block pore spaces.

Not all types of additives are used in a single well. The combination of additives and specific chemicals used would depend on the particular shale, well and well operator / service company.

2.7 Summary

Large volumes of water and proppant are used in hydraulic fracturing operations. Small quantities of several additives are used to facilitate and enhance fracturing. This section identified 12 classes of additives that may be used in shale fracturing. These 12 classes may encompass over one thousand chemicals used around the globe. Table 2-2 lists the primary constituents found in approximately 200 products used or proposed for use in hydraulic fracturing operations in New York.

3 FLOWBACK FLUIDS

3.1 Introduction

Flowback is one of several waste fluids generated from a gas well. Waste fluids from a gas well may be grouped into several categories: top-hole fluids; bottom hole fluids; stimulation fluids; and production fluids [6].

- Top-hole fluids consist of ‘waste’ fluids generated due to fresh water aquifers that may be encountered within the first few hundred feet of drilling. Top-hole fluids do not intermingle within the well bore the way bottom hole and stimulation fluids do.
- Bottom-hole fluids typically consist of fluids generated due to deep salt water zones encountered.
- Stimulation / fracturing fluids are waste fluids generated due to the water, proppants and other additives pumped into the shale to improve gas recovery.
- Production fluids (or Produced Water) are the waste fluids produced with natural gas after the well is put into production; their composition is typically similar to bottom hole fluids.

The flowback fluids discussed in this section consist mostly of stimulation fluids and bottom-hole fluids.

3.2 Flowback Fluid Volume

The volume of flowback fluid from a gas well depends on a variety of factors, including the particular shale, the depth and age of the well, and the drilling technique (horizontal vs. vertical).

Typical water usage for hydraulic fracturing is approximately 1 million gallons (MG) per vertical well and between 2.5 and 3.5 MG per horizontal well. Limited data indicate that water usage may be as little as 0.5 MG or as much as 1.5 million gallons (MG) per vertical well, and as much as 6 MG per horizontal well.

Based on limited data reported to NYSDEC and information from operators in Pennsylvania, flowback from Marcellus Shale operations, which includes both vertical and horizontal wells, is approximately 35 - 40 percent of fracturing fluids used[6], with up to 62 percent from a vertical well, and between 9 and 35 percent from horizontal wells reported.

---

[6] Typical flowback from operations based in Marcellus Shale, as estimated by URS Corporation.

3.3 Trends in Flowback Fluid Volume

Flowback occurs over 2-3 weeks after fracturing, and the flowback rate changes with time; the actual rate may depend on a variety of factors. Limited time-series data indicates that approximately 60 percent of the total flowback occurs in the first four days after fracturing. After day 4, the daily flowback rate declines sharply to between approximately 2 – 5 percent of the total flowback for approximately 2 weeks.

3.4 Flowback Fluid Composition

Flowback fluids include the fracturing fluids pumped into the well, and consist of water and additives discussed in the previous section, any new compounds that may have formed due to reactions between additives, and substances mobilized from within the shale formation due to the fracturing operation. Some portion of the proppant may return to the surface with flowback, but operators strive to minimize proppant return: the ultimate goal of hydraulic fracturing is to convey and deposit the proppant within fractures in the shale to maximize gas flow.

Marcellus Shale is of marine origin and, therefore, contains high levels of salt [4]. This is further evidenced by analytical results of flowback provided to NYSDEC by well operators from operations based in Pennsylvania. The results were in different levels of detail. Some companies provided analytical results for one day for several wells, while other companies provided several analytical results for different days of the same well (i.e. time-series). Flowback parameters were organized by Chemicals Abstract Service (CAS) number, whenever available.

Typical classes of parameters present in flowback fluid are [1 and 7]:

- Dissolved Solids (chlorides, sulfates, and calcium)
- Metals (calcium, magnesium, barium, strontium)
- Suspended solids
- Mineral scales (calcium carbonate and barium sulfate)
- Bacteria - acid producing bacteria and sulfate reducing bacteria
- Friction Reducers
- Iron solids (iron oxide and iron sulfide)
- Dispersed clay fines, colloids & silts
- Acid Gases (carbon dioxide, hydrogen sulfide)

A list of parameters detected in a limited set of analytical results is provided in the following table. Typical concentrations of parameters, based on limited data from PA and WV, are provided in Table 4-5.

Table 3-1 - Parameters present in a limited set of flowback analytical results

CAS#	Parameters Detected in Flowback from PA and WV Operations
00067-64-1	Acetone
07439-90-5	Aluminum
07440-36-0	Antimony
07664-41-7	Aqueous ammonia
07440-38-2	Arsenic
07440-39-3	Barium
00071-43-2	Benzene
07440-41-7	Beryllium
00117-81-7	Bis(2-ethylhexyl)phthalate
07440-42-8	Boron
24959-67-9	Bromide
00075-25-2	Bromoform
07440-43-9	Cadmium
07440-70-2	Calcium
00124-38-9	Carbon Dioxide
00124-48-1	Chlorodibromomethane
07440-47-3	Chromium
07440-48-4	Cobalt
07440-50-8	Copper
00057-12-5	Cyanide
00075-27-4	Dichlorobromomethane
00100-41-4	Ethyl Benzene
16984-48-8	Fluoride
07439-89-6	Iron
07439-92-1	Lead
07439-93-2	Lithium
07439-95-4	Magnesium
07439-96-5	Manganese
07439-97-6	Mercury
00074-83-9	Methyl Bromide
00074-87-3	Methyl Chloride
07439-98-7	Molybdenum
00091-20-3	Naphthalene
07440-02-0	Nickel
00108-95-2	Phenol
57723-14-0	Phosphorus
07440-09-7	Potassium
07782-49-2	Selenium
07440-22-4	Silver
07440-23-5	Sodium
07440-24-6	Strontium
14808-79-8	Sulfate
14265-45-3	Sulfite
00127-18-4	Tetrachloroethylene
07440-28-0	Thallium
07440-32-6	Titanium
00108-88-3	Toluene
07440-62-2	Vanadium
07440-66-6	Zinc

Parameters Detected in Flowback from PA and WV Operations

Alkalinity
Alkalinity, Carbonate, as $CaCO_3$
Alpha radiation
Aluminum, Dissolved
Barium Strontium P.S.
Barium, Dissolved
Beta radiation
Bicarbonates
Biochemical Oxygen Demand
Cadmium, Dissolved
Calcium, Dissolved
Cesium 137
Chemical Oxygen Demand
Chloride
Chromium (VI)
Chromium (VI), dissolved
Chromium, (III)
Chromium, Dissolved
Cobalt, dissolved
Coliform
Color
Conductivity
Hardness
Heterotrophic plate count
Iron, Dissolved
Lithium, Dissolved
Magnesium, Dissolved
Manganese, Dissolved
Nickel, Dissolved
Nitrate, as N
Nitrogen, Total as N
Oil and Grease
Petroleum hydrocarbons
pH
Phenols
Potassium, Dissolved
Radium
Radium 226
Radium 228
Salt
Scale Inhibitor
Selenium, Dissolved
Silver, Dissolved
Sodium, Dissolved
Strontium, Dissolved
Sulfide
Surfactants
Total Alkalinity
Total Dissolved Solids
Total Kjeldahl Nitrogen
Total Organic Carbon

Parameters Detected in Flowback from PA and WV Operations
Total Suspended Solids
Xylenes
Zinc, Dissolved
Zirconium

Note that the parameters listed in Table 2-2 are based on the composition of additives used or proposed for use in New York. Table 3-1 parameters are based on analytical results of flowback from operations in Pennsylvania or West Virginia. All information is for operations in the Marcellus Shale.

Some parameters found in analytical results are due to additives used in fracturing, some are due to reactions between different additives, while others may have been mobilized from within the formation; still other parameters may have been contributed from both sources. Further study would be required to identify the specific origin of each parameter.

3.5 Temporal Trends in Flowback Fluids Composition

The composition of flowback changes with time, depending on a variety of factors. Limited time-series Marcellus Shale flowback data from Pennsylvania operations indicate that:

- The concentrations of total dissolved solids (TDS), chloride, and barium increase [6];
- The levels of radioactivity increase[7], and sometimes exceed Maximum Contaminant Levels (MCLs) (see Table 4-2 - Primary Drinking Water Standards);
- Calcium and magnesium hardness increases;
- Iron concentrations increase, unless iron-controlling additives are used;
- Sulfate levels decrease;
- Alkalinity levels decrease, likely due to use of acid; and
- Concentrations of metals increase[8].

Available literature [1] corroborates the above summary regarding the changes in composition with time for TDS, chlorides, and barium. Fracturing fluids pumped into the well, and mobilization of materials within the shale may be contributing to the changes

[7] Limited data from operations in PA and WV have reported the following ranges of radioactivity: alpha 22.41 – 18950 pCi/L; beta 9.68 – 7445 pCi/L; Radium^{226} 2.58 - 33 pCi/L.

[8] Metals such as aluminum, antimony, arsenic, barium, boron, cadmium, calcium, cobalt, copper, iron, lead, lithium, magnesium, manganese, molybdenum, nickel, potassium, radium, selenium, silver, sodium, strontium, thallium, titanium, and zinc have been reported in flowback analyses. It is important to note that each well did not report the presence of all these metals.

seen in hardness, sulfate, and metals. The specific changes would likely depend on the shale formation, fracturing fluids used and fracture operations control.

3.6 Summary

Flowback consist of fracturing fluids injected into the shale formation, new compounds that may form due to decomposition or reactions between additives, and mobilization of substances in the shale formation. The flowback rate and composition change with time. Typically, approximately 35-40 percent of fracturing fluids return to the surface over a period of approximately 2-3 weeks. Flowback from almost all shale formations appears to have high concentrations of TDS (primarily due to chlorides); flowback from the Marcellus Shale consists of high concentrations of TDS and barium, and several other parameters (reported in Table 3-1).

4 SUFFICIENCY OF REGULATIONS AND GUIDELINES

This section summarizes existing environmental regulations and guidelines that govern the use of water associated with well drilling and hydraulic fracturing in New York State. The sufficiency of these regulations and guidelines in regulating these activities may then be assessed.

4.1 Background

Water for use at the well pads may be obtained from a variety of sources including surface water, groundwater, public water supplies, and treatment system effluents. The water is trucked or pumped to the well pads and stored in tanks, pits or engineered impoundments[9] until used for any of a variety of purposes including well drilling and completion, testing of pipelines, and dust control. By far, the largest use of water is for hydraulic fracturing. Hydraulic fracturing of the Marcellus Shale will require larger volumes of water to fracture the rocks than have previously been utilized in fracturing operations at other gas wells in New York. Each well may use between 0.5 and 6 million gallons of water.

As discussed in Section 2.4 hydraulic fracturing fluid typically contains additives which increase the effectiveness of the fracturing operations by ensuring that the proppant is delivered and remains in the fractures, while preventing corrosion of the well casing materials. The well must be constructed so that the fracturing fluid is only pumped into the zone targeted for fracturing.

A large portion of the fluid pumped during hydraulic fracturing remains in the shale formation (i.e., is considered consumed), but a significant portion (approximately 35 to 40 percent) normally returns to the surface as flowback and must be managed in accordance with applicable regulations. Existing well construction and fluid containment requirements are intended to prohibit any uncontrolled release of fluids to the environment.

The oil and gas industry has provided information and data to NYSDEC regarding the formulation of additives that may be used. The constituents of the fluid may then be subjected to evaluation to identify potential areas of concern where additional regulatory controls may be needed to sufficiently protect the environment.

Currently, applicants seeking permits to drill horizontal Marcellus Shale wells where high-volume hydraulic fracturing will be utilized are required to complete a site-specific Environmental Impact Statement (EIS), which must take into account the same issues being considered in the Supplemental GEIS process and must be consistent with the

[9] A pit is typically associated with just one well pad, whereas an engineered impoundment is a centralized temporary water storage location that services several well pads.

requirements of the State Environmental Quality Review Act and the State Environmental Conservation Law (ECL).

The ECL is the body of law that established NYSDEC and authorizes its programs; the State Public Health Law similarly relates to the New York State Department of Health (NYSDOH). The regulations that implement the ECL and the Public Health Law are contained in the New York Codes, Rules and Regulations (NYCRR). Of relevance to this project are the regulations contained in Title 6 - Environmental Conservation (6NYCRR), and Title 10 – Health (10NYCRR). New York environmental and health regulations draw in large measure from federal regulations that implement the Clean Water Act (CWA), the Safe Drinking Water Act (SDWA), and other legislation. A summary of the applicable regulations follows.

4.2 Water Use Classifications

Surface water and groundwater sources are classified by the best type use that is or could be made of the source. The preservation of these uses is a regulatory requirement in New York. 6NYCRR Part 701 identifies and assigns the classifications of surface waters and groundwaters in New York [8].

In general, the discharge of sewage, industrial waste or other wastes may not cause impairment of the best usages of the receiving water as specified by the water classifications at the location of discharge and at other locations that may be affected by such discharge. In addition, for higher quality waters, NYSDEC may impose discharge restrictions (described below) in order to protect public health, or the quality of distinguished value or sensitive waters.

A table of water use classifications, usages, and restrictions follows.

Table 4-1 - New York Water Use Classifications [8]

Water Use Class	Water Type	Best Usages and Suitability	Notes
N	Fresh Surface	1, 2	
AA-Special	Fresh Surface	3, 4, 5, 6	Note a
A-Special	Fresh Surface	3, 4, 5, 6	Note b
AA	Fresh Surface	3, 4, 5, 6	Note c
A	Fresh Surface	3, 4, 5, 6	Note d
B	Fresh Surface	4, 5, 6	
C	Fresh Surface	5, 6, 7	
D	Fresh Surface	5, 7, 8	
SA	Saline Surface	4, 5, 6, 9	
SB	Saline Surface	4, 5, 6,	
SC	Saline Surface	5, 6, 7	
I	Saline Surface	5, 6, 10	
SD	Saline Surface	5, 8	
GA	Fresh Groundwater	11	
GSA	Saline Groundwater	12	Note e
GSB	Saline Groundwater	13	Note f
Other – T/TS	Fresh Surface	Trout/Trout Spawning	
Other – Discharge Restriction Category	All Types	N/A	See descriptions below

Best Usage/Suitability Categories [Column 3 of Table 4-1 above]

1. Best usage for enjoyment of water in its natural condition and, where compatible, as a source of water for drinking or culinary purposes, bathing, fishing, fish propagation, and recreation
2. Suitable for shellfish and wildlife propagation and survival, and fish survival
3. Best usage as source of water supply for drinking, culinary or food processing purposes
4. Best usage for primary and secondary contact recreation
5. Best usage for fishing.
6. Suitable for fish, shellfish, and wildlife propagation and survival.
7. Suitable for primary and secondary contact recreation, although other factors may limit the use for these purposes.
8. Suitable for fish, shellfish, and wildlife survival (not propagation)
9. Best usage for shellfishing for market purposes
10. Best usage for secondary, but not primary, contact recreation
11. Best usage for potable water supply
12. Best usage for source of potable mineral waters, or conversion to fresh potable waters, or as raw material for the manufacture of sodium chloride or its derivatives or similar products

13. Best usage is as receiving water for disposal of wastes (may not be assigned to any groundwaters of the State, unless the commissioner finds that adjacent and tributary groundwaters and the best usages thereof will not be impaired by such classification)

Discharge Restriction Categories – Based on a number of relevant factors and local conditions, per 6 NYCRR 701.20, discharge restriction categories may be assigned to: (1) waters of particular public health concern; (2) significant recreational or ecological waters where the quality of the water is critical to maintaining the value for which the waters are distinguished; and (3) other sensitive waters where NYSDEC has determined that existing standards are not adequate to maintain water quality.

1. Per 6 NYCRR 701.22, new discharges may be permitted for waters where discharge restriction categories are assigned when such discharges result from environmental remediation projects, from projects correcting environmental or public health emergencies, or when such discharges result in a reduction of pollutants for the designated waters. In all cases, best usages and standards will be maintained.

2. Per 6 NYCRR 701.23, except for storm water discharges, no new discharges shall be permitted and no increase in any existing discharges shall be permitted.

3. Per 6 NYCRR 701.24, specified substance shall not be permitted in new discharges, and no increase in the release of the specified substance shall be permitted for any existing discharges. Storm water discharges are an exception to these restrictions. The substance will be specified at the time the waters are designated.

Notes [Column 4 of Table 4-1 above]

a. These waters shall contain no floating solids, settleable solids, oil, sludge deposits, toxic wastes, deleterious substances, colored or other wastes or heated liquids attributable to sewage, industrial wastes or other wastes; there shall be no discharge or disposal of sewage, industrial wastes or other wastes into these waters; these waters shall contain no phosphorus and nitrogen in amounts that will result in growths of algae, weeds and slimes that will impair the waters for their best usages; there shall be no alteration to flow that will impair the waters for their best usages; there shall be no increase in turbidity that will cause a substantial visible contrast to natural conditions.

b. This classification may be given to those international boundary waters that, if subjected to approved treatment, equal to coagulation, sedimentation, filtration and disinfection with additional treatment, if necessary, to reduce naturally present impurities, meet or will meet NYSDOH drinking water standards and are or will be considered safe and satisfactory for drinking water purposes.

c. This classification may be given to those waters that if subjected to pre-approved disinfection treatment, with additional treatment if necessary to remove naturally present impurities, meet or will meet NYSDOH drinking water standards and are or will be considered safe and satisfactory for drinking water purposes.

d. This classification may be given to those waters that, if subjected to approved treatment equal to coagulation, sedimentation, filtration and disinfection, with additional treatment if necessary to reduce naturally present impurities, meet or will meet NYSDOH drinking water standards and are or will be considered safe and satisfactory for drinking water purposes.

e. Class GSA waters are saline groundwaters. The best usages of these waters are as a source of potable mineral waters, or conversion to fresh potable waters, or as raw material for the manufacture of sodium chloride or its derivatives or similar products.

f. Class GSB waters are saline groundwaters that have a chloride concentration in excess of 1,000 milligrams per liter or a total dissolved solids concentration in excess of 2,000 milligrams per liter; it shall not be assigned to any groundwaters of the State, unless the NYSDEC finds that adjacent and tributary groundwaters and the best usages thereof will not be impaired by such classification.

Water use classifications are assigned to surface waters and groundwaters throughout New York. Regulations governing gas drilling in the Marcellus Shale formation are intended to prevent the degradation of water quality that would impair the best use or suitability as assigned.

4.3 Drinking Water

The protection of drinking water sources and supplies is extremely important for the maintenance of public health, and the protection of this water use type is paramount. Chemical or biological parameters that are inadvertently released into surface water or groundwater sources that are designated for drinking water use can adversely impact or disqualify such usage if there are constituents that conflict with applicable standards for drinking water. These standards are discussed below.

4.3.1 Federal

The SDWA, passed in 1974 and amended in 1986 and 1996, gives the United States Environmental Protection Agency (USEPA) the authority to set drinking water standards. There are two categories of drinking water standards: primary and secondary. Primary standards are legally enforceable and apply to public water supply systems. The secondary standards are non-enforceable guidelines that are recommended as standards for drinking water. Public water supply systems are not required to comply with secondary standards unless a state chooses to adopt them as enforceable standards. New York encourages but does not enforce the secondary standards.

The primary standards are designed to protect drinking water quality by limiting the levels of specific contaminants that can adversely affect public health and are known or anticipated to occur in drinking water. The determinations of which contaminants to regulate are based on peer-reviewed science research and data that evaluates the following factors [9]:

- Occurrence in the environment and in public water supply systems at levels of concern;
- Human exposure and risks of adverse health effects in the general population and sensitive subpopulations;

- Analytical methods of detection;
- Technical feasibility; and
- Impacts of regulation on water systems, the economy and public health.

After reviewing health effects studies and considering the risk to sensitive subpopulations, USEPA sets a non-enforceable Maximum Contaminant Level Goal (MCLG) for each contaminant as public health goals. This is the maximum level of a contaminant in drinking water at which no known or anticipated adverse effect on the health of persons would occur, and which allows an adequate margin of safety. MCLGs only consider public health and may not be achievable given the limits of detection and best available treatment technologies. The SDWA prescribes limits in terms of Maximum Contaminant Levels (MCLs) or Treatment Techniques, which are achievable at a reasonable cost, to serve as the primary drinking water standards. A contaminant generally is classified as microbial in nature or as a carcinogenic/non-carcinogenic chemical [10].

Secondary contaminants may cause cosmetic effects (such as skin or tooth discoloration) or aesthetic effects (such as taste, odor, or color) in drinking water. The numerical secondary standards are designed to control these effects to a level desirable to consumers [11].

Table 4-2 and Table 4-3, respectively at the end of this section, list contaminants regulated by federal primary and secondary drinking water standards [10].

In addition to the primary and secondary standards, the USEPA, on March 2, 1998, published a National Drinking Water Contaminant Candidate List (CCL), which lists contaminants that are [12]:

- Not already regulated under SDWA, but nevertheless may have adverse health effects;
- Are known or anticipated to occur in public water systems; and
- May require regulations under SDWA.

Contaminants on the CCL are prioritized and studied, including monitoring for presence/level of selected contaminants[10] in selected existing larger public water supply systems. If, after the requisite studies and monitoring are completed, the USEPA determines regulations are necessary, then the USEPA proceeds with drafting them. Every five years, USEPA will repeat the cycle of revising the CCL, making regulatory determinations for contaminants and identifying contaminants for unregulated monitoring. In addition, every six years, USEPA will re-evaluate existing regulations to determine if modifications are necessary [13].

---

[10] Most of the unregulated contaminants with potential of occurring in drinking water are pesticides and microbes.

In most cases, the USEPA delegates responsibility for implementing drinking water standards to the states.

4.3.2 New York State

In New York, a state with delegated authority in this area, drinking water is addressed in Article 15, Title 15 of the ECL and administered by the NYSDEC via implementing regulations contained in Part 601 of 6NYCRR.

Anyone planning to operate or operating a public water supply system must obtain a Water Supply Permit from NYSDEC before undertaking any of the regulated activities.

Contact with NYSDEC and submission of a Water Supply Permit application will automatically involve the NYSDOH. The NYSDOH has a regulatory role in water quality and other sanitary aspects of a project relating to human health. Through the State Sanitary Code (Chapter 1 of 10NYCRR), the NYSDOH oversees the suitability of water for human consumption. Section 5-1.30 of 10 NYCRR prescribes the required treatment for public water systems, which at a minimum includes filtration and disinfection. To assure the safety of drinking water in New York, NYSDOH, in cooperation with its partners, the county health departments, regulates the operation, design and quality of public water supplies; assures water sources are adequately protected, and sets standards for constructing individual water supplies.

The NYSDOH regulates contaminants consistent with the national drinking water standards. Section 5-1.51 of 10 NYCRR prescribes the maximum contaminant levels, maximum residual disinfectant levels and treatment technique requirements, which are listed in section 5-1.52 tables 1 through 7 of 10 NYCRR. These tables replicate the national primary and secondary standards and CCL. A comparison of constituents contained in hydraulic fracturing fluids and the contaminants listed in these tables is provided in Table 4-4.

It should be noted that the federal Energy Policy Act of 2005 amended the Underground Injection Control (UIC) provisions of the SDWA to exclude hydraulic fracturing from the definition of "underground injection." The objective of the federal UIC program is to protect underground sources of drinking water from contamination by underground injection of hazardous and non-hazardous fluids. However, protection of groundwater resources during oil and gas extraction activities is a responsibility of state government, and the cited federal amendment does not diminish the NYSDEC's authority over oil and gas well development in New York, including oversight of hydraulic fracturing activities to ensure protection of potable groundwater resources.

4.4 Discharge Limits – SPDES

The direct or indirect discharge of flowback that includes residuals from additives is subject to regulation under New York’s State Pollutant Discharge Elimination System

(SPDES). Limitations on discharges from point sources, which are derived from federal, regional, and state standards and programs, are imposed in New York via the SPDES permit program. The USEPA has approved New York's program for the control of wastewater and stormwater discharges in accordance with the Clean Water Act (CWA). Under New York State law, the SPDES program is broader in scope than the CWA in that it controls point source discharges to groundwaters as well as surface waters. Discharges related to gas drilling activities are subject to these controls.

Applicable water quality standards and effluent limitations are those State and Federal water quality standards and effluent limitations to which a discharge is subject under the CWA or State law, including but not limited to water quality standards, effluent limitations, best management practices, standards of performance, toxic effluent standards and prohibitions, pretreatment standards, and ocean discharge criteria.

Per 6 NYCRR Section 750-1.3, certain discharges are absolutely prohibited, including any radiological, chemical or biological warfare agent or high-level radioactive waste, any obstruction to anchorage or navigation, and other highly objectionable, conflicting or non-compliant discharges.

Subsection (a) of 6 NYCRR Section 750-1.11 covers the provisions of SPDES permits and lists the citations for the various effluent limitations from the Federal Register (FR) and the Code of Federal Regulations (CFR). NYSDEC is responsible to administer these applicable effluent limitations and other requirements in the SPDES permits, whenever applicable, as required by the CWA and as may be promulgated by the NYSDEC. These include the following:

(1) Best Practicable Control Technology currently available (BPT) effluent limitations under Section 301 of the CWA and 40 CFR Parts 120, 125, 133 and 405-471, inclusive, (see section 750-1.24 of this Part);

(2) Best Conventional Pollutant Control Technology (BCT) new source performance standards (NSPS), and other new source performance standards under Section 306 of the CWA and 40 CFR Parts 122.29, 129 and 405-471, inclusive (see section 750-1.24 of this Part);

(3) Best Available Technology (BAT) effluent limitation guidelines, effluent prohibitions, and pretreatment standards for existing sources under Section 307 of the CWA and 40 CFR Parts 129 and 405-471, inclusive (see section 750-1.24 of this Part);

(4) Ocean discharge criteria adopted by the Federal government pursuant to Section 403 of the CWA and 40 CFR Part 125, sections 125.120 - 125.124 (see section 750-1.24 of this Part);

(5) Any more stringent limitations, including those:

(i) Necessary to meet water quality standards, guidance values, effluent limitations or schedules of compliance, established pursuant to any state law or regulation consistent with Section 510 of the CWA, or the requirements of 40 CFR Part 132 (see section 750-1.24 of this Part);

(ii) Necessary to implement a total maximum daily load/waste load allocation/load allocation established pursuant to Section 303(d) of the CWA and 40 CFR Part 130.7 (see section 750-1.24 of this Part); or

(iii) Necessary to meet any other State or Federal law or regulation;

(6) Any more stringent requirements necessary to comply with a plan approved pursuant to Section 208(b) of the CWA and 40 CFR Part 35 (see section 750-1.24 of this Part):

(7) Prior to promulgation by the administrator of applicable effluent standards and limitations, BPT effluent limitations and such conditions as the commissioner determines are necessary to carry out the provisions of this Part pursuant to Section 402 of the CWA and 40 CFR Part 125 (see section 750-1.24 of this Part).

(8) As provided in Section 402(g) of the CWA (see section 750-1.24 of this Part), if the SPDES permit is for the discharge of pollutants into the navigable waters of the State from a vessel or other floating craft, any applicable regulations promulgated by the U.S. Department of Commerce, establishing specifications for safe transportation, handling, carriage, storage, and stowage of pollutants.

(9) Unless otherwise required or authorized by this Part, the provisions or requirements of 40 CFR. 122.23 Concentrated animal feeding operations, 40 CFR. Part 122.24 - Concentrated aquatic animal production facilities, 40 CFR Part 122.25 - Aquaculture projects, 40 CFR Parts 122.26, 122.30 to 122.37, and 122.42(c) & (d) - Storm Water Discharges, 40 CFR Part 122.27 - Silvicultural activities (applicable to SPDES), 40 CFR Part 122.44 - Establishing limitations, standards, and other permit conditions, 40 CFR Part 122.45 - Calculating NPDES permit conditions, 40 CFR Part 125 - Criteria and Standards for NPDES, 40 CFR Part 133 - Secondary Treatment Regulation, 40 CFR Part 401 - General Provisions and 40 CFR Part 403 - General Pretreatment Regulations, except 40 CFR Part 403.10 (see section 750-1.24 of this Part).

(10) 40 CFR 122.50 (see section 750-1.24 of this Part).

(11) The requirements or provisions of this Part.

Subsection (b) of 6NYCRR Section 750-1.11 covers industrial waste discharges into publicly owned treatment works, which must comply with toxic effluent limitations and pretreatment standards and with monitoring, reporting, recording, sampling and entry requirements provided by Section 307 of the CWA and 40 CFR Parts 129 and 405-471, inclusive; and Section 308 of the CWA and 40 CFR Parts 122 and 125 (see section 750-1.24 of this Part); or ECL Article 17, or adopted pursuant to ECL Article 17 of this Title.

The SPDES permit application requires any applicant to provide analytical results for several classes of pollutants listed in the following tables:

Table 6 - Priority Pollutants;
Table 7 - Other Significant Pollutants with NYSDEC Standards/Guidance Values and USEPA/NYSDEC Promulgated Analytical Methods;
Table 8 - Other Significant Pollutants with USEPA/NYSDEC Promulgated Analytical Methods;
Table 9 - Other Significant Pollutants with NYSDEC Standards/Guidance Values; and
Table 10 - Other Pollutants and Hazardous Substances Required to be Identified in ICS by Applicants if Present at Facility in Significant Levels.

4.5 Ambient Water Quality Standards and Guidance Values and Groundwater Effluent Limitations

Included in the above discussion are those rules and regulations that establish standards that generally apply to industrial activities, but that also have applicability to the oil, gas, and solution mining industrial category. In addition, a guidance value may be used where a standard for a substance or group of substances has not been established for a particular water class and type of value [53].

Division of Water Technical and Operational Guidance Series 1.1.1 (TOGS111) - Ambient Water Quality Standards and Guidance Values and Groundwater Effluent Limitations is a compilation of ambient water quality guidance values and groundwater effluent limitations for use where there are no standards (in 6 NYCRR 703.5) or regulatory effluent limitations (in 6 NYCRR 703.6).

4.6 Lists of Chemicals in Additives and Flowback Addressed in NY Regulations or Guidances

Table 4-4, at the end of this section, lists chemical constituents of additives and parameters found in a limited number of analytical samples of flowback fluids received via NYSDEC. Columns 5-9 of Table 4-4 indicate if any of these chemicals/parameters are regulated by the federal primary or secondary drinking water standards, covered in Tables 6-10 of the SPDES program, or in Table 1 or 5 of TOGS111.

Table 4-5 lists parameters found in limited flowback analyses from PA and WV that are regulated in NY. Column 3 is the number of samples that analyzed for the particular parameter; column 4 is the number in which the parameter was detected. Columns 5, 6 and 7 provide the minimum, median and maximum concentrations detected.

Table 4-6 lists parameters found in limited flowback analyses from PA and WV that are not regulated in NY. Column 2 is the number of samples that analyzed for the particular parameter; column 3 is the number in which the parameter was detected. Table 4-7 provides basic statistics for these parameters; however, given the limited number of analyses performed on these parameters, the results and statistics should be used with caution.

4.7 Rules and Regulations Applicable to Oil, Gas, and Solution Mining Category

4.7.1 Federal

40 CFR Part 435 provides guidelines on effluent limitations for the Oil and Gas Extraction Point Source Category. These guidelines are taken into consideration when the permitting authority develops discharge permit limitations for a point source discharger in this category. Subpart C of 40 CFR 435 specifically applies to facilities engaged in the production, field exploration, drilling, well completion and well treatment in the oil and gas extraction industry that are located on land (i.e., excludes offshore and coastal locations).

The applicable limits in this subcategory reflect BPT: there shall be no discharge of waste water pollutants into navigable waters from any source associated with production, field exploration, drilling, well completion, or well treatment (*i.e.*, produced water, drilling muds, drill cuttings, and produced sand).

4.7.2 New York State

NYSDEC's Division of Mineral Resources administers regulations and a permitting program to mitigate to the greatest extent possible any potential environmental impact of gas drilling and well operation.

6 NYCCR Part 554 addresses drilling practices applicable to oil, gas, and solution salt mining activities. Subpart 554.1 prescribes requirements for pollution and migration prevention. These requirements include:

- The prevention of pollution associated with the drilling, casing and completion program adopted for any well.
- A prohibition on pollution of the land and/or of fresh surface water or fresh groundwater resulting from exploration or drilling.
- Prior to the issuance of a well-drilling permit for any operation in which the probability exists that brine, salt water or other polluting fluids will be produced or obtained during drilling operations in sufficient quantities to be deleterious to the surrounding environment, the need for the operator to submit and receive approval of a plan for the environmentally safe and proper ultimate disposal of such fluids (excluding drilling muds, which, as specified by regulation, are not considered to be polluting fluids for the purposes of 6 NYCRR 554.1(c)(1)).
    - Depending on the method of disposal chosen by the applicant, a permit for discharge and/or disposal may be required by the NYSDEC in addition to the well-drilling permit.

    - An applicant may also be required to submit an acceptable contingency plan, the use of which shall be required if the primary plan is unsafe or impracticable at the time of disposal.

- A prohibition on the impounding of brine or salt water in an earthen pit where the soil underlying the pit is porous and/or is closely underlaid by a gravel, rock or sand stratum unless the pit is lined with watertight material.

    - Brine or salt water may be temporarily stored prior to disposal in any watertight tank, container or an earthen pit, if underlaid by soil such as heavy clay or hardpan.

    - The tank, container or earthen pit must be constructed and maintained so as to prevent escape of any fluids, including any amounts that may be added by natural precipitation.

    - Storage of brine, salt water or other polluting fluids in such watertight tanks or earthen pits, prior to disposal, is limited to a maximum of 45 days after cessation of drilling operations, unless NYSDEC approves an extension.

- The installation of surface casing in all wells to a depth below the deepest potable fresh water level.

    - The drilling, casing and completion program adopted for any well must be such as to:

        - Prevent the migration of oil, gas or other fluids from one pool or stratum to another; and

        - Exclude oil, gas or other fluids from any underground mining properties or rights and to protect them in accordance with prudent operations.

- ECL23-0305(8)(d) provides authority to NYSDEC to require the operator to remedy any contamination of a water supply well, and ECL 71-1307 provides authority to direct a violator to “reclaim and repair” any impairment to a water supply well.

The regulation summarized above is supplemented by required casing and cementing practices, enforced as permit conditions on each drilling permit. Surface casing must extend at least 75 feet beyond the deepest fresh water zone, or 75 feet into competent rock, whichever is deeper [14]. In primary and principal aquifers, surface casing must be set at least 100 feet below the deepest fresh water zone and at least 100 feet into bedrock. Additionally, as stated in the GEIS (p. 9-32), although the cited regulations do mention clay and hardpan as options in pit construction, NYSDEC has consistently required plastic liners in all temporary earthen drilling pits [15].

4.8 Other Agencies and Activities with Jurisdiction

New York State is a member of compacts established to regulate and protect important interstate water resources. These include the Susquehanna River Basin Commission, the Delaware River Basin Commission, and the Great Lakes Commission.

In addition, New York has specific programs, plans, and procedures in place that are focused on maintaining or improving ambient water quality in targeted watersheds. These include total maximum daily loads, and state or local watershed management or protection plans.

Although these commissions, programs, plans, and procedures carry the force of law, they are specific to individual water bodies or watersheds and, therefore, are not included in this review.

The Emergency Planning and Community Right-to-Know Act (EPCRA) applies to the manufacturing sector, in which the oil and gas extraction activities do not fall, and are not among the additional industry sectors added to EPCRA in 1997. However, existing well construction and fluid containment requirements sufficiently prohibit any uncontrolled release of fluids to the environment. Also, well permit Applicants are required to submit information on hydraulic fracturing fluid composition prior to well permit issuance, subject to regulations that protect information identified by Applicants as trade secret or confidential commercial information.

Additional environmental laws exist to address other activities related to gas well drilling in the New York Marcellus Shale area. These include the Resource Conservation and Recovery Act (RCRA) regarding hazardous waste, the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) regarding toxic substances, and the Clean Air Act (CAA) regarding emissions. A review of the federal and New York regulations that implement these laws and their applicability to the oil and gas industry is beyond the scope of this review.

4.9 Conclusions

This section provides a summary of federal and New York State environmental regulations and guidelines that apply to gas well drilling and extraction in the New York portion of Marcellus Shale region related to water use. They are intended to address concerns that the oil and gas industry may not be fully subject to certain key provisions of the SWDA, CWA, and other water resource-related environmental laws.

This review provides information regarding the sufficiency of regulatory controls in place in New York to protect specified water uses, including drinking water sources, from drilling activities, injection of fluids for hydraulic fracturing, and management of flowback or brines that flow back to surface during well development or operation. These controls are implemented in the permitting process for well drilling and completion, and for point source discharges via the SPDES program.

Table 4-2 - Primary Drinking Water Standards

Microorganisms

Contaminant	MCLG (mg/L)	MCL or TT (mg/L)
Cryptosporidium	0	TT
Giardia lamblia	0	TT
Heterotrophic plate count	n/a	TT
Legionella	0	TT
Total Coliforms (including fecal coliform and E. coli)	0	5%
Turbidity	n/a	TT
Viruses (enteric)	0	TT

MCLG: Maximum contaminant level goal
MCL: Maximum contaminant level
TT: Treatment technology

Disinfection Byproducts

Contaminant	MCLG (mg/L)	MCL or TT (mg/L)
Bromate	0	0.01
Chlorite	0.8	1
Haloacetic acids (HAA5)	n/a	0.06
Total Trihalomethanes (TTHMs)	n/a	0.08

Disinfectants

Contaminant	MRDLG (mg/L)	MRDL (mg/L)
Chloramines (as Cl_2)	4.0	4.0
Chlorine (as Cl_2)	4.0	4.0
Chlorine dioxide (as ClO_2)	0.8	0.8

MRDL: Maximum Residual Disinfectant Level
MRDLG: Maximum Residual Disinfectant Level Goal

Inorganic Chemicals

Contaminant	CAS number	MCLG (mg/L)	MCL or TT (mg/L)
Antimony	07440-36-0	0.006	0.006
Arsenic	07440-38-2	0	0.01 as of 01/23/06
Asbestos (fiber >10 micrometers)	01332-21-5	7 million fibers per liter	7 MFL
Barium	07440-39-3	2	2
Beryllium	07440-41-7	0.004	0.004
Cadmium	07440-43-9	0.005	0.005
Chromium (total)	07440-47-3	0.1	0.1
Copper	07440-50-8	1.3	TT; Action Level=1.3
Cyanide (as free cyanide)	00057-12-5	0.2	0.2
Fluoride	16984-48-8	4	4
Lead	07439-92-1	0	TT; Action Level=0.015

Inorganic Chemicals

Contaminant	CAS number	MCLG (mg/L)	MCL or TT (mg/L)
Mercury (inorganic)	07439-97-6	0.002	0.002
Nitrate (measured as Nitrogen)		10	10
Nitrite (measured as Nitrogen)		1	1
Selenium	07782-49-2	0.05	0.05
Thallium	07440-28-0	0.0005	0.002

Organic Chemicals

Contaminant	CAS number	MCLG (mg/L)	MCL or TT (mg/L)
Acrylamide	00079-06-1	0	TT
Alachlor	15972-60-8	0	0.002
Atrazine	01912-24-9	0.003	0.003
Benzene	00071-43-2	0	0.005
Benzo(a)pyrene (PAHs)	00050-32-8	0	0.0002
Carbofuran	01563-66-2	0.04	0.04
Carbon tetrachloride	00056-23-5	0	0.005
Chlordane	00057-74-9	0	0.002
Chlorobenzene	00108-907	0.1	0.1
2,4-Dichloro-phenoxyacetic acid (2,4-D)	00094-75-7	0.07	0.07
Dalapon	00075-99-0	0.2	0.2
1,2-Dibromo-3-chloropropane (DBCP)	00096-12-8	0	0.0002
o-Dichlorobenzene	00095-50-1	0.6	0.6
p-Dichlorobenzene	00106-46-7	0.075	0.075
1,2-Dichloroethane	00107-06-2	0	0.005
1,1-Dichloroethylene	00075-35-4	0.007	0.007
cis-1,2-Dichloroethylene	00156-59-2	0.07	0.07
trans-1,2-Dichloroethylene	00156-60-5	0.1	0.1
Dichloromethane	00074-87-3	0	0.005
1,2-Dichloropropane	00078-87-5	0	0.005
Di(2-ethylhexyl) adipate	00103-23-1	0.4	0.4
Di(2-ethylhexyl) phthalate	00117-81-7	0	0.006
Dinoseb	00088-85-7	0.007	0.007
Dioxin (2,3,7,8-TCDD)	01746-01-6	0	0.00000003
Diquat		0.02	0.02
Endothall	00145-73-3	0.1	0.1
Endrin	00072-20-8	0.002	0.002
Epichlorohydrin		0	TT
Ethylbenzene	00100-41-4	0.7	0.7
Ethylene dibromide	00106-93-4	0	0.00005
Glyphosate	01071-83-6	0.7	0.7
Heptachlor	00076-44-8	0	0.0004
Heptachlor epoxide	01024-57-3	0	0.0002
Hexachlorobenzene	00118-74-1	0	0.001
Hexachlorocyclopentadiene	00077-47-4	0.05	0.05

Organic Chemicals

Contaminant	CAS number	MCLG (mg/L)	MCL or TT (mg/L)
Lindane	00058-89-9	0.0002	0.0002
Methoxychlor	00072-43-5	0.04	0.04
Oxamyl (Vydate)	23135-22-0	0.2	0.2
Polychlorinated biphenyls (PCBs)		0	0.0005
Pentachlorophenol	00087-86-5	0	0.001
Picloram	01918-02-1	0.5	0.5
Simazine	00122-34-9	0.004	0.004
Styrene	00100-42-5	0.1	0.1
Tetrachloroethylene	00127-18-4	0	0.005
Toluene	00108-88-3	1	1
Toxaphene	08001-35-2	0	0.003
2,4,5-TP (Silvex)	00093-72-1	0.05	0.05
1,2,4-Trichlorobenzene	00120-82-1	0.07	0.07
1,1,1-Trichloroethane	00071-55-6	0.2	0.2
1,1,2-Trichloroethane	00079-00-5	0.003	0.005
Trichloroethylene	00079-01-6	0	0.005
Vinyl chloride	00075-01-4	0	0.002
Xylenes (total)		10	10

Radionuclides

Contaminant	MCLG (mg/L)	MCL or TT (mg/L)
Alpha particles	none ------------- zero	15 picocuries per Liter (pCi/L)
Beta particles and photon emitters	none ------------- zero	4 millirems per year
Radium 226 and Radium 228 (combined)	none ------------- zero	5 pCi/L
Uranium	zero	30 ug/L

Table 4-3 - Secondary Drinking Water Standards

Contaminant	CAS number	Standard
Aluminum	07439-90-5	0.05 to 0.2 mg/L
Chloride		250 mg/L
Color		15 (color units)
Copper	07440-50-8	1.0 mg/L
Corrosivity		noncorrosive
Fluoride	16984-48-8	2.0 mg/L
Foaming Agents (surfactants)		0.5 mg/L
Iron	07439-89-6	0.3 mg/L
Manganese	07439-96-5	0.05 mg/L
Odor		3 threshold odor number
pH		6.5-8.5
Silver	07440-22-4	0.10 mg/L
Sulfate	14808-79-8	250 mg/L
Total Dissolved Solids		500 mg/L
Zinc	07440-66-6	5 mg/L

Table 4-4 – Comparison of additives used or proposed for use in NY, parameters detected in analytical results of flowback from the Marcellus operations in PA and WV, and parameters regulated via primary and secondary drinking water standards, SPDES Program or listed in TOGS111

CAS Number	Parameter Name	Used in Additives[11]	Found in Flowback[12]	MCLG (mg/L)[13]	MCL or TT (mg/L)	SPDES Tables[14]	TOGS111
02634-33-5	1,2 Benzisothiazolin-2-one / 1,2-benzisothiazolin-3-one	Yes					
00095-63-6	1,2,4 trimethylbenzene	Yes				Table 9	Tables 1,5
00123-91-1	1,4 Dioxane	Yes				Table 8	
03452-07-1	1-eicosene	Yes					
00629-73-2	1-hexadecene	Yes					
00112-88-9	1-octadecene	Yes					
01120-36-1	1-tetradecene	Yes					
10222-01-2	2,2 Dibromo-3-nitrilopropionamide	Yes				Table 9	Tables 1,5
27776-21-2	2,2'-azobis-{2-(imidazlin-2-yl)propane}-dihydrochloride	Yes					
73003-80-2	2,2-Dobromomalonamide	Yes					
15214-89-8	2-Acrylamido-2-methylpropanesulphonic acid sodium salt polymer	Yes					
46830-22-2	2-acryloyloxyethyl(benzyl)dimethylammonium chloride	Yes					
00052-51-7	2-Bromo-2-nitro-1,3-propanediol	Yes				Table 10	
00111-76-2	2-Butoxy ethanol	Yes					

11 As with Table 2-2, information in the "Used in Additives" column is based on the composition of additives used or proposed for use in New York.

12 As with Table 3-1, information in the "Found in Flowback" column is based on analytical results of flowback from operations in Pennsylvania or West Virginia. There are/may be products used in fracturing operations in Pennsylvania that have not yet been proposed for use in New York for which, therefore, the NYSDEC does not have chemical composition data.

13 Limits marked with a pound sign (#) are based on secondary drinking water standards.

14 SPDES or TOGS typically regulates or provides guidance for the total substance, e.g. iron; and rarely regulates or provides guidance for only its dissolved portion, e.g. dissolved iron. The dissolved component is implicitly covered in the total substance. Therefore, the dissolved component is not included in Table 4-4. Flowback analyses provided information for the total and dissolved components of metals, which are listed in Table 3-1 and in Table 4-5. Understanding the dissolved vs. suspended portions of a substance is valuable when determining potential treatment techniques.

CAS Number	Parameter Name	Used in Additives[11]	Found in Flowback[12]	MCLG (mg/L)[13]	MCL or TT (mg/L)	SPDES Tables[14]	TOGS111
01113-55-9	2-Dibromo-3-Nitriloprionamide (2-Monobromo-3-nitriilopropionamide)	Yes					
00104-76-7	2-Ethyl Hexanol	Yes					
00067-63-0	2-Propanol / Isopropyl Alcohol / Isopropanol / Propan-2-ol	Yes				Table 10	
26062-79-3	2-Propen-1-aminium, N,N-dimethyl-N-2-propenyl-chloride, homopolymer	Yes					
09003-03-6	2-propenoic acid, homopolymer, ammonium salt	Yes					
25987-30-8	2-Propenoic acid, polymer with 2 p-propenamide, sodium salt / Copolymer of acrylamide and sodium acrylate	Yes					
71050-62-9	2-Propenoic acid, polymer with sodium phosphinate (1:1)	Yes					
66019-18-9	2-propenoic acid, telomer with sodium hydrogen sulfite	Yes					
00107-19-7	2-Propyn-1-ol / Progargyl Alcohol	Yes					
51229-78-8	3,5,7-Triaza-1-azoniatricyclo[3.3.1.13,7]decane, 1-(3-chloro-2-propenyl)-chloride,	Yes					
00115-19-5	3-methyl-1-butyn-3-ol	Yes					
127087-87-0	4-Nonylphenol Polyethylene Glycol Ether Branched / Nonylphenol ethoxylated / Oxyalkylated Phenol	Yes					
00064-19-7	Acetic acid	Yes				Table 10	
68442-62-6	Acetic acid, hydroxy-, reaction products with triethanolamine	Yes					
00108-24-7	Acetic Anhydride	Yes				Table 10	
00067-64-1	Acetone	Yes	Yes			Table 7	Tables 1,5
00079-06-1	Acrylamide	Yes		0	TT	Table 9	Tables 1,5
38193-60-1	Acrylamide - sodium 2-acrylamido-2-methylpropane sulfonate copolymer	Yes					
25085-02-3	Acrylamide - Sodium Acrylate Copolymer or Anionic Polyacrylamide	Yes					
69418-26-4	Acrylamide polymer with N,N,N-trimethyl-2[1-oxo-2-propenyl]oxy Ethanaminium chloride	Yes					
15085-02-3	Acrylamide-sodium acrylate copolymer	Yes					
68551-12-2	Alcohols, C12-C16, Ethoxylated (a.k.a. Ethoxylated alcohol)	Yes					
	Aliphatic acids	Yes					
	Aliphatic alcohol glycol ether	Yes					

CAS Number	Parameter Name	Used in Additives[11]	Found in Flowback[12]	MCLG (mg/L)[13]	MCL or TT (mg/L)	SPDES Tables[14]	TOGS111
64742-47-8	Aliphatic Hydrocarbon / Hydrotreated light distillate / Petroleum Distillates / Isoparaffinic Solvent / Paraffin Solvent / Napthenic Solvent	Yes					
	Alkalinity, Carbonate, as CaCO3		Yes			Table 10	
64743-02-8	Alkenes	Yes					
68439-57-6	Alkyl (C14-C16) olefin sulfonate, sodium salt	Yes					
	Alkyl Aryl Polyethoxy Ethanol	Yes					
	Alkylaryl Sulfonate	Yes					
09016-45-9	Alkylphenol ethoxylate surfactants	Yes		0.5 mg/L[#]			
	Alpha, Radiation		Yes	none ---------- 0	15 picocuries per Liter (pCi/L)	Table 7	Tables 1,5
07439-90-5	Aluminum		Yes	0.05 to 0.2 mg/L[#]		Table 7	Tables 1,5
01327-41-9	Aluminum chloride	Yes					
73138-27-9	Amines, C12-14-tert-alkyl, ethoxylated	Yes					
71011-04-6	Amines, Ditallow alkyl, ethoxylated	Yes					
68551-33-7	Amines, tallow alkyl, ethoxylated, acetates	Yes					
01336-21-6	Ammonia	Yes				Yes	
00631-61-8	Ammonium acetate	Yes				Table 10	
68037-05-8	Ammonium Alcohol Ether Sulfate	Yes					
07783-20-2	Ammonium bisulfate	Yes					
10192-30-0	Ammonium Bisulphite	Yes					
12125-02-9	Ammonium Chloride	Yes				Table 10	
07632-50-0	Ammonium citrate	Yes					
37475-88-0	Ammonium Cumene Sulfonate	Yes					
01341-49-7	Ammonium hydrogen-difluoride	Yes					
06484-52-2	Ammonium nitrate	Yes					
07727-54-0	Ammonium Persulfate / Diammonium peroxidisulphate	Yes					
01762-95-4	Ammonium Thiocyanate	Yes				Table 10	
07440-36-0	Antimony		Yes	0.006	0.006	Table 6	Tables 1,5
07664-41-7	Aqueous ammonia	Yes	Yes			Table 7	Tables 1,5

CAS Number	Parameter Name	Used in Additives[11]	Found in Flowback[12]	MCLG (mg/L)[13]	MCL or TT (mg/L)	SPDES Tables[14]	TOGS111
	Aromatic hydrocarbons	Yes					
	Aromatic ketones	Yes					
07440-38-2	Arsenic		Yes	0	0.01	Table 6	Tables 1,5
07440-39-3	Barium		Yes	2	2	Table 7	Tables 1,5
	Barium Strontium P.S. (mg/L)		Yes				
121888-68-4	Bentonite, benzyl(hydrogenated tallow alkyl) dimethylammonium stearate complex / organophilic clay	Yes					
00071-43-2	Benzene	Yes	Yes	0	0.005	Table 6	Tables 1,5
119345-04-9	Benzene, 1,1'-oxybis, tetratpropylene derivatives, sulfonated, sodium salts	Yes					
74153-51-8	Benzenemethanaminium, N,N-dimethyl-N-[2-[(1-oxo-2-propenyl)oxy]ethyl]-, chloride, polymer with 2-propenamide	Yes					
07440-41-7	Beryllium		Yes	0.004	0.004	Table 6	Tables 1,5
	Beta, Radiation		Yes	none ---------- 0	4 millirems per year	Table 7	Tables 1,5
	Bicarbonates (mg/L)		Yes			Table 10	
	Biochemical Oxygen Demand		Yes			Yes	
00117-81-7	Bis(2-ethylhexyl)phthalate		Yes	0	0.006	Table 6	Tables 1,5
10043-35-3	Boric acid	Yes					
01303-86-2	Boric oxide / Boric Anhydride	Yes					
07440-42-8	Boron		Yes			Table 7	Tables 1,5
24959-67-9	Bromide		Yes			Table 7	Tables 1,5
00075-25-2	Bromoform		Yes			Table 6	Tables 1,5
00071-36-3	Butan-1-ol	Yes				Table 10	Tables 1,5
68002-97-1	C10 - C16 Ethoxylated Alcohol	Yes					
68131-39-5	C12-15 Alcohol, Ethoxylated	Yes					
07440-43-9	Cadmium		Yes	0.005	0.005	Table 6	Tables 1,5
07440-70-2	Calcium		Yes			Table 8	
10043-52-4	Calcium chloride	Yes					
00124-38-9	Carbon Dioxide	Yes	Yes				
68130-15-4	Carboxymethylhydroxypropyl guar	Yes					

CAS Number	Parameter Name	Used in Additives[11]	Found in Flowback[12]	MCLG (mg/L)[13]	MCL or TT (mg/L)	SPDES Tables[14]	TOGS111
09012-54-8	Cellulase / Hemicellulase Enzyme	Yes					
09004-34-6	Cellulose	Yes					
	Cesium 137		Yes		Via beta radiation		
	Chemical Oxygen Demand		Yes			Yes	
	Chloride		Yes	250 mg/L[#]		Table 7	Tables 1,5
10049-04-4	Chlorine Dioxide	Yes		MRDLG=0.8	MRDL=0.8	Table 10	
00124-48-1	Chlorodibromomethane		Yes			Table 6	Tables 1,5
07440-47-3	Chromium		Yes	0.1	0.1	Table 6	Tables 1,5
00077-92-9	Citric Acid	Yes					
94266-47-4	Citrus Terpenes	Yes					
07440-48-4	Cobalt		Yes			Table 7	Table 1
61789-40-0	Cocamidopropyl Betaine	Yes					
68155-09-9	Cocamidopropylamine Oxide	Yes					
68424-94-2	Coco-betaine	Yes					
	Coliform, Total		Yes	0	0.05	Table 7	
	Color		Yes	15 (Color Units)[#]		Table 7	
07440-50-8	Copper		Yes	1.0[#]	TT; Action Level=1.3	Table 6	Tables 1,5
07758-98-7	Copper (II) Sulfate	Yes					
31726-34-8	Crissanol A-55 (Poly(oxy-1,2-ethanediyl),alpha-hexyl-omega-hydroxy)	Yes					
14808-60-7	Crystalline Silica (Quartz)	Yes					
07447-39-4	Cupric chloride dihydrate	Yes					
00057-12-5	Cyanide		Yes	0.2	0.2	Table 6	Tables 1,5
01120-24-7	Decyldimethyl Amine	Yes					
02605-79-0	Decyl-dimethyl Amine Oxide	Yes					
03252-43-5	Dibromoacetonitrile	Yes				Table 9	Tables 1
00075-27-4	Dichlorobromomethane		Yes			Table 6	Tables 1,5

CAS Number	Parameter Name	Used in Additives[11]	Found in Flowback[12]	MCLG (mg/L)[13]	MCL or TT (mg/L)	SPDES Tables[14]	TOGS111
25340-17-4	Diethylbenzene	Yes					
00111-46-6	Diethylene Glycol	Yes				Table 10	
22042-96-2	Diethylenetriamine penta (methylenephonic acid) sodium salt	Yes					
28757-00-8	Diisopropyl naphthalenesulfonic acid	Yes					
68607-28-3	Dimethylcocoamine, bis(chloroethyl) ether, diquaternary ammonium salt	Yes					
07398-69-8	Dimethyldiallylammonium chloride	Yes					
25265-71-8	Dipropylene glycol	Yes					
00139-33-3	Disodium Ethylene Diamine Tetra Acetate	Yes					
05989-27-5	D-Limonene	Yes					
00123-01-3	Dodecylbenzene	Yes					
27176-87-0	Dodecylbenzene sulfonic acid	Yes					
42504-46-1	Dodecylbenzenesulfonate isopropanolamine	Yes					
00050-70-4	D-Sorbitol / Sorbitol	Yes					
37288-54-3	Endo-1,4-beta-mannanase, or Hemicellulase	Yes					
149879-98-1	Erucic Amidopropyl Dimethyl Betaine	Yes					
00089-65-6	Erythorbic acid, anhydrous	Yes					
54076-97-0	Ethanaminium, N,N,N-trimethyl-2-[(1-oxo-2-propenyl)oxy]-, chloride, homopolymer	Yes					
00107-21-1	Ethane-1,2-diol / Ethylene Glycol	Yes				Table 7	Tables 1,5
09002-93-1	Ethoxylated 4-tert-octylphenol	Yes					
68439-50-9	Ethoxylated alcohol	Yes					
126950-60-5	Ethoxylated alcohol	Yes					
68951-67-7	Ethoxylated alcohol (C14-15)	Yes					
68439-46-3	Ethoxylated alcohol (C9-11)	Yes					
66455-15-0	Ethoxylated Alcohols	Yes					
67254-71-1	Ethoxylated Alcohols (C10-12)	Yes					
84133-50-6	Ethoxylated Alcohols (C12-14 Secondary)	Yes					
68439-51-0	Ethoxylated Alcohols (C12-14)	Yes					
78330-21-9	Ethoxylated branch alcohol	Yes					
34398-01-1	Ethoxylated C11 alcohol	Yes					

CAS Number	Parameter Name	Used in Additives[11]	Found in Flowback[12]	MCLG (mg/L)[13]	MCL or TT (mg/L)	SPDES Tables[14]	TOGS111
61791-12-6	Ethoxylated Castor Oil	Yes					
61791-29-5	Ethoxylated fatty acid, coco	Yes					
61791-08-0	Ethoxylated fatty acid, coco, reaction product with ethanolamine	Yes					
68439-45-2	Ethoxylated hexanol	Yes					
09036-19-5	Ethoxylated octylphenol	Yes					
09005-67-8	Ethoxylated Sorbitan Monostearate	Yes					
09004-70-3	Ethoxylated Sorbitan Trioleate	Yes					
00064-17-5	Ethyl alcohol / ethanol	Yes					
00100-41-4	Ethyl Benzene	Yes	Yes	0.7	0.7	Table 6	Tables 1,5
00097-64-3	Ethyl Lactate	Yes					
09003-11-6	Ethylene Glycol-Propylene Glycol Copolymer (Oxirane, methyl-, polymer with oxirane)	Yes					
00075-21-8	Ethylene oxide	Yes				Table 9	Tables 1,5
05877-42-9	Ethyloctynol	Yes					
68526-86-3	Exxal 13 (Alcohols, C11-14-iso-, C13-rich)	Yes					
61790-12-3	Fatty Acids	Yes					
68188-40-9	Fatty acids, tall oil reaction products w/ acetophenone, formaldehyde & thiourea	Yes					
09043-30-5	Fatty alcohol polyglycol ether surfactant	Yes		0.5 mg/L[#]			
07705-08-0	Ferric chloride	Yes				Table 10	
07782-63-0	Ferrous sulfate, heptahydrate	Yes					
16984-48-8	Fluoride		Yes	2[#]	4	Table 7	Tables 1,5
00050-00-0	Formaldehyde	Yes				Table 8	Tables 1,5
29316-47-0	Formaldehyde polymer with 4,1,1-dimethylethyl phenolmethyl oxirane	Yes					
153795-76-7	Formaldehyde, polymers with branched 4-nonylphenol, ethylene oxide and propylene oxide	Yes					
00075-12-7	Formamide	Yes					
00064-18-6	Formic acid	Yes				Table 10	
00110-17-8	Fumaric acid	Yes				Table 10	

CAS Number	Parameter Name	Used in Additives[11]	Found in Flowback[12]	MCLG (mg/L)[13]	MCL or TT (mg/L)	SPDES Tables[14]	TOGS111
65997-17-3	Glassy calcium magnesium phosphate	Yes					
00111-30-8	Glutaraldehyde	Yes					
00056-81-5	Glycerol / glycerine	Yes					
09000-30-0	Guar Gum	Yes					
9000-30-01	Guar Gum	Yes					
64742-94-5	Heavy aromatic petroleum naphtha	Yes					
09025-56-3	Hemicellulase	Yes					
	Heterotrophic plate count		Yes	n/a	TT[15]		
07647-01-0	Hydrochloric Acid / Hydrogen Chloride / muriatic acid	Yes					
07722-84-1	Hydrogen Peroxide	Yes				Table 10	
00079-14-1	Hydroxy acetic acid	Yes					
35249-89-9	Hydroxyacetic acid ammonium salt	Yes					
09004-62-0	Hydroxyethyl cellulose	Yes					
05470-11-1	Hydroxylamine hydrochloride	Yes					
39421-75-5	Hydroxypropyl guar	Yes					
07439-89-6	Iron		Yes	0.3 mg/L[#]		Table 7	Tables 1,5
35674-56-7	Isomeric Aromatic Ammonium Salt	Yes					
64742-88-7	Isoparaffinic Petroleum Hydrocarbons, Synthetic	Yes					
00064-63-0	Isopropanol	Yes				Table 10	
00098-82-8	Isopropylbenzene (cumene)	Yes				Table 9	Tables 1,5
68909-80-8	Isoquinoline, reaction products with benzyl chloride and quinoline	Yes					
08008-20-6	Kerosene	Yes					
64742-81-0	Kerosine, hydrodesulfurized	Yes					
00063-42-3	Lactose	Yes					

[15] Treatment Technology specified.

CAS Number	Parameter Name	Used in Additives[11]	Found in Flowback[12]	MCLG (mg/L)[13]	MCL or TT (mg/L)	SPDES Tables[14]	TOGS111
07439-92-1	Lead		Yes	0	TT; Action Level 0.015	Table 6	Tables 1,5
64742-95-6	Light aromatic solvent naphtha	Yes					
01120-21-4	Light Paraffin Oil	Yes					
	Lithium		Yes			Table 10	
07439-95-4	Magnesium		Yes			Table 7	Tables 1,5
14807-96-6	Magnesium Silicate Hydrate (Talc)	Yes					
07439-96-5	Manganese		Yes	0.05 mg/L[#]		Table 7	Tables 1,5
07439-97-6	Mercury		Yes	0.002	0.002	Table 6	Tables 1,5
01184-78-7	Methanamine, N,N-dimethyl-, N-oxide	Yes					
00067-56-1	Methanol	Yes				Table 10	
00074-83-9	Methyl Bromide		Yes			Table 6	Tables 1,5
00074-87-3	Methyl Chloride		Yes	0	0.005	Table 6	Tables 1,5
68891-11-2	Methyloxirane polymer with oxirane, mono (nonylphenol) ether, branched	Yes					
08052-41-3	Mineral spirits / Stoddard Solvent	Yes					
07439-98-7	Molybdenum		Yes			Table 7	
00141-43-5	Monoethanolamine	Yes					
44992-01-0	N,N,N-trimethyl-2[1-oxo-2-propenyl]oxy Ethanaminium chloride	Yes					
64742-48-9	Naphtha (petroleum), hydrotreated heavy	Yes					
00091-20-3	Naphthalene	Yes	Yes			Table 6	Tables 1,5
38640-62-9	Naphthalene bis(1-methylethyl)	Yes					
00093-18-5	Naphthalene, 2-ethoxy-	Yes					
68909-18-2	N-benzyl-alkyl-pyridinium chloride	Yes					
68139-30-0	N-Cocoamidopropyl-N,N-dimethyl-N-2-hydroxypropylsulfobetaine	Yes					
07440-02-0	Nickel		Yes			Table 6	Tables 1,5
	Nitrate, as N		Yes	10	10	Table 7	Tables 1,5
07727-37-9	Nitrogen, Liquid form	Yes					

CAS Number	Parameter Name	Used in Additives[11]	Found in Flowback[12]	MCLG (mg/L)[13]	MCL or TT (mg/L)	SPDES Tables[14]	TOGS111
	Nitrogen, Total as N		Yes				Table 5
68412-54-4	Nonylphenol Polyethoxylate	Yes					
	Oil and Grease		Yes				Table 5
121888-66-2	Organophilic Clays	Yes					
	Oxyalkylated alkylphenol	Yes					
64742-65-0	Petroleum Base Oil	Yes					
	Petroleum distillate blend	Yes					
	Petroleum hydrocarbons		Yes				
64741-68-0	Petroleum naphtha	Yes					
	pH		Yes	6.5-8.5[#]			Table 5
00108-95-2	Phenol		Yes			Table 6	Tables 1,5
	Phenols		Yes			Table 6	Tables 1,5
70714-66-8	Phosphonic acid, [[(phosphonomethyl)imino]bis[2,1-ethanediylnitrilobis(methylene)]]tetrakis-, ammonium salt	Yes					
57723-14-0	Phosphorus		Yes			Table 7	Table 1
08000-41-7	Pine Oil	Yes					
24938-91-8	Poly(oxy-1,2-ethanediyl), α-tridecyl-ω-hydroxy-	Yes					
60828-78-6	Poly(oxy-1,2-ethanediyl), a-[3,5-dimethyl-1-(2-methylpropyl)hexyl]-w-hydroxy-	Yes					
25322-68-3	Poly(oxy-1,2-ethanediyl), a-hydro-w-hydroxy / Polyethylene Glycol	Yes					
51838-31-4	Polyepichlorohydrin, trimethylamine quaternized	Yes					
56449-46-8	polyethlene glycol oleate ester	Yes					
	Polyethoxylated alkanol	Yes					
62649-23-4	Polymer with 2-propenoic acid and sodium 2-propenoate	Yes					
	Polymeric Hydrocarbons	Yes					
09005-65-6	Polyoxyethylene Sorbitan Monooleate	Yes					
61791-26-2	Polyoxylated fatty amine salt	Yes					
07440-09-7	Potassium		Yes			Table 8	
00127-08-2	Potassium acetate	Yes					
12712-38-8	Potassium borate	Yes					

CAS Number	Parameter Name	Used in Additives[11]	Found in Flowback[12]	MCLG (mg/L)[13]	MCL or TT (mg/L)	SPDES Tables[14]	TOGS111
1332-77-0	Potassium borate	Yes					
20786-60-1	Potassium borate	Yes					
00584-08-7	Potassium carbonate	Yes					
07447-40-7	Potassium chloride	Yes					
00590-29-4	Potassium formate	Yes					
01310-58-3	Potassium Hydroxide	Yes				Table 10	
13709-94-9	Potassium metaborate	Yes					
24634-61-5	Potassium Sorbate	Yes					
112926-00-8	Precipitated silica / silica gel	Yes					
00057-55-6	Propane-1,2-diol, or Propylene glycol	Yes					Tables 1,5
00107-98-2	Propylene glycol monomethyl ether	Yes				Table 10	
68953-58-2	Quaternary Ammonium Compounds	Yes				Table 9	Tables 1
62763-89-7	Quinoline,2-methyl-, hydrochloride	Yes					
15619-48-4	Quinolinium, 1-(phenylmethl),chloride	Yes					
	Radium		Yes			Table 7	
	Radium 226		Yes	none ------------ zero	5 pCi/L	Table 7	Tables 1,5
	Radium 228		Yes	none ------------ zero	5 pCi/L		Tables 1,5
	Salt of amine-carbonyl condensate	Yes					
	Salt of fatty acid/polyamine reaction product	Yes					
	Scale Inhibitor (mg/L)		Yes				
07782-49-2	Selenium		Yes	0.05	0.05	Table 6	Tables 1,5
07631-86-9	Silica, Dissolved	Yes				Table 8	
07440-22-4	Silver		Yes	0.10 mg/L[#]		Table 6	Tables 1,5
07440-23-5	Sodium		Yes			Table 7	Tables 1,5
05324-84-5	Sodium 1-octanesulfonate	Yes					
00127-09-3	Sodium acetate	Yes					
95371-16-7	Sodium Alpha-olefin Sulfonate	Yes					
00532-32-1	Sodium Benzoate	Yes					

CAS Number	Parameter Name	Used in Additives[11]	Found in Flowback[12]	MCLG (mg/L)[13]	MCL or TT (mg/L)	SPDES Tables[14]	TOGS111
00144-55-8	Sodium bicarbonate	Yes					
07631-90-5	Sodium bisulfate	Yes					
07647-15-6	Sodium Bromide	Yes					
00497-19-8	Sodium carbonate	Yes					
07647-14-5	Sodium Chloride	Yes					
07758-19-2	Sodium chlorite	Yes					
03926-62-3	Sodium Chloroacetate	Yes					
00068-04-2	Sodium citrate	Yes					
06381-77-7	Sodium erythorbate / isoascorbic acid, sodium salt	Yes					
02836-32-0	Sodium Glycolate	Yes					
01310-73-2	Sodium Hydroxide	Yes				Table 10	
07681-52-9	Sodium hypochlorite	Yes				Table 10	
07775-19-1	Sodium Metaborate .8H2O	Yes					
10486-00-7	Sodium perborate tetrahydrate	Yes					
07775-27-1	Sodium persulphate	Yes					
09003-04-7	Sodium polyacrylate	Yes					
07757-82-6	Sodium sulfate	Yes				Table 10	
01303-96-4	Sodium tetraborate decahydrate	Yes					
07772-98-7	Sodium Thiosulfate	Yes					
01338-43-8	Sorbitan Monooleate	Yes					
	Specific Conductivity		Yes				
07440-24-6	Strontium		Yes			Table 9	Table 1
00057-50-1	Sucrose	Yes					
	Sugar	Yes					
05329-14-6	Sulfamic acid	Yes					
14808-79-8	Sulfate		Yes	250 mg/L[#]		Table 7	Tables 1,5
	Sulfide		Yes			Table 7	Tables 1,5
14265-45-3	Sulfite		Yes			Table 7	Table 1
	Surfactant blend	Yes		0.5 mg/L[#]			
	Surfactants MBAS		Yes	0.5 mg/L[#]			
112945-52-5	Syntthetic Amorphous / Pyrogenic Silica / Amorphous Silica	Yes					

CAS Number	Parameter Name	Used in Additives[11]	Found in Flowback[12]	MCLG (mg/L)[13]	MCL or TT (mg/L)	SPDES Tables[14]	TOGS111
68155-20-4	Tall Oil Fatty Acid Diethanolamine	Yes					
08052-48-0	Tallow fatty acids sodium salt	Yes					
72480-70-7	Tar bases, quinoline derivs., benzyl chloride-quaternized	Yes					
68647-72-3	Terpene and terpenoids	Yes					
68956-56-9	Terpene hydrocarbon byproducts	Yes					
00127-18-4	Tetrachloroethylene		Yes	0	0.005	Table 6	Tables 1,5
00533-74-4	Tetrahydro-3,5-dimethyl-2H-1,3,5-thiadiazine-2-thione (a.k.a. Dazomet)	Yes					
55566-30-8	Tetrakis(hydroxymethyl)phosphonium sulfate (THPS)	Yes					
00075-57-0	Tetramethyl ammonium chloride	Yes					
00064-02-8	Tetrasodium Ethylenediaminetetraacetate	Yes					
07440-28-0	Thallium		Yes	0.0005	0.002	Table 6	Tables 1,5
00068-11-1	Thioglycolic acid	Yes					
00062-56-6	Thiourea	Yes				Table 10	
68527-49-1	Thiourea, polymer with formaldehyde and 1-phenylethanone	Yes					
07440-32-6	Titanium		Yes			Table 7	
00108-88-3	Toluene	Yes	Yes	1	1	Table 6	Tables 1,5
	Total Dissolved Solids		Yes	500 mg/L[#]			Table 5
	Total Kjeldahl Nitrogen		Yes			Yes	
	Total Organic Carbon		Yes			Yes	
	Total Suspended Solids		Yes			Yes	
81741-28-8	Tributyl tetradecyl phosphonium chloride	Yes					
68299-02-5	Triethanolamine hydroxyacetate	Yes					
00112-27-6	Triethylene Glycol	Yes					
52624-57-4	Trimethylolpropane, Ethoxylated, Propoxylated	Yes					
00150-38-9	Trisodium Ethylenediaminetetraacetate	Yes					
05064-31-3	Trisodium Nitrilotriacetate	Yes					
07601-54-9	Trisodium ortho phosphate	Yes					
00057-13-6	Urea	Yes					
07440-62-2	Vanadium		Yes			Table 7	Table 1
25038-72-6	Vinylidene Chloride/Methylacrylate Copolymer	Yes					

CAS Number	Parameter Name	Used in Additives[11]	Found in Flowback[12]	MCLG (mg/L)[13]	MCL or TT (mg/L)	SPDES Tables[14]	TOGS111
7732-18-5	Water	Yes					
1330-20-7	Xylenes	Yes	Yes	10	10		Table 1,5
07440-66-6	Zinc		Yes	5 mg/L[#]		Table 6	Tables 1,5
	Zirconium		Yes				

Table 4-5 – Typical concentrations of flowback constituents based on limited samples from PA and WV, and regulated in NY[16]

CAS #	Parameter Name	Total Number of Samples	Number of Detects	Min	Median	Max	Units
00067-64-1	Acetone	3	1	681	681	681	µg/L
	Acidity, Total	4	4	101	240	874	mg/L
	Alkalinity [17]	155	155	0	153	384	mg/L
	Alkalinity, Carbonate, as CaCO3	164	163	0	9485	48336	mg/L
	Total Alkalinity	5	5	28	91	94	mg/L
	Alpha, Radiation	15	15	0	166	18950	pCi/L
07439-90-5	Aluminum	43	12	0.02	0.07	1.2	mg/L
	Aluminum, Dissolved	22	1	1.37	1.37	1.37	mg/L
07440-36-0	Antimony	34	1	0.26	0.26	0.26	mg/L

[16] Information presented in Table 4-5 and Table 4-6 is based on limited data from Pennsylvania and West Virginia. Characteristics of flowback from the Marcellus Shale in New York are expected to be similar to flowback from Pennsylvania and West Virginia, but not identical. In addition, the raw data for these tables came from several sources, with likely varying degrees of reliability. Also, the analytical methods used were not all the same for given parameters. Sometimes laboratories need to use different analytical methods depending on the consistency and quality of the sample; sometimes the laboratories are only required to provide a certain level of accuracy. Therefore, the method detection limits may be different. The quality and composition of flowback from a single well can also change within a few days soon after the well is fractured. This data does not control for any of these variables.

[17] Different data sources reported alkalinity in different and valid forms. Total alkalinity reported here is smaller than carbonate alkalinity because the data came from different sources.

CAS #	Parameter Name	Total Number of Samples	Number of Detects	Min	Median	Max	Units
07664-41-7	Aqueous ammonia	48	45	11.3	44.8	382	mg/L
07440-38-2	Arsenic	43	7	0.015	0.09	0.123	mg/L
07440-39-3	Barium	48	47	0.553	1450	15700	mg/L
	Barium, Dissolved	22	22	0.313	212	19200	mg/L
00071-43-2	Benzene	35	14	15.7	479.5	1950	µg/L
07440-41-7	Beryllium	43	1	422	422	422	mg/L
	Beta, Radiation	15	15	0	62	7445	pCi/L
	Bicarbonates	150	150	0	183	1708	mg/L
	Biochemical Oxygen Demand	38	37	3	200	4450	mg/L
00117-81-7	Bis(2-ethylhexyl)phthalate	20	2	10.3	15.9	21.5	µg/L
07440-42-8	Boron	23	9	0.539	2.06	26.8	mg/L
24959-67-9	Bromide	15	15	11.3	607	3070	mg/L
00075-25-2	Bromoform	26	2	34.8	36.65	38.5	µg/L
07440-43-9	Cadmium	43	6	0.007	0.025	1.2	mg/L
	Cadmium, Dissolved	22	2	0.017	0.026	0.035	mg/L
07440-70-2	Calcium	187	186	29.9	4241	123000	mg/L
	Calcium, Dissolved	3	3	2360	22300	31500	mg/L
	Cesium 137 [18]	16	2	9.9	10.2	10.5	pCi/L
	Chemical Oxygen Demand	38	38	223	5645	33300	mg/L
	Chloride	193	192	287	38000	228000	mg/L
00124-48-1	Chlorodibromomethane	26	2	3.28	3.67	4.06	µg/L
07440-47-3	Chromium	43	9	0.009	0.082	760	mg/L
	Chromium (VI), dissolved	19	10	0.0126	0.539	7.81	mg/L
	Chromium, Dissolved	22	2	0.058	0.075	0.092	mg/L
07440-48-4	Cobalt	30	6	0.03	0.3975	0.62	mg/L
	Cobalt, dissolved	19	1	0.489	0.489	0.489	mg/L
	Coliform, Total	5	2	1	42	83	Col/100mL
	Color	3	3	200	1000	1250	PCU
07440-50-8	Copper	43	8	0.01	0.0245	0.157	mg/L

[18] Regulated under beta particles [56].

CAS #	Parameter Name	Total Number of Samples	Number of Detects	Min	Median	Max	Units
00057-12-5	Cyanide	7	2	0.006	0.0125	0.019	mg/L
00075-27-4	Dichlorobromomethane	29	1	2.24	2.24	2.24	µg/L
00100-41-4	Ethyl Benzene	38	14	3.3	53.6	164	µg/L
16984-48-8	Fluoride	4	2	5.23	392.615	780	mg/L
	Heterotrophic plate count	5	3	25	50	565	CFU/mL
07439-89-6	Iron	193	168	0	29.2	810	mg/L
	Iron, Dissolved	34	26	6.75	63.25	196	mg/L
07439-92-1	Lead	43	6	0.008	0.035	27.4	mg/L
	Lithium	13	13	34.4	90.4	297	mg/L
	Lithium, Dissolved	4	4	24.5	61.35	144	mg/L
07439-95-4	Magnesium	193	180	9	177	3190	mg/L
	Magnesium, Dissolved	3	3	218	2170	3160	mg/L
	Mg as CaCO3	145	145	36	547	8208	mg/L
07439-96-5	Manganese	43	29	0.15	1.89	97.6	mg/L
	Manganese, Dissolved	22	12	0.401	2.975	18	mg/L
07439-97-6	Mercury	30	2	6E-04	0.295	0.59	mg/L
00074-83-9	Methyl Bromide	26	1	2.04	2.04	2.04	µg/L
00074-87-3	Methyl Chloride	26	1	15.6	15.6	15.6	µg/L
07439-98-7	Molybdenum	34	12	0.16	0.44	1.08	mg/L
00091-20-3	Naphthalene	23	1	11.3	11.3	11.3	µg/L
07440-02-0	Nickel	43	15	0.01	0.03	0.137	mg/L
	Nickel, Dissolved	22	2	0.03	0.0715	0.113	mg/L
	Nitrate, as N	1	1	0.025	0.025	0.025	mg/L
	Nitrogen, Total as N	1	1	13.4	13.4	13.4	mg/L
	Oil and Grease	39	9	5	17	1470	mg/L
	pH	191	191	0	6.6	8.58	S.U.
00108-95-2	Phenol	20	1	459	459	459	µg/L
	Phenols	35	5	0.05	0.191	0.44	mg/L
57723-14-0	Phosphorus, as P	3	3	0.89	1.85	4.46	mg/L
07440-09-7	Potassium	33	17	15.5	125	7810	mg/L
	Potassium, Dissolved	3	3	84.2	327	7080	mg/L
	Radium	6	3	7.7	9.7	24	pCi/L
	Radium 226	3	3	2.58	4.67	33	pCi/L

CAS #	Parameter Name	Total Number of Samples	Number of Detects	Min	Median	Max	Units
	Radium 228	3	3	1.15	4.66	18.41	pCi/L
07782-49-2	Selenium	34	1	0.058	0.058	0.058	mg/L
	Selenium, Dissolved	22	1	1.06	1.06	1.06	mg/L
07440-22-4	Silver	43	3	0.129	0.204	6.3	mg/L
	Silver, Dissolved	22	2	0.056	0.0825	0.109	mg/L
07440-23-5	Sodium	42	41	83.1	23500	96700	mg/L
	Sodium, Dissolved	3	3	9290	54800	77400	mg/L
07440-24-6	Strontium	36	36	0.501	1115	5841	mg/L
	Strontium, Dissolved	22	21	8.47	629	7290	mg/L
14808-79-8	Sulfate (as SO4)	193	169	0	1	1270	mg/L
	Sulfide (as S)	8	1	29.5	29.5	29.5	mg/L
14265-45-3	Sulfite (as SO3)	3	3	2.56	64	64	mg/L
	Surfactants [19]	12	12	0.1	0.21	0.61	mg/L
00127-18-4	Tetrachloroethylene	26	1	5.01	5.01	5.01	µg/L
07440-28-0	Thallium	34	2	0.1	0.18	0.26	mg/L
07440-32-6	Titanium	25	1	0.06	0.06	0.06	mg/L
00108-88-3	Toluene	38	15	2.3	833	3190	µg/L
	Total Dissolved Solids	193	193	1530	63800	337000	mg/L
07440-62-2	Vanadium	24	1	40.4	40.4	40.4	mg/L
	Total Kjeldahl Nitrogen	25	25	37.5	122	585	mg/L
	Total Organic Carbon [20]	28	23	69.2	449	1080	mg/L
	Total Suspended Solids	43	43	16	129	2080	mg/L
1330-20-7	Xylenes	38	15	15.3	444	2670	µg/L
07440-66-6	Zinc	43	18	0.011	0.036	8570	mg/L
	Zinc, Dissolved	22	1	0.07	0.07	0.07	mg/L
	Fluid Density	145	145	8.39004	8.7	9.2	lb/gal
	Hardness by Calculation	170	170	203	11354	98000	mg CaCO3/L
	Salt %	145	145	0.9	5.8	13.9	%

[19] Regulated under foaming agents.

[20] Regulated via BOD, COD and the different classes/compounds of organic carbon.

CAS #	Parameter Name	Total Number of Samples	Number of Detects	Min	Median	Max	Units
	Specific Conductivity	15	15	1030	110000	165000	pmhos/cm
	Specific Gravity	150	154	0	1.04	1.201	
	Temperature	31	31	0	15.3	32	°C
	Temperature	145	145	24.9	68	76.1	°F

Table 4-6 – Unregulated parameters analyzed for and detected in limited flowback samples from PA and WV

Parameter Name [21]	Total Number of Samples	Detects
Barium Strontium P.S.	145	145
Carbon Dioxide	5	5
Petroleum hydrocarbons	1	1
Scale Inhibitor	145	145
Zirconium	19	1

Table 4-7 - Typical concentrations of parameters that are not regulated, based on limited flowback analyses from PA and WV

Parameter Name	Total Number of Samples	Detects	Min	Median	Max	Units
Barium Strontium P.S.	145	145	17	1320	6400	mg/L
Carbon Dioxide	5	5	193	232	294	mg/l
Petroleum hydrocarbons	1	1	0.21	0.21	0.21	mg/l
Scale Inhibitor	145	145	315	744	1346	mg/L
Zirconium	19	1	0.054	0.054	0.054	mg/L

[21] This survey did not identify direct regulations for the chemical compounds listed in this table. It is likely that they are indirectly regulated. E.g. Scale inhibitors are composed of several chemical compounds that are likely separately regulated, but the analytical results did not provide the composition of the scale inhibitors. Similarly, specific petroleum hydrocarbons may be regulated, but the analytical results did not provide the composition it tested for.

5 ON-SITE FLOWBACK FLUIDS TREATMENT OR RECYCLING TECHNOLOGIES

5.1 Introduction

New hydraulic fracturing methods are enabling the recovery of valuable onshore natural gas reserves. These new methods also require large volumes of water for the fracturing process and then produce flowback fluid with residual additives and high concentrations of several parameters, particularly TDS.

Reasonably good quality water is typically needed to harness the full benefit of fracturing fluid additives. Freshwater is therefore an obvious choice. But use of freshwater in hydraulic fracturing operations imposes an additional constraint on the resource.

Flowback fluid disposal is also difficult. Variable percentages of fracturing fluids return to the wellbore as flowback. Presently, dilution and re-use at subsequent wells, trucking to approved publicly-owned treatment works (POTW) or out-of-state industrial treatment plants, or underground injection wells[22] are the available options for disposal. However, treating flowback fluid at POTWs can cause POTW excursion of its permit limits; also, trucking the water is costly. Underground injection removes the water from the natural water cycle.

On-site treatment (with offsite disposal of the contaminants removed) or recycling is seen as the more environmentally sound method for managing flowback. This section surveys on-site treatment or recycling options currently used; provides a preliminary evaluation of the extent and conditions of such use; and assesses the general applicability of these technologies at hydraulic fracturing sites in New York State.

5.2 Flowback Recycling

Recycling flowback in hydraulic fracturing operations presently entails blending known amounts of flowback with freshwater; this practice is in a pilot testing phase at Marcellus-based operations in other states [3]. Recycling the flowback reduces freshwater needs. However, high concentrations of different parameters adversely affect the desired fracturing fluid properties. Concentrations of chlorides, calcium, magnesium, barium, carbonates, sulfates, solids, microbes, etc. in the flowback are too high to use as-is [1]. The demand for friction reducers increases when the chloride concentration increases [1]; the demand for scale inhibitors increases when concentrations of calcium, magnesium, barium, carbonates, or sulfates increase [1]; biocide requirements increase when the concentration of microbes increases [5]. The current recycling practice of

[22] It should be noted that while three fully permitted injection wells are operating for private oil and gas production brine disposal in New York, there are no currently operating commercial injection wells and none have been permitted for flowback injection.

blending flowback with freshwater attempts to balance the additional freshwater water needs with the additional additives needs.

Some form of physical and/or chemical separation (discussed later) is typically needed prior to recycling flowback.

One operator who shared analytical results after using a 50-50 blend of recycled flowback and freshwater assessed the blended water's corrosivity and scaling potential. Field experience suggests performing compatibility mixing studies prior to the actual blending flowback and freshwater in the field [16]. In addition, experts in the field suggest that flowback fluid and freshwater be evaluated multiple times during the year to assess potential seasonal variations and their impact on bacterial activity and water quality. Use of friction reducers, scale inhibitors, biocides, etc. would need to be modulated based on the composition and characteristics of the blend [16].

5.3 On-site Treatment

Regardless of the treatment objective, whether for reuse or direct discharge, the three basic issues that need consideration when developing water treatment technologies are:

1. Influent [i.e. flowback] parameters and their concentrations
2. Parameters and their concentrations allowable in the effluent [i.e. in the reuse water]
3. Disposal of residuals

5.3.1 Influent parameters and their concentrations

Flowback consists of several parameters, most in high concentrations. Table 4-5 and Table 4-6 provide typical concentrations of parameters in flowback. The median value would likely be the appropriate indicator of typical concentration. There is no single on-site treatment technique or on-site treatment unit that could treat all parameters. Therefore, a series of on-site treatment technologies is needed to produce a usable treated flowback stream. Stringing together several treatment units is costly. However, treating the flowback on-site would reduce freshwater needs, reduce flowback disposal costs, and depending on the final quality of the treated flowback, reduce the cost and need for additives.

5.3.2 Parameters and their concentrations allowable in the effluent

All experts and operators agree that freshwater meets the water quality needs for fracturing fluids; they also agree that somewhat lower quality water would be usable for fracturing operations. But there is no consensus on the minimum allowable water quality for a fracturing operation: different experts suggest different limits for TDS, chloride, calcium, etc.

Table 5-1 – Minimum allowable water quality requirements for fracturing fluids, based on input from one expert panel on Barnett Shale [1]

Constituent	Concentration
Chlorides	3,000 - 90,000 mg/l
Calcium	350 - 1,000 mg/l
Suspended Solids	< 50 mg/l
Entrained oil and soluble organics	< 25 mg/l
Bacteria	Cells/100 ml < 100
Barium	Low levels

Flowback characteristics based on limited data from PA and WV are provided in Table 4-5 and Table 4-6.

5.3.3 Disposal of residuals

Presently there is limited on-site treatment of flowback. Based on feedback from a few operators, when on-site treatment is provided, the residuals are injected into deep and stable strata (UIC wells).

5.3.4 Factors affecting on-site treatment

Several factors would influence the decision to utilize on-site treatment and the selection of specific treatment options. These include:

<u>Operational</u>

- Flowback fluid characteristics, including scaling and fouling tendencies
- On-site space availability
- Processing capacity needed
- Solids concentration in flowback fluid, and solids reduction required
- Concentrations of hydrocarbons in flowback fluid, and targeted reduction in hydrocarbon[23]
- Species and levels of radioactivity in flowback
- Access to freshwater sources

[23] Liquid hydrocarbons have not been detected in all Marcellus Shale gas analyses.

- Targeted recovery rate
- Impact of treated water on efficacy of additives
- Availability of residuals disposal options

Cost

- Capital costs associated with treatment system
- Transportation costs associated with freshwater
- Increase or decrease in fluid additives from using treated flowback fluid

Environmental

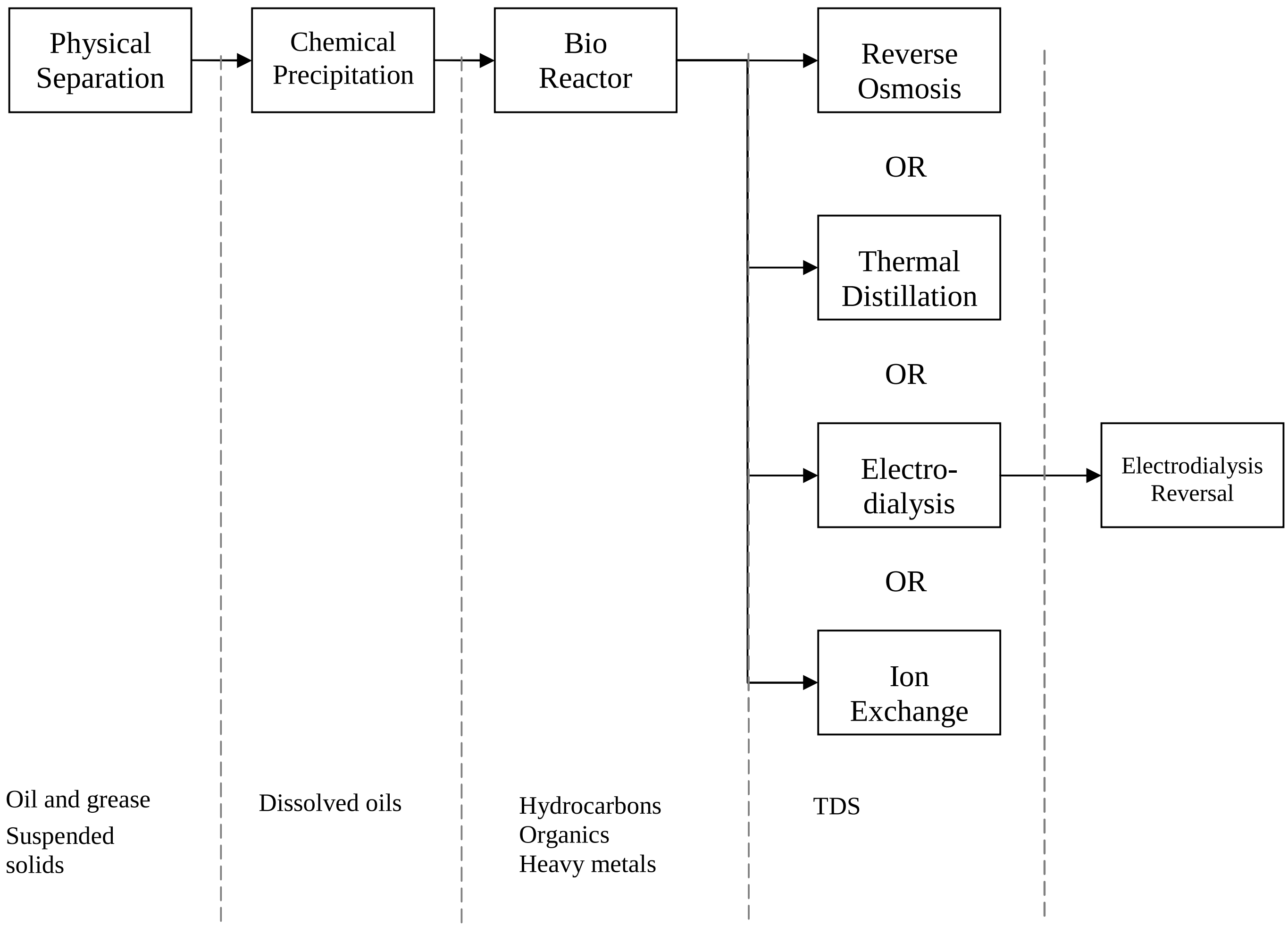
- On-site topography
- Density of neighboring population
- Proximity to freshwater sources
- Other demands on freshwater in the vicinity
- Regulatory environment

5.4 On-site Treatment Technologies

One of the several on-site treatment technology configurations is illustrated in Figure 5-1[24]. The parameters treated are listed at the bottom of the figure. The next few sections present several on-site treatment technologies that have been used to some extent in the Barnett Shale or Powder River Basin gas extraction operations. These may be further developed or retrofitted for use in the Marcellus Shale.

[24] All treatment steps illustrated in Figure 5-1 may not be necessary at for flowback from each well. The particular characteristics of flowback would determine the specific steps.

Figure 5-1 - One configuration of potential on-site treatment technologies



5.4.1 Physical and Chemical Separation

Some form of physical and/or chemical separation will be required as a part of on-site treatment. Physical and chemical separation technologies typically focus on the removal of oil and grease[25] and suspended matter from flowback.

The physical separation technologies include hydrocyclones, filters, and centrifuges; the size of constituents in flowback fluid drives separation efficiency. Chemical separation utilizes coagulants and flocculants to break emulsions (dissolved oil) and to remove suspended particles.

Modular physical and chemical separation units have been used in the Barnett Shale and Powder River Basin.

5.4.2 Membranes / Reverse Osmosis

Membranes are an advanced form of filtration, and may be used to treat TDS in flowback. The technology allows water to pass through the membrane - the permeate - but the membrane blocks passage of suspended or dissolved particles larger than the membrane pore size. This method may be able to treat TDS concentrations up to approximately 30,000 mg/L, and produce water with TDS concentrations between 200 and 500 mg/L. This technology generates a residual – the concentrate – that would need proper disposal. The flowback recovery rate for most membrane technologies is typically between 50-75 percent. Membrane performance may be impacted by scaling and/or microbiological fouling. Flowback would likely require extensive pretreatment before it is sent through a membrane.

Reverse osmosis (RO) is a membrane technology that uses osmotic pressure on the membrane to provide passage of high quality water.

Modular membrane technology units have been used in the Barnett Shale [17].

5.4.3 Thermal Distillation

Thermal distillation utilizes evaporation and crystallization techniques that integrate a multi-effect distillation column, and this technology may be used to treat flowback with a large range of parameter concentrations. For example, thermal distillation may be able to treat TDS concentrations from 5,000 to over 150,000 mg/L, and produce water with TDS concentrations between 50 and 150 mg/L. The resulting residual salt would need

[25] Oil and grease is not expected in the Marcellus.

appropriate disposal. This technology is resilient to fouling and scaling, but is energy intensive and has a large footprint.

Modular thermal distillation units have been used in the Barnett Shale.

5.4.4 Ion Exchange

Ion exchange units utilize different resins to preferentially remove certain ions. When treating flowback, the resin would be selected to preferentially remove sodium ions. The required resin volume and size of the ion exchange vessel would depend on the salt concentration and flowback volume treated.

The Higgins Loop is one version of ion exchange that has been successfully used in Midwest coal bed methane applications. The Higgins Loop uses a continuous countercurrent of flowback fluid and ion exchange resin. High sodium flowback fluid can be fed into the absorption chamber to exchange for hydrogen ions. The strong acid cation resin is advanced to the absorption chamber through a unique resin pulsing system [18].

Modular ion exchange units have been used in the Barnett Shale.

5.4.5 Electrodialysis

These treatment units are configured with alternating stacks of cation and anion membranes that allow passage of flowback fluid. The electric current applied to the stacks forces anions and cations to migrate in different directions.

Electrodialysis Reversal (EDR) is similar to electrodialysis, but its electric current polarity may be reversed as needed. This current reversal acts as a backwash cycle for the stacks, which reduces scaling on membranes. EDR offers lower electricity usage than standard reverse osmosis systems and can potentially reduce salt concentrations in the treated water to less than 200 mg/L.

Table 5-2 compares EDR and RO by outlining key characteristics of both technologies.

Table 5-2 - Treatment capabilities of EDR and RO Systems

Criteria	EDR	RO
Acceptable influent TDS (mg/L)	400-3,000	100-15,000
Salt removal capacity	50-95%	90-99%
Water recovery rate	85-94%	50-75%
Allowable Influent Turbidity	Silt Density Index (SDI) < 12	SDI < 5
Operating Pressure	<50 psi	> 100 psi

Criteria	EDR	RO
Power Consumption	Lower for <2,500 mg/L TDS	Lower for >2,500 mg/L TDS
Typical Membrane Life	7-10 years	3-5 years

Modular electrodialysis units have been used in the Barnett Shale and Powder River Basin.

5.4.6 Ozone/Ultrasonic/Ultraviolet

These technologies are expected to oxidize and separate hydrocarbons, heavy metals, oxidize biological films and bacteria from flowback fluid. The microscopic air bubbles in supersaturated ozonated water and/or ultrasonic transducers cause oils and suspended solids to float.

5.4.7 Comparison of potential on-site treatment technologies

A comparison of performance characteristics associated with on-site treatment technologies is provided in Table 5-3.

Table 5-3 - Summary of Characteristics of On-site Flowback Fluid Treatment Technologies

Characteristics	Filtration	Ion Exchange	Reverse Osmosis	EDR	Thermal Distillation
Energy Cost	Low	Low	Moderate	High	High
Energy Usage vs. TDS	N/A	Low	Increase	High Increase	Independent
Applicable to	All Water types	All Water types	Moderate TDS	High TDS	High TDS
Plant / Unit size	Small / Modular	Small / Modular	Modular	Modular	Large
Microbiological Fouling	Possible	Possible	Possible	Low	N/A
Complexity of Technology	Easy	Easy	Moderate / High Maintenance	Regular Maintenance	Complex
Scaling Potential	Low	Low	High	Low	Low
Theoretical TDS Feed Limit (mg/L)	N/A	N/A	32,000	40,000	100,000+

Characteristics	Filtration	Ion Exchange	Reverse Osmosis	EDR	Thermal Distillation
Pretreatment Requirement	N/A	Filtration	Extensive	Filtration	Minimal
Final Water TDS	No impact	200-500 ppm	200-500 ppm	200-1000 ppm	< 10 mg/L
Recovery Rate (Feed TDS >20,000 mg/L)	N/A	N/A	30-50%	60-80%	75-85%

5.5 Summary

The reduction in freshwater withdrawals and transportation needs, and reduction in flowback disposal are likely the primary benefits of recycling and/or treating flowback fluid.

However, on-site treatment of flowback is costly, and technology is not necessarily readily available. On-site treatment technologies would likely evolve more rapidly fueled by industry need and regulatory requirements. Low quality fracturing fluids typically require larger quantities of additives. The uncertainties associated with minimum water quality that may be utilized in fracturing operations, the large variations and fluctuations in flowback quality, the differences in quality of flowback from different shale formations and potential difficulties with residuals disposal are likely the main challenges to developing on-site treatment technologies. Several technologies have been utilized, albeit to a limited extent, in the Barnett Shale and Powder River Basin.

Flowback recycling presently involves blending minimally treated flowback with freshwater for fracturing operations.

6 POTENTIAL ENVIRONMENTALLY-FRIENDLY FRACTURING AND STIMULATION TECHNOLOGIES

6.1 Introduction

Hydraulic fracturing operations involve the use of significant quantities of additives/products, albeit in low concentrations, which potentially could have an adverse impact on the environment if not properly controlled. The recognition of potential hazards has motivated investigation into environmentally-friendly alternatives for hydraulic fracturing technologies and chemical additives.

It is important to note that use of ‘environmentally friendly’ or ‘green’ alternatives may reduce, but not entirely eliminate, adverse environmental impacts. Therefore, further research into each alternative is warranted to fully understand the potential environmental impacts and benefits of using any of the alternatives. In addition, the ‘greenness’ needs to be evaluated in a holistic manner, considering the full lifecycle impact of the technology or chemical.

6.2 Environmentally-Friendly Fracturing Technology Alternatives

The following environmentally-friendly technology alternatives have been identified as being in use in the Marcellus Shale, with other fracturing/stimulation applications or under investigation for possible use in Marcellus Shale operations:

- Liquid carbon dioxide alternative – The use of a liquid carbon dioxide and proppant mixture reduces the use of other additives [19]. Carbon dioxide vaporizes leaving only the proppant in the fractures. The use of this technique in the US has been limited to demonstrations [20].

- Nitrogen-based foam alternative – Nitrogen-based foam fracturing was used in vertical shale wells in the Appalachian Basin until recently [21]. Nitrogen gas is unable to carry appreciable amounts of proppant and the nitrogen foam was found to introduce liquid components that can cause formation damage [22].

- Liquefied Petroleum Gas (LPG) – The use of LPG, consisting primarily of propane, has the advantages of carbon dioxide and nitrogen cited above; additionally, LPG is known to be a good carrier of proppant due to the higher viscosity of propane gel [55]. Further, mixing LPG with natural gas does not ‘contaminate’ natural gas; and the mixture may be separated at the gas plant and recycled [55]. LPG’s high volatility, low weight, and high recovery potential make it a good fracturing agent. This technology is in limited use in Canada, and has not yet been used in the US.

- Horizontal and directional wells – These techniques are already in use in the Marcellus Shale. While these techniques require larger quantities of water and additives per well, horizontal and directional wells are considered to be more environmentally-friendly because these types of wells provide access to a larger volume of gas/oil than a typical vertical well [20, 23].

Several unconventional drilling techniques (e.g. slimhole drilling, coiled tubing, multilateral drilling, and dual-well configuration[26]) have made advances in recent decades and are considered to be more environmentally-friendly [24, 25, 20, 25, 26, 52] because of their smaller footprint. But there are no known instances of their use at shale plays similar to the Marcellus.

Locating multiple wells in a single pad, particularly multiple horizontal wells in a single pad, is a widely used technique that reduces the overall surface footprint.

The use of alternative chemical additives in hydraulic fracturing is another facet to the ‘environmentally- friendly’ development in recent years.

6.3 Environmentally-Friendly Chemical Alternatives

The most significant environmentally friendly change made to date in hydraulic fracturing operations in the United States has been the switching from a diesel- (also called oil- or synthetic-) based fluid to water based fluid. In 2003, BJ Services Company, Halliburton Energy Services, Inc., and Schlumberger Technology Corporation and the USEPA signed a voluntary Memorandum of Agreement by which diesel fuel use in hydraulic fracturing fluids injected into underground sources of drinking water during hydraulic fracturing of coalbed methane wells was eliminated [27, 28]. Diesel contains benzene, naphthalene, toluene, ethylbenzene, xylenes, and other potentially harmful compounds. While this agreement was limited to shallow coalbed methane wells, diesel was not among the listed constituents used for hydraulic fracturing by operators or their service providers who shared data with NYSDEC, and its use as a primary component of hydraulic fracturing fluid is not within the scope of the SGEIS. While chemical additives are still involved, the fluid used in hydraulic fracturing operations is now water-based.

There are several US-based chemical suppliers who advertise ‘green’ hydraulic fracturing additives. For example, Earth-friendly GreenSlurry system from Schlumberger used in both the U.K. North Sea and the Gulf of Mexico [29]; Ecosurf EH surfactants by Dow Chemicals; or ‘Green’ Chemicals for the North Sea from BASF. USEPA has published the twelve principles of green chemistry and a sustainable chemistry hierarchy [30], listed below, yet these do not provide a common measure of environmental-friendliness to assess ‘green’ hydraulic fracturing additives.

---

[26] The dual-well configuration combines a vertical and intersecting horizontal wellbore systems to access greater extents of gas resources with a single well site. This has been applied in low-medium permeability formations.

USEPA's twelve principles of green chemistry

1. Prevent waste: Design chemical syntheses to prevent waste, leaving no waste to treat or clean up.

2. Design safer chemicals and products: Design chemical products to be fully effective, yet have little or no toxicity.

3. Design less hazardous chemical syntheses: Design syntheses to use and generate substances with little or no toxicity to humans and the environment.

4. Use renewable feedstocks: Use raw materials and feedstocks that are renewable rather than depleting. Renewable feedstocks are often made from agricultural products or are the wastes of other processes; depleting feedstocks are made from fossil fuels (petroleum, natural gas, or coal) or are mined.

5. Use catalysts, not stoichiometric reagents: Minimize waste by using catalytic reactions. Catalysts are used in small amounts and can carry out a single reaction many times. They are preferable to stoichiometric reagents, which are used in excess and work only once.

6. Avoid chemical derivatives: Avoid using blocking or protecting groups or any temporary modifications if possible. Derivatives use additional reagents and generate waste.

7. Maximize atom economy: Design syntheses so that the final product contains the maximum proportion of the starting materials. There should be few, if any, wasted atoms.

8. Use safer solvents and reaction conditions: Avoid using solvents, separation agents, or other auxiliary chemicals. If these chemicals are necessary, use innocuous chemicals.

9. Increase energy efficiency: Run chemical reactions at ambient temperature and pressure whenever possible.

10. Design chemicals and products to degrade after use: Design chemical products to break down to innocuous substances after use so that they do not accumulate in the environment.

11. Analyze in real time to prevent pollution: Include in-process real-time monitoring and control during syntheses to minimize or eliminate the formation of byproducts.

12. Minimize the potential for accidents: Design chemicals and their forms (solid, liquid, or gas) to minimize the potential for chemical accidents including explosions, fires, and releases to the environment.

While these twelve principles of green chemistry and a sustainable chemistry hierarchy set general characteristics of an environmentally-friendly chemical or technique, they do not provide an objective metric for evaluating the environmentally-friendliness. Presently, environmentally-friendliness of chemicals used in hydraulic fracturing in the US has been measured only subjectively. Vendors/suppliers claim their products are environmentally-friendly, but presently, there is no established method in the US to assess the life-cycle impact or impact on all relevant media of these chemicals. The next few sections discuss objective metrics used elsewhere in the world.

6.3.1 Experience from Drilling in the North Sea

Much of the knowledge regarding environmentally-friendly chemicals used with gas exploration is based on drilling operations in the North Sea. Strict environmental guidelines regulate the amounts and types of chemicals that may be discharged into the North Sea. Two of the initiatives are:

- The Offshore Chemical Notification Scheme (OCNS) that manages chemical use and discharge by the United Kingdom (UK) and Netherlands offshore petroleum industries.
- The European Union legislation regarding the Environmental Impact Assessment (EIA) that requires a comprehensive assessment of the effects of projects on the environment.

An outcome of these initiatives was a regulation that prohibited the discharge of cuttings generated from drilling with synthetic- (i.e. oil/diesel) based drilling fluids where the synthetic oil on the cuttings is greater than 1% [31]. Additionally, the UK government proposed to phase out the discharge of cuttings contaminated with additional chemicals by December 31, 2000 [32]. Since oil-based fluids that are often used currently must be ‘skipped and shipped’ (i.e. containerized and transported back to land for disposal) due to these environmental regulations, there is an effort within the industry to develop ‘environmentally-friendly’ chemical additives that work as well as the traditional chemicals.

6.3.2 Environmental Coordination in Europe

The Convention for the Protection of the Marine Environment of the North-East Atlantic (known as the "OSPAR Convention") is the basis for national laws governing the discharge of offshore drilling wastes in the waters of the fifteen OSPAR signatory states [33, 18, 51]. The effort started in 1972 with the Oslo Convention against dumping; then, in 1974, the efforts were broadened by the Paris Convention to cover land-based sources and the offshore industry. These two conventions were unified, updated and extended by the 1992 OSPAR Convention.

The Paris Commission facilitated a thorough review of the use and manufacture of additives in order to establish the best environmental practice or best available techniques to prevent pollution [33]. The OSPAR list of substances that may be used or discharged offshore which are considered by OSPAR to Pose Little or No Risk to the Environment (PLONOR) contains substances whose use or discharge offshore are subject to expert judgment by the competent national authorities or do not need to be strongly regulated. The list of these chemicals may be found at http://www.ospar.org/documents/dbase/decrecs/agreements/04-10_plonor%202008%20revision.doc.

The "main environmental acceptability criterion" for the UK government's decision was biodegradation [32], which is consistent with Principle 10 of the Twelve Principles of Green Chemistry [34] adopted by the USEPA as part of its Green Chemistry initiative. In the Norwegian sector of the North Sea, chemical products must pass biodegradation, bioaccumulation, toxicity, and taint tests in order to be permitted for use [35]. Organisation for Economic Co-Operation and Development (OECD) North Sea countries require chemicals to be tested for ecotoxicity, biodegradation, and bio-concentration/bioaccumulation [32, 33].

6.3.2.1 Offshore Chemical Notification Scheme (OCNS)

The Offshore Chemical Notification Scheme (OCNS) manages chemical use and discharge by the UK and Netherlands offshore petroleum industries [36]. OCNS classifies chemicals using test protocols approved by OSPAR Harmonised Offshore Chemical Notification Format (HOCNF) coordinates the testing requirements for oilfield chemicals throughout the Northeast Atlantic sector.

To assess the potential environmental hazard associated with chemical products that may be used in offshore drilling operations, OCNS uses toxicity, biodegradation and bioaccumulation data for each chemical to calculate the ratio of Predicted Effect Concentration (PEC) against No Effect Concentration (NEC), and publishes the ratio as the Hazard Quotient (HQ). HQ is then used to rank products. Several lists of approved products that may be used for Production, Completion / Workover, Drilling or Cementing, ranked by their HQ may be found at http://www.cefas.co.uk/offshore-chemical-notification-scheme-(ocns)/hazard-assessment.aspx.

In the UK, OCNS is regulated by the Department of Energy and Climate Change (DECC) with scientific and environmental input from the Centre for Environment, Fisheries and Aquaculture Science (Cefas) and the Fisheries Research Services (FRS). In the Netherlands, OCNS is regulated by the State Supervision of Mines (SSM) with scientific and environmental advice from Cefas and Netherlands government agencies [37].

6.3.1.1 Cefas

Cefas assigns product ratings for additives used by the petroleum industry based on the physical, chemical and ecotoxicological properties of products. The assigned hazard groups vary from category A (most hazardous) through E (least hazardous), and HQ color from purple (most hazardous), through orange, blue, white, and silver, to gold (least hazardous) [38].

$$HazardQuotient(HQ) = \frac{PredictedEffectConcentration}{NoEffectConcentration}$$

Table 6-1 - Cefas Chemicals Categories based on Hazard Quotient (HQ)

Minimum HQ	Maximum HQ	Category	
>0	<1	Gold	Hazard Level Increases
>=1	<30	Silver	
>=30	<100	White	
>=100	<300	Blue	
>=300	<1000	Orange	
>=1000		Purple	

Several of the product names provided to NYSDEC by operators on the Marcellus Shale are on the OCNS; the OCNS-approved product list and may be found at http://www.cefas.co.uk/offshore-chemical-notification-scheme-(ocns)/hazard-assessment.aspx. OCNS-approved products that were also submitted for approval to NYSDEC are not cross-referenced here.

6.3.2.2 Products Approved by Norway

Norway is considered to have the most stringent regulatory environment among the OSPAR countries. Norwegian State Pollution Control Authority (SFT) also regulates the use of drilling muds through discharge permits. SFT assesses water-based fluids using data on bio-accumulation potential and bio-degradability. SFT encourages limiting use and discharges of even these approved products. Discharge of unused chemicals into the sea is forbidden [39].

6.3.3 Environmental Coordination in Canada

Canada-Newfoundland and Labrador Offshore Petroleum Board (C-NLOPB) in Canada utilizes a system called Offshore Chemical Selection Guidelines for Drilling & Production Activities on Frontier Lands. C_NLOPB follows the OCNS to a great extent.

6.4 Summary

The ‘environmentally-friendly’ aspect of hydraulic fracturing of deep shale formations presently stem from drilling techniques, like horizontal drilling and mutli-well pads with smaller overall footprint, and from the use of environmentally-friendly chemicals.

Several US-based chemicals suppliers advertise ‘green’ chemicals, but there does not seem to be a US-based metric to evaluate the environmental-friendliness of these chemicals.

The most significant environmentally conscious hydraulic fracturing operations and regulations to date are likely in the North Sea. Several countries have established criteria that define environmental-friendliness, and utilize models and databases to track chemicals’ overall hazardousness against those criteria. Similar to NYSDEC, the regulatory authorities in Europe request proprietary information from chemicals suppliers, and do not release any proprietary information into the public domain. The proprietary recipes for chemical additives are used to assess their potential hazard to the environment, and regulate their use as necessary.

If applicable, New York could choose to adopt the criteria used in Europe, or New York might choose to adapt the European criteria, as appropriate, or the US might choose to set up an independent scientific entity to evaluate all chemicals proposed for use within US territories. However, at this time, it may not be feasible to require the use of ‘green’ chemicals because presently there is no metric or chemicals approvals process in place in the US. The evaluation of the ‘greenness’ of a chemical needs to consider the life-cycle impacts associated with that chemicals; and setting up a metric that provides a comprehensive evaluation is difficult.

It is important to note that several products manufactured by US-based companies, and used or proposed for use in the Marcellus Shale in New York, may be found in the European approved chemicals lists.

7 ALTERNATE WATER SOURCES FOR HYDRAULIC FRACTURING OPERATIONS

7.1 Introduction

Hydraulic fracturing operations require the use of large quantities of water. Data from the Marcellus Shale operations indicate that typical usage is approximately 1 million gallons (MG) for a vertical well and between 2.5 and 3.5 MG for a horizontal well, with maximum usage up to 6 MG.

The water sources that are used initially are those that are the most readily accessible at a reasonable cost. These sources tend to be municipal (potable) water, surface water, and groundwater. Utilizing potable water is more costly and subject to quantity limitations; utilizing fresh surface water or groundwater may be less costly but may deplete limited fresh water resources, may not be available for withdrawal at the rate needed at all times, may be subject to restrictions on interbasin transfers, and may have quality concerns (e.g., affected by abandoned mine drainage). Using alternate water sources may be beneficial in replacing or supplementing the more conventional sources.

7.2 Potential Alternate Water Sources

Alternate hydraulic fracturing water sources that should be considered, where available, include:

- Effluent from municipal or industrial wastewater treatment plants
- Partial re-use of fracturing water (discussed in Section 5)
- Non-contact cooling water discharges from industrial plants
- Saline aquifers
- Stormwater ponds
- Impoundments (lakes, reservoirs, quarries)
- Mine discharges
- Deep mine pools

Alternate water sources need to meet a number of criteria before they may be considered for hydraulic fracturing, as discussed below.

7.3 Factors that Affect Usability of Alternate Water Sources

Operators should consider several factors when evaluating the usability of any particular water source. Decisions regarding use vs. non-use could change with time depending on innovations in technology and other competing uses for water. Factors affecting usability include:

Availability – The “owner” of the source needs to be identified, contact made, and agreements negotiated.

Distance/route from the source to the point of use – The costs of trucking large quantities of water increases and water supply efficiency decreases when longer distances and travel times are involved. Also, the selected routes need to consider roadway wear, bridge weight limits, local zoning limits, impacts on residents, and related traffic concerns.

Available quantity – Fewer larger water sources avoids the need to utilize multiple smaller sources.

Reliability – A source that is less prone to supply fluctuations or periods of unavailability would be more highly valued than an intermittent and less steady source.

Accessibility –Water from deep mines and saline aquifers may be more difficult to access than a surface water source unless adequate infrastructure is in place. Access to a municipal or industrial plant or reservoir may be inconvenient due to security or other concerns. Access to a stream may be difficult due to terrain, competing land uses, or other issues.

Quality of water – The fracturing fluid serves a very specific purpose at different stages of the fracturing process. The composition of the water could affect the efficacy of the additives and equipment used. The water may require pre-treatment or additional additives may be needed to overcome problematic characteristics.

Potential concerns with water quality include scaling from precipitation of barium sulfate and calcium sulfate [1]; high concentrations of chlorides, which could increase the need for friction reducers; very high or low pH (e.g. water from mines); high concentrations of iron (water from quarries or mines) which could potentially plug fractures [1]; microbes that can accelerate corrosion, scaling or other gas production [5]; and high concentrations of sulfur (e.g. water from flu gas desulfurization impoundments), which could contaminate natural gas. In addition, water sources of variable quality could present difficulties.

Similar to reusing or recycling flowback for hydraulic fracturing, experts on hydraulic fracturing agree that high quality water is easy and convenient to use, and that somewhat lower quality water may also be utilizable for hydraulic fracturing [1]. Perhaps due to the additional cost and inconvenience of withdrawing and transporting alternate water sources, expectations of water quality are higher of alternate water sources than of recycled flowback. Based on the applicable water quality specifications, several of the alternate water sources identified in Section 7.2 (such as flowback, saline aquifers, mine discharges and deep mine pools) may be usable only after appropriate treatment.

Permittability – Applicable permits and approvals would need to be identified and assessed as to feasibility and schedule for obtaining approvals, conditions and limitations on approval that could impact the activity or require mitigation, and initial and ongoing fees and charges. Preliminary discussions with regulating authorities would be prudent to identify fatal flaws or obstacles.

Disposal – Proper disposal of flowback from hydraulic fracturing will be necessary, or appropriate treatment for re-use provided. Utilizing an alternate source with sub-standard quality water could add to treatment and disposal costs.

Cost – Sources that have a higher associated cost to acquire, treat, transport, permit, access or dispose, typically will be less desirable by industry.

7.4 Summary

Theoretically, any water source may be utilized for hydraulic fracturing. But in practice, several factors could affect the usability and suitability of these sources. The perceptions of usability and suitability would likely change with time based on the value of natural gas recovered, innovations in technology related to water treatment, regulations, and costs. Each service company and operation would need to evaluate local conditions to determine the availability of alternate water sources to a particular gas well.

8 WATER WELL SAMPLING NEEDS

8.1 Introduction

Based on experiences in other states, there is concern that high-volume hydraulic fracturing operations may impact private water wells in the State of New York (the State) by contaminating the water well or depleting the resource [40, 41, 42]. However, the USEPA found no threat to water sources from hydraulic fracturing [43, 54]. Additionally, Interstate Oil and Gas Compact Commission (IOGCC) member states have all stated that there have been no cases where hydraulic fracturing has been verified to have contaminated drinking water [54]. This section summarizes available information on private water well sampling, testing, and monitoring activities performed in a number of states in conjunction with hydraulic fracturing of deep shale formations. The desktop research identified relevant information for New York, Pennsylvania, Ohio, Kentucky and Texas.

This section also proposes ‘indicator’ compounds/elements to monitor before and after drilling/fracturing to indicate whether there may be a connection between private water well contamination and hydraulic fracturing operations. These indicators have been selected using limited analytical results of flowback from the Marcellus Shale from operations in New York and Pennsylvania.

8.2 Water Well Sampling Requirements in Pennsylvania

Section 208 of Pennsylvania’s Oil and Gas Act - Protection of water supplies – requires ‘any well operator who affects a public or private water supply by pollution or diminution [to] restore or replace the affected supply with an alternate source of water adequate in quantity or quality for the purposes served by the supply’ [44].

The gas well operator may be held responsible for any drinking water well supply contamination or reduction within 1,000 feet of the gas well that is discovered within 6 months of gas well completion [6]. Pre-drilling monitoring of water wells within 1,000 feet of the gas well may, therefore, be driven by both the drinking water supply owner and the gas well operator, at the gas well operator’s expense. Post-drilling water supply well monitoring by the well operator is presently not required in Pennsylvania. While the drinking well supply owner may use a ‘Do-it-yourself’ sampling kit, a state-certified laboratory needs to perform the analyses if legal action were later required based on the analytical results.

8.3 Water Well Sampling Requirements in Ohio

Ohio Department of Natural Resources administers a pre-drilling water sampling program in Ohio. This program requires gas well operators to prepare a sampling plan; the actual sampling requirements are determined on a case-by-case basis and may be contingent on a variety of factors, including hydrology, geology, and aquifer characteristics. The program may require the gas well operator to sample all domestic water supply wells in a given area; the actual size of the sampling area varies by operation.

The State of Ohio requires analyses of the following parameters to characterize pre-drilling water quality: alkalinity, barium, calcium, chloride, conductivity, iron, magnesium, pH, potassium, sodium, sulfate, and total dissolved solids (TDS) [45].

8.4 Water Well Sampling Requirements in Texas

The Railroad Commission of Texas has rules in place to protect groundwater and surface water resources in Texas. Texas Administrative Code Title 16 Economic Regulation, Part 1- Railroad Commission of Texas, Chapter 3 Oil and Gas Division, Rule §3.8 Water Protection provides guidance on anti-degradation. Specific information or guidance on water supply well protection was not readily found.

8.5 Water Well Sampling Requirements in Kentucky

The Kentucky Department of Environmental Protection's Division of Water does "not regulate contaminants in private wells" [46]. Kentucky Administrative Regulations have general requirements and guidelines for groundwater protection, but the desktop search did not find any specific water supply monitoring requirements associated with natural gas drilling in the Devonian Shale [47].

8.6 Existing Water Well Protection in New York

Article 23, Title 3 of the Environmental Conservation Law (ECL) authorizes the New York State Department of Environmental Conservation (NYSDEC) to require that oil or gas wells be drilled, constructed, operated and plugged, and the surrounding land reclaimed, to prevent or remedy "the escape of oil, gas, brine or water out of one stratum into another" and "the pollution of freshwater supplies by oil, gas, salt water or other contaminants" [48].

NYSDEC requires a full environmental assessment if a proposed oil or gas well is within 2,000 feet of a municipal well and a supplemental Environmental Impact Statement if the proposed oil or gas well is within 1,000 feet. Strict oil or gas well construction requirements are expected to protect all groundwater resources, including private wells [49].

8.7 Enhanced Water Well Protection in New York

NYSDEC appears to have a comprehensive program in place to protect municipal wells in the State, while protection of private water supply wells is based on gas well construction requirements. The State could potentially enhance its protection of private water well supplies by implementing the following:

- NYSDEC may be able to draw from Ohio's requirements and enhance the State's requirements by providing to potential gas well operators a succinct list of parameters to monitor, at the producer's expense, in private water wells within a certain distance of a proposed gas well, before and after a fracturing operation.

- NYSDEC could draw from Pennsylvania's requirements and require any gas well operator who affects the quantity or quality of a private water supply to restore or replace, within a reasonable timeframe, the affected private water supply with an alternate source of water similar in quantity and quality to the original supply.

8.8 Indicator Compounds/Elements of Potential Contamination due to Hydraulic Fracturing

Limited time-series data of flowback from Marcellus Shale gas wells in Pennsylvania show that concentrations of several parameters in flowback increased over the 2 to 3 week period. These parameters include: TDS, hardness, calcium, magnesium, bromide, chloride, fluoride, chemical oxygen demand, barium, and manganese. Concentrations of sulfates, bicarbonates, total Kjeldahl nitrogen, 5-day biological oxygen demand, phosphorus and alkalinity decreased with time, likely due to additives used.

Literature based on flowback data from other shale formations indicates that the concentrations of chlorides and TDS (likely heavily influenced by chlorides) increase over the flowback period; literature based on flowback data from the Marcellus indicates that the concentrations of TDS and barium increase over the flowback period. While other parameters may be influenced by mobilization of materials in the shale formation or due to fracturing fluids, there is insufficient data at this time to make a definitive determination that these other parameters would always be found primarily/exclusively due to fracturing operations in the Marcellus Shale area.

In order to determine if a private water supply well has been contaminated due to hydraulic fracturing operations, comprehensive pre- and post-drilling water quality monitoring may be warranted[27]. Such monitoring may be costly, though.

[27] Many water wells in New York are completed in shale formations. Based on NYSDEC's experience with investigating water well complaints, pre-drilling private water well quality may vary due to impact of even an undeveloped shale.

Monitoring for parameters such as barium, TDS and pH could indicate if the private water well has been contaminated due to the fracturing operation. Monitoring for strontium, sodium, chloride, hardness (calcium and magnesium), surfactants, total suspended solids (TSS), iron, carbonates and bicarbonates could provide a better understanding of the extent of potential contamination [6].

Diesel is no longer used in fracturing operations, but is used to fuel equipment. Therefore, sampling for benzene, which is contained in diesel, could indicate above ground spills.

8.9 Summary

There is concern among the public, particularly among property owners and private water supply well owners near hydraulic fracturing operations, about potential well water contamination due to fracturing operations. This section surveyed existing private water well sampling, testing and monitoring requirements in New York, Pennsylvania, Ohio, Kentucky and Texas.

Barium and TDS are recommended as indicator substances to monitor for, at a minimum, in private water supply wells, before and after gas well drilling/fracturing to determine potential contamination from the operation. Private water well quality depends on a number of factors, including water well construction, potential pre-existing contamination, and natural water quantity variations. Therefore, establishing pre-drilling well water conditions is important to determine the potential impact of the fracturing operation.

The frequency and length of monitoring would likely depend on the specific location; but may be pre-drilling, then once per month from the start of operations until six months after completing fracturing operations; and then once per six months until the well is capped. As with other water-quality-related permits, the frequency may be reduced if the operator maintains its record of compliance. Monitoring for additional parameters like pH, strontium, sodium, chloride, calcium, magnesium, surfactants, TSS, iron, carbonates, bicarbonates and diesel would provide a better understanding of potential contamination of private water well supplies due to hydraulic fracturing operations or above ground spills.

9 SUMMARY AND CLOSING

The process of horizontal drilling and high-volume hydraulic fracturing uses large volumes of water with small concentrations of chemical additives to assist and enhance drilling and fracturing. A portion of the fracturing fluids returns to the surface as flowback. This fluid contains variations of additives, new compounds formed due to reactions between additives and substances mobilized within the shale formation.

There is concern among the public that the chemical additives used for fracturing or flowback fluid could contaminate some of the State's water resources and, as a result, interfere with the use of those sources in accordance with their designated use classifications. This study addresses this issue, subject to the limited amount of data available for evaluation.

9.1 Summary

Section 2 presents 12 classes of chemical additives that may potentially be used in hydraulic fracturing operations and, based on proprietary information and MSDS received from service companies and operators via the NYSDEC, presents a list of basic compounds and elements found in more than 125 chemicals.

Section 3 discusses volumes and composition of flowback based on publicly available literature and data from well operators, and trends in volume and composition observed based on information from one well operator. This section presents a list of compounds and elements based on analytical results of flowback from the Marcellus Shale.

Section 4 surveys the sufficiency of federal and New York State regulations and guidelines to protect water resources in the State. This section provides a preliminary comparison of constituents found in additives (in Section 2) and flowback (in Section 3) with contaminants/pollutants regulated by the federal drinking water standards, the SPDES program, or which have guidance through TOGS111.

Section 5 is a preliminary survey of flowback recycling and on-site treatment technologies currently used to a limited extent for other drilling/fracturing operations. On-site treatment of flowback is costly, and technology is not necessarily readily available for use in the Marcellus Shale. However, these technologies are evolving to meet industry need and regulatory requirements. Low quality fracturing fluids typically require larger quantities of additives. The very high TDS concentrations in flowback from the Marcellus Shale, the uncertainties associated with minimum water quality that may be utilized in fracturing operations, the large variations and fluctuations in flowback quality, the differences in quality of flowback from different shale formations, and potential difficulties with disposal of residuals are likely the main challenges to developing on-site treatment technologies. These technologies may have the potential to function appropriately at the Marcellus Shale after further adaptation. Flowback recycling presently involves blending flowback with freshwater for fracturing operations.

A reduction in freshwater withdrawals and transportation needs, and a reduction in flowback fluid disposal are likely the primary benefits of recycling and/or on-site treatment of flowback fluids. The value of natural gas from the Marcellus and the regulatory environment would likely drive innovation of on-site treatment technologies. On-site treatment technologies do not appear to be ready yet for industry-wide use.

Section 6 surveyed 'environmentally-friendly' hydraulic fracturing technologies and chemicals. It appears that environmentally-friendly technologies are in experimental phases or have only been used under conditions different from the Marcellus. The 'environmentally-friendly' aspect of hydraulic fracturing of deep shale formations presently stems from drilling techniques, such as horizontal drilling and multi-well pads with smaller overall footprint, and from the use of environmentally-friendly chemicals. While there are claims of green or environmentally-friendly chemicals and technologies, their lifecycle environmental performance has not yet been evaluated.

There is multinational cooperation in Europe regarding oil and gas drilling in the North Sea. This study did not evaluate the robustness or efficacy of European efforts, but suggests that the OSPAR Convention and the Offshore Chemical Notification Scheme (OCNS) serve as the starting point for setting up a framework in New York State (or the US) to promote environmentally-conscious hydraulic fracturing operations. The specific concerns associated with onshore vs. offshore operations would likely be different, but the framework, approach and lessons learned from offshore operations would likely be applicable at onshore operations as well.

Section 7 is a survey of alternate water sources that may be utilized for hydraulic fracturing operations. Several alternate sources might potentially be available in New York, but they are not well-bore-ready. Each alternate source has its limitations. Effluent from wastewater treatment plants or non-contact once-through cooling water discharge from industrial facilities may presently be a significant component of a waterbody[28], and its use would likely require approvals and permit modifications from waterbody commissions or other agencies. Water from saline aquifers, quarries, or mines would likely require significant treatment. These sources already contain high concentrations of TDS – the parameter likely of greatest operational concern in flowback. Treatment is costly. Innovations in treatment technologies and potential use of alternate water sources would likely depend on the value of natural gas that may be harvested from the Marcellus, the availability, costs and other competing uses of freshwater in the general area, and regulations and guidelines on withdrawal, use, consumption, treatment and disposal (i.e. the complete life-cycle) of water used in hydraulic fracturing.

There is concern that hydraulic fracturing operations may contaminate private water wells in the vicinity. Section 8 surveys efforts in Pennsylvania and Ohio to potentially preserve water quality and quantity in private water wells. NYSDEC has the authority to

[28] Particularly during low flow period, the relatively reliable discharge rate from POTWs is important to maintain minimum flow rates in small waterbodies.

protect water resources in the State, and has a comprehensive program to protect municipal water wells. Section 8 draws from experiences and guidelines in Pennsylvania and Ohio to suggest enhancements to water resource protection (particularly private water well supplies) in the State. In addition, based on analytical results of flowback from the Marcellus obtained from operators and published literature, Section 8 suggests a series of parameters to test and monitor for in private well water before and after drilling/fracturing a gas well.

9.2 Limitations of the Survey

This study looked at a variety of subjects associated with hydraulic fracturing within a very short period of time. The information is based on limited interactions with service companies, telephone interviews and articles from industry experts, or information published on websites, and is not based exclusively on peer-reviewed published literature. Composition of additives and analytical results of flowback are from a handful of service companies and operators who voluntarily shared proprietary information with NYSDEC. Such information was used in this study under a strict confidentiality agreement. The level of detail of information and data from different sources is not consistent. Given these study conditions, information presented in this report may be refined in the future as more information becomes available.

This study likely captures all the classes of chemical additives used in fracturing operations. As additional service companies, operators and chemicals suppliers share more information, the table with basic constituents in additives (Table 3-1) may be further expanded.

The different analyses of flowback data tested for different sets of parameters. In addition, different detection methods (which have different detection limits) have been used to test for the same parameter. All operators testing and reporting concentrations for the same comprehensive list of parameters, guidelines on allowable detection methods under different conditions, along with the composition and quantity of water and additives used would provide a better understanding of constituents in flowback. Flowback composition changes with time. All operators monitoring flowback at several pre-specified points in time would also improve understanding of flowback.

On-site treatment and recycling are in pilot phases, and much of the information is presently considered to be proprietary. Incentives to innovate and share information would help understand the industry’s progress in on-site treatment and recycling.

Several US-based companies advertise ‘green’ chemicals. But there does not appear to be a common metric in place to evaluate environmental-friendliness in the US. New York State may be able to draw from experiences in Europe and formulate a metric to objectively measure the environmental-friendliness of chemicals or technologies so the industry has a specific goal to work towards, and the environmental impact of hydraulic fracturing may be measured more objectively. Significant differences between European countries and the US include the size, the state-based governance system, and offshore vs. onshore operations. European countries are smaller than the US and most environmental regulations and requirements apply to the entire country, while in the US regulations and requirements are often administered at the state-level. It is imperative that these regulations and requirements continue to be administered at the state-level. Interstate collaboration with respect to shale development similar to riverbasin commissions would be beneficial.

This study suggests a few parameters to test and monitor for in private water wells before and after drilling a gas well in the vicinity. A pilot study to evaluate the appropriateness of these parameters may lend greater credibility to the perceived need for a State-wide private well testing program.

9.3 Closing

The oil and gas industry has developed innovative technologies to harness natural gas from the low-permeability Marcellus Shale formation at depths of several thousand feet. Adequate safeguards are necessary to carry out these drilling and fracturing operations in an environmentally sensitive manner. The industry has shared proprietary information and experiences regarding hydraulic fracturing operations which have been utilized in this report.

As with other states in the core Marcellus Shale region, New York State is tasked with promoting efforts to develop natural gas resources in support of federal and state energy policies while protecting and preserving other important resources of the State. This balance is reflected in the laws and regulations that have been promulgated to address public needs for energy and environmental health.

Natural gas harvesting from the Marcellus Shale provides an opportunity for agencies, industry and the public to work together to develop one resource while protecting and preserving other resources and respecting the competing public demands on the State.

10 REFERENCES

[1] Gas Technology Institute (September 26, 2007). Proceedings and Minutes of the Hydraulic Fracturing Expert Panel, XTO Facilities, Fort Worth, TX, compiled by Tom Hayes of GTI.

[2] Parshall, J. (undated). Barnett Shale Showcases Tight-gas Development. Journal of Petroleum Technology, in: ALL Consulting. 2008. Hydraulic Fracturing Considerations for Natural Gas Wells of the Marcellus Shale.

[3] All Consulting, LLC (2008). Evaluating the Environmental Implications of Hydraulic Fracturing in Shale Gas Reservoirs, presented at International Petroleum & Biofuels Environmental Conference Albuquerque, NM, November 11-13, 2008.

[4] New York State Water Resources Institute at Cornell University (visited 2009). Waste Management of Cuttings, Drilling Fluids, Hydrofrac Water and Produced Water, at http://wri.eas.cornell.edu/gas_wells_waste.html.

[5] Fichter, J.K., Johnson, K., French, K. an Oden, R. 2008. "Use of Microbiocides in Barnett Shale Gas Well Fracturing Fluids to Control Bacterially-Related Problems." NACE International Corrosion 2008 Conference and Expo. Paper 08658. I pp. 2, 3. http://content.nace.org/Store/Downloads/7B772A1BA1- 6E44-DD11-889D-0017A446694E.pdf

[6] Pennsylvania State University (2009). Gas Well Drilling and Your Private Water Supply: Water Facts #28.
URL: http://resources.cas.psu.edu/WaterResources/pdfs/gasdrilling.pdf

[7] ASWCMC {June 30, 2008) Appalachian Shale Water Conservation and Management Committee.

[8] NYSDEC (visited June 2009). Classification – Surface Waters and Groundwaters (6 NYCRR 701), at http://www.dec.ny.gov/regs/4592.html#15979.

[9] USEPA (visited June 2009). Setting Standards for Safe Drinking Water, at http://www.epa.gov/ogwdw/standard/setting.html.

[10] USEPA (visited June 2009). Drinking water contaminants, at http://www.epa.gov/safewater/contaminants/index.html.

[11] USEPA (visited June 2009). Secondary Drinking Water Regulations: Guidance for Nuisance Chemicals, at http://www.epa.gov/OGWDW/consumer/2ndstandards.html.

[12] USEPA (visited June 2009). Drinking Water Contaminant Candidate List and Regulatory Determinations, at http://www.epa.gov/OGWDW/ccl/index.html.

[13] USEPA (visited June 2009). Six Year Review of Drinking Water Standards, at http://www.epa.gov/OGWDW/review.html.

[14] NYSDEC (visited June 2009). Casing and Cementing Practices, at http://www.dec.ny.gov/energy/1757.html.

[15] NYSDEC (1992). Generic Environmental Impact Statement on the Oil, Gas and Solution Mining Regulatory Program (GEIS), at http://www.dec.ny.gov/energy/45912.html.

[16] Fichter, J.K. et al. (2008) Use of microbiocides in Barnett Shale gas well fracturing fluids to control bacteria related problems, presented at the National Association of Corrosion Engineers (NACE) International Corrosion 2008 Conference and Expo.

[17] Washington Group International (undated). Water in the West: Treatment, Disposal, and Reuse of Produced Water from Natural Gas Exploration in the Rocky Mountain Region, prepared by Tim Rollenhagen, Barry Friedman, Jeff Matthews and Sally Cuffin, of Washington Group International, Denver, CO.

[18] National Energy Technology Laboratory (visited April 2009). Produced Water Technology Description – Fact sheet – Ion Exchange, at http://www.netl.doe.gov/technologies/pwmis/techdesc/ionex/index.html.

[19] Natural Gas and Technology (2004), at http://www.naturalgas.org/environment/technology.asp.

[20] USDOE (1999). Environmental Benefits of Advanced Oil and Gas Exploration and Production Technology, prepared by the office of Fossil Energy of the United States Department of Energy.

[21] Hill et al. (undated). Fractured Shale Gas Potential in New York, prepared by David G. Hill and Tracy E. Lombardi of TICORA Geosciences, Inc., and John P. Martin of NYSERDA.

[22] National Energy Technology Laboratory: Home Page (visited June 2009). Petroleum Consulting Services Production Verification Tests, DE-AC21-90MC26025, at http://www.netl.doe.gov/technologies/oil-gas/NaturalGas/Projects_n/EP/DCS/DCS_C_26025PetrolConsult.html.

[23] NUMA (visited April 2009). Undated. Project Summaries, Horizontal Drilling Project, United Kingdom. http://www.numahammers.com/newsitems/PS-EIL_shropshire.html.

[24] TAMU (Texas A&M University) (2003). Drilling for Natural Gas – an Environmental Friendly Process. The Texas Institute for Advancement of Chemical Technology (TIACT). October 10, 2003. http://cheweb.tamu.edu/tiact/.

[25] CDX Gas (2007). About Z-Pinnate Technology, at http://www.cdxgas.com/technology.php.

[26] Rae, P., A. N. Martin, and B. Sinanan (1999). Skin bypass fracs: Proof that size is not important. SPE annual technical conference and exhibition, 3-6 October 1999. Volume delta: Drilling and completion. SPE annual technical conference, Houston TX , ETATS-UNIS (03/10/1999) 1999, pp. 129-141 (23 ref.).

[27] USEPA (2003). A Memorandum of Agreement between the United States Environmental Protection Agency and BJ Services Company, Halliburton Energy Services, Inc., and Schlumberger Technology Corporation for Elimination of Diesel Fuel in Hydraulic Fracturing Fluids Injected into Underground Sources of Drinking Water During Hydraulic Fracturing of Coalbed Methane Wells, dated 12 December 2003.

[28] USDOE (2009). State Oil and Natural Gas Regulations Designed to Protect Water Resources, prepared by the office of Fossil Energy of the United States Department of Energy, and the National Energy Technology Laboratory.

[29] Schlumberger (visited April 2009). Green Chemistry: Earth-friendly GreenSlurry system for uniform marine performance, at http://www.slb.com/content/services/stimulation/execution/greenslurry.asp

[30] USEPA (visited April 2009). Introduction to the Concept Of Green Chemistry, at http://www.epa.gov/oppt/greenchemistry/pubs/about_gc.html?.

[31] Cameron, C., A. Florence, and C. Temple (2004). Water-Based Drilling Fluid Helps Achieve Oil-Mud Performance. AADE-04-DF-HO-01. Presented at the AADE 2004 Drilling Fluids Conference, Houston, Texas, April 6-7, 2004.

[32] Cobby, G. L. and R. J. Craddock (1999). Western Australian Government Decision-Making Criteria Involved In the Regulation of Drilling Fluids Offshore. APPEA Journal, pp 600-605.

[33] Wills, Jonathan (2000). A Survey of Offshore Oilfield Drilling Wastes and Disposal Techniques to Reduce the Ecological Impact of Sea Dumping- The Law on Offshore Wastes Discharges in Different Jurisdictions, at http://www.offshore-environment.com/unitedkingdom.html.

[34] Anastas, P. and J. C. Warner (1998). Green Chemistry: Theory and Practice. Oxford University Press: New York. 152 pp.

[35] Journal of Petroleum Technology Online (2006). Summary of Society of Petroleum Engineers paper 102908, “Meeting the Environmental Challenge: A New Acid Corrosion Inhibitor for the Norwegian Sector of the North Sea,” by M. Vorderbruggen, SPE and H. Kaarlgstad, SPE, prepared for ATCE 2006, San Antonio, TX, 24-27 September.

[36] Cefas (visited April 2009). Description of Offshore Chemical Notification Scheme (OCNS), at http://www.cefas.co.uk/offshore-chemical-notification-scheme-(ocns).aspx

[37] Schlumberger (visited April 2009). Earth-friendly GreenSlurry system for uniform marine performance, at http://www.slb.com/media/services/stimulation/execution/greenslurry.pdf.

[38] National Energy Board of Canada (April 2009). Offshore Chemical Selection Guidelines for Drilling & Production Activities On Frontier Lands, at http://www.cnlopb.nl.ca/pdfs/guidelines/ocsg.pdf.

[39] Wills, Jonathan (2000). A Survey of Offshore Oilfield Drilling Wastes and Disposal Techniques to Reduce the Ecological Impact of Sea Dumping- The Law on Offshore Wastes Discharges in Different Jurisdictions - Norway, at http://www.offshore-environment.com/norway.html

[40] Scott M. Stringer (2009). Uncalculated Risk: How plans to drill for gas in Upstate New York could threaten New York City's water system. A report based on statement by Manhattan Borough President.

[41] Lustgarten, Abrahm (November 11, 2008). *Does Natural-Gas Drilling Endanger Water Supplies?* in Business Week November 11, 2008.

[42] Witter et al. (September 15, 2008). Potential Exposure-Related Human Health Effects of Oil and Gas Development: A White Paper, prepared by Roxana Witter, Kaylan Stinson, Holly Sackett, Stefanie Putter, Gregory Kinney, Daniel Teitelbaum, and Lee Newman.

[43] USEPA (June, 2004). Evaluation of Impacts to Underground Sources of Drinking Water by Hydraulic Fracturing of Coalbed Methane Reservoirs. EPA 816-R-04-003.

[44] Pennsylvania Statutes and Consolidated Statutes Annotated, Title 58 - Oil And Gas, Chapter 11 - Oil And Gas Act

[45] Ohio Department of Natural Resources: Mineral Resources Management (April 28, 2005). Best Management Practices for Pre-Drilling Water Sampling, at http://www.dnr.state.oh.us/Portals/11/oil/pdf/BMP_PRE-DRILLING_WATER_SAMPLING.pdf.

[46] Well testing information published on Kentucky Division of Water website at http://www.water.ky.gov/dw/profi/tips/welltest.htm

[47] Kentucky Administrative Regulations: Title 401 - Energy and Environment Cabinet Department for Environmental Protection published at http://www.lrc.ky.gov/kar/TITLE401.HTM

[48] NYSDEC (visited April 2009). Protecting the Environment During Well Drilling and Operation - Environmental Protections for Oil and Gas Development, at http://www.dec.ny.gov/energy/1536.html.

[49] NYSDEC (visited April 2009). Protecting the Environment, Water Resources and Public Water Supplies at http://www.dec.ny.gov/energy/46288.html.

[51] Wills, Jonathan (2000). A Survey of Offshore Oilfield Drilling Wastes and Disposal Techniques to Reduce the Ecological Impact of Sea Dumping- Drilling Waste Streams from Offshore Oil and Gas Installations, at http://www.offshore-environment.com/drillwastestream.html.

[52] D. B. Burnett Global Petroleum (visited April 2009). Undated. Environmentally Friendly Drilling Systems Background & Current Programs, at http://www.bismarckstate.edu/gpee/presentations/pdfs/BurnettDaveGPEEPresentation.pdf.

[53] Division of Water (June 1998). Division of Water Technical and Operational Guidance Series 1.1.1. - Ambient Water Quality Standards and Guidance Values and Groundwater Effluent Limitations, at http://www.dec.ny.gov/regulations/2652.html.

[54] Interstate Oil and Gas Compact Commission (undated). Is Hydraulic Fracturing Safe?, at http://www.iogcc.state.ok.us/hydraulic-fracturing visited August 2009.

[55] Maurice Smith (September 2008). Frac Forward: Startup Cracks Propane Fracture Puzzle, Provides 'Green' Solution, in New Technology Magazine.

[56] USEPA (2002). EPA Facts about Cesium-137. At http www.epa.gov superfund health contaminants radiation pdfs cesium.pdf.