Frac Water Recycling Technologies
Feasibility Study

FRAC FLUID REPORT
Draft 5.6b

Prepared for
Petroleum Technologies Alliance Canada

Prepared by
M-I SWACO

January 3, 2012

Table of Contents

Glossary of Terms

List of Figures

List of Tables

ACKNOWLEDGEMENTS

PTAC Petroleum Technology Alliance Canada (PTAC) would like to gratefully acknowledge the vision of CAPP, SCEK and Alberta Innovates for co-funding this project. This report is a companion document to a report entitled Frac Water Recycling Technologies Feasibility Study – Frac Fluid Reuse – Guidance Document.

PTAC wishes to acknowledge the contributions of the following individuals for providing guidance and peer review:

Keith Minnich, Talisman
Scott Hillier, Conoco Phillips
Brian Thompson, SCEK
Mayka Kennedy, BC Oil and Gas Commission
John Faltinson, Alberta Innovates
Sarah Fulton, PennWest
Michael Duncan, Quicksilver

The participation and contribution of the following Schlumberger/M-I SWACO personnel in providing technical input and oversight is gratefully recognized:

Nicole Mikic, M-I SWACO
Doug Pipchuk, Schlumberger
Susan Mahmoudi Darinsou, M-I SWACO
Debbie Larond, Lonkar Testing
Ken Charney, Silvertip Testing
Joe Lima, Schlumberger
Paul Howard, Schlumberger
Adriana Ovalle, M-I SWACO
Taunnya Child, M-I SWACO

In addition, the input of the PTAC Water Innovation and Planning Committee in launching, and administering the execution of this study is gratefully acknowledged.

DISCLAIMER

This document was prepared for and under the direction of PTAC. M-I SWACO and Schlumberger and its participating subsidiaries disclaim any warranty, express or implied, that the information in this report is accurate and complete, or will be useful or reliable for any purposes. The user assumes the entire risk of inaccuracy or incompleteness or that the information will be useful or reliable, regardless of any fault or any negligence on the part of PTAC and M-I SWACO.

PREFACE

The documents that have been produced as part of this project are intended to be usable by:

- Oilfield operators, hydraulic fracturing service companies, chemical manufacturers, and water treatment companies in the design of fracs and the management of water needs and issues associated with hydraulic fracturing in the energy sector.
- Regulators in providing direction and developing policy regarding fracture treatment operations and water management issues.
- Other stake holders with an interest in water management to understand the fracturing process and the considerations that must be taken into account in the use and reuse of water for fracture treatment operations.

The objective of the study is to identify a methodology so that producers can work with service companies to determine the limiting factors and mitigation or control scenarios for using water with high salinity or other undesirable constituents for making up frac fluid. The methodology and technologies that have been suggested incorporate the science and practice of hydraulic fracturing with frac fluid management and treatment technologies.

Significant portions of the input to this report has been extracted, in some cases verbatim, from existing documents prepared by individuals experienced in the engineering and implementation of hydraulic fracturing operations and water management. In preparing this document, we have attempted to give credit to the authors of those documents. We apologize for any oversights in citing the appropriate references to any of the materials included.

For maximum utility, this document should be considered alongside its companion report “Guideline to the Re-use of Fracture Treatment Flowback Water” prepared as part of this project, and published by Petroleum Technology Alliance Canada.

ABSTRACT OR EXECUTIVE SUMMARY

Integrated Water Management Plan

Desirable Frac Fluid Characteristics

Generic Fac Additives and Conditioners

Frac Flowback Characteristics

Sensitive Water Constituents

Decision Tree

Remedial Options

1.0 INTRODUCTION

During the last decade of gas shale development, projected recovery of shale gas-in-place has increased from about 2% to estimates of about 50%; mainly through the development and adaptation of technologies to fit shale gas developments. Adapting technologies, including multi-stage fracturing of horizontal wells, slickwater fluids with minimum viscosity and simultaneous fracturing, have evolved to increase formation-face contact of the fracture system. These technologies have made possible development of enormous gas reserves that were completely unavailable only a few years ago. Current and next generation technologies promise even more energy availability with advances in hybrid fracs, fracture complexity, fracture flow stability and methods of re-using water used in fracturing.40

As part of an effort to recycle flowback and produced water through optimization of water use and chemical additives, there has emerged a need to understand the factors that influence the use and performance of water conditioners and hydraulic fracturing additives, and the factors that influence the reuse of frac flowback water in hydraulic fracturing operations.

An outcome of the consideration of these issues is the recognition that cost effective use of chemicals and water management warrant the application of more intensive planning and engineering. Ultimately, the refinement of the science and practice of hydraulic fracturing will lead to the development of more formalized work flows and operating procedures that will evolve in response to continuing development and of operating experience in shale gas and tight oil development.

In addition, the need for transparency creates a need to outline the role of the various chemical conditioners and additives used in the various types of hydraulic fracturing methods.

The documents produced as part of this project are intended to be usable by:

- Oilfield operators, hydraulic fracturing service companies, chemical manufacturers, and water treatment companies in the design of fracturing treatment and management of water needs and issues.
- Regulators in providing direction and developing policy regarding fracturing treatments and water management issues.
- Other stake holders with an interest in water management to understand the fracturing process and the considerations that must be taken into account in the use and reuse of water for fracturing operations.

As drilling and completion technologies have advanced, similarly stimulation techniques have developed that are specifically effective in the stimulation of horizontal wells in Shale Gas zones. Not only have the number of stages increased, and the volume of frac fluids pumped per stage increased, but the addition of combinations of specific chemical additives to the frac fluid has made frac completions more effective.

While the technology related to the design of large fracture treatments being conducted in the shale gas development areas and the management and treatment of frac fluid flowback water continues to evolve, a need has arisen to understand the physical and chemical nature of frac fluid flowback and to clarify the factors that influence the reuse of frac fluid flowback water. Reuse of frac flowback has multiple benefits:

- Reduces demand for fresh water
- Reduces water disposed
- Ideally reduces overall production costs

Water reuse and/or recycling can be a key enabler to large scale future development. Pursuing this water conservation option, however, requires planning and knowledge of chemical additives likely to be used in hydraulic fracturing operations, and a detailed evaluation of the physical and chemical composition of the source water, flow back and produced water. Reuse and/or recycling practices require the selection of compatible additives, with focused efforts on the use of environmentally benign constituents that do not impede water treatment initiatives. The judicious selection of water conditioners and frac additives may enhance the quantity and compatibility of fluids available and provide more options for ultimate use and/or disposal.HF2

There are no optimum, one-size-fits-all completion or stimulation designs for shale gas wells.40 No two shale formations are alike. Shales vary aerially and vertically within a trend, even along the wellbore, so there is no "silver bullet" in terms of frac design or frac fluid configuration. Nonetheless, workflows have been developed that formalize the logic and process of evaluating the needs for developing and designing cost effective hydraulic fracturing fluid packages that optimize the utilization of water conditioners and frac additives, and reuse of flowback water.40

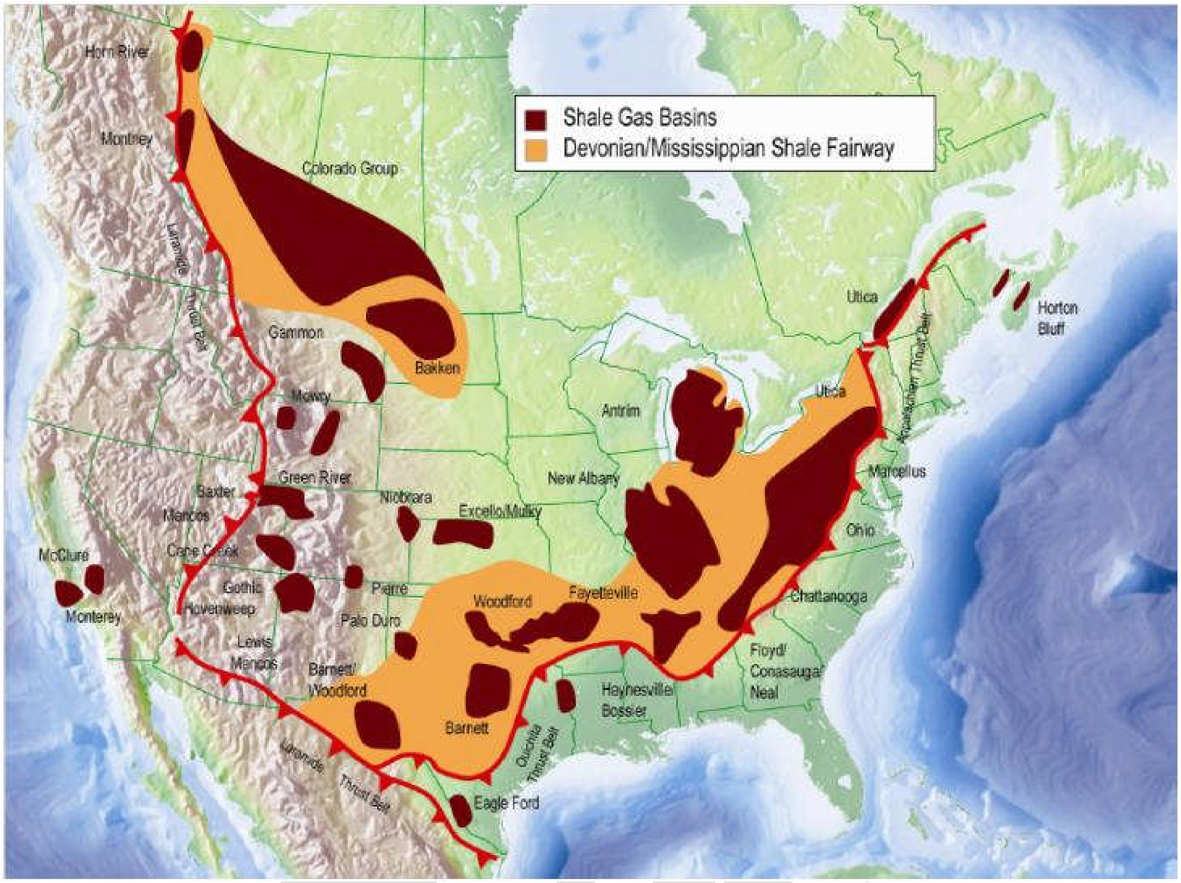


Figure 1 Shale Gas Development Areas of North America (Source Doc 10)

1.1 Scope Of Report

The purpose of this project is to examine and critically evaluate the performance of water conditioners and frac fluid additives that are employed in hydraulic fracturing of shale gas reservoirs and prepare guidelines for selecting additives that will optimize performance during pumping, fluid recovery and production.41

While the focus of the project is on the influence of the water constituents on frac additives and the need to condition or treat source water or flowback water; the secondary focus is to understand how decisions regarding the re-use of frac water and the decisions regarding frac fluid conditioning may have implications with regard to other elements of the water management plan and infrastructure needs of hydraulic fracturing operations.

This report provides that insight, consolidating information related to fracturing treatment, frac additives, frac flowback, and treatment of frac flowback into a single document that will provide guidance on frac flowback issues, treatment and management. As such, it is intended to act as a first cut at the development of a more formalized approach to frac fluid design and management.

The FRAC FLUID REPORT provides the basis for the preparation of the FRAC FLUID REUSE GUIDELINE for producers and service companies to use in the evaluation of the reuse of flowback fluids and the selection of water management and treatment technologies. The FRAC FLUID REPORT will become a supplement to the FRAC FLUID REUSE GUIDELINE which is the second core deliverable of the project.

A substantial amount of the technical information needed to meet the requirements of this project was already in existence, but was dispersed, in fragmentary form, in various public documents, within proprietary frac design documents and manuals, and in client confidential databases. Additional raw data in the form of flowback test data and time series chemical analyses from source water, flowback water and produced water was provided by operators. This data was synthesized by M-I SWACO staff before being incorporated into the project report. To protect confidentiality of proprietary information, specific references to operator's names, well names and locations have been deleted. Similarly, trade names for specific commercially available product have not been used.

In developing a scope of work for the project, a list of pertinent questions related to hydraulic fracturing and frac fluid reuse was prepared to provide direction to the scoping exercise.

Questions that need answers and which are addressed in the project deliverables include:

- What do I need to know about my frac fluid, formation fluid, and flowback water in order to manage it cost effectively?
- How do the chemical constituents in the source water influence the performance of frac fluids and additives?
- What is the optimum water quality for the various types of fracture treatments? What are the outside limits? What are the implications of being outside the recommended limits of various frac water constituents?
- How does the occurrence and quality of the flowback water from fracturing treatment influence the re-used of flowback water for subsequent fracturing operations?
- What other characteristics of flowback water complicate its re-use for fracturing operations? What technologies are available to modify undesirable flowback water characteristics to make re-use and management of frac flowback more cost effective?
- What are my water treatment design objectives? Partial reduction? Complete removal?
- How will treatment of flowback fluids impact on the other elements of the Water Balance and Water Management Plan and the infrastructure needs?

1.2 Evolution of Shale Gas Development and Hydraulic Fracturing Technology

A key element in the emergence of shale gas production has been the refinement of cost-effective horizontal drilling and hydraulic fracturing technologies. These two technologies, along with the implementation of protective environmental management practices, have allowed shale gas development to move into areas that previously would not have been economically developable.

Hydraulic fracturing has played an important role in the development of North America's oil and gas resources for nearly 60 years. Hydraulic fracturing is a technology that was developed in the 1940s and has since helped produce more than 600 trillion cubic feet of natural gas and 7 billion barrels of oil. In the U.S., an estimated 35,000 wells are hydraulically fractured annually and it is estimated that over one million wells have been hydraulically fractured since the first well in the late 1940s. As production from conventional oil and gas fields continues to mature, and the shift in focus to non-conventional resources increases, the importance of hydraulic fracturing in the development of these resources will also increase.17

Hydraulic fracture stimulation is continuously being refined as technology improves and more detailed information is gathered on the process.33Today, there are numerous different types of fracturing methods using a variety of fluids and proppant and injection techniques which vary depending upon the reservoir characteristics.

1.2.1 Horizontal Drilling Technology

Horizontal drilling commonly involves drilling several (up to a dozen or more) wells from a single drilling pad. The use of the drilling pad concept reduces the footprint of drilling and completions operations, but also makes for more cost effective investment in water management infrastructure 40 The longer horizontal wells translates into more stages per well requiring fracture treatment, with a corresponding increase in the volume of water needed per well, and an increase in flowback volume

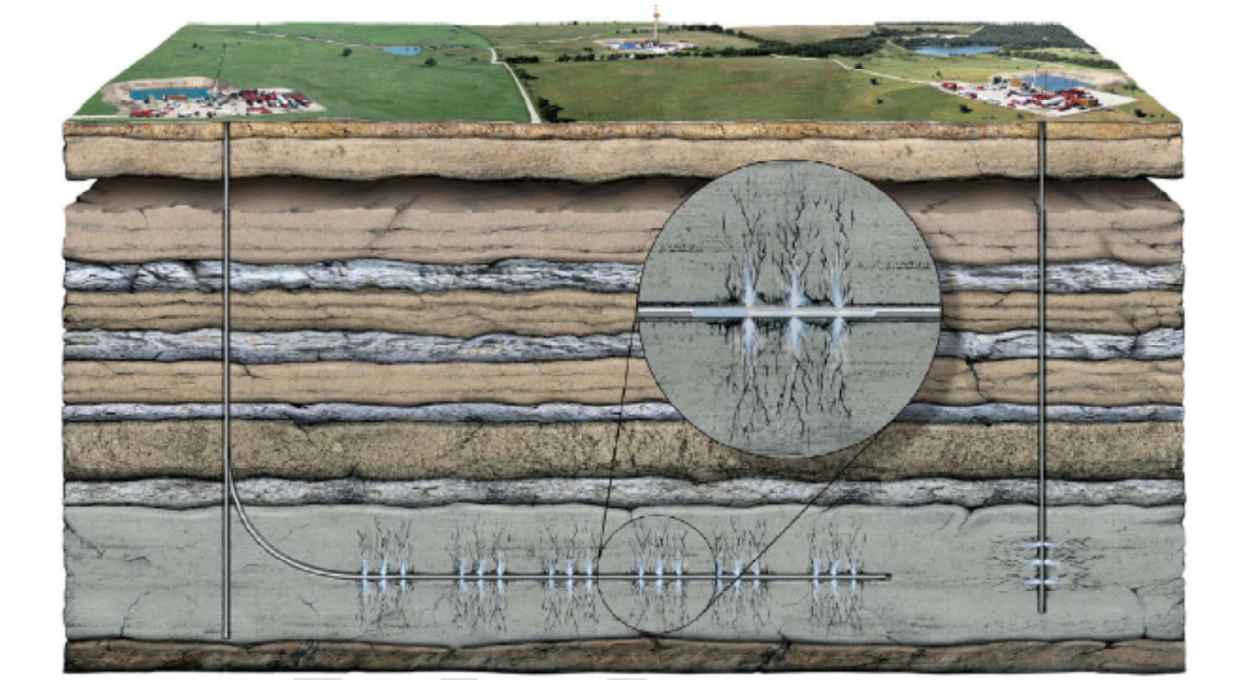


Figure 2 Vertical vs Horizontal Drilling

The lengths of the horizontals which began with well lengths on the order of a few hundred meters have increased to several thousand meters as confidence in the drilling phase has grown. Longer well lengths usually deliver lower cost per foot if frac stages are increased to effectively break up the shale formation exposed by the extended wellbore reach. The increased length of the horizontal translates into more fracture stages, and conversely more frac fluid utilized per well completed.

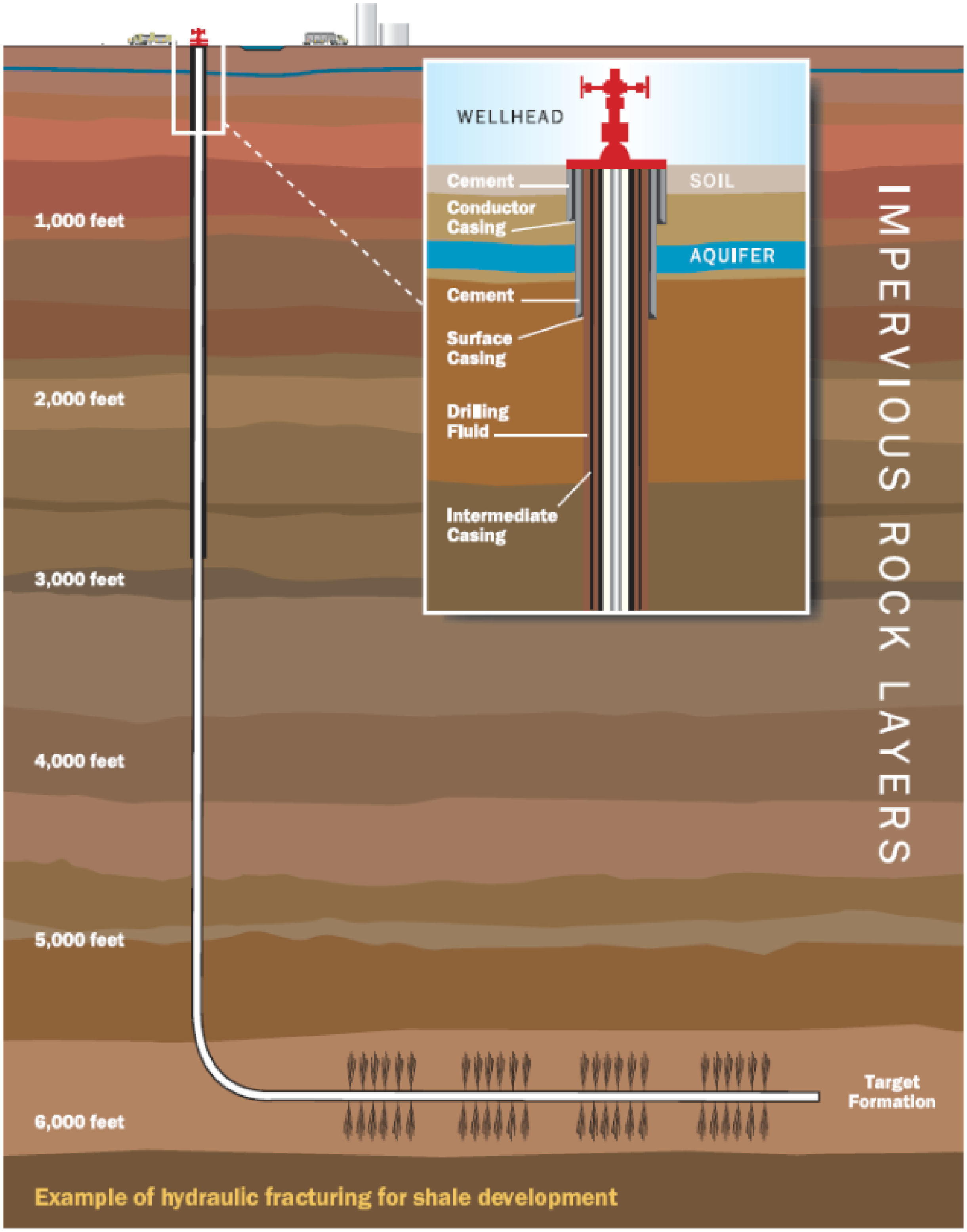


Figure 2b Horizontally Drilled Well

1.2.2 Hydraulic Fracturing Technology

Hydraulic fracturing is widely used by the oil and gas industry to improve low permeability reservoirs. Fluid (often water, carbon dioxide, nitrogen gas, or propane) is pumped down the well until the pressure surpasses the rock strength and causes the reservoir to crack (Figure 5). The “frac” fluid pumped down the well is loaded with proppant that infiltrate the formation and help to prop the fractures open, which are at risk of closing once the pressure is released.

Hydraulic fracturing has traditionally been used in vertical wells that accessed only a specific portion of the producing zone. Multi-stage fracturing treatments in horizontal wellbores are capable of accessing significantly larger producing zones, maximizing the amount of resources being recovered and minimizing the amount of surface space required.71

1.3 Development of Shale Gas Areas

Much useful insight into water management needs and responses has been be gained from the experiences in the development of shale gas areas which have undergone, or are undergoing extensive development, such as the Barnett Shale and the Marcellus in the United States and the Horn River Basin and the Montney area of Western Canada. However, each shale gas development areas is substantially different from all others, such that a unique set of field development procedures and water management approaches must be developed for each area.

During the initial period of pilot scale development of a shale gas area, different drilling and completion technologies are applied in an attempt to find the most cost effective combination of reservoir properties, drilling configuration and hydraulic fracturing technology needed to optimize gas production from the low permeability shale deposits. The Barnett Shale in the Forth Worth Basin of north-central Texas was the first modern commercially developed shale play, but it took almost two decades to become the success it is today.33

Typically, the development of a shale gas play follows a process of pilot develop whereby different drilling and completions techniques are applied until the right combination of technologies proves that development of an area can be achieved cost effectively before the operating company commits to “full field development”.

Typically, exploitation of a shale play proceeds through three distinct phases; from the discovery stage, through drilling and reservoir evaluation, to production. Discovery and planning is the stage during which all of the initial reservoir knowledge is gathered. Extensive analysis including coring establishes the economic viability of the play during this phase, and helps determine the techniques to be used to optimize the development. The effectiveness of planning accomplished in the discovery stage depends largely upon knowledge of the reservoir. Drilling and reservoir evaluation is the operational phase. During this stage, the focus is on applying the planned techniques most efficiently to maximize reservoir contact and lower cost per unit. It is in this stage of development that the issues concerning infrastructure and practical efficiencies are addressed. And this is the present state of several currently active shale plays.

Shale gas development is occurring in 34 US states and in British Columbia, Alberta, Saskatchewan[3], Quebec and New Brunswick. Further, the effectiveness of both horizontal drilling and hydraulic fracturing technology has been proven in several of the liquids rich gas fields of Canada and the US.

Because the cost of horizontal drilling and large scale hydraulic fracturing is large compared to conventional vertical well completions and hydraulic fracturing, companies engaged in shale gas development continue to commit significant engineering resources on an ongoing basis to monitor and modify hydraulic fracturing procedures in response to insights gained from previously executed fracturing treatments.

2.0 HYDRAULIC FRACTURING IN SHALE GAS DEVELOPMENT

Modern hydraulic fracturing practices are sophisticated, engineered, processes designed to create single fractures or multiple fractures in specific rock strata. These hydraulic fracture treatments are controlled and monitored processes designed for site specific conditions of the reservoir (see Figure 5). These conditions are based on the target product (natural gas or crude oil), the target formation properties and rock fracturing characteristics, the formation water characteristics, the anticipated water production (formation water versus fracturing flow back water), and the type of well drilled (horizontal or vertical)HF2

2.1 Hydraulic Fracturing Technology

Hydraulic fracturing designs are continually refined to optimize fracture networking and maximize gas production. While the concepts and general practices are similar, the details of a specific fracture operation can vary substantially from basin to basin and from well to well. Fracture design can incorporate many sophisticated and state-of-the art techniques to create effective, economic, and highly successful fracture stimulations. Some of these techniques include modeling, microseismic fracture mapping, and tilt-meter analysis.[2]

The marginal flow properties and recovery factors of most unconventional reservoirs make necessary a continuous effort to reduce costs and improve efficiencies in all aspects of drilling, completing and producing these wells. Many of the recent improvements and innovations in well completions and hydraulic fracturing have been focused as much on the cost aspect as with improving well productivity.129

Hydraulic Fracturing Objectives

The objective of a fracturing treatment is to place a proppant into the created fracture to maintain the open crack and provide a high-permeability pathway for reservoir fluids to the wellbore. The fluid system provides the means to create the fracture and place the proppant in it. The stimulating benefit of a fracturing treatment comes from the proppant holding the fracture open. The fluid system only facilitates the proppant placement and it must be recovered from the well before production can commence.125

In any hydraulic fracturing procedure, the objective is to limit fractures to the target formation. Excessive fracturing is undesirable from a cost standpoint because of the expense associated with unnecessary use of time and materials.55 Economics would dictate limiting the use of water, additives and proppant, as well as the need for fluid storage and handling equipment, to what is needed to treat the target formation.56 In addition, if adjacent rock formations contain water, then fracturing into them would bring water into the reservoir formation and the well. This could result in added costs to handle produced water, or could result in loss of economic hydrocarbon production from the well.57 13

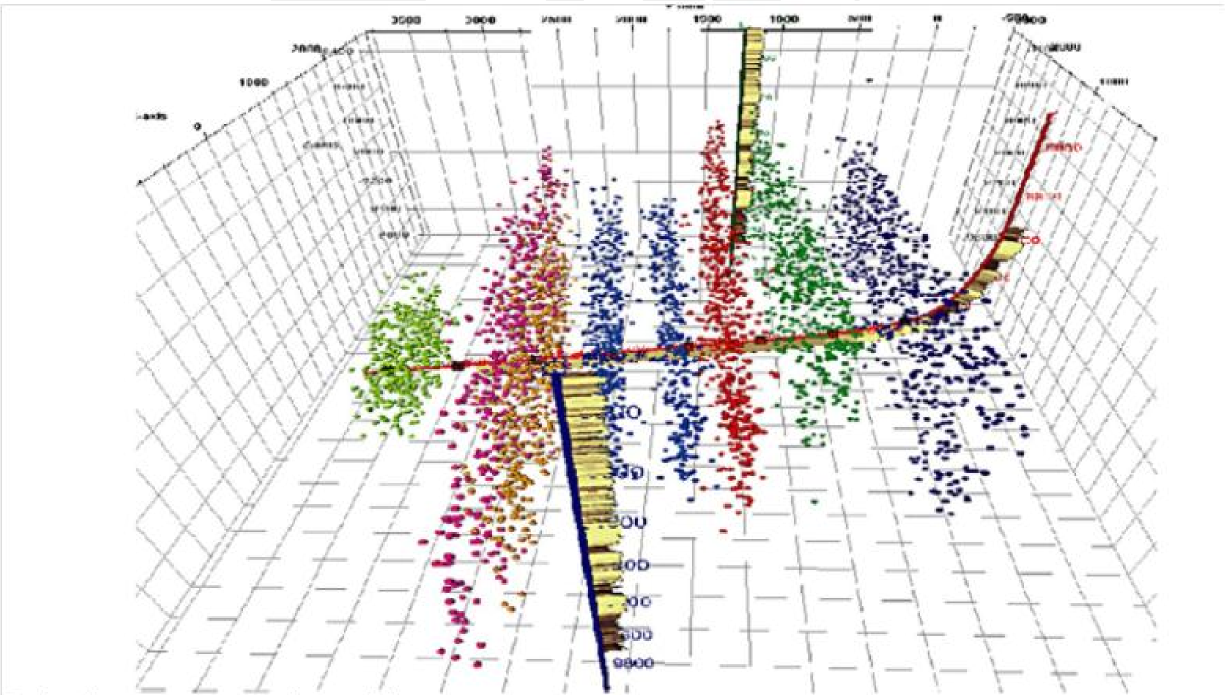
The process of hydraulic fracturing increases the exposed area of the producing formation, creating a high conductivity path that extends from the wellbore through a targeted hydrocarbon bearing formation for a significant distance, so that hydrocarbons and other fluids can flow more easily from the formation rock, into the fracture, and ultimately to the wellbore. Hydraulic fracturing treatments are designed by specialists and utilize state-of-the-art software programs and are an integral part of the design and construction of the well. HF1

Pre-Design Considerations

Understanding the in-situ reservoir conditions is critical to successful stimulations, and in the design of the fracture treatment and fluid used. Hydraulic fracturing designs are continually refined, both during the fracture stimulation itself, as well as over time as more about fracturing the target formation is learned from experience. Thus, while the concepts and general practices are similar, the details of a specific fracture operation can vary substantially from resource to resource, from area to area, from operator to operator, and even from well to well. The ideal properties of a fracturing fluid relate to its compatibility with the formation rock; its compatibility with the formation fluids; its ability to transfer enough pressure throughout the entire fracture to create a wide fracture, and be able to transport the proppant into the fracture, while breaking back down to a low viscosity fluid for cleanup after the treatment. Finally, and most importantly, the fracture treatment must meet necessary performance specifications.

2.1.1 Hydraulic Fracturing Design

Service companies design hydraulic fracturing procedures based on the rock properties of the prospective hydrocarbon reservoir. For any given area and formation, hydraulic fracturing design is an iterative process, i.e., it is continually improved and refined as development progresses and more data is collected. In a new area, it may begin with computer modeling to simulate various fracturing designs and their effect on the height, length and orientation of the induced fractures.49 After the procedure is actually performed, the data gathered can be used to optimize future treatments.50 Data to define the extent and orientation of fracturing may be gathered during fracture treatments by use of microseismic fracture mapping, tilt measurements, tracers, or proppant tagging.51, 52 13



Each color represents a single staged frac.

Source: Schlumberger, 2007.

Figure 3 Microseismic Imaging of a Multistage Fracture Treatment

The design of hydraulic fracture stimulations takes into consideration the type of geologic formation, anticipated well spacing, and the selection of proppant material. Other considerations include the formation temperature and pressure, length of the productive interval to be fractured, reservoir depth, formation rock properties, and the type of fracture fluid available. Long productive intervals may require the hydraulic fracture stimulation to be pumped in several cycles or stages. Each stage of the process is made up of different fluid mixtures that are pumped sequentially with the objective of creating and propagating the hydraulic fracture and placing the proppant. As a matter of course, it takes less than eight hours to pump one stage of a fracture treatment and some wells may require many stages.

When developing hydraulic fracturing plans, in addition to considerations associated with successfully fracturing the target formations, operators should carefully consider the fluid management and disposal implications of their fracture fluid formulations. The best practice is to use additives that pose minimal risk of possible adverse human health effects to the extent possible in delivering needed fracture effectiveness. While desirable, this type of product substitution is not currently possible in all situations, since effective alternatives are not available for all additives.HF2

Post - Fracture Treatment Design Adjustment

Throughout the stimulation process, numerous data are collected. Wellhead and down-hole pressures are monitored, pumping rates are recorded, fracture fluid slurry density is measured, water and additive volumes are tracked, and equipment function is monitored. The collection of the massive amounts of data constitutes a highly-controlled process and its analysis and interpretation allows operators to ensure there are no unforeseen problems.33

Hydraulically stimulating a well is an iterative process. As monitors collect more resource specific data, a more optimized fracture pattern within the target formation is developed to increase gas production while ensuring that the fractures do not grow beyond the formation [*Arthur et al*., 2009d]. Micro-seismic imaging is often undertaken to actively monitor multi-stage hydraulic fracture stimulation [*Arthur et al*., 2008b]. Real-time data collected from micro-seismic imaging is a method that can be used by industry to determine how far, how extensively, and in what directions the shale cracks under induced pressure [*NEB*, 2009].33

Shale gas production economics dictate that fractures be limited to the target formation and not extend into adjacent rock strata Allowing fractures to extend beyond the target formation and into adjacent strata could cause excessive amounts of water to be produced from adjacent wet formations. Confining fractures to the target formation also saves time, materials, and money. Pressures used for hydraulically stimulating shale are not excessive enough to produce extensive fractures vertically. This is because the weight of the rock layers above is so great that fracture growth is limited vertically. Stresses in the horizontal direction are much lower, which allows fractures to extend much further horizontally. [*Arthur et al*., 2009; *GPC and ALL Consulting*, 2009; *NYSDEC*, 2009].

The other factor is the shale's internal pressure. Overpressured shale develops during the generation of natural gas: because of the low permeability, much of the gas cannot escape and builds in place, increasing the internal pressure of the rock. Therefore, the artificially created fracture network can penetrate further into the formation because the shale is already closer to the breaking point than in normally pressured shale formations. The Horn River, Montney, and Utica shales are all considered to be overpressured. The Colorado Shale is underpressured

Figure 4a Frac Van (Source Doc20)

Figure 4b Frac Monitoring and Data Collection(Source Doc)

Figure 4c Data Measurement and Monitoring Interface (Source 77)

2.1.2 Hydraulic Fracturing Process

As described above, the current practice for hydraulic fracture treatments of shale gas reservoirs is to apply a sequenced pumping event during which water-based fracturing fluids mixed with proppant materials are pumped in a controlled and monitored manner into the target shale formation above fracture pressure.

Wells may be fractured either in a single stage or in multiple stages as determined by the total length of the injection zone. Vertical wells can be fractured in a single stage or multiple stages while horizontal wells typically require multiple stages due to the overall length of the horizontal leg. In a multi-stage fracture of a horizontal well, the fracturing operation typically begins with the stage furthest from the wellhead until the entire length of the horizontal leg has been fractured. The actual fracturing process within each stage consists of a series of injections using different volumes and compositions of fracturing fluids. After the combination is pumped, a water flush is used to begin flushing out the fracturing fluid.138

Staging/Sub-staging of Hydraulic Fracturing

Today, hydraulic fracture stimulation of wells is done in multiple stages because it is not possible to maintain pressures sufficient to induce fractures over the complete length of a lateral leg that can be several thousand meters long [*Arthur et al.*, 2008d].

Stages

Hydraulic fracturing of horizontal shale gas wells is performed in stages. Lateral lengths in horizontal wells for shale gas development may range from 1,000 feet to more than 5,000 feet. Because of the length of exposed wellbore, it is usually not possible to maintain a downhole pressure sufficient to stimulate the entire length of a lateral in a single stimulation event275. Because of the lengths of the laterals, hydraulic fracture treatments of horizontal shale gas wells are usually performed by isolating smaller portions of the lateral. The fracturing of each portion of the lateral wellbore is called a stage. Stages are fractured sequentially beginning with the section at the farthest end of the wellbore, moving uphole as each stage of the treatment is completed until the entire lateral well has been stimulated276. Horizontal wells in the various gas shale basins may be treated using two or more stages to fracture the entire perforated interval of the well. Each stage of a horizontal well fracture treatment is similar to a fracture treatment for a vertical shale gas well.[2]

Sub-stages

For each stage of a fracture treatment, a series of different volumes of fracture fluids, called sub-stages, with specific additives and proppant concentrations, is injected sequentially. Table ---- is an example of the sub-stages of a single-stage hydraulic fracture treatment for a well completed in the Marcellus Shale278. This is a single-stage treatment typical of what might be performed on a vertical shale well or for each stage of a multi-stage horizontal well treatment. The total volume of the sub-stages in Table is 2189 m3 (578,000 gallons). If this were one stage of a four-stage horizontal well, the entire fracture operation would require approximately four times this amount, or 8758 m3 (2.3 million gallons of water.[2]) Table 1 shows an example of the sequence of pumping the sub-stages of a Hydraulic Fracture Treatment[2]

Table 1: Example of a single stage of a sequenced Hydraulic Fracture treatment

Stage	Volume (gallons)	Rate (gal/min)	Fluid Type	Proppant size
Acid	5,000	500	15% HCl acid	None
Pad	100,000	3,000	Slickwater	None
Prop 0.1	50,000	3,000	Slickwater	100 Mesh
Prop 0.3	50,000	3,000	Slickwater	100 Mesh
Prop 0.5	40,000	3,000	Slickwater	100 Mesh
Prop 0.75	40,000	3,000	Slickwater	100 Mesh
Prop 1	40,000	3,000	Slickwater	100 Mesh
Prop 2	30,000	3,000	Slickwater	100 Mesh
Prop 3	30,000	3,000	Slickwater	100 Mesh
Prop 0.25	20,000	3,000	Slickwater	40/70
Prop 0.5	20,000	3,000	Slickwater	40/70
Prop 0.75	20,000	3,000	Slickwater	40/70
Prop 1	20,000	3,000	Slickwater	40/70
Prop 2	20,000	3,000	Slickwater	40/70
Prop 3	20,000	3,000	Slickwater	40/70
Prop 4	10,000	3,000	Slickwater	40/70
Prop 5	10,000	3,000	Slickwater	40/70
Flush	13,000	3,000	Slickwater	None

Volumes are presented in gallons (42 gals=one barrel, 5,000 gals= 120 bbls).
Rates are expressed in gals/minute. 42 gals/minute= 1 bbl/min. 500 gals/min= 12 bbl/min.
Flush volumes are based on the total volume of open borehole; therefore as each stage is completed the volume of flush decreases as the volumes of borehole is decreased.

Within each fracturing stage is a series of sub-stages, or steps.74,75**.** Each stage in the hydraulic fracturing process is carried out in predetermined order that can be altered depending on the site-specific conditions, or if necessary during the treatment. In general, these steps can be described as follows:

- pre-pad
- pad
- prop or slurry
- flush.115

Pre-pad

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, and to remove near wellbore damage created in the cementing and perforating process..

- A *dilute acid solution*, as described in the first stage, used during the initial sequence of the fracturing treatment. This cleans out cement and debris around the perforations to facilitate the subsequent slickwater solutions employed in fracturing the formation. An *acid stage*, may consist of several thousand gallons of water mixed with a dilute acid, such as hydrochloric or muriatic acid. This serves to clear cement debris in the wellbore and provide an open conduit for other frac fluids, by dissolving carbonate minerals and opening fractures near the wellbore

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

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

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

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

The purpose for a pre-pad is to:

- cool down the tubulars to prevent premature crosslinking,
- cool down the fracture face in high-temperature wells to prevent premature viscosity breakdown of the pad and slurry fluid stages of the fracturing treatment,
- perform an Instantaneous Shut-In Pressure (ISIP) to verify the closure,
- pressure of the formation.115

Pad

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 is used to prevent the growth of bacteria, which can reduce the ability of the fluid to carry proppant into the fractures [5].

- A *biocide or disinfectant*, used to prevent the growth of bacteria in the well that may interfere with the hydraulic fracturing operation. Biocides typically consist of bromine based solutions or glutaraldehyde.

- *Gelling agents*, such as guar gum (a common food additive), may be used in small amounts to thicken the water-based solution to help transport the proppant material.

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

The *pad stage*, consists of approximately several hundred cubic meters of slickwater fluid without proppant material. The slickwater pad stage fills the wellbore with the slickwater solution (described below), opens the formation and helps to facilitate the flow and placement of proppant material.

Fractures form during this stage when the fluid pressure exceeds the minimum normal stress in the rock mass plus whatever minimal tensile stress exists.76 The fractures are filled with fluid, and as the fracture width grows, more fluid must be pumped at the same or greater pressure to maintain and propagate the fractures.77

The fracture is initiated in the targeted formation during the initial pumping of the pad. From this point forward, the fracture is propagated into the formation. Typically, no proppant is pumped during the pad; however, in some cases, very small amounts of sand may be added in short bursts in order to abrade or fully open the perforations. Another purpose of the pad is to provide enough fluid volume within the fracture to account for fluid leakoff into the targeted formations that could occur throughout the treatment.

The pad initiates and propagates the fracture. The treatment must be designed with enough pad volume to allow for the desired half-length to be obtained. A pad volume that is too small will result in a premature screen out. A pad volume that is too large will increase the job cost without necessarily increasing well productivity and can leave excess guar residue in the tip of the fracture.115

Proppant or Slurry Stages

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

As proppant is added, other additives such as a gelling agent and crosslinker may be used to increase viscosity and improve the fluid’s capacity to carry proppant. Use of friction reducers allows fracturing fluids to be injected at optimum rates. Fine-grained proppant is added first, and carried deepest into the newly induced fractures, followed by coarser-grained proppant. 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

Once the proppant is conveyed to the formation, the proppant needs to be released into the formation. Therefore a breaker may be used to reduce the viscosity of the fluid and release the proppant into fractures and to enhance the recovery of the fracturing fluid.

Displacement Stage

The final step in the hydraulic fracturing process is a freshwater flush to clean out the wellbore. The purpose of the displacement or flushing stage is to flush the previous sand laden stage to a depth just above the perforations. This is done so that the pipe is not left full of sand, and so that most of the proppant pumped will end up in the fractures created in the targeted formation. Sometimes called the flush, the displacement stage is where the last fluid is pumped into the well. Sometimes this fluid is plain water with no additives, or it may be the same fluid that has been pumped into the well up to that point in time.

In wells with long producing intervals (e.g. horizontal wells), this process may be done in multiple stages or cycles, working from the bottom to the top of the productive interval. Staging the treatments allows for better control and monitoring of the fracture process.HF1 It is important not to pump the flush fluid through the perforations, as this will result in a pinch point in the fracture at the wellbore that can choke back the production rate of the formation fluids in the fracture. 115

Post-Fracture Treatment Testing

Subsequent to the flushing stage' the well is available for "testing". During the testing operation, the well is flowed under controlled conditions and data critical to the evaluation of well and formation productivity is collected. Data and flowback fluid samples essential lo the evaluations of frac flowback water are also collected over the testing period. Water related data collected during the flowback testing includes:

- Elapsed time since testing commenced
- Volume of water produced over the measurement time period
- Cumulative flowback water produced
- Water Salinity
- Water Temperature
- Detailed water chemistry (water samples collected and submitted to analytical lab for detailed analysis and determination of temporal variation in flowback water chemistry
- H_2S and CO_2 gas

Since the testing is being conducted for purposes other than water management, the acquisition of the water related elements is very cost effective to acquire.

.

2.1.3 Hydraulic Fracturing Types

Dozens of hydraulic fracturing techniques have been developed over the years that are particularly effective for specific reservoir and geological stimulation needs. The stimulation techniques that are effective for shale gas development have been developed through an iterative process of careful engineering and monitoring of performances. While the current hydraulic fracturing technique of choice is the "slickwater" method, several other variations, or combinations of fracture treatment techniques are available. The most commonly considered fracture treatment techniques for shale gas completions include:

- Slickwater
- Linear Gel
- Cross-linked Gel
- Foam Systems
- Viscoelastic (VES)

Each of these fracture treatment techniques, the additives commonly used, and the sensitivity to source water and flowback water constituents are be discussed in Sections 6.0 of this report..

Before Barnett Shale was fractured in 1997, many fracture treatments were carried out with a cross-linked fluid and large amounts of proppant. The difficulty in cleaning the wells and the low return made many wells uneconomical. 41 Eventually, the state of the art has evolved to high rate slickwater fracs with fewer chemical additives. The question to be addressed is - how do the various additives perform in shale and how do we select which additives are necessary particularly in light of the fact that most fracturing treatments are now conducted with produced and/or flowback water from previous fracs.41

Slickwater fracs require much more water than a typical sand and gel frac. This type of fracture treatment has proven to be a cost effective system in the Barnett Shale and is being expanded into Haynesville, Marcellus, Woodruff, and Fayetteville shales.63 28. Recent slickwater fracs conducted in the Horn River basin used up to 5,000 m^3/stage and 150,000 m^3/well.

While slickwater treatments have become the stimulation method of choice in shale gas hydraulic fracturing, it is important to note that several other stimulation and completion techniques have been employed that have resulted in economic and commercially viable shale gas production over the last 20 years.131

For dry shale or those shale reservoirs that contain clays, making them particularly sensitive to contact with fresh water, foam fracturing—the use of foam as the carrier for the propping agent applied under high pressure—has been the predominant method used for stimulation. Such techniques have been employed for over 30 years and the foam application continues to be the method of choice in some settings. Nitrogen or carbon dioxide gas has also been used when fracturing dry shale reservoirs in many basins in the U.S., but success has been limited to relatively shallow shale formations that are very brittle.17.

With the recent shift in exploration focus to liquids rich gas plays, the process of determining the most cost effective method of hydraulic fracturing is under ongoing review. Oil-based and energized viscoelastic and other treatments are being used. While this shift in fracturing treatment practice may result in the use of less water per well fracturing treatment, the reduction in water use may be offset by an increase in the number of wells undergoing fracturing treatment. The need for water management in the areas where liquids rich development is taking place is beginning to emerge in the US, where development is more aggressive than in Canada. In any case, a complication in any consideration of re-use or treatment of flowback fluids will be the need to separate produced oil and frac oil from flowback and produced water.

2.1.4 Hydraulic Fracturing Equipment and Fluids

The hydraulic fracturing process requires an array of specialized equipment and materials. This section will describe the materials and equipment that are necessary to carry out typical hydraulic fracture operations in vertical and horizontal wells

2.1.4.1 Hydraulic Fracturing Equipment

The equipment required to carry out a hydraulic fracturing treatment includes fluid storage tanks, proppant transport equipment, blending equipment, pumping equipment, and all ancillary equipment such as hoses, piping, valves, and manifolds. Hydraulic fracturing service companies also provide specialized monitoring and control equipment that is necessary in order to carry out a successful treatment. Figure --- is a diagram showing schematically how this equipment typically functions. During the fracture treatment, data are being collected from the various units, and sent to monitoring equipment; in some cases this is a “frac van.” Data being measured include fluid rate coming from the storage tanks, slurry rate being delivered to the high-pressure pumps, wellhead treatment pressure, density of the slurry, sand concentration, chemical rate, etc.HF1

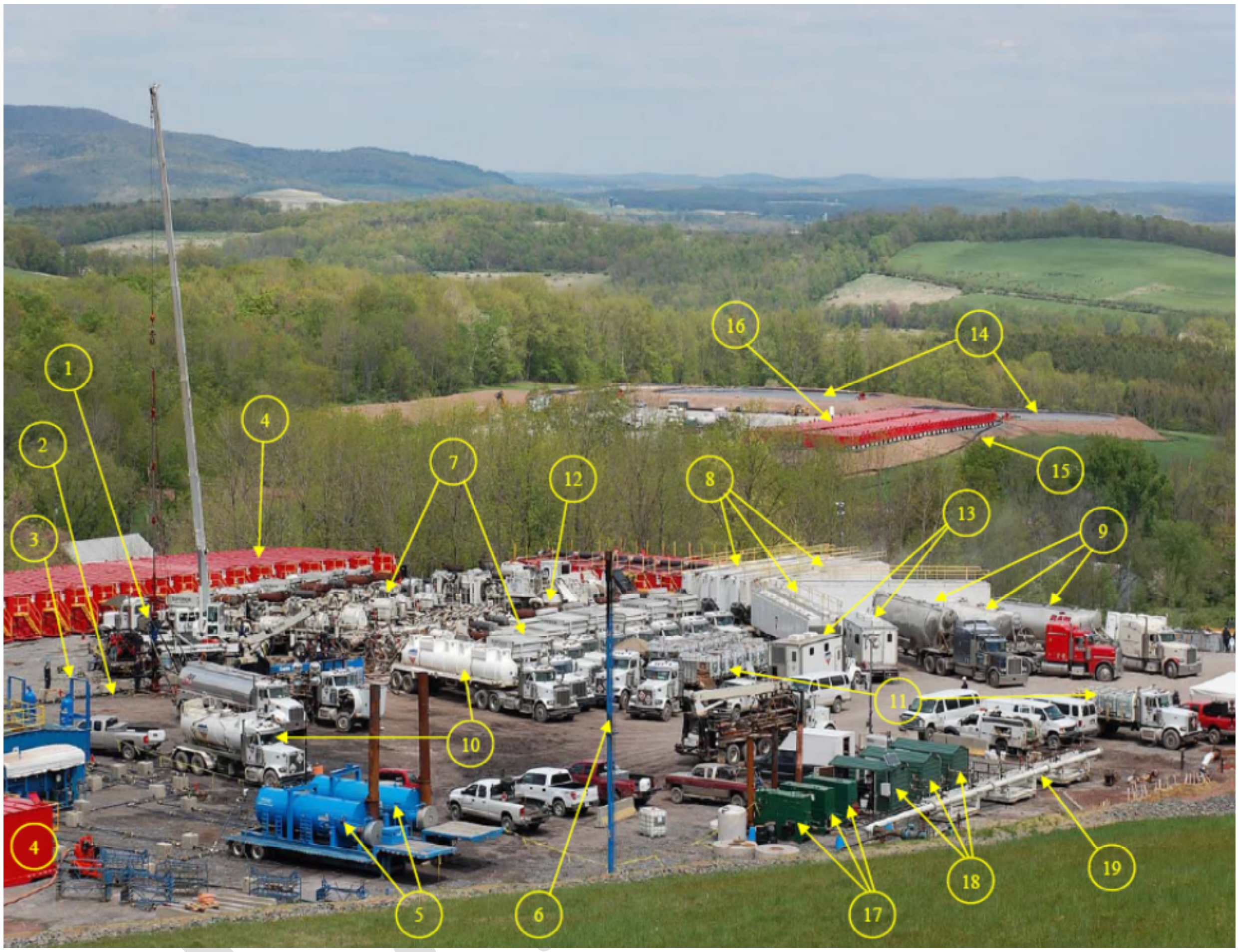


Figure 5 Equipment Setup For Hydraulic Fracturing (Source Doc 4)

Table 2 Hydraulic Fracturing Operation Equipment

Hydraulic Fracturing Operation Equipment

1) Well head and frac tree with “Goat Head”
2) Flow line (for flowback & testing)
3) Sand separator for flowback
4) Flowback tanks
5) Line heaters
6) Flare stack
7) Pump trucks
8) Sand hogs
9) Sand trucks
10) Acid trucks
11) Frac additive trucks
12) Blender
13) Frac treatment control and monitoring center
14) Fresh water impoundment
15) Fresh water supply pipeline
16) Extra tanks

Production Equipment

17) Line Heaters
18) Separator- meter skid
19) Production manifold

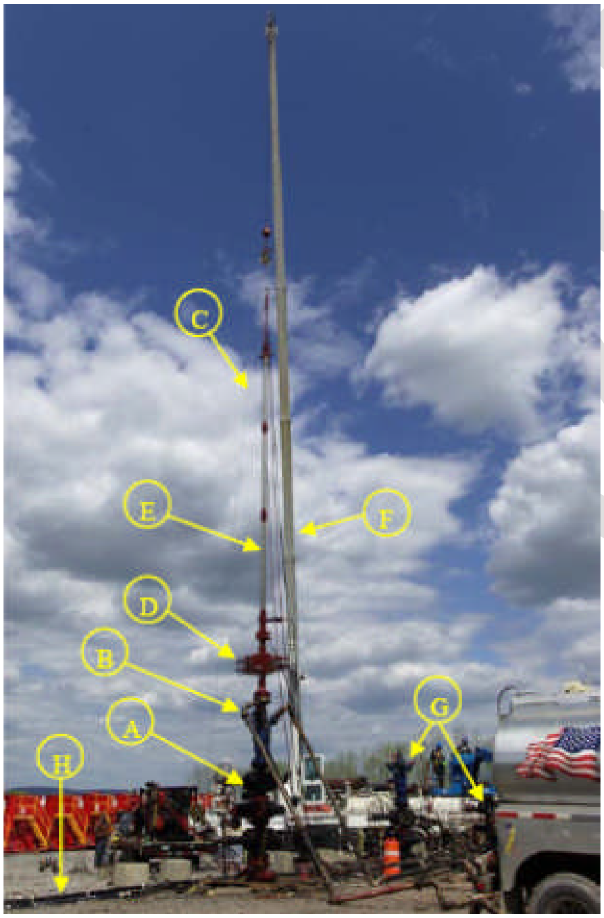


Table 3 Listing of Wellhead Components

A. Wellhead and Frac Tree Valves
B. Goat Head (for frac flow connections
C. Wireline (used to convey equipment into wellbore
D. Wireline Blow Out Preventer
E. Wireline Lubricator
F. Crane to support wireline Equipment
G. Additional Wells
H. Flow line (for flowback and testing)

Figure Wellhead Setup For Fracture Treatment (Source Doc 4)

2.1.4.2 Desirable Properties of Fracturing Fluids

In fracturing operations, the frac fluid fulfills two functions: to create and propagate the fracture in the formation, and; to transport proppant throughout the length of the fracture to ensure that the fracture remains open after the fracturing pressure has been released

The ideal injection fluid would be of such a quality as to have no detrimental interactions with, or effects upon, the treating equipment, the fluids and rocks of the producing reservoir, or the rate, amount and properties of the recovered fluids.

The important fluid characteristics for fracturing fluids include:

- viscosity
- efficiency
- compatibility
- stability
- friction pressure
- controllable break and cleanup
- economy.115

Viscosity

Viscosity is the resistance to flow. The higher the viscosity of the fracturing fluid, the more difficult it is to inject the fluid into the formation. Since the fluid must transport the proppant, the fluid must be sufficiently viscous to prevent setting out of proppant before the end of the treatment.115

Fluid Efficiency

Fluid efficiency is defined as the volume of the hydraulic fracture divided by the volume of fluid injected into the fracture. Since the success of the fracturing job depends upon improved production to warrant the expense, the more efficient the fluid is the more profitable the fracturing job (all other factors—transport, cleanup, etc.—being equal).115

Compatibility

When determining the compatibility of a fracturing fluid, it is important to determine:

- the compatibility of the frac fluid with formation fluids, and
- the compatibility of the fracturing fluid with additives used in the fracturing treatment

Incompatible fluids or additives can result in emulsions, water blocks or solid precipitates that prevent the fractured well from producing at anticipated levels.115

Stability

The fracturing fluid is often designed so that the fluid stability of the fluid pumped at the end of the treatment is much less than that of the fluids pumped in the earlier stages. A fluid that is stable for only 15 minutes can be acceptable or even desirable at the end of the treatment. This allows for the well to be flowed back earlier with a minimum amount of proppant being transported back to the surface.115

Friction Pressure

The lower the friction pressure, the more economical the treatment will be due to lower horsepower costs. In addition, higher friction pressures result in higher pumping pressures. This can be a serious safety concern and precautions must be taken to protect personnel and surface equipment.115

Controllable Break and Cleanup

To ensure the stability and efficiency of the fluid, the time required to break the fluid must be controllable. Establishing the correct timing for breaking of the fluid will result in faster cleanup and a more economical fracturing treatment. Controllable breaking of the fluid usually defines the fluid stability discussed previously.115

Economy

Fracturing treatments to improve the productivity of the well, the operation must result in an acceptable return on investment (ROI) within a reasonable period of time. The cost-benefit ratio of the fracturing treatment can be greatly improved by:

- reduced horsepower costs from lower friction pressures
- utilizing correct fluid types and volumes
- reducing cleanup times through proper selection of fracturing fluids and breakers.

In the planning stage of a frac design, specialized software incorporating an optimization module is used to evaluate various fracture treatment configurations and to identify the optimum cost-benefit ratio for the job. 115

Hydraulic Fracturing Materials

Chemical 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 effect 11

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.

Water is the primary component for most hydraulic fracture treatments, representing the vast majority of the total volume of fluid injected during fracturing operations. Ideal frac water does not exist. In all cases, water from some source must be treated to approach the desired requirements. The challenges in design and operation of water treating equipment for injection are:

- To determine the minimum acceptable quality requirements for a specific water flood;
- To design and construct minimal, low cost, safe, and effective treating equipment and processes to achieve the required quality; and
- To operate the facilities in a safe and cost-effective manner while still producing injection water of the required quality.

The proppant is the next largest constituent. Proppant is a granular material, usually sand, which is mixed with the fracture fluids to hold or prop open the fractures that allow gas and water to flow to the well. Proppant materials are selected based on the strength needed to hold the fracture open after the job is completed while maintaining the desired fracture conductivity.HF2

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 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 fracturing treatment design and operation.[3]

The additives mentioned above are relatively-common components of a water-based frac solution used in tight gas formations such as the Marcellus Shale in Pennsylvania. However, it is important to note that not all of the additives listed here are used in every hydraulic fracturing operation; the exact “blend” and proportions of additives will vary based on the site-specific depth, thickness and other characteristics of the target formation.

Water is used in fracture treatment operations as the carrier fluid in varying amounts depending on the fracturing technique and numerous factors. Slickwater fracs are the most intensive use of water, so most discussion regarding water management will focus on that particular fracturing technique. The predominant fluids currently being used for fracture treatments in the gas shale plays are water-based fracturing fluids mixed with friction-reducing additives (called slickwater).

The addition of friction reducers allows fracturing fluids and proppant to be pumped to the target zone at a higher rate and reduced pressure than if water alone were used. In addition to friction reducers, other frac additives include: biocides to prevent microorganism growth and to reduce biofouling of the fractures;

oxygen scavengers and other stabilizers to prevent corrosion of metal pipes; and acids that are used to remove drilling mud damage within the near-wellbore area. These fluids are used not only to create the fractures in the formation but also to carry a propping agent (typically silica sand) which is deposited in the induced fractures.

Figure------ demonstrates the volumetric percentages of additives that were used for a nine-stage hydraulic fracturing treatment of a Fayetteville Shale horizontal well. The make-up of fracturing fluid varies from one geologic basin or formation to another. Evaluating the relative volumes of the components of a fracturing fluid reveals the relatively small volume of additives that are present.

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

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. 11

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.11

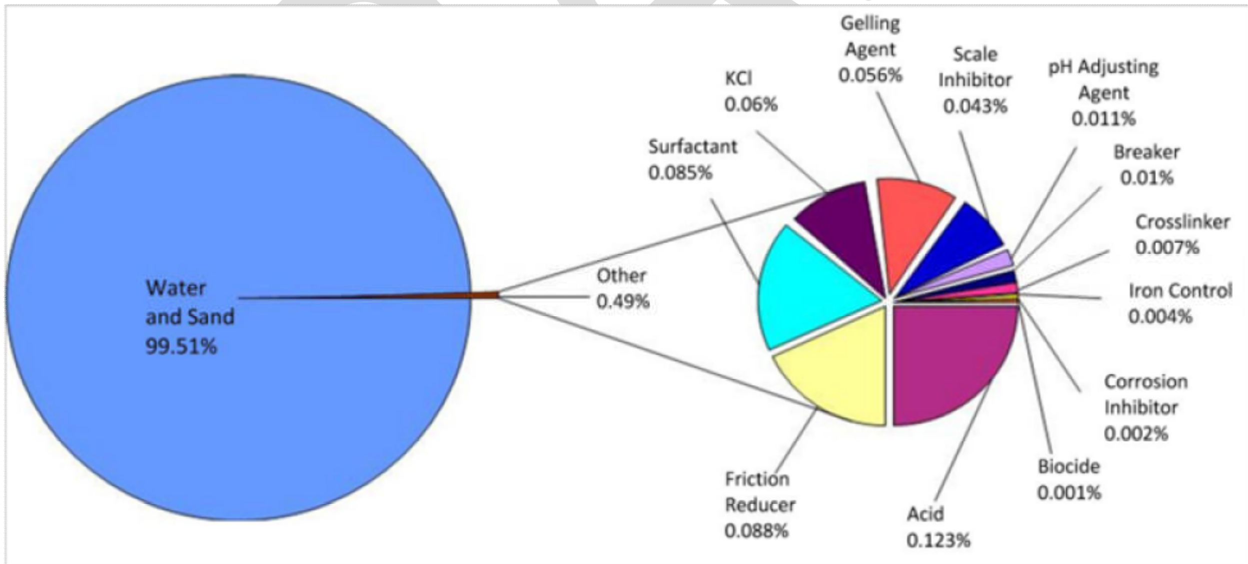


Figure 7 Frac Materials and Additives (Source)

While several types of additives may be used in a single well, they are not all 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 is described in Section 2.1.2 Hydraulic Fracturing Process

Mixing

In the preparation of the frac fluid, the selected constituents may be batch mixed or continuously mixed. For batch mixed, water-based fluids, the bactericide, polymer, salt, clay stabilizer etc are mixed together before pumping. The polymer is given sufficient time to hydrate in the tanks before the job begins. The pH of the gel is adjusted for optimum crosslinking. Crosslinker is added on the fly in the case of transition metal (Ti and Zr) crosslinkers. Because borate crosslinking occurs only at a high pH, boric acid can be added to the polymer in the tanks, and a base such as sodium hydroxide (NaOH) can then be added on the fly to raise the pH and to initiate crosslinking.

2.2 Water Quality Needed to Maintain Hydraulic Fracturing Effectiveness.

Given that water constitutes a high percentage of the frac fluid used to carry the proppant during fracturing operations, any water quality issues that have the potential to impact on the performance of the frac fluid, or the cost of water conditioners and/or frac fluid additives will be of concern to the frac designer. An understanding of the water quality issues and the mitigation options available to the frac designer provides an effective basis for optimizing the frac fluid design.

Water quality used in the fracturing process is usually considered at several (number) specific points during the fracturing process:

- Compatibility of the source water with the water in the formation being hydraulically fractured. These compatibility issues commonly related to scaling tendencies, and biological issues.

- Compatibility of the source water being considered for use as a carrier fluid with the rock fabric. These issues are commonly related to the swelling and mobilization of clays in the rock mass.

- The third water quality issue is related to the compatibility or sensitivity of fracturing additives with specific constituents in the source water used for the fracturing treatment.

- The flowback water commonly has elevated concentrations of naturally occurring constituents. A determination must be made regarding the level of effort required to make the flowback water reusable for hydraulic fracturing.

- If a decision is made not to reuse the frac water the flowback water is normally disposed of in an injection well. In this case, the chemistry of the flowback water must be made acceptable for injection.

The ideal water for hydraulic fracturing would have the following characteristics:

- no suspended solid particles,
- no harmful dissolved solids causing scaling or corrosion,
- no dissolved gases,
- no bacteria ,

- no adverse effects on the formation , such as clay swelling ,
- no detrimental effects when mixed with formation fluids, and
- non-conductive to prevent galvanic corrosion.

Because this fluid does not exist in nature, some degree of adjustment may be necessary to minimize the impact of objectionable water quality issues on fracture performance. The degree of adjustment may vary from minor adjustment of pH to treatment of a number of water constituents with a complex water treatment train, including a variety of chemical additives and advanced treatment techniques.

The quality of water associated with hydraulic fracturing of shale gas must be considered at 4 specific junctures of a hydraulic fracturing job: 1) as part of pre-fracture treatment selection of additives; 2) as part of pre-fracture treatment source water/formation fluid compatibility assessment; 3) Flowback water reuse considerations, and; 4) in the consideration of flowback fluid or residue disposal requirements.

Source Water/ Formation Fluid Compatibility

Whenever fluids are being injected into a subsurface geological unit, the chemical compatibility of the injected fluid and the formation fluid and formation matrix must be considered at the outset to ensure geochemical compatibility. The identification of compatibility issues on the basis of water analyses and geochemical simulations provides a basis for the development of a program to address compatibly issues through the use of water conditioners including scale inhibitors, or the application of more advanced treatment technologies

Pre-Fracture Treatment Additives Selection

The initial consideration of water quality occurs during early planning of the fracturing treatment. The sensitivity of frac additives to constituents in source water must be considered. Most hydraulic fracturing service providers will identify what the sensitivity is of the various additives that they use to commonly occurring water constituents. During this initial stage of fracture treatment planning, the compatibility of the water from the various source water options (be they surface water, groundwater or produced water) must be evaluated and physical and chemical parameters needing adjustment identified as part of the process of selecting the frac fluid and the source water The sensitivity of the various frac additives is discussed in more detail in Section ---------

Flowback Water Reuse Considerations

After a hydraulic fracture treatment, when the pumping pressure has been relieved from the well, the water based fracturing fluid begins to flow back through the well casing to the wellhead. After the hydraulic fracturing procedure is completed and pressure is released, the direction of fluid flow reverses. The well is "cleaned up" by allowing water and excess proppant to flow up through the wellbore to the surface. Both the process and the returned water are commonly referred to as “flowback.” This produced water consists of spent fracturing fluids and, in some cases, dissolved constituents from the formation; the dissolved constituents vary from one shale play to the next or even by area within a shale play. Produced water from shale gas can vary from fresh (less than 5,000 mg/L total dissolved solids) to varying degrees of salinity (5,000–400,000 mg/L TDS).10 29

After the fracturing of the well is completed, water is produced along with the natural gas. Some of this water is returned frac fluid and some is natural formation water. Regardless of the source, these produced waters that move back through the wellhead with the gas represent a stream that must be managed.

Along with the introduced additive components, frac fluids in close contact with the shale during the course of the stimulation treatment may, when recovered, contain a wide variety of dissolved constituents such as salts, metals and other constituents. These constituents can make wastewater disposal difficult and expensive, and can potentially impair gas production by yielding damaging precipitants within the fractures, perforations and wellbore.110

In shale gas development settings where the availability of source water for fracturing purposes is limited or very expensive; and the costs associated with disposal of flowback water are high or the injection capacity is limited, there is an incentive for the operator to consider reuse of frac flowback water. The reuse of flowback fluids is part of a complex set of integrated water management elements (Figure 3).

States, local governments, and shale gas operators seek to manage produced water in a way that protects surface and ground water resources and, if possible, reduces future demands for fresh water. By pursuing the pollution prevention hierarchy of “Reduce, Re-use, and Recycle” these groups are examining both traditional and innovative approaches to managing shale gas produced water. This water is currently managed through a variety of mechanisms, including underground injection, treatment and discharge, and recycling. New water treatment technologies and new applications of existing technologies are being developed and used to treat shale gas produced water for reuse in a variety of applications. This allows shale gas-associated produced water to be viewed as a potential resource in its own right.[2]

Disposal Requirements

In some cases, a decision may be taken not to reuse flowback water from hydraulic fracturing operations. In such cases, and also when lesser volumes of frac flowback water requires disposal at the end of a drilling season, there is a need to consider the requirement to condition or treat the quality of the flowback water to make it acceptable for injection.

2.2.1 Water Quality Objectives

Water quality can be defined as the sum total of all the chemical, physical and microbiological properties required for a water to be suitable for a specific application. Water Quality Objectives take into account the intended use of the water, and the water quality characteristics that have an influence on the intended use. Water quality objectives are determined by compatibility considerations and the potential for interference with frac additives.

2.2.2 Rate Requirements

The minimum rate that water must be made available at a lease or pad at which a hydraulic treatment will be conducted is equal to the rate at which the frac treatment will be pumped, unless the entire volume of frac water is pre-staged on the lease. With larger hydraulic fracture treatments it may not be possible to store all the water on the lease or pad, and water must be replenished at or about the rate that it is used. On pads where a number of fracture treatments are conducted “back to back” the rate of replenishment of water in lease based storage becomes more important, and the water storage facilities on or near the lease must be adequately sized to accommodate the total water needs.

2.2.3 Water Quality Characteristics

Water quality specifications may cover a wide variety of properties such as temperature, color or turbidity; dissolved components including inorganic and organic solids, liquids and gases; suspended material including solids from corrosion or scale forming reactions or dispersed oil from separation facilities; or even microscopic biological components that can produce fouling, plugging, corrosive, and toxic materials. All of these factors influence the performance of the frac fluid and the subsequent productivity of the well. Suspended solids could plug the pore spaces in the formation or build up an impermeable filter cake on the face of the reservoir rock that would impede water injection. Bacteria may contribute to corrosion and corrosion products, resulting in plugging of the injection well. Bacterial growths themselves can sometimes result in plugging. Corrosive water not only damages the system but may produce corrosive products which can plug the well. A common example of this is iron sulfide formed from corrosion by hydrogen sulfide.

The suitability of a water of certain characteristics for use in a hydraulic fracturing project is determined from water analysis, compatibility tests, clay swelling tests, and water quality evaluation. If the water is not suitable for use in a fracturing treatment, but is the only supply available, it must be treated to change its characteristics and make it suitable for use. (96)

Each hydraulic fracturing application will have its own set of water quality requirements. Water quality requirements are application – and site specific. They may be set by the application or they may be determined by some regulatory agency.

The challenge is to determine the quality requirements for a particular application, to devise a treatment process to achieve the required quality, to operate the equipment in a cost effective and environmentally acceptable manner, and to monitor over all plant operations to assure the required water quality is being achieved.(96)

2.2.4 Water Constituents

The physical and chemical characteristics that require quantification as part of the characterization of waters for sourcing purposes and for determining compatibility of formation fluids are listed below.

Table 4 Physical and Chemical Water Characteristics

pH 6.7
Electrical Conductivity
Temperature (°F)
Specific Gravity
Fluid Density (lb/gal)
Titrated Chlorides (mg/L)
Total Suspended Solids (TSS)
Total Dissolved Solids -TDS (mg/L)
Salt %

Total Hardness (mg/L)
Sodium Na
Potassium K
Calcium as CaCO3 (mg/L)
Calcium Ca2+ (mg/L)
Magnesium Mg as CaCO3 (mg/L)
Magnesium Mg2+ (mg/L)
Total Iron (mg/L)
Sulfates (mg/L)
Carbonate Alkalinity (mg/L)
Bicarbonate Alkalinity (mg/L)
Total Alkalinity (mg/L)
Scale Inhibitor (mg/L)
Barium
Strontium P.S. (mg/L) 41
Bacteria
Petroleum Hydrocarbons
Dissolved Oxygen

Other optional parameters that may be quantified as part of the water characterization includes: residual frac additives, dissolved metals as may be warranted, and radioactive constituents. Sampling plans and analytical protocols should consider the seasonal or temporal variability of the physical and chemical constituents in potential water sources.

2.2.5 Integrated Water Management Plan

The scale of hydraulic fracturing operations of shale gas wells and the enormous water requirements for completions on an annual basis require the expenditure of enormous amounts of capital, and may require a significant lead time to stage and develop plans to source and implement cost effective water management systems.

Because the development of a water management plan consists of the implementation of a number of related elements, it is essential that the elements of the Water Management Plan be integrated not only with the drilling and completion plan, but the elements of the plan

A Water Management Plan may cover a single drilling plan covering a single year, or, the drilling plan may include dozens of wells and completions for a multi-year period, the Water Management Plan may cover a period of time adequate for the development of a significant water management capability for a 10 -20 year period.

The drilling plan that is to be the basis for development of the Integrated Water Management Plan should include, as a minimum:

- Number and location of vertical wells to be drilled
- Duration of drilling/hydraulic fracturing season
- Number of stages to be fractured in vertical wells

- Type of fracture treatment for vertical wells
- Volume of water to be used per vertical stage fractured
- Expected flowback from vertical wells as percentage of pumped volume
- Number and location of horizontal wells to be drilled
- Number of stages to be fractured in horizontal wells
- Type of fracture treatment for horizontal wells
- Volume of water to be used per horizontal stage hydraulically fractured
- Expected flowback from horizontal wells as a percentage of pumped volume
- Determination which wells are single well per lease or multi-well per pad
- Identification where wells are to be drilled to identify where water is required.
- Projections of conceivable drilling scenarios in subsequent years

The evaluation of water needs developed from this understanding will be an iterative process worked out with the operating companies drilling department. Since no drilling plan stays the same for very long, the water management plan must be capable of rapid and frequent adjustment. Depending on the complexity of the drilling plan, and the time duration of the drilling/completion plan, the projection of water needs may consist of more than two dozen spread sheets that covers a time period of up to 15 – 20 years. The duration of the Water Management Plan will be driven by the need to create the lead time needed to provide for fiscal planning and water infrastructure development.

Elements of Integrated Water Management Plan

Once a water needs calculation has been prepared based on a given drilling/completion plan, the initiation of the Integrated Water Plan can begin in earnest. The elements of an Integrated Water Management Plan include the following elements:

- Water Sourcing
- Water Delivery and Logistics
- Water Storage
- Water Treatment and Reuse
- Water Disposal

The need for an integrated water management plan lies in the fact that changes in one of the elements of the water management plan is likely to have a significant impact on the other elements. A graphic portrayal of an Integrated Water Management Plan is shown in Figure ------- An example of a change that would have an impact on other elements of the water management is a change in the decision regarding how much flowback will be reused for subsequent fracture treatments. This decision will affect the volume of water needed at source, and the volume of flowback fluid that must be disposed.

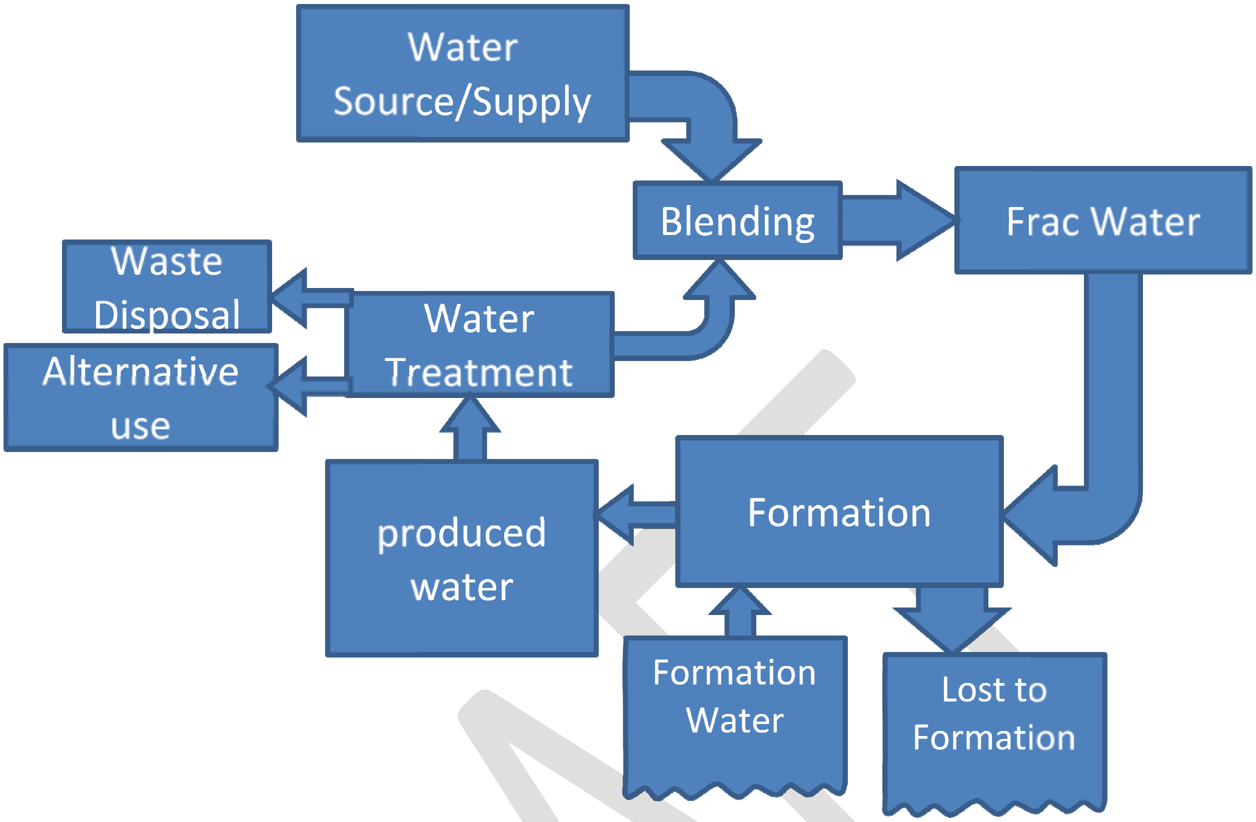


Figure 8 Elements of Integrated Water Management Plan (Source ????)

Considerations associated with water acquisition, use, and management in hydraulic fracturing operations can be categorized in the following different phases:

Source Water Acquisition—Where will the water supplies needed for hydraulic fracturing operations be acquired?

Transport—How does the water get from the source to the well site and from the well site to the point of treatment and/or disposal? 17

Storage—What requirements and constraints exist for water storage on site, and how do source water considerations and fracture fluid requirements affect storage requirements?

Use—How will the water be used, what volume is required, over what period of time and what must be done (e.g. the addition of proppant and additives) to achieve the fracturing objectives?

Treatment and Reuse/Recycle—Can the water produced from the fracturing operation be treated and recycled for reuse?

Treatment and Disposal—If the water is not to be recycled and or reused, what must be done either prior to disposal or with any treatment byproducts?17

3.0 MECHANICS OF FRAC FLUID FLOWBACK

Flowback of frac fluids occurs after the frac pumps have been shut down. These frac flowback fluids must be managed and preferably reused if technically and economically feasible. In order to develop an effective management strategy for managing flowback fluids, an understanding of the nature of flowback mechanics is necessary.

Frac Flowback

The management and disposal of water after it is used for hydraulic fracturing operations present additional challenges for operators. After a fracture treatment is complete, the fluids returning to the surface within the first seven to fourteen days (often called flowback) will often require treatment for beneficial reuse and/or recycling or be disposed of by injection. This water may contain dissolved constituents from the formation itself along with some of the fracturing fluid constituents initially pumped into the well.17

Once it reaches the surface, flowback is stored either in an open evaporation pit located on the drilling site, or in enclosed tanks. From there, the flowback may be treated for reuse in the fracturing process or taken off site for disposal. 139

Operators have found that most flowback and produced formation fluid from the fracturing and production of shale gas wells can be used satisfactory in frac fluid for subsequent frac treatments with proper chemical additives and laboratory testing.125 and treatment.

Reuse of Flowback Water

The volumes of water used and flowback water generated has increased to the point that consideration is now commonly given to the feasibility of reusing the flowback fluid as a water conservation measure, and to offset or reduce the volume of waste fluids that must be injected or otherwise disposed of.

Primary potential destinations for flow back/production fluids generally include the following:

- injection wells, which are regulated under either a state or federal UIC program;
- municipal waste water treatment facilities;
- industrial waste treatment facilities;
- other industrial uses;
- frac flow back water recycling/reuse.

Geochemical control also enables operators to tailor frac flowback so it can be reused in subsequent fracturing operations while minimizing concerns of subsequent formation damage due to geochemical precipitation. Specific reductions in frac fluid expense have been observed from the reuse of flowback, due to the reduction in transportation costs of the frac water, purchases of fresh water and water disposal volume.110

Reuse of frac flowback should not be considered an operation that must be undertaken “at all costs”. The reuse of frac water should only be undertaken when it can be documented that it can be done economically and in an environmentally acceptable manner. The cost of facilitating the reuse of frac flowback is generally worth considering if the incremental cost of reusing the frac flowback is less than the combined cost of alternative source water plus the cost of disposal of the frac fluid if it is not used.

While the decision to reuse flowback fluid is seemingly a simple one, the level of effort and resources and logistical resources required to make reuse work may be considerable. Therefore, the decision to reuse should be undertaken based on a clear understanding of the frac flowback characteristics and chemical characteristics with time, and the treatment and logistical requirements.

Much of the planning and evaluation of options for managing and reusing frac flowback can be done during the planning and pilot stages of the shale gas field development. The nature and variability of frac flowback can initially be determined through the collection of appropriate data and sampling during the initial testing of the gas well following completion operations. Since the gas well testing function will be undertaken regardless of whether the frac flowback fluids are to be reused or not, the incremental costs associated with acquiring the appropriate flowback information is modest.

3.1 Flowback Fluid Volumes

Flowback volume or "load recovery" is generally calculated as a percentage of the total frac fluid volume pumped. Of the total amount of fluid that is pumped into wells, typically between 10% and 70% is retrievable. Figure ------ shows the cumulative flowback from a number of shale gas wells completed in the Marcellus.

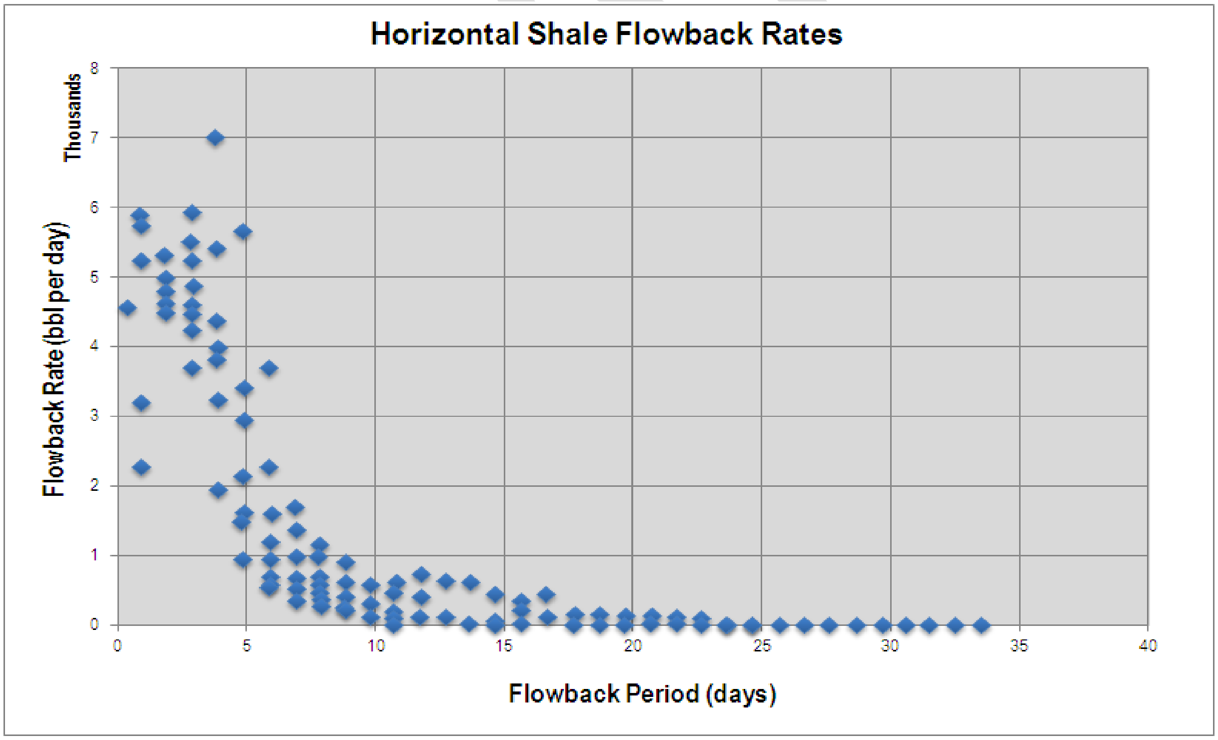


Figure 9 Decline in Flowback Rate (Source -------)

The amount of fracture fluid recovery from fracture of treatment of shale-gas wells varies with the shale character, the frac design and the type of fluid as the main drivers. Fractures that are more conventional with long reach and minimum complexity often flow back quickly and the percentage of frac fluid recovered is high. In shale fracs where extensive complexity is developed or the shale is mildly reactive, the amount of fluid recovered may be on the order to 10 to 70% of the total pumped and the time for fluid recovery may stretch over several weeks. This relationship depends on system energy and closure stresses. Controlling back pressure to use available formation gas energy to most efficiently remove the load water from the fracturing treatment may have significant benefits.40 Flowback from foam based fracture treatments may be close to 100%. (Doug Pipchuk Personal communication)

The initial flow rate at which the flowback exits the well can be relatively high (e.g., > 400m3 per day) for the first few days. However, this flow diminishes rapidly with time, ultimately dropping to the normal rate of produced water flow from a natural gas well (e.g., 50 gallons per day) (Chesapeake Energy, 2010; Hayes, 2009b). While there is no clear transition between flowback and produced water, produced water is generally considered to be the fluid that exits the well during oil or gas production (API, 2010a; Clark and Veil, 2009). Generally there is no set volume for when flow-back ends and production begins (Anadarko) Figure ------ demonstrates the rapid decrease in flowback volume following the initiation of flow testing.

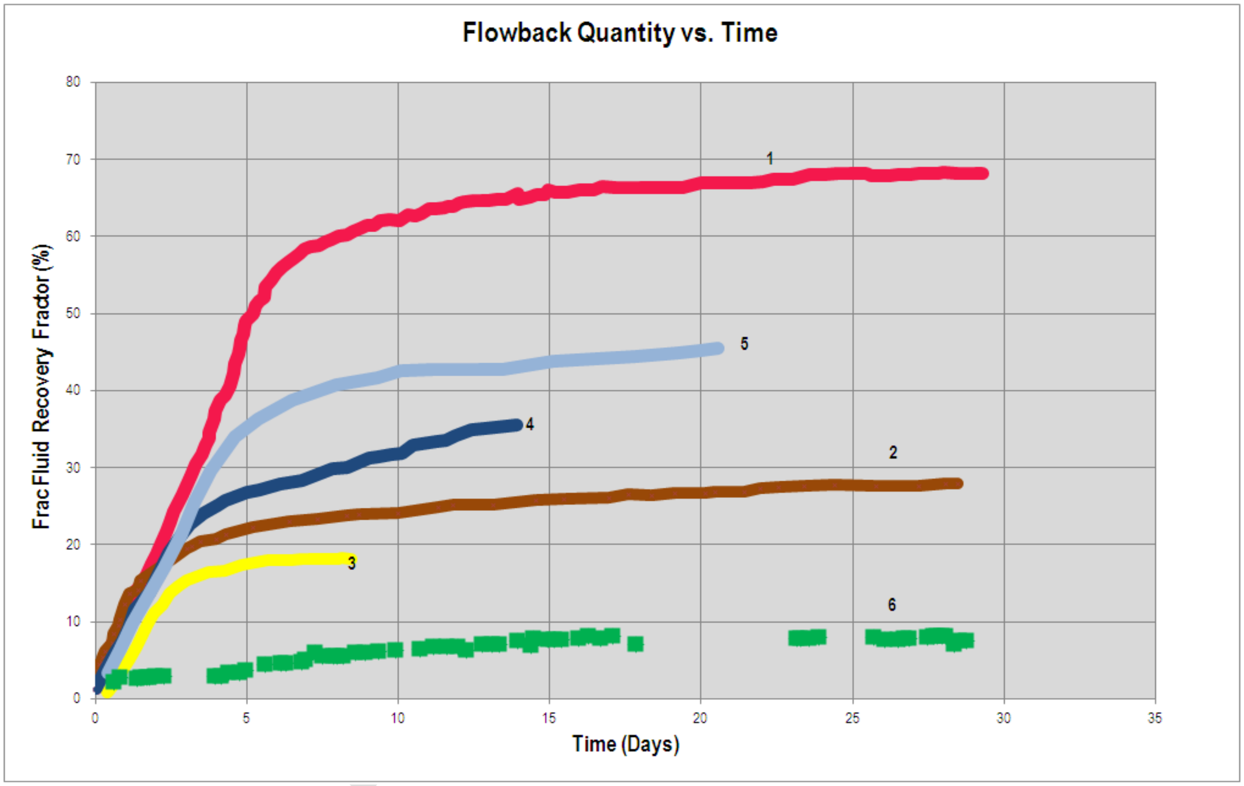


Figure 10 Percentage of Flowback Recovery (Source------)

Flow back volumes and recovery percentages may be influenced arbitrarily by decisions by the operator regarding when testing ends and production begins. Similarly, limiting the rate at which a well is tested (due to limited capacity to handle storage, transmission of treatment of the flowback water) may result in lower load recovery during the testing period, and slower build up of formation fluid in the flowback. This is the situation in some wells in the Horn River Basin where flowback water contains H_2S which must be treated before the flowback water can be reused or disposed of. The capacity to treat creates a limitation on the rate that flowback fluid can be produced during testing. The result of this constraint is that at the end of the testing period, load recovery may be limited and significant frac fluid is still being produced.

After the first few weeks or months, the amount of water produced from a well considerably decreases. During the initial period, large volumes of spent fracturing fluids, ranging from 15 % to 35 % of the initial hydraulic fracture stimulation fluid volume, are returned to the surface [*Arthur and Cornue*, 2010].

The flowback techniques and results discussed here deal mainly with slickwater fracs. Gelled fracs have an entirely different dependency on cleanup Wells fractured by gels may benefit in some cases by forced closure methods and liquid recovery rates as fast as 6 barrels per minute (bpm) if proppant is not moved out of the fracture, however, this technique is not a universal suggestion for shale fracture treatments, particularly those using slickwater fracs. Forced closure may not be optimum for removal of water from micro-fractures. Slower water recovery has increased IP in some cases. 40 A conceptualized flowback volume decline curve is shown in Figure --------

3.2 Duration of Flowback

Generally, the flowback period in shale gas reservoirs is several weeks Flowback usually 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% of the total flowback occurs in the first four days after fracturing. After day four, the daily flowback rate declines sharply to between approximately 2% – 5% of the total flowback for approximately two weeks.[3](URS Corporation, 2009),

If there is a delay in flowing back the well after fracture treatment, this may result in higher total dissolve solids concentrations in the flowback water as shown in Figure -----. This increase in salinity may influence treatment requirements.

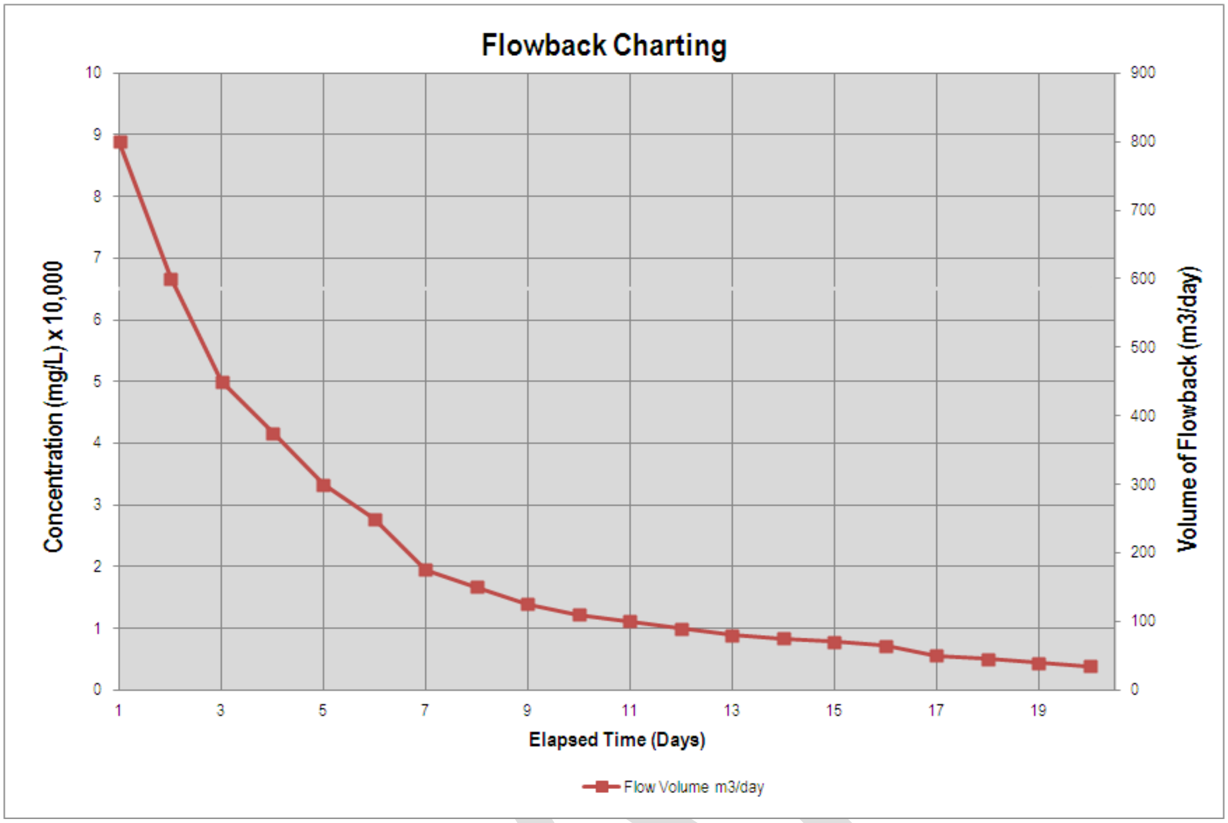


Figure 11 Generalized Flowback Rate vs Elapsed Time (Source…….)

Load Recovery

During the fracturing process, some fracturing fluid may flow from the created fractures to other areas within the gas-containing formation in a phenomenon known as “fluid leakoff.” In the case of leakoff, the fluid may flow into the micropore or pore spaces within the formation, existing natural factures in the formation, or small fractures opened into the formation by the pressure in the induced fracture. Fluid leakoff during hydraulic fracturing can exceed 70% of the injected volume. (API, 2009; Economides et al., 2007).

3.3 Flowback Chemistry

The chemistry of flowback water can vary from location to location and is largely dictated by the chemical makeup of the fracturing fluid and the nature of the formation fluid. Many of these waters are contaminated with heavy metals such as zinc and iron. The flowback water may contain corrosive elements such as H_2S, CO_2, and/or salt, solids (inorganic scales like $FeCO_3$), and traces of organic materials like oil. As they are used in fracturing treatments, the flowback water returns with additional material in the fluid such as broken polymer and/or other residuals from the original fracturing treatment. All these different species in the flowback water can have detrimental chemical affects on additives envisioned to be used for future treatments (e.g. disruption with biocide efficacy, ability of polymer to induce drag reduction, etc).

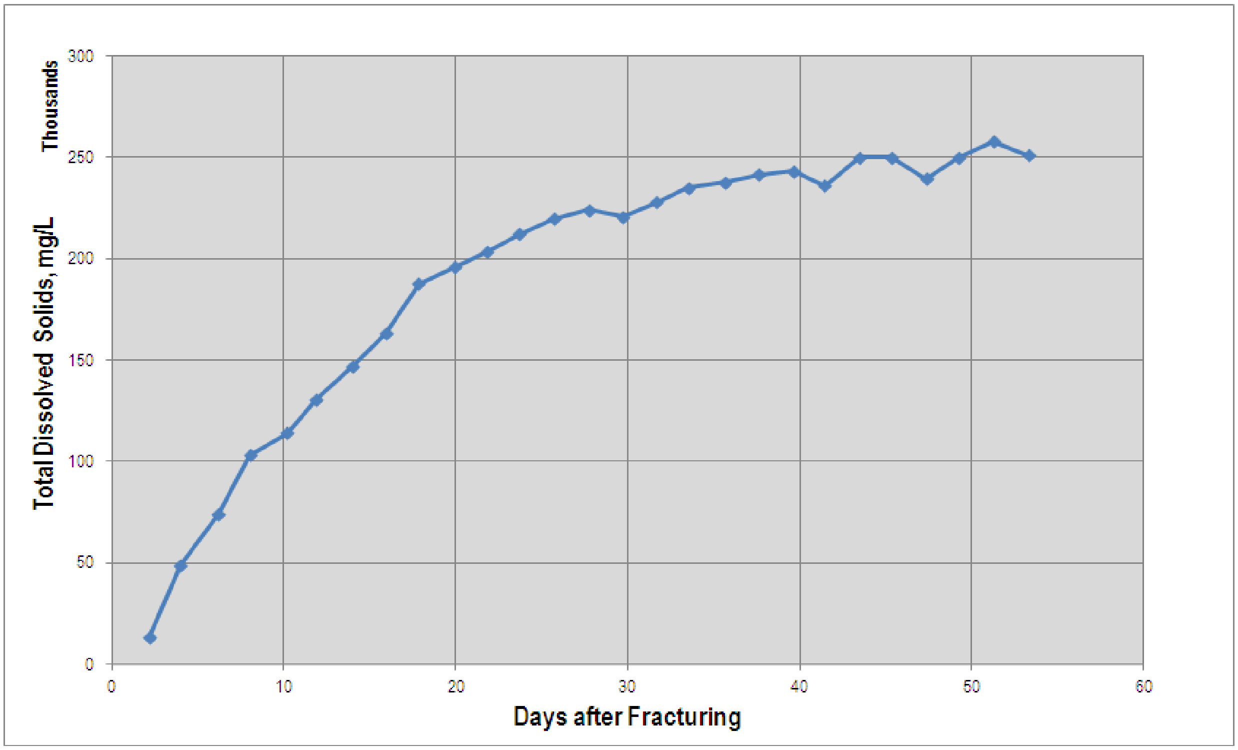


Figure 1 Total Dissolved Solids Buildup With Time (Source------)

In general, analyses of flowback from various reports show that concentrations of Total Dissolved Solids can range from 5,000 mg/L (Horn, 2009) to more than 100,000 mg/L and may even reach 200,000 mg/L These high values can be reached in a matter of two weeks. Along with high TDS values, flowback can have high concentrations of major ions (e.g., barium, bromide, calcium, chloride, iron, magnesium, sodium, strontium, bicarbonate), with concentrations of calcium and strontium sometimes reported to be as high as thousands of milligrams per liter Flowback may also contain radionuclides as well as volatile organic compounds (VOC), including benzene, toluene, xylenes, and acetone.

Additionally, flowback has been reported to have pH values ranging from 5 to 8 A limited time series monitoring program of post-fracturing flowback fluids in the Marcellus Shale indicated increased concentrations through time of TDS, chloride, barium, and calcium; water hardness; and levels of radioactivity 138

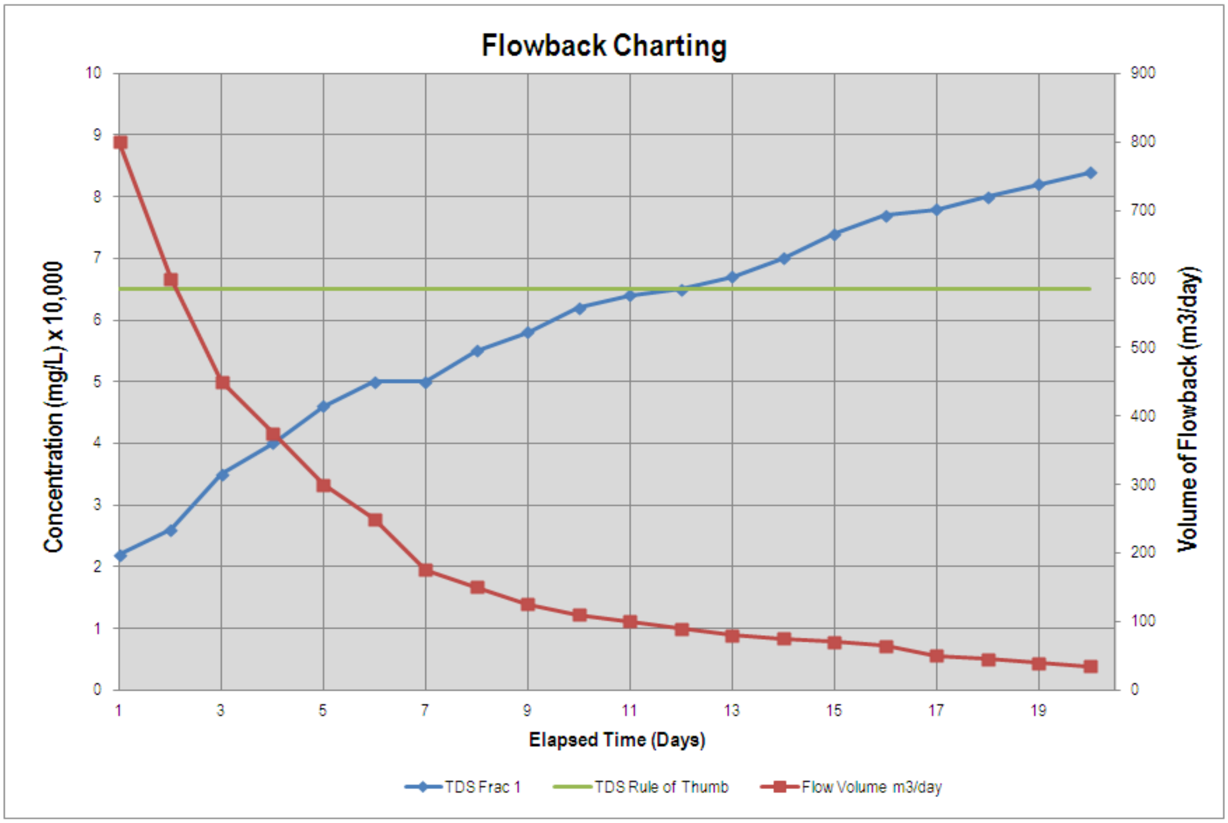


Figure 13 Generalized Total Dissolved Solids vs Flowback Rate (Source----)

The presence of the many possible contaminants can impact the performance of the fracturing fluid additives. For example, surfactants and clay stabilizers can be adsorbed onto the colloidal solids. The presence of solids, residual gel and bacteria can also impair permeability of the formation

Typical classes of parameters present in produced and flowback fluid are:

- Dissolved Solids (chlorides, sulfates, and calcium)
- Metals - Monovalent and Divalent (calcium, magnesium, barium, strontium)
- Suspended solids - Solids, Clays, Sand, Silt
- Mineral scales (calcium carbonate and barium sulfate)
- Bacteria - acid producing bacteria and sulfate reducing bacteria
- Friction Reducers (Polymer & Gel)
- Iron solids (iron oxide and iron sulfide)
- Dispersed clay fines, colloids & silts
- Acid Gases (carbon dioxide, hydrogen sulfide)
- Oily Solids
- Soluble Hydrocarbon
- Scale & Corrosion Inhibitors SPE 119900

As they are used in fracturing treatments, the flowback water returns with additional material in the fluid such as broken polymer and/or other residuals from the original fracturing treatment

3.3.1 Naturally Occurring Constituents in Flowback

Natural formation water has been in contact with the reservoir formation for millions of years and thus contains minerals native to the reservoir rock. The salinity, TDS, and overall quality of formation water vary by geologic basin and specific rock strata. After initial production, produced water can vary from brackish (5,000 mg/L to 35,000 mg/L TDS), to saline (35,000 mg/L to 50,000 mg/l TDS), to supersaturated brine (50,000 mg/L to >200,000 mg/L TDS)2,97, and some operators report TDS values greater than 400,000 mg/L 2,98. The variation in composition changes primarily with changes in the natural formation water chemistry.[2]

Type of Contaminant	Example (s)
Formation fluid	Brine[a]
Gases	Natural gas[b] (e.g. methane, ethane), carbon dioxide, hydrogen sulfide, nitrogen, helium
Trace elements	Mercury, lead, arsenic [c]
Naturally occurring radioactive material	Radium, thorium, uranium[c]
Organic material	Organic acids, polycyclic aromatic hydrocarbons, volatile and semi-volatile organic components

Table 5 Naturally Occurring Substances that may be found in hydrocarbon- containing formations

Chemical	Common valence states	Ref.
Aluminum	III	1
Antimony	V, III, -III	1
Arsenic	V, III, O , -III	1
Barium	II	1
Beryllium	II	1
Boron	III	1
Cadmium	II	1
Calcium	II	1
Chromium	VI, III	1
Cobalt	III, II	1
copper	II, I	1
Hydrogen sulfide	N/A	2
Iron	III, I	1
Lead	IV, II	1
Magnesium	II	1
Molybdenum	VI, III	1

Nickel	II	1
Radium (226)	II	2
Radium (228)	II	2
Selenium	VI, IV, II, O, -II	1
Silver	I	1
Sodium	I	1
Thallium	III, I	1
Thorium	IV	2
Tin	IV, II, -IV	1
Titanium	IV	1
Uranium	VI, IV	2
Vanadium	V	1
Yttrium	III	1
Zinc	II	1

Table ------ Naturally Occurring Substances Mobilized By Fracturing Activities (Source---)

3.3.2 Presence of Residual Concentrations of Frac Additives

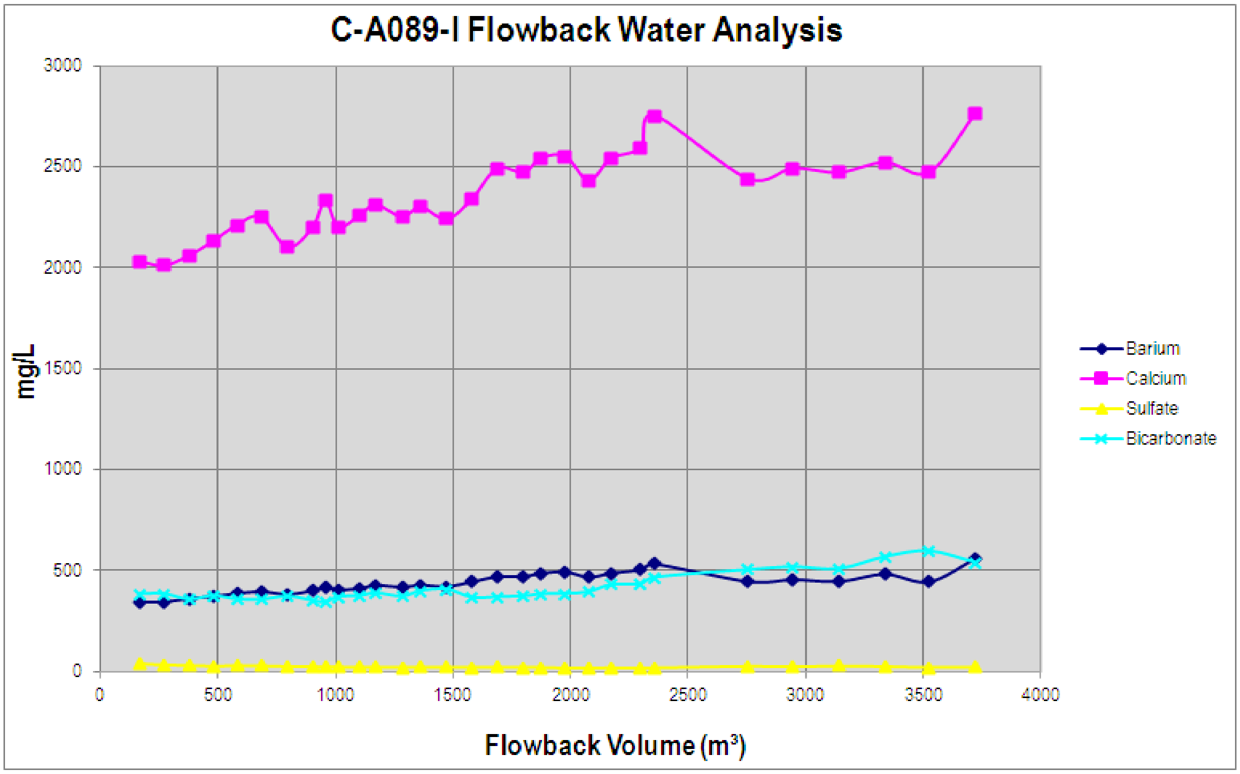


Figure 13 Time Series Flowback Chemistry – Montney Formation???

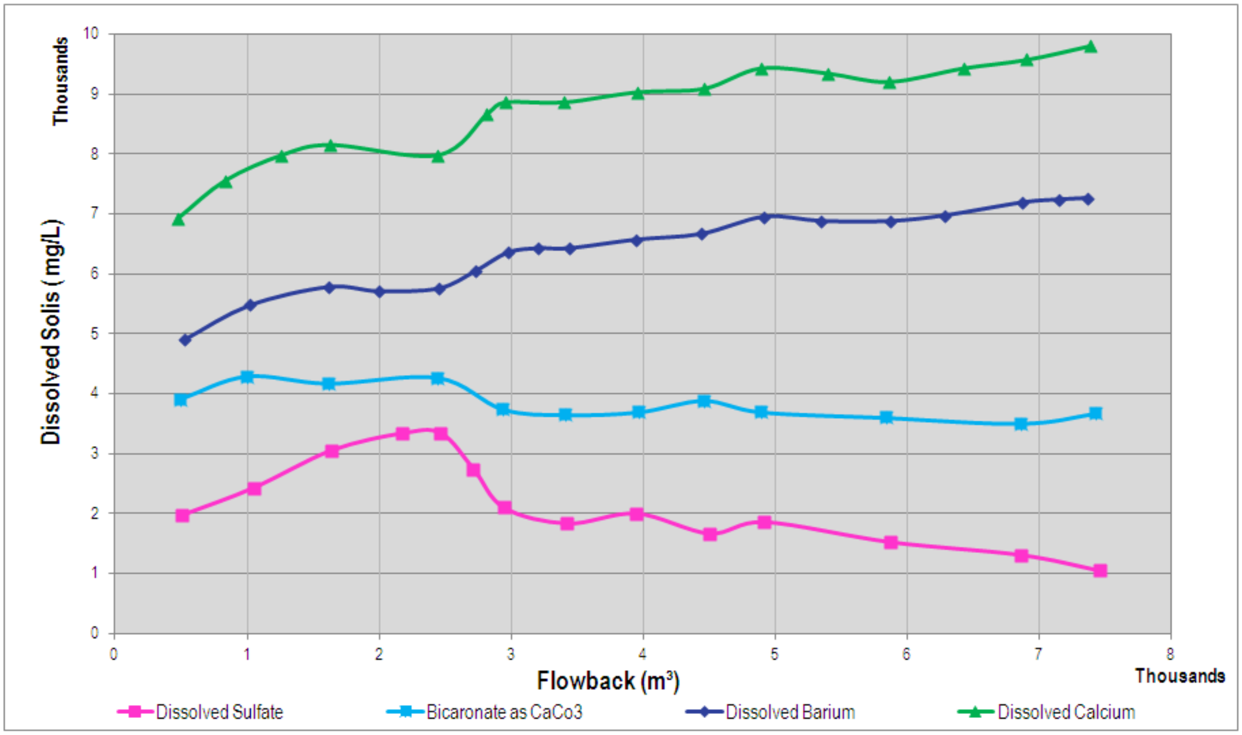


Figure 14 Time Series Flowback Chemistry – Montney Formation ???

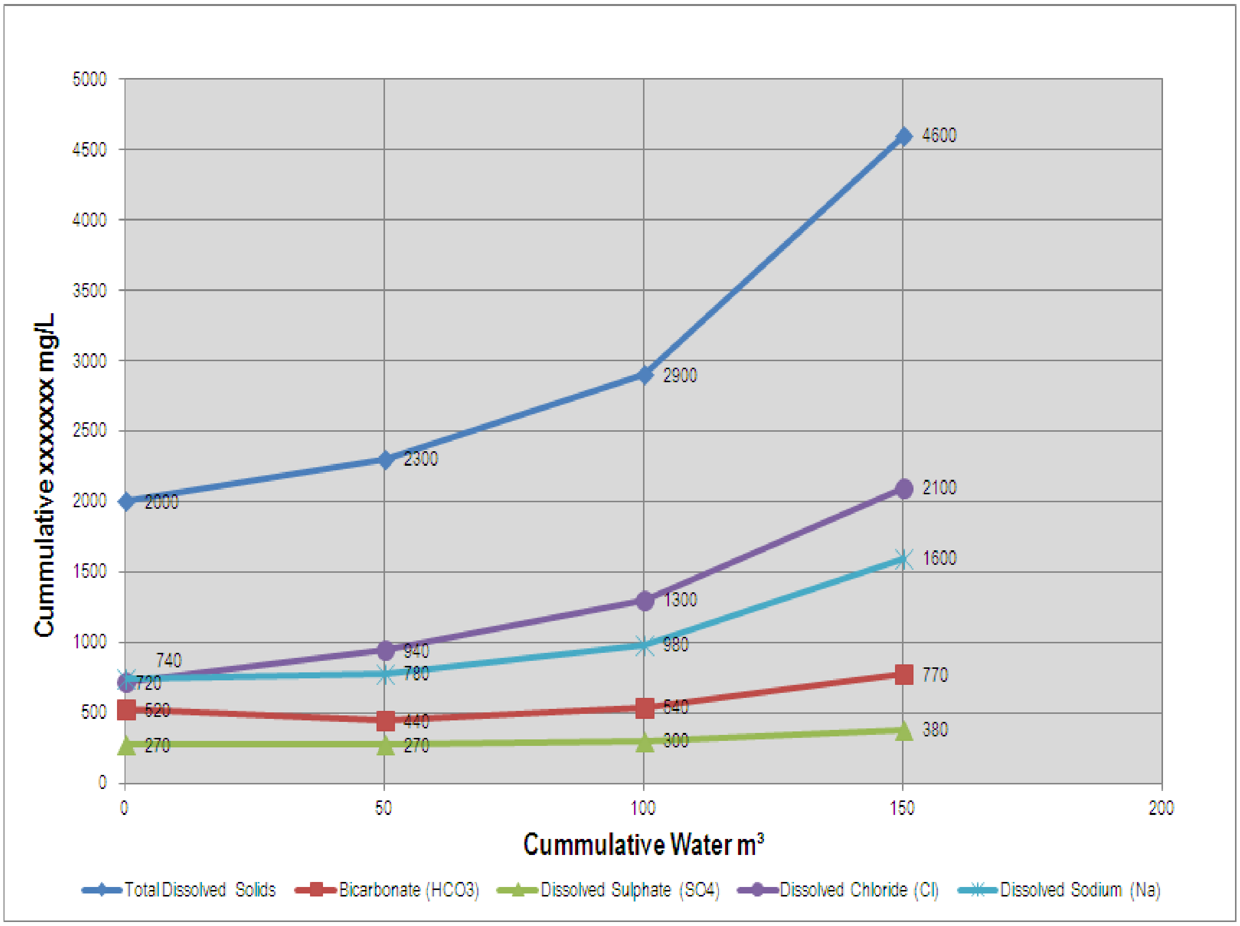


Figure 16 Time Series Flowback Chemistry – Cardium Formation

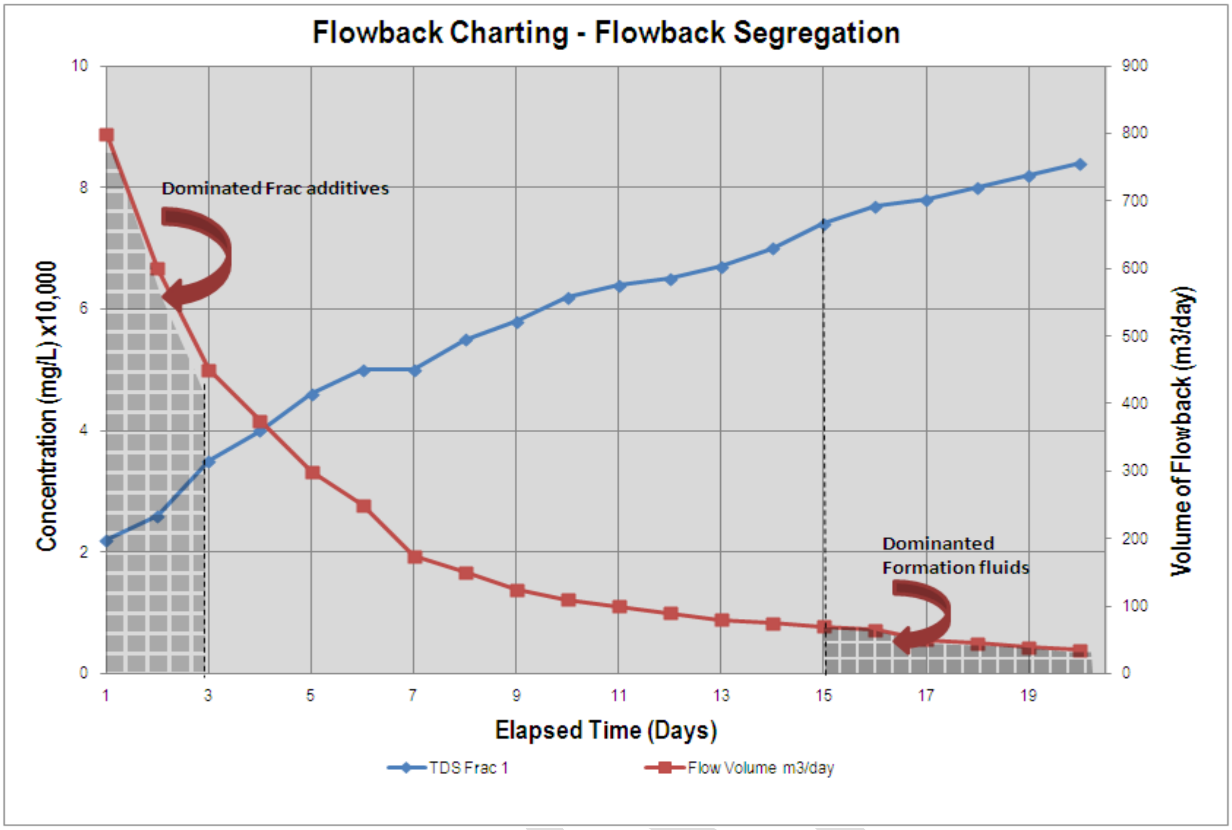


Figure 17 Flowback Chemical Segregation

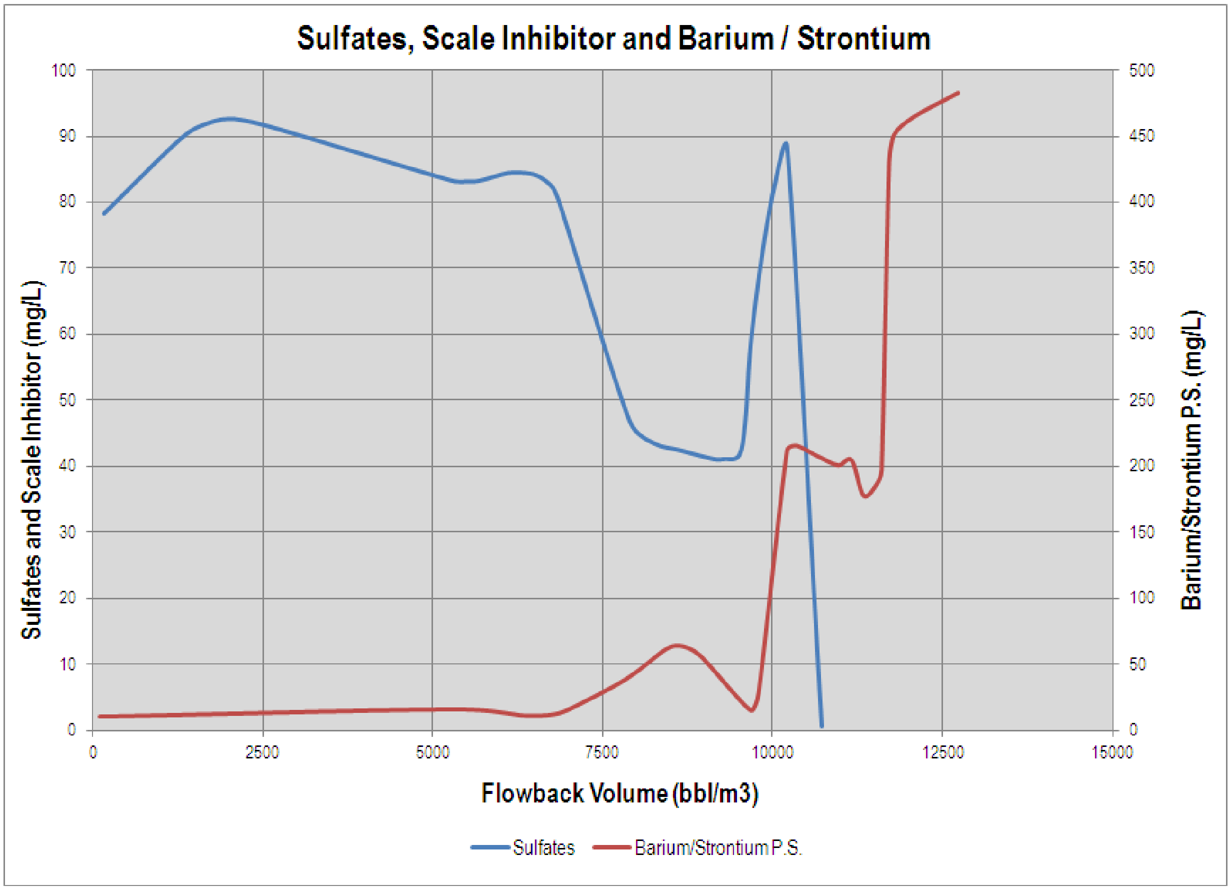


Figure 17 Variability in Flowback Chemistry (Source -----)

Return chemicals may include quantities of friction reducer (normally a polyacrylamide molecule or a guar in a few cases) and a very small amount of biocide in the first part of the flowback (the last fluid pumped). Most added frac chemicals with surface active nature adsorb in the formation and will not usually return in significant quantities. Polymer debris may be present, although often highly diluted, but also reported in very high concentrations when leakoff results in the buildup of a skin of polymer on the fracture face. This polymer debris is subsequently returned to surface with the flowback and may plug filtration equipment. It is known that the dilution of the injected fluid does occur with time, so at a minimum, we expect to see a reduction in the concentration of residual frac chemicals in response to simple mixing and dilution by formation fluids.

If the presence of residual frac additives and chemicals are an impediment to the reuse of the flowback fluids it may be desirable to batch the early flowback fluids for treatment or disposal. Therefore it is (again) important to understand the nature of the flowback for a number of conditioners and additives.

3.4 Process of Optimizing Frac Fluids From Flowback Water

The process of utilizing flowback frac fluid can be optimized through by following a series of steps that together constitute a formal workflow.

STEP 1: WATER ANALYSIS

A water analysis is the first of a series of tests that should be performed when designing and optimizing a fracturing fluid. The composition and quality of flowback water can vary greatly from location to location.

STEP 2: BIOCIDE SELECTION

One of the most severe threats in recycling waters for fracturing treatment is the control of bacteria including sulfate reducing bacteria (SRBs) and other forms such as acid producing bacteria (APB), iron fixing bacteria and slime formers. SRBs have created souring of some conventional reservoirs from injection of waters, both produced and semi-fresh, which have established a presence in the reservoirs and create H_2S gas and iron sulfide problems. Local well fouling problems are common where SRBs are spiked into the formation from drilling or completion fluids. This type of H_2S occurrence may cause local corrosion, but not usually a problem for conventional reservoirs in the absence of water flooding. In shale, however, the effect of uncontrolled bacteria is a general unknown, given the extremely large volumes of surface water used in slick water fracturing. Thus bacterial control is a necessity. Promising developments of no-residual biocides include trials using ultraviolet light and chlorine dioxide 40

The chemistry of the water will impact the additives to be recommended. For example, a biocide like glutaraldehyde gives optimal killing action in alkaline systems. This is because the mode of action for glutaraldehyde on bacteria is dependent on the pH of the surrounding medium. In acidic systems, the reactivity of glutaraldehyde is reduced and would require additional chemical to effect cidal action would be needed. Biocide like glutaraldehyde gives optimal killing action in alkaline systems This is because the mode of action for glutaraldehyde on bacteria is dependent on the pH of the surrounding medium. In acidic systems, the reactivity of glutaraldehyde is reduced and would require additional chemical to effect cidal action would be needed. SPE 125336

STEP 3: SCALE INHIBITOR

A scale control mechanism is required to simultaneously protect against three types of known scale or precipitate found in flowback from shale reservoirs: carbonate, sulfate, and iron-based scale depositions. As seen in many shale completions, the frac water picks up significant levels of ions from the formation that have the potential to cause production impairment. Unprotected, this unique geochemical environment can lead to geochemical precipitates within the created fracture network and potential scale to accumulate in perforations, piping, and surface impoundments. Many surface source waters also exhibit a need for scale control 125

Once the biological activity and biocide recommendation has been accomplished, a scale prediction analysis should be performed on the water. There are several ways to indirectly predict the amount of scale potential of water based on its composition. The Langelier saturation index (LSI) and Stiff-Davis index (SI) are the most commonly used indicators to predict water scale potential LSI only considers the thermodynamic driving force for calcium carbonate scale formation and growth based on the pH of the given water sample. The SI value relies more heavily on the pH of saturation than LSI method to determine the potential for scale making it more useful in waters that have a higher salt concentration or higher TDS. However, the SI model has the same shortcomings as the LSI with respect to its inability to predict other types of scale and the limitation to predict scale at reservoir conditions (e.g. temperature and pressure effects). SPE 125336

A more comprehensive scale prediction method is the Gibb's Free Energy minimization method because it incorporates reservoir conditions into the modeling process,. This approach can predict additional scales (e.g. sulfates and other divalent carbonates) and can be accomplished using a software modeling program Table 3 reports the scaling tendency of the flowback water composition listed for the Piceance water in Table ------ using a software modeling program based on the Gibb's Free Energy minimization method. SPE 125336 (Oddo and Tomson, 1994)

The reservoir conditions used to predict the scale were a bottom hole static temperature of 190 ° F [88 ° C] and 1500 psi. For this flowback water sample, the amount of scale predicted under the reservoir conditions included only a small amount of iron carbonate ($FeCO_3$) and higher amounts of calcium carbonate ($CaCO_3$). SPE 125336

The publically available software modeling programs referred to in Section ----- contains an algorithm for scale prediction using information obtained from water analysis done on field mix water samples. The concentration of each species detected in the water analysis was input into the software program along with the reservoir pressure and temperature. The program then generates the different scaling species expected under such conditions and the relative amounts expected to scale out of solution. This information is then used to recommend an appropriate scale inhibitor for treatment.

STEP 4: FRICTION REDUCER

With so many different friction reducers available on the market, the next step in the process should be performance testing of the friction reducer in the flowback water. The ability to test the performance of a friction reducer in the flowback water will ensure that the most cost effective and efficient friction reducer is selected for the treatment.

Fig.------ illustrates the effect of concentration of three different friction reducers in a synthetic flowback water system. Each point on this plot comes from the maximum percent drag reduction for each friction reducer fluid evaluated at different concentrations on a friction loop. The maximum percent drag reduction (%DR) value for an anionic friction reducer (Friction Reducer A), a more environmentally friendly anionic friction reducer (Friction Reducer B), and a cationic friction reducer (Friction Reducer C) in a 33,000 TDS synthetic flowback water evaluated at various concentrations on a friction loop in 3/8-in. pipe, (Error + 5%).

These results indicate that a robust friction reducer can perform well at low concentrations (e.g. 0.5 gallons /tone (gpt) in flowback water, and that there is little benefit in performance at higher concentrations (e.g. 1 gpt) for Friction Reducer A and B. Friction reducer C is the least efficient of the friction reducers tested and would require elevated amounts of polymer (1.0 gpt) to reach the performance level of the other two friction reducers. Friction reducer A is the least expensive of those tested and would result in cost savings relative to the other polymers tested. SPE 125336

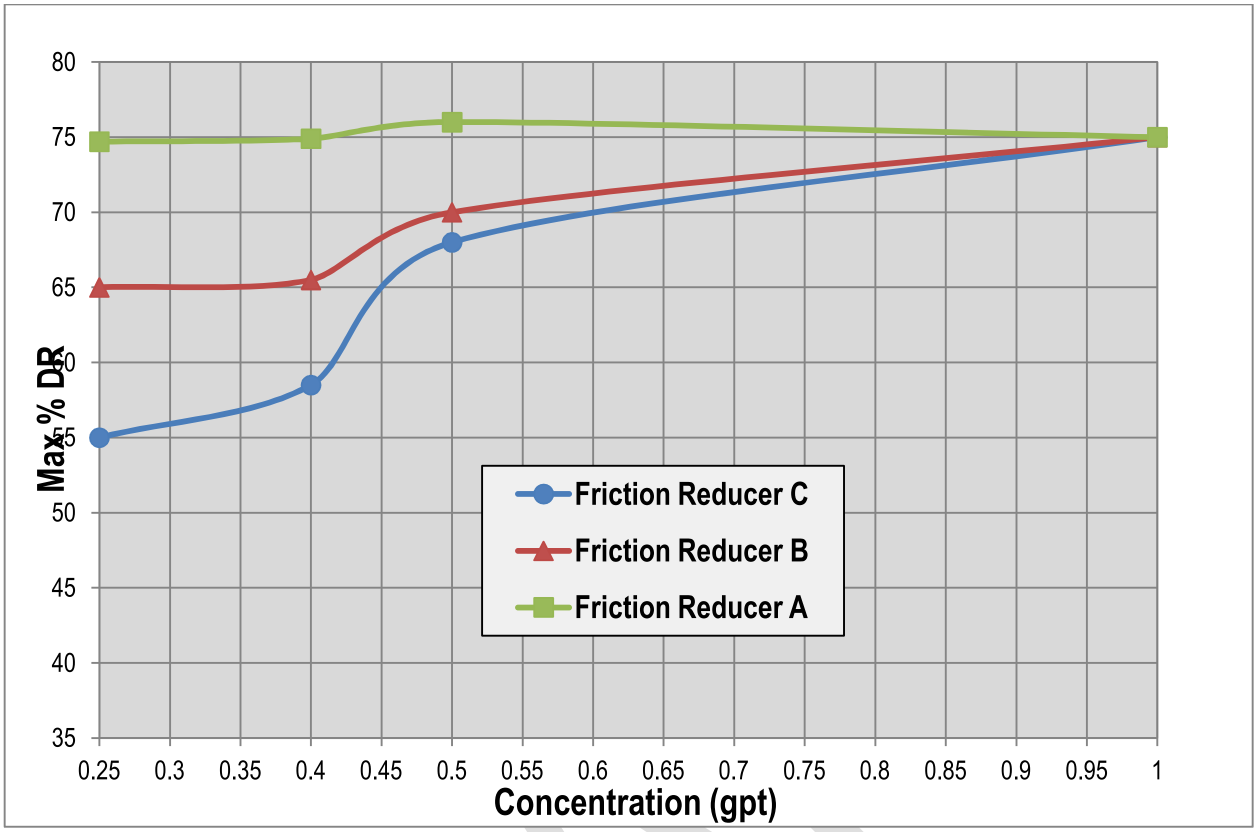


Figure 18 Friction Reducers Performance in Flowback Water (Source SPE 125336)

STEP 5: CLAY STABILIZATION

The next step in the process is to determine if the reservoir is sensitive to water. Capillary suction time (CST) test measures the retention time of a particular fluid in a slurry containing crushed rock (30/70 mesh) and a fracturing fluid. The slurry is placed in a funnel atop chromatography paper. The timer measures the time it takes for the fluid to be extracted from the slurry by adsorption onto the chromatography paper. Fluids that disperse clays in the slurry will result in long CST retention times. Fluids that do not swell the clays in the slurry result in a short CST retention time. SPE 125336 High CST ratios indicate increased colloid formation and more potential formation damage.

$$CST\ Ratio = \frac{CST\ Time - Blank\ Time}{Blank\ Time}$$

Where CST Time = the retention time (sec) it takes for a fluid to pass through the core sample and filter paper and reach the electrode. The Blank Time = the retention time (sec) for a fluid to pass through the filter paper without a core sample present.

If the reservoir is known to be sensitive to clays and core samples are available, performing a CST analysis is recommended. Different fluids containing various clay stabilizing additives can be readily screened and the optimum concentration and type of additive that stabilizes clays in the core sample can be determined. SPE 125336

STEP 6: COMPATIBILITY CHECK

The final step in the process is a compatibility check. All additives that have been identified throughout the process should be checked for incompatibilities and evaluated on the friction loop to confirm performance of the optimized fluid. If flocculation or incompatibilities result at this stage of the process, a different additive should be suggested and retested with the appropriate analytical tool listed earlier.SPE 125336

It is important to do a water analysis and follow through on efficacy testing for each type of additive expected to be used in the fracturing fluid. The final compatibility check is critical to ensure that all the different additives are working together in concert to optimize well performance. If the compatibility step is ignored, problems with bacteria and scale may result.

4.0 HYDRAULIC FRACTURING FLUID CONSIDERATIONS

The types and use of fracturing fluids have evolved greatly over the past 60 years and continue to evolve. To select the fracturing fluid for a specific well, it is necessary to understand the properties of the fluid and how these properties may be modified to accomplish desired effects.

In classifying fracturing fluids and their additives it is important to realize that service companies that provide these additives have developed a number of compounds with similar functional properties to be used for the same purpose in different well environments. The difference between additive formulations may be as small as a change in concentration of a specific compound. Although the hydraulic fracturing industry may have a number of compounds that can be used in a hydraulic fracturing fluid, any single fracturing job would only use a few of the available additives. It is not uncommon for some fracturing recipes to omit some compound categories if their properties are not required for the specific application.

Each of the various fracturing treatment types and formations are sensitivity to differing fluid quality issues. The design of effective fracture treatments and the determination of the need for treatment of frac flowback fluids require a clear understanding of the water quality issues. Various water quality issues influence frac performance in different ways.

Geochemical control also enables operators to tailor frac flowback water so it can be used in subsequent fracturing operations while minimizing concerns of subsequent formation damage due to geochemical precipitation. Significant reductions in frac fluid expense have been observed from the reuse of flowback, due to the reductions in transportation costs of frac water, purchases of freshwater and water disposal volume.110

Composition of Fracturing Fluids

To achieve successful stimulation, the fracturing fluid must have certain physical and chemical properties.

1) It should be compatible with the formation material
2) It should be compatible with the formation fluids
3) It should be capable of suspending proppant and transporting them deep into the fracture
4) It should be capable, through its inherent viscosity, to develop the necessary fracture width to accept proppant or to allow deep acid penetration.
5) It should be an efficient fluid (i.e., have low fluid loss)
6) It should be easy to remove from the formation
7) It should have low friction pressure
8) Preparation of the fluid should be simple and easy to perform in the field
9) It should be stable so that it will retain its viscosity throughout the treatment.
10) The fracturing fluid should be cost effective

The first characteristic may be the most critical. If the chemical nature of the fracturing fluid causes swelling of naturally occurring clays in the formation, thereby plugging pore channels, the treatment will be a failure. If the fracturing fluid causes migration of fines and/or clays, the success of the treatment will be nullified. If the fracturing fluid creates emulsions and/or sludges, then the plugging rather than stimulation will occur. The fracturing fluid should not cause scaling. Compatibility is therefore a critical and necessary characteristic of a fracturing fluid.

Another important characteristic of a fracturing fluid is its ability to transport the proppant down the tubular goods, through perforations, and deep into the fracture. Depending on the nature of the fracture, it may perfectly suspend the proppant or, as is the case of linear fluids, allow for some settling and banking of the proppant in the fracture. Large viscosities are needed to transport proppant and to develop the fracture width needed to create and to prop long fractures. It is well known that insufficient fracture width from insufficient viscosity will not allow proppant to be transported very far into the fracture.

The ideal fracturing fluid should be moderately efficient. A high percentage of fluid should remain in the fracture and not be lost to the formation. Fluid efficiency is normally attained by combining high fluid viscosity with fluid–loss additives. These fluid loss additives may consist of plastering agents, bridging agents, microemulsions, or emulsified gas. A low efficiency fracturing fluid would not create the desired fracture volume, carry the proppant or achieve the desired formation penetration if most of the fracturing fluid leakoffs during treatment

Another important characteristic of a fracturing fluid is its ability to revert from high viscosity to low viscosity upon residing in the formation. Viscosity reduction is necessary so that the treating fluid can be removed from the formation easily. High fluid viscosities in the fracture or in the formation near the fracture can reduce hydrocarbon production. Fracture fluid viscosity is normally reduced by thermal degradation in high temperature wells or by controlled degradation through the use of such breaking agents as enzymes, oxidizers, or weak acids. Controlled degradation is essential for the fluid to maintain its viscosity during the treatment but to degrade and lose its viscosity after the treatment.

Many fracturing-fluid systems used during the 1950’s and 1960’s had high viscosity and the ability to degrade; however, they were extremely difficult to pump down small tubular goods. Modern fracturing –fluid systems have been developed that allow for high viscosity but have reduced friction properties. In fact, most of these fluids will pump at pressures lower than low viscosity base fluids, such as water or oil, through turbulence suppression by long-chain polymer systems. If a fluid cannot be pumped easily, it normally is not acceptable as a fracturing fluid. Exceptions to this case are high viscosity crude oils used in shallow casing jobs. These high-viscosity, Newtonian fluids, however, are not acceptable for pumping down small tubular goods.

Fracture fluid stability at high temperature is a critical aspect of any fluid. A fluid that rapidly loses its viscosity because of thermal thinning or degradation is not applicable for treatment of high temperature wells. A fracturing fluid should be able to maintain the designed viscosity with minimal viscosity loss vs time at bottomhole temperature (BHT)

Finally, fracture fluids should be cost effective and easy to mix in the field. One of the most important selection criteria for a fracturing fluid is cost-effectiveness in treating the formation under study. Quite obviously, a fluid that has all these attributes but will not yield cost effective stimulation will not be an ideal fluid.

Factors Influencing Fracturing Fluid Composition

As described in 4.4, there are a wide variety of additives that could be included in the fracturing fluid mix to achieve successful fracturing. The mix could include proppant, gel and foaming agents, salts, acids, and other fluid additives. Today, operators and service companies are working to maximize the utilization of environmentally benign additives and minimize the amount of additives required. The characteristics of the resource target determine the required fracture fluid composition. For example, gas shale may contain various naturally occurring trace metals and compounds that are leached from rocks by acidic water, oxidation, and the action of ions found in brines. Numerous compounds have been formed naturally in the shale, and a stimulation fluid pumped into a well may require various chemicals to counteract any negative effects these compounds may have in the well or the reservoir. Iron compounds found within the Fayetteville shale require an iron sequestering agent so that the compounds of iron will not precipitate out of the fracturing fluid and be deposited within the pore spaces of the reservoir, reducing the reservoir's permeability.

4.1Compatibility Testing and Water Issues

An optimized frac fluid can be attained with a systematic approach to the fluid design. Each case requires specific analysis and testing to maximize fluid performance116. The key to the effective design and management of frac fluid lies in establishing a detailed understanding of how the various chemical will interact and function when mixed with the other components in the frac fluids. A characterization of the physical and chemical characteristics is required for:

1. Evaluation of compatibility of the source water and the formation water.
2. Evaluation of compatibility of the source water with the rock framework
3. Evaluation of the source water and proposed conditioners and frac fluids

Waters that are compatible can be mixed without producing undesirable chemical reactions between components dissolved in the individual waters. Undesirable reactions are those that produce insoluble products such as calcium and carbonate ions, forming calcium carbonate; barium and sulfate ions, forming barium sulfate; or ferrous iron and oxygen forming iron oxide. Insoluble products produced from these reactions can decrease flow in lines, plug injection wells, or reduce permeability.

When water that is not compatible with interstitial water is injected into a reservoir, deposits will form only where the waters make contact and mix. If there is a small degree of mixing, deposits will form in only a small volume of water; conversely, a large degree of mixing will result in deposits forming in a large volume of water. A breakthrough of injection water into the bore of a producing well would mix large amounts of incompatible waters and cause severe damage to the well.

Compatibility – Water Rock and Water/Water Interactions and Formation Damage

Whenever there is a significant difference in either the composition or concentration of the injected water and the formation water that has been in contact with reservoir rocks for long periods of time, a potential for detrimental interactions exists. This is frequently the case when a source water used for injection, is different from the produced water.

We will consider two types of compatibility or reactions as they are related to water quality and water injection. The first is concerned with chemical and physical reactions and interactions between the injection water and the formation rock in the injection zones. These reactions occur because of differences in chemical composition and concentration between the injection water and the water with which the rock has been in equilibrium. The second type of compatibility is concerned with precipitation reactions that might occur between the water that is being injected into the formation and the water that is already in the formation – this may be connate water or some other previously injected water. This type of interaction will be discussed later in the section on scale control. (98)

Waters that are compatible can be mixed without producing undesirable chemical reactions between components dissolved in the individual waters. Undesirable reactions are those that produce insoluble products such as calcium and carbonate ions, forming calcium carbonate; barium and sulfate ions, forming barium sulfate; or ferrous iron and oxygen forming iron oxide. Insoluble products produced from these reactions can decrease flow in lines, plug injection wells, or reduce permeability.

There are two general mechanisms for formation damage or permeability impairment from injected water/formation rock interactions. The first mechanism is concerned with the formation and liberation of fines. The fines then move with the water flow until they become lodged in a pore throat. Processes involved in this mechanism include: (1) clay swelling, (2) clay flocculation, (3) mica alteration, and (4) critical flow velocity.

The second mechanism involves solution of formation minerals. In some cases, damage occurs when the dissolved minerals re-precipitate. In the other case, the solution of some minerals frees less soluble minerals that can move with the water flow and plug pore throats.

The key to maximizing injection efficiency (rates and profiles) is to identify the potential problem before hand and then to treat to prevent or control the damage. The less efficient procedure is to try to identify the damage mechanism after it has occurred and then to try remedial treatments. Generally the best option is to be proactive rather than reactive.

There are a number of test procedures available to detect and identify possible damage upon water injection. They include:

- Core flow tests (not to be confused with core flow tests to determine required water quality for injection)
- Mineral analysis of the formation rock; and,
- Chemical analysis of the waters involved in the flood.

The tests are usually run in the order listed. The rational for this order is first to run the core flow tests to see if there is a problem, and then if there is, the mineralogical and chemical analyses can be used to determine the cause of the problem in the rock and water phases, respectively.

If several water sources are available, choosing the least damaging is the most economical. This is particularly true if produced water is available in sufficient volumes. Since the produced water came from the formation, it should be less damaging when re-injected into the same formation, particularly if care has been exercised to minimize chemical and physical changes in the water during production, separation, treatment and injection.

Modifying the completion techniques and the injection procedures can be especially helpful when the damage mechanism is fines migration from high flow rates. Lower injection rates and completion techniques (higher perforation density, openhole completions, etc) that increase the cross-sectional area for flow may reduce the velocity below the critical value, particularly around the injection wells where velocities are the highest.

Changing the water chemistry by the addition of divalent cations or potassium salts is usually not economical for the volumes involved in an injection project. Such treatments may be justified for low volume conditions such as drilling or completion fluids.

There are two variations available for protecting the formation rock around a wellbore prior to injection of a damaging water. First, inject a calcium chloride, potassium chloride, or ammonium chloride brine. Or second, inject a commercially available clay stabilizer. The first treatment is less expensive but not long lasting as the second.

Water Compatibilities (STP 641)

Water used for hydraulic fracturing usually contains a number of inorganic salts and sometimes organic salts in solution. It is common practice to test the compatibility of the injection water and water in the formation before starting an injection operation. Often this test is performed by mixing the injection water with the formation water in a glass container and observing to determine if a precipitate forms. The precipitate or scale can be analyzed to determine its composition. Waters are compatible if they can be mixed without producing chemical reactions between the dissolved solids in the waters which precipitate insoluble compounds

Two waters are mixed in definite proportion to test their compatibility. If an induction period is required before salt deposition occurs, it is important that the test be observed for a considerable length of time. If no reaction occurs that produces a deposit, it is advisable to seed the test waters with a crystal of the salt most likely to deposit. From the water analysis data of the individual waters, it is possible to calculate the composition of the mixed water. A prediction of which salt will be most likely to deposit can then be made. A few small crystals of this salt can be used to salt the test mixtures. A procedure for making a compatibility test is found in the Appendix (64)

4.1.1 Databases

In the early stages of planning of drilling and hydraulic fracturing plans, a detailed understanding of the water quality of potential water sources or the formation characteristics of the formation to be fractured is frequently not known. Nonetheless, preliminary information regarding water chemistry and quality may be available from existing oilfield and environmental databases. While water quality information available from these databases may be incomplete, they provide the basis for a first approximation of the water quality of the water sourcing options and the formation fluid. Any problematic water constituents identified during this initial characterization that would preclude the use of that water for fracturing may result in significant savings in water development costs. Databases that may provide initial insight into water quality include:

- Hydrogeological Databases maintained by provincial governments:
- Water well files (AE)
- Water Quality data reported by Facilities operating under Environmental Approvals (AE)
- Hydrogeological base maps (AGS)
- Reports In Support of Application to Divert under Water Act (AE)

- Surface water databases
- Oilfield databases ERCB
- Oilfield databases (private by subscription)

4.1.2 Water Sampling and Laboratory Analysis

Water analysis testing is prudent and needed for each well and all source waters considered for high volume and rate fracturing. Blending of surface source waters and flowback waters can only be achieved successfully with up-front laboratory water analysis and flow-loop testing.125

The first step in any study involving waters is the determination of the dissolved solids and gases in the waters. Obtaining representative samples of water is the most important aspect of a water problem.

A water analysis is the first of a series of tests that should be performed when designing and optimizing a fracturing fluid. The composition and quality of flowback water can vary greatly from location to location.116 Each property of the water can influence the performance of the fracturing fluid. Selection of polymer, biocide, scale inhibitor and other additives are dependent on different water characteristics.11

Samples of all waters involved should be collected and analyzed. These samples should include water present in the oil reservoir, as well as all available sources of potential injection water. Often the only analyses of waters in formation s above the oil reservoir that might be considered as supply water are those obtained from a drill stem test taken during drilling of the oil well. This emphasizes the importance of taking the necessary time and precautions essential to obtaining reliable DST water samples.

All samples collected should be submitted to a reliable laboratory for analysis. These analyses should include determination s for carbonate, bicarbonate, sulfate, chloride, iron, calcium, magnesium, sodium, dissolved oxygen, total dissolved solids, alkalinity, pH, and specific gravity. If the dissolved sulfate, a barium analysis should be included. When the odor of hydrogen sulfide is detected, the water should be analyzed for this gas.

Some estimate of the corrosively of the waters can be obtained from the analytical data. Water analyses showing appreciable dissolved solids, dissolved oxygen and low pH will obviously indicate corrosive water. In designing the water handling system and treatment plant, measures for preventing corrosion can be included. This is more effective and less costly than discovering the water is corrosive after the system has been constructed and then trying to modify the system to minimize corrosion.

Throughout the operating life of the system, periodic water analyses should be made. If the injection project is large, these analyses should be made on samples taken simultaneously from different parts of the system. These analyses made every three to six months will enable the operator to detect changes in water composition and often prevent potential problems in he system before they become severe.

Analyses and calculations are very useful in estimating characteristics and behavior of water. Whenever samples of the actual waters involved are available, tests designed to verify predictions made from analyses and calculations should be performed. (64)

Sample Type	Case Study Site	Parameters
Surface and ground water (e.g. existing wells, new wells) Soil/sediments, soil gas	Prospective and retrospective (collect as much historical data as available)	• General water quality (e.g. pH, redox, dissolved Oxygen) and water chemistry parameters (e.g. cations and anions) • Dissolved gases (e.g. methane) • Stable isotopes (e.g. Sr, Ra, C, H) • Metals • Radionuclides • Volatile and semi-volatile organic components, polycyclic aromatic hydrocarbons • Soil gas sampling in vicinity of proposed/actual hydraulic fracturing well location (e.g. Ar, He, H_2, O_2N_2, CO_2, CH_4, C_2H_6, C_3H_8, iC_4H_{10}, nC_4H_{10}, iC_5H_{12}).
Flowback and produced water	Prospective	• General water quality (e.g. pH, redox, dissolved oxygen, total dissolved solids) and water chemistry parameters (e.g., cations and anions) • Metal • Radionuclides • Volatile and semi-volatile organic components, polycyclic aromatic hydrocarbons • Sample fracturing fluids (time series sampling) o Chemical concentrations o Volumes injected o Volumes recovered
Drill cuttings, core samples	Prospective	• Metal • Radionuclides • Mineralogical analyses

Table 7 Monitoring and Measurement Parameters

4.1.3 Mixing Tests

Mixing tests or “jar tests” are a simple yet effective method of validating the results of predictive determinations of compatibility, inversion times, and viscosity characteristics. Mixing of several additives, conditioners, and source waters at selected blending ratios is conducted in jars, and the results observed. A particular advantage of this procedure is that it is relatively simple, and can be conducted in the field in response to changes in fluid characteristics not anticipated during the fluid design. A jar test being conducted on a frac site is shown in Figure ----------

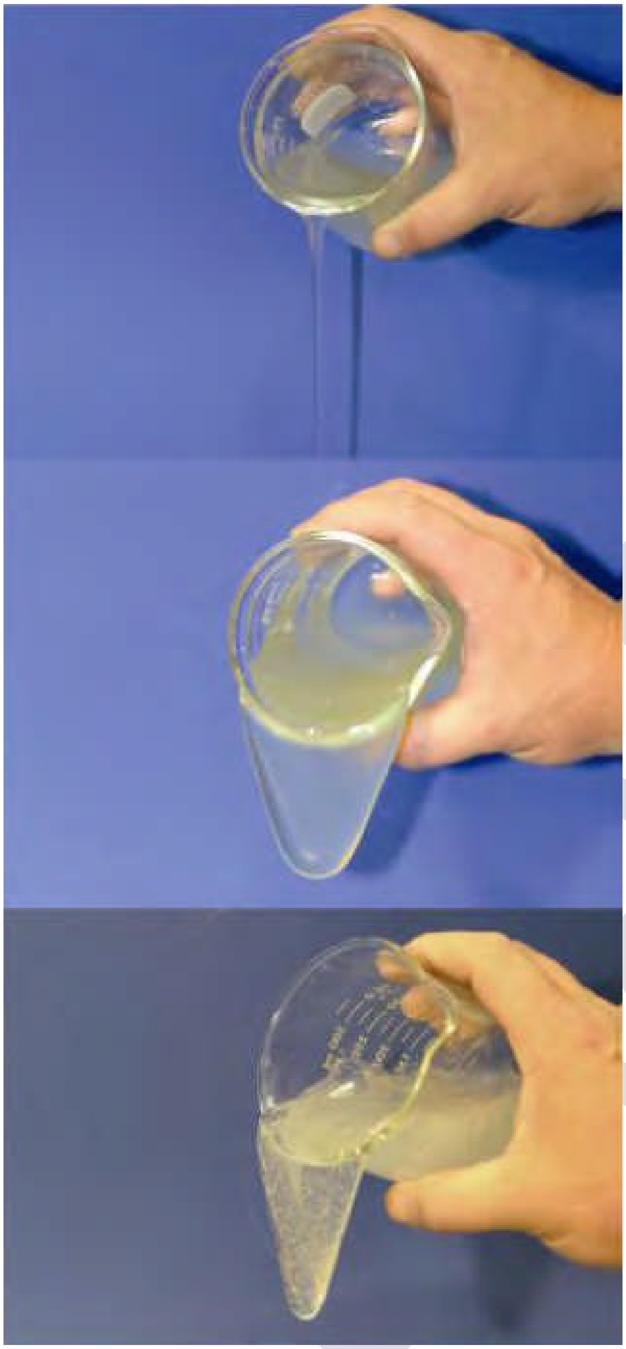


Figure 20a Viscosity Test

Figure 20b Jar Test (Source 87)

Figure 20c Jar Test Source ???

4.1.4 Geochemical Computer Modeling

A geochemical simulator may be used to predict the tendency for a wide range of geochemical precipitation from the shale completion flowback fluid. A geochemical simulator shows the tendency for specific mineral precipitates such as barium sulfate and iron carbonate to form. This process is used to ensure that the appropriate level of protection is being provided by the control chemical 110

The most basic solution for obtaining usable fracturing water from flowback fluids is to blend with fresh water. This option is commonly considered prior to more extensive and more costly remediation options. In applying such strategy, it does require extensive laboratory testing and evaluation as previously described. **Fig 6** illustrates an example testing suite where problematic flowback water was tested for straight blending rather than pre-conditioning or remediation. As can be seen, a functional performance limit is observed based on percent friction flow loop laboratory testing. In this example, a blend ratio of only 5% flowback water could be used in the final blend without further remediation. This information is critical to the proper design of a particular well's water sourcing and water management planning and requires rapid turn-around testing with specific waters from the specific sources being considered.125

Because of the complexity of scale formation and the difficulty of conduction the necessary thermodynamic and kinetic calculation to predict scaling, many computer programs have been produced to aid the engineer. There are several general purpose geochemical models available in the public domain that can be used to predict formation of oilfield scale. Most of the models are available at no or minimal charge from the internet and have been extensively reviewed in texts on aqueous chemistry. Geochemical Models specifically adapted for oilfield scale prediction are also available but tend to be more expensive. An exception is the "Water Mixing and Scale Affinity Model" developed through the US Department of Energy. The databases of thermodynamic properties required for scale prediction also tend to be better maintained and calibrated. In addition to these models there are several proprietary scale prediction models that appear in the literature, but the access to these models is available through consulting agreement or with membership to the consortium of companies responsible for its development. The geochemistry software programs/models available include:

- EQ3/6
- PHREEQC and PHRQPITZ
- MINTEQA2/Visual MINTEQ
- The Geochemist's Workbench
- SOLMINEQ.88
- ScaleChem
- MultiScale
- ScaleSoftPitzer
- OKSCALE
- Downhole
- AquaChem
- Water Mixing and Scale Affinity Model

An example of the report output from the "ScaleSoftPitzer" is shown in Table -------

MI SWACO
A Schlumberger Company

Oilfield Water Management

Scale-Potential Analysis: Single Fluid

Company Name:	Chevron	**Analysis Requested:**	Scaling Potential
Field:	Haynesville	**Technical Request No:**	CVX001
Sample ID:	Flowback Water (AVE)	**Date Requested:**	6/17/2011
Date Sampled:	6/17/2011	**Date Reported:**	6/19/2011
M-I SWACO Rep:	Adriana Ovalle	**Reported By:**	Jesse Farrell

Scale Prediction results are conducted using ScaleSoftPitzer SSP2010. This is a program that calculates the solubility of ions and minerals in water. It then identifies the scaling formation potential of mineral solids on individual brines or when two or more waters are mixed. The modeling software can reflect seven potential types of mineral scale precipitation including Calcite, Barite, and Halite.

Scale Precipitation Risk Matrix				
Less than 0 No Scale	0 to 1 Minor Risk	1 to 2 Moderate Risk	2 to 3 Severe Risk	Greater than 3 Extreme Risk

Table No.1 Scale Prediction Results

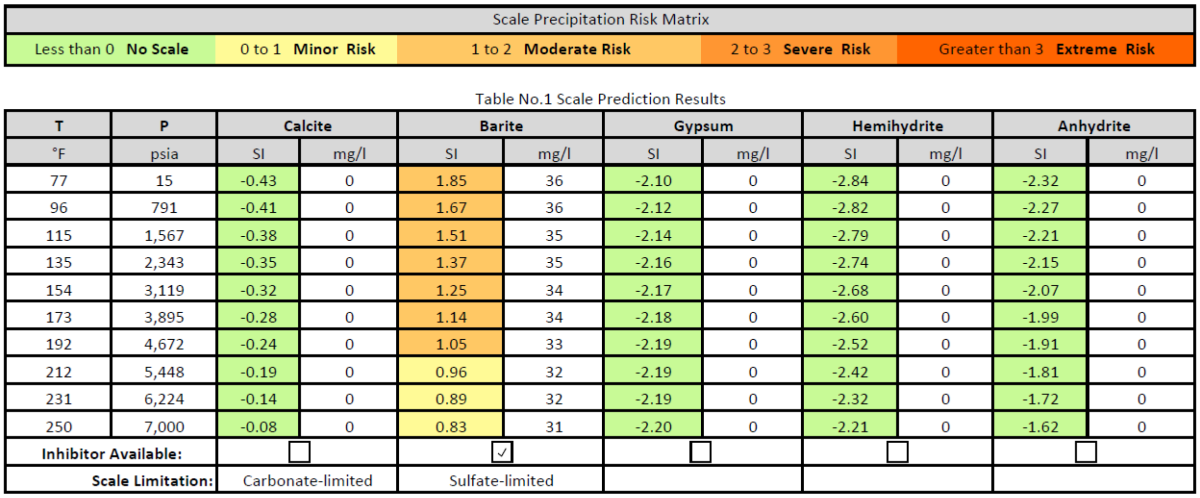
T	P	Calcite		Barite		Gypsum		Hemihydrite		Anhydrite	
°F	psia	SI	mg/l	SI	mg/l	SI	mg/l	SI	mg/l	SI	mg/l
77	15	-0.43	0	1.85	36	-2.10	0	-2.84	0	-2.32	0
96	791	-0.41	0	1.67	36	-2.12	0	-2.82	0	-2.27	0
115	1,567	-0.38	0	1.51	35	-2.14	0	-2.79	0	-2.21	0
135	2,343	-0.35	0	1.37	35	-2.16	0	-2.74	0	-2.15	0
154	3,119	-0.32	0	1.25	34	-2.17	0	-2.68	0	-2.07	0
173	3,895	-0.28	0	1.14	34	-2.18	0	-2.60	0	-1.99	0
192	4,672	-0.24	0	1.05	33	-2.19	0	-2.52	0	-1.91	0
212	5,448	-0.19	0	0.96	32	-2.19	0	-2.42	0	-1.81	0
231	6,224	-0.14	0	0.89	32	-2.19	0	-2.32	0	-1.72	0
250	7,000	-0.08	0	0.83	31	-2.20	0	-2.21	0	-1.62	0
Inhibitor Available:		☐		☑		☐		☐		☐	
Scale Limitation:		Carbonate-limited		Sulfate-limited							

Table No.1 Scale Prediction Results (cont.)

T	P	Halite			Celestite		FeS		$FeCO_3$		
°F	psia	SI	Delta SI	mg/l	SI	mg/l	SI	mg/l	SI	Delta SI	mg/l
77	15	-1.77	0.00	0	-0.79	0		0	-0.53	0.00	0
96	791	-1.80	-0.03	0	-0.82	0		0	-0.44	0.08	0
115	1,567	-1.82	-0.05	0	-0.85	0		0	-0.37	0.16	0
135	2,343	-1.84	-0.07	0	-0.87	0		0	-0.30	0.23	0
154	3,119	-1.86	-0.09	0	-0.88	0		0	-0.24	0.29	0
173	3,895	-1.87	-0.10	0	-0.89	0		0	-0.19	0.34	0
192	4,672	-1.88	-0.11	0	-0.88	0		0	-0.15	0.38	0
212	5,448	-1.89	-0.12	0	-0.87	0		0	-0.11	0.41	0
231	6,224	-1.89	-0.12	0	-0.86	0		0	-0.09	0.44	0
250	7,000	-1.89	-0.12	0	-0.83	0		0	-0.06	0.46	0
Inhibitor Available:			☐		☐		☐		☐		
Scale Limitation:					Sulfate-limited				Iron-limited		

Comments:

At average Haynesville flowback water composition, barite (NORM) scale remains a significant concern. If this flowback water is mixed with high sulfate water, the potential for and quantity of barite scale will continue to increase.
The recommended barite inhibitor and corresponding concentration can be made available upon request.
Calcite scale is carbonate limited, therefore, care should be taken when blending this flowback water with high alkalinity water or high pH water.



Scale Precipitation Risk Matrix

Less than 0 **No Scale**	0 to 1 **Minor Risk**	1 to 2 **Moderate Risk**	2 to 3 **Severe Risk**	Greater than 3 **Extreme Risk**

Table No.1 Scale Prediction Results

T	**P**	**Calcite**		**Barite**		**Gypsum**		**Hemihydrite**		**Anhydrite**	
°F	psia	SI	mg/l	SI	mg/l	SI	mg/l	SI	mg/l	SI	mg/l
77	15	-0.43	0	1.85	36	-2.10	0	-2.84	0	-2.32	0
96	791	-0.41	0	1.67	36	-2.12	0	-2.82	0	-2.27	0
115	1,567	-0.38	0	1.51	35	-2.14	0	-2.79	0	-2.21	0
135	2,343	-0.35	0	1.37	35	-2.16	0	-2.74	0	-2.15	0
154	3,119	-0.32	0	1.25	34	-2.17	0	-2.68	0	-2.07	0
173	3,895	-0.28	0	1.14	34	-2.18	0	-2.60	0	-1.99	0
192	4,672	-0.24	0	1.05	33	-2.19	0	-2.52	0	-1.91	0
212	5,448	-0.19	0	0.96	32	-2.19	0	-2.42	0	-1.81	0
231	6,224	-0.14	0	0.89	32	-2.19	0	-2.32	0	-1.72	0
250	7,000	-0.08	0	0.83	31	-2.20	0	-2.21	0	-1.62	0
Inhibitor Available:		☐		☑		☐		☐		☐	
Scale Limitation:		Carbonate-limited		Sulfate-limited							

Figure 20 Output From Geochemical Simulator (Source M-I SWACO)

Scaling Index	**Risk**
Less than Zero	**No Scale**
0 - 1	**Minor risk**
1 - 2	**Moderate Risk**
2 - 3	**Severe Risk**
>3	**Extreme Risk**

Table ------- Scaling Tendency Risk

Friction Loop Testing

Friction Flow Loops are used for testing the effects of friction reducers by circulating at high rates through different pipe diameters. Friction Loop designs vary based on the application required. Data collected from the friction-loop tests can be used to predict and calculate friction pressures of the test-fluid formulations in downhole conditions.

A friction loop consists of a pump, a pipe of known dimensions; a tank connected to the closed loop, and the tank feeds the pump and collects the effluent from the pipe section during pump operation. The friction loop allows for the measurement of the frictional pressure drop across the pipe section at different flow rates.116

For variable rate tests, a prepared frac fluid is added to the friction loop hopper, and the test fluid is pumped for predetermined periods at incremental rates and %DR (drag reduction) is calculated using the following formula:

$$\%DR = \frac{\Delta PWater - \ \Delta P\ Fluid}{\Delta PWater} \cdot 100$$

Where ΔPWater = differential pressure of water in 3/8 in. (0.952 cm) tubing, psi; ΔPFluid = differential pressure of the fluid in 3/8 in. tubing psi; and %DR = percent drag reduction with respect to water, dimensionless.

Inversion Tests are used to quantify the length of time from polymer addition to evidence of reduced friction. For inversion tests, a selected amount of additive for the fracture treatment is mixed with the source water in a tank, and differential pressure gauges record the ΔP as time elapses.

Figure 21 Friction Loop Tester (Source- Schlumberger)

4.2 Hydraulic Fracturing Water Issues

Water quality issues are commonly addressed at specific points in the fracturing process. At each of these points, there is an opportunity to identify and respond to water issues that may impact on the effectiveness of the fracture treatment or the water management plan. Inevitably, the response to these issues comes down to the cost effectiveness of the frac design and the water management plan.

Pre-Fracture Treatment

During the pre-fracture treatment period, the water samples from the water sourcing options, detailed chemical analysis of water samples from the various surface water, groundwater, produced water, and other sources will be evaluated against the chemical characteristics of the water in the formation that will be fractured. At this point, the primary consideration is the compatibility of the fluids. In addition to the fluid compatibility, the mineralogy of the formation to be fractured will be assessed to determine whether there are water sensitive clays that will require stabilization.

The outcome of the Pre-Frac Assessment is the determination of the need for adjustment of water quality parameters through the application of water conditioners or water treatment technologies. The next step in the frac fluid planning process involves a comparison of the constituents in the “conditioned” source water against the frac additives that are proposed for the frac method selected.

Based on the results of the review of the sensitivities of the proposed frac additives to constituents in the conditioned source water, the conditioners and additives may require adjustment in terms of dosages, and types of additives being proposed for the fracture treatment.

In a worst case scenario, water quality issues identified at the planning stage may require a change in the choice of source water, or a change in the type of fracture treatment being proposed.

Flowback

If the reuse of frac flowback fluids is being considered, then a detailed characterization of the likely chemical constituents in the flowback must be determined. . In addition to the parameters indicated in Table ---- the characterization should include the presence of frac additives that are included in the frac plan. The evaluation of flowback water includes the same parameters implicit in the pre-frac selection of source water for the fracture treatment, plus the additives and conditioners that have been added to the frac fluid including H2S and CO2 and Temperature. This characterization and the characterization of the source water will be used to determine what if any supplemental water conditioning or treatment is needed before the frac flowback water can be reused for hydraulic fracturing purposes. Because the characteristics of flowback fluids changes with time, it is important that the characterization of flowback characteristics include a time series of analyses over the flowback period.

Pre-disposal

Waters which do not meet water quality specifications for hydraulic fracturing and cannot be cost-effectively conditioned or treated; or waters that become surplus to the needs of the hydraulic fracturing program (such as at the end of the fracturing season) may require disposal. Determination of the chemical and physical characteristics of the waste stream must be considered as part of the disposal process. These disposal streams may include treatment wastes, and NORMs bearing sludges for treatment processes. Different wastes and disposal technologies will determine the parameters that need to be quantified as part of this process.

The final step in the process is a compatibility check. All additives that have been identified throughout the process should be checked for incompatibilities and evaluated on the friction loop to confirm performance of the optimized fluid. If flocculation or incompatibilities result at this stage of the process, a different additive should be suggested and retested with the appropriate analytical tool listed earlier. A compatible anionic friction reducer, biocide and surfactant were found to work well with the flowback water (Fig. 6) on the friction loop. The TDS of the flowback water was 13,000 mg/L and the scale software modeling program did not predict the need for a scale inhibitor with this flowback water. The slickwater fluid mixed with flowback water showed moderate to good performance on the friction loop (more than 75% drag reduction at higher rates). It contained 0.4 gpt of an anionic friction reducer, 0.25 gpt of a biocide, and 0.5 gpt of a surfactant.116

The impurities that affect the desired frac fluid properties (as per Question 1) include:

- Chlorides increase demand for friction reducers and scale inhibitors
- Scale potential [f(Ca, Mg, Ba, SO4, CO3…)]
- Suspended solids (>25 microns)
- Bacterial growth (SRB and APB)
- Crude oil effects on friction reducer
- Scale & corrosive materials affect downhole and surface production facilities
- Adding inhibitors affects friction reducers (XTO)

4.2.1 Total Dissolved Solids

In the reservoir, the Total Dissolved Solids (TDS) can reach several hundred thousand mg/L. The precise composition has a complex dependence on mineral digenesis and other types of alteration encountered as formation fluids flow and mix over geological time. Scale begins to form when the state of any natural fluid is disturbed, such that the solubility limit for one or more components is exceeded. Actual mineral solubilities have a more complicated dependence on temperature and pressure. (95)

Total Dissolved Solids is a measure of the combined content of all inorganic and organic substances contained in: molecular, ionized or micro-granular suspended form. Generally the operational definition is that the solids must be small enough to survive filtration through a sieve of 2.0 µm 255. The chemicals may be cations, anions, molecules or agglomerations on the order of one thousand or fewer molecules, so long as a soluble micro-granule is formed. The presence of agglomerations in source water and flowback fluids provides a partial explanation of the apparent effectiveness of flocculation- coagulation treatment methods in reducing the TDS of the fluids.

Total Dissolved Solids is the sum of the solubilized minerals that are present in water (cation, anions, and metals). The total dissolved solids concentration is not an issue, other than the fact that if TDS is high, other solubilized constituents that are objectionable (i.e. chloride, sulfate, calcium, barium, strontium) are also likely to be present in concentrations that are problematic for the frac fluid Therefore, the frac fluid package cannot be designed based on the TDS alone. A detailed chemical analysis of source, flowback and formation fluids is needed also.

There appears to be little currently measurable damage in most gas shales from short term contact with water – fresh or saline. Use of more saline source water would probably be beneficial in the longer term contact areas.40

More saline fluids are also perfectly acceptable to most shale, although some early chemical additives such as friction reducers did not work well above 30,000 mg/L TDS, a problem that has now been resolved. In lower clay content gas-shale rocks, (on the order of less than 30% clays), fresh to moderately saline (~30,000 mg/L) fluids are normally a first choice and higher salinity waters that match the formation water salinity (normally 50,000 to 70,000 mg/L) will likely work, but chemical compatibility and rock sensitivity tests are recommended (Jones, 1964).40

4.2.2 Suspended Solids

Total dissolved solids are differentiated from total suspended solids (TSS) in that the latter cannot pass through a sieve of 2 μm and yet are indefinitely suspended in solution 255A. The term "settleable solids" refers to materials of any size that will not remain suspended or dissolved in a holding tank not subject to motion. Settleable solids may include larger particulate matter of insoluble molecules

Solids entrained in the source water or flowback water can be effectively dealt with through a combination of settlement in storage (whether in tanks or pits) and centrifuging and or filtration. Flocculation then can be used to polish water that has had the big lumps removed through mechanical means.

Suspended solids carried by water may be sand grains from the water-sand, corrosion products such as iron sulfide or iron oxide, free sulfur, or bacterial growths. If allowed to enter the well being hydraulically fractured, these materials will either plug the wells completely or cause increases in injection pressures, or reduce the effectiveness of frac additives. These materials are often present in water in finely divided state and in amounts small enough so that their presence is not easily detected by looking at the water. Yet, when large volumes of water are injected, even small amounts of suspended solids can from an appreciable filter cake or deposit in an injection well bore. Figure 13.1 shows that water carrying only 2 mg/L suspended solids could deposit 7 pounds of solids from 10,000 bbls if the formation were of sufficiently fine pore size to filter this from the water. After 10 days injection, this would amount to 70 pounds, or about 0.22 to 0.48 cubic feet, as shown in Table 13.1. Larger volumes of water and longer injection periods could produce correspondingly greater amounts of solids and eventually fill the well bore if the formation were sufficiently tight. (96)

When particle damage is known to have occurred because of the use of unfiltered or poor quality fluid, cleanup depends on finding a solvent or acid that can either remove the particles or break the structure of the bridges formed in the formation or fracture system. Surfactants, acids and mutual solvents are usually the most beneficial materials. The addition of N2 to provide a high-energy boost may also be beneficial.

The decision of which surfactant or mutual solvent to use should be based on core tests or field response. Including a gas such as N2 or CO@ is based on fluid and solids recovery requirements and wellbore unloading ability. For designing cleanup operations for particulate damage, flowing the well back quickly after treatment helps in the removal of the particles. Lower Pressure formations may require a gas boost. In higher pressure formations, natural flow is usually adequate to unload these solids, especially when a properly designed fluid has been used and the solids are no deeper than the wellbore wall. (SLBRS)

Produced water can contain precipitated solids, sand and silt, carbonates, clays, proppant, corrosion products, and other suspended solids derived from the producing formation and from well bore operations. Quantities can range from insignificant to a solids slurry, which can cause the well or the produced water treatment system to shut down. The solids can influence produced water fate and effects, and fine-grained solids can reduce the removal efficiency of oil/water separators, leading to exceedances of oil and grease limits in discharged produced water Some can form oily sludges in production equipment and require periodic removal and disposal

It is important to determine the amount and chemical composition of suspended solids in the water. This is accomplished by removing the solids by filtration from a given volume of water. The solids can then be analyzed. If the chemical composition of the suspended solids is known, it is frequently possible to take corrective measures that will either eliminate the source of the solids or remove them before injection.

Suspended solids and dispersed oil are the principal quality parameters for injection water. They are responsible for most of the plugging and injection losses that occur. Most of the capital and operating costs in injection water treatment operations are associated with the removal and control of these two components. (98)

Particulates are defined as disperse (free) oil or suspended solids. They are present in separated produced waters. Dispersed oil is usually not found in source waters if the pickup point for the source water is remote from any produced water discharges. Suspended solids are frequently present in source waters, particularly surface sources. Since oil and solids occur together in produced water, they will be lumped together in the first part of this discussion.

This item refers to all suspended solids in frac water, whether the frac water is produced water or sources water. Solids injected into a formation usually reduce the effective pore throat size in the reservoir rock, in essence causing a restriction or barrier to flow. The solids injected into an injection well can cause a filter cake to be built up on the formation face or can enter the rock pore space and cause restrictions in the pores. Whatever the scenario, the outcome is the same: a loss in effective permeability of the injection zone which usually manifests itself as an increase in injection pressure. To determine the potential injectivity loss caused by solids in the injection water, on-site corefloods are usually carried out. This is the preferred approach to determining the effect of solids but if no suitable core material is available, some "rules of thumb" exist for relating the size of suspended solids to the tendency of the water to plug the formation. These are known as the 1/3-1/7 Rules. Briefly stated, these rules are as follows:

1. Particles having a median diameter at least one-third the median pore throat diameter will not invade the formation but will bridge and form an external filter cake

2. Particles having a median diameter between one-third and one-seventh the median pore throat diameter can invade the formation causing an internal filter cake which will cause plugging and permeability decline
3. Particles having a median diameter smaller than one-seventh the median pore throat diameter will pass through the porous medium

4.2.3 Petroleum Hydrocarbons and Organics

Petroleum hydrocarbons are commonly considered in two forms; dispersed oil, and solubilized hydrocarbons**.**

Dispersed Oil

Dispersed oil in injection water is detrimental for three reasons. First, bacteria utilize certain components in the crude oil as food. Second, oil is strongly adsorbed on iron sulfides and other scale deposits, which makes it difficult to remove these deposits with acid treatments. Third, oil reduces the relative permeability to water in the well. As relative permeability to water decreases, it requires more pressure to inject the same amount of water. Dispersed oil in injection water can be reduced by proper use of a demulsifier and by better design of the water system.

Factors that affect the concentration of dispersed oil in produced water include oil density, interfacial tension between oil and water phases, type and efficiency of chemical treatment, and type, size, and efficiency of the physical separation equipment (Ali et al. 1999). Oil and Grease. No problem at levels up to 200 mg/L (by unanimous agreement)

Soluble organics and treatment chemicals in produced water decrease the interfacial tension between oil and water. Also, because precipitated droplets are often 4-6 microns in size, and current treatment systems typically cannot remove droplets smaller than 10 microns, the small droplets can interfere with water processing operations

The presence of oil in produced water or flowback water has not been a major problem gas in dry shale gas plays. However, in the liquids rich plays, the need to manage oil/water flowback is inherent.

Dissolved or Soluble Organic Components

Hydrocarbons that occur naturally in produced water include organic acids, polycyclic aromatic hydrocarbons (PAHs), phenols, and volatiles. Soluble organics are not easily removed from produced water.

Generally, the concentration of organic compounds in produced water increases as the molecular weight of the compound decreases. The lighter weight compounds (BTEX and naphthalene) are less influenced by the efficiency of the oil/water separation process than the higher molecular weight PAHs and are not measured by the oil and grease analytical method. Volatile hydrocarbons can occur naturally in produced water. Concentrations of these compounds are usually higher in produced water from gas-condensate-producing platforms than in produced water from oil-producing platforms.

Organic components that are very soluble in produced water consist of low molecular weight (C2-C5) carboxylic acids (fatty acids), ketones, and alcohols. They include acetic and propionic acid, acetone, and methanol. In some produced waters, the concentration of these components is greater than 5,000 mg/L. Due to their high solubility, the organic solvent used in oil and grease analysis extracts virtually none of them, and therefore, despite their large concentrations in produced water, they do not contribute significantly to the oil and grease measurements

4.2.4 Scaling and Tendency

Scales can form when ions in a supersaturated produced water react to form precipitates when pressures and temperatures are decreased during production.. They can clog flow lines, form oily sludges that must be removed, and form emulsions that are difficult to break

Most waters have the potential to form mineral scale deposits. These deposits vary in composition due to differing compositions of the waters. Usually, at least one form of scale is encountered, resulting from the water produced in association with the petroleum. The precipitated insoluble compounds are undesirable because they can reduce the permeability of porous petroleum producing rock formation, plug input wells and production wells, and cause scale formation in injection equipment, such as water pumps and lines.

Scale can be detrimental to the production of the well. As the well is fractured, water dissolves minerals in the shale, and if the conditions are right, scale can form. If produced water is used then the problem of scale is exacerbated. The dissolved salts can potentially cause scale deposition. Many times the flowback fluid is diluted with fresh water to achieve the desired level of salts such as barium (Ba) and strontium (Sr). Table 2 shows a frac fluid water analysis and Figure 5 shows the resulting amount of Ba and Sr found in flowback waters of the same well. Clearly, this well has potential for severe scaling problems

The amount of scale that will precipitate out of water is dependent on temperature, pressure, water incompatibility and mineral content. Because these variables often fluctuate, predicting and controlling the type and amount of scale inhibitor to use can be difficult requiring constant operations adjustments to account for these fluctuating parameters

Before a well is drilled and completed, the fluids in the formation are in equilibrium with the surroundings. However, when the well is drilled and starts to flow, the equilibrium is disturbed, and solids may start to precipitate. Inorganic deposits are called “scales” 95

Figure 23 Scale Deposits in Pipe (Source ---- -----)

Scaling Process and Types of Scaling Problems

Some of the more common ions that frequently occur in oilfield waters and that cause precipitation in incompatible waters are: $Ca^{+2,}$ Sr^{+2}, Ba^{+2}, Fe^{+2}, HCO_3^{-1}, and SO_4^{-2}.

Common reactions are as follows:

$CaCl_2 + Na_2SO_4 \rightarrow 2NaCl + CaSO_4 \downarrow$
$CaCl_2 + MgSO_4 \rightarrow MgCl_2 + CaSO_4 \downarrow$
$Ca(HCO_3)_2 \rightarrow CO_2 + H_2O + CaCO_3 \downarrow$
$CaCl_2 + 2NaHCO_3 \rightarrow 2NaCl + CO_2 + H_2O + CaCO_3 \downarrow$
$SrCl_2 + NaSO_4 \rightarrow 2NaCl + SrSO_4 \downarrow$
$SrCl_2 + MgSO_4 \rightarrow MgCl_2 + SrSO_4 \downarrow$
$BaCl_2 + NaSO_4 \rightarrow 2NaCl + BaSO_4 \downarrow$
$BaCl_2 + MgSO_4 \rightarrow MgCl_2 + BaSO_4 \downarrow$
$Fe + H_2S \rightarrow H_2 + FeS \downarrow$

$2FeO_3 + 6H_2S \rightarrow 6H_2O + 2Fe_2S_3 \downarrow$

There are three types of scales that occur most frequently in oilfield waters. They are: calcium carbonate ($CaCO_3$), calcium sulfate ($CaSO_4.2H_2O$), and barium sulfate ($BaSO_4$). Strontium is frequently co-precipitated with barium sulfate.

4.2.4.2 Carbonate Scale

Calcium carbonate is by far the most common form of scale encountered and occurs in fresh water as well as oilfield brines.. Calcium carbonate scale can result from reactions between calcium ions (Ca++) and bicarbonate ions (HCO_3-), carbonate ions (CO_3--), or indirectly from carbon dioxide (CO_3--). The following chemical equations show the possible reactions just described
Insert from page 69and 70

Calcium carbonate or calcite can form from mixing two incompatible waters or from a single unstable water. Calcium carbonate ($CaCO_3$) is present in water solution as calcium carbonate [$Ca(HCO_3)_2$]. Its solubility is dependent upon ionic strength, calcium ion concentration, bicarbonate ion concentration, pressure of carbon dioxide, and temperature. A change in carbon dioxide pressure or temperature can cause $CaCO_3$ to precipitate. If the solubility product is exceeded, solid $CaCO_3$ will deposit. 96

When two waters are mixed, the concentration of dissolved ions becomes the average concentration of the respective ions in the two waters. If mixing the waters produces a concentration of calcium carbonate in excess of the amount permissible on the basis of the solubility product, the water is said to be supersaturated. This condition is adjusted to saturation by precipitation of the excess amount of calcium carbonate. This precipitation may occur rapidly if the excess concentration is large, or require a waiting period if the excess concentration is small. This waiting period, called an induction period represents the time necessary for calcium carbonate crystal nuclei to form. Once formed, other calcium carbonate molecules adhere to the nuclei to form crystal and finally precipitate as a solid. The more supersaturated the water is with calcium carbonate, the shorter the induction period. At the end of the induction period, solid calcium carbonate forms and settles out of the water. Its concentration in solution declines, as shown by the curves. If solid calcium carbonate is present, there is no induction period for the formation of crystal nuclei. 96

Calcium Carbonate Scale is generally predicted with saturation indices [3,7] that compare the amount of scaling constituents in solution to the solubility. The original Langliers[8] saturation index was proposed for corrosion control in municipal water distribution systems. Numerous corrections for temperature, pressure and ionic strength have been proposed for the Langlier index, and most of the corrections have been in the form of either data tables or plots and figures. In addition to the standard difficulties with sampling and analyses, all the above indices require measurement of the brine pH. In gas and oil wells, realistic pH measurements are rarely feasible. In the original version of the $CaCO_3$ saturation indices the effects of the changes in the fugacity of CO_2 and the partitioning of CO_2 were ignored as were the effects of weak acids on the alkalinity. All of these effects have been included in the up dated version113

Typically, an increase in temperature increases the water solubility of a mineral. More ions are dissolved at higher temperature. Similarly, decreasing pressure tends to decrease solubility's and, as a rule of thumb, the solubility of most minerals decreases by a factor of two for every 7000 psi (48 mPa) decrease in pressure. Not all minerals conform to the typical temperature trend (e.g. CaCO3 shows the inverse trend of increasing water solubility with decreasing temperature). The solubility of barium sulfate increases by a factor of two in the temperature range 25 to 100C (77 to 212F) and then decreases by about the same magnitude as temperatures approach 200 C (392F). This trend is influenced by the background brine salinity. Additional trends are described in Sec 2,2,3 95

An additional complexity is the solubility of carbonate minerals in the presence of additional acid gases such as hydrogen sulfide (H_2S). Carbonate solubility increases as fluid acidity increases, and CO_2 or H_2S at a high pressure supplies significant acidity. Consequently, formation waters, in contact with both carbonate rocks and acid gases can be rich in dissolved carbonate. 95

Improvements to the original saturation index[9] for $CaCO_3$ include algorithms to calculate the partitioning or changing mole fraction of CO_2 with varying temperature and pressure conditions, the inclusion of both oil and CH_4. Some factors affecting the solubility of calcium carbonate in an aqueous solution are:

- Temperature
- Partial Pressure of CO in the water
- pH
- Pressure Drops
- Salinity, and
- Concentration of calcium, bicarbonate, and carbonate ions

Calcium carbonate has an inverse solubility characteristic in water. As the temperature of the water increases, the solubility of calcium carbonate in solution decreases, depositing $CaCO_3$ scale. The effect of increased temperature will result in dissolved CO_2 being liberated, or the bicarbonate ion is further ionized to CO_3.

4.2.4.2 Sulfate Scale

Three different calcium sulfates occur, each with different amounts of water of hydration as follows: 95

- Anhydrite ($CaSO_4$)
- Hemihydrate ($CaSO_4 \cdot 1/2H_2O$)
- Gypsum ($CaSO_4 \cdot 2H_2O$)

Calcium sulfate

CaSO4 poses a unique problem for the salts under consideration because it occurs with various regularity as one of three different phases. Gypsum, the most common scale former[3], occurs at relatively low temperatures. At higher temperatures [above about 100°C (212°F)], the stable phase predicted is anhydrite ($CaSO_4$). However, hemihydrates have been known to form at about 212 to 250°F, especially in non-turbulent systems and in high-ionic-strength brines. Field or lab simulations should be conducted to gain insight into the kinetically preferred phase.113

Below 176°F, the most likely phase will be gypsum in brine solutions. Between 176 and 250°F, any of the three phases may form, with qypsum being more likely at the low end and anhydrite at the high end. However, in this temperature range, hemihydrates is commonly found in non-turbulent system with high ionic strength, which means that a scaling problem may not be as severe as one might think if prediction equations for the less soluble anhydrite were used. Above 250°F, the produced scale will almost certainly be anhydrire.113

Calcium sulfate scale in the form of gypsum ($CaSO.2H_20$) is the second most prevalent type of mineral scale in petroleum related aqueous systems. The chemical reaction that results in the Formation of calcium sulfate scale is as follows:

$$Ca^{++} + SO_4^{--} \rightarrow CaSO_4$$

The solubility of gypsum or anhydrite is influenced by:

1. Temperature,
2. Salts
3. Pressure, and
4. Concentration of Scaling species

Gypsum solubility increases slightly as the temperature increases over range 0 to 40° C in distilled water. As the temperature increases from 40 to 100°C, the solubility of gypsum decreases by about 6 mg/L as reported by Stiff and Davis (5). Data presented by Ostroff and Metler (6) show similar increase and decrease solubility trends as Stiff and Davis. Ostroff and Metler report solubility of gypsum to be 1900± mg/L at 100°C at 100 kPa (1 bar) pressure. This data shows that gypsum may increase somewhat with temperature where calcium carbonate solubility decreases.

The solubility of gypsum increases from approximately 2000 to 7000 mg/L by increasing the concentration of sodium chloride from 0 to 120,000 mg/L in solution at 32°C. As the sodium chloride concentration increases above 120,000 mg/L the gypsum solubility begins to decrease at 101.3 kPa (1 atm) pressure. Similar trends in solubility were also observed for anhydrite ($CaSO_4$) (7) The addition of $MgCl_2$ to the sodium chloride brines in small quantities increases the solubility of gypsum up to approximately 15,000 mg/L, but above this sodium chloride concentration, gypsum solubility decreases.

As pressure increases, the solubility of calcium sulfate increases in aqueous solutions. Pressure increases the solubility of anhydride dramatically at 100°C, but this increase in solubility is essentially offset when the temperature is increased to 275°C.

Gypsum solubility is much greater than calcium carbonate. As a result, a water containing sulfate and carbonate ions in the presence of calcium ions, calcium carbonate will precipitate first.

Calcium sulfate occurs in three forms: (a) gypsum, $CaSO_4 \cdot 2H_2O$; (b) anhydrite, $CaSO_4$; and (c) Plaster of Paris $CaSO_4 \cdot ½H_2O$. Temperature of the system dictates which crystal form the calcium sulfate will take.
Calcium sulfate scales are not soluble in common mineral acids at ambient temperature of 25°C. Gypsum and anhydrite can be disintegrated in 8 to 16 hours at temperatures up to about 80°C in the presence of certain proprietary chemical. This type of chemical has been used successfully in West Texas to remove

gypsum scale from the tubing wall downhole in pumping oil wells. After the scale disintegrates, it is pumped from the well with the produced fluids

Barium Sulfate

BaS04 scale occurs during gas and oil production in many places throughout the world and in the Unites States including the Michigan Basin the Gulf Coast, Oklahoma and Alaska. It is formed due to the inherent chemistry of the produced brine and the production parameters, by the commingling of waters from different produced zones in the same well and by the mixing of incompatible waters. The low solubility I-4 of BaS04 is demonstrated by the extreme likelihood that the scale will form when water containing even relatively low concentrations of sulfate is mixed with water containing relatively low concentrations of barium.126

During the production process, both pressure decreases and the lowering of temperature as the fluids are produced contribute to the likelihood that $BaS0_4$ will precipitate. Unlike $CaC0_3$ whose solubility increases with decreases in temperature, the solubility of $BaS0_4$ decreases significantly as the temperature decreases.3 As a rule of thumb, $BaS0_4$ is about half as soluble at 77 F (25 C) as it is at 203 F (95 *C),* regardless of the salt concentration.5Further, the solubility is about half as much at atmospheric pressure as it is at 6250 psi.3 126

Barium sulfate is less prevalent than the two types of calcium scale previously discussed. However, like the calcium scales, barium sulfate scale is not isolated to any one geographic region.

This form of mineral scale follows the normal solubility characteristics in an aqueous solution, that is, the warmer the solution, the more soluble the barium sulfate becomes. Barium sulfate (BaSO4) is the least soluble of these three types of mineral scale in an aqueous solution. Barium sulfate has a solubility of only 2.3 mg/L at 25°C and 3.9 mg/L at 100°C (212°F) in distilled water at 101.3 kPa (1 atm) (8). It solubility increases with increasing salinity. Actual solubility data obtained by Templeton indicated the solubility of $BaSO_4$ increased by a factor of 2.6 with increased temperature from 25 to 65°C (77 to 149°F) at 55,000 mg/L sodium chloride(9)

Barium sulfate scale is the most critical type of scale deposit in surface and downhole equipment in oil, gas, or water supply wells, because it is not soluble in hydrochloric acid. Dissolution of a metal sulfate requires sequestration of the scaling metal ion, thus dissolution of sulfate scale requires the use of chelation chemistry. Strontium sulfate, frequently deposited with barium sulfate has a higher solubility (114 mg/L) in distilled water than barium sulfate (10)

As long as the salts are at equilibrium, and are in solution, they do not present a problem. However, if a water containing sulfate is mixed with a water containing barium, a chemical reaction will occur, resulting in the precipitation of barium sulfate.

The most effective method of preventing $BaSO_4$ formation is to avoid mixing incompatible waters, although this may not always be an option. When mixing of incompatible waters is likely to result in $BaSO_4$ formation, the use of scale control chemicals is indicated. Commonly used chemicals include chelating or sequestering agents.

4.2.4.3 Iron Scale

An iron-control compound is necessary that chemically maintains the iron in formation fluids in the reduced-valence state and prevents both precipitation and re-precipitation of iron compounds and minerals. The iron control agent should inhibit the iron from converting to insoluble particulates that can damage fracture conductivity and reduce the production potential of the formation .1 The compound must provide adequate iron control at a low dosage rate without lowering the system pH and, thus reducing FR performance. The chemical additive should work synergistically with scale-control additives both in preventing precipitation of difficult post–fracture treatment geochemical species such as siderite (which can form in hydraulic fractures), and in enhancing performance of FR chemistry

- Iron Carbonate – $FeCO_3$
- Iron Scales (Soluble in HCL, THPS)
- Iron Sulfides
- Iron Carbonate
- Iron oxides

Traditional iron-reducing and chelating agents consist of acidic chemicals such as citric acid, acetic acid and ethylenediaminetetraacetic acid (EDTA), which keep the iron in formation in a soluble or reduced form (ferrous iron) through pH reduction and chelation chemistry. This method of iron control performs inconsistently, particularly when the formation acts to neutralize the acid and the acids capability to control iron and other metals. Acids and chelants also reduce frac fluid pH and, thus can adversely affect FR and other chemical performance. Alternative iron control additives should be sought that avoid these drawbacks, thus allowing optimal performance of the FR, scale control agents and biocide.110

Figure 1 illustrates the need for integrating iron control into the frac fluid, even though the initial water used in the fracture treatment may contain no iron. Upon contact with the downhole environments, iron and other metals are leached and/or released into the frac flowback water. If not controlled, free iron may be available to form a number of iron species that can be damaging to gas production and potentially to the unloading of the frac fluid during well cleanup. For example, geochemical simulation has shown that siderite (FeCO3) can be a problematic iron precipitate.110

4.2.4.4 Prediction of Scaling Tendency

Prediction of scaling tendencies can be accomplished if the composition of the water downhole is known with a high degree of accuracy. 95

Once the biological activity and biocide recommendation has been accomplished, a scale prediction analysis should be performed on the flowback water. There are several ways to indirectly predict the amount of scale potential of water based on its composition. The Langelier saturation index (LSI) and Stiff-Davis index (SI) are the most commonly used indicators to predict water scale potential LSI only considers the thermodynamic driving force for calcium carbonate scale formation and growth based on the pH of the given water sample. The SI value relies more heavily on the pH of saturation than LSI method to determine the potential for scale making it more useful in waters that have a higher salt concentration or higher TDS (Stiff and Davis, 1952). However, the SI model has the same shortcomings as the LSI with respect to its inability to predict other types of scale and the limitation to predict scale at reservoir conditions (e.g. temperature and pressure effects).

A more comprehensive prediction method is the Gibb's Free Energy minimization method because it incorporates reservoir conditions into the modeling process. This approach can predict additional scales (e.g. sulfates and other divalent carbonates) and can be accomplished using a software modeling program (Bartko et al., 1998). Table 3 reports the scaling tendency of the flowback water composition listed for the Piceance water in Table 1 using a software modeling program based on the Gibb's Free Energy minimization method116

Predicting potential scaling problems can be difficult, and numerous saturation indices and computer algorithms have been developed to determine if, when, and where scaling will occur. The Langlier, Stiff-Davis and Oddo-Tompson saturation indices are all widely used in the oil field. 113

Oddo-Tompson suggest an updated version for barium, strontium and calcium sulfate scale formation. The calcium Carbonate saturation index does not require a measured pH and can accommodate the presence of weak acids, such as H_2S and weak organic acids. The sulfate prediction methods (for gypsum, hemihydrates, and anhydrite) are easy to use, reliable, and designed for field use by an operator who may be untrained in chemistry. The prediction methods can be applied to any production well where calcium carbonate, calcium sulfate, strontium sulfate, or barium sulfate scale occurs113

The water analysis data are used to compute the scaling index for calcium carbonate, calcium sulfate, and barium sulfate scale. The calcium carbonate scaling index for oilfield water was developed by Stiff and Davis. The scaling index can be calculated for calcium sulfate using the Skillman Method (11). The barium sulfate scaling index can be calculated from solubility product constant for barium sulfate that varies with temperature, salinity, barium, and sulfate ion concentrations. This method gives only approximate results, since the effects of ionic species other than chloride, barium and sulfate are neglected.

It is particularly useful to incorporate the necessary data from each scale index computation into a computer program that covers a temperature range of 15.6 to 126.7°C (60 to 250°F) for each of the forms of mineral scale. This allows the investigator to enter the water analysis data into the computer and receive the scale indexes computed over a wide range that covers most operating temperatures.

A problem frequently encountered in water flooding operations is mixing of waters from different sources. The scale index may indicate each water source is free of scaling tendencies. Yet when the waters are mixed, serious scale deposition problems occur. This problem is most critical when waters containing sulfate ions, are mixed with waters containing barium or calcium. Another problem of this type occurs when surface water from a lake is mixed with water from the producing zone. The surface water usually has a higher pH than formation water. It is common for the surface water to contain large concentrations of bicarbonate alkalinity. Calcium carbonate scale results when the formation water containing high concentrations of calcium ions is mixed with surface water of higher pH and higher concentrations of bicarbonate ions.

In some systems, several waters are commingled simply to be injected in a common disposal well. An analysis of the mixed water must be performed in order to compute a scale index prior to startup. Id this cannot be accomplished, the investigator can calculate an analysis of the mixed waters by knowing the percent by volume of each water type in the system having and accurate analysis of each water type. A scale index can be calculated on the hypothetical mixture of water types Using calculated compositions is particularly useful when more than two waters are mixed in widely varying ratios.

Once the scale indexes are computed or scale analysis is completed, a comprehensive scale inhibitor program can be initiated if scale deposition is indicated. The type of scale inhibitor used in the system is based on the specific type of scale and the treating technique to be used.

4.2.4.6 Corrosion

Dissolved gases frequently found in injection waters are oxygen, carbon dioxide and hydrogen sulfide. All three enhance corrosion problems. Oxygen can be removed by an oxygen scavenger, such as cobalt-catalyzed sodium bisulfite. Proper gas blanketing of water tanks also minimizes oxygen entry. Hydrogen sulfide can be oxidized to sulfur with oxygen or sulfur dioxide, or to sulfate with hypochlorite. Removal of carbon dioxide from the water can be achieved by stripping with an inert gas, such as nitrogen, but the cost generally exceeds the benefit.

Corrosion control will consider reactions between the waters and the metal structures involved in the production/treating/injection system. Primary concern will be on how corrosion reactions affect water quality and injection rates. The corrosion reactions and their effect upon the structural materials of the system will receive less emphasis.98 The chemical corrosivity of produced fluids is most commonly associated with the presence of hydrogen sulfide, carbon dioxide, or oxygen. Chemical corrosion is one area where the application of technology, through the use of corrosion resistant metallurgy, can reduce the use, hence the potential discharge, of chemicals. Well designed equipment coupled with a sound chemical treatment program can reduce chemical consumption by as much as 90% while significantly improving the operational safety and longevity of a facility. That in turn reduces the risk of a catastrophic failure that can result in a loss of resources (oil and gas), human injury, or spills.

Carbon dioxide is the most common corrodent, while hydrogen sulfide poses the most significant risk to human health and the environment. Oxygen is not typically found in unaltered produced fluids. Oxygen is usually introduced as the produced fluids are treated. Most corrosion inhibitors work by adsorbing onto exposed metal surfaces.

Corrosion inhibitors are very complex compounds that can be sorted into four generic groups: amine imidazolines, amines and amine salts, quaternary ammonium salts, and nitrogen heterocyclics. Oil soluble corrosion inhibitors are most commonly used since they are usually the most effective at providing a stable, durable film. The concentration of active ingredient in bulk corrosion inhibitors is usually 30 - 40%. The remaining material (inert ingredients) is usually a hydrocarbon based solvent like heavy aromatic naphtha. When improved water solubility is required, dispersants or surfactants may be added, or water soluble corrosion inhibitors such as quaternary amines can be used. Oil soluble inhibitors will follow the oil stream to the refinery and water-soluble inhibitors will stay with the water phase. Selection of a particular corrosion inhibitor is usually made based on the type of corrodent, the type of production, prior experience, and laboratory or field testing.

Corrosion caused by oxygen is controlled by chemical reaction rather than adsorption. Oxygen inhibitors (scavengers) are usually some form of sulfite, with ammonium bisulfite the most common form being used. These compounds and their reaction products (sulfates) are highly water soluble and will be discharged with the produced water. Far more frequently, oxygen scavengers are used to treat injection water.

There are three standard treatment methods used for corrosion inhibition, continuous treatment, displacement treatment, and squeeze treatment. Continuous treatment involves continuous injection of corrosion inhibitor into the production stream. Treatment concentrations normally range between 5 - 15 mg/L for liquid production depending on the concentration of the corrodent. Displacement treatments involve filling the production tubing with corrosion inhibitor, allowing it to stay in contact with the tubing for a period of time (up to several hours) and then producing the inhibitor back through the production equipment. Squeeze treatments are similar to displacement treatments except that the corrosion inhibitor is pumped into the formation. For both displacement and squeeze treatments, the return concentrations on inhibitor may initially be several thousand mg/L. This initial slug is quickly produced and concentrations return below 100 mg/l. These two treatment methods are usually used in wells with lower production rates.

The concentration of an oil soluble corrosion inhibitor in discharged produced water will be quite low. The inhibitor that remains in the produced water would make up a portion of the hydrocarbons measured in the dispersed oil and grease analysis. As an example, if produced water with 40 mg/L oil and grease comes from a production stream containing 500 mg/L corrosion inhibitor in the oil, the concentration of corrosion inhibitor in the discharged produced water is 0.020 mg/Lat the point of discharge.27

4.2.4.7 Resolution of Scaling Issues

The chemical treatment of water associated with oil and gas includes the application of scale inhibitors, such as phosphonates, to help maintain the integrity of equipment that is used during the drilling and production phases.

Prevention is your best option!

Calcium, Magnesium, Carbonate. These parameters can be managed collectively through the use of scaling models (eg Oddo-Tompson Model)

Scale inhibitors

Three types of scale or geochemical precipitates are of concern to shale gas producers: carbonate, sulfate, and iron-based depositions. In many shale completions, the frac flowback water contains significant concentrations of ions that can impair production. Unmanaged, this geochemical environment can spawn precipitates within the created fracture network and cause scale to accumulate in perforations, piping and surface equipment. Preventing such accumulations requires analysis of the flowback water to identify and evaluate geochemical deposit- producing potential. An effective treatment method is twofold:

1. Based on the geochemistry analysis, apply an appropriate select ion and dose of scale control that is designed not to negatively affect the fluid pH and resultant friction reducer (FR) performance.
2. When necessary, conduct remediation of the water for certain problem species. The ideal treatment should address all scale situations predicted during post-fracture treatment flowback; conform to National Pollutant Discharge Elimination System (NPDES) standards; and pass appropriate aquatic toxicity standards if surface disposal is required.110

Most available scale inhibitors are phosphonates and organophosphonates which are anionic. This can create incompatibilities with some additives such as friction reducers and clay stabilizers. Some novel solutions to this problem have been tried in recent history. The organophosphonates can be reacted with calcium chloride to render them insoluble in order to successfully pump from the surface to the formation. The insoluble material can be made into the proppant matrix541

The accumulation of scale can reduce flow rates or for instance, lower efficiencies in heat exchangers. Scale inhibiting chemicals can be applied up or down hole of the wellhead and are in general, classified into four categories: Oil-Miscible, Totally Water Free, Emulsified and Solid. Depending on the mineral content present in the water, duration of the project and operation needs, the chemical(s) can be applied continuously or in scale squeeze applications.55

Available scale inhibiting chemicals are effective at preventing mineral deposits caused by compounds such as calcium carbonate, strontium sulfate, calcium sulfate, barium sulfate, iron sulfide and iron oxide. Selection of the appropriate scale inhibitor and dose will include water testing to identify the types and concentrations of scale forming compounds present in the water. For example, phosphonate-based scale inhibitors are effective at preventing carbonate and sulfate scales whereas, polymer-base scale inhibitors are effective for sulfate/carbonate scales of barium, strontium and calcium.55

Because the amount and type of scale that can precipitate out of water is dependent on many factors, a cost associated with application is variable. However, the volume of application is low relative to the overall composition of water for fracture treatment. For example, approximately 0.08% or 0.043% of fracture water in the Marcellus Basin and Fayetteville respectively, is composed of scale inhibiting chemicals.55

4.2.5 Biological Activity

In any water handling system it is advisable to guard against the growth of microorganisms. Conditions for their growth and methods of controlling it are discussed in Chapter 6. Water selected for injection should be examined microbiologically to determine the type and number of bacteria present. If the examination indicates that microorganisms could present a problem, the system should be designed to minimize such problems. “Dead” or stagnant areas where microorganisms could colonize should be eliminated. Where this is not practical, provisions should be made to allow periodic flushing of the dead areas. Lines should be sized so that velocities are sufficient to avoid buildup of solids in the lines. Provisions should be made to add a suitable bactericide to the water if required. Periodic ally during the life of the system , water samples should be examined microbiologically to determine the effectiveness of any bactericide added or to tell whether the water is still relatively free of microbial growth.96

The nature of the recovered fluid provides an ideal media for bacteria to grow under certain conditions, which can lead to a change in the expected fluid properties. Therefore, preservatives are used for long-term storage. The preservation is effectively accomplished using conventional biocides. Because fluid volumes are large and generally stored in large tanks on location, it is best to treat the fluid as it is transferred into the storage tanks. This is done with an in-line additive system. The additive system is composed of a flow meter and injector to treat the fluid with a liquid biocide as shown in **Fig. 3**. Another system that uses a solid biocide to treat the fluid on the way to the storage tank is shown in **Figs. 4 and 5**. Simple chemical, on-site analyses were performed to confirm biocide concentrations.125

Bacterial and microbiological effects will consider such items as plugging of wells and fouling of surfaces by bacteria and biomass, microbial production of toxic and corrosive gases such as hydrogen sulfide and carbon dioxide, and microbial reservoir souring.98

The next step in the process is to determine which biocide is best for the expected biological activity in the flowback water. This step in the process should be iterative. For example, the biocide that is recommended based on killing action in the flowback water is not compatible with other additives expected to be used in the fracturing fluid (e.g. friction reducer), a different biocide should be considered. If the biocide selected is the only chemical available in a region for use, then a different additive (e.g. friction reducer) should be selected that is compatible with the biocide to ensure that the efficacy of the biocide is preserved in the fluid.116

Outside of its container, the biocide should exhibit a short life and have known breakdown pathways.125
Biocides in general are the most environmentally problematic constituent found in the fracturing fluid system and therefore must be carefully considered and thoroughly evaluated.125

Microbial Population

Three classes of *microorganisms* found in water used in the oil field are algae, fungi, and bacteria, with bacteria representing the most serious problem in fracturing treatments. They range in size from 0.2 to 10 μm.

The number and type of bacteria present in injection water affect the quality of the water. Bacteria can contribute to corrosion or produce plugging. Desulfovibrio or sulfate reducing bacteria utilized oxygen in sulfate ion to oxidize organic compounds. Corrosive hydrogen sulfide is produced in the process. Increases in sulfide content of water within the water handling system are caused by sulfate reducers. Desulfovibro are nearly always present, but, when conditions are not right for their growth, they are not a serious problem.

The total bacterial count is indicative of the number of all varieties of bacteria in the water. Large growths of bacteria can result in colonies of the microorganisms plugging the injection well or otherwise fouling equipment.

The reuse of fracture water is of special concern due to the potential amount of bacteria is in the produced water. Again these bacteria can attack the polymer and reduce its effectiveness, and a registered biocide is recommended in the frac tank.41

Sulfate–reducing and iron-metabolizing microbes play an important role in the formation of geochemical precipitates and must therefore be considered in any geochemical discussion. Control measures must be followed to negate the effects of downhole “extremophile” sulfate-reducing microbes and conventional spore-forming bacteria. A 20% active, liquid brominated propionamide, commonly referred to as DBNPA is an effective choice for biochemical control. DBNPA works in the presence of hydrocarbons, begins to kill instantly, and will decontaminate a system within 1 hour. One benefit of DBNPA is its short half-life in the environment. DBNPA is considered one of the safest biocides when used or spilled; it breaks down into the innocuous components bromine, nitrogen, and water. The non-foaming biocide is effective against both aerobic and anaerobic microorganisms. It is water soluble, easy to mix and dilute, and registered with the

US Environmental Protection Agency as non-persistent. DBNPA is also not affected by hard water or salts.110

Control of Microorganisms

The growth of organisms is sometimes a problem in water handling systems. Uncontrolled growth of slime forming bacteria can plug injection wells and clog equipment. Sulfate reducing bacteria contribute to corrosion and can cause the formation of iron sulfide in the water. Iron bacteria Crenothrix and Gallionella precipitate iron from water, forming a red scum that is a potential plugging material. Bacteria can clog equipment and pipelines. They can also form difficult-to-break emulsions and hydrogen sulfide, which can be corrosive. Bacteria are controlled using biocide chemicals and removed by filtration.15

Biocides are used in slickwater fracturing applications to prevent bacteria growth and may alter the physical characteristics of fluids such as viscosity by degrading the polymer. The degradation of the polymer can be caused by free radicals usually from oxygen. Therefore potentially there is a compatibility issue between oxygen scavenger or biocide. Compatibility of biocide with other chemicals such as corrosion inhibitors, scale inhibitors, polymers, and other well treatment fluids is critical. Some attributes necessary for a biocide are safety, cost effectiveness, compatibility with fluids or other additives, and handling. In the well the bacteria can cause other problems. These include but are not limited to producing acid (acid producing bacteria, APB), sulfate reducing bacteria (SRB), and production of carbon dioxide and oxygen.

Common biocides are quaternary amines, glutaraldehyde (glut) and tetra-kis-hydroxylmethylphosphonium sulfate (THPS). A relative new comer to the oilfield applications is tetrahydro- 3,5-dimethyl-1,3,5-thiadiazinane-2-thione; this biocide (Thione) has been shown that it does not interfere with friction reducer, and is extremely effective in killing APB bacteria , and is a broad spectrum biocide3. It is also a longer term kill biocide that is compatible with oxygen scavengers. Even if a biocide is effective in killing, testing should be done to determine compatibility of biocide with the friction reducer. Figure 3 illustrates the effect of 500mg/L biocides on a post inversion viscosity at the samples have been heated at 180°F and then measured at 77 °F. As seen in Figure 3, the polymer viscosity degrades with heat over time. After four hours at 180 °F, the control (no biocide), aqueous Thione, and emulsified Thione show a slight decrease in viscosity, whereas the glut maintains its viscosity. This can de deleterious in flowback of the polymer.

Biocide effectiveness is the main concern with this parameter. Most Biocides work best below pH 7, though many biocides will still work between pH 7 and pH 8. Highly alkaline frac waters (above pH 8) should be avoided

4.2.6 Water Sensitive Formations

The water sensitivity of the reservoir rock has traditionally prompted a division between water-base fluids and oil-base fluids. However, this consideration is often the cause of inappropriate fluid selection and less-than-optimum fracturing treatments. Essentially, if the reservoir is mildly-to-moderately water sensitive, the selection process outlined for a gas well should be followed. While the use of oil-base fluids in oil wells is often suggested, these fracturing fluids deserve certain additional considerations. The cost of pumping an oil-base fluid is usually much greater than the cost of pumping a water-base fluid because of the cost of the oil. Oil-base fluids, because of their inordinately high friction pressure losses, typically exhibit high hydraulic horsepower requirements. Safety considerations must also be addressed because of the flammability of the oil. Any problem leading to fluid leakage has the potential for extreme fire hazard.

Certain reservoir rocks are subject to permeability damage when infiltrated by fresh water. This damage is caused by swelling of indigenous clays that constrict pores, and the dispersion of indigenous non-swelling particles during fluid flow. Many water injection projects have suffered reduced efficiency because reservoir rock was plugged by clay which swelled when contacted with water. For this reason, when extraneous waters are used, it is advisable to determine the composition and clay content of the reservoir rock before selecting a water source. 96

When contacted with water, some clays swell as a result of water adsorption or exchange of basic radicals from foreign water. Montmorillinites, mixed layer clays, and some illites are the most common swelling clays. It is possible for water to penetrate between the plates of montmorillinite and cause swelling sufficient to separate the plates and disperses the clay particles. The degree of swelling when reservoir clay minerals contact water depends upon the type of clay and the amount of water held by the mineral since sedimentary deposition. Clays which have held the maximum amount of water will not appreciably increase in volume. Clays which are capable of absorbing additional water will increase in volume when contacted by water.96

Swelling of clays is also related to salinity of water. Clays susceptible to swelling are more sensitive to fresh water than saline waters containing a minimum of 2% to 5% sodium chloride. Clay swelling often results when saline interstitial water is displaced by relatively fresh water. Water sensitivity increases with decreasing salinity.96

Permeability reduction can result from mechanical plugging caused by dislodgement and transport of particles during fluid flow. Clay swelling can contribute to this by loosening the cementation binding the clays and inert particles, so that these particles are more easily removed by turbulence of fluid flow. The sensitivity of reservoir rock to water should be determined by using rock core samples before injection of water into the reservoir is started. A series of permeability measurements can determine the effect of water salinity on the rock. Analysis of the rock by X-ray diffraction can determine the presence or absence of swelling clays. If swelling clays are present, and permeability measurements show reduction in permeability with reduced water salinity, the cause of the reduction is established.

If no swelling clays are present and permeability reduction occurs, then particle mobility and plugging are causing the reduction. To determine adequately the presence, cause, and magnitude of water sensitivity permeability measurements, physical swelling tests, x-ray identification of clay and non-clay minerals, and the microscopic examination should be made of the reservoir rock. On-site testing to reveal any chemical interaction between water and core materials have been suggested 96

The next step in the process is to determine if the reservoir is sensitive to water. Fig. 4 records the CST results of tap water and flowback water on three core samples obtained from the Piceance basin. In this case, the salinity of the flowback water helped stabilize the reservoir without addition of clay stabilizers. However, if the reservoir is known to be sensitive to clays and core samples are available, performing a CST analysis is recommended (Fig. 5). Different fluids containing various clay stabilizing additives can be readily screened and the optimum concentration and type of additive that stabilizes clays in the core sample can be determined.116

In Fig. 5, CST ratios were determined on a Bakken shale sample with three different test fluids in fresh water. The shale sample was oil wet and required cleaning before analysis. A surfactant was tested in this series due to the wettability of the shale sample submitted. All the fluids tested resulted in CST ratios less than 2.0 (a desired result). There seemed to be a slight benefit to using 3 gpt surfactant on these core samples but the values of the 2 wt% potassium chloride and the 3 gpt surfactant both fell within the error of the experiment. In this case, 2 wt% potassium chloride was recommended to be added to the slickwater fluid based on economics116

4.2.7 NORMs

Occurrence

NORM originates in geological formations and can be brought to the surface with produced water. The most abundant NORM compounds in produced water are radium- 226 and radium_228, which are derived from the radioactive decay of uranium and thorium associated with feldspars, micas, clay minerals, and other common and abundant silicate minerals in the hydrocarbon reservoir (Utvik 2003). Radium, which is slightly soluble, can be mobilized in the liquid phases of a formation and transported to the surface in the produced water stream. As the water approaches the surface, temperature changes cause radioactive elements to precipitate. The resulting scales and sludges may accumulate in water separation systems.

Organic-rich shale has higher radioactivity responses than typical shale because the organic matter tends to concentrate uranium ions that otherwise would be scattered throughout the sediment As a result, many organic-rich shales have uranium and thorium contents that are greater than 10 parts per million and that may approach 100 parts per million,

Conditions that appear to affect radium solubility and precipitation include water chemistry (primarily salinity), temperature, and pressure. Radium 226 and 228 in produced waters may react with barium sulfate to form a scale in well tubulars and surface equipment; or may occur in sludge that accumulates in pits and tanks; and which will show up on a gamma-ray log as higher-than-normal gamma-ray responses. Comparisons of gamma-ray logs with drill cuttings show a fairly strong correlation between higher-than-normal radioactivity and black color in shale derived from the organic content.

Issues

NORM is a naturally occurring material that is all around us and may also be present at oilfield sites in varying amounts. The levels of radioactive substances are typically so low; the NORM in produced waters and natural gas is not a problem “unless it becomes concentrated in some manner.”91

In everyday operations, NORM does not cause a problem. The principal concern for NORM in the oil and gas industry is that, over time, it can become concentrated in field production equipment325 and as sludge or sediment inside tanks and process vessels that have an extended history of contact with formation water326.. Studies have shown that exposure risks for workers and the public are low for conventional oil and gas operations327, 328

Management

NORMs have been recognized as an issue by the oil and gas sector since the 1930’s, and regulations and guidelines that are protective of human health and the environment have been in place in Canada and the United States have for several decades.

With proper detection, measurement, along with the use of appropriate work practices, the potential risks from oilfield NORM to oilfield workers and the public can be effectively managed to ensure their safety and health.43 Work procedures are recommended when maintaining NORM contaminated equipment such as pipelines, filters, pumps, lines, sludge or wellhead equipment. The exposure risk is highest when grinding, cutting, polishing or performing other work that may generate dust.44

The definitive document on radiation protection requirements for incidentally exposed workers is the *Canadian Guidelines for the Management of Naturally Occurring Radioactive Materials (NORM*) published by Health Canada on the www.hc-sc.gc.ca website. This document was developed by the Federal Provincial Territorial Radiation Protection Committee and has been endorsed by all provinces and territories as well as the federal government 46

Currently, there are no regulations for NORM management in Canada; however, the ERCB provides guidelines outlining NORM waste disposal options in *Guide 58: Oilfield Waste Management Requirements for the Upstream Petroleum Industry*.45

API also has published several documents providing guidance on the management of NORM in oil and gas operations. [29]HF2

In the US, NORM contained in the discharge of fracturing fluids or production brine may be subject to discharge limitations. The Environmental Sciences Division of Argonne National Laboratory has addressed exploration and production (E&P) NORM disposal options in detail and maintains a Drilling Waste Management Information System website [28] that links to regulatory agencies in all oil and gas producing states.

Simultaneously, state agencies have promulgated NORM regulations that establish new, more restrictive standards for the management and disposal of NORM wastes. These actions have served to limit the number of available disposal options for NORM wastes, thereby increasing waste management costs.

The largest volume oil and gas waste stream that contains NORM is produced water. At this time, the radium content of produced water going to injection wells is not regulated. Consequently, radium that stays in solution in the produced water stream does not present a significant waste management problem from a regulatory perspective.

The occurrence of NORMs in the oil and gas sector is widely recognized in the oil and gas sector. Wastes associated with NORMS are considered to be adequately managed through a combination of work practices and regulation. In the development of shale gas properties, the need for the management of wastes containing NORMs should be considered as part of the Integrated Water Management Plan, and the likelihood of generation of NORMS in scale should be considered as part of the evaluation of scaling tendencies conducted as part of the frac fluid design. Since the occurrence of NORMs in oil and gas production is not unique to the shale gas sector, it is not considered further in this study.

4.2.8 Hydrogen Sulfide

Hydrogen sulfide (H_2S) gas occurs naturally in some geologic formations and in groundwater from those formations. It is formed from decomposing underground deposits of organic matter such as decaying plant material. It may be found in deep or shallow wells. H_2S often is present in wells drilled in shale or sandstone, or near coal or peat deposits or oil fields.107

Although most of rthe shale gas basins have not identified hydrogen sulfide as being a significant problem, the presence of H_2S in both source water and flowback water has been a significant issue in the Horn River. Reports indicate that H_2S has been measured in waters originating in the Debolt Formation at concentrations ranging from 200 mg/L up to 8000 mg/l with an average concentration of 5000 mg/L. In addition, flowback water with concentrations in the order of several hundred mg/L has been encountered.
Treatment of both the Debolt water and frac flowback water is necessary before the water is used for fracturing treatment

Pumping equipment, and other oilfield equipment is susceptible to damage on exposure to H2S either in vapor phase or solubililized in water, to say nothing of the worker safety issues. For this reason it is desirable to eliminate H_2S from both source water and flowback water prior to use or reuse of the water.

If H_2S is encountered in production fluids, both regulators and operators are well equipped to implement appropriate safety measures. States have well-established public safety and worker protection requirements in place and operators have access to proven procedures for working with natural gas contaminated with H_2S.[2]

The American Petroleum Institute (API) has a Recommended Practice (RP 49) for Drilling and Well Servicing Operations Involving H_2S 336. Producers voluntarily follow this practice to minimize the release of and exposure to H_2S.

4.2.9 Temperature

Extreme temperatures and temperature variations in frac fluids can have an impact on equipment integrity and frac fluid performance. The optimum temperature for frac fluid is approximately, 15 ° C. The source water from the deeper aquifers (including the Debolt) can be in the range of 100 to 160 ° C. Inversion of slick-water polymer dispersions will occur faster at +100 °F and aid friction reduction. The suggested 15 °C (60 °F) lower limit was to ensure that adequate inversion/hydration time for the friction-reducer, and minimize any potential freezing problems in suction/discharge lines. As temperatures increase toward 150-deg °F (65 °C), then we begin to get into potential rubber seal and suction/discharge hose problems. The butterfly valve seals and rubber hoses soften enough where soft discharge hoses can slip from clamps and separate. Valve packing and inserts can also fail/leak (considerations for packing-grease used, etc.) In addition, QHSE issues also come into play, since the waters may be hot enough to scald, as the POD-Blender can potentially add 10° F to the fluids, due to high shear energy imparted. As such, special consideration must be given to the direct use of these heated fluids for fracturing treatments. If cooling time is required, additional storage capacity for source water or flowback may be required, and mechanical cooling of water may be necessary. In the winter months, the heat of deep groundwater or flowback water will offset the energy requirements to prevent freezing at surface while in temporary pre-frac storage.

Stabilizers are used to prevent degradation of polysaccharide gels at temperatures above 200 °F. The common stabilizers are methanol and sodium thiosulfate ($Na_2S_2O_3$). Methanol is more hazardous to handle and is used as 5% to 10% of the fluid volume. Sodium Thiosulfate is generally used at 10 to 20 lb/1000 gal. Sodium thiosulfate is the more effective of the two, increasing the viscosity at elevated temperatures by a factor of 2 to 10, depending on the temperature and time of exposure to temperature. Fluid pH should be considered in maximizing fluid stability. Guar and its derivatives are hydrolyzed at low pH, especially at elevated temperatures (>200 °F). Therefore, if long-term fluid stability is desired, a high pH (eg 9-11) fluid should be used. (SLBRS)

The temperature of flowback fluids can be an issue that must be handled as part of water management planning, and operationally due to safety and operational constraints imposed by high temperature. The rule of thumb for the temperature of frac fluids is approximately 15 °C. At approximately 65 °C, the temperature of the frac fluid becomes a safety issue, and begins to impact pumping equipment. (Pope, personal communication). Several of the hydraulic fracturing additives and water conditioners used in the injection process do not perform well at elevated temperatures, and alternatives that function adequately at elevated temperature may need to be considered. Bachu (2002) indicates that in the Horn River, temperatures up to 120 °C can be anticipated, and in the Montney, bottom hole temperatures in the range of 30 to 140 °C.

- Health and Safety Issue
- Impact on Frac Additives – some sensitive, some not
- impact on scaling tendencies
- Impact on pumping equipment

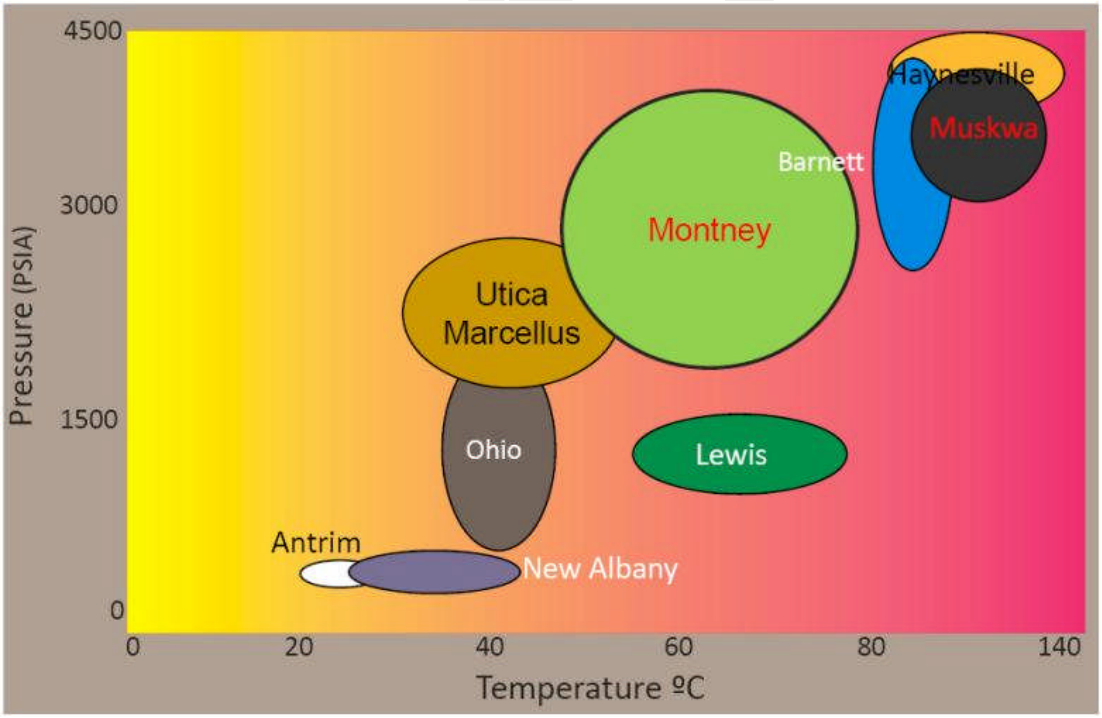


Figure 24 Temperature – Pressure Relationship of Various Shale Gas Plays (Source Doc 74)

5.0 GENERIC FRAC ADDITIVES

A number of chemical additives are utilized in the various fracs commonly used in the stimulation of unconventional reservoirs. The chemicals have differing purposes, characteristics, and are used in varying concentrations. Documentation will be provided of the nature, purpose, concentrations of the various chemicals that are used in the various frac types, as well as the sequencing of injection. In addition to the discussion of these issues within the text of the report, summary spreadsheets and tables will be prepared that provide guidance information to frac designers and other stakeholders. The generic groups of chemicals used in fraccing operations may include:

Acids	KCL
Biocides	Oxygen Scavenger
Breakers	pH Adjusting Agent
Corrosion Inhibitors	Proppant
Crosslinker	Scale Inhibitor
Friction Reducer	Surfactant
Gel	Iron Control

In addition to water and proppant other additives are essential to successful fracture stimulation. The chemical additives used in the process of hydraulic fracturing typically represent less than 1 % of the volume of the fluid pumped (99 % sand and water) during a “hydraulic fracture treatment” and in many cases can be even less (see Figure 3). [13] Chemical additives may consist of acids, surfactants, biocides, bactericides, pH stabilizers, gel breakers, in addition to both clay and iron inhibitors along with corrosion and scale inhibitors.

Chemical additives may consist of acids, surfactants, biocides, bactericides, pH stabilizers, gel breakers, in addition to both clay and iron inhibitors along with corrosion and scale inhibitors. These additives, along with the characteristics of water in the formation being fractured, can often dictate the water management and disposal options that will be technically feasible. [16]

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.

Following the proppant, the major additive in most jobs will be the friction reducer which is required to reduce the friction pressure while pumping at the extreme rates of 50 to 120 barrels per minute (bpm). The second concern should be additives to treat bacteriological activity. The injection of water will ultimately result in the cultivation of sulfate reducing bacteria which produce Hydrogen sulfide (H2S) and byproducts such as black iron sulfide on the surface if not treated properly. Scale inhibitors become vitally important as water dissolves salts from the formation. Finally, the use of surfactants can be beneficial in promoting the flowback of injected fluids to restore the relative permeability to gas

Service companies have developed a number of different oil- and water-based fluids and treatments to more efficiently induce and maintain permeable and productive fractures. The composition of these fluids varies significantly, from simple water and sand to complex polymeric substances with a multitude of additives. Each type of fracturing fluid has unique characteristics, and each possesses its own positive and negative performance traits. For ideal performance, fracturing fluids should possess the following four qualities (adapted from Powell et al., 1999):

- Be viscous enough to create a fracture of adequate width.
- Maximize fluid travel distance to extend fracture length.
- Be able to transport large amounts of proppant into the fracture.
- Require minimal gelling agent to allow for easier degradation or “breaking” and reduced cost. 30

5.1 Acids/Buffers

The use of acid as a frac breakdown aid has been demonstrated in most shales, even when there was little or no acid reactivity in the formation. Using acid in an area where calcite cementation or fill is common in the fractures is well recognized but can lead to plugging problems with excessive amounts of calcite cement and acid (Broacha, 2009). In other areas, the ability to inject any aqueous fluid into a rock may lower its strength and promote fracturing. This is a commonly-known rock mechanics fact: wet rock is weaker than dry rock. Although most shale formations have at least moderate water saturations, adding water, regardless of salt content, seems to reduce rock strength. Hydrochloric acid is commonly used at 10% to 15% concentration as a breakdown tool because it is inexpensive, works wells and spends gradually on acid soluble material. However, acid may not be needed in every case.40

The leading edge of an otherwise effective mutual solvent and acid system can be loaded with debris cleaned off the walls of the tanks and tubing. For this reason, the leading edge of the acid job is circulated out of the well using a process called pickling the tubing if the completion configuration allows. In this treatment, acid and solvents are injected down the tubing to disperse and dissolve iron, pipe dope, and mud and other debris from the tubing and are then circulated or reversed out of the well without being injected into formation. These jobs are extremely effective when the tubing has not been cleaned or its condition is unknown. Volumes of both acids and additive treatments range from 1 to 2 tubing volumes depending on the condition of the tubular. Minimum acid and solvent volumes typically range from 250 to 500 gal. Coated tubing can reduce iron scale significantly, but other contaminants, such as scale and pipe dope, may still be present. If load-fluid recovery influences well production, surfactants or mutual solvents that reduce surface and interfacial tension are usually beneficial. The treatment volumes depend on the fluid, formation and amount of load fluid lost. 94

In general, most flowback and produced waters are circum-neutral with pH values between 6 and 8. Buffering is usually provided through the presence of bicarbonate. In the normal storage and handling of produced waters, pH values will remain neutral unless caustics or acids are added in the course of treatment.

The pH of the water affects the polymer hydration rate. If the pH of the water is low, hydration may be rapid and lumping of the gel results. If the water pH is too high, the gel hydrates too slowly. Water temperature also affects hydration rate. Increasing the water temperature causes faster polymer hydration (viscosity development). A sample of polymer from location should be used to prepare a linear gel with the water from the fracture tanks. Testing should ensure that proper dispersion (no lumps) and hydration (viscosity development) will be obtained on location. 94

Buffers

Buffers are weak acids or bases that are added to water-base fracturing fluids to maintain a desired pH value. The buffers will maintain the pH value at a desired level even if an extraneous acid or base is introduced (for example, through contaminated water or proppant). This is especially important when using enzyme breakers. The optimum pH range for enzyme breakers is 3.5 to 5.0. Enzyme breakers are deactivated when the fluid pH value is greater than 9.0. Buffers are also used to maintain the proper pH value for crosslinked fluids. This is important because crosslinking rate and polymer stability are affected by the fluid pH value. Crosslinked fluids are generally formulated to work best in a narrow pH range (±0.25 units from the optimum). Guar and HPG can be crosslinked at a pH range of 3 to 10, depending on the type of crosslinker used. Buffers also promote hydration of the polymer. For example, guar and hydroxypropylguar (HPG) are treated to be dispersible and nonhydrating at a high pH value. Initially, the water pH value should be high to allow polymer dispersion. After the polymer is dispersed, the water pH should be lowered to promote hydration. The pH value can be lowered by adding an acidic buffer after the polymer is dispersed.

Activators

Activators are strong bases that enable crosslinking by raising the pH value in the borate-crosslinked fluids.

5.2 Friction Reducers

Fluids such as water and low-viscosity oil achieve turbulence when pumped through small tubulars at high rates. This creates high friction pressures. Dramatic decreases in friction pressure are observed when turbulence is suppressed by adding polymers (friction reducers) to the fluid.

Friction reducers offer no advantage unless the fluid is in turbulent flow. An already viscosified water- or oil-base fracturing fluid will not benefit from the addition of friction reducers. Similarly, a viscous oil pumped at low rate through casing or large diameter tubing exhibits little opportunity for enhanced friction reduction by adding friction reducers. High turbulence must be a factor before friction reducers are effective.

Friction Reducers for Water

Polymers are high-molecular-weight molecules that have an affinity for water molecules. The polymer deters turbulence by controlling migration of the individual water molecules. Low concentrations (10 to 20 lbm/1000 gal) of guar or HPG polymers and copolymers of polyacrylamide are the most efficient friction reducers for water.

Friction Reducers for Oil

The friction reducer for oil is a copolymer. Friction reduction of as much as 55% may be obtained using Oil Friction Reducing Agent in crude oil. Used in refined oils, friction reduction of as much as 70% may be obtained. The oil viscosity is unaffected by friction reducers. Friction in oil may also be reduced with low concentrations of an aluminum phosphate ester gelling agent and an activator.

With the success of slickwater fracs especially in the Barnett Shale, friction reducers have grown in popularity. Friction reducers are used to decrease the friction pressure allowing higher pressure from the same number of pumping trucks. Common friction reducers are polyacrylamide based and have a usual loading range from 0.25 gallon of friction reducer per one thousand gallons (gpt) of water to 1.0 gpt of water.

There are three types of polyacrylamide friction reducers, anionic, cationic and nonionic. They do have thermal stability up to about 200 °C and readily decompose after 280 °C. Chemical and thermal degradation of the polymer lowers its effectiveness.41

Care must be taken when selecting a friction reducer. Figure 1 illustrates the variations in commercially available friction reducers. Six friction reducers were supplied by a major operating company for independent evaluations. The conditions are: flow at 5 gallons per minute through a tubing length of fifty feet, a dimension of one half inch outer diameter, a total volume including tank is 5 gallons, pressure ports ten feet apart, and concentration of friction reducer was 0.25 gpt in two percent (%wt) potassium chloride (KCl). At 20 seconds polymers hydrate at different rates; in fact the friction reduction between the lowest and highest values is roughly 50%. At 20 seconds the polymer has made two complete passes through the loop. At ten minutes (600 seconds), or 60passes through a progressive cavity pump, the difference between the lowest and highest values is roughly 20%

With so many different friction reducers available on the market, the next step in the process should be performance testing of the friction reducer in the flowback water. The ability to test the performance of a friction reducer in the flowback water will ensure that the most cost effective and efficient friction reducer is selected for the treatment. Figure. 3 illustrates the effect of concentration of three different friction reducers in a synthetic flowback water system (See Piceance basin water analysis in Table 1). Each point on this plot comes from the maximum percent drag reduction for each friction reducer fluid evaluated at different concentrations on a friction loop.

Given that the practice in the field is “rule of thumb” adjustment for the friction reducer, the efficiency of fluids can be lost. This may be the case in today’s market but the cost considerations could be better optimized. It is plain from the data that adding more that about 0.5 gpt of the current commercial materials yields little increase in friction reduction. If the treatment fluid requires concentrations above that level, then there may be interactions between the different additives occurring to reduce the effectiveness.137

As shown earlier, some friction reducers are more salt tolerant than others. The operator must ensure that the correct type of friction reducer is used. If the wrong friction reducer is used, then a higher concentration is pumped to achieve the same effect, and potentially more formation damage will occur or more breaker is needed.41 at higher costs.

Most friction reducers used in slickwater fracture stimulation are high molecular- weight polyacrylamide emulsions. Since these friction reducers are typically pumped at low concentrations The industry belief has been that these polymers are causing minimal damage to the formation.130
There are several kinds of polyacrylamides (anionic, cationic and nonionic) used for different conditions and compatibilities. These can be used in a variety of water types from fresh to produced brines.130

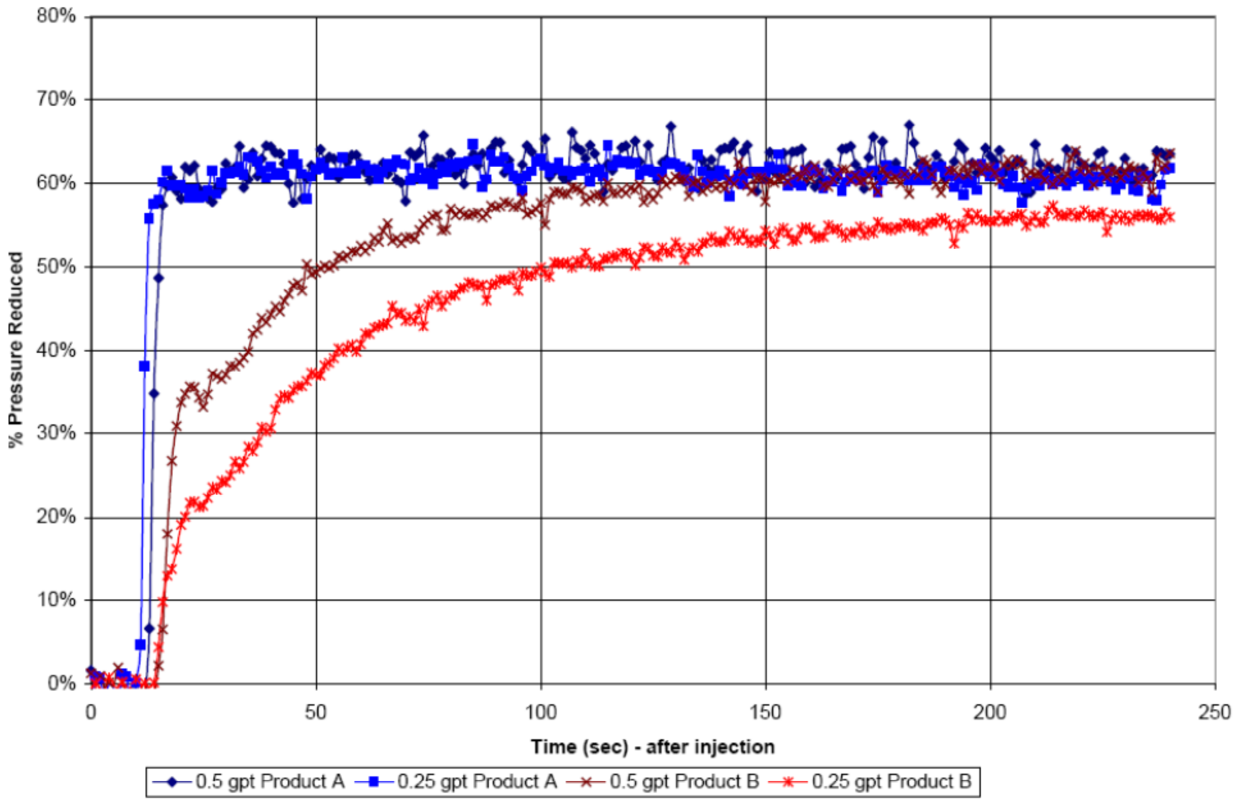


Figure 25 Doc 31 Comparison of Various Commercially Available Friction Reducers: Data generated during the first 60 seconds after injection into the flow loop. On the right, friction reduction recorded up to 10 minutes

Friction reducers do cause formation damage and may need a breaker; some breakers are delayed to allow the friction to be reduced in the tubing where it is most effective. At even low concentrations of 0.25 gallon/1000 gallons of water, results in 250 gallons of potential polymer damage. Once past the perforations, the breaker will break the polymer to reduce damage and encourage polymer flowback. Carmen et al 2 did a study of oxidative breakers on a fresh water and brine-based polyacrylamide friction reducer used in slickwater fracture treatments. All breakers tested worked at 180°F to some extent. The results were generated using a techniques called molecular weight cut off (MWCO), and shows that the persulfate breakers worked best at 180°F, and is effective at 100°F at concentration of 5 and 10 pounds per thousand (ppt) of water. Flow loop data showed no degradation of polymer at a persulfate concentration of 1 gpt up to 105°F, nor did the breaker have detrimental effects on hydration of the polymer.

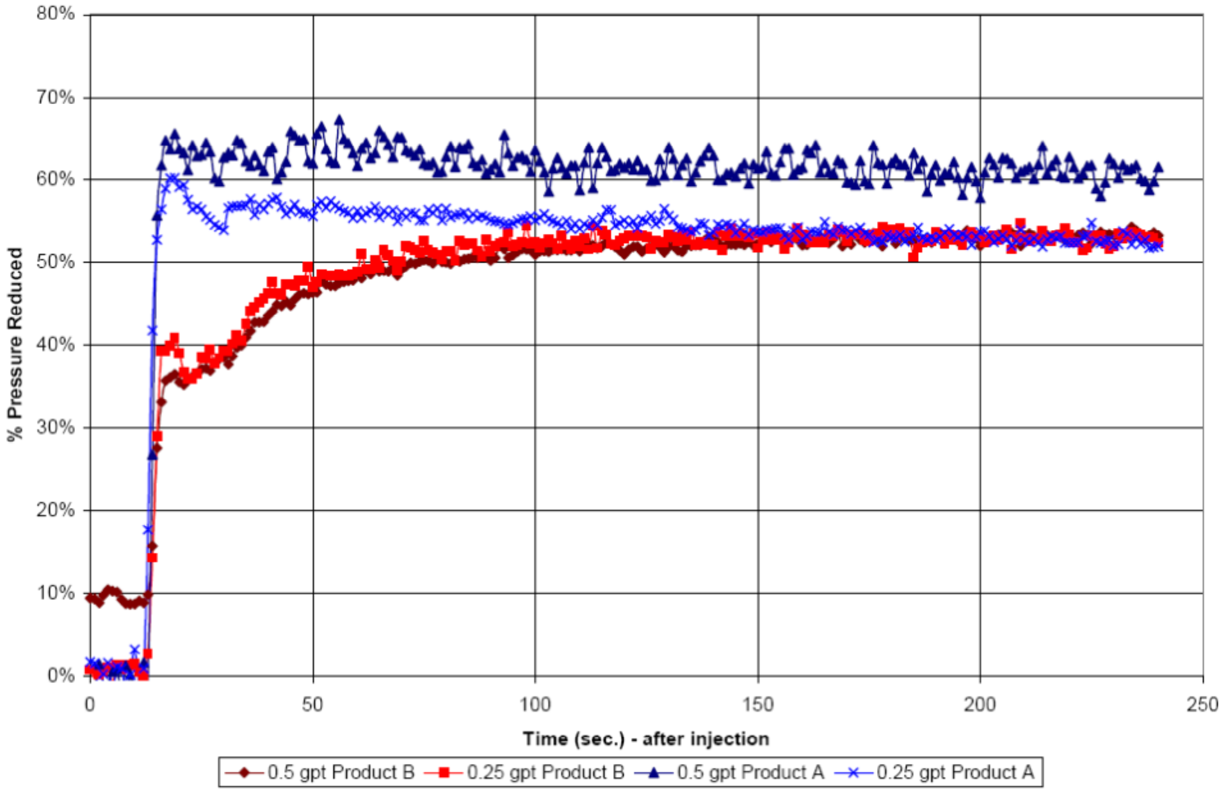


Figure 26: Comparison of Various Commercially Available
Friction Reducers: Data generated after 10 minutes after injecting into the flow loop

Anionic Friction Reducers

As one balances the compatibility and efficacy of the biocides and other additives in the fluid, it is tempting to prescribe a cationic or non-ionic friction reducer

The commercial friction reducers are therefore made with very high molecular weight. The polyacylamide copolymers also have an advantage because they are charged (polyelectrolytes) which increases this radius. Raising the ionic strength of the fluid reduces the radius of gyration of the polymers and thus their drag reduction. This is why the anionic polyacylamides give greater fraction reduction in fresh water. Waters with added potassium chloride (KCl) or produced waters usually require additional friction reducer to attain the same level of drag reduction as in fresh water.137

Salt Sensitivity

As the theories predict, anionic polyacylamide friction reducers are affected by salts in the treatment water. This is a large issue as the industry continues to use more produced water for fracturing treatments. It is clear from Fig. 2 that higher salt concentrations reduce the effectiveness of the friction reducers. It is also worth noting that there is little improvement in drag reduction for the fluid once the polymer concentration exceeds 0.5 gpt. Adding more does not improve the result.137

Slickwater pumped at high rates with low sand concentration has been very effective at treating shale gas formations. An ideal slickwater additive has been found to be a liquid-polymer emulsion that is a salt tolerant friction reducer (STFR) designed especially for compatibility with the specific shale lithology. Use with brine liquids at NaCl concentrations from 2% to 12% is feasible.2,3 Salt tolerance allows frac fluid of high salt concentration to be reused repeatedly provided that other geochemical properties are controlled.110

Cationic Friction Reducers

The typical oil field cationic friction reducers are used in acidizing or with heavy brines. These polymers would work in fracturing treatments and be compatible with cationic biocides. The cost of these materials is far higher than the normal anionic friction reducers. Another possibility is to use the polysaccharides as friction reducers. These materials are also compatible with cationic biocides. However, it requires 10 times as much polysaccharide to achieve the same drag reduction as with an anionic polyacrylamide friction reducer. Therefore, the use of these alternative materials becomes an economic issue.137

Insert Figure from DOC 41

If one uses a cationic friction reducer again care must be taken to ensure enough friction reducer is used depending on the water, meaning the salt concentration, if the cations are monovalent or divalent, is fresh water or is produced water being used. Figure 2 illustrates the effects of certain salts on two different cationic friction reducers; FR-A (friction reducer A) behaves much superior in the first 60 seconds compared to FR-B (Friction Reducer B), in all salts and concentrations tested. In the first 60 seconds FR-B is strongly affected by the different salts such as 4% NaCl, 7% CaCl2, and 7% KCl, whereas FR-A shows very little effect at 0.25 gpt concentration. At 60 seconds the friction reducers have made six passes through the positive displacement pump41

Sensitivity to Biocide

In general, the wrong or incompatible biocide will reduce the effectiveness of your friction reducer. This will require more friction reducer to be added to the fluid to control the pressure drop while pumping. In addition, the flocculated polymer-biocide complexes could plug the formation. It is outside the testing from this study, but presumably the polymer biocide complexes consume the biocide and reduce its effectiveness against killing bacteria.137

Evaluating the effect of the biocides, it is clear that a detrimental effect can occur when incompatible materials are mixed together. The incompatibility between the anionic friction reducer and the cationic quaternary ammonium biocide can be seen via flocculation in the bottle. This effectively consumes friction reducer resulting in less being available to give the fluid drag reduction. This is seen in Fig. 3. The drag reduction of the fluid drops by 25%. Fig. 6 shows that this effect is not just a laboratory curiosity, but scales up to a field pumping example. In this case, the addition of an incompatible biocide results in a pumping pressure increase of 1000 psi. In a real slickwater treatment, the biocide would be added before the friction reducer, and the incompatibility would not be noticed. In all eventualities, the concentration of friction reducer would be increased to overcome the negative effects.137

The reuse of fracture water is of special concern due to the potential amount of bacteria is in the produced water. Again these bacteria can attack the polymer and reduce its effectiveness, and a registered biocide is recommended in the frac tank.41

Temperature Sensitivity

Polyacrylamides have very good thermal stability up to 200°C. However they do begin to break down between 200°C and 300°C. Above 300°C the decomposition of the main chain and other bonds will occur.130

Summary

In summary, the graphs show that the performance level for a friction reducer can vary widely, based on the contents of the base fluid. The friction loop used to collect the data depicted in Figs. 1 and 2 is an invaluable tool for comparing friction-reducer effectiveness in fracture waters of varying composition.
As freshwater scarcity increases and state agencies tighten regulations concerning water use and disposal, a growing number of shale-gas wells will be stimulated using produced water. This will escalate the importance of developing more robust and versatile friction reducers. In addition, this will escalate the importance of the other chemical additives used in slickwater fracturing. More specifically, scale inhibitors and biocides will be required in most treatments to avoid fouling. These and other fracturing additives need to be tested for compatibility with each other, with the friction reducer, as well as with the base fluid to ensure that they will function as expected.20

Taking a more systematic approach to product selection can prevent overtreating and provide substantial cost savings. Current efforts involve compiling data on fracture-additive compatibility, and a report detailing the problem and appropriate solutions is forthcoming

5.3 Biocides

The polymers used in water-base fracturing fluids are excellent food sources for bacteria. Bactericides are added to water-base fracturing fluids to prevent bacterial degradation of the polymer and to protect the formation from bacterial growth. Common practice is to add a bactericide to the frac tanks before water is added to ensure that the bacterial enzyme count remains low. No water-base fracturing fluid should be pumped into a well without some type of bactericide present. Bactericides are unnecessary in oil-base fracturing fluids. Bacteria may be aerobic or anaerobic. Aerobic bacteria require oxygen for survival. Anaerobic bacteria can exist in the absence of oxygen. Aerobic bacteria produce enzymes that degrade the polymers used in water-base fracturing fluids resulting in a viscosity loss and premature break of the fluid. Anaerobic bacteria, introduced by the fracturing fluid, can create severe reservoir problems. The bacteria can multiply in such numbers that they reduce permeability and, consequently, damage the formation. Certain types of anaerobic bacteria chemically reduce sulfate ions to produce hydrogen sulfide, creating a safety hazard. Hydrogen sulfide also corrodes tubular goods and production equipment.

Bactericides are added to polymer-containing aqueous fracturing fluids to prevent viscosity loss caused by bacterial degradation of the polymer. The polysaccharides (sugar polymers) used to thicken water are an excellent food source for bacteria, Bacteria not only ruin gel by reducing the molecular weight of the polymer, but some can turn the reservoir fluids sour. Once introduced into the reservoir, some bacteria can survive and reduce sulfate ions to hydrogen sulfide (H_2S), and extremely dangerous gas with characteristic rotten-egg odor.

Materials such as glutaraldehyde, chlorophenates, quaternary amines and isothiazoline are used to control bacteria. Usually the materials kill the bacteria, but they do not always inactivate the enzymes that are responsible for breaking down the polysaccharides. For this reason it is common practice to add bactericide to fracture tanks before the water is added to ensure that the bacterial enzyme levels is kept low.

Prevention of polymer destruction by bacteria is usually handled with bactericides and tank monitoring. Control of bacteria down hole is more difficult and involves scraping or treatments with hypochlorite or other oxidizers followed by acidizing and then treatment with an effective biocide at a level at least 1.2 times the minimum kill level. Frequent rotation of the type of biocide is also necessary to prevent the development of biocide-resistant strains of bacteria. (SLBRS)

The biocide needs to be selected to be compatible with the FR and breaker system. A system that has both short term and long term kill is recommended for shales to avoid future production problems.41

Biocides are used in slickwater applications to prevent bacteria growth and may alter the physical characteristics of fluids such as viscosity by degrading the polymer. The degradation of the polymer can be caused by free radicals usually from oxygen. Therefore potentially there is a compatibility issue between oxygen scavenger or biocide. Compatibility of biocide with other chemicals such as corrosion inhibitors, scale inhibitors, polymers, and other well treatment fluids is critical.41

In the well the bacteria can cause other problems. These include but are not limited to producing acid (acid producing bacteria, APB), sulfate reducing bacteria (SRB), and production of carbon dioxide and oxygen. Common biocides are quaternary amines, glutaraldehyde (glut) and tetra-kis-hydroxylmethylphosphonium sulfate (THPS). A relative new comer to the oilfield applications is tetrahydro- 3,5-dimethyl-1,3,5-thiadiazinane-2-thione; this biocide (Thione) has been shown that it does not interfere with friction reducer, and is extremely effective in killing APB bacteria , and is a broad spectrum biocide3. It is also a longer term kill biocide that is compatible with oxygen scavengers. Even if a biocide is effective in killing, testing should be done to determine compatibility of biocide with the friction reducer. Figure 3 illustrates the effect of 500 mg/L biocides on a post inversion viscosity at the samples have been heated at 180°F and then measured at 77 °F. As seen in Figure 3, the polymer viscosity degrades with heat over time. After four hours at 180 °F, the control (no biocide), aqueous Thione, and emulsified Thione show a slight decrease in viscosity, whereas the glut maintains its viscosity. This can de deleterious in flowback of the polymer.41

The reuse of fracture water is of special concern due to the potential amount of bacteria is in the produced water. Again these bacteria can attack the polymer and reduce its effectiveness, and a registered biocide is recommended in the frac tank.41

Polysaccharides, such as guar and guar derivatives, are susceptible to bacterial damage. Bacteria can synthesize enzymes, such as cellulose (including hemicellulose), glycoside hydrolases, and amylase, that catalyze the breakdown of polysaccharides (Fodge, et al., 1996; Gupta, et al., 1995; Tjon Joe Pin, et al., 1993; Shell and Hitzman, 1992; Dawson, 1991). Biocide (bactericide) is often added as an additive to suppress or kill bacteria, thus preventing the degradation of the polymer fluid and the growth of a large biomass in the formation. Commonly used biocides in oilfield may include glutaraldehyde, 2,2-dibromo-3-nitrilopropionamide (DBNPA), tetrakishydroxymethyl phosphonium sulfate (THPS), and quaternary ammonium compounds (QACs), to name a few (Paulus, 2005).

When fracturing fluids, for example, polysaccharide-based fracturing fluids, are prepared using clean water or brine, normal dosage of the common biocides is usually sufficiently protective (Paulus, 2005). This may not always be the case when produced water is used to make fracturing fluids, as produced water typically contains much higher concentrations of bacteria and/or bacterial enzymes. The biocides may be depleted quickly by overwhelming populations of bacteria and/or high concentrations of ions in produced water. At the same time, biocide is usually applied at low dose (sufficient for clean water) because of environmental and economical considerations and may not denature (disable) bacterial enzymes at all. These enzymes will then continue to decompose polysaccharides even after the bacteria can be killed or suppressed.

Historically, biocides have been added to protect biopolymer-based fracturing fluids (e.g. guar) from degrading during a fracturing treatment to preserve the proppant carrying capacity. In slickwater applications, the polymer most often used is a synthetic acrylamide co-polymer that does not readily degrade in the presence of bacteria. Instead, the biocide is added to prevent souring of the asset by SRB. Fig. 2 illustrated the different abilities each type of biocide had in killing bacteria in flowback water after 7 days.116

One of the common incompatibilities can be between cationic additives such as biocides, and the anionic friction reducer polymers. In water, the two oppositely charged moieties would form complexes. These complexes may be insoluble, and will render available materials ineffective. This will require more FR to be added to the fluid to control the pressure drop while pumping. In addition, the flocculated polymer-biocide complexes could cause formation damage.137

The goal of any stimulation fluid should be that all components are compatible. As expected, some biocides complex with oppositely charged friction reducers. This results in the formation of flocks of insoluble polymers in the fluid. Laboratory testing and a field example indicate that the quaternary ammonium biocides reduce the drag reduction seen with the common friction reducer. In comparison, nonionic biocides such as glutaraldehyde do not interact with the friction reducer.137

In contrast, using a non-ionic biocide like glutaraldehyde, results in no interaction with the friction reducer. This can be seen at all scales for the bottle tests through to the field pumping example. Biocide choice needs to be made to most effectively control the bacteria present in the treatment water, but also for compatibility with the other components of the fluid. There are other non-oxidizing biocide classes that are compatible with anionic friction reducers (e.g. DBNBA or other bromine complexes, Carpenter and Nalepa, 2005). Each of these different types of biocides has their strengths and weaknesses for use in the oilfield.137

Sulfate-reducing and iron-metabolizing microbes play an important role in the formation of geochemical precipitates and must therefore be considered in any geochemical discussion. Control measures must be followed to negate the effects of downhole “extremophile” sulfate-reducing microbes and conventional spore-forming bacteria. A 20% active, liquid brominated propionamide, commonly referred to as DBNMA, is effective choice for geochemical control. DBNPA works in the presence of hydrocarbons, begins to kill instantly, and will decontaminate a system within one hour. One benefit of DBNPA is its short half-life in the environment. DBNPA is considered one of the safest biocides when used or spilled; it breaks down into the innocuous components bromine, nitrogen, and water. The non-foaming biocide is effective against both aerobic and anaerobic microorganism. It is water soluble, easy to mix and dilute, and registered with the US Environmental Protection Agency as non-persistent. DBNPA is also not affected by hard water or salts.110

Designing the biocide package for the produced water without considering interactions with the friction reducer could lead to a less than optimal system and extra added cost. It could also lead to a sour well and increased formation damage. Ultimately, using additives that work in concert will both optimize fluid performance and maximize the return on invenstment.137

Another continuing issue in the various shale reservoirs around North America is produced water and scale (Szymczak et. al., 2007). Operators have naturally addressed the problems of treating flowback and produced water from these fields with traditional production chemicals. Given that a large amount of the water is flowback, they have adopted the treatment of the slickwater water being pumped into the wells.

The polyacrylamide co-polymers are minimally susceptible to biological degradation; but pumping 7154 m3 (60,000 bbl) of water into the formation has high potential for a problem with sulfate reducing bacteria. There are a range of biocide chemistries which can be used, and have varying effectiveness to control sulfate reducing bacteria (SRB). There are several popular and effective biocide choices: glutaraldehyde, quaternary ammonium salts, isothiazolin, and 2,2-dibromo-3-nitrilopropionamide (DBNPA).137

Biocides are used in slickwater application to prevent bacteria growth and may alter the physical characteristics of fluids such as viscosity by degrading the polymer. The degradation of the polymer can be caused by free radical usually from oxygen. Therefore potentially there is a compatibility issue between oxygen scavenger or biocide. Compatibility of biocide with other chemicals such as corrosion inhibitors, scale inhibitors, polymers, and other well treatment fluids is critical. Some attributes necessary for a biocide are safety, cost effectiveness, compatibility with fluids or other additives, and handling. In the well the bacteria can cause other problems. These include but are not limited to producing acid (acid producing bacteria, APB), sulfate reducing bacteria (SRB) and production of carbon dioxide and oxygen.41

Common biocides are quaternary amines, glutaraldehyde (glut) and tetra-kis-htdroxylmethylphosphonium sulfate (THPS). A relatively new comer to the oilfield applications is tetrahydro- 3,5-dimethyl-1,3,5-thiadiazinane-2thione; this biocide (Thione) has been shown that it does not interfere with friction reducer, and is extremely effective in killing APB bacteria, and is a broad spectrum biocide[3]. It is also a longer term kill biocide that is compatible with oxygen scavengers.41

Even if a biocide is effective in killing, testing should be done to determine compatibility of biocide with the friction reducer. Figure ----- illustrates the effect of 500 mg/L biocides on a post inversion viscosity at the samples have been heated at 180°F, the control (no biocide), aqueous Thione, and emulsified Thione show a slight decrease in viscosity, whereas glut maintains its viscosity. This can be deleterious in flowback of the polymer.41

The reuse of fracture water is of special concern due to the potential amount of bacteria that is in the produced water. Again these bacteria can attack the polymer and reduces its effectiveness, and a registered biocide is recommended in the frac tank.41

One hydraulic fracturing design problem that arises when using organic polymers in fracturing fluids is the incidence of bacterial growth within the fluids. Due to the presence of organic constituents, the fracturing fluids provide a medium for bacterial growth. As the bacteria grow, they secrete enzymes that break down the gelling agent, which reduces the viscosity of the fracturing fluid. Reduced viscosity translates into poor proppant placement and poor fracturing performance. To alleviate this degradation in performance, biocides, bactericides, or microbicides are added to the mixing tanks with the polymeric gelling agents to kill any existing microorganisms (e.g., sulfate-reducing bacteria, slime-forming bacteria, algae), and to inhibit bacterial growth and deleterious enzyme production. Bactericides are typically hazardous by nature (Messina, Inc. Web site, 2001). They may contain hazardous constituents, including polycyclic organic matter (POM) and polynuclear aromatic hydrocarbons (PAHs) (U.S. Department of the Interior, CO State BLM, 1998).

These concentrated products are substantially diluted prior to injection into the subsurface. Typical dilution in the make-up water is 0.1 to 0.2 gallons of microbiocide in 1,000 gallons of water (Halliburton, Inc., Virginia Site Visit, 2001; Schlumberger, Ltd., 2001).

Sulfate reducing bacteria (SRB) are the most common biological problem found in oil and gas production facilities. SRB reduce the sulfate ion to hydrogen sulfide, which causes chemical corrosion, steel embrittlement, and fouling of equipment by formation of iron sulfide. There are three common chemical types used as bactericides in offshore production operations, quaternary amine salt, amine acetate, and glutaraldehyde. Each of these bactericides are highly water soluble and are sold as aqueous solutions with bulk concentrations ranging from 10% - 50%. Application of bactericides is either through slug treatments or continuous treatment. For a slug treatment typical concentrations will be between 100 – 200 mg/L for 2 to6 hours, once or twice a week, depending on the type of production, volume of produced water and size and complexity of the production system being treated. Continuous treatment concentrations usually range between 5 – 20 mg/L and will vary based on the same factors just mentioned.27

Glutaraldehyde based biocide has good compatibility with Friction Reducers at concentration of approximately 200 mg/l. If the pH is more acidic an increase in dosage is recommended. If the temperature increases above 38 degrees C increase dosage

5.4 Gels

Water alone is not always adequate for fracturing certain formations because its low viscosity limits its ability to transport proppant. In response to this problem, the industry developed linear and cross-linked fluids, which are higher viscosity fracturing fluids. Water gellants or thickeners are used to create these gelled fluids. Gellant selection is based on formation characteristics such as pressure, temperature, permeability, porosity, and zone thickness. These gelled fluids are described in more detail below.

A substantial number of fracturing treatments are completed using thickened, water-based linear gels. The gelling agents used in these fracturing fluids are typically guar gum, guar derivatives such as hydroxypropylguar (HPG) and carboxymethylhydroxypropylguar (CMHPG), or cellulose derivatives such as carboxymethylguar or hydroxyethylcellulose (HEC). In general, these products are biodegradable.

Guar Gum

Guar is a polymeric substance derived from the seed of the guar plant.Guar gum, on its own, is non-toxic and, in fact, is a food-grade product commonly used to increase the viscosity and elasticity of foods such as ice cream.

Guar is a long-chain polymer composed of mannose and galactose sugars. Polymers composed of sugar units are called polysaccharides. The guar polymer has a very high affinity for water. When the polymer is added to water, guar particles "swell" and "hydrate," which means the polymer molecules become associated with many water molecules and unfold and extend out into the solution. The guar solution on the molecular level can be pictured as long, bloated strands suspended in water. The strands tend to overlap and hinder motion, which causes an increase in the viscosity of the solution.

Most systems currently use water soluble polymers composed of guar or guar derivatives. Additional materials are used to optimize the fluid characteristics for the application and also to degrade the water-soluble polymer to make it easier to recover from the well prior to production.125

Guar gums are preferred as thickeners for Enhanced Oil Recovery (EOR), guar gum and its derivatives account for most of the gelled fracturing fluids. Guar is more water soluble than other gums, and it is also a better emulsifier, because it has more galactose branch points. Guar gum shows high low-shear viscosity, but it is strongly shear-thinning. Being non-ionic, it is not affected by ionic strength or pH but will degrade at low pH at moderate temperature (pH 3 at 50°C). Guar's derivatives demonstrate stability in high temperature and pH environments. Guar use allows for achieving exceptionally high viscosities, which improves the ability of the fracturing liquid to transport proppant. Guar hydrates fairly rapidly in cold water to give highly viscous pseudoplastic solutions of, generally, greater low-shear viscosity than other hydrocolloids. The colloidal solids present in guar make fluids more efficient by creating less filter cake. Proppant pack conductivity is maintained by utilizing a fluid that has excellent fluid loss control, such as the colloidal solids present in guar gum. Guar has up to eight times the thickening power of starch.

Hydroxypropylguar (HPG)

Guar gum comes from the endosperm of guar beans. The process used to produce guar powder does not completely separate the guar from other plant materials, which are not soluble in water. Consequently, as much as 10% of the guar powder will not dissolve.

Derivatization of guar gum leads to subtle changes in properties, such as, decreased hydrogen bonding, increased solubility in water-alcohol mixture, and improved electrolyte compatibility. These changes in properties result in increased use in different fields, like textile printing, explosives, and oil-water fracturing applications.19

Guar can be derivitivized with propylene oxide, to produce hydroxyopropylguar (HPG). HPG is more stable at an elevated temperature than guar; therefore HPG is better suited for use in high temperature (>300F [150C]) wells.94 The additional processing and washing removes much of the plant material from the polymer, so HPG typically contains only about 2 to 4% insoluble residue. It has generally been considered to be less damaging to the formation face and proppant pack than guar, although recent studies have indicated that guar and HPG cause about the same degree of pack damage. Hydroxypropylguar substitution makes HPG more stable at an elevated temperature than guar; therefore, HPG is better suited for use in high-temperature wells. The addition of the less-hydrophilic hydroxypropyl substituent also makes the HPG more soluble in alcohol.

5.5 Scale Inhibitor

Scale inhibition is concerned with detecting and controlling chemical precipitation and deposition reactions that might occur from chemical and physical changes happening in the water or from mixing of two incompatible waters 98

Calcium sulfate, calcium carbonate and barium sulfate can cause scale problems if the concentration is high enough, and conditions such as pressure differential is high enough and the temperature is low enough. Scale can be detrimental to the production of the well.

If produced water is used then the problem of scale is exacerbated. The dissolved salts can potentially cause scale deposition. Many times the flowback fluid is diluted with fresh water to achieve the desired level of salts such as barium (Ba) and strontium (Sr). Table 2 shows a frac fluid water analysis and Figure 5 shows the resulting amount of Ba and Sr found in flowback waters of the same well.

The dissolved salts can potentially cause scale deposition. Many times the flowback fluid is diluted with fresh water to achieve the desired level of salts such as barium (Ba) and strontium (Sr). Table 2 shows a frac fluid water analysis and Figure 5 shows the resulting amount of Ba and Sr found in flowback waters of the same well.41

Control of mineral scales is through chemical treatment alone. All of the chemicals used for control of mineral scales work by interfering with crystal growth. There are three common types of chemical compounds used for this purpose, phosphate esters, phosphonates, and acid polymers. All scale inhibitors are highly water-soluble and will stay with the produced water to discharge. Typical treatment concentrations are 3 - 5 mg/L. Scale inhibitors are used either in squeeze treatments into the producing formation or by continuous injection.27

The compatibility of the fracturing fluid is a main factor that determines if and SI can be pumped in a fracture treatment. The inhibitor should not adversely affect fracturing fluid rheology, and conversely, the fracturing fluid should not reduce the inhibitor efficiency. Traditional SIs are typically low-pH systems which are not compatible with high-pH borate fracturing fluids. To allow SI placement during a fracturing treatment, a modified PPA SI was created to be applied in high pH borate fracturing fluid and not interact with borate crosslinkers. The inhibitor has a pH of 7.8 to 8.8. The inhibitor is compatible with the borates and has minimal effects on fluid rheology for a guar loading of 30 lbs/thousand gallons or more and some viscosity reduction for low-gel systems (20 ppt or less) 95

The use of other additives like scale inhibitors and clay stabilizers may interfere with compatibility and performance as well. It is important to use a scale inhibitor that is compatible with the anionic friction reducer as well as effective in the mix water type. Scale inhibitors that have been formulated to work in alkaline conditions (e.g. pH up to 9) have shown good compatibility with anionic friction reducers and do not inhibit performance (Fig. 7).

Most available scale inhibitors are phosponates and organo phosphonates which are anionic. This can create incompatibilities with some additives such as friction reducers and clay stabilizers. Some novel solutions to this problem have been tried in recent history. The organo phosponates can be reacted with calcium chloride to render them insoluble in order to successfully pump from the surface to the formation. The insoluble material can be made into the proppant matrix5. 41

Iron Control -

The three methods currently used to help keep iron in solution are pH control, sequestering agents and reducing agents (also effective as oxygen scavengers). These may be used individually or in combination, depending on the source and amount of iron dissolution expected.

pH control

pH control is accomplished by the addition of a weak acid that is very slow to react so that a low pH is maintained after the HCl has spent. Acetic acid is typically used for this purpose. A low pH aids in preventing the secondary precipitation of iron. SLBRS

Sequestering agents

Sequestering agents bond to the iron and hold it in solution so that it cannot precipitate. Citric acid, ethylenediaminetetraacectic acid (EDTA) and nitrilotriacetic acid (NTA) are some of the more commonly used sequestering agents. SLBRS

Reducing Agents

Reducing agents convert ferric (Fe3+) to ferrous (Fe2+) iron. The secondary precipitation of ferric iron occurs at about a pH of about 2.0. The secondary precipitation of ferrous iron hydroxides does not occur until the pH is above 7.0. Returned spent acids never have a pH this high. Erythorbic acid and sodium erythorbate are commonly used as reducing agents. Erythorbic acid is preferred over sodium erythorbate in sandstone acidizing because the addition of sodium salts of either sequestering or reducing agents to mud acid can lead to the precipitation of insoluble hexafluosilicate and acidity e. Hall and Dill reported that erythorbic acid is unstable in hot HCL and decomposes to form an insoluble precipitate. Although this is true, the decomposition process is slow and the acid normally spends long before precipitation can occur.

Most reducing agents also act as oxygen scavengers move dissolved oxygen from the fluid. The scavengers prevent the oxidation of ferrous iron to ferric iron. This maintains iron in solution by preventing the precipitation of ferric iron. The amount of iron that can be reduced depends on the quantity of chemical added. Aeration of the solution can introduce additional oxygen. SLBRS

Table ------ compares iron control additives showing t heir advantages and disadvantage, and the amount of each required in 1000 gal of 15%HCl to sequester 5000 mg/L of ferric iron at 65 °C (150 °F) for a minimum of 2 days.

The safest way to prevent damage to the reservoir from precipitated iron hydroxide is to clean or pickle the pipe with acid before acidizing the formation. The acid should contain large quantities of iron control additives and should be circulated out of the well, not pumped into the formation. In conjunction with this treatment a dispersed hydrocarbon phase should be incorporated or used as a pre-flush to remove pipe dope that could plug the perforation

The treatment of sour wells presents an entirely different type of precipitation problem. In addition to free sulfur precipitation, by the reaction of Fe3+ with H2S, the dissolved Fe2+ also precipitates as ferrous sulfide (FeS) on spending the acid. FeS precipitates at a pH of about 2. Laboratory and field data show that a combination of NTA, EGMBE, and a sulfide modifier is an effective system for controlling the precipitation of FeS and free sulfur when acidizing sour wells.

Crowe previously proposed a two-component system to address sour well problems. The system incorporates erythorbic acids to reduce ferric iron to ferrous iron, and EDTA to chelate ferrous iron and eliminate the precipitation of FeS.

Iron compounds found within the Fayetteville shale require an iron sequestering agent so that the compounds of iron will not precipitate out of the fracturing fluid and be deposited within the pore spaces of the reservoir, reducing the reservoir's permeability. SLBRS

5.6 Crosslinkers

Crosslinking agents enable the individual polymeric molecules to form a complex network of entangled polymer with the associated hydrated water. This results in higher molecular weight (higher viscosity) and less freedom of random motion (greater resistance to deformation) for the solvent and polymer. Not only does crosslinking result in higher viscosity, it lends stability to viscosity loss with time at elevated temperatures.

One of the simplest crosslinkers, the borate ion, is used to produce very viscous gels with guar and HPG that can be stable above 300F. At a pH above 8, borate ions and guar form an extremely viscous gel in a matter of seconds. To maximize the thermal stability of the crosslinked gel, the pH and borate concentration must be increased with an optimum pH of 10 to 12 depending on the borate compound and borate ion concentration.

Increasing the temperature reduces the pH, resulting in a lower crosslinker concentration and lower viscosity. Attempting to compensate for the detrimental effects of temperature by increasing the H3BO3 concentration can cause sysersis (overcrosslinking) of the gel 94

Regardless of the gel composition or viscosity, all fracturing gels thin with shear and heat. However, some gels return to their original state once shear or heat is removed. Typically, borate crosslinking is reversible; crosslinks form and then break, only to form again. If the polymer is not thermally degraded, this reversible behavior continues to accommodate changes in shear rate or temperature. 94

The composition of the crosslinked fluids is carefully optimized to obtain the desired performance (rheology and proppant transport, thermal stability, crosslinking rate, cleanup, etc). Many factors influencing the performance must be considered during the selection of a fracturing fluid candidate and monitored during onsite preparation. To obtain the best possible performance from a crosslinked fluid, the following issues must be addressed:

1. Crosslinker Concentration

   Each fluid composition has an optimum range for crosslinker concentration dictated by the type of polymer, polymer concentration, and fluid pH. If the crosslinker concentration is too low, the crosslinking rate will be slower and the viscosity development will be lower than anticipated. If the crosslinker concentration exceeds the optimum range, the crosslinking rate will be faster than anticipated and the final viscosity may be much lower because of sysersis. Sysersis is the precipitation of the polymer from solution caused by the collapse of the polymer network. In the most severe cases, “free water may be observed at ambient sampling conditions. However, detection of sysersis in delayed crosslinked fluids usually requires heating the fluid to the anticipated downhole temperature to fully react all the crosslinker.

2. pH Control

   All crosslinked fluids have a specific pH range for optimum performance. If this pH is not maintained, the desired crosslinking range and thermal stability cannot be obtained. To minimize pH variation in crosslinked fluid, buffers are included with the crosslinked fluid. However, gross contamination of the fracturing fluid can overwhelm these buffers and compromise crosslinked-fluid performance. Proper pH control is critical to crosslinked-fluid performance and must be monitored diligently.

3. Chemical Contamination

A variety of common compounds and oilfield products can interfere with the performance of crosslinker compounds. Typically, these contaminant reduce or eliminate crosslinking and produce a fluid with a slow rate of viscosity development (extremely long crosslink time) and significantly lower viscosity. In the most obvious cases, no viscosity increase may be produced by the crosslinker. Among the “naturally occurring compounds that can be present in mix water are bicarbonate, phosphate and silicates. The source of many of these contaminants is the mix water used to prepare the fracturing fluid. In addition to naturally occurring contaminants, many surfactants, clay stabilizers and foaming agents can interfere with crosslinked-fluid performance. To avoid contamination with incompatible additives, fracture tanks and mixing equipment should be empty and clean before the mix water is loaded and fracturing fluid prepared. Furthermore, substitution of additives should not be approved without compatibility testing (typically, rheology testing at the anticipated fluid temperature) (SLBRS)

5.7 Surfactants

A surface active agent, or surfactant, is a material that at low concentration adsorbs at the interface between two immiscible substances. The two immiscible substances may be two liquids, such as oil and water ,a liquid and a gas, or a liquid and a solid. The surfactant becomes involved in the interface and lowers the amount required to expand the interface. Finally, the use of surfactants can be beneficial in promoting the flowback of injected fluids to restore the relative permeability to gas.41 Some bactericides and clay control agents are surfactants 94

Common surfactants are adsorbed rapidly onto a shale matrix. The formulation of the surfactants into a microemulsions (ME) allows the surfactant to travel further into the matrix allowing the surfactant to remain with the leading edge of the penetrating fluid. The addition of ME to the fracture treatment s has resulted in more than 50 to 100 % increase in load recovery and gas production41

Remarkably, in the design of most well treatments, surfactants are selected with little or no laboratory data to support the choice and sometimes without full knowledge of their properties at the conditions in which they will be applied. Improper surfactant selection can lead to results contrary to those intended and may be detrimental to the process of the treatment.

Surfactants owe their properties to their “dipolar” composition. The surfactant molecule consists of a water soluble (hydrophilic) group and an oil-soluble (lipophilic) group, which are separated from each other although linked by a strong covalent chemical bond. The molecules are classified into five groups according to the ionic charge carried by the water soluble group:

- Anionic
- Cationic

- Nonionic
- Amphoteric
- Fluorocarbons

Anionic Surfactants

Anionic Surfactants are commonly added to treatment fluids. These surfactants carry a negative charge when they ionize in an aqueous solution. Because most reservoir minerals are also negatively charged at near neutral and higher pH values, anionic surfactants exhibit minimal adsorption. Some examples of anionic Surfactants are:

- Sulfates
- Sulponates
- Phosphates
- Phosphonates

Of these, the most common anionic surfactants are sulfates and sulfonates. Anionic surfactants are sensitive to the multivalent ions Ca2+ and Mg2+. These tend to precipitate anionic surfactants, although this tendency can be overcome to some extent by increasing the surfactant concentration. Anionic Surfactants are used primarily as nonemulsifying agents, retarding agents and cleaning agents.

Cationic Surfactants

Cationic surfactants carry a positive charge when they ionize in aqueous solutions. There are two general categories of cationic surfactants. The first category consists of long-chain primary, secondary and tertiary amines. They are soluble only in acidic solutions where they ionize to form a long-chained cation and simple anion salt.

- Primary amine
- Tertiary Amine
- Quaternary Amine

The second important category of cationic surfactants is the quaternary ammonium compounds. These ionize to form long-chained cations over a long range of solution pH. Cationic surfactants experience the same sensitivity to multivalent ions or increased concentrations of dissolved solids as anionic surfactants; therefore, the same care must be exercised in their application as with anionic surfactants. Cationic and Anionic Surfactants are generally incompatible. When mixed, they tend to precipitate in aqueous solutions.

Nonionic Surfactants

Nonionic surfactants have no charge at all in the hydrophilic group and a long chain organic for the lipophilic group. The water-soluble group is a polymer made from either ethylene oxide or propylene oxide. Other types include alkyanol amine condensates and amine oxides. The general products are as follows:

- Ethylene oxide polymer
- Propylene oxide polymer
- Alkyanol amine condensate
- Amine oxides

Nonionic surfactants obtain their water solubility by attaching the long hydrocarbon chain to a highly soluble molecule such as polyhydric alcohol or by reacting it with ethylene oxide. Most of the compounds in this classification are esters, ethers and ether-esters. The lipophilic group may be derived from natural oils and fats, petroleum oils or synthesized hydrocarbons. The hydrophoilic group is usually a polyhydric alcohol or an alkyd oxide polymer. These surfactants are used as non emulsifiers and foaming agents.

Surfactants, or surface-active agents are used in acidizing to break undesirable emulsions, reduce surface and/or interfacial tension, alter wettability, speed cleanup, disperse additives and prevent sludge formation. The use of surfactants requires careful selection of and appropriate molecule.

Amphotoric Surfactants

Amphotoric surfactants have a hydrophilic group that changes from cationic to nonanionic to anionic with increasing pH. In other words, if the solution is acidic, the amphoteric surfactant acts like a cationic surfactant; if the solution is neutral, it acts like a nonionic surfactant; and if the solution is basic, it acts like an anionic surfactant. These properties are derived from the two groups of opposite charge on the surfactant head. The amphotoric are usually either amine sulphonates or amine phosphates. The general chemical are:

- Amine Sulphonates
- Amine Phosphonates

Fluorocarbon Surfactants

Fluorocarbons form surfaces of lower free energy than hydrocarbon surfaces. Consequently, fluorocarbon surfactants lower the surface tension of solutions to a greater extent than hydrocarbon surfactants. Surface tensions as low as 30 dynes/cm can be obtained using surfactants with a hydrocarbon tail. Values as low as 17 dynes/cm have been reported using fluorocarbon surfactants. Fluorocarbons are commercially available in anionic, cationic, and nonionic forms. 94

5.8 Clay Stabilizers

Clay swelling is caused by the introduction of incompatible fluid or relatively fresh water (water of lower salinity or ionicity than the original pore solution) into the pores. Once clay particles are dispersed, they can block pore spaces in the rock and reduce permeability.

Clays can swell or migrate (or both), resulting in permeability damage. Severity of damage caused by swelling clay and clay migration is dependent on the following parameters:

- clay type
- clay content
- clay distribution
- pore-size distribution
- grain-size distribution
- quantity of cementing materials (for example, calcite, siderite, and silica)

Susceptibility to damage is evaluated using X-ray diffraction, a scanning electron microscope, and thin-section point counting.

Three methods of clay control are known to be effective. These are:

- Ionic neutralization
- Organic barrier
- Particle fusion

Ionic neutralization is commonly used in hydraulic fracturing and is accomplished using brines, polyvalent inorganic cations, and quaternary amine polymers. In the formation, the clays are generally not dispersed as long as their chemical environment is not changed. For this reason, brines are not nearly so damaging to sandstone as is freshwater. Solutions containing 1% to 3 % KCl are commonly used as the base liquid in fracturing fluid to stabilize clays and prevent swelling. KCl is used more often than NaCl or NH4Cl because K+ stabilizes clays better against invasion of water and, consequently, prevents swelling. All of these salts help maintain the chemical environment of the clay particles, but they do not provide permanent stabilization.

Many flow tests and Capillary Suction Time (CST) evaluations show that 2% KCl has a marginal effect on swelling clays. To get the most benefit, tests show 4% (wt) KCl is often better. Cost then becomes the issue, so what are the alternatives? A common KCl substitute or tetramethyl ammonium chloride shows very little impact at 2 gpt in this test. 2% KCl with 2gt clay stabilizer is similar to 2% KCl at 21 sec. 15 sec was obtained at 5 gpt. 41

Temporary clay stabilizers are designed to prevent dispersion of clay particles with a positively charged nitrogen molecule. Such products are intended replacements for KCl as a temporary clay-control additive. If not treated, clay particles in the reservoir rock may swell (if they contain an expandable clay layer) and/or migrate to damage fracture conductivity from migration of labile shale particles. 125

The organic tetramethyl ammonium chloride is an effective stabilizer. All these salts help maintain the chemical environment of the clay particles, but they do not provide permanent protection. More permanent methods for controlling clay migration involve the use of quaternary amines or inorganic polynuclear cations. The latter materials, such as zirconium oxychloride and hydroxyaluminum are used primarily in matrix –acidizing treatments to neutralize the surface face charge on clays. Unfortunately, they have limited compatibility with higher pH fracturing fluids

The use of other additives like clay stabilizers may interfere with compatibility and performance. Some clay stabilizers can possess a strong cationic nature (e.g. quaternary ammonium compounds). However, not all quaternary ammonium compounds have the same affinity for water. The quaternary ammonium compounds found in some biocides have a hydrophobic moiety on the molecule that may explain why these compounds prefer to associate with the polymer versus stay in bulk solution (e.g. presence of a precipitate). The permanent clay stabilizers have a strong cationic nature and have been shown to precipitate out of solution with anionic reducers.

.

A polynuclear ion with a net charge of +8, +12, or more may be several million times more attracted to a clay particle than monovalent or divalent cations. Consequently, from electrostatic considerations alone, polynuclear ions should almost immediately displace all of the exchangeable cations and be very tightly held to the clay surface. These however have tendency to crosslink frac fluids so are not used with most stimulation fluids. A monomolecular film of quaternary amine polymer is strongly adsorbed on the surface of the clays by cation exchange. More permanent stabilization is claimed since the clay particles are bridged together by multiple cationic sites along the polymer chain. To destabilize the clays, simultaneous release of all cationic sites is required for exchange with other ions in the formation brine. Quaternary amine polymers are water soluble and leave the formation water-wet. Quaternary amine polymers may be used in water-base fracturing fluids under acidic, neutral, and basic conditions.

Organic barrier include some cationic surfactants that prevent deflocculation of clays by their adsorption on the clay surface (cation exchange). These cationic surfactants make clay and sandstone surfaces oil-wet. The oil-wet condition prevents the adsorption of water which would otherwise deflocculate the clays.. This method temporarily reverses the wettability of the rock, resulting in a decrease in the permeability of the oil due to water entrapment. In most cases, reversing the wettability of the rock is undesirable.

Particle Fusion method is technically an anionic stabilization. In this method, the repulsive forces between the dispersing clay particles are destroyed by simply destroying part of the clay mineral itself. This can be accomplished by the use of the various anions of fluoride, phosphate, borate, and to some extent hydroxide.

Low-toxicity clay stabilizer (LTCS) products have recently become popular effective alternative replacement for the highly toxic temporary clay stabilizers that are composed of the tetraallyl ammonium chloride (TAAC) salt, tetramethyl ammonium chloride (TMAC). Such chemistry becomes an important consideration for HVR fracturing and water reuse.

5.9 Breakers

Breaker fluids are used to degrade the fracturing fluid viscosity, which helps to enhance post-fracturing fluid recovery, or flowback. Breakers can be mixed with the fracturing fluid during pumping, or they can be introduced later as an independent fluid. There are a variety of breaker types including time-release and temperature-dependent types. Most breakers are typically acids, oxidizers, or enzymes (Messina, Inc. Web site, 2001).

Thermal breaking of the polymer backbone generally occurs in wells with bottomhole temperatures greater than 107°C. A breaker should be added to the fracturing fluid when the bottomhole temperature is less than 107°C. Breakers are added to fracturing fluids for two reasons:

- To reduce the viscosity of the fluid so that the fracturing fluid can be cleaned up quickly following a treatment.
- To degrade the fluid and thus reduce proppant-pack conductivity damage.

Breakers perform both these tasks by attacking the backbone of the polymer and reducing its size. The fluid viscosity decreases as the polymer molecular weight decreases.

The breakers currently used in water-base fluids are enzyme breakers and oxidative breakers. Enzyme breakers such as hemicellulose begin to degrade the polymer immediately. These enzymes are similar to those that bacteria use to digest the polymer. The most common oxidative breakers are peroxydisulfates. Thermal decomposition of peroxydisulfate produces highly reactive sulfate radicals which attack the polymer backbone. Thermal decomposition is slow at temperatures less than 52°C. These breakers can be expanded into lower temperature applications 16° to 52°C if an amine is concurrently added to catalyze the reaction. Oxidative breakers are effective over a wide pH range (3 to 14) and demonstrate breaking properties superior to enzyme breakers (based on observed proppant-pack permeability reduction

Which type of breaker is best is currently a topic for much debate. Both of the common types of breakers have strengths and weaknesses.

1) Performance at high temperature

   Oxidizers have been identified for high-temperature applications. Current enzymes have some activity up to 225F (105C). Higher temperature versions will most likely be identified in the future.

2) Completeness of break

Theoretically, enzymes should have an advantage because of their catalytic nature. However, enzyme sensitivity to temperature, pH and other chemicals can significantly shorten the life-time of the enzyme. Under ideal conditions (less than approximately 180F (80C), pH 5-8, enzymes break the polymer into smaller fragments than oxidizers do, but there is no information in the literature to document that significant production of simple sugars results.

3) Duration of Breaking

Enzymes, unless exposed to extremes of pH or temperature react with the polymer over a more extended time period (days) than oxidizers (hours)

4) Fast Break

A fast break to allow quick turnaround of the well is accomplished much better with oxidizers.

5) Chemical sensitivity

Enzymes are highly sensitive to pH so control of pH within a limited range is necessary for predictable performance. Oxidizers are affected by the presence of curable-resin-coated proppant, whereas enzymes are not.

Currently, field users when asked by clients to use a breaker for slickwater fluid formulations have been using J218 at 1-2 ppt for their wells at 170 degrees F and 110 degF (inTouch Ticket 4289732). We do not recommend the use of M91 as a breaker in slick water systems. (SLBRS)

5.10 Oxygen Scavengers

Oxygen scavengers like ammonium bisulphate or sodium thiosulfate have been known to generate free radicals that can degrade polyacrylamide solutions (See SPE 9299, SPE 14232, SPE 12008). With parts per billion (ppb) concentrations of catalysts like cobalt (Co) or iron (Fe); O2 scavengers like ammonium bisulphate can degrade (up to 80% loss of viscosity) polyacrylamide polymers in minutes at moderate temperatures

5.11 Corrosion Inhibitors

The chemical corrosivity of produced fluids is most commonly associated with the presence of hydrogen sulfide, carbon dioxide, or oxygen

A corrosion inhibitor is a chemical that slows the attack of acid corrosion on drill pipe, tubing or any other metal that the acid attacks during treatment. Brief explanations of corrosion mechanisms, corrosion inhibition and techniques for evaluating inhibitor performance are presented in this section.

Any additive that alters the tendency of the corrosion inhibitor to adsorb will also change its effectiveness. For example, surfactants added to acid for various purposes may form miscelles that solubilize the inhibitor, thereby decreasing the tendency for the inhibitor to absorb on the metal surface. Inorganic salts and mutual solvents can also interfere with the inhibitor adsorption. If possible, additives that reduce the effectiveness of inhibitors should be included in a pre-flush or over flush rather than in the acid flush.

Chemical corrosion is one area where the application of technology, through the use of corrosion resistant metallurgy, can reduce the use, hence the potential discharge, of chemicals. Well designed equipment coupled with a sound chemical treatment program can reduce chemical consumption by as much as 90% while significantly improving the operational safety and longevity of a facility. That in turn reduces the risk of a catastrophic failure that can result in a loss of resources (oil and gas), human injury, or spills. Carbon dioxide is the most common corrodent, while hydrogen sulfide poses the most significant risk to human health and the environment.

Oxygen

Oxygen is not typically found in unaltered produced fluids. Oxygen is usually introduced as the produced fluids are treated. Most corrosion inhibitors work by adsorbing onto exposed metal surfaces. Corrosion inhibitors are very complex compounds that can be sorted into four generic groups:

- amine imidazolines,
- amines and amine salts,
- quaternary ammonium salts, and
- nitrogen heterocyclics.

Oil soluble corrosion inhibitors are most commonly used since they are usually the most effective at providing a stable, durable film. The concentration of active ingredient in bulk corrosion inhibitors is usually 30 - 40%. The remaining material (inert ingredients) is usually a hydrocarbon based solvent like heavy aromatic naphtha. When improved water solubility is required, dispersants or surfactants may be added, or water soluble corrosion inhibitors such as quaternary amines can be used. Oil soluble inhibitors will follow the oil stream to the refinery and water-soluble inhibitors will stay with the water phase. Selection of a particular corrosion inhibitor is usually made based on the type of corrodent, the type of production, prior experience, and laboratory or field testing. Corrosion caused by oxygen is controlled by chemical reaction rather than adsorption. Oxygen inhibitors (scavengers) are usually some form of sulfite, with ammonium bisulfite the most common form being used. These compounds and their reaction products (sulfates) are highly water soluble and will be discharged with the produced water. Oxygen scavengers are typically used at concentrations of less than 100 ppm. Oxygen scavengers are frequently used to treat injection water.

Corrosion inhibitors are required in acid fluid mixtures because acids will corrode steel tubing, well casings, tools, and tanks. The solvent acetone is a common additive in corrosion inhibitors. These products are diluted to a concentration of 1 gallon per 1,000 gallons of make-up water and acid mixture (Halliburton, Inc., Virginia Site Visit, 2001; Schlumberger, Ltd., 2001).

Fluid-Loss Additives

Fluid-loss additives restrict leakoff of the fracturing fluid into the exposed rock at the fracture face. Because the additives prevent excessive leakoff, fracturing fluid effectiveness and integrity are maintained. Fluid-loss additives of the past and present include bridging materials such as 100 mesh sand, 100 mesh soluble resin, and silica flour, or plastering materials such as starch blends, talc silica flour, and clay (Ely, 1985).

Fluid-loss control is essential for an efficient and successful fracturing treatment. The loss of fracturing fluid into the formation is generally considered to be detrimental because it decreases the fluid efficiency (or decreases the fracture

Temperature Stabilizers

Stabilizers are used to prevent degradation of water-base fracturing fluids at temperatures greater than 200°F (93°C). The temperature stability of a fracturing fluid is dependent on the following:

- The stability of the polymer. Guar is less stable than HPG.
- The fluid pH value. Guar and guar derivatives are hydrolyzed at a low pH value, especially at elevated temperature. A high-pH fluid should be used to enhance long-term fluid stability.
- The presence of breakers. Fracturing fluids are degraded by breakers.

5.12 Proppant

The amount of proppant used in slickwater fracs is relatively6 SPE 119900 small when compared to conventional fracs. Selection of proppant is critical in a slickwater design. With the use of extremely large volumes of water of over 5 millions of gallon, proppant placement can be an issue. Brannon et al 7 have studied the placement of proppant in slickwater applications. Their findings showed that a 20/40 mesh lightweight proppant with a specific gravity of 1.25 in viscosified 9.4 lb/gallon brine had virtually no proppant settling. For proppant placement there are several factors to keep in mind while designing a frac job, they are specific gravity of the fluid and proppant, flow rate of slurry, and fluid viscosity.

Proppant Transport

Viscosity and flow rate both affect the ability of the fluid to keep the proppant in suspension. The preferred fluid for most of these fracture treatments has been slickwater with low concentrations of proppant: usually 20/40 or smaller size sand.137

The bulk of proppant that do not become entrained in the fracture s created by the frac job are removed during the post frac flush. These tend to settle out in the P tank on surface with lesser amounts entrained in the FR that is carried back to surface with the Flowback. Commonly, aggressive flowback may result in erosion of the frac sand from the near wellbore formation.

For proppant placement there are several factors to keep in mind while designing a frac job, they are specific gravity of the fluid and proppant, flow rate of slurry, and fluid viscosity.41

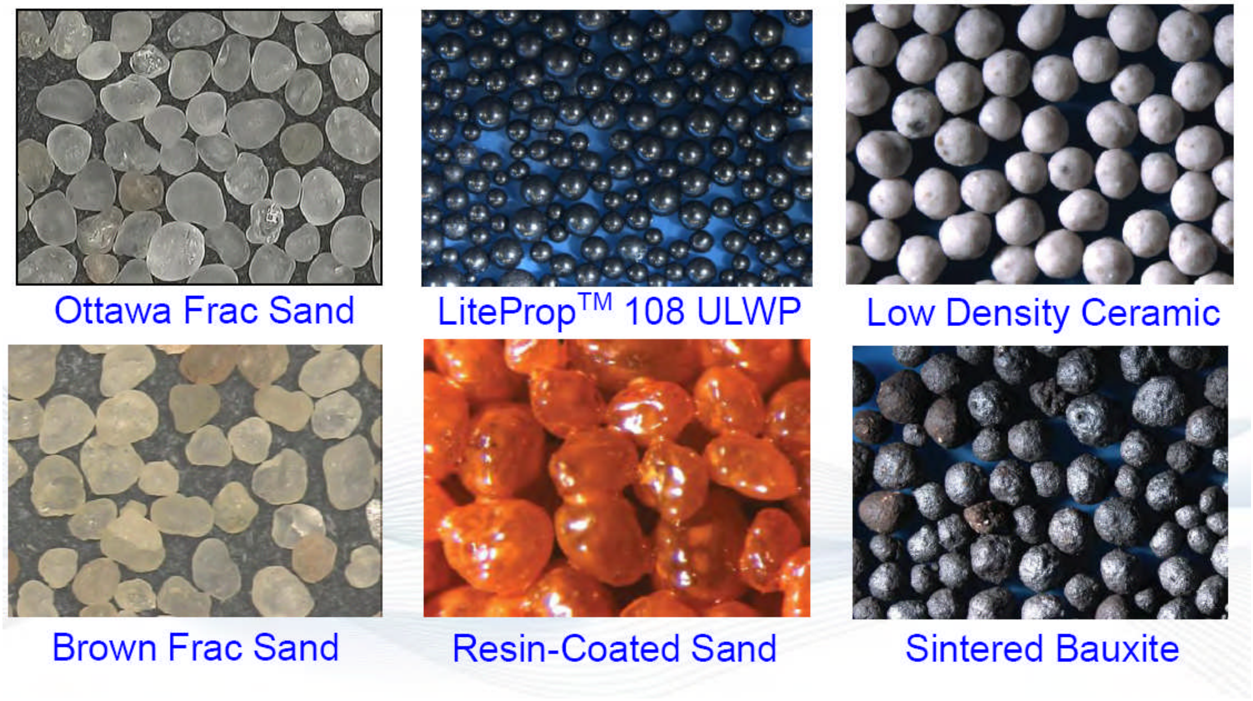


Figure 26 Source 84

Figure 27 Source ?????

Water-Base Fluids

Water-base fluids are the most widely used fracturing fluids because of their low cost, high performance, and ease of handling. Potential problems with water-base fluids are damage to highly water-sensitive formations and proppant-pack damage caused by concentrated polymer.

Polymers

Polymers are water-soluble, high-molecular-weight molecules that can be added to water to make a viscosified solution capable of suspending propping agents.

6.0 TYPES OF FRACS

Introduction

In most cases where the well type, bottomhole temperatures and other formation properties do not demand extreme design measures, several fluids can be considered as probable candidates. Since reservoirs vary significantly in terms of temperature, permeability, rock composition, and pore-pressure, many types of fluids have been developed to provide the characteristics described above. The design engineer must then narrow down the available options that suit the given conditions. Several important fluid, formations, economic and logistical characteristics should be considered when selecting fluids that are appropriate for particular job. This section will give an overview of those criteria. The following types of fluids will be discussed specifically:

- Slickwater
- Linear water-base fluids
- Crosslinked water-base fluids
- Foamed fluids
- Viscoelastic Fluids

6.1 Fracturing Fluid Selection General

Fracturing fluids are required to efficiently open and propagate a fracture and transport proppant throughout the length of the fracture. The selection of appropriate fluids for a treatment has significant influence on the treatment effectiveness and cost. A number of considerations must govern fracturing fluid selection. These are (in order of importance)

- Ability to create a fracture with adequate conductivity (that is, transport required slurry concentrations)
- Result in as little polymer-induced proppant-pack damage as possible
- Require lower pumping and treatment pressure capacity by reducing the friction pressure drop.
- The fluid should provide good fluid-loss control.
- The fluid should break and clean up rapidly after pumping.
- The fluid should be as economical as possible.

All these considerations are affected by the polymer concentration and type that controls both the fluid viscosity and the resulting friction pressure. Thus, the polymer concentration must be engineered appropriately so that the concentration is adequate but not excessive. There are other less important considerations in fluid selection. While these should be taken into account, they should not govern the fluid selection to the detriment of the previously mentioned important concerns. These include minimization of fracture-face damage, which would be the result of unavoidable leakoff, and compatibility problems between the fracturing fluid and reservoir fluids and rock. In addition, there has been much industry concern about post-treatment cleanup. This concern has led to the use of energized and foam fluids. Although these fluids have a decided edge on cleanup, energized and foam fluids become impractical when super-high proppant concentrations are necessary because proppant is added exclusively to the liquid portion of the fluid. The super-high proppant concentrations may exceed the capabilities of the mixing and blending equipment. Foam fluids may be more appropriate in very tight formations where fracture conductivity is less important.

Rheological Properties and Viscosity Requirements

The fracturing fluid will almost totally suspend propping agents if the viscosity is maintained at 100 cp ±25 cp at 170 sec-1 during pumping. When designing a fluid to meet this requirement, the reservoir temperature must be known. The pad and half of the slurry will be exposed to the bottomhole static temperature (BHST). The fracturing fluid viscosity will decrease as a function of both increasing temperature and increasing exposure time at this temperature. Reservoirs with temperatures greater than 150 deg c require fracturing fluids with higher polymer concentrations for the pad fluid and for the early treating fluid stages.

Polymer concentration may be reduced as the treatment progresses because the later portion of the treatment will not be exposed to BHST for an extended period of time. Another issue considered in the fluid selection is the viscosity needed at the entrance of the fracture to avoid any proppant bridge. That is, the fracture must have a minimum width, which is a function of proppant size, concentration and volume injected, to be able to admit the proppant. Proppant bridge at the wellbore will bring serious consequences for the success of the fracture treatment. The additional pressure drop near the wellbore when tortuosity and/or parallel fractures occur can be decreased using very viscous fracturing fluids. A better solution is to recognize and minimized near well bore abnormally with adequate perforating practice. Indeed when the NWB restriction is large a higher viscosity is required to create sufficient width and force the entry in the fracture. It is known that fracture width is a function of the fracturing fluid viscosity and Young modulus. In soft formations, characterized by low Young modulus (<1x106 psi), the same viscosity requirement for suspending proppant is enough to avoid proppant bridge. However, previous experiences and a fracturing simulator should be used to confirm that for each case. In high Young Modulus (>5x106), high viscosity may be needed to create enough fracture width to avoid any wellbore restriction. Previous experience is the most reliable information to try to identify near wellbore restriction problems.

Fracturing fluid pumped during the process is generally in turbulent flow in the well bore and perforations and in laminar flow in the fracture. The accurate characterization of the rheological properties of the fluid is necessary for the successful application of the hydraulic fracturing process. The turbulent flow frictional loss in the well bore and perforations is important to design and perform a fracturing treatment. The frictional losses are used to predict the surface treating pressure and injection rate.

The laminar flow behaviour of the fluid in the fracture is critical to the design of proppant transport and fracture geometry. The fracture geometry and extension during the treatment depends to a high degree on the rheological properties of the clean as well as proppant-laden fluid. Fracturing fluids are generally classified into three types: aqueous-based, oil, and foam fluids. Aqueous-based fracturing fluids have been widely used in the oil and gas wells because of their low cost, high performance, greater suspending power, environmentally acceptable and ease of handling.20

Fluid Friction Pressure

The surface pressure during a fracturing treatment is a function of fracture gradient, net pressure, the hydrostatic of the fracturing fluid, the friction pressure in the tubulars of the fracturing fluid, and the perforations and near-wellbore friction. Reducing the surface pressure has considerable advantage on cost and reduce the wear of the fracturing equipment. Fluid friction pressure in tubulars, through the perforations and along the fracture has a direct relationship with fluid viscosity. Hydrostatic pressure is a function of the fluid density. Therefore; the two important parameters to consider in the fluid selection are the hydrostatic pressure and friction in the tubulars. As an example, foam fluids have less hydrostatic head and result in higher surface pressures than water-base fluids. Oil-base fluids have also lower density than water-base fluids. Similarly, the higher friction pressure in the tubulars, the higher surface pressure is needed for the same fracture gradient (or same bottomhole pressure). On deep wells, it is preferred to have fracture fluids with a fluid density such that the surface treating pressure is not too high. Fluid friction pressure through the perforations and along the fracture is usually low, and is therefore neglected. A polymer concentration increase will cause a friction pressure increase. Large differences will be observed at low flow rates in small diameters. On the other hand, using a lower density fluid is an advantage to flow back a well more rapidly when reservoir pressure is low. This is one of the main reasons for the selection of foamed or energized systems and to some extent for gelled oil.

Fluid Compatibility with Reservoir Fluid and Rock

Chemical analysis of the reservoir fluid and rock may be considered when selecting a fracturing fluid. Clay content, iron precipitation, asphaltene and paraffin deposition, are among the compatibility considerations.

The water sensitivity of the reservoir rock has traditionally prompted a division between water-base fluids and oil-base fluids. However, this consideration is often the cause of inappropriate fluid selection and less-than-optimum fracturing treatments. Essentially, if the reservoir is mildly-to-moderately water sensitive, the selection process outlined for a gas well should be followed.

While the use of oil-base fluids in oil wells is often suggested, these fracturing fluids deserve certain additional considerations. The cost of pumping an oil-base fluid is usually much greater than the cost of pumping a water-base fluid because of the cost of the oil. Oil-base fluids, because of their inordinately high friction pressure losses, typically exhibit high hydraulic horsepower requirements.

Safety considerations must also be addressed because of the flammability of the oil. Any problem leading to fluid leakage has the potential for extreme fire hazard.

The perceived advantage of oil-base fluids is that the reservoir is exposed only to a fluid that is related to the reservoir fluids. However, several studies have shown that fluid leakoff and relative permeability-induced damage are not usually severe problems. Fracture face damage should never be a criterion for the fracturing fluid selection to the detriment of fracture conductivity.

The water sensitivity of sandstone is a phenomenon whereby the permeability of the sandstone is decreased rapidly and significantly after the sandstone is contacted with water. Most of the literature concurs that the water sensitivity results from clay swelling, clay particle migration, or combination of these effects, depending on the composition of the rock. The clay particles that migrate can bridge across the pore throats near the fracture face region and in extreme cases can reduce the well productivity of the well. Similarly, Clays may change volume as the salinity of the fluid flowing through the formation changes. The most common migratory clay is kaolinite and the most common swelling clay is the smectite. Traditionally, the control of clay swelling and migration has been done in water-base fluids using several salts. The most common salts used today are potassium chloride, amine and polymeric amine compounds. The water sensitivity of the reservoir rock has traditionally made a division between water-base fluids and oil-base fluids. Clay dispersion may have a major impact in an unfractured well and a marginal impact in a fractured well under normal conditions. The reason for this difference is that a fracture increase dramatically the contact area and it can tolerate high fracture face damage without affecting much the gain of productivity (even a very small fracture can ` increase the surface contact in a wellbore by greater than 300 times). Several studies (Analytical and reservoir simulations, explained later in cleanup section) have shown that a not very deep damaged zone around fracture has minimal effect on production as long as the fracture has adequate conductivity. The number of additives available in water-base fluids and its cost effectiveness should always be considered in the fluid type selection. The cost of pumping an oil-base fluid is usually much greater than the cost of pumping a water-base fluid because of the cost of the oil. Additionally, oil-base fluids have higher friction pressure losses than water-base fluids and always present a greater risk of fire or contamination on location

Leakoff

The rate of fluid leakoff to the formation is one of the most critical factors involved in determining fracture geometry for a given treatment design. The volume of fluid lost during the treatment determines the fracturing fluid efficiency or the ratio of fracture volume to volume pumped. The fluid loss to the formation is a filtration process that is controlled by the fracturing fluid composition, differential pressure between the fracture and the reservoir, reservoir transmissibility (kh/mu) and diffusivity. Since each fluid type and polymer concentration have a different leakoff coefficient (even for the same rock conditions), it is important to consider it in the fracturing fluid selection. The best way to determine the leakoff coefficient of a fracturing fluid in a given reservoir rock, is to perform a calibration test.

Fluid Cleanup

Fracturing fluid cleanup is the ability of flowing back all the components of the fracturing fluid. Cleanup is governed by several mechanisms and the composition of the fracturing fluid affects drastically the cleanup process. It is known that polymeric fracturing fluids leave residues in the near fracture face region and in the proppant pack, thus decreasing the productivity of the well. On the contrary, Viscoelastic (VES) fluids are a free-polymer fluid that almost does not leave residues in the fracture, giving high conductivity fractures. During a fracture treatment, the fracturing fluid starts creating the fracture and as the fracture is progressively growing the fluid leaks off into the formation. If a polymeric or wall building fluid is used, a polymeric filter cake is built on the fracture face and the concentration of the polymer of the fluid that remains in the fracture increases as the fluid leaks off into the formation. At the end of the job, the fracturing fluid inside the fracture could have a polymer concentration of about 10 times (or more) of the designed fracturing fluid. Non-wall building fracturing fluids such as slickwater and VES fluids will not create a filter cake on the fracture face and the fracturing fluid can enter the formation rock around the formation face if there is suitable permeability.

Therefore, when a polymeric fracturing fluid is used in a fracturing treatment, the conditions at the end of the job are as follows:

- A proppant pack in the fracture full of a very high viscous fluid with high concentration of polymer.
- Fracture faces with a polymer filter cake.
- A near fracture face region (around the fracture) of the formation with high saturation of fracturing fluid filtrate. This filtrate will have a viscosity value very close to the water at reservoir temperature.

And when a non-wall building fluid is used, the following scenario is obtained at the end of the job:

- A proppant pack in the fracture full of the non-wall building fluid.
- A near fracture face region (around the fracture) of the formation with high saturation of the non-wall building fracturing fluid.

With one of the above scenarios, the well is put on production and it is expected that the base fluid, the filtrate and the polymer (if any) will flowback to the wellbore. This flowback of the components of the fracturing fluid is known as cleanup. It is well known that fracturing fluid cleanup could dramatically affect the hydrocarbon production rate and cumulative recovery but its mechanisms are not very well established yet.

6.2 Slickwater

According to Schlumberger, slickwater (a low-viscosity water-based fluid and proppant) is more commonly used in deeper high-pressure shales, while nitrogen-foamed fracturing fluids are commonly pumped on shallower shales and shales with low reservoir pressures.64 At least two companies operating in the Marcellus shale agree with this analysis.

Description

Slickwater treatments are designed to be pumped with little or no viscosity added to the frac fluid. The objective of a slickwater treatment is to maximize creation of surface area with the least amount of fluid damage for the smallest cost. To this end they are pumped at the high rate with relatively low proppant concentrations due to the poor proppant transport characteristics of the low viscosity fluid. Leakoff is not a concern with these fluids as they are pumped in extremely low permeability reservoirs. Leakoff can arguably only occur though secondary permeability networks and create complexity in the fracture network which will allow access to more surface area which can be ultimately beneficial to production. To be economic the fluids are generally simple with usually only three additives added by the service company.

Friction Reducer

Large polymers called friction reducers are added to the fracturing fluid whose only function is to decrease the fluid friction. The reduction of friction reduction is to either maximize rate or decrease amount of required horsepower and/or maximum pressure rating of surface equipment. Friction reducers are added at order of magnitude smaller concentrations relative to polymer addition in other fracturing fluids. Each friction reducer has different capacity for drag reduction with respect to water depending on the ionic strength of the mix water used to blend the fluid. The use of source water, produced water, flowback water or a combination of these is common for high rate fracturing in tight gas formations. The presence of salts or scales in these waters can present issues in fluid performance (e.g. flocculation of solids). The salts will reduce the effectiveness of the friction reducer. Divalent ions such as calcium and magnesium are especially detrimental. The increased salt concentration causes less drag reduction per gpt of friction reducer added. This can be overcome by adding additional friction reducer to the fluid.

Bactericide

The bacteria in the water will not degrade the friction reducer (unlike guar based fluids) because friction reducers are synthetic polymers. There are different types of bacteria that oilfield applications typically are concerned with and these bacteria types include: general heterotopic bacteria (GHB), acid producing bacteria (APB), and sulfate reducing bacteria (SRB) bacteria. GHB and APB are aerobic bacteria and cause issues in the oilfield like corrosion or loss of viscosity in biopolymer fluids. The anaerobic sulfate reducing bacteria (SRB's) will sour the well and are usually of most concern.

Scale Inhibitors

Another issue with produced water is the solids/salts in the water that may precipitate. Options include filtering the water or adding flocculants for cleaning. If the goal is to prevent precipitation or scale formation when mixing different source waters, a scale inhibitor can be added to the fracture treatment.

Applications

Slickwater applications are generally for formations that have a low to very low permeability. The goal of all slickwater fracs is to maximize surface area contact. Slickwater has proven to be effective technique with appropriately mature shales with adequate organic content where contact area is strongly correlated to production. Also appropriate for formations with large amount of secondary porosity in which connection to these networks is desired. Slickwater is also desirable in formation where we are creating a large amount of complexity. This is seen in brittle rock with low stress anisotropy such as seen in many shale plays.

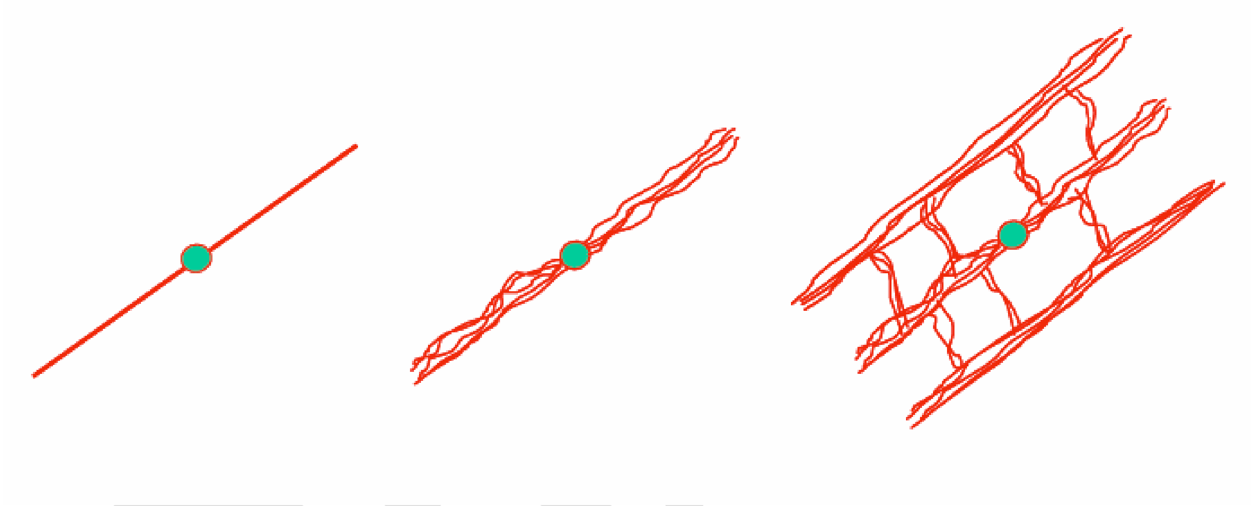


Figure 28 Complex Fracture Development

Fluid Use

The volumes expected on this are the highest because of the large fracture extent desired and the low prop concentrations. Since the use of the fluid is to create massive fairways in a lowly conductive rock the use of water is further amplified because not only are there large volume stages but the number of stages is large as well as it usually applied in horizontal multi stage completions.

Recyclability

Slickwater is the most forgiving in terms of its ability to be reused. A large range of fluid properties are permissible to get acceptable fluid performance. The biggest concern on these fluids is the presence of H_2S causing HSE and corrosion concerns upon surface handling of the fluids. Also of concern is the presence of excessive divalent cations that can act to inhibit friction reducer performance.

Slickwater			
Water Quality	**Range**	**Occurring Problems**	**Remedial Options**
Temperature (F)	38-350	Lower temperatures may prolong hydration of Fiction reducer	Use hydration Unit
pH	5.0- 8.5	pH below 5 may cause prolonged hydration , and pH greater than 8.5 may result in inadequate gelling	
		pH should be kept below 7.5 so that ferrous iron remain in solution	
Chloride (mg/L)	<90,000	High chloride concentration inhibits hydration	Blending, Mechanical Vapor Recompression, Recerse Osmosis. Ionization, Electrocoagulation
Divalent Cations	<5000	Inhibits hydration	Blending, Floc/coag, Ion ex, Electrocoagulation

Figure 30 Slickwater Sensitivities

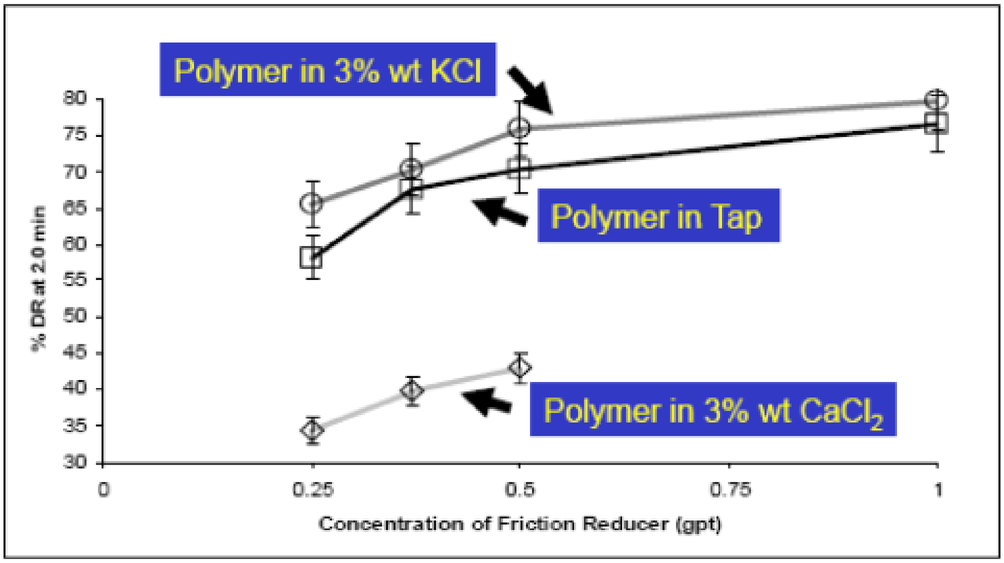


Figure 11 Effect of Ions on Friction Reducer Performance

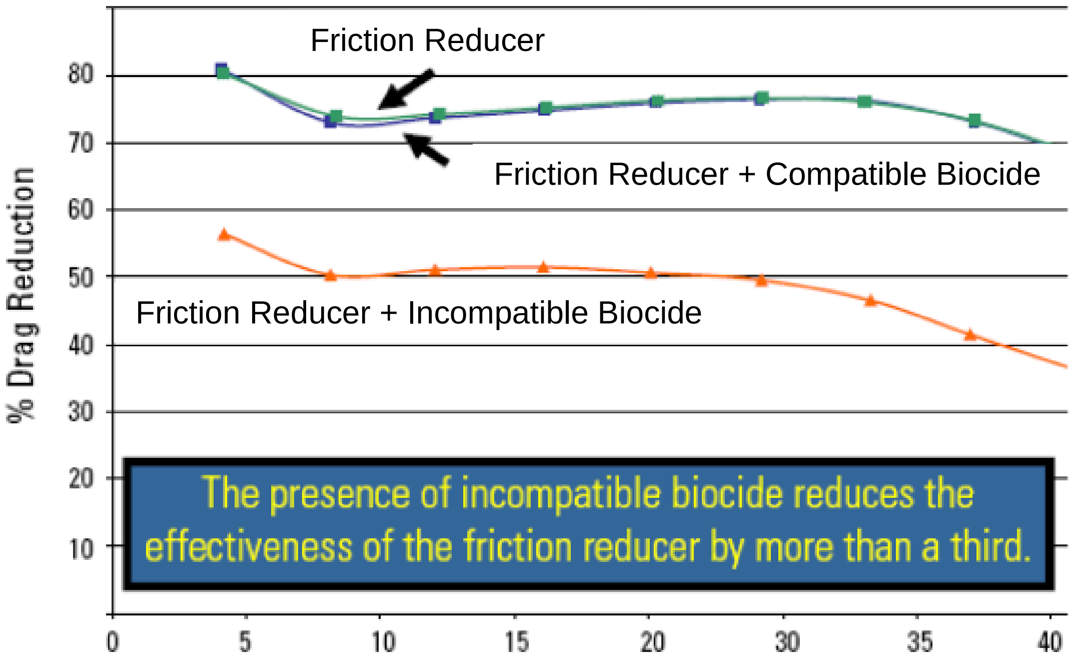


Figure 32 Effect of Incompatible Additives on Friction Reduction

Concerns

Low viscosity fluids provide poor proppant transport, which necessitates high pump rates, low proppant concentrations, and high volumes. The proppant transport can prove to be a problem for efficiency of propped height as a function of total frac geometry created. The volumes expected on this are the highest because of the large fracture extent desired and Low prop concentrations. These jobs are logistically the most demanding for fluid volume, horsepower, surface footprint and sand volumes. They also require extra consideration on flowback due to total volumes. Since a large amount of fluid is pumped and a large amount of surface area contacted on typical slickwater jobs then a large amount of ions can be dissolved and returned to surface in flowback which will have to be dealt with on disposal.

Although slick water fracturing has proved itself in many types of shale, there are many cases where SWF has not provided sufficient propped flow capacity to develop a gas or oil productive shale. For these cases, a hybrid fluid using SWF to open the fissures and a more viscous fluid to place the main body of the proppant may be warranted.40

6.3 Linear Gel Based Fluids

Description

Water-base fluids are the most widely used fracturing fluids because of their low cost, high performance, and ease of handling. Potential problems with water-base fluids are damage to highly water-sensitive formations and proppant-pack damage caused by concentrated polymer. Linear (non-crosslinked) fluids use gels of fresh water, seawater, or potassium chloride (KCl) brines as efficient and economical fracturing fluids.

Polymers

Polymers are water-soluble, high-molecular-weight molecules that can be added to water to make a viscosified solution capable of suspending propping agents. The two most common types are guar and hydroxypropylguar

Guar Gum

Guar is a long-chain polymer composed of mannose and galactose sugars. Polymers composed of sugar units are called polysaccharides. The guar polymer has a very high affinity for water. When the polymer is added to water, guar particles "swell" and "hydrate," which means the polymer molecules become associated with many water molecules and unfold and extend out into the solution. The guar solution on the molecular level can be pictured as long, bloated strands suspended in water. The strands tend to overlap and hinder motion, which causes an increase in the viscosity of the solution.

Hydroxypropylguar (HPG)

Guar gum comes from the endosperm of guar beans. The process used to produce guar powder does not completely separate the guar from other plant materials, which are not soluble in water. Consequently, as much as 10% of the guar powder will not dissolve. Guar can be derivatized with propylene oxide to produce hydroxypropylguar (HPG). The additional processing and washing removes much of the plant material from the polymer, so HPG typically contains only about 2 to 4% insoluble residue. It has generally been considered to be less damaging to the formation face and proppant pack than guar, although recent studies have indicated that guar and HPG cause about the same degree of pack damage. Hydroxypropylguar substitution makes HPG more stable at an elevated temperature than guar; therefore, HPG is better suited for use in high-temperature wells. The addition of the less-hydrophilic hydroxypropyl substituents also makes the HPG more soluble in alcohol.

Hydroxyethylcellulose

Hydroxyethylcellulose (HEC) is used when a very clean fluid is desired. These polymers have a backbone composed of glucose sugar units which appears to be similar to the mannose backbone of guar, but there is a significant difference. Guar contains hydroxl pairs which are positioned on the same side of the sugar molecule (cis orientation). In HEC, the –OH groups are on adjacent carbons, but they are on opposite sides of the ring (trans orientation). The cis arrangement is easily crosslinked, while the trans is not.

Xanthan

Xanthan is a biopolymer, produced metabolically by a microorganism. Xanthan solutions behave as power-law fluids even at very low shear rates, while HPG solutions become Newtonian. At shear rates less that 10 sec^{-1}, xanthan solutions suspend proppant better than HPG. Xanthan is more expensive than guar or cellulose derivatives and is used less frequently

Carboxymethylhydroxypropylguar

Carboxymethylhydroxypropylguar (CMHPG) is a "double derivatized" guar that contains the hydroxypropyl functionality of HPG as well as a carboxylic acid substituent. CMHPG is crosslinked with aluminum or zirconium complexes

Applications

- Linear frac fluids perform best in the following applications.
- depleted or underpressured wells
- low-permeability gas wells
- fracture treatments where leakoff is not critical to control
- Fracture geometries where height growth is a concern
- Economic optimization as it is a cost effective fluid
- Low temperature applications
- Substitute for Slickwater in large fracs for better proppant transport

Fluid Use

The volumes of linear gels used tend to be generally much lower than in slickwater operations on the order of 1/2 on stage size as well as usually less stages by ½ so up to ¼ of water demand. This is not, however, true if dilute linear gels are used in place of slickwater for a large complex fracture geometry objective. If it is directly substituted then water volumes are the same but fracture treatment cost is probably much higher in this case because base fluid cost is higher.

Recyclability

Linear gel can be reused but has some limitations. Of particular concern are residual bacteria which can metabolize the gel affecting the viscosity and the performance of the fracture treatment. Bacteria can also be an issue because recycled fluid contains residual gel that bacteria can use as a substrate to grow when contacted in surface storage and then introduced into the well causing souring or damage to the reservoir. Residual gel in fluid can also be a problem because polymers can accumulate and concentrate resulting in difficulty handling and more potential damage when reintroduced into the well. Linear gels require that the recycled water be appropriate for hydration of the new polymer to be added and there are many parameters that can inhibit hydration. The pH of the fluid and salinity of the fluid are the two key components to inhibit polymer hydration.

.

Sensitivities

Linear Gels			
Water Quality	**Range**	**Occurring Problems**	**Remedial Options**
Temperature (C)	15deg - 40 deg	Lower temperatures may prolong hydration of gel polymers	Passive cooling in tanks or ponds, heat exchanger; Hydration Unit
pH	6.0 - 8.0	pH below 6 may cause prolonged hydration of gel, and pH greater than 8 may result in inadequate gelling	Treat with Caustic
		pH should be kept below 7.5 so that ferrous iron remain in solution	
Chloride (mg/L)	<50,000	High chloride concentration destabilizes fluid	Blending, Mechanical Vapor Recompression, Recerse Osmosis. Ionization, Electrocoagulation
Iron (mg/L)	<25	Degrades and breaks polymers in gel, causing premature break and crosslink problems.	Iron Sequestration,oxidization
		Ferric iron will precipitate at the pH of natural environment becoming detrimental to the stimulation	
Sulfate (mg/L)	<1000	Causes scaling problems	Blending, Ion Ex, MVR, RO
Sodium (mg/L)	<1000	Destabilizes the fluid	Blending, Ion Ex, MVR, RO
Silica (mg/L)	<35	May inhibit the crosslinking of polymer gel	
Bacteria	0	Degrade gel viscosity,	Biocide, Ozone

Figure 32 Linear Gel Sensitivities

Concerns

Linear gels have relatively low viscosity and the only way to enhance the viscosity in linear gel is to add more polymer. The addition of temperature will further reduce the viscosity of these fluids. A balance must be found with these fluids for placement performance, resulting cost of extra polymer and damage introduced to the proppant pack as result of total polymer introduced.

7.4 Crosslinked Fluids

Description

Polymers produce viscous solutions at ambient temperature; however, as the temperature increases, these solutions thin significantly. The polymer concentration can be increased to offset the thermal effects, but this approach is expensive and damaging. Instead, crosslinking agents are used to dramatically increase the effective molecular weight of the polymer by binding polymer chains, resulting in high fluid viscosities at relatively low polymer concentrations. Inorganic species such as borate salts and organometallic complexes react with guar and HPG When the polymer solution is concentrated enough that the molecules overlap (for HPG, at least 0.25% wt/wt), the complex can react with an overlapping polymer so that the two are linked together. A species is created that has two times the molecular weight of the polymer alone. Each polymer chain can be crosslinked at more than one site. Very high-molecular-weight networks develop, especially under static conditions, resulting in highly viscous solutions.

Borate

Boric acid and borate salts are used to produce crosslinked fluids with guar and HPG that are stable to 163°C. At a pH value greater than 8, an extremely viscous fluid forms in a matter of seconds. A high pH value is required for crosslinked fluid stability, with a pH value of 9 to 12 as optimum. Viscosity control of borate-crosslinked fluids is achieved by adjusting polymer concentration or crosslinker concentration.

Organometallic

Organometallic crosslinkers were developed for fracturing high-temperature reservoirs. The stability of the polymer backbone, rather than of the polymer-metal ion bond is the limiting factor. A well with a BHST greater than 204°C can be fractured with these fluids if the treatment is designed to provide adequate cool down.

The organometallic-polymer bond is very sensitive to shear. High shear irreversibly degrades organometallic-crosslinked fluid. Unlike the borate crosslinker, once the bond between the organometallic crosslinker and polymer is broken, it does not reform. Crosslinking occurring in a high-shear region is not desirable because an irreversible loss of viscosity results.

The two heavy metal organometallic crosslinker families are:

- titanates and
- zirconates

Conductivity Considerations for Crosslink fluids

The following should be considered when designing jobs with crosslinked fluid which otherwise might be considered conductivity limited because of the damaging effects of water-base fracturing fluids. Polymer that is concentrated within the proppant pack due to fluid leakoff and volume reduction during fracture closure is the primary cause of proppant-pack damage. The severity of damage increases as the polymer concentration increases, and is strongly dependent on fluid type, crosslinker type and breaker type Borate fluids are less damaging than the organo-metallic-crosslinked fluids at temperatures less than 82°C. *CfD* and post-closure polymer concentrations should be used as guidelines to determine conductivity-limited fracturing treatments. Factors that can adversely affect *CfD* and/or post-closure polymer concentration are

- Low fluid efficiencies and/or large pad volumes
- Low proppant concentration
- Moderate to high formation permeabilities
- Long fracture half-lengths
- Small fracture widths
- Initial polymer concentrations greater than 25 lbm/1000 gallon

Applications

Crosslinked frac fluids perform best in the following applications.

- Normally pressured wells
- Low rate fracs where proppant transport is a concern
- Fracture treatments where leakoff is critical to control
- Fracture geometries where generating adequate width is a concern
- Economic optimization as it is a cost effective fluid
- Higher temperature applications
- Combination with slickwater on hybrid treatments for better proppant transport

Fluid Use

The volumes are for crosslinked gels tend to be generally much lower than slickwater operations on the order of 1/2 on stage size as well as usually less stages by ½ so up to ¼ of water demand. If hybrid treatments are being performed the fluid volumes are very similar or might even exceed a standard slickwater design.

Recyclability

Crosslinked gels are the most difficult fluids to reuse as they have all the same concerns as linear gels for hydration and bacteria. It can be reused but with limitations. Of particular concern are residual bacteria which can metabolize the gel effecting the viscosity and the performance. Bacteria can also be an issue because recycled fluid contains residual gel that bacteria can use as a substrate to grow when contacted in surface storage and then introduced into the well causing souring or damage to the reservoir. Residual gel in fluid can also be a problem because polymers can accumulate and concentrate resulting in difficulty handling and more potential damage when reintroduced into the well. Linear gels require that the recycled water be appropriate for hydration of the new polymer to be added and there are many parameters that can inhibit hydration. The pH of the fluid and salinity of the fluid are the two key components to inhibit polymer hydration. The crosslinker is particularly sensitive to pH and buffers such as bicarbonate in solution that will interfere with the crosslinking mechanism. Residual borate is also a problem as it can act to overcrosslink the polymer resulting in decreased performance.

Crosslink Fluids

Water Quality	Range	Occurring Problems	Remedial Options
Temperature (C)	15 deg-40 deg	Lower temperatures may prolong hydration of gel polymers	Passive cooling in tanks or ponds, heat exchanger
pH	6.0 - 8.0	pH below 6 may cause prolonged hydration of gel, and pH greater than 8 may result in inadequate gelling	CaOH
		pH should be kept below 7.5 so that ferrous iron remain in solution	
Chloride (mg/L)	<30,000	High chloride concentration destabilizes fluid and creates problems with crosslinking	Blending, Mechanical Vapor Recompression, Recerse Osmosis. Ionization, Electrocoagulation
Iron (mg/L)	<25	Degrades and breaks polymers in gel, causing premature break and crosslink problems.	Iron Sequestration,oxidization
		Ferric iron will precipitate at the pH of natural environment becoming detrimental to the stimulation	
Carbonate (mg/L)	<600	Acts as a pH Buffer, thus higher concentrations of crosslinker activator may be needed for desired	Blending, Scale inhibitor, ionization, MVR
Bicarbonate (mg/L)	<600	Acts as a pH Buffer, thus higher concentrations of crosslinker activator may be needed for desired	Blending, Scale Inhibitor, Ionization, MVR
Hydroxide (mg/L)	<600	Acts as a pH Buffer, thus higher concentrations of crosslinker activator may be needed for desired	Blending, ??
Calcium (mg/L)	<100	Calcium + Magnesium should be less than 100 ppm, if greater than 100 the pH will not be in proper range	Blending, Floc/coag, Ion ex, Electrocoagulation
Magnesium (mg/L)	<100	Calcium + Magnesium should be less than 100 ppm, if greater than 100 the pH will not be in proper range	Blending, Floc/coag, Ion ex, Electrocoagulation
Sulfate (mg/L)	<1000	Causes scaling problems	Blending, Ion Ex, MVR, RO
Sodium (mg/L)	<1000	Destabilizes the fluid	Blending, Ion Ex, MVR, RO
Silica (mg/L)	<35	May inhibit the crosslinking of polymer gel	
Bacteria	0	Degrade gel viscosity	Biocide, Ozone

Figure 34 Crosslink Fluid Sensitivities

Low Ph Crosslink Fluids

Water Quality	Range	Occurring Problem	Remedial Options
Temperature (C)	15-40	Lower temperatures may prolong hydration of gel polymers	Use hydration Unit Heat Water
pH	5.0-7.0	pH below 6 may cause prolonged hydration of gel, and pH greater than 8 may result in inadequate gelling	
		pH should be kept below 7.5 so that ferrous iron remain in solution	
Chloride (mg/L)	<30,000	High chloride concentration destabilizes fluid and creates problems with crosslinking	Blending, Mechanical Vapor Recompression, Recerse Osmosis. Ionization, Electrocoagulation
Iron (mg/L)	<25	Degrades and breaks polymers in gel, causing premature break and crosslink	Blending, Floc/coag, Ion ex, Electrocoagulation
		Iron Ferric will precipitate at the pH of natural environment becoming detrimental to the stimulation	Blending, Floc/coag, Ion ex, Electrocoagulation
Carbonate (mg/L)	<400	Acts as a pH Buffer, thus higher concentrations of crosslinker activator may be needed for desired	Blending, Ion Ex, MVR, RO
Bicarbonate (mg/L)	<400	Acts as a pH Buffer, thus higher concentrations of crosslinker activator may be needed for desired	Blending, Ion Ex, MVR, RO
Hydroxide (mg/L)	<400	Acts as a pH Buffer, thus higher concentrations of crosslinker activator may be needed for desired	
Calcium (mg/L)	<100	Calcium + Magnesium should be less than 100 ppm, if greater than 100 the pH will not be in proper range	Biocide, Ozone
Magnesium (mg/L)	<100	Calcium + Magnesium should be less than 100 ppm, if greater than 100 the pH will not be in proper range	NA
Sulfate (mg/L)	<1000	Causes scaling problems	
Sodium (mg/L)	<1000	Destabilizes the fluid	
Silica (mg/L)	<35	May inhibit the crosslinking of polymer gel	
Bacteria	0	Degrade gel viscosity,	

Figure 35 Low pH Crosslink Fluid Sensitivities

6.5 Foam Fracture Treatment

Description

A foam fracturing fluid is a stable emulsion composed of a liquid (external or continuous) phase surrounding a gas (internal, dispersed, or non-continuous) phase and a surfactant (foaming agent). Foam fracturing fluids are characterized by their "quality." The quality of foam (Q) is defined as the ratio of gas volume to the liquid and gas volume. Foam fracturing fluids, as compared to non-foam fluids, are particularly well suited for fracturing because of some very unique properties. These include:stored

- compressed gas for better cleanup
- good fluid efficiency
- low fracture conductivity damage
- equivalent rheological performance at reduced polymer loading

The most common and most versatile types of foams are aqueous-base foams containing a polymer in the liquid phase and nitrogen as the gas phase. Foams containing alcohol, oil or carbon dioxide are used to improve performance based on a specific requirement.

Foam stability is critical to the foam performance in the fracture. Stability maintains the dispersion of the gas in the liquid which in turn controls the rheology and fluid loss properties of the foam. Factors affecting stability are:

- surfactant type
- surfactant concentration
- foam quality
- polymer type and concentration
- mixing energy

The stability of foam is normally measured under static conditions at low temperature and pressure. These laboratory tests do not represent the actual downhole stability and only serve as a guide to determine which polymer or surfactant offers the most stability. A foam is a stable dispersion of a gas in a liquid. An unstable dispersion is also a foam, but only for a short period of time. Once segregation of the phases occurs, the properties of the foam also disappear and the fluid becomes only an energized fluid. Nitrogen and or Carbon dioxide can be used for production of foam.

.

Comparison of Nitrogen and Carbon Dioxide Foam Fluid

Property	**Nitrogen**	**Carbon Dioxide**
Hydrostatic Head	**Low**	**High**
Reactive	Inert	Yes
Solubility in Water	Low	Moderate
Solubility in Oil	Low	High
Surface Tension Reduction	None	Good
Compressibility	High	Low
Temperature	(38°C)	(-7° to 4°C)

Table 9 Comparison of Properties of N2 and CO2 Foam Fluid

Applications

Foam fracturing fluids, as compared to non-foam fluids, are particularly well suited for fracturing because of some very unique properties. These include:

- stored compressed gas for better cleanup
- good fluid efficiency
- low fracture conductivity damage
- equivalent rheological performance at reduced polymer loading

Foam fracturing fluids perform best in the following applications.

- depleted or underpressured wells
- water-sensitive formations
- low-permeability gas wells

.

Fluid Use

The volumes for foamed fluids gels tend to be generally much lower both then slickwater operations on the order of 1/2 on stage size as well as usually less stages by ½ so up to ¼ of total fluid. The water demand is even less because only 30% is water and the rest is nitrogen or CO_2. Foamed fluids are the best way to minimize water usage apart from fracturing with hydrocarbons

Recyclability

Foamed fluids ability to be recycled is governed by the ability of the surfactant to form stable foam. The presence of hydrocarbon will vastly inhibit proper micelle formation therefore the fluid must be hydrocarbon free for water base foams. The foam is also governed by the state of the stabilizing agent in water phase so if it is a linear gel, control of bacteria and effective hydration are necessary. Of particular concern are residual bacteria which can metabolize the gel affecting the viscosity and the performance of the frac fluid. Bacteria can also be an issue because recycled fluid contains residual gel that bacteria can use as a substrate to grow when contacted in surface storage and then introduced into the well causing souring or damage to the reservoir. Residual gel in fluid can also be a problem because polymers can accumulate and concentrate resulting in difficulty handling and more potential damage when reintroduced into the well. Linear gels require that the recycled water be appropriate for hydration of the new polymer to be added and there are many parameters that can inhibit hydration.

Foam Fracturing

A foam fracturing fluid is a stable emulsion composed of a liquid (external or continuous) phase surrounding a gas (internal, dispersed, or non-continuous) phase and a surfactant (foaming agent). Foam fracturing fluids are characterized by their "quality." The quality of foam is defined as the ratio of gas volume to the liquid and gas volume.

Foam fracturing fluids, as compared to non-foam fluids, are particularly well suited for fracturing because of some very unique properties. These include:

- stored compressed gas for better cleanup
- good fluid efficiency
- low fracture conductivity damage
- equivalent rheological performance at reduced polymer loading

The most common and most versatile types of foams are aqueous-base foams containing a polymer in the liquid phase and nitrogen as the gas phase. Foams containing alcohol, oil or carbon dioxide are used to improve performance based on a specific requirement.

Foam stability is critical to the foam performance in the fracture. Stability maintains the dispersion of the gas in the liquid which in turn controls the rheology and fluid loss properties of the foam. Factors affecting stability are:

- surfactant type
- surfactant concentration
- foam quality
- polymer type and concentration
- mixing energy

The stability of foam frac fluid is normally measured under static conditions at low temperature and pressure. These laboratory tests do not represent the actual downhole stability and only serve as a guide to determine which polymer or surfactant offers the most stability. Foam is a stable dispersion of a gas in a liquid. An unstable dispersion is also a foam, but only for a short period of time. Once segregation of the phases occurs, the properties of the foam also disappear and the fluid becomes only an energized fluid. Three conditions are necessary to create stable foam:

- A foaming surfactant at sufficient concentration and free of contaminants must be used
- The liquid and gas must be in the proper ratio. Segregation between the liquid and gas phases will readily occur if an insufficient quantity of gas is present. The foam may invert to a mist with the gas as the outside phase if too much gas is present.
- The mixing energy must be sufficient to create the foam.

.

6.6 VES Fluids

Description

VES stimulation fluids are polymer free, water based fluids prepared by diluting a viscoelastic surfactant (VES) in brine. Filtered seawater may also be used. Unique features of VES fluid are:

- No polymer hydration is necessary, and there is no need to add crosslinker or breakers.
- The breaker for VES fluid is the produced hydrocarbon, or dilution by other formation fluids
- Solids-free fluid. Consequently, the retained permeabilities of proppant packs placed with VES fluids are typically greater than 90%.

Performance factors include:

- Good fluid efficiency
- Predictable leakoff control based on fluid viscosity
- No filter cake formation
- No residue in the proppant pack to impair well productivity
- Optimizes fracture length and height
- Reduces friction pressure losses

.

Applications

VES fluids are very versatile and can be used in wide variety of applications

- Oil, gas, and condensate reservoirs with bottomhole temperatures up to 135 °C
- Gravel-pack and Frac-pack operations
- Coiled tubing stimulation treatments

- Onshore and offshore treatments (seawater compatible)

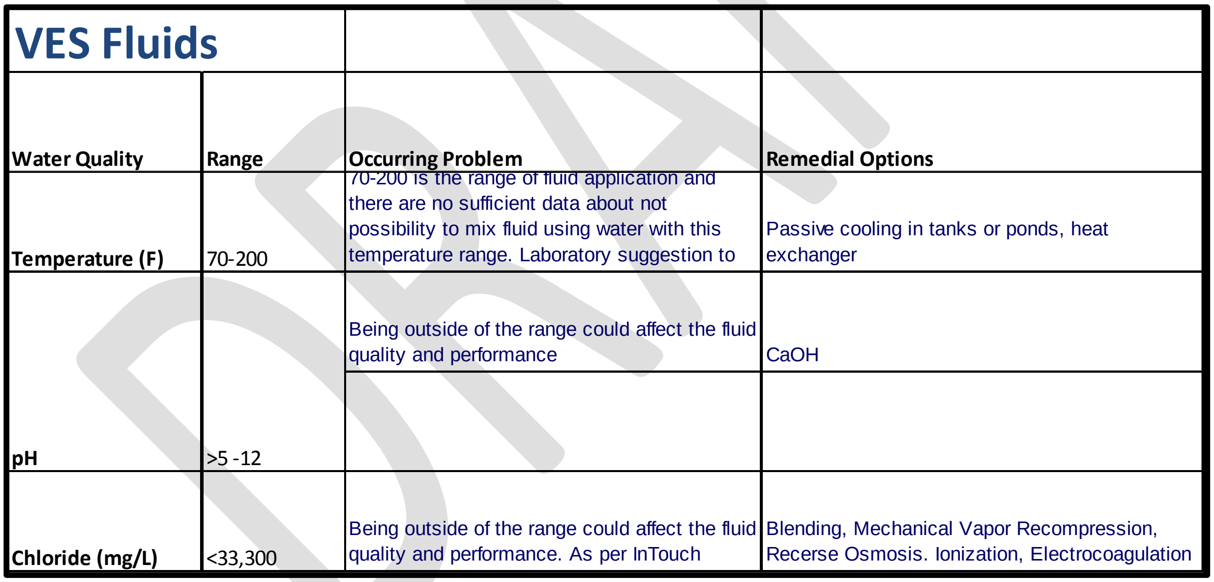
Fluid Use

The volumes for VES fluids tend to be generally much lower both then slickwater operations on the order of 1/2 on stage size as well as usually less stages by ½ so up to ¼ of total fluid. If the VES is foamed which is a common application, the water demand is even less because only 30% is water and the rest is nitrogen or CO_2. Foamed fluids are the best way to minimize water usage apart from fracturing with hydrocarbons

Recyclability

VES fluids are relatively insensitive to both ions and pH as compared to other fluids. They are also relatively inert to bacteria. The VES fluids are a suitable candidate for recycled waters as long as no residual hydrocarbons and or surfactants are present in recycled fluid.

Sensitivity



VES Fluids			
Water Quality	**Range**	**Occurring Problem**	**Remedial Options**
Temperature (F)	70-200	70-200 is the range of fluid application and there are no sufficient data about not possibility to mix fluid using water with this temperature range. Laboratory suggestion to	Passive cooling in tanks or ponds, heat exchanger
pH	>5 -12	Being outside of the range could affect the fluid quality and performance	CaOH
Chloride (mg/L)	<33,300	Being outside of the range could affect the fluid quality and performance. As per InTouch	Blending, Mechanical Vapor Recompression, Recerse Osmosis. Ionization, Electrocoagulation

Figure 36 VES Fluid Sensitivities

Several hydraulic fracturing techniques, or combinations of techniques referred to as “hybrids” are used in the fracturing of shale gas formations

7.0 FUTURE TRENDS IN FRACCING AND TREATMENT

Service companies invest millions of dollars annually developing techniques and chemicals that allow fracturing operations to be executed providing superior performance or cost effectiveness.

Research direction that might be anticipated might include:

- Alternative stimulation techniques that are as effective as slickwater fracturing treatments, but that are less water intensive.
- Frac additives that are salinity tolerant, allowing higher salinity produced fluids and flowback water to be considered for fracturing treatments without extensive treatment.
- Frac chemicals that are more environmentally friendly (ie less toxic, and quicker to degrade.

Early indications are that the hydraulic fracturing techniques applied in the liquids rich plays are requiring only about 15% of the water used in a comparable slick water fracture treatment. From a water conservation standpoint, this reduction in water use is a positive. Service providers caution however (Pipchuk, 2011, personal communication) that the number of fracture treatments that will be executed in the liquids rich areas will be significantly greater than the number of fracture treatments currently being executed in the conventional shale gas plays.

8.0. SUMMARY

Re-use of fracturing fluids is being evaluated by service companies and operators to determine the degree of treatment and make-up water necessary for re-use301. The practical use of on-site, self contained treatment facilities and the treatment methods employed will be dictated by flow rate and total water volumes to be treated, constituents and their concentrations requiring removal, treatment objectives and water reuse or discharge requirements. In some cases it would be more practical to treat the water to a quality that could be reused for a subsequent hydraulic fracturing job, or other industrial use, rather than treating to discharge to a surface water body or for use as drinking water. At the time this Primer was developed there were plans to construct commercial waste water treatment facilities specifically designed for the treatment of produced water associated with shale gas development in some locations around the country302. The completion and success of such plants no doubt will be closely tied to the successful expansion of production in the various shale gas plays.

While challenges still exist, progress is being made. New technologies and new variations of established technologies are being introduced on a regular basis, and some industry researchers are pursuing ways to reduce the amount of treatment needed. In early 2009, studies were underway to determine the minimum quality of water that could successfully be used in hydraulic fracturing. If hydraulic fracturing procedures or fluid additives can be developed that will allow use of water with a high TDS content, then more treatment options become viable and more water can be reused. Treatment and re-use of produced water could reduce water withdrawal needs as well as the need for additional disposal options. This approach could also help to resolve many of the concerns associated with these withdrawals.2

Controlling cost of development is of paramount importance in the economic development of shale gas resources in the Horn River Basin in northern British Columbia. Slick water fracs, which are an integral part of gas well completions in the Horn River Basin require huge amounts of water, and full field development will place pressure on existing water availability. Surface water, which is being used for initial small scale development is unlikely to be able to meet the water needs of full field development scenarios. Most developers in the Horn River Basin are looking at groundwater to meet long term water needs. While the Debolt Formation has been the focus of early attention, the Debolt is present in only a part of the Horn River Basin. In addition, the Debolt has drawbacks in terms of the presence of H2S and elevated temperatures which make it costly to develop. Aquifers in the Devonian, which have documented high permeability and would likely produce at high rates, are costly to drill and have severe water chemistry and temperature issues making treatment necessary. Aquifers in the Cretaceous are expected to show better water chemistry, but lower permeabilities, requiring well field scale development to meet water needs.

Further, flow back from slick water fracs is nominally expected to be 20 -30 % of the original injected volume. There chemical quality and temperature of the flow back water makes special handling requirements and treatment a consideration if re-use is being contemplated.

Ultimate disposal of frac water can be facilitated through deep well injection. The geological targets that are being considered for water sourcing also become the targets for disposal. The concept of using the same zone for sourcing as for disposal (Aquifer Storage and Recovery) albeit with widely spaced source and disposal wells is being explored by Encana.

Given the complexity of the many aspects of water management; which include sourcing, transportation, storage, treatment, and ultimate disposal; an integrated approach to management provides the best opportunity for cost minimization and environmental performanceKWC1

9.0 REFERENCES

The provisional References listing will be finalized as part of final editing of the text

1) Rimassa S and Howard, P., 2008, “NSA Stimulation Client Support Tech Memo, Part 1 Section 01 Slickwater Fluid Design Guidelines” confidential Schlumberger document
2) “Modern Shale Gas Development in the United States: A Primer”, 2009, prepared by GWPC and ALL Consulting
3) URS Corp, 2009, “Water Related Issues Associated with Gas Production from the Marcellus Shale”, prepared for NYSERDA, Contract no. 10666
4)T “Chapter 5, Natural Gas Development Activities and High Volume Hydraulic Fracturing – Draft SGEIS” 2009 prepared for --------- by ----------
5) Reynolds, R.R., 2003, “Produced Water and Associated Issues” Oklahoma Geological Survey Open-File Report 6-2003
6) “Technical Assistance For the Draft Supplemental Generic EIS: Oil, Gas and Solution Mining Regulatory Program Well Permit Issuance For Horizontal Drilling For High Volume Hydraulic Fracturing to Develop the Marcellus Shale and Other Low Permeability Gas Reservoirs”, 2009, prepared by ICF for NYSERDA
7)T “An Integrated Framework For Treatment and Management of Produced Water” – RSEA Project 07122-12, prepared by Colorado School of Mine
8) Harper, J.A., 2008, “The Marcellus Shale– An Old “New” Gas Reservoir in Pennsylvania”, Pennsylvania Geology, Vol. 38, No. 1
10) NEB (National Energy Board), 2009, A Primer For understanding Canadian Shale Gas
11)T URS, Water Related Issues Associated With Gas Production In The Marcellus Shale
12) EPA, CBM Evaluation of Impacts to Underground Sources of Drinking Water By Hydraulic Fracturing
13)T Chapter 5 Natural Gas Development And High Volume Hydraulic Fracturing
14) Pennsylvania Geology – Vol 38 No. 1
15) Produced Water And Associated Issues
16) Shale Gas 2007
17) API, 2010, “Water Management Associated With Hydraulic Fracturing”, API Guidance Document HF2
18) DOE, White Paper Describing Produced Water From Production of Crude Oil
19) “ Fraccing Fluid Systems” accessed 2008, prepared by Chem Total
20) Feguson, M.L., and Johnson, M.A.2009, “Comparing Friction Reducers Performance in Produced Water From Tight Gas Shales”, Journal of Petroleum Technology, Nov, 2009
21) Shale Gas White Paper
22) Tulissi, M.G, and May R.E., 2002, “A Comparison of Three Different CO_2 Energized Frac Fluids: A Case History” SPE 75681S
23) ThermaFOAM, CO2 Foam Systems For High Temperature Wells
24) “High TDS Waters Scoping Study: Produced Water Beneficial Re-Use – High TDS Waters”, 2007, prepared by Fossil Water
25) Aquapure, “Managing The Volatility of Process Affected Water in SAGD”
26) “Low TDS Water: Scoping Study: Produced Water Beneficial Re-Use – Low TDS Waters”, 2007, prepared by Fossil Water
27) CAPP, Offshore
28) Shale Gas, Focus on the Marcellus Shale

29) J. Daniel Arthur, Bohm, B, and Layne, Mark. 2009, “Consideration For Development of Marcellus Shale Gas”, World Oil , July, 2009

30) EPA 816-R-04-003, Hydraulic Fracture Fluids

31) BJ, A Novel Nondamaging Friction Reducer

32) EV Norms

33) Considerations For Responsible Gas Development of The Frederick Brook Shale in New Brunswick

34) Produced Water Issues With Shale Gas Production - PP

35) All, Summary and Applicability to Canada

36) CAPP, Responsible Water Management

37) CSUG, An Overview of Canadas Natural Gas Resources

37A) “Shale Gas in Canada – An Overview” 2010, a presentation prepared by CSUG

38) Hydraulic Fracturing – The Fuss, The Facts, The Future

38A) 2010 “Hydraulic Fracturing – A History Of An Enduring Technology” Journal of Petroleum Technology, December 2010

39) “Freeing Up Energy” 2010, American Petroleum Institute

40) King, E.K. 2010, “Thirty years of Gas Shale Fracturing”, SPE 133456 PP

41) Kaufman, P., and Penny, G.S., “Critical Evaluation of Additives Used in Shale Slickwater Fracs”, SPE 119900

42) Canadian Guidelines For Management of Naturally Occurring NORMS

43) Naturally Occurring Radioactive Material in North American Oilfields”, 2004, American Petroleum Institute

44) Oilweek, Radioactive in The Patch

46) BC Radiation Protection Guidelines

47) Memo, Radioactivity in Marcellus

48) “Waste Management of Cuttings, Drilling Fluids, Hydrofrack Water and Produced Water” Cornell University web site http://wri.eas.cornell.edu/gas_wells_waste.html

49) 1999, “An Investigation of Naturally Occurring Radioactive Materials (NORM) in Oil and Gas Wells in New York State”, New York State Department of Environmental Conservation

50) 2011, “Chemical Description for Marcellus Shale Wells”, Talisman Chemical Additives

51) Pad To Pad Transfer of Flowback Water

52) Radon in BC

53) NORMs – Salt Caverns

54) Scaling PP

55) Alls, Scale Inhibitors

56) Bamidela, O.A., Chunfang, Fan, Zhang. P., Alsajari, H., Kan A., 2009, “Effects of Oilfield Scale Deposition on Oil Production From Horizontal Wells” Petroleum and Oil, 51, 2009

57) M.E. Lauch, R.R. Myers, T.R. Moore, B.A. Lipinski. N.A. Houston, 2009 “Marcellus Shale Post-Frac Flowback Waters – Where is All the Salt Coming From and What are the Implications?”, SPE 125740

58) 2009, “Integration of Kinetics into Scale Prediction Software, ScaleSoftPitzer”, SPE 121681-MS

59) Adesina, F.A.S., Olugbenga, F., and Samuel, A., 2010, “Oilfield Scale-Induced Permeability Damage Management During Waterflooding”, SPE 126116

60) Dyer, S.J., Graham, G.M. 2002 “The Effect of Temperature and On Oilfield Scale Formation” Journal of Petroleum Science and Engineering, 35, (2002) 95-107

61) Yeboah, Y.D., Somuah, S.K., and Saeed, M.R., 1993, “A New and Reliable Model For Predicting Oilfield Scale Formation, SPE 25166

62) Gaudlip, A., Paugh, L.O., and Hayes, I.D.2002, Marcellus Shale Water Management Challenges in Pennsylvania", SPE 119898
63) Canyon Servicing – Needs To Be Cracked
64) Maximizing Shale Gas Production
65) A New Trend In Hydro Fraccing
67) Apache Frederick Brook?
69) Baker Hughes
70) Anadarko
71) Shein. Gary, 2005, "The Application and Technology of Slickwater Fracturing" a presentation to SPE
72) DOB - Montney
73) Reeise? Thesis
74) Trican
75) Thermofoam
76) GMRX
77) All – Injection Versus Hydro Fraccing
78) An Update
79) Ft Worth
80) Fracture Stimulation
81) " Northern Great Plains Water Consortium - Bakken Water Opportunities Assessment" 2009, prepared by EERC, presented at Water Opportunities Meeting, Bismark N.D December 10, 2009
82) Hydro Frac Illustration
83) Anadarko
84) Lefollette
85) BJ
86) SPE Presentation
87) "Stimulation 101", presentation bt CarboCeramics at Dallas YP Luncheon, SPE
88) "Water Generated During Natural Gas Production" from Water Use - Chesapeake – Barnett Water
89) Shale Gas 2007
90) DOE
91) USGS
92) Campbell K.W., 2010," Management of Water Issues in the Development of Shale Gas in the Horn River Basin" presented at the Canadian Institute Conference , Calgary, 2010
93) Bachu, S., 2002, "Suitability of the Subsurface in Northeastern British Columbia for Geological Sequestration of Anthropogenic Carbon Dioxide", Alberta Geological Survey
94) Economides, Michael.J., Nolte, Kenneth G ed.2000 "Reservoir Stimulation Third Edition" Schlumberger
95) Frenier, W.W. and Zaiuddin. M, 2008, "Formation, Removal, and Inhibition of Inorganic Scale in the Oilfield Environment" SPE
96) Ostoff, A.G., 1979, "Introduction to Oilfield Water Technology" National Association of Corrosion Engineers
97) Wright. C.C., Cross, D., Ostoff, A.G and Stanford J.R ed. "Oilfield Subsurface Injection of Water" ASTM 641
98) Thakur, G.C., and Satter, Abdus. 1998,"Integrated Waterflood Asset Management" PennWell Publishing Company
99) Gidley. John L., Holditch. S.A, Nierode, D.E and Veatch. R.W., 1989, "Recent Advances in Hydraulic Fracturing Monograph Volume 12" SPE

100) Stephen C. Rose, Buckwalter, J.F., and Woodhall, R.J, 1989, “The Design Engineering Aspects of Waterflooding Monograph Volume 11”, SPE

101) Hayes, T.,2008, “Proceedings and Minutes of the Hydraulic Fracturing Expert Panel , XTO Facilities” Fort Worth, September 26, 2007, prepared by GTI

102) Arthur, J.D, Coughlin, B.J., and Layne, M., 2008, Hydraulic Fraturing Considerations For Natural Gas Wells of the Fayetteville Shale”, prepared by ALL Consulting

103) Arthur, J.D, Coughlin, B.J., and Layne, M., 2008, Hydraulic Fraturing Considerations For Natural Gas Wells of the Marcellus Shale”, prepared by ALL Consulting

104) Hayes, T., 2010, “Produced Water Research Projects”, a presentation at RPSEA Unconventional Gas Conference, 2010, Golden, Colorado

105) Vidic, R.D., 2010 “Sustainable Water Management For the Marcellus Shale Development” a presentation at…..

106) Alexander, M.D, Qian, L., Ryan, T.A., and Herron, J., 2011, “Considerations For Responsible Gas Development of the Frederick Brook Shale in New Brunswick”

107) Hydraulic Fracturing Overview – author unknown

108) “US Shale Gas – An Unconventional Resource, Unconventional Challenges, White Paper”, 2008, prepared by Halliburton

109) “Optimized Water Frac Services For Unconventional Reservoirs” presentation by Halliburton

110) “Shale Energy: Developing the Eagleford” 2011, World Oil Vol 231 No. 7

111) “Managing Water Resource Challenges In Select Natural Gas Plays”, 2008, a presentation by Chesapeake Energy at GWPC Annual Forum, Sept 20-24, 2008

112) Bachu, S., 2002, “Suitability of the Subsurface in Northeastern British Columbia For Geological Sequestration of Anthropogenic Carbon Dioxide.” Alberta Geological Survey

113) Oddo, J.E., and Tomson, M.B., 1994, “Why Scale Forms and How to Predict It”, SPE --

114) Paktinat,J, Pinkhouse, J.A., and Fontaine, J., 2007 “Investigation of Methods to improve Utica Shale Hydraulic Fracturing in the Appalachian Basin”. SPE 111063

115) “Fracturing Fluid”, 2005, Schlumberger Internal Document

116) Rimassa, S.M., Howard, P.R., and Blow, K.A., 2009, “Optimizing Fracture Fluids From Flowback Water”, SPE 125336

117) Kaufman, P., and Penny, G.S., “Critical Evaluation of Additives Used in Shale Slickwater Fracs”, SPE 119900

118) Gupta, D.V.S., Hlidek, B.T., 2009,” Frac Fluid Recycling and Water Conservation – A Case History”, SPE 119478

119) Li, L., Eliseeva, K., Bustos, O.A., England, K., Howard, P.R., Boney, C.L., Parris, M.D., and Ali, S.A., “ 2009, “Well Treatment Fluids Prepared With Oilfield Produced Water” SPE124212

120) Yang, B.H. and Flippen, M.C., 1997, “Improved Flowback Analysis to Assess Polymer Damage”, SPE 37444

121) “Shale Energy: Developing the Eagleford” 2011, World Oil Vol 231 No. 7

122) Bennion, D.B., Thomas, F.B., Bietz, R., and Bennion, D.W.1995, “Advances in Laboratory Coreflow Evaluation to Minimize Formation Damage Concerns With Vertical/Horizontal Drilling applications”, CAODC

123) API- HF3

124) Palisch. T.T., Vincent, M.C., Handren. P.J., 2010, Slickwater Fracturing: Food for Thought”, SPE 115766

125) Blauch, M.E., 2010, “Developing Effective and Environmentally Suitable Fracturing Fluids Using Hydraulic Fracturing Flowback Waters”,SPE 131784

126) Oddo, J.E., Amal, A., Ortiz, I., Anthony, R., Pope, D.H., Hill, D.G., Linz, D.G., Frank, J., Becker, D.M., and Tomson, M.B.,1993, "The Chemistry Prediction and Treatment of Scale Containing Naturally Occurring Radioactive Materials (NORM) in Antrim Gas Fields, Michigan",SPE 25485

125A) Parker, M., Slabaugh, B., Walters, H., Weaver, J. and Hanes, R., 2003, "New Hydraulic Fracturing Fluid Technology Reduces Impact on the Environment Through Recovery and Reuse ", SPE 80590

128) Gaudlip, A.W., Paugh, L.O., and Hayes, T.D., 2008, "Marcellus Shale Water Management Challenges in Pennsylvania", SPE 119898

129) Cramer,D.D.,2008, "Stimulating Unconventional Reservoirs: Lessons Learned, Successful Practices, Areas For Improvement", SPE 114172

130) Carman, P.S., Cawiezel, K.E., 2007, "Successful Breaker Optimization for Poly acrylamide Friction Reducers Used in Slickwatwer Fracturing", SPE 106162

131) Matthews, H.L., Shein, G., and Malone,M., 2007, "Stimulation of Gas Shales: They're All the Same
– Right?", SPE 106070

132) Kaufman. P., Penny. G.S., Paktinat, J., 2008, "Crtiical Evaluations of Additives Used in Shale Slickwater Fracs" SPE 119900

133) Parker, M., Slabaugh, B., Walters, H., Hoyt, T., Haley, W., Harper, J., and Weaver, J., 2003, " New Hydraulic Fracturing-Fluid Technology Increases Production in the Barnett Shale and Reduces Impact on the Environment" SPE 80912

130/134)Carman, P.S., and Cawiezel, K.E.2007, "Successful Breaker Optimization For Polyacrylamide Friction Reducer Used in Slickwater Fracturing", SPE 106162

135) Bluach, M.E., Myers, R,.R., Moore, T.R., Lipinski, B.A., and Houston, N.A., 2009, "Marcwellus Shale Post-Frac Flowback Waters – Where Is All the Salt Coming From and What Are the Implications?",SPE 125740

136) Willberg, D.M., Card, R.J., Britt, L.K., Samuel, M., England, K.W., Cawieze, K.E., and Krus, H. 1997, "Determination of the Effect of Formation Water on Fracture Fluid Cleanup Through Field Testing in the East Texas Cotton Valley", SPE 38620

137) Rimassa,S.M., Howard, P.R., Arnold, M.O., "Are We Buying Too Much Friction Reducer Because of Biocides?", SPE 119569

138) USEPA Draft Plan to Study the Potential Impacts of Hydraulic Fracturing on Drinking Water Resources, EPA/600/D-11/001/

139) Carroll, D., 2011, "On Site Waste Water Containment for Hydraulically Fractured Wells" Unpublished Memorandum

140) Rimassa, S.M., Howard, P.R., Kristel, A.B., 2009, "Optimizing Fracturing Fluids from Flowback",
SPE 125336

141) Russell, D., 2001, "Recycling of Water and Minimizing Fresh Water Usage", presented at PTAC Forum on Shallow Gas, Calgary, Canada, June 21

143) Tulissi, M.G, and May R.E., 2002, "A Comparison of Three Different CO_2 Energized Frac Fluids" A Case History" SPE 75681S

144) King, E.G. 2010, "Thirty years of Gas Shale Fracturing", SPE 133456

145) Bennion, D.B, and Thomas F.B, 1996, "Low Permeability Gas Reservoirs: Problems, Opportunities and Solutions for Drilling, Completion, Stimulation and Production" SPE 35577

146) Fontana C., and Muruaga E. 2007, "Successful Application of a High Temperature Viscoelastic Surfactant (VES) Fracturing Fluids under Extreme Condition in Patagonian Wells, San Jorge Basin" SPE 107277

147) Gdanski, R., Weaver J., 2007, "A New Model for Matching Fracturing Fluid Flow back Composition" SPE 1 06040

148) Robinson B.M, and Holdtch S.A, 1988, "Minimizing Damage to a Propped Fracture by Controlled Flow back Procedures" Journal of Petroleum Technology

149) Crafton, W. James, 2008, "Modeling Flow back Behavior or Flow back Equals "Slow back", SPE 119894

150) Bazrafshan, Idris, Mahvi, Amirhossein, Naseri, Simin, and Mesdaghian, Ali Reza, 2006, "Performance Evaluation of Electro coagulation"

151) Armenante, Priero.M, "Coagulation and Flocculation", NJIT PowerPoint Presentation

152) Gaudlip A.W, and Paugh L.O., 2008, "Marcellus Shale Water Management Challenges in Pennsylvania" SPE 119898

153) Penny G.S. and Soliman M.Y., 1983, "Enhanced Load Water-Recovery Technique Improves Stimulation Results", SPE 12149

154) Willberg D.M., and Steinsberger, N., 1998, "Optimization of Fracture Cleanup Using Flow back Analysis", SPE 39920

155) Pope, D. and Britt, L., 1995, "Field Study of Guar Removal from Hydraulic Fractures" SPE 31094

156)A Samuelson, M.L., and Constien, V.G, "Effects of High Temperature on Polymer Degradation and Cleanup" SPE 36495.

156) B Paktinat, J., and Pinhouse, J., 2005, "Post-Frac Fluid Recovery Improvements of Appalachian Basin Gas Reservoirs" A Case History, SPE 97365

157) StormWaterX, ,2011, "Total Suspended Solids or Suspended Solids", Website

158) Willberg, D.M,1998, "Optimization of Fracture Cleanup Using Flowback Analysis", SPE 39920

159) Wikipedia, 2011, "Sedimentation"

160) Ryles R.G., 1983, "Elevated Temperature Testing of Mobility Control Reagents", SPE 12008

161) ….. 2011, "Ferric Chloride Solution"

162) Gulbardson, 2011, "Industrial Waste Water Treatment: Suspended Solids Removal"

163) Gulbardson, 2011, "Ferrous Iron Solution"

164) Gulbardson, 2011, "Industrial Waste Water Treatment: Suspended Solids Removal"

165) Eaton, 2011 "Bag and Cartridge Filtration" website

166) Robinson B.M, and Holdltch, 1988, "Minimizing Damage to a Propped Fracture by Controlled Flowback Procedure", SPE

167) Murphy, Sheila,2011, "General Information on Solids", USGS Water Quality Monitoring

168) General Electric, 2011 "Water Purification Handbook Chapter 23- Cooling Water Systems - Heat Transfer"

169) General Electric, 2011 "Water Purification Handbook Chapter 09- Membrane Systems"

170) General Electric, 2011 "Water Purification Handbook Chapter 07- Precipitation and Softening"

171) General Electric, 2011 "Water Purification Handbook Chapter 05 – Clarification"

172) General Electric, 2011 "Water Purification Handbook Chapter 06 – Filtration"

173) OAS, 2011, "Filtration Systems", website

174) Ecolotran Inc., 2011, "Electrocoagulation Solutions", website,

175) Holt, Peter, Barton, Geoffrey, and Mitchell Cynthia; 2006; "Electrocoagulation As a Wastewater Treatment", Third Annual Australian Environmental Engineering Research Event, 23-26 November, Castlemaine, Victoria

176) CENEMES, 2011, "Wastewater Treatment by Electrocoagulation (EC)"

177) Universal Systems Inc, 2011, "Electrocoagulation – Wastewater Treatment Process Through Electrocoagulation"

178) Powell Water Systems Inc., 2011, "Electrocoagulation and Wastewater Treatment Systems"

164) Replacement Wikipedia, 2011, "Electrocoagulation in Wastewater Treatment"

179) Western Regional Aquaculture Center, 2001, "Settling Basin Design", WROC-106

180) Schlicher, Ron, Haas, Lynn, and Mostoller, Larry, 2011, “An Inovative Approach to Managing Produced Water and Frac Flow back in the Marcellus Shale”, Montgomery, Watson, Harza

181) Manz, David H, 2010, “Economic treatment of Frac Flow Back Water to Recyclable Condition Using Physical Chemical Process”, Pure filtered Water international Ltd.

182) ”Frac Flowback Water Treatment and Recovery Systems”

183) Daniel Arthur. J, SPEC, P.E, 2011, “Water Management Planning in the Eagle Ford Shale Play”, SPEC

204) A.Veil, John, and G. Puder, Markus, 2004, “Produced Water from production of Crude Oil, Natural Gas, and Coal Bed Methan”, Contract no. W-31-109-Eng-38

206) E&P, 2011, “Gas Well Treated with 100% Reused Frac Fluid”, Website

207) Barkley Naomi.P, and Williams, Tracie, 1993, “Electro-Pure Alternating Current Electro coagulation”, EPA/540/S-93/504

214) Fossil Water Corporation, 2007, “produced Water Beneficial Re-Use High TDS Waters”,

251) Colorado School of Mines, 2009, “An Integrated Framework for Treatment and Management of Produced Watyer”, RPSEA project 07122-12

255 TimPope, personal communication.

GLOSSARY OF TERMS

alternative water
Water from outside an operators asset boundary which does not meet the definition of fresh water. Alternative water sources include; acid mine drainage, municipal or industrial wastewater, brackish water, saline Water, or non-fresh water from a different operators asset.

aquifer
A subsurface formation that is sufficiently permeable to conduct groundwater and to yield economically significant quantities of water to wells and springs.

basin
A closed geologic structure in which the beds dip toward a central location; the youngest rocks are at the center of a basin and are partly or completely ringed by progressively older rocks.

brackish water
Water that has total dissolved solids (TDS) greater than 500 ppm and less than or equal to 10,000 ppm.

casing
Steel piping positioned in a wellbore and cemented in place to prevent the soil or rock from caving in. It also serves to isolate fluids, such as water, gas, and oil, from the surrounding geologic formations.

coal bed methane/coal bed natural gas
CBM/CBNG
A clean-burning natural gas found deep inside and around coal seams. The gas has an affinity to coal and is held in place by pressure from groundwater. CBNG is produced by drilling a wellbore into the coal seam(s), pumping out large volumes of groundwater to reduce the hydrostatic pressure, allowing the gas to dissociate from the coal and flow to the surface.

completion
The activities and methods to prepare a well for production and following drilling. Includes installation of equipment for production from a gas well.

disposal well
A well which injects produced water into an underground formation for disposal.

directional drilling
The technique of drilling at an angle from a surface location to reach a target formation not located directly underneath the well pad.

flow back
The fracture fluids that return to surface after a hydraulic fracture is completed.

flowback water
Water produced as a result of hydraulic fracking while completions has responsibility for the well. After a well has been stimulated to fracture the formation and the pressure is reduced some of hydraulic injection fluid will flow back out of the well. Flowback Water is a subset of the industry definition of Produced Water.

formation (geologic)
A rock body distinguishable from other rock bodies and useful for mapping or description. Formations may be combined into groups or subdivided into members.

fracturing fluids
A mixture of water, proppant (often sand), and additives used to hydraulically induce cracks in the target formation.

fresh water
Water that has total dissolved solids (TDS) less than or equal to 500 ppm. fresh water sources include; Surface water bodies, groundwater, or fresh water suppliers/utilities.

gelling agent
Chemical compounds used to enhance the viscosity and increase the amount of proppant a fracturing fluid can carry.

groundwater
Subsurface water that is in the zone of saturation; source of water for wells, seepage, and springs. The top surface of the groundwater is the "water table."

horizontal drilling
A drilling procedure in which the wellbore is drilled vertically to a kickoff depth above the target formation and then angled through a wide 90° arc such that the producing portion of the well extends horizontally through the target formation.

hydraulic fracturing
Injecting fracturing fluids into the target formation at a force exceeding the parting pressure of the rock thus inducing fractures through which oil or natural gas can flow to the wellbore.

hydrocarbons
Any of numerous organic compounds, such methane (the primarily component of natural gas), that contain only carbon and hydrogen.

hydrostatic pressure:
The pressure exerted by a fluid at rest due to its inherent physical properties and the amount of pressure being exerted on it from outside forces.

injection well
A well used to inject fluids into an underground formation either for enhanced recovery or disposal.

Inversion time
Inversion time is defined as the amount of time it takes for 0.25 gpt friction reducer to reach 90% of the maximum drag reduction reported

naturally occurring radioactive material

NORM
Low-level, radioactive material that naturally exists in native materials.

original gas in place
The entire volume of gas contained in the reservoir, regardless of the ability to produce it.

perforations
The holes created between the casing and liner into the reservoir (subsurface hydrocarbon bearing formation). These holes create the mechanism by which fluid can flow from the reservoir to the inside of the casing, through which oil or gas is produced.

permeability
A rock's capacity to transmit a fluid; dependent upon the size and shape of pores and interconnecting pore throats. A rock may have significant porosity (many microscopic pores) but have low permeability if the pores are not interconnected. Permeability may also exist or be enhanced through fractures that connect the pores.

porosity
The voids or openings in a rock, generally defined as the ratio of the volume of all the pores in a geologic formation to the volume of the entire formation.

primacy
A right that can be granted to state by the federal government that allows state agencies to implement programs with federal oversight. Usually, the states develop their own set of regulations. By statute, states may adopt their own standards, however, these must be at least as protective as the federal standards they replace, and may be even more protective in order to address local conditions. Once these state programs are approved by the relevant federal agency (usually the EPA), the state then has primacy jurisdiction.

produced water
Water flowing from a well after responsibility for the well has been transferred to production.

Note: Industry defines "produced water" as any water that flows from a well as a result of oil and gas exploration or production activity.

propping agents/proppant
Silica sand or other particles pumped into a formation during a hydraulic fracturing operation to keep fractures open and maintain permeability.

Rate of replenishment
The rate that water used in fraccing individual stages can be replenished from the water source or primary storage. The rate of replenishment must allow the lease based storage capability to deliver water to the pumpers at a rate equal to the rate that water is being pumped.

reclamation
Rehabilitation of a disturbed area to make it acceptable for designated uses. This normally involves regarding, replacement of topsoil, revegetation, and other work necessary to restore it.

reservoir
Subsurface hydrocarbon bearing formation.

reused water
Flowback Water and/or Produced Water generated within an operators asset and subsequently used again within that same asset whether treated or not.

recycled water
Water taken from any internal waste (effluent) stream and treated to a level suitable for further use, where it is used safely and sustainably for beneficial purposes. Recycled water is a subset of reused water.

saline water
Water that has total dissolved solids (TDS) greater than 10,000 ppm. Saline water is sourced from underground formations using wells drilled or converted for the purpose of water withdrawal

shale gas
Natural gas produced from low permeability shale formations.

slick water
A water based fluid mixed with friction reducing agents, commonly potassium chloride.

solid waste
Any solid, semi-solid, liquid, or contained gaseous material that is intended for disposal.

stimulation
Any of several processes used to enhance near wellbore permeability and reservoir permeability, including hydraulic fracturing

tight gas
Natural gas trapped in a hard rock, sandstone, or limestone formation that is relatively impermeable.

total dissolved solids
TDS
The dry weight of dissolved material, organic and inorganic, contained in water and usually expressed in parts per million.

underground injection control program
UIC
A program administered by the Environmental Protection Agency, primacy state, or Indian tribe under the Safe Drinking Water Act to ensure that subsurface emplacement of fluids does not endanger underground sources of drinking water.

underground source of drinking water
USDW
Defined in 40 *CFR* Section 144.3, as follows: “An aquifer or its portion:
(a) (1) Which supplies any public water system; or

(2) Which contains a sufficient quantity of groundwater to supply a public water system;
and
(i) Currently supplies drinking water for human consumption; or
(ii) Contains fewer than 10,000 mg/l total dissolved solids; and
(b) Which is not an exempted aquifer."

water quality
The chemical, physical, and biological characteristics of water with respect to its suitability for a particular use.

water withdrawal
Water withdrawal is the process of sourcing fresh water or alternative water.

watershed
All lands which are enclosed by a continuous hydrologic drainage divide and lay upslope from a specified point on a stream.

well completion
See **completion**. 17