Fracturing Fluid
Flowback Reuse Project

Prepared by M-I SWACO, a Schlumberger Company
for Petroleum Technology Alliance of Canada
and the Science and Community Environmental Knowledge (SCEK)
Fund

Decision Tree & Guidance Manual

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Executive Summary

This document is intended for:

- **Oilfield operators, hydraulic fracturing service companies, chemical manufacturers,** and **water treatment companies** in the design of fracturing processes and management of water needs and issues.
- **Regulators** who provide direction and develop policy regarding hydraulic fracturing operations and water management issues.
- **Other stakeholders** with an interest in water management, to understand the hydraulic fracturing process and the considerations that must be taken into account in the use and reuse of water for hydraulic fracturing operations.

Water has become a major economic factor in current fracturing technologies. The industry has learned that water need not be fresh, but may be reused if the chemistry is correct or can be adapted.

This study aims to identify a methodology, in the form of a Decision Tree and Guidance Manual, and supporting Appendices and Case Studies, 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 fracturing fluid. The methodology and technologies that have been suggested incorporate the science and practice of hydraulic fracturing with fracturing fluid management and treatment technologies.

1.0 Introduction and Background

Previous projected recovery rates for shale gas-in-place were about 2%. Shale gas development has advanced so that this has increased to estimates of about 50%. [40] As shown in Figure 1.1, shale gas exists in many places in North America.

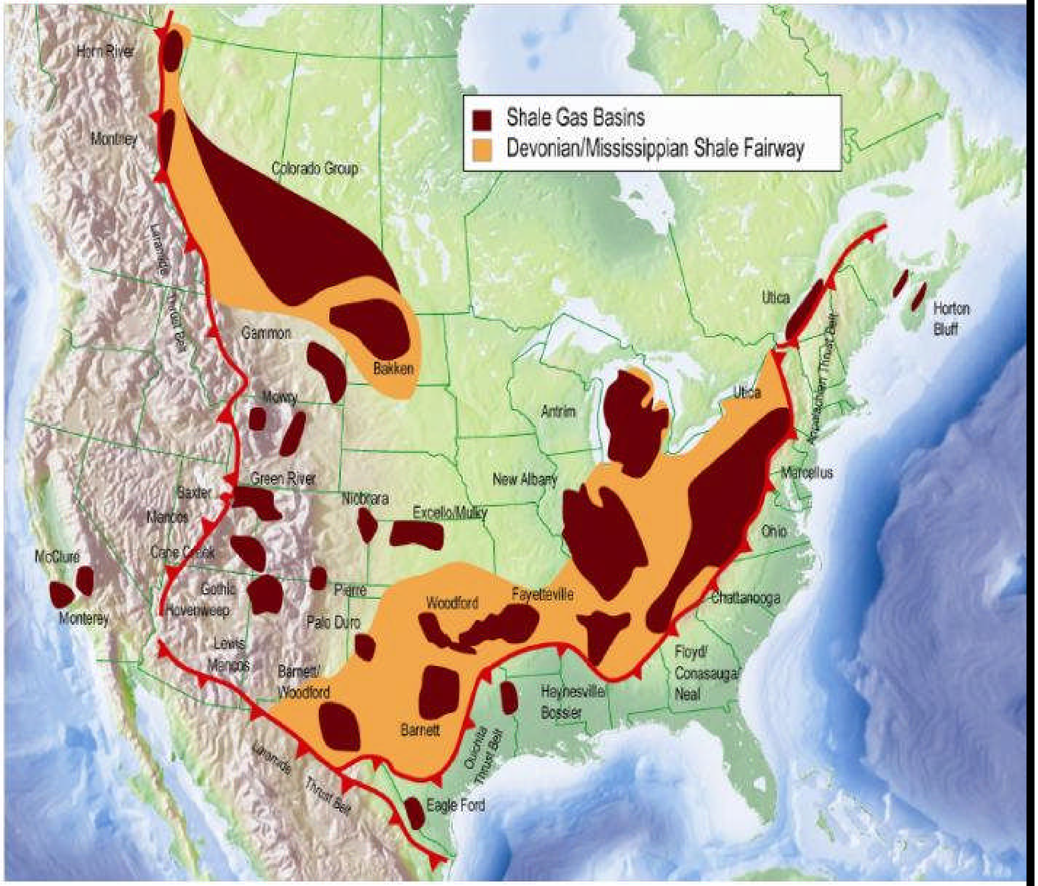


Figure 1.1 Shale Gas Development Areas of North America. [48]

Technologies that have been developed to increase the formation-face contact of the fracture system include:

- *multi-stage fracturing of horizontal wells,*
- *slickwater fluids with minimum viscosity,*
- *simultaneous fracturing.*

Future advances are likely to include

- *hybrid fracturing,*
- *fracture complexity,*
- *fracture flow stability,*
- *methods of re-using water.*

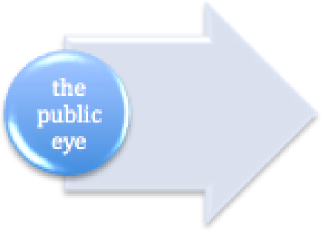
Newly advanced technologies mean that gas reserves that were completely unavailable only a few years ago can now be developed. However, these new technologies (see sidebar) all require large volumes of water.

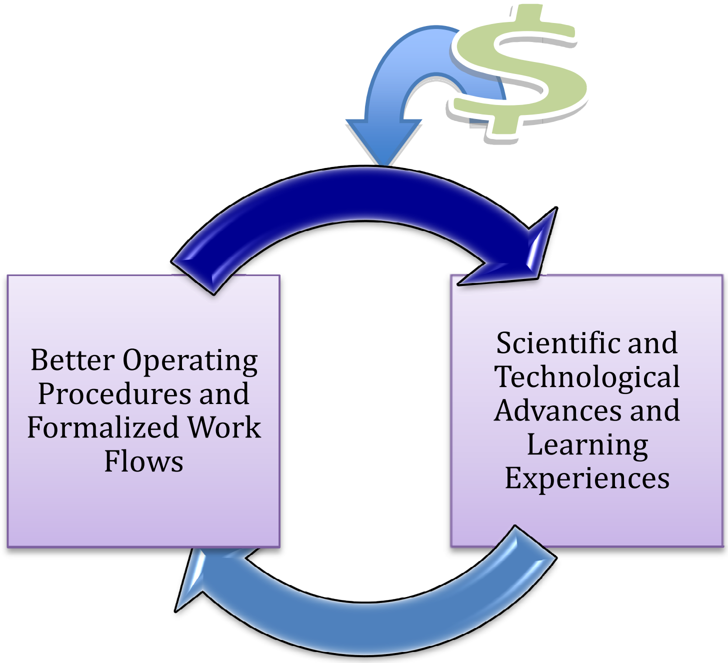
Optimization of water use will require a thorough and accurate understanding of the factors that influence the reuse of fracturing flowback water in hydraulic fracturing operations, including the use and performance of water conditioners and hydraulic fracturing additives.

Cost-effective use of chemicals and water management will require intensive planning and engineering. Ultimately, the refinement of the science and experience with hydraulic fracturing will lead to the development of more formalized work flows and operating procedures. These, in turn, will evolve in response to continuing development and operating experience in shale gas and tight oil development.

Reuse of fracturing flowback:

- *reduces the demand for fresh water,*
- *reduces the amount of water that needs to be disposed,*
- *ideally, reduces overall production costs.*





The recent call for more transparent operations also makes it desirable to outline the roles of the various conditioners and additives used in the various types of hydraulic fracturing methods.

As drilling and completion technologies have advanced, stimulation techniques have developed that are specifically effective in the stimulation of horizontal wells in shale gas zones.

The number of stages and the volume of fracturing fluids pumped per stage have increased. Completions have also been made more effective by the addition of combinations of specific chemical additives to the fracturing fluids.

Factors that influence the reuse of fracturing fluid flowback water must also be thoroughly researched to optimize the process. These include:

- Chemical additives likely to be used in hydraulic fracturing operations.
- A detailed evaluation of the physical and chemical composition and compatibility of the source water.
- Flowback water.
- Produced water.
- Chemical additives.
- Formation.

These factors and the methods of evaluation are discussed in the Decision Tree and the accompanying document.

Reuse and/or recycling practices require the selection of compatible additives (which means that they do not participate in chemical reactions that would be detrimental to any of the processes required for the hydraulic fracturing procedure).

Effort is focused on environmentally benign constituents.

Wise selection of additives may enhance the quantity and compatibility of fluids available and provide more options for use and disposal [17].

There are no optimum, one-size-fits-all completion or stimulation designs for fracturing or fracturing fluid configuration for shale gas wells because no two shales are alike. However, this paper aims to help formalize the logic and process of evaluating the needs for developing and designing cost-effective hydraulic fracturing fluid packages that optimize the use of water conditioners and fracturing additives, and reuse of flowback water.

2.0 Shale Gas Development and Hydraulic Fracturing Technologies

2.1 Introduction

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.

There are now numerous different types of fracturing methods using a variety of fluids and proppant and injection techniques, which vary depending upon the reservoir characteristics.

Hydraulic fracturing technology was developed in the 1940s, and since then, about a million wells have been fractured and billions of cubic meters of natural gas and barrels of oil have been produced.

Hydraulic fracturing allows production from wells that were not previously available. Therefore, it will continue to be an important technology as production from conventional oil and gas fields continues to mature, and the shift in focus to non-conventional resources increases.

2.2 Horizontal Drilling Technology

Horizontal drilling involves drilling many (10+) wells from a single drilling pad. The use of the drilling pad concept reduces the footprint of drilling and completions operations and creates a cost-effective water management infrastructure.

Longer horizontal wells require more stages per well. Each stage receives a fracture treatment, which requires water, so there is an increase in the flowback volume that must be managed.

Horizontal drilling and hydraulic fracturing are costly compared to conventional vertical well completions and hydraulic fracturing, so companies engaged in shale gas development continue to commit significant engineering resources on an ongoing basis to monitor and optimize hydraulic fracturing procedures.

The lengths of the horizontal wells, which began with wells on the order of a few hundred meters, have increased to several thousand meters as operator confidence in the drilling and completion process has grown.

Longer well lengths usually deliver a lower cost per foot as fracturing 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 more fracturing fluid used per well completed.

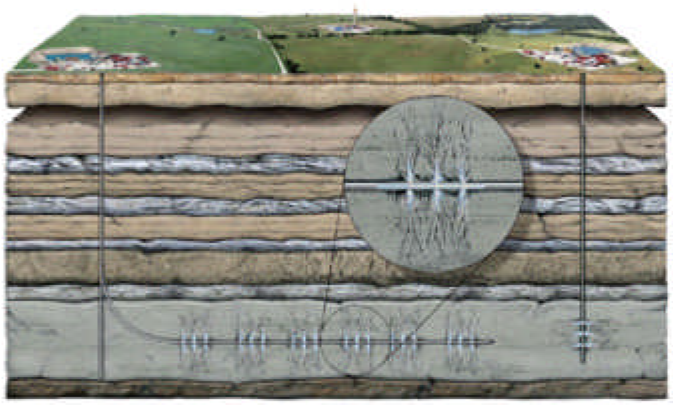


Figure 2.1 Vertical vs Horizontal Drilling with Hydraulic Fracturing [37].

2.3 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. The fracturing fluid pumped down the well is loaded with propping agent, or proppant, which infiltrates the formation and helps to prop the fractures open, as they are at risk of closing once the pressure is released. See Figure 2.2 for some common proppant materials currently in use in Canada.

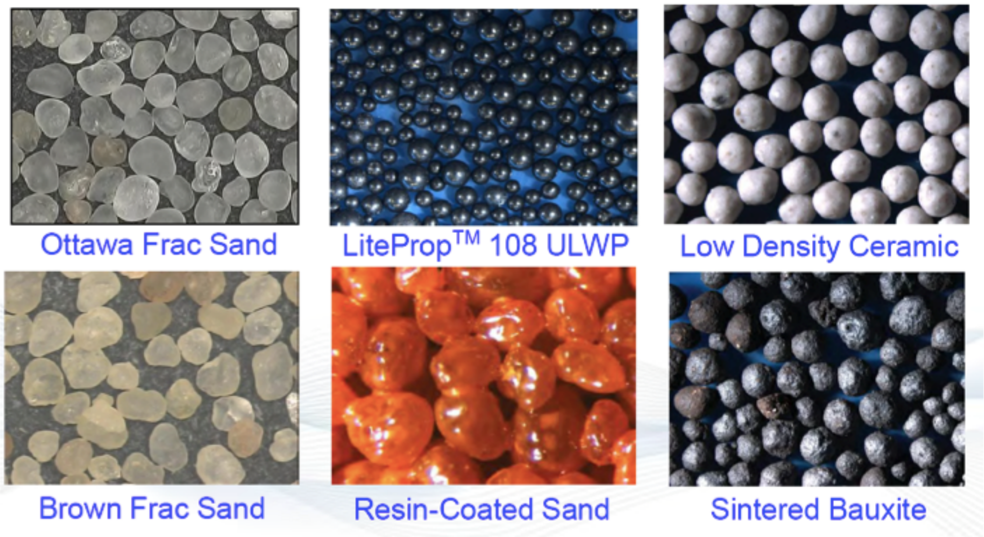


Figure 2.2 some common proppants used in hydraulic fracturing.

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 now capable of accessing significantly larger producing zones, maximizing the amount of resources being recovered and minimizing the amount of surface space required [175].

2.4 Development of Shale Gas Areas

Much useful insight into water management needs and responses has been gained from experiences in the development of shale gas areas such as the Barnett Shale and the Marcellus in the United States, and the Horn River Basin and the Montney areas of Western Canada.

Each shale gas development area is substantially unique. As it undergoes its own development process, it will require its own set of field development procedures and water management approaches.

Shale gas development is occurring in British Columbia, Alberta, Saskatchewan, Quebec, New Brunswick, and thirty-four US states.

Normally, exploitation of a shale play proceeds through five distinct phases: discovery, drilling and reservoir evaluation, completion, production, and shut down and remediation [87].

1. Discovery

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 in the discovery stage depends largely upon knowledge of the reservoir [87].

2. Drilling and Reservoir Evaluation

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 reduce the cost per unit. It is in this stage of development that the issues concerning infrastructure and practical efficiencies are addressed. This is the present state of several currently active shale plays [87].

3. Completion

Completion includes all of the activities and methods to prepare a well for production after drilling, including hydraulic fracturing and installation of equipment for production from a gas well.

4. Production

Production is the phase of development where commercial amounts of hydrocarbons are produced by the well. The production of a well typically lasts from a few years to a few decades [87].

5. Shut Down/Remediation

Shut down and remediation of wells that have produced all their economically viable petroleum must proceed in an environmentally responsible manner. This consideration should be taken into account at the outset of the project. Where will used flowback fluid be disposed of? Will any hazards be introduced by the production procedures? What reclamation procedures will be needed?

3.0 Integrated Water Management Plan

Water volumes for fracturing operations are on the rise, and it is essential to consider how much water will actually be available when planning operations. The cost of treatment and environmental issues are limiting factors that can be mitigated by smart use of water through treatment, reuse and recycling.

Application of advanced treatment technologies and chemical conditioners is expensive, and can easily reach to millions of dollars over the life of the project, so it is essential that the operator arrives at a rationalized decision regarding water management and chemical use early in the project development to minimize costs.

An Integrated Water Management Plan should include the following elements:

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

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 fracturing processes. This decision will affect the volume of water needed at source, and the volume of flowback fluid that must be disposed. This diagram is basically a brief introduction to the broad issues more thoroughly explained in the Decision Tree included in this report.

A change in one of the elements of the water management plan is likely to have a significant impact on the other elements. A water needs assessment is a first step, but needs may be reduced or re-evaluated as innovative solutions arise.

A graphic portrayal of an Integrated Water Management Plan is shown in Figure 3.1.

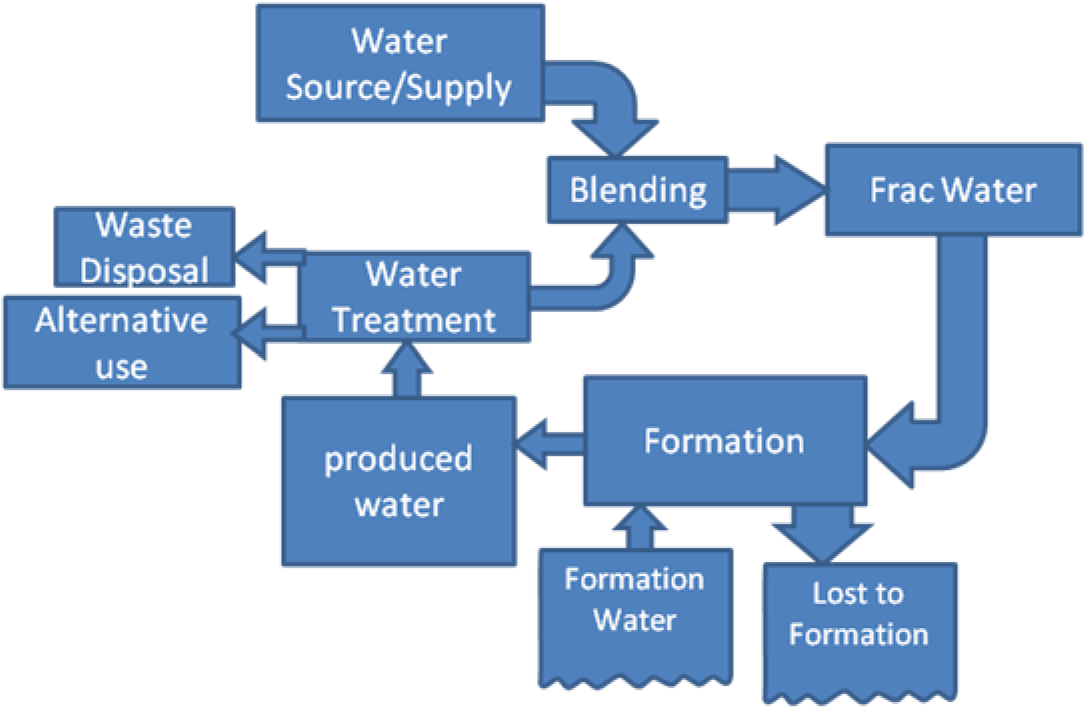


Figure 3.1 Elements of Integrated Water Management Plan.

Questions associated with such a plan include the following:

- **Source Water Acquisition**
    - Where will the water supplies needed for hydraulic fracturing operations be acquired [2]?
- **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 [2]?
- **Storage**
    - What requirements and constraints exist for water storage on site, and how do source water considerations and fracture fluid requirements affect storage requirements [2]?
- **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 [2]?

- **Treatment and Reuse/Recycle**
    - Can the water produced from the fracturing operation be treated and recycled for reuse [2]?
- **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 [2]?

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/fracturing season.
- Number of stages to be fractured in vertical wells.
- Type of fracturing 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 fracturing for horizontal wells.
- Volume of water to be used per horizontal stage 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 will be an iterative process worked out with the operator's 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 and time duration of the drilling/completion plan, the projection of water needs may cover a time period of up to 15 – 20 years. The duration of the Water Management Plan will be driven by the necessary lead time to allow for fiscal planning and water infrastructure development.

A "do nothing" approach might be a valid option. Many factors need to be weighed.

The first option with regard to management of flowback water is to do nothing. Under this scenario, the operator may choose to use the flowback water directly in the next fracturing treatment, or to send all flowback water to disposal. If direct reuse is chosen, they may be subject to higher pumping costs, equipment failures, loss of viscosity, scale deposits on equipment and in the formation, and increased formation damage resulting from poorer fracturing fluid performance. The other “do nothing” approach is to dispose of the untreated flowback water as an oilfield waste. The volumes of fluid requiring disposal are often quite high (20 - 30% of the original volume of water used in the fracturing is in the order of 19,000 m^3). Assuming 40 m^3 per truck load, that equates to 4750 loads sent to the nearest disposal well. If an operator chooses this route, it should first consider the economic viability of other reuse alternatives.

3.1 Change Source Water

In cases where water quality issues arise because the source water contains constituents that are incompatible with the flowback, the formation water and/or the fracturing additives, it may be possible to address the incompatibilities by changing the chosen source water to a water that is more physically or chemically compatible with the fluids and additives being considered for the fracturing treatment, thus eliminating or reducing the need for using expensive conditioners or advanced treatment technologies.

Alternative water sources with more chemically suitable water are not always available. The evaluation of water source options and chemical compatibility is normally conducted as part of the planning process in the development of the Integrated Water Management Plan.

3.2 Blending or Dilution

The most basic solution for obtaining usable fracturing water from flowback fluids is to blend with fresh water. This option is commonly considered before more extensive and more costly remediation options.

3.3 Blending Process

The simplest treatment approach is to dilute or “blend” the poor quality water with a water of better chemical or physical quality until the desired concentration of troublesome chemical parameters is reached.

The kinds of scenarios that might be workable is if there is a desire to use flowback water that has a chloride content above 60,000 mg/L but that the high chloride pushes the cost of water conditioning and fracturing additives to unacceptable levels. If water of better quality is available, such as surface water from a nearby lake, then simple dilution of the flow back water with surface water will bring the mixed water, now to be used for fracturing, into a chloride range below 60,000 mg/L, in which case lower amounts of less expensive fracturing additives can be used. The economics of this scenario is improved by the fact that the flowback water is essentially free, except for the cost of storage and minimal costs associated with removal of solids.

Blending is most effective in situations where it is desirable to reuse flowback water. This is relatively straightforward when the salinity of the flowback is low to moderate and the flowback load recovery is low.

There are two drivers that lead to the consideration of blending to address water management issues:

- Reduce the need for source water.

In cases where there is a limited amount of source water available for hydraulic fracturing, or if the cost of source water is very high, consideration may be given to supplementing the source water (commonly a surface water or groundwater) with flowback water from hydraulic fracturing operations, or produced water that has been generated as part of ongoing oilfield production operations.

- Reduce the cost of disposal of flowback water.

Hydraulic fracturing operations generate flowback water that requires management. The volume of water that flows back from fracturing operations varies from well to well, but can be significant. Because the flowback must be disposed of if a use cannot be identified, it becomes a financial liability to the operator. By virtue of the volume of flowback water that is created, the liability is significant. Commonly, flowback water and other produced waters are disposed of by deep well injection. In cases where the cost of deep well injection is very high, consideration may be given to reducing disposal costs by using the flowback water, usually for subsequent hydraulic fracturing operations to reduce the need to dispose of produced water.

Similarly, the use of water from very saline aquifers where water salinities are in the order of 120,000 mg/L (such as in some of the Devonian zones) can be made attractive through the dilution with surface water. This approach minimizes the volume of fresh water required in a system, or makes using saline aquifers more economically attractive. This presupposes that there is a surface water supply that is available by permit, but there is either not enough surface water available either because of hydrologic factors or regulatory constraints to be a viable single source supply.

In scenarios where the original source water has high salinity and the flowback load recovery is high and formation fluid salinity is very high, the blending capacity may be limited.

An initial determination is a simple calculation of the dilution of one fluid in a second fluid. Simple calculations allow the determination of the concentration of blended constituents in the fixed proportions. Following the determination and selection of the constituents in the blended fluid, it is advisable to run the chemistry of the two fluids to be blended to determine if there are compatibility issues at the blending concentrations selected. If compatibility issues are present, some adjustment in using scale inhibitors may be necessary.

While blending water from multiple sources may resolve issues related to the volume of source water needed, blending waters from a variety of sources tends to create problems in water quality and compatibility that may require the application of advanced treatments after blending is completed.

Whereas blending is an effective mechanism to reduce the concentration of chlorides or other objectionable water constituents, blending may or may not be an effective mechanism to reduce scaling tendencies. Case studies conducted as part of this project suggest that scaling tendencies may in fact increase with blending of waters of differing chemical makeup.

In situations where access to source water is limited, and/or using produced water is compelling the source water being considered for fracturing purposes may be a mixture of water from a variety of sources, including produced water, surface water, or groundwater. This introduces the need to consider a formalized blending process in order to reduce concentrations of objectionable constituents, and to keep water quality as stable as possible. When blending flowback water, care must be taken in confirming that the chemistry used in the blending calculation matches the actual chemistry of the flowback water.

In settings where the salinity of the flowback fluids is high, and the flowback load recovery is high, the phenomena of “salinity creep“ may be observed whereby the salinity of the flowback of the source water increases with each successive fracturing event, requiring that the blending ratio be re-calculated prior to each time that the flowback is used.

For practical purposes, the reuse of flowback water can be accomplished for six to eight fracturing treatments before the quality of the flowback water deteriorates due to the presence of residual chemicals. These residual chemicals make its continued reuse unattractive. In such cases, the flowback water is commonly used in a “slickwater fracture” and new water is introduced to the fracturing process.

Advantages of blending techniques include:

- Only simple calculations are needed to determine effectiveness of blending.
- It can be very cost effective.

- No chemicals are needed beyond possible adjustment of pre-fracturing water conditioners.
- No waste products are made from the blending process.
- Only relatively simple logistics and oversight are needed.

Disadvantages of blending techniques include that they:

- May be limited by volume and concentration of flowback fluids produced.
- May require additional storage capacity for pre- and post-treatment storage.
- May have to be combined with using water conditioners or more advanced water treatment techniques.
- May not resolve scaling problems.

3.4 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 waters, 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-fracturing 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 fracturing fluid planning process involves a comparison of the constituents in the “conditioned” source water against the fracturing additives that are proposed for the fracturing method selected.

Based on the results of the review of the sensitivities of the proposed fracturing 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.

The impurities that affect the desired fracturing fluid properties include:

- Chlorides increase demand for friction reducers and scale inhibitors.
- Scale potential.
- Suspended solids (> 25 microns).
- Bacterial growth.
- Crude oil effects on friction reducer.
- Scale & corrosive materials affect downhole and surface production facilities.
- Adding inhibitors affects friction reducers.

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.

3.5 Flowback Period

If the reuse of flowback fluids is being considered, then a detailed characterization of the likely chemical constituents in the flowback, including the presence of fracturing additives that are included in the fracturing plan must be examined. The evaluation of flowback water includes the same parameters implicit in the pre-fracturing selection of source water for the fracture treatment, plus the additives and conditioners that have been added to the fracturing fluid including H_2S, CO_2 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 fracturing 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.

3.6 Pre-Disposal

Waters that do not meet water quality specifications for hydraulic fracturing and cannot be cost-effectively conditioned or treated become surplus to the needs of the hydraulic fracturing program (such as at the end of the fracturing season) and 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 Naturally Occurring Radioactive Materials (NORM) 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.

4.0 Characterization of Source Water and Flowback

A detailed understanding of the chemical constituents present in source water, formation water, and fracturing flowback fluids is essential to effective management and decison making.

Samples of all waters to be involved in the hydraulic fracturing operations should be collected according to procedures and protocols that will ensure that results are representative and usable. These samples should include water present in the oil reservoir, as well as all available sources of potential injection water. The characterization of the source water chemicals must be adequate to understand any seasonal variability in water chemistry that might be inherent in the water source.

Often the only water analyses in formations above the oil reservoir that might be considered as supply water are those obtained from a drill stem test (DST) 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 and information from existing databases.

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 industry or they may be determined by some regulatory agency.

4.1 Flowback Fluid Composition

Sampling programs have identified the typical components of shale gas fracturing flowback fluids. While proportions vary among formations, there is a consistent list of core components.

The range of total dissolved constituents varies from 10,000 - 250,000 mg/L; the salinity ranges are similar, pH typically ranges between 5.0 - 8.0, and most flowback contains:

- Additives used in fracturing.
- Products of reactions between different additives.
- Substances mobilized from within the formation.
- Substances contributed by multiple sources.

Flowback components detected in one set of analytical results included:

- Components of fracturing fluid.
- Dissolved solids (chlorides, sulfates, calcium).
- Metals (calcium, magnesium, barium, strontium).
- Suspended solids.
- Mineral scales (calcium carbonate; barium sulfate).
- Bacteria (acid producing bacteria; sulfate reducing bacteria).
- Friction reducers.
- Iron solids (iron oxide; iron sulfide).
- Dispersed solids (clay fines, colloids, silts).
- Acid gases (carbon dioxide; hydrogen sulfide).

Since flowback components are influenced by many different factors, they may vary over time. Limited time-series field data from Montney Shale flowback, taken at different times, showed:

- Increased concentrations of total dissolved solids, chloride, and barium.

- Increased radioactivity levels.
- Increased calcium and magnesium hardness.
- Increased concentrations of iron-controlling additives were not used.
- Decreased sulfate levels.
- Decreased alkalinity levels (likely due to acid use).
- Increased metal concentrations.

Fracturing fluids pumped into the well and materials mobilized within the shale contribute to changes in hardness, sulfate, and metals. Specific changes depend on the shale formation, the fracturing fluids used, and fracture operations control.

While some fracturing fluid additives are consumed in the well (e.g. strong acids) or react during fracturing to form different products (e.g. polymer precursors), most additives will be present in flowback water. The Generic Environmental Impact Statement (GEIS) identified several flowback components as significant environmental concerns:

- High Total Dissolved Solids (TDS).
- Chlorides.
- Surfactants.
- Gelling Agents.
- Metals.

Other additives of concern not identified in the GEIS include corrosion inhibitors, friction reducers, and microbiocides.

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 4.1 Physical and Chemical Water Characteristics.

pH	Electrical Conductivity	Temperature (°C)	Specific Gravity	Fluid Density (kg/m^3)
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 $CaCO_3$ (mg/L)	Calcium Ca^{2+} (mg/L)	Magnesium as $MgCO_3$ (mg/L)
Magnesium Mg^{2+} (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, Ba^{2+}	Strontium P.S. (mg/L)	Bacteria
Petroleum Hydrocarbons	Dissolved Oxygen			

Other optional parameters that may be quantified as part of the water characterization include residual fracturing additives, dissolved metals, 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.

Sequential flowback sampling (every 80 m^3 of flowback is recommended for the initial sequential testing) is a method to gain an understanding of the interactions between the fracture fluid, formation, and connate water. Figures 4.1, 4.2, and 4.3 are examples of sequential flowback analysis.

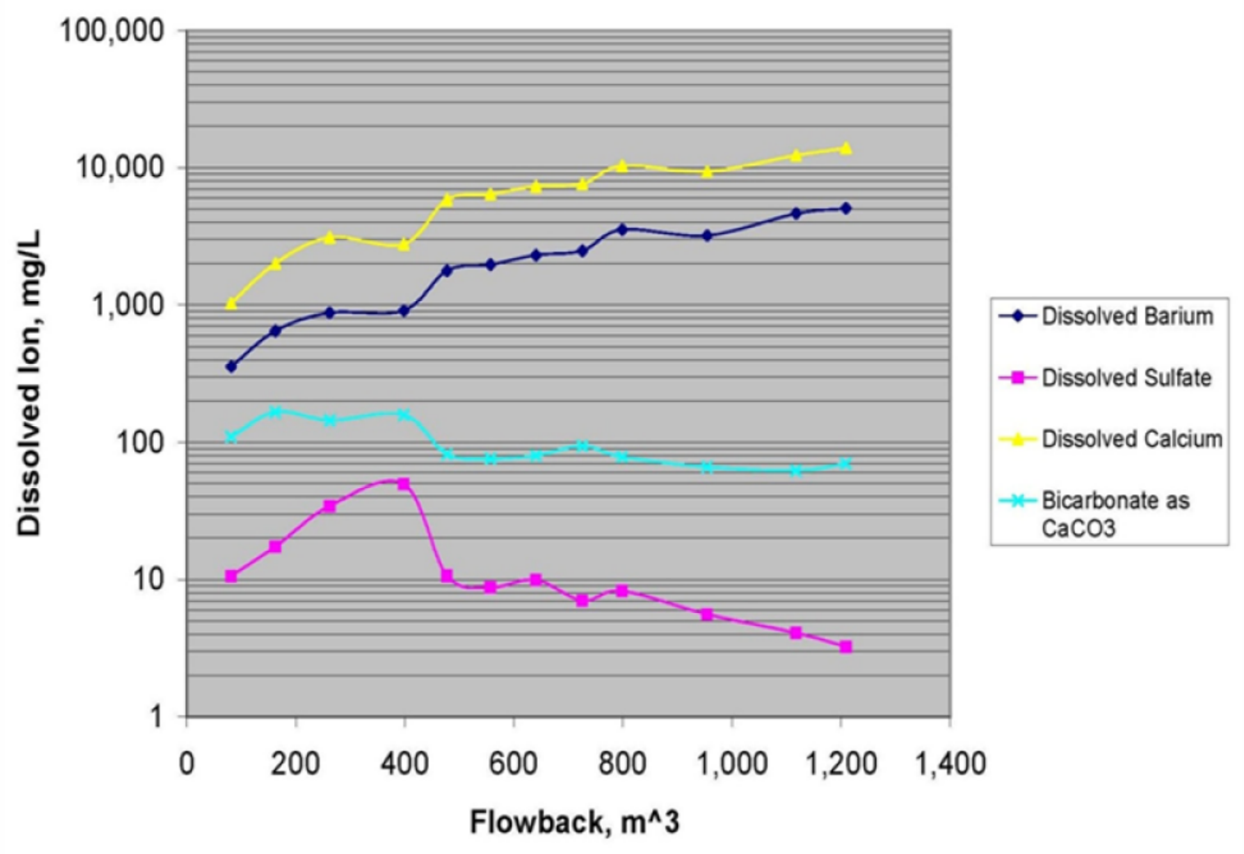


Figure 4.1 Concentrations of several typical scaling constituents in flowback fluid.

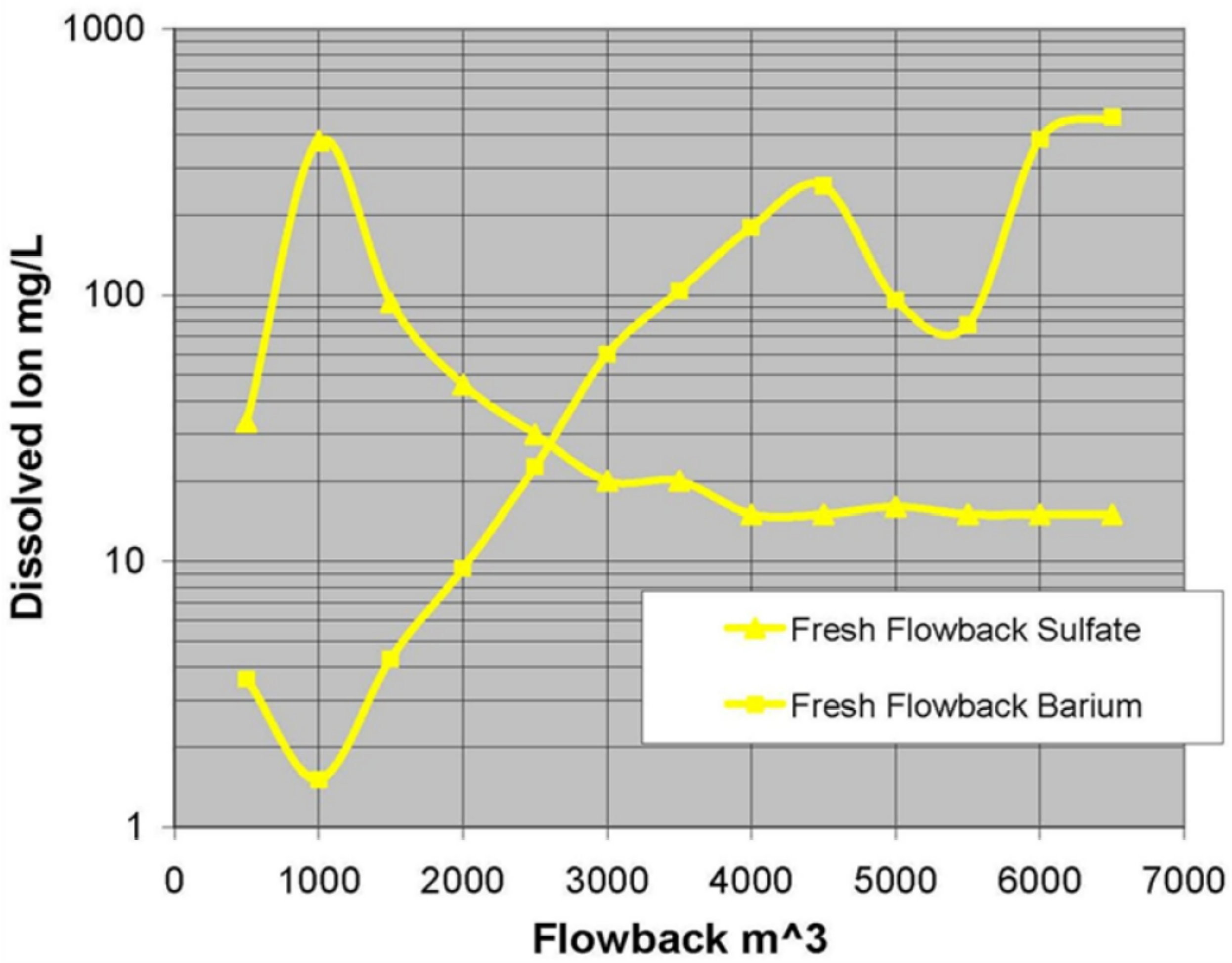


Figure 4.2 Flowback analysis of sulfate and barium from a fresh water based hydraulic fluid.

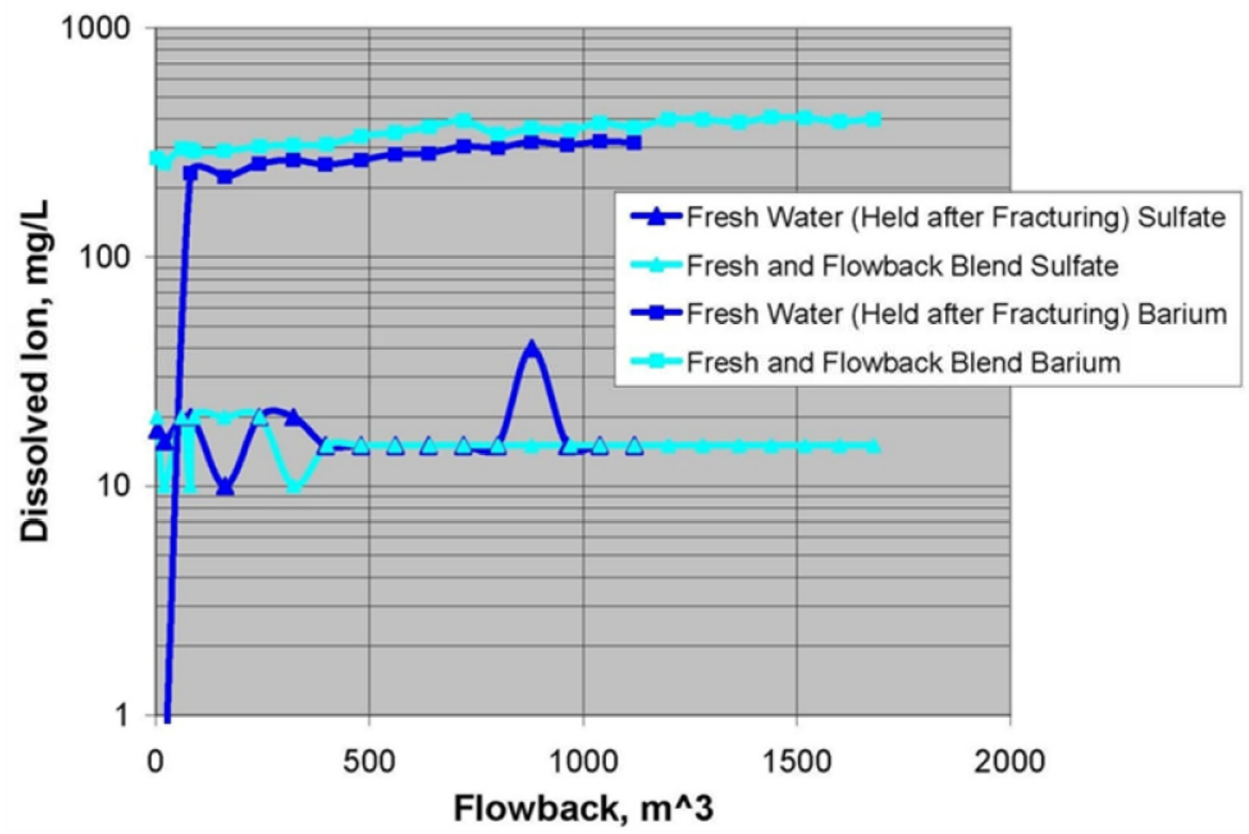


Figure 4.3 Flowback analysis of sulfate and barium from a blend of flowback and fresh water based hydraulic fluid.

4.2 Residual Fracturing Additives in Flowback

One concept for estimating the potential of chemical ingredients in additives to concentrate through successive reuse is that of concentration factor.

When we discuss concentration factor of residual additives we must first define it. Concentration Factor as we are going to define it is going to be the additive effect of a particular chemical ingredient, and its degradation products, in the fluid over successive reuse cycles.

An example of the impact of successive reuse is shown in Figure 4.4. The figure illustrates the accumulation of an additive when all of the flowback is reused for four wells (Wells 2 through 5). It is assumed that there is no degradation of additive and that none of the additive is absorbed or adsorbed in the formation. The volume of hydraulic fracture fluid in the example is 20,000 m^3

and additive is dosed at rate of 0.3 L/m^3. Flowback recovery is 50% of the hydraulic fracture fluid.

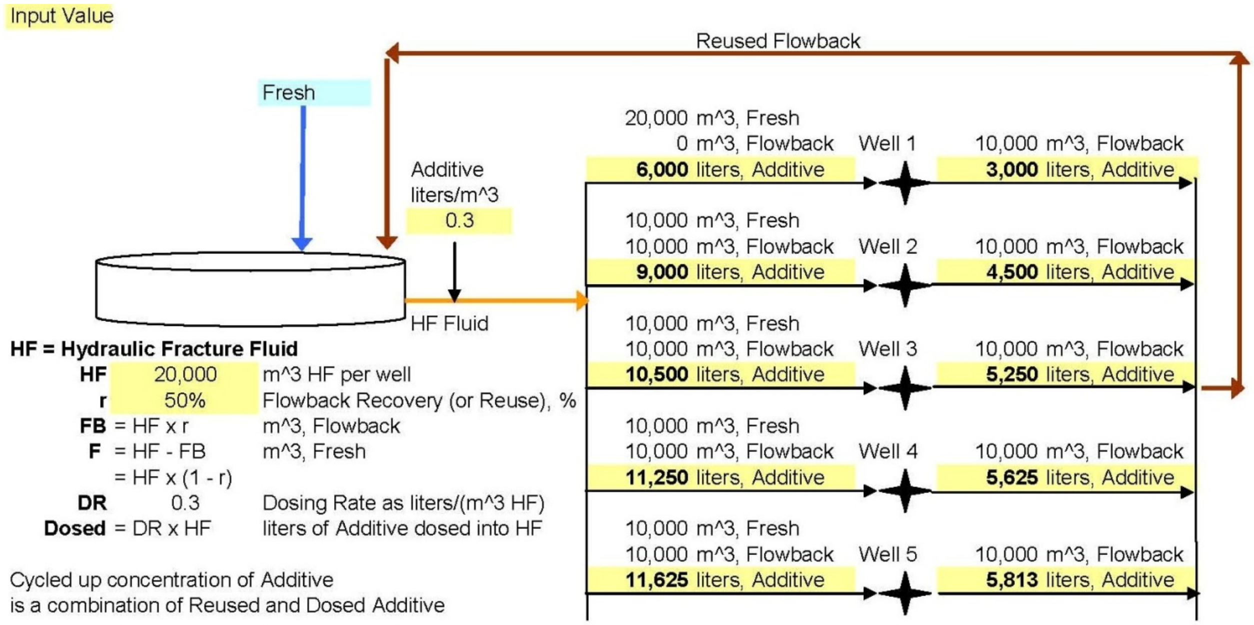


Figure 4.4 Impact of successive reuse.

The hydraulic fracture fluid for Well 1 is 20,000 m^3 of fresh water with 6,000 L of additive. Assuming no degradation of additive and that none of the additive is absorbed or adsorbed in the formation and that flowback recovery is 50%, then the flowback is 10,000 m^3 of fluid which has 3,000 L of additive. The other half of the fluid and additive remains in the formation. This fluid is mixed with fresh water for the fracturing of Well 2.

The hydraulic fracture fluid for Well 2 is 10,000 m^3 of fresh water and 10,000 m^3 of flowback. The flowback has 3,000 L of additive. Additive is dosed into this 20,000 m^3 blend at the rate of 0.3 L/m^3, which means that 6,000 L of fresh additive is added to the blend. The total additive in the blend is 9,000 L. Assuming no degradation of additive and that none of the additive is absorbed or adsorbed in the formation and that flowback recovery is 50%, then the flowback is 10,000 m^3 of fluid which has 4,500 L of additive. This fluid is mixed with fresh water for the fracturing of Well 3.

This process is repeated for Wells 3, 4 and 5. The blend fluid injected into Well 5 contains 11,625 L of additive. The loss of additive in the formation and the addition of fresh additive eventually reach a steady state balance. At this point there is 12,000 L of additive in the blend of fresh water and flowback. In this example the steady state concentration factor is 2. The steady state Concentration Factor can be expressed by the following formula:

$$\textbf{Steady State Concentration Factor} = \frac{\mathbf{1}}{\mathbf{(1 - \%\ Reused\ Flowback\ in\ Blend)}}$$

It is important to note that Concentration Factor does not depend on dosing rate of the additive. It depends only on the % of reused flowback in the blend.

Figure 4.5 shows the impact of % of reused fluid in the blend on Concentration Factor. It is also noted that the time required to reach steady state is longer at higher % reuse.

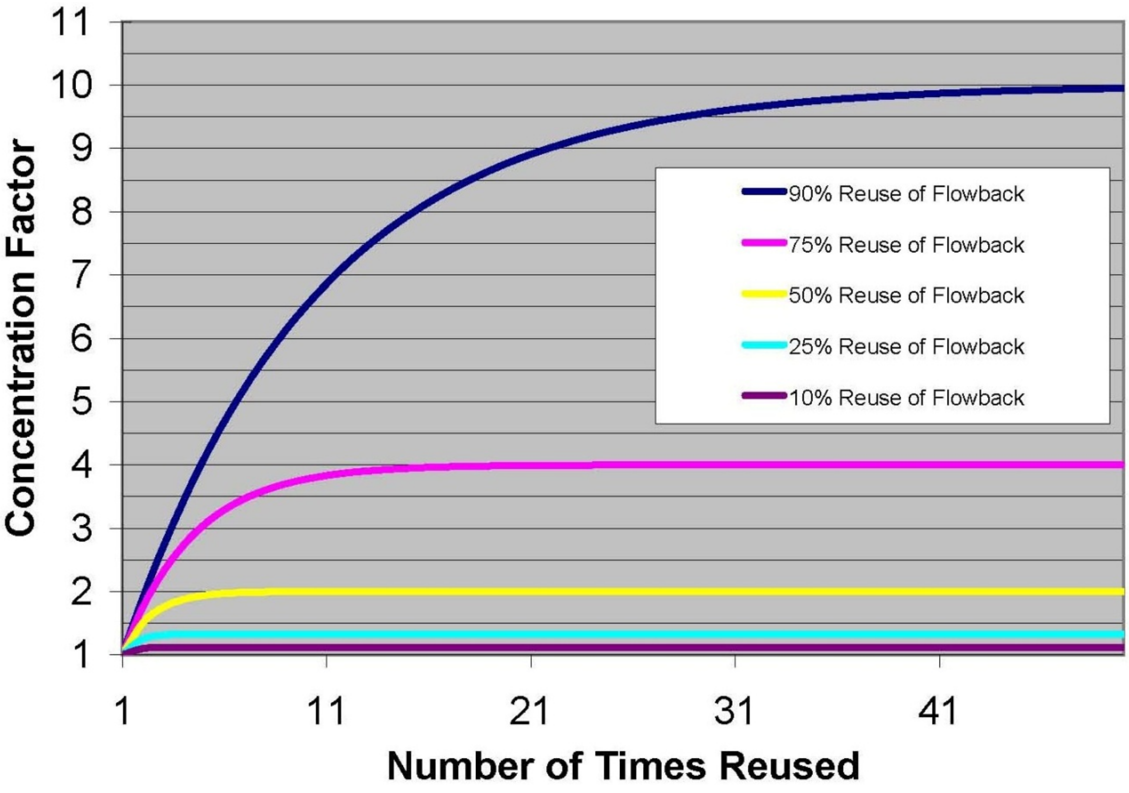


Figure 4.5 Impact of reused fluid.

The actual Concentration Factor of residual fracture additives is the result of a number of factors that all must be considered. The persistence of the additive itself is one of the main governing factors. That is the amount of a specific additive that does not either permanently associate with other components in situ or is degraded into a different form. The in situ associations can take the form of adherence to the rock through chemical interactions of active groups or phase associations with organic or inorganic states. Complexes can also be from dissolution products reacting with the additive to make new species. The complexes or associations can be temporary as environment changes such as temperature, pressure and fluid shear can act to remobilize these constituents resulting in different amounts being returned at different times during flowback cycle.

Additive degradation can occur through chemical reaction with fluid components, exposure to temperature and mechanical shear. These can all act to degrade the additive into a non usable form that may have nuisance or harmful side effects, or that might not have any impact.

The other factor effecting concentration is the differential mobility of carrier fluid to the component of concern. This is most prevalent in polymers that will be mechanically retained while allowing carrying fluid to leakoff. This is a result of molecular size of polymer being effectively filtered and carrying fluid to be removed from the cycle as a irretrievable filtrate.

This is important because as the component is concentrated a point can be reached that a maximum amount of component exists that the fluid will not be useful anymore due to interference of its function or side effects of high concentrations such as formation damage.

The additives which could be expected to accumulate to a measurable level include friction reducers, corrosion inhibitors, scale inhibitors and some biocides.

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). This could lead to souring of the well or scaling of the wellbore.

There has been little or no discussion in the literature on how the residual additives can affect performance of these fracturing fluids and this is an area of further study.

As an example, reuse of flowback from crosslink fluids might create problems with fresh additives because two key components must be kept within a tight window. The crosslinker must be kept within a given concentration range, if this range is exceeded over crosslinking can occur that severely changes fluid performance. If this range is exceeded in base fluid before additive addition, it is impossible to get fluid performance without conditioning the water first. Likewise if too many buffering agents accumulate in flowback cycles a fluid of adequate performance is impossible to achieve. With all these factors it is very important to manage the residual additives and their concentration as part of the water management strategy.

4.3 Databases

In the early stages of planning the drilling and fracturing programs for shale gas development, 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, it provides the basis for a first approximation of the water quality of the water sourcing options and the formation fluid. Identification of any prohibitively problematic water constituents identified during this initial characterization can result in significant savings in water development costs.

Databases that may provide initial insight into water quality include:

- Hydrogeological Databases maintained by provincial governments.
- Waterwell files (Alberta Environment, AE).

- Water Quality data reported by Facilities operating under Environmental Approvals (Alberta Environment, AE).
- Hydrogeological base maps (Alberta Geological Survey, AGS).
- Reports In Support of Application to Divert under Water Act (Alberta Environment, AE),
- Surface water databases.
- Oilfield databases (Energy Resources Conservation Board, ERCB).
- Oilfield databases (private by subscription).

5.0 Decision Tree

The Decision Tree is intended to provide a method for the evaluation of reusing flowback in hydraulic fracturing operations. The Decision Tree is not intended to serve a prescriptive method. It is intended to provide a method and framework for a consistent approach to answering a set of interdependent questions. The Decision Tree can also serve to evaluate the use of alternative sources of water, such as saline water or municipal wastewater.

Step 1 of the process presumes a certain amount of information, data, and knowledge about the formation and flowback water characteristics. This information will not likely be available in the early stages of development and forces the user to make assumptions until the data becomes available.

The Decision Tree is most useful when the characteristics of the formation, flowback fluid, and the presence of residual additives are well understood. The next sections describe that characterization.

Step 1. Select the percentage of flowback to blend with source water.

The initial step in the decision tree process is to collect the necessary information and assumptions required to develop an approach to managing the flowback water and managing the water issues.

Water management using the tree is an iterative process, and some initial assumptions regarding the fracturing are necessary. The information required in Step 1 includes assumptions regarding the hydraulic fracturing that is being proposed, including:

- Fracturing Treatment Type.
- Volume of Fluid to be Pumped.
- Water Conditioning and Fracturing Additives.
- Fracturing Fluid Recovery.
- Bottomhole Pressure and Temperature.
- Assumption of Blending Ratio.
- Chemical Analysis - Rock Core.

Fracturing Treatment Type

The provisional selection of the fracture type will allow the identification of sensitive constituents in the source, flowback, and formation waters to be identified and addressed. Dozens of fracturing types and hybrids are available, however, for the purposes of this decision making process, the four fracturing types most commonly applied in shale development have been integrated into the decision tree. These are:

- Slickwater.
- Linear Gel.
- Crosslinked Gel.
- Viscoelastic.

Each of the fracturing types requires different chemicals or additives, and has differing sensitivities to the chemical constituents in the source water, flowback water, and formation water.

Fracturing treatment types are discussed in Section 2.0 of Appendix C.

Volume of Water to be Pumped

The volume of water to be pumped during the fracturing is the basis for projecting the volume of flowback that will be generated, and which must be reused or otherwise managed.

For horizontal wells, the total volume pumped is the product of the number of stages pumped and the volume of fluid pumped per stage.

Water Conditioning and Fracturing Additives Likely to be Needed.

There are two types of chemicals used during a hydraulic fracturing operation:

1. Chemical additives are added to the hydraulic fluid to act as conditioners to modify the properties of the water to achieve a desired purpose (e.g. reduce friction, suspend proppant, reduce scaling, bacteria, and corrosion). These conditioners may include:

- Acids.
- Biocides.
- Scale Inhibitors.
- Iron Sequesters.

2. Certain chemical additives are required by each specific fracturing type. These additives include:

- Friction Reducers.
- Gels.
- Crosslinkers.
- Breakers.

These chemical additives are discussed in Section 1.0 of Appendix C.

Fracturing Fluid Recovery

The volume of fracturing fluid that flows back from a fractured well after pumping stops is known as flowback recovery and is commonly expressed as a percentage of the total volume of fracturing fluid pumped into the well during the fracturing operation. The flowback recovery is variable from formation to formation, and from area to area within a specific shale gas development area. The observed flowback recovery varies between 5% and 70%. A rule of thumb, in the absence of actual data, is a flowback recovery of 30%. As the history of fracturing and flowback recovery in any particular shale gas area becomes more extensive, trends begin to appear and the recovery percentage estimate can be adjusted.

An estimate of the flowback recovery is an essential part of the decision tree process. The flowback recovery becomes the basis for generating blending ratios, which determine the chemical characteristics of the hydraulic fluid.

Bottomhole Pressure and Temperature

Compatibility of source water, flowback, and formation water is a function of the chemical constituents and concentrations, as well as temperature and pressure. Bottomhole pressure and temperature are required to make a determination of compatibility. Water chemistry and geochemical simulators can be used to calculate scaling indices over a range of pressures and temperatures.

Assumption of Blending Ratio

The selection of the blending ratio that is initially being considered may be based on the objective of:

- Avoiding disposal costs of the flowback fluid.
- Reducing source water needs.

As an example, if the total fracturing volume is 20,000 m^3, and the flowback is expected to be 30%, that means that a blending ratio of 70% fresh and 30% flowback is needed to use all of the flowback. The blending ratio is often expressed as a percentage to facilitate determining the compatibility of fluids for a range of mixes using the geochemical simulator. The above blend would be expressed as 70:30.

The selection of a blending ratio is usually not relevant for the first fracturing treatment conducted in a drilling season when no flowback water is available, and the fracturing fluid is made from 100% source water. In this case, move to Step 2 without setting the blending ratio.

Chemical Analysis – Rock Core

In addition to the chemical analyses conducted on the fluid, it is necessary to determine the presence of sensitive clays (Section 5.0 Appendix A), which may be present in the rock formation. The common clays that account for most of the real and perceived clay problems are kaolinite, smectite (montmorillonite), illite and chlorite. Predicting the response of a certain clay to water flow is almost impossible without testing. The common technique for identifying the clay mineralogy is with a Scanning Electron Microscope. After identification of sensitive clay types, laboratory core flow tests are typically required to determine if clays are reactive with the fracturing fluid. The results of the analyses of rock core will be used to identify the need for clay stabilizers.

When the physical and chemical characteristics of the source water, flowback water, and formation water have been appropriately determined, and a provisional blending ratio has been selected, go to Step 2.

Step 2. Run compatibility model on the blend to check for fluid scaling.

The chemical analyses generated in Step 1 become the input that is used in this step. The scaling tendency of the source water, formation water, and the flowback water are determined using a geochemical simulator (see below). In addition to the scaling tendency of the individual fluids, the scaling tendency for a range of blends of fluids (source water blended with flowback, water) can be determined.

Examples of the output from a compatibility simulation are shown in the Case Studies section. Positive output from the geochemical simulator is indicative of a positive scaling tendency, while negative output is indicative of a corrosive condition. As a rule of thumb, for a scaling index of 1 or more for a carbonate scale, the use of a scale inhibitor is suggested. Any positive scaling index for a barite scale warrants consideration of the use of a scale inhibitor.

A standard set of geochemical simulations would include scaling indices for the following:

- Source water.
- Flowback water.
- Formation water.
- A blend of source water and flowback water.
- A blend of flowback water and formation water.
- A selected mix of blended source water and flowback water and formation water.

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 [14].

The software modeling program developed by Schlumberger 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 is 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.

Because of the complexity of scale formation and the difficulty of the calculations, and the necessary thermodynamic and kinetic calculations to predict scaling, many computer programs have been produced to aid the user.

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 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 the following:

- 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

Once the scale indices 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.

Another way to evaluate compatibility is to mix the waters 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.

Step 3. Are the source water and flowback fluid compatible from scaling, bacteria, and corrosion perspectives?

Scaling

The results of the geochemical simulations in Step 2 are used to determine the compatibility of the source water and flowback water.

Bacteria

Bacteria in the fracturing fluid, if injected into the formation, can result in damage to the formation. In Section 2.0 of Appendix A, information about biocides is discussed to provide a basis for determining if the biocide of choice is compatible with the blend of source and flowback.

Corrosivity

Substances such as salts, acids, hydrogen sulfide, carbon dioxide and oxygen can result in damaging corrosion of tubular and surface equipment. Corrosion inhibition is discussed in Section 4.0 of Appendix A.

If the source water and flowback water are compatible, go to Step 9 to determine if the blend and the formation are compatible. If the source water and flowback water are not compatible with the formation, go to Step 4.

Step 4. Dilution.

Dilution is possible when disposal is inexpensive or storage is available.

Step 5. Water conditioning by chemical addition.

If the source water and the flowback are not compatible it is often possible to address the issues by chemical addition. Table A on the flow chart lists options for "Water Conditioning by Chemical Addition". The chemical addition options are discussed in Appendix A.

Step 6. Is water conditioning by chemical addition a good option?

The use of chemicals as a conditioner in fracturing fluids is almost invariably a good option. As a rule of thumb, it is suggested that the least costly, simplest treatment technologies be used to meet treatment needs for fracturing fluids. There is a long history of the use of conditioners in the oil and gas sector, and the effectiveness of conditioners is well understood. Chemical conditioners have a wide range of uses and ultimately several conditioners are likely to be used in any fracturing job:

- Biocide.
- Corrosion Inhibition.
- Iron.
- Scale.
- Clay Stabilization.

Chemical conditioners are discussed in Appendix A.

The use of chemical conditioners may be integrated into a fracturing fluid design that includes pretreatment and or blending. In this step, the application of chemical conditioners in Table A is evaluated for the water issues expected during the fracture treatment, and the scaling tendencies identified in Step 2. This evaluation provides a basis for comparison to more treatment and management techniques identified in Step 8.

If the water conditioning by chemical additives is considered a good option, go back to Step 2 and confirm that the chemical addition addresses the incompatibility. If the water conditioning by chemical additives is not considered to be a good option, the use of more aggressive physical /chemical treatment techniques should be evaluated in Step 7.

Step 7. Evaluate water conditioning by physical/chemical water treatment to resolve identified problem.

If the source water and the flowback are not compatible and conditioning by chemical addition will not address the compatibility issues, then physical/chemical treatment options are evaluated. Table B lists options for "Water Conditioning by Physical/Chemical Treatment". The treatment options are discussed in Appendix B.

Step 8. Is water conditioning by physical/chemical treatment a good option?

The use of physical/chemical treatment technologies becomes an option when other simpler or less costly techniques for achieving water quality objectives are not possible, and if there is a compelling need to reuse the flowback water.

The cost of the technologies must be evaluated against other options, such as disposal.

Application of advanced treatment technologies is expensive (easily in the millions of dollars over the life of the project) so it is essential that the operator arrive at rational decisions regarding water management and chemical use early in the project development to minimize costs. Implementation of an Integrated Water Management Plan, which is the recommended context for evaluating the implementation of physical/chemical treatment, is discussed in Section 3.0 of this manual.

Once the physical/chemical treatment technologies in Table B have been considered, and the water treatment technologies have been confirmed as a good option, return to Step 2 and confirm that the chemical addition addresses the incompatibility. If the physical /chemical treatment options are not considered good options, go to Step 19A.

Step 9. Are the blend and formation compatible?

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 source water used for injection is different from the produced water.

Two types of compatibility or reactions related to water quality and water injection need consideration.

The first 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. The testing described in Step 2 is appropriate for this compatibility evaluation. It is also noted that in the case of reused flowback, 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.

The second 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.

There are two general mechanisms for formation damage or permeability impairment from injected water/formation rock interactions:

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

The second 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.

There are a number of test procedures available to detect and identify possible damage. 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.
- Chemical analysis of the waters involved in the fracture.
- Chemical analysis of the flowback.

The tests are usually run in the order listed. The rationale for this order is first to run the core flow tests to see if there is a problem. 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.

Step 10. Select hydraulic fracturing process.

The selection of the fracture fluid type is normally made by the completions team.

A mutual understanding between the water management team and the completions team improves the overall effectiveness of the program.

Step 11. Are the blend (including residual additives from flow back and added conditioners) and the hydraulic fracturing additives compatible?

The chemistry of recycled flowback becomes more complex with each successive cycle. Measuring the concentration of residual chemical ingredients and the degradation products against a high salinity background is a complicated task. The potential accumulation of residual chemical ingredients and their degradation products is discussed and a method for estimating the maximum concentration using the concept of concentration factor is presented in Section 2.0 of this document.

There is very limited information on the impact of residual chemical ingredients and their degradation products on fresh hydraulic fluid additives. Generally, slickwater fluids are the least sensitive, and cross-linked fluids are the most sensitive as noted in Appendix C.

Table 5.1 provides guidelines for evaluating the impact of concentrated residual chemical ingredients. Field testing is recommended for confirmation.

Table 5.1 Sensitivity of Fracture Fluids to Concentration Factor.

Hydraulic Fracture Fluid Type	Suggested Concentration Factor Threshold Requiring Additional Investigation	Additive or Additive Residuals which can impact fresh Fracture Fluid	Remedial Options
Slickwater Fluids	2	Friction Reducer	Breaker
Linear Gels	2	Polymer	Breaker
Cross Link Fluids	Field Tests Required	Borate	Disposal of Flowback or Physical/Chemical Water Treatment for Dissolved Solids
	2	Polymer	Breaker

	Field Tests Required	Buffers	Disposal of Flowback or Physical/Chemical Water Treatment for Dissolved Solids

Step 12. Conduct tests using field samples.

Once the conditioners and additives to be used in the fracturing are identified and provisional dosages are selected, the fracturing fluid design is tested using actual fluid samples collected from the field for the source water, formation water and flowback water using field samples. The objective of the test is to confirm that the fracturing fluid design will perform as predicted. These tests are routinely conducted by the hydraulic fracturing service provider or the operator's reservoir engineer. The tests may include bench scale tests, mixing or jar tests, and friction loop tests.

If field samples of the source water, flowback water, and formation water are not available, it is possible to recreate the chemical makeup of a fluid based on a historical analysis. These manufactured fluids then can be used to test the viability of the fracturing fluid design.

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 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 (Figure 5.1). The friction loop allows for the measurement of the frictional pressure drop across the pipe section at different flow rates [19].

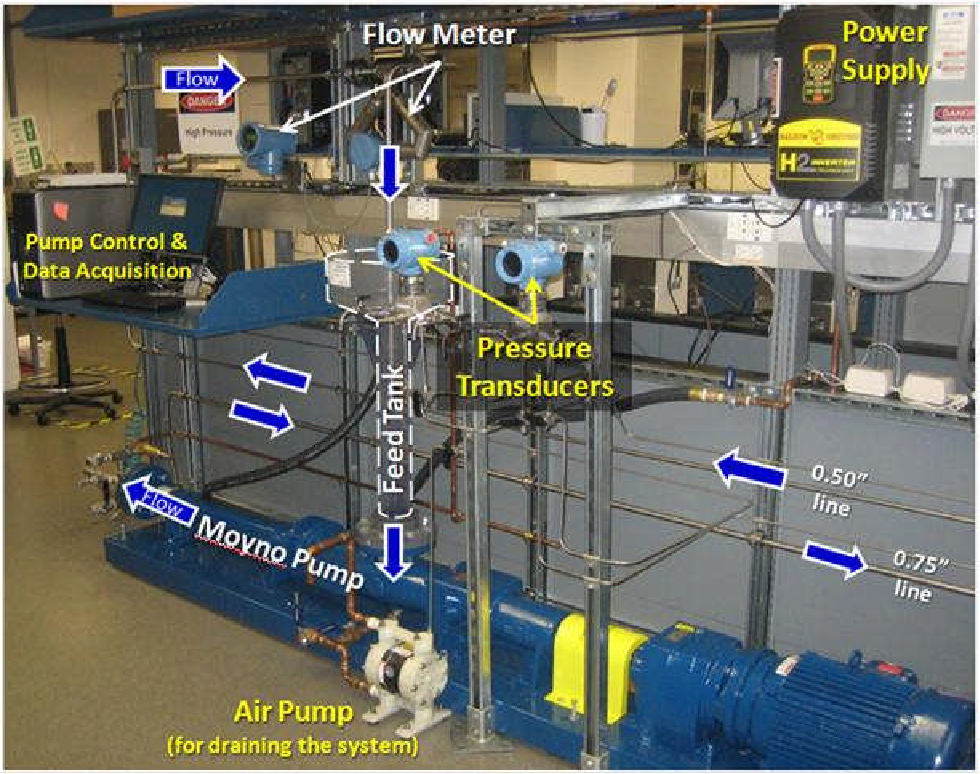


Figure 5.1 Friction Loop Tester.

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

$$\%DR = (dP_{Water} - dP_{Fluid}) / dP_{Water} \text{ x } 100$$

Where;
dP_{Water} = differential pressure of water in 3/8 in. (0.952 cm) tubing, psi
dP_{Fluid} = differential pressure of the fluid in 3/8 in. tubing, psi
%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 fracturing operation is mixed with the source water in a tank, and differential pressure gauges record the dP as time elapses.

Jar Tests

In spite of the power of existing geochemical models and the detailed analyses that are commonly conducted to identify water issues, questions regarding compatibility remain enormously complex, and it is common practice to conduct "mixing" tests in the lab or in the field using samples of the actual source water and conditioners and additives to verify the predicted chemical responses under operational conditions. The mixing tests, or "jar tests" are shown in Figure 5.2.

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 that precipitate insoluble compounds.

Figure 5.2 Jar Test.

When the field testing work is complete, go to Step 13.

Step 13. Does HF fluid meet performance expectations?

The determination regarding the performance of the fracturing fluid is normally made by the fracturing service provider or the operator's reservoir engineer. If there are shortcomings in the performance of the fracturing fluid, adjustments may be made either based on pre-fracturing testing, or during the execution of the fracturing itself.

If the testing indicates that there are shortcomings in the performance of the fracturing fluid, the design of the proposed fracturing fluid is revisited (go to Step 11A). If the testing indicates that the performance of the fracturing fluid meets expectation, the execution of the fracturing can proceed (go to Step 14).

Step 14. Conduct HF process.

In Step 14, the hydraulic fracturing for which the fracturing fluid program is has been designed is executed using the fracturing fluid design. The elements of hydraulic fracturing are described in Section 2.0 of this manual.

When the fracturing is complete, go to Step 15.

Step 15. Collect flowback and as necessary perform analysis to characterize chemistry.

When the fracturing operation is complete, the next step is the completion of the well. The well test is conducted by a well testing contractor to determine the production characteristics of the well. The well is allowed to flow in a controlled manner for a period of time, which may extend several weeks.

In order to characterize the flowback process, it is desirable to monitor fluid production and collect water samples for analysis over the duration of the flowback test to establish the chemical characteristics of flowback with time (every 80 m^3 of flowback is recommended for the initial sequential testing). The parameters that should be analyzed are discussed in Section 4.0 of this manual. During initial sequential testing in a formation, field measurements of temperature, pH, conductivity, H_2S, flow rate and cumulative volume of water produced should be recorded hourly during the flowback period.

When the chemical and flow characteristics of the flowback have been documented, go to Step 16.

Step 16. Evaluate for health, safety and environmental considerations.

The sampling and monitoring of fluid properties produced should be conducted within the framework of a safety plan prepared and implemented by the operator's health and Safety Team. Thousands of shale gas wells have been drilled and completed using hydraulic fracturing techniques, and the need for safety measures and practices is well understood by the industry and regulators.

When health, safety, and environmental considerations have been identified, go to Step 17.

Step 17. Is the fluid nonflammable?

Fluids recovered from flowback commonly consist of a mixture of gas and fracturing fluid. Both the natural gas and the free phase hydrocarbon should be considered to be flammable (go to Step 17A). If the flowback is not considered flammable, go to Step 18.

Step 17A. Degas or treat with separator.

It is necessary to separate the gas from the fracturing fluid. If the produced fluids also contain free phase hydrocarbons it will be necessary to conduct phase separation of the flowback water and the liquid hydrocarbons as part of the fluid recovery process. Once flammable gases and liquids have been separated from the flowback water, go to Step 18.

Step 18. Is it sour by NACE MR-0175 requirements?

Flowback and produced water from the shale gas wells may contain H_2S gas. As a rule of thumb, if the H_2S is present in the gas phase, it will also be present in the liquid phase at a concentration approximately 1/10 of the concentration of H_2S in the gas phase.

If the water is considered to be sour, then go to Step 18A. If the water is not considered to be sour, go to Step 19.

Step 18A. Remove H_2S gas.

If H_2S is present in the water phase, the H_2S can be removed using chemicals or through stripping before it can be incorporated into a fracturing fluid. The requirement to remove H_2S from produced water is dictated by provincial regulation. Hydraulic fracturing service providers have established working limits for H_2S concentrations, above which the operator will not handle the fluid because of risk to pumping equipment. Refer to Section 4.0 of Appendix A.

Once the H_2S gas has been removed from the flowback water, go to Step 19.

Step 19. Can the flowback be reused safely?

Correct Health and Safety work practices should be used in handling chemicals and work practices. A safety plan should be prepared by the operator's Health and Safety team to ensure that management of chemicals and fluids are handled appropriately. The major safety issues related to reuse of flowback fluid are:

- H_2S.
- Temperature.
- NORMS management.

The application of oilfield safety and best working practices should allow flowback water to be re-used in a manner that is safe and protective of the environment.

If a safety evaluation determines that the flowback water can be reused safely, return to Step 1 to begin the preparation of the next fracturing fluid design. If the flowback cannot be used safely or if no other use for the flowback is found, go to Step 19A.

Step 19A. Dispose as per local regulations.

If the flowback fluids cannot be reused safely, or the flowback fluids have no further use, such as at the end of a fracturing program, the fluids should be disposed of according to approved industry standards and procedures. The most likely scenario that would lead to disposal of fracturing flowback is when there is no further opportunity to reuse the flowback.

If the cost of source water is low, injection costs are low, and the cost of treatment is high, there is an economic disincentive to reuse the flowback water. There are still other considerations, such as the environmental benefit of reuse.

At the end of the drilling season, there may not be a need or ability to reuse flowback water, and other disposal methods must be considered. The most common practice is to inject the water fluid back into the formation.

PTAC Water Decision TREE

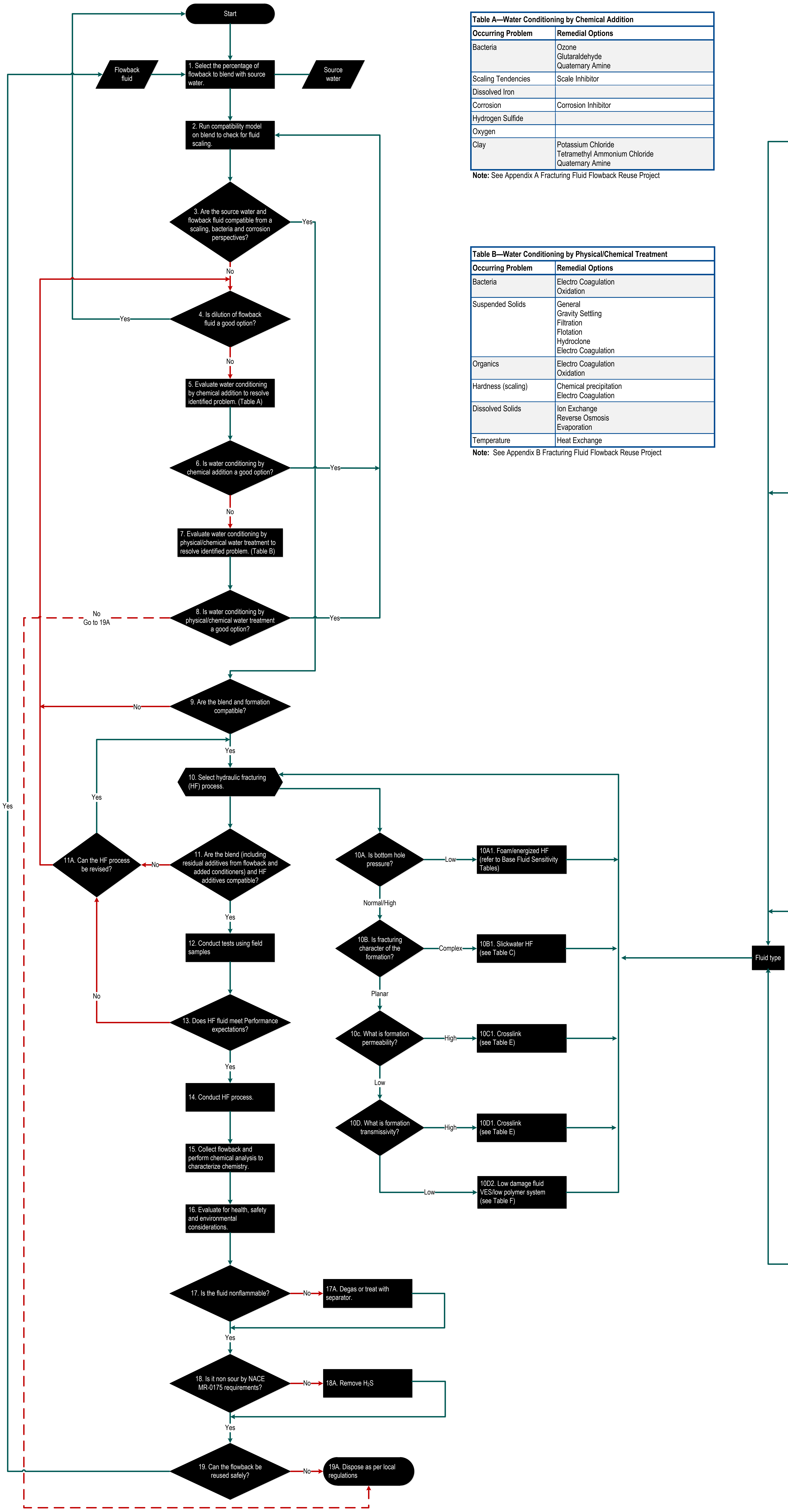


Table A—Water Conditioning by Chemical Addition

Occurring Problem	Remedial Options
Bacteria	Ozone Glutaraldehyde Quaternary Amine
Scaling Tendencies	Scale Inhibitor
Dissolved Iron	
Corrosion	Corrosion Inhibitor
Hydrogen Sulfide	
Oxygen	
Clay	Potassium Chloride Tetramethyl Ammonium Chloride Quaternary Amine

Note: See Appendix A Fracturing Fluid Flowback Reuse Project

Table B—Water Conditioning by Physical/Chemical Treatment

Occurring Problem	Remedial Options
Bacteria	Electro Coagulation Oxidation
Suspended Solids	General Gravity Settling Filtration Flotation Hydroclone Electro Coagulation
Organics	Electro Coagulation Oxidation
Hardness (scaling)	Chemical precipitation Electro Coagulation
Dissolved Solids	Ion Exchange Reverse Osmosis Evaporation
Temperature	Heat Exchange

Note: See Appendix B Fracturing Fluid Flowback Reuse Project

Table C—Slickwater

Water Quality	Range	Problem	Remedial Options
Temperature (degC)	3–40	Temp for safe handling of fluid at surface lower temperatures may cause freezing problems	Use a hydration unit for mixing of water and friction reducer
pH	5.0–8.0	pH < 5 may cause prolonged hydration pH > 8.0 may result in inadequate gelling	NaOH or HCl
Chloride (mg/L)	<90,000	High chloride concentration inhibits hydration. Greater amounts of friction reducer maybe required.	Mechanical vapour recompression, ionization, reverse osmosis, electrocoagulation
Hardness (mg/L $CaCO_3$)	<15,000	Divalent cations inhibits hydration	flocculation and coagulation, ion exchange, electrocoagulation
Concentration Factor for Residual Additive Ingredients	2	Friction reducer impact on formation	Breaker
Suspended Solids (mg/L)	50 (< 100 um)	Possible damage to reservoir	Settling or filtration

Table D—Linear Gels

Water Quality	Range	Problem	Remedial Options
Temperature (degC)	15–40	Lower temperatures may prolong the hydration of gel polymers	Passive cooling in tanks or ponds Heat exchanger
pH	6.0–8.0	A pH < 6 may cause prolonged hydration of gel A pH > 8 may result in inadequate gelling	NaOH or HCl
Chloride (mg/L)	<50,000	High chlorides concentration destabilizes the fluid and hydration	Mechanical vapour recompression (MVR), ionization, reverse osmosis (RO), electrocoagulation
Iron (mg/L)	<25	Iron degrades and breaks polymers in gels, causing premature breaking and crosslinking	Iron sequestration, oxidization
Sodium (mg/L)	<1000	Excess sodium destabilizes the fluid	Ion exchange, MVR, RO
Bacteria (CFU)	0	The presence of bacteria degrade the gel viscosity	Biocide, ozone
Concentration Factor for Residual Additive Ingredients	2	Polymer impact on formation and fresh additive	Breaker
Suspended Solids (mg/L)	50 (< 100 um)	Possible damage to Reservoir	Settling or filtration

Table E—Crosslink Fluids

Water Quality	Range	Problem	Remedial Options
Temperature (degC)	15–40	Temperature range for safe handling of fluid at surface and hydration of gel.	Passive cooling in tanks or ponds. Heat exchanger.
pH	6.0–8.0	pH < 6 may cause prolonged hydration of gel pH > 8 may result in inadequate gelling	NaOH or HCl
Chloride (mg/L)	<30,000	High Cl^- concentration destabilizes the fluid and creates problems with crosslinking	Mechanical vapour recompression (MVR), ionization, reverse osmosis (RO), electrocoagulation
Iron (mg/L)	<25	Iron degrades and breaks polymers in gels, causing premature breaking. Iron can also create premature crosslinking	Iron sequestration, oxidization
Alkalinity (mg/L $CaCO_3$)	<600	Acts as a pH buffer, so high concentrations of crosslinking activator may be needed	Ionization, mechanical vapour recompression, scale inhibitor
Sodium (mg/L)	<1000	Excess sodium destabilizes the fluid	Ion exchange, MVR, RO
Silica (mg/L)	<35	Excess silica may inhibit the crosslinking of polymer gels	
Bacteria (CFU)	0	The presence of bacteria degrade the gel viscosity	Biocide, ozone
Concentration Factor for Residual Additive Ingredients	Field Tests Required	Borate impact on control of crosslinking	Disposal of flowback or physical/chemical water treatment for dissolved solids
	2	Polymer impact on formation and fresh additive	Breaker
	Field Tests Required	Buffers impact on control of crosslinking	Disposal of flowback or physical/chemical water treatment for dissolved solids
Suspended Solids (mg/L)	50 (< 100 um)	Possible damage to reservoir	Settling or filtration

Table F—Viscoelastic Fluids

Water Quality	Range	Problem	Remedial Options
Temperature (degC)	20– 40	Temperature range for safe handling of fluid at surface	Passive cooling in tanks or ponds Heat exchanger
pH	5–12	Outside this range can effect properties of surfactants. Testing required	
Chloride (mg/L)	<33,000	Being outside of this range could affect the fluid quality and performance of standard chemistry. Alternative blends can be tested above this concentration.	Blending, mechanical vapour recompression, reverse osmosis, ionization, electrocoagulation
Suspended Solids (mg/L)	50 (< 100 um)	Possible damage to reservoir	Settling or filtration

Case Studies

Fracturing Fluid
Flowback Reuse Project

Prepared by M-I SWACO, a Schlumberger Company
for Petroleum Technology Alliance of Canada
and the Science and Community Environmental Knowledge (SCEK)
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Case Studies

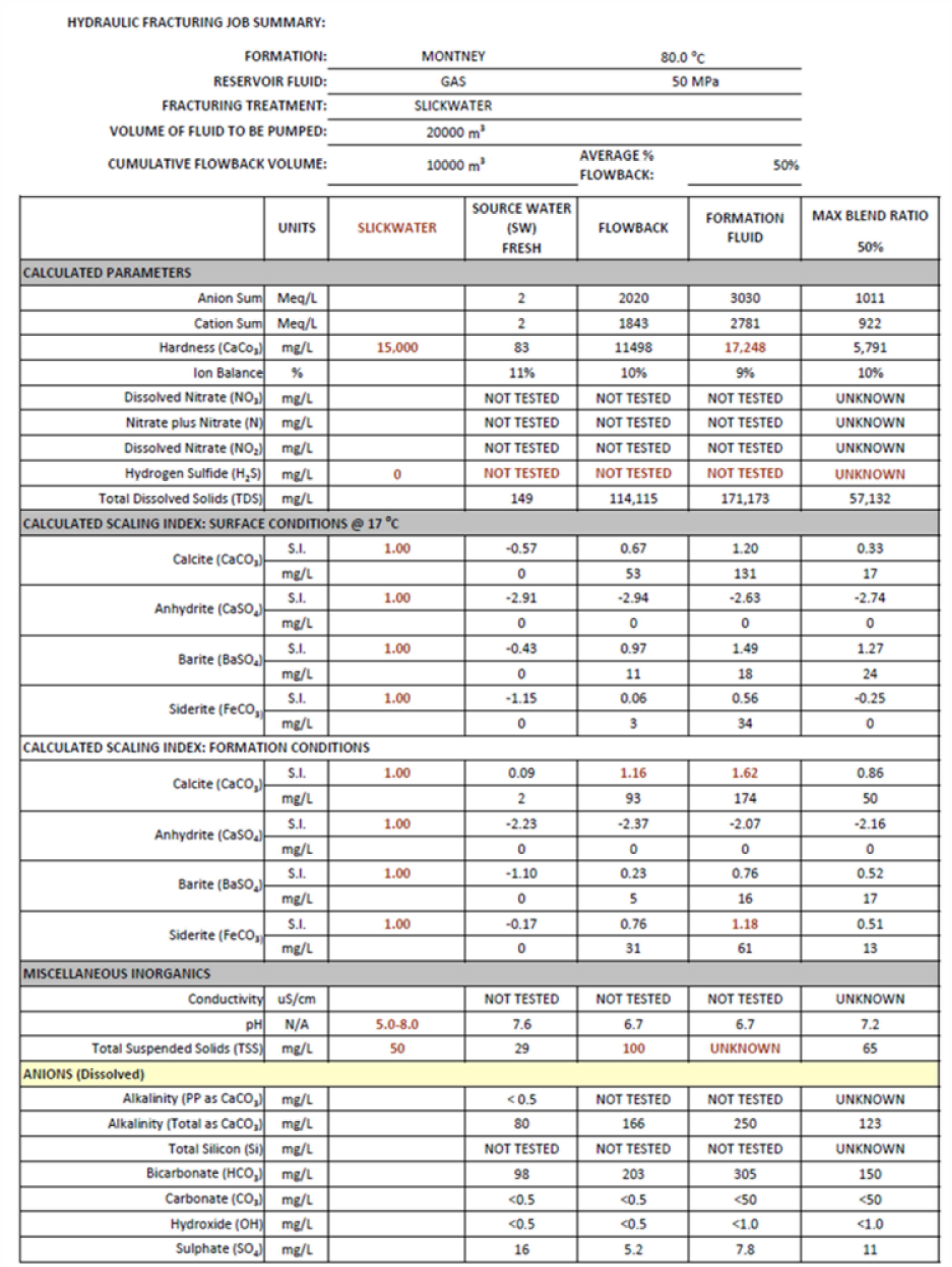
Two case studies have been prepared that demonstrate the application of the Decision Tree. The case studies are intended as a validation of the applicability of the decision-making process, and as an example for those interested in applying the Decision Tree process. The following parameters apply to these case studies:

- Each of the case studies starts from some basic assumptions regarding what type of fracturing technology will be applied.
- In each case, a fracturing treatment similar to the treatment currently being applied has been chosen.
- Similarly, for each case study, assumptions regarding flowback have been made based on current knowledge of the performance of fractures that have already been conducted.
- In each case, the starting point is the evaluation of compatibility of the three fluids: source water, formation water, and fracturing flowback water.
- The propensity of each of these fluids to generate scale (that is, a precipitate) in response to changes in temperature and pressure is determined.
- At this point, any scaling tendency observed does not take into account the scaling or incompatibility that may subsequently occur in response to mixing fluids.

This assessment is followed up with an evaluation of compatibility and scaling tendency when the fluids are mixed in various concentrations and subsurface conditions.

1.0 Decision Tree Example – Montney Formation Case Study

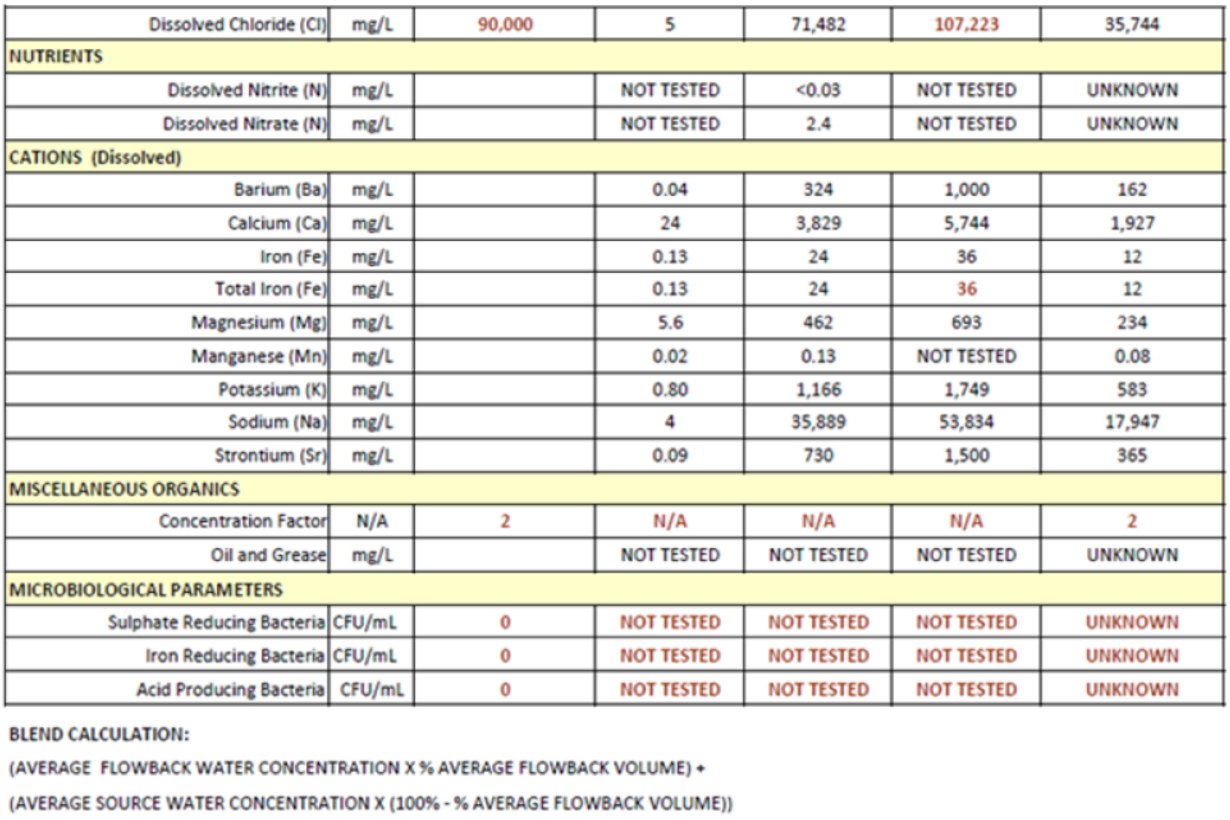
Table 1: Montney Formation Case Study Data Summary



HYDRAULIC FRACTURING JOB SUMMARY:

FORMATION:	MONTNEY		80.0 °C
RESERVOIR FLUID:	GAS		50 MPa
FRACTURING TREATMENT:	SLICKWATER		
VOLUME OF FLUID TO BE PUMPED:	20000 m^3		
CUMULATIVE FLOWBACK VOLUME:	10000 m^3	AVERAGE % FLOWBACK:	50%

	UNITS	SLICKWATER	SOURCE WATER (SW) FRESH	FLOWBACK	FORMATION FLUID	MAX BLEND RATIO 50%
CALCULATED PARAMETERS						
Anion Sum	Meq/L		2	2020	3030	1011
Cation Sum	Meq/L		2	1843	2781	922
Hardness ($CaCo_3$)	mg/L	15,000	83	11498	17,248	5,791
Ion Balance	%		11%	10%	9%	10%
Dissolved Nitrate (NO_3)	mg/L		NOT TESTED	NOT TESTED	NOT TESTED	UNKNOWN
Nitrate plus Nitrate (N)	mg/L		NOT TESTED	NOT TESTED	NOT TESTED	UNKNOWN
Dissolved Nitrate (NO_2)	mg/L		NOT TESTED	NOT TESTED	NOT TESTED	UNKNOWN
Hydrogen Sulfide (H_2S)	mg/L	0	NOT TESTED	NOT TESTED	NOT TESTED	UNKNOWN
Total Dissolved Solids (TDS)	mg/L		149	114,115	171,173	57,132
CALCULATED SCALING INDEX: SURFACE CONDITIONS @ 17 °C						
Calcite ($CaCO_3$)	S.I.	1.00	-0.57	0.67	1.20	0.33
	mg/L		0	53	131	17
Anhydrite ($CaSO_4$)	S.I.	1.00	-2.91	-2.94	-2.63	-2.74
	mg/L		0	0	0	0
Barite ($BaSO_4$)	S.I.	1.00	-0.43	0.97	1.49	1.27
	mg/L		0	11	18	24
Siderite ($FeCO_3$)	S.I.	1.00	-1.15	0.06	0.56	-0.25
	mg/L		0	3	34	0
CALCULATED SCALING INDEX: FORMATION CONDITIONS						
Calcite ($CaCO_3$)	S.I.	1.00	0.09	1.16	1.62	0.86
	mg/L		2	93	174	50
Anhydrite ($CaSO_4$)	S.I.	1.00	-2.23	-2.37	-2.07	-2.16
	mg/L		0	0	0	0
Barite ($BaSO_4$)	S.I.	1.00	-1.10	0.23	0.76	0.52
	mg/L		0	5	16	17
Siderite ($FeCO_3$)	S.I.	1.00	-0.17	0.76	1.18	0.51
	mg/L		0	31	61	13
MISCELLANEOUS INORGANICS						
Conductivity	uS/cm		NOT TESTED	NOT TESTED	NOT TESTED	UNKNOWN
pH	N/A	5.0-8.0	7.6	6.7	6.7	7.2
Total Suspended Solids (TSS)	mg/L	50	29	100	UNKNOWN	65
ANIONS (Dissolved)						
Alkalinity (PP as $CaCO_3$)	mg/L		< 0.5	NOT TESTED	NOT TESTED	UNKNOWN
Alkalinity (Total as $CaCO_3$)	mg/L		80	166	250	123
Total Silicon (Si)	mg/L		NOT TESTED	NOT TESTED	NOT TESTED	UNKNOWN
Bicarbonate (HCO_3)	mg/L		98	203	305	150
Carbonate (CO_3)	mg/L		<0.5	<0.5	<50	<50
Hydroxide (OH)	mg/L		<0.5	<0.5	<1.0	<1.0
Sulphate (SO_4)	mg/L		16	5.2	7.8	11



Dissolved Chloride (Cl)	mg/L	90,000	5	71,482	107,223	35,744
NUTRIENTS						
Dissolved Nitrite (N)	mg/L		NOT TESTED	<0.03	NOT TESTED	UNKNOWN
Dissolved Nitrate (N)	mg/L		NOT TESTED	2.4	NOT TESTED	UNKNOWN
CATIONS (Dissolved)						
Barium (Ba)	mg/L		0.04	324	1,000	162
Calcium (Ca)	mg/L		24	3,829	5,744	1,927
Iron (Fe)	mg/L		0.13	24	36	12
Total Iron (Fe)	mg/L		0.13	24	36	12
Magnesium (Mg)	mg/L		5.6	462	693	234
Manganese (Mn)	mg/L		0.02	0.13	NOT TESTED	0.08
Potassium (K)	mg/L		0.80	1,166	1,749	583
Sodium (Na)	mg/L		4	35,889	53,834	17,947
Strontium (Sr)	mg/L		0.09	730	1,500	365
MISCELLANEOUS ORGANICS						
Concentration Factor	N/A	2	N/A	N/A	N/A	2
Oil and Grease	mg/L		NOT TESTED	NOT TESTED	NOT TESTED	UNKNOWN
MICROBIOLOGICAL PARAMETERS						
Sulphate Reducing Bacteria	CFU/mL	0	NOT TESTED	NOT TESTED	NOT TESTED	UNKNOWN
Iron Reducing Bacteria	CFU/mL	0	NOT TESTED	NOT TESTED	NOT TESTED	UNKNOWN
Acid Producing Bacteria	CFU/mL	0	NOT TESTED	NOT TESTED	NOT TESTED	UNKNOWN

BLEND CALCULATION:

(AVERAGE FLOWBACK WATER CONCENTRATION X % AVERAGE FLOWBACK VOLUME) +

(AVERAGE SOURCE WATER CONCENTRATION X (100% - % AVERAGE FLOWBACK VOLUME))

Referencing the Decision Tree flowchart, an analyst may process the data above to arrive at the following decisions.

Step 1: Blend Ratio

- With an average flowback rate of 50%, the maximum blend ratio for the Montney would be 50% source water and 50% flowback.

Steps 2 & 3: Compatibility Simulations: Scaling, Bacteria & Corrosion

- The compatibility simulations suggest a minor scaling risk for a blend ratio of 50% source water and 50% flowback water for the Montney. Potential scaling concerns may be further mitigated with the application of a scale inhibitor, as outlined in Appendix A.
- Bacteria analyses were unavailable for this case study review. Therefore the potential bacteria compatibility concerns with fracturing fluid chemistry is unknown. It is

recommended to consider applying biocide as outlined in Appendix A.

- The observed pH and chloride concentrations suggest a relatively low corrosion potential. If acids are to be used in the well stimulation, it's recommended to consider applying a corrosion inhibitor as outlined in Appendix A.

Step 4: Dilution Requirements

- Source water/flowback blending at a ratio of 50:50 is not a good option for utilization of bulked flowback fluids without the consideration of the use of scale inhibitors.

Steps 5 & 6: Water Conditioning by Chemical Addition

- The evaluation of the use of conditioners indicated the need for conditioners to address calcite, barite, and FeO_3 scaling tendency.
- In addition, there is a need for the use of biocide, acid, that are more or less standard part of a fracturing fluid package. These conditioners include iron sequesters, corrosion inhibitors.
- Water conditioning is cost effective for Montney.

Steps 7 & 8: Water Conditioning by Physical/Chemical Treatment

- A total suspended solids analysis was unavailable for this case study review, so the potential solids compatibility concerns with fracturing fluid chemistry is unknown. The total suspended solids within both the source and flowback waters are likely to be present at concentrations greater than 100 mg/L with an average particle diameter size greater than 0.50 microns. Therefore, water conditioning by physical treatment with filtration as found in Appendix B may be recommended.
- An analysis for residual fracturing additives within the flowback water was unavailable for this case study, so the potential compatibility concerns with residual fracturing additive concentrations are unknown. The presence of residual gel and friction reducers are expected, so water conditioning by either physical (electrocoagulation) or chemical treatment (ozonation) as detailed in Appendix B may be needed.

Step 9: Formation Compatibility

- Neither clay mineralogy nor core tests were conducted as part of this case study; therefore formation compatibility of the source water and flowback blend is unknown. Application of clay stabilizers as outlined in Appendix A may be required.

Step 10: Selection of Hydraulic Fracturing Process

- The fracturing process selected for this case is the slickwater method. This determination considers Steps 10A to 10D, and is commonly determined by a reservoir engineer. In many cases, the decision regarding water issues is made within that context. The water constituents that are sensitive in Slickwater Fracturing treatment are indicated in Table C on the Water Decision Tree.

Step 11: Blend Compatibility with Slickwater Fluids

- From the analytical data available, the source water and flowback water blend appear to have positive compatibility with the slickwater method fluid requirements.

2.0 Decision Tree Example – Cardium Formation Case Study

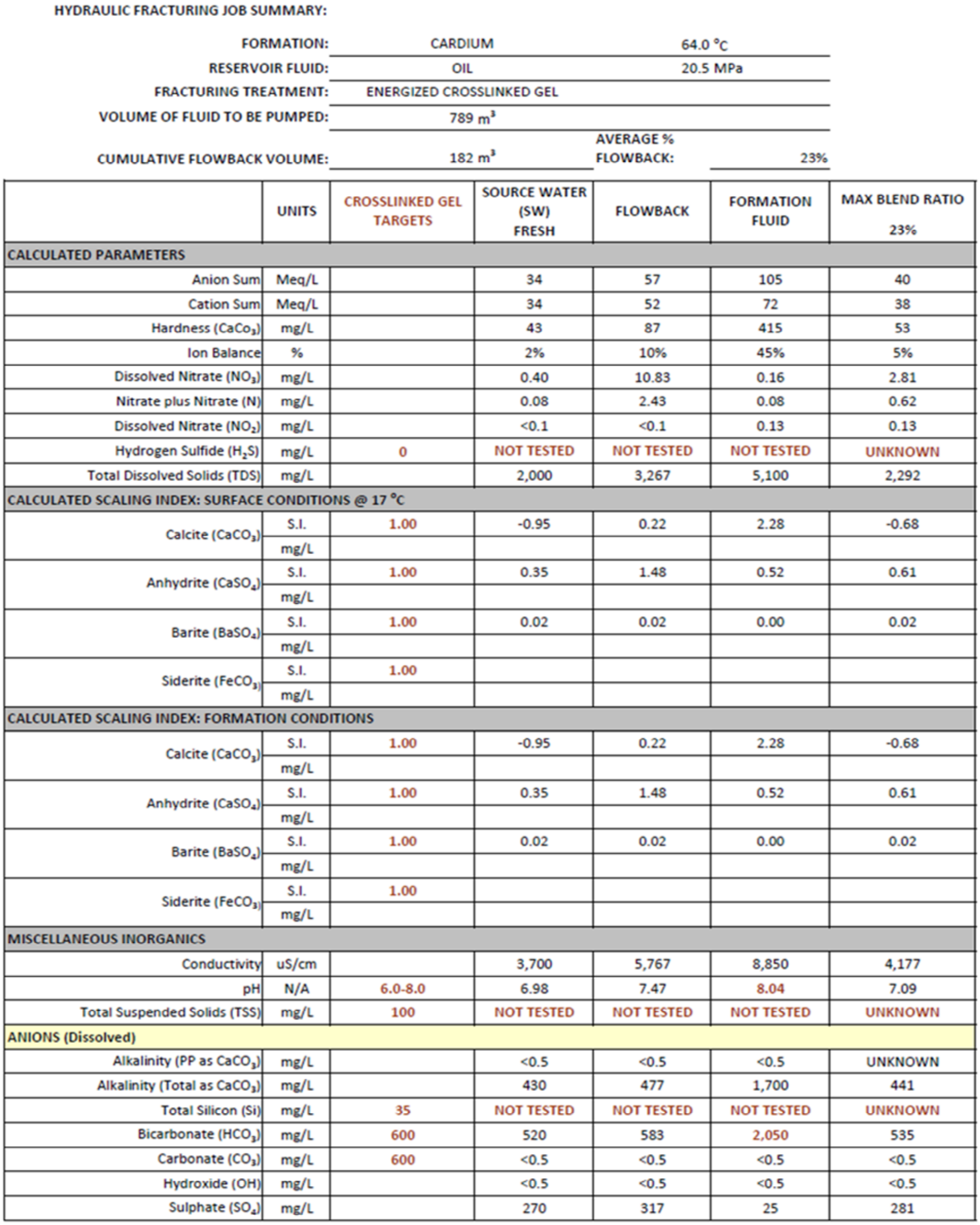
This case study evaluates compatibility considerations when recycling flowback for hydraulic fracturing with energized crosslinked gel fracturing treatments within the Cardium Formation.

This case study is based on three flowback samples acquired from the same hydraulic fracturing job at varying recovered fluid volume increments, one source water sample, and two formation water samples.

The accuracy of this case study is constrained by quality of the analytical data. It is preferable to obtain samples from multiple sources and jobs for a formation when possible.

By applying the pre-screen portion of the Decision Tree methodology (Steps 1-11) the perceived compatibility considerations were identified as follows.

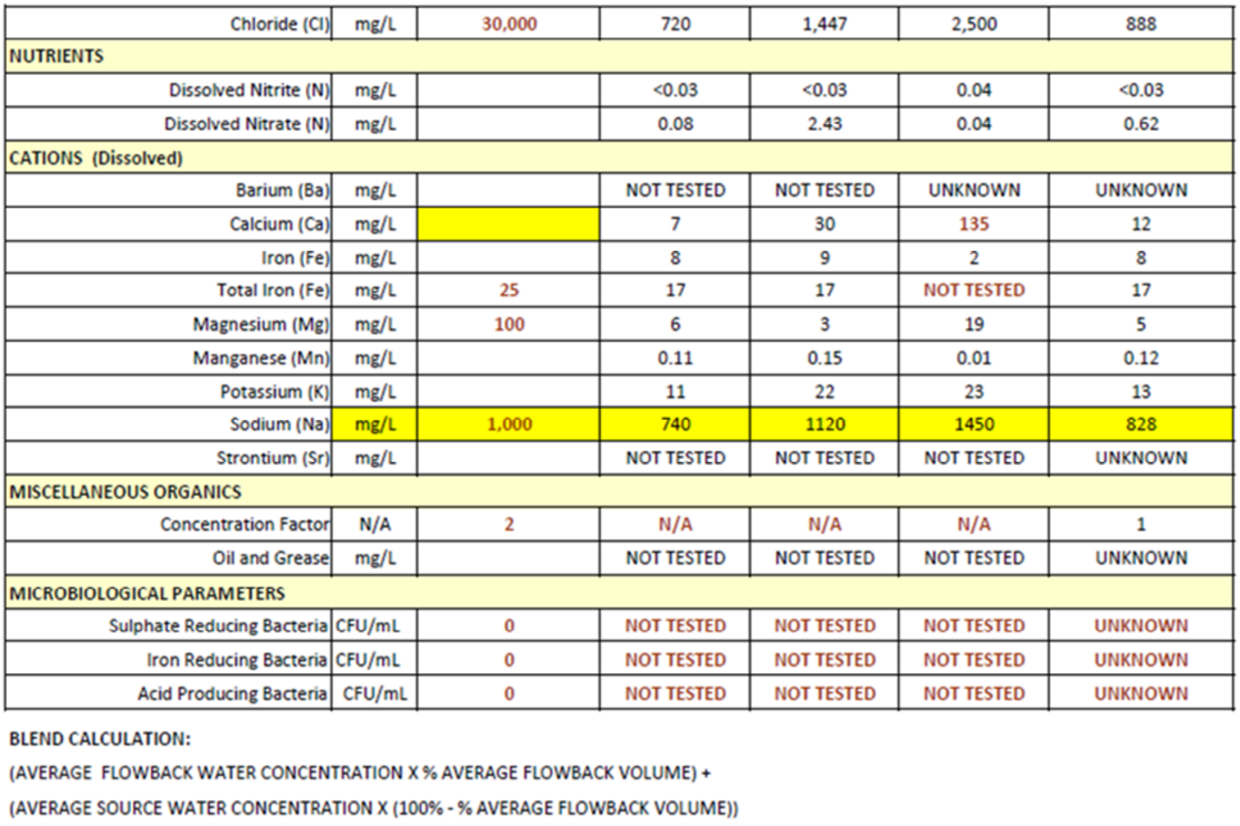
Table 2: Cardium Formation Case Study Data Summary



HYDRAULIC FRACTURING JOB SUMMARY:

FORMATION:	CARDIUM		64.0 °C	
RESERVOIR FLUID:	OIL		20.5 MPa	
FRACTURING TREATMENT:	ENERGIZED CROSSLINKED GEL			
VOLUME OF FLUID TO BE PUMPED:	789 m^3			
CUMULATIVE FLOWBACK VOLUME:	182 m^3	**AVERAGE % FLOWBACK:**		23%

	UNITS	CROSSLINKED GEL TARGETS	SOURCE WATER (SW) FRESH	FLOWBACK	FORMATION FLUID	MAX BLEND RATIO 23%
CALCULATED PARAMETERS						
Anion Sum	Meq/L		34	57	105	40
Cation Sum	Meq/L		34	52	72	38
Hardness ($CaCo_3$)	mg/L		43	87	415	53
Ion Balance	%		2%	10%	45%	5%
Dissolved Nitrate (NO_3)	mg/L		0.40	10.83	0.16	2.81
Nitrate plus Nitrate (N)	mg/L		0.08	2.43	0.08	0.62
Dissolved Nitrate (NO_2)	mg/L		<0.1	<0.1	0.13	0.13
Hydrogen Sulfide (H_2S)	mg/L	0	NOT TESTED	NOT TESTED	NOT TESTED	UNKNOWN
Total Dissolved Solids (TDS)	mg/L		2,000	3,267	5,100	2,292
CALCULATED SCALING INDEX: SURFACE CONDITIONS @ 17 °C						
Calcite ($CaCO_3$)	S.I.	1.00	-0.95	0.22	2.28	-0.68
	mg/L					
Anhydrite ($CaSO_4$)	S.I.	1.00	0.35	1.48	0.52	0.61
	mg/L					
Barite ($BaSO_4$)	S.I.	1.00	0.02	0.02	0.00	0.02
	mg/L					
Siderite ($FeCO_3$)	S.I.	1.00				
	mg/L					
CALCULATED SCALING INDEX: FORMATION CONDITIONS						
Calcite ($CaCO_3$)	S.I.	1.00	-0.95	0.22	2.28	-0.68
	mg/L					
Anhydrite ($CaSO_4$)	S.I.	1.00	0.35	1.48	0.52	0.61
	mg/L					
Barite ($BaSO_4$)	S.I.	1.00	0.02	0.02	0.00	0.02
	mg/L					
Siderite ($FeCO_3$)	S.I.	1.00				
	mg/L					
MISCELLANEOUS INORGANICS						
Conductivity	uS/cm		3,700	5,767	8,850	4,177
pH	N/A	6.0-8.0	6.98	7.47	8.04	7.09
Total Suspended Solids (TSS)	mg/L	100	NOT TESTED	NOT TESTED	NOT TESTED	UNKNOWN
ANIONS (Dissolved)						
Alkalinity (PP as $CaCO_3$)	mg/L		<0.5	<0.5	<0.5	UNKNOWN
Alkalinity (Total as $CaCO_3$)	mg/L		430	477	1,700	441
Total Silicon (Si)	mg/L	35	NOT TESTED	NOT TESTED	NOT TESTED	UNKNOWN
Bicarbonate (HCO_3)	mg/L	600	520	583	2,050	535
Carbonate (CO_3)	mg/L	600	<0.5	<0.5	<0.5	<0.5
Hydroxide (OH)	mg/L		<0.5	<0.5	<0.5	<0.5
Sulphate (SO_4)	mg/L		270	317	25	281



Chloride (Cl)	mg/L	30,000	720	1,447	2,500	888
NUTRIENTS						
Dissolved Nitrite (N)	mg/L		<0.03	<0.03	0.04	<0.03
Dissolved Nitrate (N)	mg/L		0.08	2.43	0.04	0.62
CATIONS (Dissolved)						
Barium (Ba)	mg/L		NOT TESTED	NOT TESTED	UNKNOWN	UNKNOWN
Calcium (Ca)	mg/L		7	30	135	12
Iron (Fe)	mg/L		8	9	2	8
Total Iron (Fe)	mg/L	25	17	17	NOT TESTED	17
Magnesium (Mg)	mg/L	100	6	3	19	5
Manganese (Mn)	mg/L		0.11	0.15	0.01	0.12
Potassium (K)	mg/L		11	22	23	13
Sodium (Na)	mg/L	1,000	740	1120	1450	828
Strontium (Sr)	mg/L		NOT TESTED	NOT TESTED	NOT TESTED	UNKNOWN
MISCELLANEOUS ORGANICS						
Concentration Factor	N/A	2	N/A	N/A	N/A	1
Oil and Grease	mg/L		NOT TESTED	NOT TESTED	NOT TESTED	UNKNOWN
MICROBIOLOGICAL PARAMETERS						
Sulphate Reducing Bacteria	CFU/mL	0	NOT TESTED	NOT TESTED	NOT TESTED	UNKNOWN
Iron Reducing Bacteria	CFU/mL	0	NOT TESTED	NOT TESTED	NOT TESTED	UNKNOWN
Acid Producing Bacteria	CFU/mL	0	NOT TESTED	NOT TESTED	NOT TESTED	UNKNOWN

BLEND CALCULATION:
(AVERAGE FLOWBACK WATER CONCENTRATION X % AVERAGE FLOWBACK VOLUME) +
(AVERAGE SOURCE WATER CONCENTRATION X (100% - % AVERAGE FLOWBACK VOLUME))

Step 1: Blend Ratio

- With an average flowback rate of 23%, the maximum blend ratio for the Cardium Formation would be 77% source water combined with 23% flowback.

Steps 2 & 3: Compatibility Simulations: Scaling, Bacteria & Corrosion

- The compatibility simulations suggest a minor scaling risk for a blend ratio of 77% source water and 23% flowback water for the Cardium Formation. Potential scaling concerns may be further mitigated with the application of a scale inhibitor as outlined in Appendix A.
- Bacteria analyses were unavailable for this case study review, therefore the potential bacteria compatibility concerns with fracturing fluid chemistry is unknown. It is recommended to consider applying a biocide as outlined in either Appendix A.
- The observed pH and chloride concentrations suggest a relatively low corrosion potential.

If acids are to be used in the well stimulation, it is recommended to consider applying a corrosion inhibitor as outlined in Appendix A.

Step 4: Dilution Requirements

- As no significant compatibility concerns were identified in the maximum blend ratio analysis in Table 3, no need for further dilution is anticipated.

Steps 5 & 6: Water Conditioning by Chemical Addition

- Although no immediate needs for water conditioning by chemical addition were identified in the max blend ratio as outlined in Table 3, it may be economical to add biocides, corrosion inhibitors, and scale inhibitors on an as-needed basis in this situation (Appendix A).

Steps 7 & 8: Water Conditioning by Physical/Chemical Treatment

- A total suspended solids analysis was unavailable for this case study review, therefore the potential solids compatibility concerns with fracturing fluid chemistry is unknown. Total suspended solids with an average particle diameter size greater than 0.50 mm are expected to be present within both the source and flowback waters at concentrations greater than 100 mg/L. Therefore, it is recommended to consider water conditioning by physical treatment with filtration (Appendix B).
- Analyses for residual fracturing additives within the flowback water were unavailable for this case study, so the potential compatibility concerns with residual fracturing additive concentrations are unknown. There are likely residual gel and friction reducers present, so water conditioning by either physical (electrocoagulation) or chemical treatment (ozonation) may be required as per Appendix B.

Step 9: Formation Compatibility

- Neither clay mineralogy nor core tests were conducted as part of this case study; therefore formation compatibility of the source water and flowback blend is unknown. Application of clay stabilizers as outlined in Appendix A may be required.

Step 10: Selection of Hydraulic Fracturing Process

- The hydrofracture process selected for this case is the Energized Crosslink Gel Fluid method. The water constituents that are sensitive in a Crosslinked Gel fracturing treatment are indicated in Appendix C.

Step 11: Blend Compatibility with Energized Crosslink Gel Fluids

- From the analytical data available, the source water and flowback water blend appear to have positive compatibility with Crosslink Gel fluid requirements. However, uncertainty about the overall blend compatibility will have with the hydraulic fracturing fluid is increased when any of the following are absent: hydrogen sulfide (H_2S), silica (Si), bacteria, clay mineralogy, and core testing.

In summary, results from applying the pre-screen of the Decision Tree suggest that recycling the flowback for reuse within the Cardium Formation at a maximum blend ratio of 77:23 will not result in any significant crosslink fluid compatibility concerns.

Further analysis, including field samples testing, hydrogen sulfide (H_2S), silica (Si), bacteria, clay mineralogy, and core analyses will confirm the above fluid compatibility observations and will aid in identifying any additional compatibility concerns.

If the results from the additional analyses reinforce the perceived fluid compatibilities, application of the recycled blend in subsequent hydraulic fracturing applications as outlined in Steps 12 through 19 of the Decision Tree may then be pursued.

Appendix A
Water Conditioning by Chemical Addition

Fracturing Fluid
Flowback Reuse Project

Prepared by M-I SWACO, a Schlumberger Company
for Petroleum Technology Alliance of Canada
and the Science and Community Environmental Knowledge (SCEK)
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1.0 Introduction

Water treatment can be addressed through a variety of treatment technology options. The options can differ in their inherent facility requirements; capital costs, operating expenses, and waste streams. The large space requirements for some technologies may not be feasible in smaller oil and gas installations, while others may be commercially available as small, skid-mounted units that can be easily relocated as production conditions change. Equipment costs can be significant for installations where a large amount of dedicated equipment must be purchased just for managing produced water. Increased power demand and chemical expenses could be intolerable early in the life of an oil and gas development. Waste streams derived from produced water may no longer be classified as oil and gas wastes and may be more difficult and more expensive to manage [162].

Using conditioning chemicals is common in the oil and gas sector to improve well production, and is not limited to hydraulic fracturing operations. Commonly referred to as "production chemicals" these additives may include:

- Biocides.
- Scale Inhibitors.
- Iron Sequesters.
- Corrosion Inhibitors.
- Clay Inhibitors.

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 have an 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 fracturing design and the water management plan.

2.0 Bacteria

Bacterial growth in hydraulic fracturing fluids is damaging from two perspectives. First, some of the chemicals used in water-base fracturing fluids are excellent food sources for bacteria. The bacteria secrete enzymes that break down the chemicals which reduces their effectiveness. Second, bacterial growth in the formation can cause other problems. These include producing acid (acid-producing bacteria, or APB) and reducing sulfate (sulfate-reducing bacteria or SRB). Sulfate-reducing bacteria (SRB) are commonly found in oil and gas production facilities. Iron sulfide is created when SRB reduce the sulfate ion to hydrogen sulfide causing issues such as steel embrittlement, chemical corrosion and fouling of equipment. The bacteria can multiply in such numbers that they reduce permeability and, consequently, damage the formation.

Bacteria may be aerobic or anaerobic. The two types have different characteristics, as follows:

- Aerobic bacteria require oxygen for survival. They produce enzymes that degrade the polymers used in water-base fracturing fluids, resulting in viscosity loss and premature breakdown of the fluid.
- Anaerobic bacteria can exist in the absence of oxygen and can create severe reservoir problems when introduced by the fracturing fluid. The bacteria can multiply in such numbers that they reduce permeability and, consequently, damage the formation. In addition, certain types of anaerobic bacteria chemically reduce sulfate ions to produce hydrogen sulfide, (H_2S), which is not only highly toxic and flammable but also causes chemical corrosion, steel embrittlement, and fouling of equipment by the formation of iron sulfide.

Biocides are added to the mixing tanks to kill any existing microorganisms (e.g. sulfate-reducing bacteria, slime-forming bacteria, algae), and to inhibit bacterial growth and enzyme production. Biocides are added to prevent bacterial degradation of the polymer, and to protect the formation from bacterial growth. Common practice is to add a biocide to the fracturing tanks before water is added, to ensure that the bacterial enzyme count remains low [6]. Biocides usually kill the bacteria, but they do not always inactivate the enzymes that are responsible for breaking down the polysaccharides.

The reuse of fracturing fluid is of special concern due to the potential amount of bacteria in the produced water. Again, these bacteria can attack the polymer and reduce its effectiveness, and a registered biocide is recommended in the fracturing tank [11].

When fracturing fluids (e.g. polysaccharide-based fluids) are prepared using clean water or brine, normal dosage of the common biocides is usually sufficiently protective. This may not always be the case when produced water is used to make fracturing fluids, as it typically contains much higher concentrations of bacteria and/or bacterial enzymes. In produced water, the biocides may be depleted quickly by overwhelming populations of bacteria and/or high concentrations of ions. 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 are killed or suppressed [119].

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. There is a range of biocides available, which control sulphate-reducing bacteria with varying effectiveness. Several popular and effective biocide choices are: glutaraldehyde, quaternary ammonium salts, isothiazolin, and 2,2-dibromo-3-nitrilopropionamide (DBNPA) [14].

Biocides are typically hazardous by nature, and may contain polycyclic organic matter and polynuclear aromatic hydrocarbons. Material Safety Data Sheets (MSDS) are available for biocides. These concentrated products are substantially diluted prior to injection into the subsurface. Typical dilution in the make-up water is 10 mL of biocide in 1 m^3 of water [6].

2.1 Resolution of Bacteria Issues

An ideal biocide should have the following criteria:

Performance: It must exhibit rapid kill of target organisms, with a high LC50 toward non-target organisms. It must be able to keep systems clean of biofilm. Ideally it should be able to clean up already fouled systems. It should not be consumed by materials commonly encountered in cooling systems, e.g. hydrocarbons, wood, plastic, or other treatment chemicals. Finally, it must be effective over a wide range of operating conditions [163].

Environment: Side or by-product reactions should be minimized and reaction products should be environmentally friendly. Neither it, its by-products, nor its reaction products should persist in the environment [163].

Safety: It must be safe and easy to handle [163].

Economics: It must be affordable [163].

Chlorination, oxidation by chemicals, and aeration are the most common methods adopted for water treatment. Of these three, chlorination is the oldest form of purification and it is very economical, but it is highly corrosive, will destroy some fracture fluid additives, and poses safety challenges. The oxidation agents commonly used are hydrogen peroxide, ozone, and chloride dioxide. While hydrogen peroxide and ozone are unstable and not suitable for pipelines, chlorine dioxide is comparatively stable, but difficult to transport.

Typical oilfield biocide options are broken into two groups:

- Non-oxidizers.
- Oxidizers.

2.1.1 Non-oxidizing Biocides

Non-oxidizers typically have a slower and more persistent microbial kill and are more common in the oilfield. Oxidizers are considered to be fast kill and significantly more reactive and less persistent. Due to improved efficacy and environmental benefits oxidizers are gaining position and are expected to have a greater presence in the future particularly in fracturing water due to environmental benefits [164].

Glutaraldehyde

Glutaraldehyde is dangerous, unpleasant to handle and thermally unstable. However, it is a useful antibacterial agent and is recommended for use to control anaerobic sulfate reducing bacteria in oil and gas wells [165].

Glutaraldehyde is effective against all organisms encountered in a process water system. It is also effective against anaerobic bacteria - notably SRB. It is typically added to process water systems in slug doses. Dosing on a continuous basis is sometimes done; however, slug dosing is usually a more cost-effective method of treatment. The stability of glutaraldehyde is influenced primarily by pH and temperature. Glutaraldehyde is very stable at acidic pH, and is typically supplied as either a 25% or 50% aqueous solution at pH 3.1 to 4.5. Under alkaline conditions, glutaraldehyde is used very effectively up to pH 10 [165].

To control the bacteria in the treatment water most effectively, the right biocide must be selected, which also has to be compatible with the other components of the fluid. There are other non-oxidizing biocide classes that are compatible with anionic friction reducers. Each of these different types of biocides has its strengths and weaknesses for use in the oilfield. Glutaraldehyde-based biocide has good compatibility with friction reducers at concentrations of approximately 200 mg/L. Dosage should be increased if the pH is more acidic, and if the temperature rises above $38^{o}C$ [8].

Tetrakishydroxymethyl phosphonium sulfate (THPS)

Tetrakishydroxymethyl Phosphonium Sulfate (THPS) is a non-foaming, water-soluble quaternary phosphonium compound with broad-spectrum antimicrobial efficacy. The primary biocidal mechanism of THPS is the disruption of proteins in the bacterial cell wall and/or membrane that destroy the integrity of these structures [165].

THPS microbicoide is fast-acting and effective for algae control as well as bacteria. THPS is typically shock-dosed to industrial water systems. Dosages range from 25 to 100 mg/L. THPS is compatible with most water treatment chemical additives, except halogens, at these concentrations. THPS is a cationic species and adsorbs to organic contaminants and reacts with anionic materials in the water. It also reacts with iron sulfide [165].

Quaternary Amines (Quats)

Quaternary amines are considered broad-based microbiological control agents. They are effective as algicides, and perform well against various classes of bacteria and fungi. Quats come in many types and descriptions, from the older, more commonly used alkyl dimethyl benzyl ammonium chloride (ADBAC), to the slightly newer dialkyl quats such as didecyl dimethyl ammonium chloride (DDAC). More recently, branched dialkyl quats have been introduced as well. The properties of these products can vary substantially in foam characteristics, salt tolerance, microorganism efficacy, etc [165].

Foaming varies dramatically. The dialkyl quats generally exhibit the largest volumes of foam, and often the most stable foam as well. The ADBAC variety of quat also foams extensively, although at slightly lower levels with less foam stability. The newest generations of branched dialkyl quats are extremely low in foam generation and stability [165].

Generally, as the hardness of the water used is increased, the foaming tendency increases. These products are added either continuously at low levels or on an intermittent basis, depending on the severity of the biological problem. Typical dosages range from 5 to 50 mg/L as active. They are generally added at a point in the system with extensive agitation, remote from the feedpoint of other chemical additives containing high levels of anionic ingredients [165].

Use of quaternary ammonium salts is limited, due to their interaction with oil when this is present and the fact that they can cause foaming. Quats are effectively applied at a broad range of pH levels from 6.5 to 9.5 [165].

Salinity can also adversely affect quat performance. High salinity quat tests have shown this negative influence when the tests are conducted at 1%, 1.8%, and 2.5% salinity. Generally, ADBAC quats are more negatively impacted by salinity than are dialkyl quats. Quats can complex or precipitate with anionic species, including high concentrations of bicarbonate, phosphate, or sulfate as well as with anionic polymers such as polyacrylates, and anionic surfactants [165].

Laboratory testing and field experience indicates that quaternary ammonium biocides reduce the effectiveness of common friction reducers, resulting in less drag reduction. In contrast, non-ionic biocides such as glutaraldehyde do not affect the performance of the friction reducer [8].

Tetrahydro-3,5-dimethyl-1,3,5-thiadiazinane-2-thione (Thione)

A relative newcomer to oilfield applications is tetrahydro-3,5-dimethyl-1,3,5-thiadiazinane-2-thione; it has been shown that this biocide (Thione) does not interfere with friction reducer, is extremely effective in killing APB bacteria , and is a broad spectrum biocide. 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 [11].

2,2-dibromo-3-nitrolopropionamide (DBNPA)

A 20% active, liquid brominated propionamide, commonly referred to as DBNPA, is an 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 innocuous components: bromine, nitrogen and water. 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 [14].

2.1.2 Oxidizing Biocides

A wide variety of oxidizing microbiocides are used for microbiological control in cooling water systems. These microbiocides can be grouped into five different oxidizing chemistries—chlorine, bromine, chlorine dioxide (ClO_2), ozone, and peroxides. The following sections provide details on typical oxidizing microbicide monitoring and control [165].

Chlorine

Chlorine is known to react with a wide variety of compounds. It reacts primarily through oxidation, although it can react by both substitution and addition reactions. There are many reports of the limited reaction of chlorine dioxide with organics. This indicates that much more of the chlorine dioxide added to a system is available as a biocidal agent, and is not consumed to the degree that chlorine would be under the same circumstances. In addition, chlorine will react with ammonia or any amine, while chlorine dioxide reacts very slowly with secondary amines, and not at all with primary amines or ammonia [163].

Chlorine Dioxide (ClO_2)

Chlorine dioxide (ClO_2) is an active oxidizing biocide, that is being applied more and more due to the fact that is has less damaging effects to the environment and human health than chlorine. It does not form hydrochlorous acids in water; it exists as dissolved chlorine dioxide, a compound that is a more reactive biocide at higher pH ranges. Chlorine dioxide is an explosive gas, and therefore it has to be produced or generated on site using mobile units that have proven durability in oilfield conditions with a small footprint [166].

Because of safety, environmental and community impact considerations, gaseous chlorine as a biocide for industrial applications is declining. Various alternatives have been explored, for example, bromochlorodimethyl hydantoin (BCDMH), non oxidizing biocides, ozone, and chlorine dioxide. Some unique advantages of chlorine dioxide are its selectivity, effectiveness over a wide pH range, and speed of kill. Safety and cost considerations have restricted its use as a viable replacement for chlorine [173].

Pure ClO_2 is a water-soluble gas with a slight yellow-green color with a broad efficacy range.

- Clay inhibitors.
- It is capable of utilizing dirty water and water varying in pH.
- It is not a persistent biocide and is more environmentally friendly.
- It does not hydrolyze in water.
- It does not require high residual concentrations.
- It has low corrosivity compared to other oxidants.
- It removes iron and manganese and H_2S.

Ozone (Sodium bromide, bleach)

Ozone is very effective in eliminating residual hydrocarbons in oilfield water. Complex and volatile hydrocarbons are readily oxidized using either ozone or advanced oxidation treatment. Ozone is one of the few oxidants that will easily break down carbon-carbon bonds, effectively forming smaller and smaller compounds until complete oxidation to carbon dioxide and water is achieve. Ozonation also has the added benefit of being an excellent disinfectant [167].

It is a bluish gas with a pungent odor. As temperature increases, its solubility in water decreases. For example, the maximum solubilities at 25°C for gas streams containing 1% and 3% ozone are 2.7 and 8.1 mg/L, respectively [165].

Ozone degrades with increasing pH. It is fairly stable under conditions at pH 6 and instantaneously degrades at pH 10. Ozone is a very reactive species and reacts with many chemicals including corrosion inhibitors, deposit control chemicals, and organic and inorganic chemicals [165].

Ozone is naturally unstable. It can be used as a powerful oxidizing agent, when it is generated in a reactor. It acts in much the same way as chlorine by disturbing the formation of adenosine triphosphate (ATP), so that the cell respiration of micro-organisms will be made difficult. Bacteria usually die from loss of life-sustaining cytoplasm during oxidation with ozone.

Temperature, pH, organics and solvents, and accumulated reaction products are all factors in determining the amount of ozone required during oxidation. Ozone is more environmentally friendly than chlorine, because it does not add chlorine to the water system [166].

Ozonation systems also greatly reduce the toxicity of oilfield wastewater. The removal of sulphides, heavy metals, complex chemicals, and residual hydrocarbons has the positive effect of also decreasing the toxicity of the water. Ozonation is often sufficient treatment to achieve oilfield wastewater toxicity regulations [167].

Ozone as a viable long term replacement for chlorine is being explored, due to its excellent biocidal activity. However, ozone does suffer from several serious drawbacks. Because of its strong oxidizing ability, it will not differentiate between the target organisms and the corrosion inhibitor packages used with it to control scale and corrosion. Its effectiveness on biofilm control is questionable. Ozone equipment is reported to be maintenance intensive and expensive.

2.1.3 Other Considerations in the Selection of a Biocide

Prevention of polymer destruction by bacteria is usually handled with biocides and tank monitoring. However, inappropriate or incompatible biocide may also lower the effectiveness of the friction reducer, and compounds formed by the two may plug the formation. If the biocide is added before the friction reducer, the incompatibility might not be noticed, but more would need to be used to overcome the negative effects [8].

Control of bacteria downhole 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. A biocide system that has both short-term and long-term kill ability is recommended for shales to avoid future production problems.

Frequent rotation of types of biocide is necessary to prevent the development of biocide-resistant strains of bacteria.

Cationic vs. Anionic Biocides

One of the common incompatibilities in fracturing fluids can be between cationic additives such as biocides, and the anionic friction reducer (FR) 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 [8].

The goal of any stimulation fluid should be that all components are compatible. As expected, some biocides complex with the oppositely charged friction reducers. This results in the formation of "flocs" 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 [8].

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). Each of these different types of biocides has their strengths and weaknesses for use in the oilfield [8].

3.0 Scale Formation from Dissolved Solids (Hardness)

Scale is the solid precipitate that forms in solution and on surfaces in contact with a fluid, often the result of a supersaturated condition brought on by temperature change, pressure change, or comingling of multiple solutions. The formation of scale is not unique to hydraulic fracturing of shale gas wells. The accumulation of scale can reduce flow rates or for instance, lower efficiencies in heat exchangers. The formation of scale is commonly an issue in conventional oil and gas production, enhanced oil recovery (EOR) and disposal scenarios, and there is an extensive history of successful management of oilfield scale issues.

Scales are water-soluble chemicals that precipitate out of solution in response to changes in conditions or the mixing of incompatible waters. Water-formed scale deposits are among the most troublesome damage problems. Scale usually consists of precipitates formed from mixing incompatible waters or upsetting the solution equilibrium of produced waters. Water that may be stable under reservoir conditions may become supersaturated with an ion when the pressure decreases, which allows carbon dioxide (CO_2) outgassing, or the temperature changes. The supersaturated solutions react by precipitating a compound from solution. The deposition of scale is influenced by pressure drop, temperature, dissolved gases, flow viscosity, nucleation sites and metal type - in short, anything that upsets the solution equilibrium.

While the formation of dozens of chemical scales is possible, the most common oilfield scales include:

- Gypsum ($CaSO_4 \cdot 2H_2O$).
- Hemihydrate ($CaSO_4 \cdot 0.5H_2O$).
- Anhydrite ($CaSO_4$).
- Aragonite ($CaCO_3$).
- Calcite ($CaCO_3$).
- Barite ($BaSO_4$).
- Celestite ($SrSO_4$).
- Siderite ($FeCO_3$).
- Hematite ($Fe_2O_3 \cdot nH_2O$).

Waters used for fracturing and secondary recovery projects usually contain a number of inorganic salts and sometimes organic salts in solution, which may result in the formation of scale when the chemical equilibrium is disturbed. The amount of scale that will precipitate from water is dependent on the water composition, temperature, pressure, and gas composition. Predicting and controlling the type and amount of scale inhibitor to use can be difficult because these parameters often vary, and may require constant adjustment to account for these changing parameters.

In many shale completions, the fracturing flowback water contains significant levels 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 [14].

3.1 Carbonate Scale

$CaCO_3$ is usually formed when the pressure is reduced on waters that are rich in calcium and bicarbonate ions. The deposition can be affected by CO_2 outgassing, which raises the pH value and makes the high concentrations of calcium unstable.

When surface water from a lake is mixed with water from the producing zone it could result in a scale. The surface water usually has a higher pH than formation water. Surface water usually contains high concentrations of bicarbonate alkalinity.

A problem frequently encountered with injection 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.

3.2 Sulfate Scale

Sulfates form two common types of scale: gypsum ($CaSO_4 \cdot 2H_2O$) and barium sulfate ($BaSO_4$).

3.2.1 Gypsum

Gypsum may be the most common sulfate scale in the oil industry (Cowen and Weintritt, 1976). With a chemical structure of $CaSO_4 \cdot 2H_2O$, it shares a similar composition to the hemihydrates

$CaSO_4 \cdot 1/2H_2O$, commonly called plaster of Paris or by its mineral name, bassanite. It is also formulaically similar to the evaporite mineral anhydrite ($CaSO_4$).

3.2.2 Barium Sulfate ($BaSO_4$)

$BaSO_4$ is a less common form of sulfate deposit, but it causes extensive problems. Almost any combination of barium and sulfate ions causes precipitation. It is difficult to remove, as it is not significantly soluble in acids and solvents unless it is finely ground or the structure is interrupted with impurities such as carbonate scale. Like calcium sulfate, barium sulfate is usually thought to be a product of mixing incompatible waters, with precipitation accelerated by pressure drop, outgassing or turbulence. Some barium sulfate is radioactive; this is part of Naturally Occurring Radioactive Material (NORM) scales. The radioactivity results from a concentration of uranium in the lattice of the scale. The buildup of radioactive scale can be monitored using a gamma ray logging tool. Care must be exercised when analyzing well debris to avoid mislabeling barite ($BaSO_4$) from drilling mud residue as barium sulfate scale. Strontium sulfate or celestite ($SrSO_4$) is a common substitute in the barium sulfate crystal lattice. Strontium scale can be associated with NORM scale. It may be more soluble than barium sulfate in chemical remover systems.

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).

3.3 Iron Scale

Iron scales such as iron carbonate and iron sulfide can be extremely difficult to remove. They are usually seen in wells that have both a high background iron count and a tendency to precipitate calcium carbonate. Seven different forms of iron sulfide scale have been identified. Only two of these iron sulfide forms are readily soluble in hydrochloric acid (HCl). The remaining iron sulfide scales are either slowly soluble or not significantly soluble.

Upon contact with the downhole environments, iron and other metals are leached and/or released into the fracturing 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 fracturing fluid during well cleanup. For example, geochemical simulation has shown that siderite ($FeCO_3$) can be a problematic iron precipitate [14].

3.4 Prediction of Scale

Prediction of scaling tendencies can be accomplished if the composition of the source water, flowback water and formation water is known in detail; and the downhole temperature, and bottom hole pressure are known with a high degree of accuracy.

3.4.1 Analytical Methods

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 the 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).

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

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-Tomson saturation indices are all widely used in the oil field [90].

Oddo-Tomson suggests 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 occurs [90].

The water analysis data is 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. 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.

3.4.2 Computer Methods

It is particularly useful to incorporate the necessary data from each scale index computation into a computer program that covers a range of temperatures and pressures 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.

In some systems, several waters are comingled 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. Alternatively, if the water quality and volume fraction of each component is known, the composite water can readily be calculated by scaling software. A scale index can be calculated on the hypothetical mixture. 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.

3.5 Resolution of Scale Issues

There are two basic approaches to dealing with oilfield scale:

- Preventing the formation of scale through using chemicals, and careful selection of a water source.
- The removal of scale once it forms through the application of physical methods and chemical additives.

This report will deal with the prevention of scale included in the planning process as part of the Water Management Plan, and will leave the question of removal of scale to be addressed elsewhere as a production problem.

In the oil and gas industry, the chemical treatment of water includes the application of scale inhibitors, which help bind up the scale-causing constituents, thereby maintaining the integrity of equipment that is used during the drilling and production phases. Treatment may also be used to reduce the concentration of scale forming compounds that can deposit in production wells, water and disposal wells, flow lines, and surface equipment.

An effective treatment method is twofold:

- Based on the geochemistry analysis, apply an appropriate selection and dose of scale control that is designed not to negatively affect the fluid pH and resultant friction reducer (FR) performance [14].

- When necessary, conduct remediation of the water for certain problem species. The ideal treatment should address all scale situations predicted during post-fracturing flowback [14].

Regardless of the chemical scale inhibitors that are available, the most effective management of scaling issues is realized by avoiding the creation of chemical settings where scale may be deposited. These simple measures include, for example, avoiding using source water that is incompatible with the flowback or formation water, and avoiding exposure of waters to oxygen.

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 water sources [21].

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.
- Acid polymers.

Most phosponates and organophosphonates 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 organophosponates 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 matrix

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.

The compatibility of the fracturing fluid is a main factor that determines if a scale inhibitor 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 scale inhibitors are typically low-pH systems which are not compatible with high-pH borate fracturing fluids. To allow scale inhibitors placement during a fracturing treatment, a modified phosphonic acid scale inhibitors 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 - 8.8. The inhibitor is compatible with the borates and has minimal effects on fluid rheology for a guar loading of 4 kg/1000 L or more and some viscosity reduction for low gel systems (20 ppt or less).

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 when the concentration of calcium is only a few hundred mg/L whereas; polymer-base scale inhibitors are effective for sulfate/carbonate scales when the concentration of barium, strontium and calcium ions are high [70].

Using other additives like scale inhibitors and clay stabilizers may interfere with compatibility and performance. Scale-inhibiting chemicals can be applied up or downhole of the wellhead and are available in liquid, emulsified and solid form. 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 [70].

Recent concerns about potential toxicity issues associated with scale inhibitors have led the shale gas industry to evaluate alternative scale inhibitors such as polyaspartic acid. Polyaspartic acid is a manufactured amino polycarboxylic acid that can function as a scale inhibitor, corrosion inhibitor, dispersant, chelation agent, and water absorber. According to the manufacturer, polyaspartic acid is non-toxic, biodegradable, and non-polluting.

Calcium sulfate, calcium carbonate and barium sulfate can cause scale problems if the concentration is high enough to exceed the solubility of these minerals. Conditions such as a drop in pressure, a temperature change, or a comingling with incompatible waters may initiate scaling. Scale can be detrimental to the production of the well [70].

Scale deposition potential may be indicated when ions such as barium, strontium and calcium are available in the flowback water and sufficient bicarbonate or sulfate ions are present to create supersaturation in the liquids. Ion compositions can also lend value to predict increases in corrosion, entry of extraneous water, and other production problems such as NORM scale.

Preventative treatments to block scales are highly reliable when monitoring systems are in place. Ion compositions can also lend value to predict increases in corrosion, entry of extraneous water, and other production problems such as NORM scale. Water management issues for produced and flowback water can often be at least simplified by a few actions that segregate water by contaminant or level of treating difficulty. Early flowback water volumes after a fracturing job are most often lower in total dissolved salt content. Sending these waters of lower salinity to reprocessing plants for reuse is a simple operation and usually meets targets with minimal treatment. Medium salinity waters can be diluted with the recycled fresher waste water to meet fracturing specs or treated for re-use. High salinity waters are difficult to treat to low salinity without large energy input [109].

Inclusion of the right blend of inhibitors in the treatment helps prevent formation of certain geochemical deposits by the mechanism of crystal modification. Polyacrylic acid of the proper molecular weight can further prevent the formation of calcium, barium, or strontium sulfate scales. Iron control, discussed below is an important component of the solution since the presence of iron tends to deactivate the effectiveness of conventional scale inhibitors; preventing the formation of iron-based scales has been an industry wide problem [14].

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 [70].

3.5.1 Resolution of Iron Scale Issues

An iron-control compound is necessary to chemically maintain the iron in formation fluids in the reduced-valence state and prevent 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. 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 [14].

- Iron carbonate – $FeCO_{3.}$
- Iron scales (soluble in HCL, THPS).
- Iron sulfides.
- Iron oxides.

Traditional iron-reducing and chelating agents consist of acidic chemicals such as:

- Citric acid.
- Acetic acid.
- Ethylenediaminetetraacetic acid (EDTA).

These keep the iron in formation in a soluble or reduced form (ferrous iron) through pH reduction. 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. EDTA is effective only when the concentrations of other polyvalent cations (e.g. barium, calcium, strontium) are very low [14].

Acids and chelants also reduce fracturing 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 [14].

Costs

Because the amount and type of scale that can precipitate out of water is dependent on many factors, the 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 [70].

4.0 Corrosion

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 using 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 [168].

Carbon dioxide is the most common corrosion agent, while hydrogen sulfide poses the most significant risk to human health and the environment. Most corrosion inhibitors work by adsorbing onto exposed metal surfaces [168].

4.1 Corrosion Issues

4.1.1 Hydrogen Sulfide

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

Pumping and other oilfield equipment is susceptible to damage upon exposure to H_2S either in vapor phase or solubilized 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. Agencies 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 [37].

Although most of the shale gas basins have not identified H_2S 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 fracturing flowback water is necessary before the water is used for fracturing treatment.

The American Petroleum Institute has a Recommended Practice (RP 49) for Drilling and Well Servicing Operations Involving H_2S. This practice is voluntarily followed by producers to minimize the release of and exposure to H_2S.

4.1.2 Oxygen Issues

Oxygen is not typically found in unaltered produced fluids, it is usually introduced as the produced fluids are treated.

4.1.3 Carbon Dioxide Issues

Carbon dioxide dissolved in water can contribute to the corrosion of steel. Corrosion caused by water containing dissolved carbon dioxide is characterized by clean uniformly thinned surfaces below the water line. The rate and amount of corrosion is dependent upon the salts dissolved in the water, the carbon dioxide content, the oxygen content, the temperature, and the composition of the steel. Carbon dioxide is present in water as: (1) the carbon dioxide in carbonate ions; (2) the carbon dioxide necessary to convert the carbonates to bicarbonates; (3) the amount of carbon dioxide necessary to keep the bicarbonates in solutions; and (4) any excess carbon dioxide. This excess carbon dioxide is referred to as "aggressive" carbon dioxide, and is the most corrosive form [174].

4.2 Resolution of Corrosion Issues

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.
- Nitrogen Heterocyclics [168].

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 micelles 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 preflush or over flush rather than in the acid flush.

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

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 corrosion agent, the type of production, prior experience, and laboratory or field testing. Corrosion caused by oxygen is controlled by chemical reaction rather than adsorption [168].

4.2.1 Resolution of Hydrogen Sulfide Issues

There are two basic methods of treatment of H_2S in the water stream; one, the addition of chemical scavengers, which reacts with the H_2S and eliminates it, and; two, by stripping through counter current flow of air. In the case of the addition of a triazine-based chemical, the H_2S in the water stream is chemically eliminated through direct contact and no further action is needed.

There is no solid residual from the application of triazine.

For higher concentrations of H_2S, the combination of triazine treatment and H_2S scavenger effectively reduces H_2S. The H_2S scavenger creates a chemical reaction whereby $Fe_3O_4 + H_2S = FeS_2 + H_2O$.

Whereas the application of triazine can be accomplished through direct injection, the application of a H_2S scavenger requires a treatment vessel. The spent H_2S scavenger is disposed of as an oilfield waste.

In the case of the air stripping, usually associated with higher volume/ high rate treatment, the H_2S is stripped in a stripping tower from the aqueous phase and becomes part of the vapor phase.

Once in the vapor phase, additional care must be taken of the H_2S laden air albeit at lower concentrations.

4.2.2 Resolution of Oxygen Issues

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. [168].

Oxygen scavengers such as ammonium bisulphate or sodium thiosulfate have been known to generate free radicals that can degrade polyacrylamide solutions. With ppb (parts per billion) concentrations of catalysts such as cobalt (Co) and iron (Fe); O_2 scavengers such as ammonium bisulphate can degrade polyacrylamide polymers in minutes at moderate temperatures, causing up to 80% loss of viscosity.

Corrosion inhibitors are also 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 L per 1000 L of make-up water and acid mixture [6].

4.3 Methods of Corrosion Control

There are three standard treatment methods used for corrosion inhibition:

- Continuous treatment.
- Displacement treatment.
- Squeeze treatment.

4.3.1 Continuous Treatment

Continuous treatment involves continuous injection of corrosion inhibitor into the production stream. Treatment concentrations normally range between 5 - 15 ppm for liquid production depending on the concentration of the corrosion agent. The treatment concentration for gas production may be as high as 100 ppm [168].

4.3.2 Displacement Treatment

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 [168].

4.3.3 Squeeze Treatment

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 ppm. This initial slug is quickly produced and concentrations return below 100 ppm. These two treatment methods are usually used in wells with lower production rates [168].

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 ppm oil and grease comes from a production stream containing 500 ppm corrosion inhibitor in the oil, the concentration of corrosion inhibitor in the discharged produced water is 0.020 ppm at the point of discharge.

5.0 Clay

Certain reservoir rocks are subject to permeability damage when infiltrated by fresh water. This damage, which is related to rock properties, is caused by swelling of indigenous clays that constrict pores, and the dispersion of indigenous non-swelling particles during fluid flow.

Clays can swell or migrate (or both), resulting in permeability damage. Severity of damage caused by clay swelling 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).

Clays may change volume as the salinity of the fluid flowing through the formation changes. Several authors have dealt with clay swelling in sandstones, showing either ion exchange, movement or critical salt concentration triggering clay dispersion

Changes in formation permeability resulting from the alteration of clay are due to the amount, location and type of clay minerals within the formation. The total quantity of clay inside the formation is a misleading indication of potential changes to permeability. It is the arrangement of the clay, its chemical state at the moment of contact and the location of the clay with respect to the flowing fluids that are responsible for the changes. Predicting the response of a clay to water flow is almost impossible without testing.

The most common swelling clays are smectite and smectite mixtures. Smectite swells by taking water into its structure. It can increase its volume up to 600%, significantly reducing permeability. If smectite clay occupies only the smaller pore throats and passages, it will not be a serious problem; however, if it occupies the larger pores and especially the pore throats, then it is capable of creating an almost impermeable barrier to flow if it swells. Clays or other solids from drilling, completion or workover fluids can invade the formation when these particles are smaller than the pore throat openings. Any subsequent increase in flow rate through the invaded zone will force a high concentration of particles into the rock matrix.

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.

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

When contacted with water, some clays swell as a result of water adsorption or exchange of basic radicals from foreign water. Montmorillonites, mixed layer clays, and some illites are the most common swelling clays. It is possible for water to penetrate between the plates of montmorillonite 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.

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 - 5% sodium chloride. Clay swelling often results when saline interstitial water is displaced by relatively fresh water.

Water sensitivity increases with decreasing salinity.

5.1 Determining Clay Sensitivity

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 (XRD) can determine the presence or absence of swelling clays. If swelling clays are present, and permeability measurements show a reduction in permeability with reduced water salinity, the cause of the reduction is established.

However, if the reservoir is known to be sensitive to clays and core samples are available, performing a Capillary Suction Test (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 [19].

5.1.1 Fines Migration

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.

If no swelling clays are present and permeability reduction occurs, then particle mobility and plugging are causing the reduction.

5.1.2 Resolution of Sensitive Clay Issues

Three methods of clay control known to be effective are:

- Ionic neutralization.
- Organic barrier.
- Particle fusion.

5.1.3 Potassium Chloride (KCl)

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 as damaging as is freshwater. Solutions containing 1 - 3% KCl are commonly used as the base liquid in fracturing fluid to stabilize clays and prevent swelling. KCl is used more often than Sodium Chloride (NaCl) or Ammonium Chloride (NH_4Cl) 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 CST evaluations show that 2% KCl has a marginal effect on swelling clays, and that 4% (wt) KCl is often more effective. Naturally, this increases cost. A common KCl substitute is tetramethyl ammonium chloride (TMAC) [11].

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 fracturing 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.

5.1.4 Organic Barrier

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.

5.1.5 Particle Fusion

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 using various anions, including 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 hydraulic fracturing and water reuse.

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 using 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.

5.1.6 Tetramethyl Ammonium Chloride (TMAC)

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 [23].

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.

5.1.7 Quaternary Amines

More permanent methods for controlling clay migration involve using quaternary amines or inorganic polynuclear cations. The latter materials, such as zirconium oxychloride and hydroxy-aluminum 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.

Using 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 certain biocides have a hydrophobic motiety on the molecule and we believe that this 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 are only compatible with cationic friction reducers. They have a strong cationic nature and have been shown in to precipitate out of solution with anionic reducers.

5.1.8 Dissolved Salts in Flowback

The dissolved salts in flowback can serve the same function as potassium chloride.

Appendix B
Water Conditioning by Physical/Chemical Treatment

Fracturing Fluid
Flowback Reuse Project

Prepared by M-I SWACO, a Schlumberger Company
for Petroleum Technology Alliance of Canada
and the Science and Community Environmental Knowledge (SCEK)
Fund

Table of Contents

1.0 Introduction

Chemical conditioners have limitations, and it may become necessary to consider other water management or treatment techniques. Treating produced water may include removal of suspended solids, gas and liquid hydrocarbons, H_2S and CO_2, bacterial control, cations and anions, dissolved organics, and total dissolved solids (TDS). It can also include treating flowback ion levels for reuse so that the fracturing fluid chemical additives for the subsequent fracturing will operate effectively or prevent potential scaling. Or treating to remove TDS to allow for beneficial reuse in irrigation or for surface discharge are in the formative stages. Efficiency in treating flowback and produced waters has reduced the total make-up fluid levels and has minimized dependence on fresh water for fracturing operations in some areas.

Produced water has been reused up to 100% without blending on cross-link gel fracturing operations since at least 2006 by different producers in the Pinedale Anticline Field in Wyoming. Gupta (2009) outlines successful reuse of water including attractive economics on a fifty-well recycle project. Numerous successful treatment methods have been employed, including crystallizing units, evaporation ponds, selective ion membranes, filters, chemical flocculants, reverse osmosis, and various other methods.

2.0 Treatment Technologies

The process of determining which treatment is needed depends on the water constituent that needs to be removed. Removing gross solids in the first part of the treatment. If only gross solids need to be removed, then simple filtration or sedimentation may be all that is required. If one is trying to meet discharge standards, more advanced treatments that target the removal of total dissolved solids need to be used. The end use of the water (reuse in fracturing fluid makeup or for discharge) determines the level of treatment that is necessary.

Treatment technologies can be used as standalone processes, such as filtration or oil water separation, or they can be combined into a treatment train as with total dissolved solids, where multiple processes must take place prior to the end target removal of dissolved solids.

Traditionally, the higher the water quality standard one is trying to achieve will require more steps in the treatment process.

The section below is broken down into the following processes based on constituent removal:

- Free Oil Removal.
- Total Suspended Solids (TSS) and Dispersed Oil Removal.
- Soluble Inorganics and Dissolved Organics Removal.
- Advanced Treatment – Total Dissolved Solids (TDS) Removal.
- Disinfection.

3.0 Free and Dispersed Oil

Free oil is the second part of the primary treatment. Free oil can be removed by high rate mechanical separators, or oil water separators (in the same basin where gross solids are being separated by gravity, the oil droplets will rise to the surface according to Stoke's Law).

Dispersed oil can be removed by a coalescing-type media such as walnut shells or chemically enhanced resins, and sorbent media such as organoclay, hydrophobic or oleophillic media, or granular activated carbon. The table below shows different oil-removing technologies and the minimum particle sizes that each can each remove. Dispersed oil is defined as micron-sized oil droplets that are not easily removed by separation.

Table 3.1 Comparison of Particle Size Removal.

Oil Removal Technology	Minimum size of particles removed (microns)
API gravity separator	150
Corrugated plate separator	40
Induced gas flotation (no flocculation)	25
Induced gas flotation (with flocculation)	3-5
Hydroclone	10-15
Mesh coalescer	5
Media Filter	5

Centrifuge	2-5
Membrane filter	0.01

Numerous different chemicals and technologies exist for oxidizing the organics including ozone, ultraviolet light, chlorine dioxide generators, mixed oxidant solution generators, and various chemical oxidants that can be added on the fly.

3.1 Oil Water Separator

In conjunction with the gravity settling discussed previously for gross solids separation, a gravity oil water separator can simultaneously float oils in the same basin as a first cut for free oil removal. API separators are designed to provide sufficient hydraulic residence time for oil droplets 150 micron and larger to be separated by buoyancy forces floating the oil to the surface where it can be raked or floated over a weir and be sent to a sales tank. This initial type of treatment can actually be performed in storage tanks, fracturing tanks, or impoundments. Specifically designed gravity oil water separators or compact flotation units for off-shore applications, provide designs better suited for dealing with the removal of the collected oil and solids from the residence basin, at a slightly increased cost.

3.2 Dissolved Gas Flotation

Dissolved Gas Flotation (DGF) utilizes dissolved air bubbles to adhere to the flocculated particles and float to the surface in a reasonable amount of time provided by the residence time in the DGF. Flotation is caused by introducing fine gas bubbles into the liquid phase. When the bubbles (typically air) adhere to the particles, the buoyant force of the combination is strong enough to cause them to rise to the surface. The surface of the water is then skimmed to remove the foam/flocculant at the top of the unit. Larger, heavier solids are collected as bottom sludge. A DGF system is comprised of several components including basic process equipment, chemical conditioning, and the dissolved air injection process.

Chemical selection and dosing rates are developed prior to the operation of a DGF during a bench scale analysis. Coagulants and flocculants are typically dosed into the system, either in a flocculation tube, where the microbubbles are also introduced into the water to dissolve, or in a flash mix chamber for the coagulant and a slow mix chamber for the flocculant. Air is also introduced into the unit at various locations near the front end of the floatation chamber. Exact air introduction and volumetric rates are optimized during either piloting or start up of the unit. Typically, a portion of the water is recycled and the air is dissolved into the water in a separate chamber before it is introduced to the main water flow stream.

It is important for DGF to receive wastewater with a consistent flow and a stable wastewater loading for it to work efficiently. Therefore it is essential that upstream wastewater mixtures be carefully analyzed, monitored and controlled before feeding into a DGF system. To optimize the process equalization tanks are commonly used in front of a DGF system. High fluctuations in water temperature and pH can also impact performance of a DGF. If the water quality contains significant amounts of free oil (oil droplets > 150 micron) pre-treatment of the water is normally employed prior to the use of a DGF. The pre-treatment would consist of an oil water separator.

Below are the typical specifications of the influent water quality where a DGF would be employed:

- Dispersed Oil:
    - Particle Size: 5 - 100 microns.
    - Concentrations: 25 - 500 ppm.
- Total Suspended Solids:
    - Particle Size: 5 - 100 microns.
    - Concentrations: > 30 ppm.

Induced Gas Flotation (IGF) systems are very similar to DGF systems and works under the same principle. The two technologies differ by the method used to generate gas bubbles and the resultant bubble sizes. In DGF units, gas (usually air) is fed into the flotation chamber, which is filled with a fully saturated solution. Gas is released by applying a vacuum or by creating a rapid pressure drop inside the chamber. IGF technology uses mechanical shear or propellers to create bubbles that are introduced into the bottom of the flotation chamber. Coagulation is normally used as a pre-treatment to flotation.

There are two main differences in system design that require discussion: Air versus Gas and Dissolved versus Induced. Induced or Dissolved Gas (typically nitrogen or methane) can be used in lieu of ambient air. In terms of removal efficiency between gas or air, it seems to be negligible. The advantage would be in the reduced explosive hazards associated with the head space, such as an enclosed DAF/IGF, and the air/volatile hydrocarbon mixture that could potentially exist.

In a typical refinery setting, DGF units are employed as the water being processed typically has a much higher ratio of hydrocarbons to water and thus a much more volatile and explosive environment. These volatile constituents also require capture at a refinery, because there are many other sources of emissions that require capture and destruction and the total emissions of the plant require control by regulation. Also, nitrogen gas is usually readily available at a refinery for tank blanketing. Normally, they would tie the numerous emissions sources into a centralized destructive device such as a thermal oxidizer or flare.

At a produced water treatment facility, typically there is not any other need for nitrogen gas, and thus it would become very expensive to deliver gas or purchase and operate a nitrogen generator just for the DGF/IGF. Also, the produced water, being much lower in hydrocarbon content, yields a highly reduced potentially explosive environment in comparison to those fluids being processed at a refinery. When modeling the emissions off a DAF, it is equivalent to what would come off of an oil water separator. Typically, a DAF is just left open to the air if outside, or if in a building, the unit can be covered with a blower providing air changes in the head space to ensure that no explosive environment exists.

Differences between a DGF and IGF system include:

- A dissolved flotation system is slightly smaller than an induced system. The whole purpose of a flotation system is that it reduces the footprint, and thus the mobility, over a typical coagulation-flocculation-sedimentation system that is typically removed in larger, municipal applications.

- The removal efficiency for both Total Suspended Solids (TSS) and oil is increased by reducing the hydraulic surface loading rates in $m^3/m^2/hr$. Smaller size oil droplets have slower rise rates and thus greater need for "surface area" for separation. The dissolved flotation designed for the produced water industry has hydraulic surface loading rates of < 2 ½ $m^3/m^2/hr$ versus > 10 $m^3/m^2/hr$ for a similarly sized induced flotation unit.
- The reduced surface loading rate also improves the surge handling capacity.
- The defined residence time and efficient coagulation, homogenous mixing patterns, combined with minimal shear forces on the floc produced when introducing the dissolved air or gas in a pipe flocculator results in an air or gas that is being trapped into the floc instead of smashed around the floc as is typical of induced air or gas.
- Bubble Size – dissolved air or gas is 30 - 50 micron, designed to match the size of the precipitated particles as compared to larger 70 - 100 micron bubbles provided in an induced system.

Depending on the specific project requirements, the DGF may be open to the atmosphere or covered. The location where the system is to be employed may have regulations in place or permitting requirements that force you one way or the other. In the US, the state agency that regulates and administers permits for volatile organic compound (VOC) or hazardous air pollutant (HAP) emissions sources will either have requirements in place or request that the permit applicant model or otherwise estimate expected emissions off of VOC/HAP emissions sources at a produced water treatment facility. As with other emissions sources often found at produced water treatment facilities, such as generators, oil water separators, and condensate, oil or water storage facilities, the potential emissions can be calculated and a determination will be made on whether these sources need to capture the emissions and perform some sort of destruction or collection of these wastes. In cases where emissions do not force covering the DAF unit, the client may desire to place the DAF unit inside a building in colder environments or in order to protect and secure the equipment. In this case, the unit would likely be covered to collect vapors and at least vent them to the outside so as not to cause interior odors or noxious vapors in a facility that requires mechanical air changes. Also, a client may desire to cover a system outdoors to protect against intrusion of additional water via precipitation or against animals finding their way into undesirable waters.

An enclosed DGF needs to maintain certain air changes in the head space above the water and below the enclosure in order to protect against creation of an explosive environment as the volatile, flammable hydrocarbons release from the water. These air changes can be maintained by operation of a blower, which, depending on the permit and the client's internal desires, can either be vented or routed to a gas phase treatment device such as an adsorbent media or thermal oxidizer.

Covered DGF units have a slightly increased capital cost for the covers. Operations and maintenance (O&M) costs include power costs for operating the blowers and inspection and replacement of gaskets or seals between the cover and the DAF unit. O&M costs can be significant if treatment or destructive devices are required to deal with VOC/HAP emissions. Oil and condensate storage tanks typically have much greater emissions than a DAF unit, and thus a DAF is not usually the unit that would cause a facility to exceed an emissions standard that leads to the requirement for treatment or destruction and the associated costs.

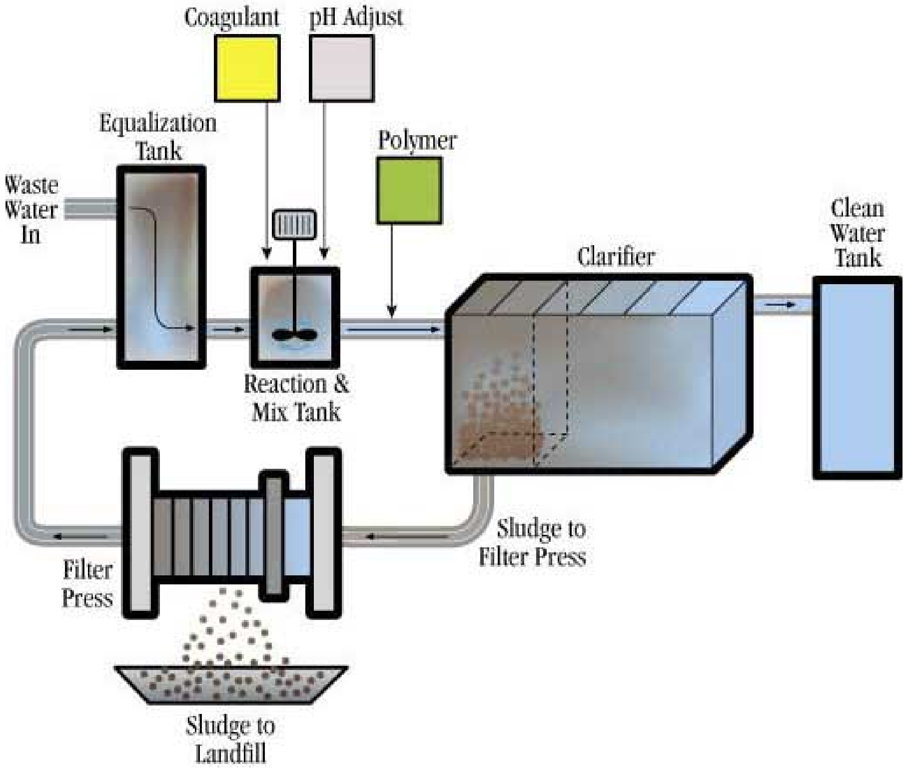

Figure 3.1 Process Diagram for Dissolved Air Flotation System.

3.3 Coalescing Media

Similar to multimedia filters, walnut shells are a media that performs some removal of solids due to particles flowing through the media and being captured in the crushed shell media. The solids are then removed in the backwash cycle similar to the multimedia filters. Although walnut shells are not as robust nor perform as effective TSS removal as properly selected mineral media, walnut shell filters provide coalescing sites for dispersed oil particles that may also be present in the influent stream. Therefore, this type of filter provides removal of both TSS and dispersed oil at least as a first cut for both constituents.

3.4 Adsorbent Media

Whereby coalesced oils can be collected and sold, adsorbent media filters encapsulate a hydrophobic or oleophillic media that traps the dispersed oil particle on its surface. When the adsorbing sites have been filled on the media, the media is removed from the filter vessel and disposed. Adsorbent media type filters include organoclays and other proprietary type filter media that claim successful results for removing the dispersed fraction

Table 3.2 Treatment Technology Comparisons for Free and Dispersed Oil.

	Oil Water Separator (API)	Dissolved Air / Gas Flotation	Electro-coagulation	Coalescing Media	Adsorbent Media
Mobility	Semi-mobile	Semi-mobile	Mobile	Mobile	Mobile
Footprint	Large	Medium – Large	Small	Small	Small
Capital Cost	Low	Medium - High	Medium - High	Low	Low
Operational Cost	Very Low	Medium	Medium - High	Low	Medium – Very high (depends on media use)
Operational Complexity	Simple	High	Very High	Low	Low
Consumables	Emulsion breaker?	Chemicals	Anodes	None	Media
Power	None	Medium – rake, compressor, mixers, chem. injection pump	Very high – electro-oxidation of anodes	Low – Pump for backwashing media	None
By-Products	Settled solids; saleable free oil	Sludge – floats, solids + chemicals; saleable oil	Sludge – floats, solids + sacrificial metal	Separated solids; saleable oil	Separated solids and media
Advantages	Simple to operate No moving parts Provides water quality equalization to improve chemical conditioning	Ability to provide a first cut of dispersed oil removal typically found in produced water Pressed floats provide saleable product	Ability to provide a first cut of dispersed oil removal typically found in produced water Provides good first cut of TSS removal	Simple to operate No Chemicals Coalesced and backwashed oil can be recovered and sold Also removes solids	Simple to operate No Chemicals Polishes to very low organics levels for reducing air emissions or to prevent biofouling

	Oil Water Separator (API)	Dissolved Air / Gas Flotation	Electro-coagulation	Coalescing Media	Adsorbent Media
	Removes free oil and gross solids	Provides good first cut of TSS removal			of RO membranes
Disadvantages	Improved efficiency based on residence time, thus large size makes less mobile Only removes free oil > 150 micron droplets VOC emissions controls may be required	Inlet water quality consistency is required for proper air bubble sizing and volume Solids processing system required in order to press out floated oils in order to sell	Field results have shown need for pre-treatment for high concentration influent Inlet water quality consistency is required for proper power conditioning Difficulty performing in varying or high TDS applications	Not suitable for large concentrations of oil or solids; pre-treatment likely required Problems seen with some backwash systems and media binding Difficult and expensive cleanup for paraffinic oils	Adsorbent Media

4.0 Total Suspended Solids

In low concentration produced water applications and depending on the level of TSS removal require, sock/cartridge or Multi-Media Filtration (MMF) units can used as water filtration technology without pre-treatment. In other cases, it can be used in-line as a polishing filtration step after bulk TSS removal by other processes. After the MMF unit a final bag/cartridge filter may be used as insurance against media breakthrough where strict adherence to a solids standard is required.

The gross solids removal in the primary treatment process only removes solids that are large enough to be removed by sedimentation. In produced and flowback waters encountered in North American unconventional plays, median particle sizes range from 1 - 50 microns with a majority in the 5 - 25 micron range. Corresponding TSS concentrations vary from less than 50 mg/L to as much as 1000 mg/L.

Fine solids are too small to be removed by gravity separation alone therefore treatment technologies such as filtration or utilizing a coagulation/flocculation process is required.

Treatment goals vary considerably depending on the end goal. Particles that are 20 - 25 microns do not cause much of an issue with infrastructure destruction, formation damage or plugging. Studies are currently ongoing to optimize what a proper cut should be, as well as concentration, for fracturing reuse applications. For water flooding or disposal by injection, the geology of the formation has major impacts on cut size and concentration of TSS. A trade-off between treatment costs to remove TSS versus production loss in flooding applications and costs associated with replacement of plugged disposal wells needs to be evaluated on a case by case basis to engineer the proper solution for a specific location.

4.1 Filtration

Filtration can be accomplished using a variety of different types of screens, bags/cartridges, or media; including: sand, anthracite, garnet or gravel, for TSS reduction. Filtration is a widely used technology for produced water. There are many vendors available that market filtration technologies specifically for produced water. Filtration does not remove TDS but it can be used for all TDS applications regardless of salt type.

In order to properly size a filtration media it is important to understand two things about the water: the amount of solids that need to be removed and the particle size distribution (PSD) of the solids in that water stream. The amount of solids that need to be removed will allow proper selection of equipment and filter size. The PSD will allow proper filtration sizing and media selection to take place.

4.1.1 Bag/Cartridge Filtration

The predominant method deployed for land-based operations for the removal of TSS in the unconventional plays where mobility is key, focuses on the implementation of basic sock and/or cartridge filtration, depicted in Figure 4.1. Typical daily throughputs are in the 800 - 1600 m^3/day range. Sock and cartridge filtration has proven to be the most flexible means of TSS removal. Bag filters are typically available in 2, 5, 10, 25 nominal micron cuts and above.

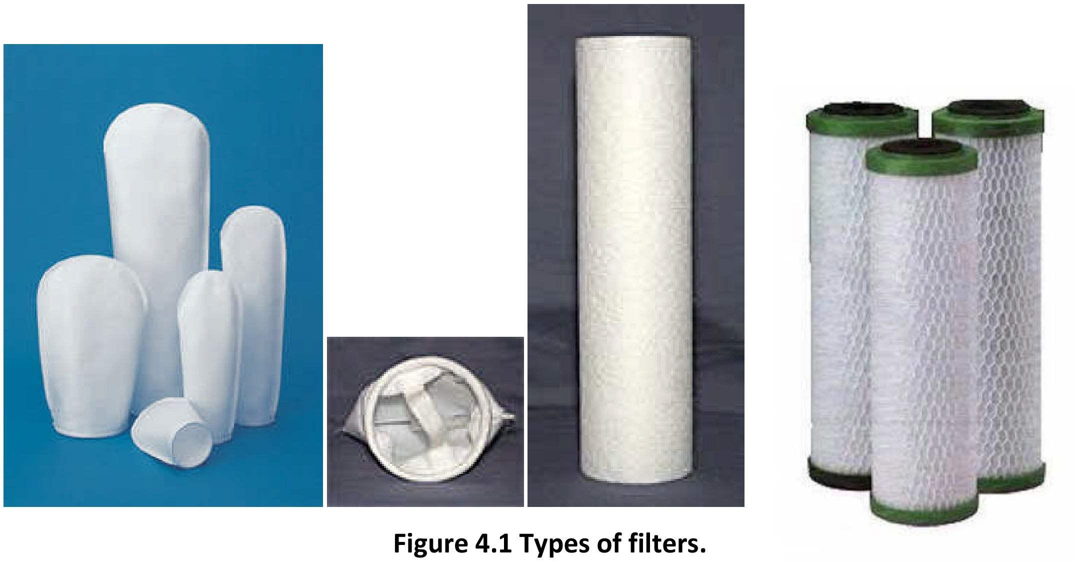

Figure 4.1 Types of filters.

A bag filter system has two components, the filter bag that removes the solid material from the media and the filter housing that contains the filter bag. Typical setup includes a primary filter for removing large particles and a secondary or polishing filter to remove particles to the final level needed to meet the micron size. As the unit is filtering, a differential pressure is built up until the point where the filter is plugged which is indicated by a decrease in flow rate and an increase in differential pressure. The filter vessels will then automatically or manually shut down and the filters will be replaced. Frequently a choice has to be made between the use of cartridge filters or bag filters.

Cartridge filters are preferable for systems with contaminations lower than 100 ppm TSS, which equate to levels lower than 0.01% by weight. A cartridge filter can be of surface or depth-type while a sock filter is predominately a surface filter. Surface filters are made of thin materials like papers, woven wire, or cloth where particles get blocked on the surface of the filter. Depth-type filters capture particles throughout the total thickness of the medium.

Surface filters are best for filtering sediment of relatively large sized particles. If all particles are around 5 microns, a pleated 5 micron filter works best because of its large surface area. Compared to pleated surface filters, depth filters have a lower surface area, with the advantage of depth. As a rule of thumb for concentrations greater than 5 mg/m^3, a surface filter is favored and for concentrations lower than 5 mg/m^3 a depth-type filter is preferred.

Both cartridge and sock filters are designed to be disposable and have to be replaced when the filter is plugged. Most cartridge filters also have absolute micron ratings to ensure that a specific micron cut point is being achieved while most bag filters have a nominal size rating. The nominal size rating allows a user to understand the average size particle that a particular filter will remove. If a specific size is required it may be necessary to select a nominal size rating below the required micron cut point to achieve the necessary level of filtration.

Figure 4.2 Typical mobile filtration trailer.

Figure 4.3 Filtration pods.

4.1.2 Multimedia Filtration

Where mobility is not required and an equalized influent water quality can be provided, coagulation/flocculation of the TSS particles followed by backwashable media filters provides a more cost effective approach as manpower and consumable (bags and cartridges) are greatly reduced.

The disadvantage of sock/cartridge filters is the amount of consumables that they require in order to operate. If the need for mobility afforded by the bag/cartridge filter is not needed and a slightly larger footprint is available utilizing sand or multi-media filtration (MMF) may save time and money.

MMF uses a filtration media such as sand, anthracite, garnet, or gravel instead of bags/cartridges for physical removal of the target solids. Removal is brought about by flowing the influent water through a vessel packed with the solid media. Gravity and the particle size of the media force the contaminated water to take a circuitous route thru the packed media. Particles larger than the media in the vessel will be trapped on the media as the water continues out the effluent side of the vessel. “Multi” refers to using different layers (size and specific gravity) to provide several micron cuts within one vessel. Each different media needs to be homogenously sized in order to not allow different particle sizes thru. As the unit collects filtered solids within the media bed, the pressure required to transmit water thru the media increases. MMF units typically include backwash systems in order to remove the filtered solids for disposal or further processing. Typically, in order to reduce manpower, backwash cycles start automatically based on either preset time periods or on pre-programmed pressure differentials monitored by pressure gauges on the influent and effluent sides of the vessel. The backwash water comes from a clean water backwash tank and the waste from the backwash cycle is collected in a solids tank. These solids can be further processed utilizing equipment such as filter presses or centrifuges in order to reduce the solid waste that needs to be hauled to a landfill.

Below are the typical specifications of the influent water quality where a MMF would be employed:

- Total Suspended Solids:
    - Particle Size: 5 - 100 microns.
    - Concentrations: > 30 ppm.

If the influent water contains significant amounts of oil (say > 20 - 50 ppm), pre-treatment of the water is normally employed prior to the use of a TSS filtration technology. High crude content or paraffinic oil may coat the media and may not be removed by backwashing. If this occurs, media replacement would be required which can be expensive in terms of new media and disposal of spent media as well as operationally intensive. Pre-treatment to remove the oil may consist of an oil water separator such as an American Petroleum Institute (API) separator, Corrugated Plate Interceptor (CPI), inclined plate separator, gun barrel tank, dissolved/induced air/gas flotation as discussed previously, or a hydrocyclone.

Backwashable screens are an additional method of filtration. This technology utilizes pre-sized screens to filter the fluid. Similar to the MMF unit, once a differential pressure or pre-designated time of running has been achieved the unit will go into a backwash cycle. Different types of screen cleaning exist, including spray and vacuum nozzles that clean just a small portion of the screen at a time as well as scrubber type mechanisms. The metal material of the screen design allows for somewhat rigorous screen cleaning techniques rather than the simple backwash fluidization provided in MFF backwashing processes. Screens are sized based on the micron level it is meant to remove. Similar to the sock/cartridge filtration unit, screen vessels can be setup in series to remove multiple micron cuts of solids. This is a key parameter in order to optimize the system.

During the backwash cycle a waste stream will form, similar to the MMF unit. One disadvantage with screen filtration is it has a hard time with filtering fluid that has gels or polymers. The gels and polymers get caught inside the filters and will go into a continuous backwash cycle, which in turns produces a large waste stream. In order to clean the screens it usually takes a manual shut down to remove the screen and put it through a full cleaning.

There are a large amount of vendors that provide different types of screen filtration. Differences between the screen filtration vessels include how the screens are backwashed and the means by which they filter the fluid.

4.2 Coagulation/Flocculation

TSS removal efficiencies can be improved by employing coagulation/flocculation upstream of the filter. This process allows smaller solids to conglomerate together to form larger, easier to remove solids. This process has been used as a traditional treatment process for decades in municipal and industrial applications to destabilize suspended particles and enhance flocculation of the now neutralized inorganic particles, as well as other inorganic species from aqueous streams, thereby permitting their removal through sedimentation, flotation, or filtration. Traditionally, the chemical coagulants used are polymers, such as aluminum sulfate and ferric chloride.

Although the words "coagulation" and "flocculation" are often used interchangeably, they refer to two distinct processes:

Coagulation indicates the process through which colloidal particles and very fine solid suspensions are destabilized so that they can begin to agglomerate if the conditions are appropriate

Flocculation refers to the process by which destabilized particles actually conglomerate into larger aggregates so that they can be separated from the wastewater [116].

Coagulation is one of the most important reactions used in water treatment. Ions (inorganic metals) and colloids (organic and inorganic) are mostly held in solution by electrical charges. By the addition of ions with opposite charges, these ions and colloids can be destabilized; coagulation can be achieved by chemical or electrical methods. The coagulant is added in the form of suitable chemical substances. Alum $[Al_2(SO_4)^3 \bullet 18H_2O]$ is such a chemical substance, which has been widely used for wastewater treatment. In each case, the charged portion of the chemical additive destabilizes and binds with the oppositely-charged contaminants in solution, causing them to coagulate and, when of sufficient mass, to precipitate [178].

Coagulants fall into two categories, aluminum based or iron based. The aluminum based coagulants include aluminum sulfate, aluminum chloride and sodium aluminate. The iron based coagulants include ferric sulfate, ferrous sulfate, ferric chloride and ferric chloride sulfate. Hydrated lime and magnesium carbonate are other chemicals used as coagulants.

Aluminum and iron coagulants are effective principally from their ability to form multi-charged polynuclear complexes with enhanced adsorption characteristics. The form of these complexes can be controlled by the pH of the system.

When the metal ions (Al and Fe) from the coagulants are added to water they hydrolyze rapidly but in a somewhat uncontrolled manner, forming a series of metal hydrolysis species. The efficiency of pH, rapid mixing and the coagulant dosage determine which hydrolysis species is effective for treatment. Bench scale testing is a necessary step to ensure the correct combination of chemicals is used. Ongoing bench scale testing during operation is also essential to make sure the process is continuing to operate at an optimized level.

Once the suspended particles are flocculated into larger particles, they can usually be removed from the liquid by sedimentation, flotation, or media filtration. The addition of a flocculant may not be required when a filtering process is used because the particles formed by the coagulation reaction may be large enough in size to allow for removal.

The effectiveness of the technology is based on the chemistry of the chemicals selected for treatment. There are a wide range of different coagulants and flocculants that can be bought off the shelf from chemical supply companies. In order to understand which chemical is appropriate for the application, bench scale studies are needed prior to field application and also during the operation. These studies will provide the optimized chemical and dosage to be used. The key to continued operational success is equalization of water. Chemical dosages are determined by very specific items in the water and how they react together, if the water to be treated widely fluctuates, a system will have difficulties operating as a continuous process as a bench scale study will be necessary or each new water type brought to the site. Equalization of all water prior to the system will help ensure a homogeneous water source and help reduce the need to change chemical dosages or even chemicals.

Figure 4.4 Flocculation Operation.

4.3 Conditioning and Settling

The basic process utilizing coagulation/flocculation is to utilize a settling step to remove the newly formed suspended particles. Sedimentation will work provided that a sufficient density difference exists between the suspended matter and the liquid. During this process the coagulant/flocculant will be mixed into the fluid and the fluid will go through a retention basin in order to allow sufficient time for settling to take place. A lamella separator is one option in order to decrease the time it takes for the suspended particles to settle. A lamella separator or clarifier is a water treatment process featuring a rack of inclined metal plates, causing flocculated material to precipitate from water flowing across the plates. Lamella clarifiers are used in the water and wastewater treatment industries to separate solids from liquids in effluent streams, such as suspended solids in produced, flowback or fresh water sources.

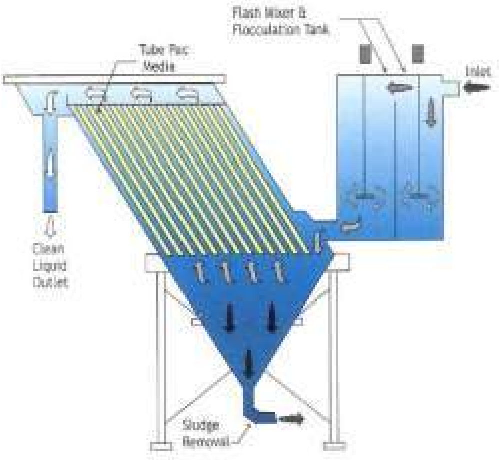

Figure 4.5 Process Diagram of Lamella Clarifier [171].

The clarifier is usually the third step in a four-stage process for conditioning and settling. The steps are:

- Collection and homogenization of feed water or water to be treated.
- pH adjustment and polymer addition.
- Clarification.
- Sludge dewatering.

One of the advantages of lamella clarifiers over conventional clarification equipment is that they require a much smaller surface footprint for a given solids removal capacity. The compact and enclosed design largely eliminates any hydraulic disturbances (such as wind or temperature changes) that can cause challenges with conventional clarifiers located outdoors. Equal flow to each plate and across the plate surface area is assured by balanced flow distribution. Pre-packaged units can be easily transported and installed at the use location. Maintenance costs tend to be low due to few moving parts.

In a typical operation, fluid enters the lamella clarifier where it is flash mixed with a polymer flocculant and then gently agitated with a separate mixer. The fluid flows down the inlet chamber onto the plate rack. Previously settled solids are not disturbed by the fluid because it enters the plate rack in a cross current motion. Then the fluid flows upward and the solids settle on the plates and discharge into the discharge hopper where the sludge is further condensed due to the sludge packing together, as is also the case with a conventional clarifier.

The clarified liquid is dispersed into collection channels leading to the clarified water outlet as it exits the plate assembly through orifices or weirs found at the top. Underflow from the sludge hopper (or sludge tank) found below the unit is removed and usually dewatered prior to disposal.

4.4 Settling

Most operators are currently already practicing sedimentation when they allow water to sit in fracturing tanks or surface impoundments prior to being reused. Sedimentation can be done in a basin (either a lined impoundment or a tank) or in a separator such as a Gun Barrel Separator, American Petroleum Institute (API) Separator, or Corrugated Plate Interceptor (CPI) Separator. Sedimentation uses the natural process of gravity to separate the solids from the liquid. The solids are allowed to settle to the bottom and be removed for further processing while the effluent can continue on to be reused or conditioned if further treatment is necessary.

Depending on the targeted particulate size and specific gravity of the particle, sedimentation basins are sized to provide the necessary hydraulic residence time to allow the particles to settle to the bottom of the basin prior to discharge based on Stoke's Law. Typically, a significant volume of water, and size of the sedimentation basin, requires a large amount of area to work properly for a typical produced water influent volume. Thus, sedimentation basins and separators are not easily moved from location to location due to their large size. A mobile unit would be something as simple as a fracturing tank that has the ability to move to different locations. The other advantage of using large tanks for sedimentation is this also allows water quality and flow equalization of fluid to take place which significantly helps during more advanced treatment processes where chemical conditioning and dosing needs to be matched to the influent water quality. Varying water quality makes dosing of chemicals very difficult to perform effectively.

4.5 Hydrocyclone

Hydrocyclones are used to separate solids from liquids based on the density of the materials to be separated. They will not remove soluble oil and grease components. Depending on the model of hydrocyclone employed, they can remove particles in the range of 5 - 15 microns. Hydrocyclones normally have a cylindrical section at the top where the liquid is fed tangentially and a conical base (Figure 4.6). The angle of the conical section determines the performance and separating capability of the hydrocyclone. Hydrocyclones can be made from metal, plastic, or ceramic and have no moving parts. The hydrocyclone has two exits, one at the bottom, called the underflow or reject for the more dense fraction and one, called the overflow or product at the top for the less dense fraction of the original stream [47].

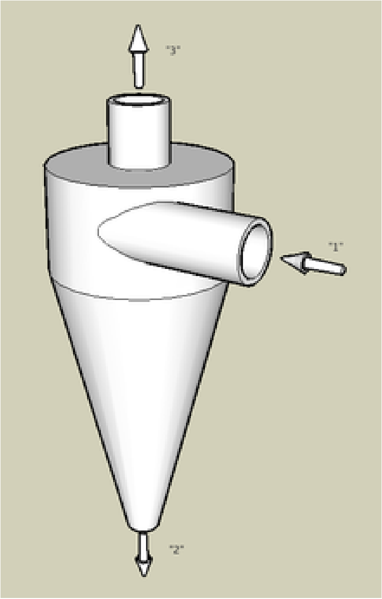

Figure 4.6 Schematic drawing of a hydrocyclone [47].

Hydrocyclones have been used extensively to treat produced water and are marketed by numerous companies for produced water treatment. Hydrocyclones were used to treat fracturing brine in the Barnett Shale play. In this research study, hydrocyclones were used in combination with organoclays as a pretreatment to reverse osmosis [47].

Hydrocyclones do not require any pre- or post-treatment. They do not require any chemicals or energy. The hydrocyclone is the only piece of equipment necessary. There are no energy requirements unless the plant setup requires a forwarding pump to deliver water to the hydrocyclone. Depending on the size and configuration of the hydrocyclone, a large pressure drop can occur across the hydrocyclone [47].

The waste generated from a hydrocyclone is slurry of concentrated solids. This is the only residual that requires disposal [47].

4.6 Electrocoagulation

Electrocoagulation (EC) is another means in which to remove suspended material from flowback/produced water. EC is a treatment method where the flocculating agent is created by electro-oxidation of a sacrificial anode, usually made of iron or aluminum. The anodes neutralize the charge on the suspended solids and oil droplets so that they coagulate and separate from the water phase. EC is performed without adding any chemical coagulant or flocculants, thus reducing the amount of sludge that must be disposed.

This process has been most commonly used in the treatment of water from metal-processing plants. Recently this technology has gained some use within the oil and gas industry for treating flowback/produced water.

In EC, dissolved ionic or electrostatically suspended contaminants are destabilized by applying alternating or direct current electricity to a cathode-anode system. During the electrolytic process, cationic species from the anode metal dissolve into the water. These cations react with the destabilized contaminants creating metal oxides and hydroxides which precipitate. If aluminum anodes are used, aluminum oxides and hydroxides form; if iron anodes are used, iron oxides and hydroxides form. The formation of the oxides and hydroxides, and their subsequent precipitation, are similar to the processes that occur during coagulation/flocculation and precipitation using alum or other chemical coagulants.

It is essential to make a careful selection of the reaction tank material along with control of the current, flow rate and pH. Depending on the wastewater to be treated and the contaminants to be removed, electrodes can be made of aluminum, iron, titanium, graphite or other materials.

EC operating conditions are highly dependent on the conductivity of the aqueous medium as well as the chemistry. Other influent characteristics such as pH, particle size, and chemical constituent concentrations will influence operating conditions. Pressure and temperature have minimal effect on the process. Characterization of the fluid prior to the unit is essential for optimum operation. Similar to other technologies, EC requires equalization of water prior to running the unit as changes in the wastewater quality greatly affect the treatment efficiency. The EC process has been combined with other treatment processes such as DGF prior to the unit and filtration after the unit. A combination of treatments may be required to successfully treat a water source.

The design of the EC process impacts its operation and efficiency. The following factors should be considered:

- Continuous versus Batch Operation.
- Reactor Geometry.
- Reactor Scale-Up.
- Current Density.

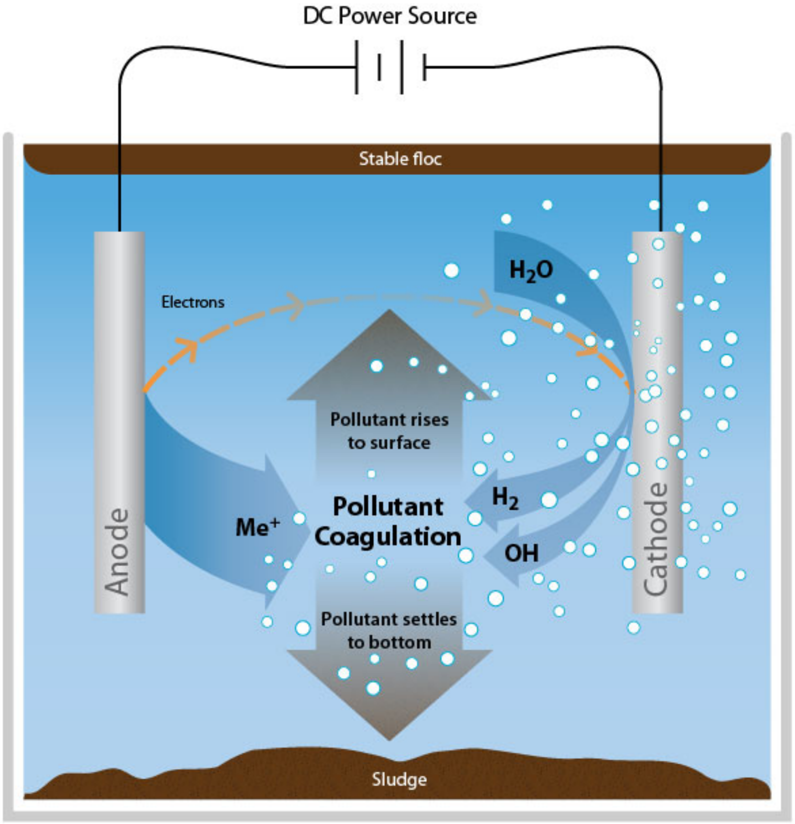

Figure 4.7 Electrocoagulation Process Diagram.

In EC, wastewater separates into three phases, a floating layer, a mineral-rich sediment, and a clear water. The first phase, or floating layer, is removed by an overflow removal method and moved to a sludge collection tank. The accumulated mass settles down via gravity and is later removed through a discharge valve at the bottom of the EC reaction tank and moved to a sludge collection tank. The treated water is pumped to a buffer tank for later disposal and/or reuse in the plant's designated process.

There are both mobile and central treatment facility designs for the EC technology.

Table 4.1 Comparison of Treatment Technologies for Total Suspended Solids.

	Gravity Settling	Filtration	Hydrocyclone - Desander	Coagulation/ Flocculation/ Sedimentation	Dissolved Air / Gas Flotation	Electro-coagulation
Mobility	Semi-mobile	Mobile	Mobile	Semi-mobile	Semi-mobile	Mobile
Footprint	Large	Small	Small	Medium – Large	Medium – Large	Small
Capital Cost	Low - High	Low	Low - Medium	Medium – High	Medium - High	Medium - High
Operational Cost	Very Low	Low - Medium	Low - Medium	Medium	Medium	Medium - High
Operational Complexity	Simple	Simple	Low	High	High	Very High
Consumables	None	Filters, media	None	Chemicals	Chemicals	Anodes
Power	None	Low – Pump for backwashable filters	High – Pump to feed unit for separation	Low – mixers, chemical injection pump	Medium – rake, compressor, mixers, chem. injection pump	Very high – electro-oxidation of anodes
By-Products	Settled solids	Solids laden bag/ cartridge filters	Separated solids	Sludge – solids + chemicals	Sludge – floats, solids + chemicals	Sludge – floats, solids + sacrificial metal
Advantages	Simple to operate No moving parts Provides water quality	Simple to operate Flexibility in handling varying influent water	Simple to operate No Chemicals Small footprint and light weight ideal	Ability to remove smaller, suspended particulate typically found in	Ability to remove smaller, suspended particulate typically found in	Ability to remove smaller, suspended particulate typically found in

	Gravity Settling	Filtration	Hydrocyclone - Desander	Coagulation/ Flocculation/ Sedimentation	Dissolved Air / Gas Flotation	Electro-coagulation
	equalization to improve chemical conditioning Removes free oil and gross solids	quality Filter media can be tailored to treatment goal	for off-shore applications	produced water Lower operational costs than an array of filters	produced water Lower operational costs than an array of filters Dispersed oil removal and saleable product w/ flotation	produced water Dispersed oil removal w/ flotation
Disadvantages	Improved efficiency based on residence time, thus size makes less mobile Does not remove small or suspended particles Controlling VOC emissions and wildlife intrusion	Can be labour intensive for frequent filter changes if sock/ cartridges are used Large amount of consumables with sock/ cartridges Does not remove oil	Limited to physical separation Subject to abrasion by particulate matter Not suitable for large concentrations of oil or sands Only removes a certain size, density of material	Inlet water quality consistency is required for proper chemical addition Increased solids may require solids processing facilities	Inlet water quality consistency is required for proper chemical addition Increased solids may require solids processing facilities	Field results have shown need for pre-treatment for high concentration influent Inlet water quality consistency is required for proper powering conditioning Increased solids may require solids

	Gravity Settling	Filtration	Hydrocyclone - Desander	Coagulation/ Flocculation/ Sedimentation	Dissolved Air / Gas Flotation	Electro-coagulation
	expensive or difficult on large impoundments		per desander			processing facilities Difficulty performing in varying or high TDS applications

5.0 Bacteria Control

Disinfection is needed on almost all fracturing jobs due to the bacterial growth in water and the issues they present with scaling and degradation of fracturing fluid additives. Traditionally chemical means, such as biocides, have been used to control the bacterial activity during the operation. As operators are looking to reduce their environmental impact and improve the chemicals they utilize, other technologies are being investigated to provide disinfection and bacterial control during fracturing operations.

Disinfectants can be classified in two categories: residual and non-residual. Residual indicates that there is a lasting chemical in the water that will continue to disinfect until the entire chemical has been consumed. A residual ensures that there is bacterial protection as the water is sent downhole. A non-residual disinfectant does not provide any lasting bacteria control. Once the water has passed through the system, if it encounters bacteria further in the piping there will be no additional bacterial kill or control.

5.1 Electrocoagulation for Bacteria

Electrocoagulation has the capacity to destroy bacteria. EC vendors claim the process can provide 90 - 99% bacterial reduction in industrial and municipal wastewaters.

5.2 Ozone

Ozone (O_3) is both a very strong oxidant and effective disinfectant. Ozone is produced when oxygen molecules are separated by an energy source into oxygen atoms and then collide with an oxygen molecule to form (O_3). Ozone is an unstable gas that decomposes to elemental oxygen in a short amount of time after generation so it is produced onsite prior to its use for different applications [170].

Air or pure oxygen can be used as the feed-gas source to produce ozone. The selected gas is passed through a dehumidifier and then to an ozone generator where the gas is exposed to an electrical charge to form ozone. The ozone will contain about 0.5 to 3.0% ozone by weight, while pure oxygen will form approximately two to four times that amount. After generation, ozone is fed into a contact chamber containing the wastewater to be disinfected. The ozone is dispersed into the water generally using bubble diffusers and the water is mechanically agitated to ensure that the ozone is contacted uniformly within the water in a short period of time, ranging from seconds to minutes, depending on the level of contamination in the water. After the water is in contact with ozone, off-gases produced in the contact chamber must be treated to destroy any remaining ozone before release of the water to the atmosphere to avoid toxicity and corrosive effects in the environment where the water is to be used.

In the disinfection of flowback water, the use of an ozone destruction system for any residual can be eliminated if the water is to be stored after disinfection to eliminate bacterial contamination in the storage equipment.

The efficiency of disinfection of any wastewater using ozone depends on the susceptibility of the target microorganisms in the water to ozone, the contact time, and the level of pre-treatment of the water prior to disinfection. High levels of TSS, metals and organics in the water reduce the ozone disinfection efficiency and higher ozone doses for disinfection could be required. Thus, adequate pre-treatment for removal of these components is recommended prior to disinfection using ozone. Ozone doses as low as 0.5 mg/L have been reported in drinking water applications for disinfection of bacteria and viruses in waters with turbidity levels of 0.2 Nephelometric Turbidity Units (NTU) accomplishing 99.99% bacterial removal. Doses of 4 - 7 mg/L have been reported in wastewater applications for wastewaters with levels of turbidity and Chemical Oxygen Demand (COD) of 12 NTU and 40 mg/L, respectively. USEPA indicates that an adequate pre-treatment system for disinfection using ozone shall provide no more than 30 mg/L of organic material and less than 30 mg/L of TSS (or turbidity less than 15 NTU).

One of the major advantages in the use of ozone compared to other disinfectants is that a 100% bacteria kill can be achieved if adequate pre-treatment is provided for sufficient contact times. In municipal wastewater treatment applications, 100% kills have been reported using a 1.9 mg/L dose, with contact times from 30 seconds to 10 minutes.

For disinfection of flowback water or alternate water sources for the preparation of fracturing fluids, ozone can be applied “on the fly” because of the low contact times required or prior to short term storage of the water. If the water is to be stored, an ozone residual compound can be left in the water to disinfect the storage equipment eliminating the use of ozone destruction equipment.

5.3 Mixed Oxidant Solutions

An alternative disinfection in fracturing operations is the mixed oxidant solution which replaces the conventional biocides used for bacterial control. The mixed oxidant solution is an onsite generated disinfectant composed of predominantly sodium hypochlorite and various mixed oxidants including, but not limited, to ozone, hydrogen peroxide, hydroxide, and chlorine ions. It is generated on site and to demand utilizing an electrolytic cell, food grade sodium chloride salt, and water. It is capable of disinfecting fresh water at pump rates up to 19 m^3/minute with an effective dose of 20 - 30 ppm. This technology is currently used worldwide in civil applications to disinfect drinking water for the public. It is a commonly used and widely accepted technique for disinfecting water.

The mixed oxidant solution reacts with bacteria, algae, manganese, iron, and ammonia. The technology is typically contained within a 20’, 30’ or one 40’ and a 20’ container depending upon the pump rates required to disinfect. The technology will arrive with salt and the equipment required and only requires the addition of water and electricity to generate the mixed oxidant solution. The water is obtained from the working tanks of the fracturing job and the electricity is created from a power generator, which is usually incorporated into the package. Depending upon the size of the equipment, which is dependent upon the pump rates of the fracturing operation, the mixed oxidant solution technology will require one to two operators per 12-hour shift.

5.4 Chlorine Dioxide

Chlorine dioxide is an alternative disinfection that is currently being explored as an option for disinfecting source water for fracturing operations. Chlorine dioxide is an onsite disinfection technology that generates the disinfectant (chlorine dioxide) on demand. Depending upon the chemistry being used the system can have a 2 or 3 chemical precursors. The most typical generating technology being used is a three chemical precursor system that utilizes sodium chlorite, sodium hypochlorite, and hydrochloric acid. The three chemicals are mixed in a specific order depending on the technology used and under a vacuum to entrain the gas in liquid immediately. The chlorine dioxide is typically in concentrations up to 3500 ppm and is dosed on the fly with effective loadings ranging from 5 - 150 ppm chlorine dioxide on pump rates up to 19 m^3/min. This technology is currently used worldwide in waste water applications to the fluid prior to surface discharge.

Chlorine dioxide reacts with bacteria, sulphides, manganese and iron within the water. It can be used to disinfect fresh water and produced/flowback water for reuse in fracturing fluid make up. As it is an oxidant, its residual concentration needs to be monitored to ensure no interference with the fracturing fluid additives. The unit is typically a 20 - 40’ container that encloses the chlorine dioxide generator, controls, pumps and pipe work. The chemical supply footprint will vary depending upon the amount required and the number of precursors used. The footprint can then grow in size from a one trailer system to a three trailer system to incorporate all the chemicals and equipment required. Typically an injection manifold is also used to dose the disinfectant into the water stream to ensure even distribution of disinfectant, especially when fresh water and produced/flowback water is used as the makeup fluid for the fracturing job.

Depending upon the size of the generator and the rate required, one or two operators are required per 12 hour shift. Due to the nature of the oilfield, two operators are required to run the chlorine dioxide disinfection unit per tour.

5.5 Ultraviolet

Ultraviolet (UV) light radiation is a widely used method for disinfection of treated wastewaters. UV disinfection is based on the photochemical damage of links in the DNA molecules of a cell in microorganisms preventing the future replication of a cell and effectively “inactivating” the microorganism. UV uses electromagnetic energy as a disinfection agent and the UV source commonly used for disinfection is mercury vapor, electric discharge lamps. The optimum disinfection wavelengths are in the range of 255 – 265 nm. The lamp systems are modular in design, oriented horizontally or vertically, mounted parallel or perpendicular to the water flow, and assembled in single or multiple channels or reactors for contact.

The main difference between chemical disinfection or ozone disinfection compared to UV is that the effect of UV radiation is manifested by the organism's inability to replicate, whereas chemical and ozone disinfection destroy the integrity of the microorganisms via oxidation processes. Thus, UV is sometimes combined with a chemical disinfection method for better disinfection results. One of the major complications using UV is the dispersion of radiation through the wastewater. Ideally all the flow entering the contact reactor should be exposed to the same level of UV for the same amount of time; a condition described as turbulent, ideal plug flow. In fact, these conditions are difficult to achieve and not all the water gets exposed to the same UV dose. The maximum reported levels of disinfection using UV are 2-log inactivation (99.99%) compared to 4 log achieved by chemical disinfection (99.9999%) and 4 log or complete kill achieved by ozone.

Furthermore, UV lamps usually do not use all input energy on the disinfection process. Only 30 - 40% is generally used.

The use of UV can be implemented for disinfection of water to be used in the preparation of fracturing fluids and its application can be "on the fly"; however the expected disinfection level considering the contaminants in the water sources may not achieve more than 99% bacteria reduction and the method may need to be used in combination with chemical treatment for better disinfection results (i.e. addition of biocide for bacteria reduction combine with UV for final disinfection).

5.6 Biological Treatment

Activated sludge is the most common type of biological wastewater treatment. Oxygen and (in some cases) nutrients are fed into a tank or basin to support a suspended biological population. The "mixed liquor" from the bioreactor then flows to clarification where treated effluent overflows out the top while settled sludge is recycled back to the front of the bioreactor or filtration. The sludge recycle helps balance the biomass population in the bioreactor. Variations of activate sludge include Fluidized Bed Reactors (FBRs) and Membrane Bioreactors (MBRs).

Anaerobic systems require much less maintenance than FBRs or MBRs but require a delicate balance of primary degraders and methanogens to break down the waste. These systems are usually very large and can sometimes have non-uniform biomass distribution. FBRs and MBRs allow for much more controlled biological systems, whereby both aerobic and anaerobic biological systems can be successfully applied.

Biological systems offer the advantage of removal of all organics and bacteria at relatively low cost, and it has historically been a mainstay in more traditional municipal and industrial treatment plants. The oil and gas industry has shown a preference for physiochemical treatment processes. However, as volatile organic compound (VOC) emissions including methanol and as pre-treatment for reverse osmosis (RO) to prevent biofouling, biological systems have recently been employed with great success on produced water treatment systems at numerous locations.

Table 5.1 Comparison of Treatment Technologies for Bacteria Control.

	Electro-coagulation	Ozone	Mixed Oxidant	Chlorine Dioxide	Ultraviolet Light Radiation
Mobility	Mobile	Mobile	Mobile	Mobile	Mobile
Footprint	1-2 Trailers	1 Trailer	1-2 Trailers	2-3 Trailers	1 Trailer
Economics					
Personnel Requirements	1-2	1-2	1-2	1-2	1-2
By-Products	Sludge		None	None	None
Advantages	Reduces suspended solids load	100% Kill	Residual disinfection Benign precursors – salt, water, electricity	Residual disinfection Able to provide a high dose due to chemical generation	Does not use a chemical
Disadvantages	pH dependent – requires equalization of flows. Not a standalone disinfection process.	Requires Pre-treatment Requires mix chambers and removal of residual – can create large	Reacts with inorganics – exerting an extra demand in some flowback/ produced waters	Chemical precursor system may require a lot of footprint Hazardous precursor	Requires Pre-treatment – highly dependent on water quality (clarity) No Residual Does Not achieve 100% kill

	Electro-coagulation	Ozone	Mixed Oxidant	Chlorine Dioxide	Ultraviolet Light Radiation
		footprint.		chemicals requires proper handling and system design	

6.0 Scale-Forming Dissolved Solids

6.1 Chemical Precipitation

Chemical precipitation utilizes the addition of chemicals to precipitate out water quality constituents such as the multivalent cations of calcium, magnesium and iron. The standard process for calcium and magnesium removal is utilizing lime softening. Lime softening utilizes the addition of lime, or calcium hydroxide, to remove hardness, i.e. precipitation of calcium and magnesium ions. The process can also be effective at removing a variety of microorganisms and dissolved organic matter. In the case of hydraulic fracturing, reduced hardness minimizes interference with fracturing fluid components and down-hole scaling that can impede lifetime and productivity of the well. Variations of the process include using dolomitic lime (with magnesium), adding soda ash, aerating, or adding a magnesium salt. Treatment temperature may be ambient (cold lime) in open tanks, close to 100^{o}C (warm lime), or above 100^{o}C (hot lime) in closed vessels. Additional chemicals can also be used during the process to precipitate specific ions such as barium.

Lime softening is a series of complex chemical reactions designed to convert the calcium and magnesium compounds in water into calcium carbonate and magnesium hydroxide. Calcium and magnesium compounds are the least soluble and as a result will settle out of the water at the lowest concentrations [170].

The pH of the water must be raised by the addition of lime in order to produce calcium carbonate and magnesium hydroxide. In water, calcium compounds will be removed at a pH of about 9.0 - 9.5 while magnesium compounds require a pH of 10.0 - 10.5. Removal of non-carbonate hardness requires an even higher pH, 10.0 - 10.5 for calcium compounds and 11.0 - 11.5 for magnesium compounds. This can be accomplished by adding soda ash or sodium hydroxide [170].

When lime is added to water the pH increases and the equilibrium of the carbonate species shifts. Dissolved carbon dioxide (CO_2) is first converted to bicarbonate (HCO_3^-) and then to carbonate

(CO_3^{2-}), which precipitates. Additionally, magnesium can be precipitated to magnesium hydroxide.

However, the reactions that remove carbonate and non-carbonate hardness from water require a very high pH. If used in this state, the high pH would cause corrosion of pipes and the excess calcium carbonate would precipitate out, causing scale. Consequently the solids must be removed and the pH neutralized to stabilize the system [170].

Lime softening is often used in combination with sedimentation and filtration in order to reduce waste streams. The process is unique in that both the calcium added with the lime and that present in the raw water as well as some of the magnesium present in the raw water are precipitated [170].

Hydrated lime and quicklime both soften water in the same way, but the equipment required for the two types is different. Hydrated lime ($Ca(OH)_2$) is also known as calcium hydroxide or slaked lime. Hydrated lime can be added to water as it is without requiring any special equipment, and is the preferred choice for small water treatment plants, and mobile operations. Quicklime (CaO), or unslaked lime, must be slaked or hydrated before use and should be avoided due to its high exothermic and hazardous characteristics, requiring special precautionary measure and equipment to ensure safe operation.

The advantages of caustic soda are its stability in storage, lower sludge formation, and easy handling. However, safety issues still apply and should be considered. Caustic soda is dangerous to the operator and can cause severe burns to the skin if handled improperly. In addition to the caustic soda, lime dust is harmful when it comes in contact with eyes, mouth, nose and skin contact can cause burns. The Material Safety Data Sheet (MSDS) should be referenced for details on the Personal Protective Equipment (PPE) and handling recommendations.

6.2 Ion Exchange

Ion exchange (IX) softening is another way of softening water. IX is a reversible chemical reaction whereby positively or negatively charged ions present in the water are replaced by similarly charged ions present on the resin. The resins are immersed in the water and are either naturally occurring inorganic zeolites or synthetically produced organic resins. When the exchange sites on the resin are exhausted, the resin is regenerated by exchange with the ions in the regeneration solution.

IX units utilize different resins to preferentially remove certain ions. When treating flowback, a resin loaded with hydrogen ions may be selected to preferentially remove sodium ions. The required resin volume and size of the IX vessel would depend on the salt concentration and flowback volume treated.

The Higgins Loop is one version of IX that has been successfully used in Midwest coal bed methane (CBM) applications. The Higgins Loop uses a continuous counter current of flowback fluid and IX resin. Flowback water with high sodium content can be fed into the absorption chamber to exchange for hydrogen ions. The strong acid cation resin is pushed into the absorption chamber through a unique resin pulsing system.

Specialty IX resins can be used to remove divalent cations for softening operations. A typical water softening system consists of a pressure tank partially filled with IX resin, consisting of plastic beads with sodium ions that can be exchanged with calcium and magnesium responsible for the hardness of the feed water, resulting in an effluent stream of softened water containing sodium ions instead of calcium and magnesium. The resin bed can be regenerated by passing sodium chloride or hydrochloric acid in the reverse direction to displace the calcium and magnesium ions attached to the resin. The backwash, or upward flow, that loosens the resin bed and flushes out suspended particles is referred to as the regeneration cycle. Backwash usually lasts about 10 minutes and then is followed by regeneration and rinse cycles. Regeneration produces concentrated brines that contain more solids than the mass of ions removed from the water. This waste would need treatment and disposal.

The technology is widely used in water treatment and is readily available both as packaged or engineered systems. Ion exchange materials may be natural (certain clays) or synthetic (zeolites, which are crystalline aluminosilicates or clays, and organic resins).
Recent research also suggests that IX may be employed to remove boron from RO permeate. IX is a well-developed process and is commonly applied to drinking water treatment for hardness removal, but is increasingly being studied for the removal of radionuclides and nitrates.

Typically, IX processes operate with minimal energy demand and may require only electricity for pumping fluids under low hydraulic pressure. Operational and management considerations for IX include occasional disinfection of the IX resin with NaOCl or H_2O_2. To make sure that fouling agents such as suspended solids, scale forming materials and oxidized metals are not present in the feed water careful management is required. Additionally, many IX resins are sensitive to free chlorine oxidation. IX processes must also be carefully managed to reduce osmotic shock occurring with high salinity waters and mechanical abrasion of IX resin, which will lead to physical loss of the resin.

Table 6.1 Comparison of Treatment Technologies for Scale-Forming Dissolved Solids.

	Chemical Precipitation	Ion Exchange
Mobility	Semi-mobile	Mobile
Footprint	Medium – Large	Small
Capital Cost	Medium – High	Low – Medium
Operational Cost	Low – High	Medium – High
Operational Complexity	Medium – High	Low
Consumables	Chemicals	Resin
Power	Low to Medium – mixers, chem. injection pumps; solids processing equipment	None to Low – Higgin’s Loop pump
By Products	Solids	Spent resin
Advantages	Straightforward, proven treatment approach Robust technique	Simplicity of operation Can remove multivalent cations to low levels

Disadvantages	Large amount of solids created at remote sites in several produced water high influent concentrations Solids processing systems required Large costs for solids dewatering and land filling	Extremely high influent concentrations often found in produced water require extreme quantities and frequencies of regeneration of resins Only applicable as polishing step or for CBM waters

7.0 Dissolved Salts

Advanced treatment technologies are needed in order to remove Total Dissolved Solids (TDS) from a waste water stream. The two main processes that have been employed in the oil field to remove TDS have been Reverse Osmosis (RO) and Mechanical Vapor Recompression (MVR). Most fracturing fluids have advanced enough today to handle the high levels of TDS seen in flowback/produced water. TDS removal may be necessary is when the fluid will be reused for a beneficial purpose or for discharge back into the environment.

The level of TDS will dictate which type of treatment is needed. Typically for TDS with concentrations less than 40,000 mg/L RO will be sufficient, as levels increase to over 40,000 mg/L MVR will be necessary. The efficiency of both technologies depend on the amount of TDS that is put through the system, typically the higher the TDS the lower the efficiency of the process. Once the TDS has reached a certain level, the efficiency of an MVR is too low to justify the cost. At this point a crystallizer would be the appropriate technology.

For both processes, significant pre-treatment is necessary to ensure that the technologies work at the highest efficiency. For the RO unit, membranes can be expensive and pre-treatment of the system allows these to run for the maximum amount of years before they begin to foul. MVR systems can have issues of scaling from high concentrations of calcium and magnesium in the water. MVR vendors have started to add a pre-treatment skid that is used prior to going through the unit. This removes or inhibits the hardness ions from precipitating out. If pre-treatment is used prior to either unit, the cost for the full treatment and the waste stream of the process will increase.

Both processes will have two streams at the end, concentrated brine for disposal and a high water quality effluent as the processed water. The concentrated brine streams are typically sent to injection wells for disposal or large brine storage / natural evaporation ponds.

7.1 Reverse Osmosis

Reverse Osmosis (RO) and Nanofiltration (NF) are examples of pressure-driven membrane processes. RO and NF are proven, widely used treatment technologies for desalination of both seawater and brackish water. Nanofiltration is yet another non-chemical means of removing water hardness using spiral wound membranes in cross-flow mode similar to Reverse Osmosis but at significantly lower pressures. Nanofiltration has the advantage of excluding any divalent or multivalent ions (heavy metals) remaining in the water after preceding pre-treatment steps. Additional advantages include the removal of nitrates and sulfates. The filtration capacity ranges from about 1 nm to 10 nm allowing the filtration of most bacteria and viruses. Recovered volumes can be up to 75% with a TDS reduction up to 70%.

Pressure-driven Membrane Technologies

Pressure-driven membrane processes utilize hydraulic pressure to overcome the osmotic pressure of the feed solution and force pure water (called permeate) to diffuse through a dense, non-porous membrane. Additional treatment technologies may be employed to further concentrate the stream towards zero liquid discharge (ZLD). Solutions of higher total dissolved solids (TDS) concentrations have greater osmotic pressures, and therefore require more hydraulic pressure to produce permeate.

RO membranes can achieve high removal of almost all ions and organics. Depending on raw water quality, polymeric membranes may require pre-treatment as minimal as cartridge filtration or as complex as individual or combination of coagulation/flocculation (or air-floatation), chemical precipitation, media filtration, ion exchange, biological process, and final cartridge filtration. Because certain produced waters may contain emulsified oil, dissolved hydrocarbons, or polymers added to hydraulic fracturing water, it is challenging to use conventional polymeric membrane processes for desalination without suitable and effective pre-treatment. Polymeric membranes are very susceptible to biofouling by oil and grease and organic polymers. Furthermore, high silica, hardness and other sparingly soluble salts in produced water can cause severe membrane scaling in high-pressure membrane applications [251].

RO uses the operating pressure higher than the osmotic pressure of salt present in the water to drive pure water through the membrane, thereby rejecting the salts. It is reversal of the osmosis process where water flows from the higher concentration solution to the lower concentration solution to attain natural equilibrium [162].

In gas-liquid separation, the pressure difference across a selective membrane is with pore size of about 0.03 micrometers (small enough to prevent water from leaking out but large enough to allow CO_2 to pass through) is applied. Gas penetrates into the membrane at a rate that depends on diffusivity and solubility of molecules in order to attain the equilibrium between the gas phase and the solute gas in liquid. The pressure difference is created by either vacuum or gas sweep through the membrane [162].

Oil and gas operators exploit the clear advantages of using mobile produced water treatment units. One of the leading manufacturers of membranes focusing on produced water treatment applications has been developing high performance compact membrane (such as spiral wound membrane) modules. These membrane modules are easy to utilize in mobile systems. The spiral wound membrane offers the most efficient packing of membrane area to provide higher membrane contact area in limited space. The performance of these membranes is reduced by higher temperature; the upper limit for operating temperature is 45 to 50°C but some of the spiral wound elements it can be used up to 90°C. Higher temperature operations require more pressure differential across the membranes and so more energy is required to achieve desired separation. However, higher temperature reduces the viscosity of the solution which somewhat offsets the temperature effect. The pH of the solution is also an important factor during the membrane filtration operations. High pH RO operation effectively removes boron if the membrane can sustain high pH [162].

Higher flow rate through the membrane module can produce enough shear near the membrane to avoid accumulation of oil and fouling agents. The utilization of energy recovery devices to recycle hydraulic pressure within the RO system can substantially reduce energy costs. RO processes are also easily automated and are relatively simple to operate. Depending on the chemical composition of the RO feed water, system failure may occur with changing feed water quality. Residual management costs may be substantial. RO systems have been previously employed for various types of produced water treatment. Early pilot studies were conducted without consideration for adequate pre-treatment; subsequently the RO membranes were irreversibly damaged by foulants [162].

Later, systems with rigorous pre-treatment trains were employed with RO as a final desalination stage.

Membrane fouling and scaling is a primary concern when operating RO systems. RO frequently requires pre-treatment to remove organic foulants, and may require the addition of scale inhibitors to condition feed water prior to contact with the membranes. Constituents of primary concern for all pressure-driven membrane processes include organic acids, metal oxides, and sparingly soluble salts (e.g. $CaSO_4$, CaF_2, and $BaSO_4$).

Practical limits are imposed on the process by pump energy and component manufacturing costs associated with operating at hydraulic pressures exceeding 1,000 psig. For this reason, pressure-driven membrane processes are typically used for treatment of saline streams with TDS concentrations ranging from 500 - 40,000 mg/L; however this technology has been used to treat water with 50,000 mg/L TDS.

Table 7.1 Applications of Advanced Membrane Filtration Technologies.

Membrane Filtration	Separation Specifications	Applications/Removal
Microfiltration (MF)	> 100,000 Daltons 10 – 0.1 m	bacteria, viruses, suspended solids etc
Ultrafiltration (UF)	10,000 – 100,000 Daltons $0.05 - 5 \times 10^{-3}$ m	proteins, starch, viruses, colloid silica, organics, dyes, fats, paint solids etc
Nanofiltration (NF)	1,000 – 100,000 Daltons $5 \times 10^{-4} - 5 \times 10^{-3}$ m	starch, sugar, pesticides, herbicides, divalent ions, organics, BOD, COD, detergents etc
Reverse Osmosis (RO)	salts and lower MWCO 1×10^{-4} m - 1×10^{-5} m	metal ions, acids, sugars, aqueous salts, dyes, natural resins, monovalent salts, BOD, COD, ions etc
Gas Liquid Membrane	CO_2, H_2S	decarbonation, hydrogen sulfide removal

7.2 Mechanical Vapor Recompression

Mechanical Vapor Recompression (MVR) consists of evaporating the water, leaving non-volatile contaminants in the liquid phase. The vapors are then condensed, producing a high quality condensate (or distillate) that may contain volatile components. Water is generally heated with steam or with vapors. The heat exchanger may be internal (e.g. vertical falling film or calandria / flooded, tubular, or dimple plate) or external (tubular or plate). Liquid recirculation is generally needed in either case.

Two basic types of evaporators are in widespread use. Multiple effect evaporators consist of a number of evaporation vessels connected in series for the flow of water, which gets more concentrated in contaminants as it moves from one to the next. These vessels usually operate under a vacuum. Steam is used in the last one. The vapors produced in the last vessel are fed to the previous one in the liquid train, and so on. Each “effect” produces some condensate, the sum of which is the “distilled” water. A single effect (classic still) requires almost twice as much steam as a two effects evaporator.

The other type is a mechanical vapor recompression (MVR). The vapors generated in the vessel are compressed using a blower, which also heats them up, and fed to the vapor side of the exchanger, where they condense at a higher temperature (and pressure) than the liquid phase.
Through advances in technology, much of the energy needed to distill water can now be recovered and re-used in the distillation process as shown in Figure 7.1, while the process creates a condensed brine as a blowdown product.

The mechanical side of conventional Mechanical Vapor Recompression has made its application difficult and servicing challenging in an oilfield setting. Periodic servicing related to the removal of scale from the tower designs was time consuming, requiring special lifting equipment. Many of the drawbacks of the earlier tower design have been overcome by the redesigned units which are both modular, no longer requiring a specially constructed foundation, and are simpler to service.

The mechanical vapor technology has been successfully applied in the Barnett shale. The Barnett Shale has flowback water with TDS in the order of 15,000 - 70,000 mg/L. In order to reuse the flowback water other contaminants, such as organic materials (bacteria present in the rock formation, and fracturing chemicals), polymers (the friction reducers and cross-linked gels), residual hydrocarbons (trace oil, and volatile organic compounds such as benzene and toluene), and suspended solids need to be removed.

In the Barnett, fracturing flowback water from various wells is collected and hauled by vacuum truck to the water treatment facility. The flowback water is unloaded into an aboveground lined impoundment that acts as an oversized gravity oil water separator. The water is then processed through chemical precipitation treatment equipment before it is passed through the MVR units. The clean water is then trucked to the subsequent fracturing jobs to use instead of fresh water.

The adaptation of the modular unit to operate in Canadian winters has made this technology package usable in both the Horn River and Montney settings.

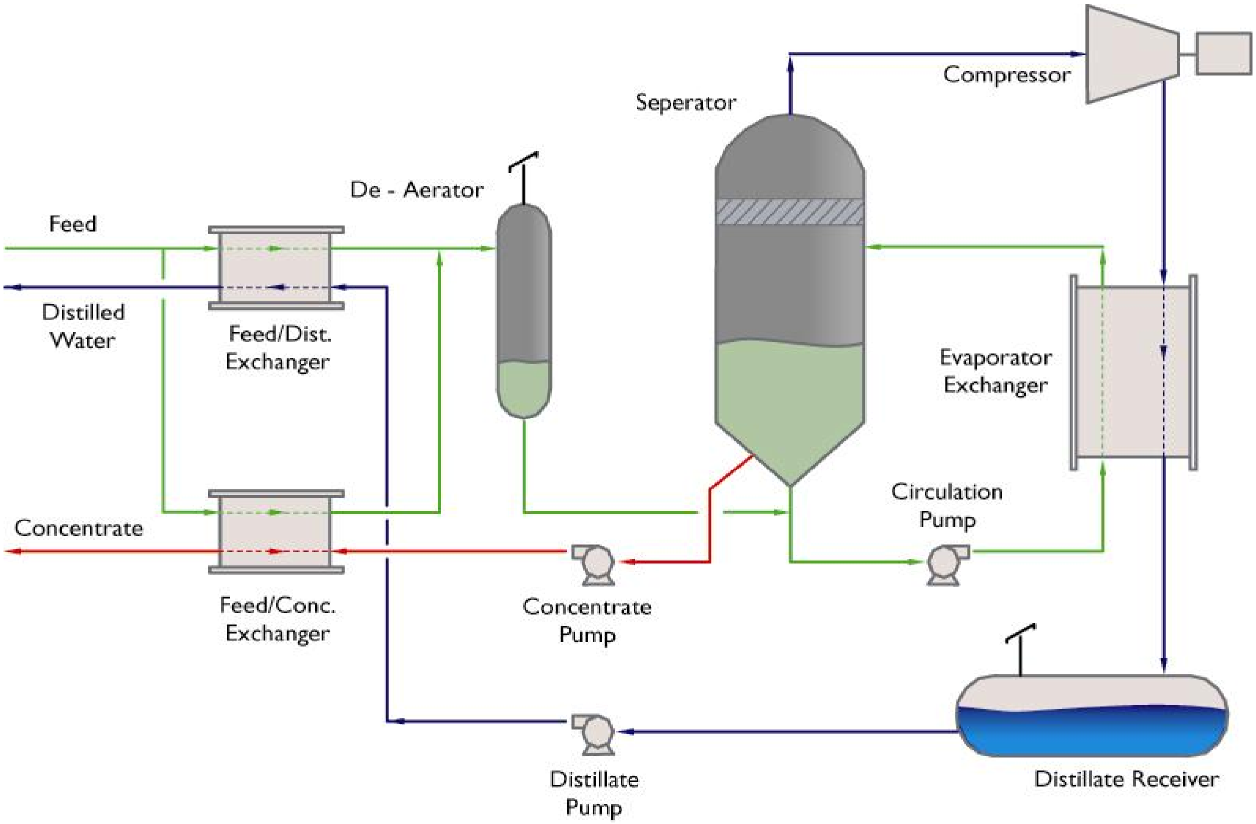

Figure 7.1 Mechanical Vapor Recompression Process Diagram.

Table 7.2 Comparison of Treatment Technologies for Dissolved Salts.

	Ion Exchange	Reverse Osmosis	MVR Evaporation / Distillation
Mobility	Mobile	Mobile	Mobile
Footprint	Small	Small – Medium	Medium
Capital Cost	Low – Medium	Medium - High	Very High
Operational Cost	Medium – High	Medium - High	Very High
Operational Complexity	Low	High	High
Consumables	Resin	Antiscalant chemicals	None
Power	None to Low	Medium – pump pressure	Very high
By-Products	Spent resin	Concentrate – 5 – 50%	Concentrate – 5 – 50% of

	Ion Exchange	Reverse Osmosis	MVR Evaporation / Distillation
		of influent stream	influent stream
Advantages	Simplicity of operation	Proven technology in desalination applications Inexpensive compared to evaporative techniques up to 40,000 mg/L TDS influent concentrations	Only technology capable of reducing TDS at influent concentrations > 50,000 mg/L removes boron
Disadvantages	Extremely high influent concentrations often found in produced water require extreme quantities and frequencies of regeneration of resins Only applicable as polishing step or for CBM waters	Poorly rejects Boron and methanol Rigorous pre-treatment required to prevent biofouling or scaling of the membrane	Extremely high energy costs Requires significant pre-treatment to prevent scaling of unit Does not remove dissolved organics

8.0 Temperature

Extreme temperatures and temperature variations in fracturing fluids can have an impact on equipment integrity and fracturing fluid performance. The optimum temperature for fracturing fluid is approximately, 15°C. The source water from the deeper aquifers (including the Debolt) can be in the range of 100 - 160°C. Inversion of slick-water polymer dispersions will occur faster at > 38°C and aid friction reduction. The suggested 15°C (60°F) lower limit was to ensure we have adequate inversion/hydration time for the friction-reducer, and minimize any potential freezing problems in suction/discharge lines. As temperatures increase toward 65°C (150°F), 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, Quality, Health, Safety & Environment (QHSE) issues also come into play, since the waters may be hot enough to scald, as the blender can potentially add 10°C to the fluids, due to high shear energy imparted. As such, special consideration must be given to the direct use of these fluids for fracturing. If cooling time is required, additional storage and cooling energy of water at these elevated temperatures. 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-fracturing storage.

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 fracturing fluids is approximately 15°C. At approximately 65°C, the temperature of the fracturing fluid becomes a safety issue, and begins to impact pumping equipment. 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 - 140°C [81].

Parameters Treated and Effectiveness

Temperature stabilizers are used to prevent degradation of polysaccharide gels at temperatures above 93°C. The common stabilizers are methanol and sodium thiosulfate ($Na_2S_2O_3$). Methanol is more hazardous to handle and is used as 5 - 10% of the fluid volume. Sodium thiosulfate is generally used at 2.5 kg/1000 L. Sodium thiosulfate is the more effective of the two, increasing the viscosity at elevated temperatures by a factor of 2 - 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 (> 93°C). Therefore, if long-term fluid stability is desired, a high pH (e.g. 9 - 11) fluid should be used.

9.0 Sludge and Residue Management

Produced water treatment technologies convert poor quality produced water into good quality water by removing contaminants and impurities. As discussed earlier, many of such treatment technologies decontaminate inlet-produced water, producing a waste stream with higher concentration of contaminants and a treated water stream. For example, membrane systems separate influent water into cleaner product water and a more concentrated stream that is called concentrate in RO, NF, and EC systems and backwash in filtration systems. Considering large scale of produced water treatment, the amount of concentrated waste volume needs to be considered when planning water treatment facilities.

The selection of concentrate disposal practice depends on several factors such as regional disposal availability (geology, geographical climate, etc.), local availability (existence of suitable disposal site, distance, compatibility, etc.), volume of concentrate stream, applicable environmental regulations, environmental impacts, public reception, cost, etc. Along with cost contributing factors such as transportation, treatment, development of disposal site, etc; environmental regulations also have major impact on the feasibility of any particular concentrate disposal method.

As a rule of thumb, undrainable tank bottoms amount to approximately 7% of the pumped volume, which will require management, regardless of the treatment approach selected for the flowback.

9.1 Fluid Disposal

Underground injection has traditionally been the primary disposal option for oil and gas produced water. In most settings, this may be the best option for shale gas produced water. This process uses salt water disposal wells to place the water thousands of feet underground in porous rock formations that are separated from treatable groundwater by multiple layers of impermeable rock thousands of feet thick. Underground injection of the produced water is not possible in every play as suitable injection zones may not be available. If such is not locally available, it may be possible to transport the produced water to a more distant injection site. In well developed urban plays such as the Barnett Shale around the City of Fort Worth, pipelines have been constructed to transport produced water to injection well disposal sites. This minimizes trucking the water and the resultant traffic, exhaust emissions, and wear on local roads [37].

Operators should prepare for proper management and disposal of fluids associated with hydraulic fracturing operations. Considerations for fluid management should include flow back water disposition, including the planned transport off the well pad (truck or piping), and information about any proposed piping; planned disposition (e.g. treatment facility, disposal well, reuse, centralized surface impoundment or centralized tank facility); identification and permit numbers for any proposed treatment facility or disposal well, and the location and construction and operational information for any proposed centralized flow back water surface impoundment.

9.2 Disposal of Residuals

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

Waste products are specific to each technology; for example desalinization can result in a residue consisting of 20% of the input stream or a residue made up of 1% of the input. The 1% residue will be more concentrated brine than the 20% residue, however, both may no longer be classified as oil and gas wastes. Produced water can usually be disposed of by way of an exemption from standard industrial waste regulations. The oil and gas exemption means that produced water can be sent to deep disposal wells that inject the water back into deep, salt water bearing reservoirs with minimal regulatory requirements and cost. Industrial brines are subject to increased regulatory compliance costs.

Applications might include specific oil and gas operations as well as general producing situations. Applications include the treatment objective and the desired beneficial use or disposal route being employed. Geological and hydrologic settings for common oil and gas fields are also part of the description of certain applications.

9.3 Solids Disposal

Naturally Occurring Radioactive Materials (NORMs)

The occurrence of NORM in the oil and gas sector is widely recognized. Wastes associated with NORM 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 NORM should be considered as part of the Integrated Water Management Plan, and the likelihood of generation of NORM in scale should be considered as part of the evaluation of scaling tendencies conducted as part of the fracturing fluid design. Since the occurrence of NORM in oil and gas production is not unique to shale gas, it is not considered further in this study beyond this section.

In oil and gas production, NORM originating in geological oil and gas formations is usually brought to the surface in produced water. As the water approaches the surface, temperature changes cause radioactive elements to precipitate. Resulting scales and sludge may collect in water separation systems. Radium is usually found in this type of NORM [52].

Issues

In everyday operations, NORMs do not cause a problem. The principal concern for NORMs in the oil and gas industry is that, over time, it can become concentrated in field production equipment and as sludge or sediment inside tanks and process vessels that have an extended history of contact with formation water. Studies have shown that exposure risks for workers and the public are low for conventional oil and gas operations [37].

Management

NORMs have been recognized as an issue by the oil and gas sector since the 1930s, and regulations and guidelines that are protective of human health and the environment have been in place in Canada and the United States for several decades. The potential risks from oilfield NORM to humans can be effectively managed to ensure their safety and health with appropriate work practices such as proper detection and measurement.

The Canadian Guidelines for the Management of Naturally Occurring Radioactive Materials (NORM) published by Health Canada (www.hc-sc.gc.ca) outlines radiation protection requirements for incidentally exposed workers.

Currently, there are no regulations for NORM management in Canada, however, the ERCB provides guidelines outlining NORM waste disposal options in Directive 058: Oilfield Waste Management Requirements for the Upstream Petroleum Industry.

The largest-volume oil and gas waste stream that contains NORMs 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 [172].

Treatment

NORMs such as radium get mobilized from the oil or gas formations because of the solubility in the presence of chloride ions that are present in the water within formation. The solubility of radionuclide is very low in sulfate species. The low solubility precipitates scale containing high concentrations of radium in the form of barium sulfate or barite under the effects of varying temperature and pressure during the production operations. The handling and treatment of the precipitated sulfate deposits containing decaying radioactive materials is absolute necessity because of the dangers of radioactivity.

MI SWACO
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Appendix C
Hydraulic Fracturing Fluids & Flowback

Fracturing Fluid
Flowback Reuse Project

Prepared by M-I SWACO, a Schlumberger Company
for Petroleum Technology Alliance of Canada
and the Science and Community Environmental Knowledge (SCEK)
Fund

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1.0 Fracturing Fluid Additives

Water-based fluids are the most widely used fracturing fluids because of their low cost, high performance, and ease of handling. It is relatively simple to dissolve many additives in water. The selection of hydraulic fracturing additives is driven by many factors, including the formation chemistry and the available water sources. Figure 1.1 shows a typical recipe for additives. This section describes these additives in greater detail.

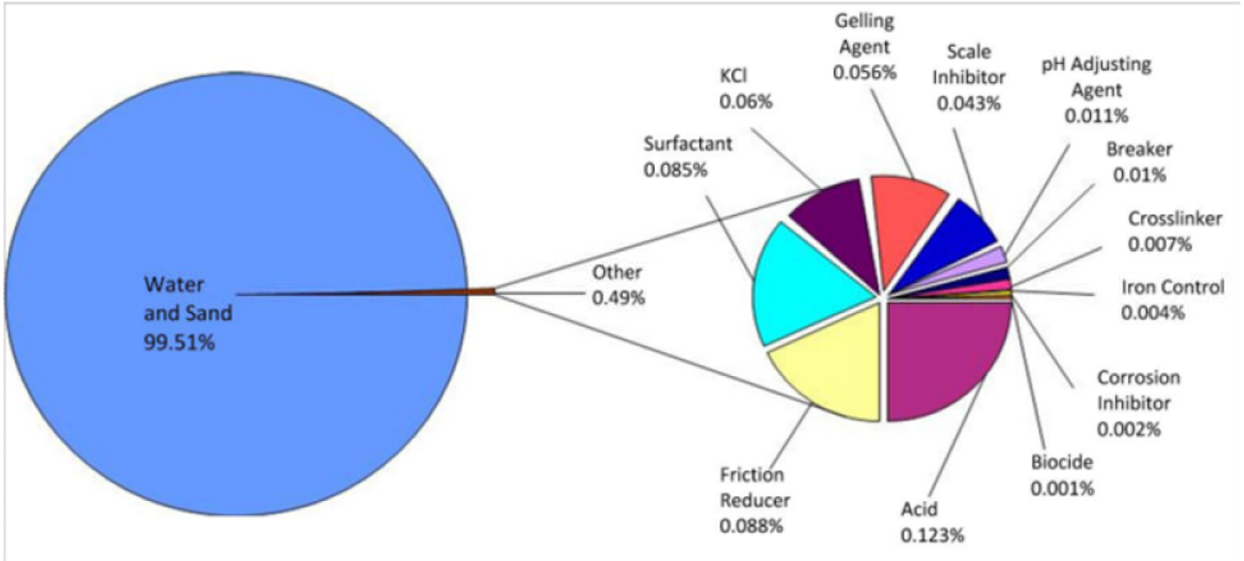

Figure 1.1 Fracturing Materials and Additives [37].

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 specific fracturing fluid characteristics at different phases of the operation.

A number of chemical additives are used in the fracturing techniques common in the stimulation of unconventional reservoirs.

These additives include acids, surfactants, biocides, bactericides, pH stabilizers, gel breakers, clay and iron inhibitors, and corrosion and scale inhibitors. Along with the characteristics of water in the formation being fractured, they can often dictate the water management and disposal options that will be technically feasible.

The optimal composition of the fracturing fluid may vary from one geologic basin/formation to another, but the range of additive types available remains the same. Each additive type has several different products; but typically only one product is used for an individual gas well. Product selection is based on formation and interaction between additives. Additionally, not every fracturing job requires the use of every type of additive.

Following the proppant, the major additive in most jobs will be a friction reducer, which is needed to reduce the friction pressure while pumping at the extreme rates of 8 – 19 m^3/minute. The next concern is additives to treat bacteriological activity. The injection of water results in the cultivation of sulfate-reducing bacteria (SRB), which, if not treated properly, produce hydrogen sulfide (H_2S) and by-products such as black iron sulfide. As water dissolves salts from the formation, scale inhibitors become vitally important. Finally, the use of surfactants can be beneficial in promoting the flowback of injected fluids to restore the fracture’s relative permeability to gas [11].

Permeable and productive fractures can be induced and maintained with a variety of oil- and water-based fluids. The fluids comprise a range of components: from simple water and sand to complex polymeric substances with a multitude of additives. As the US EPA finds, “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 by the EPA 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” at reduced cost [6].

1.1 Acid

Acidizing involves pumping acid (usually hydrochloric acid), into the formation. The acid dissolves the rock material so that the rock pores open and hydraulic fracturing fluid flows more quickly. The acid helps dissolve minerals and initiate cracks in the rock.

1.2 Proppant

Proppants are small particles that are carried by the fracturing fluid down into the formation. They are deposited into the cracks created by the fracture process. Optimally, the fluid that deposited the proppant will all flow back to the surface, while the proppant remains to hold the cracks open so that the gas can flow to the surface.

There are several factors to keep in mind when deciding on proppant placement in a fracturing job: specific gravity of the fluid and proppant, flow rate of the slurry, and fluid viscosity.

Proppant Transport

Viscosity and flow rate affect the ability of the fluid to keep the proppant in suspension. The preferred fluid for most fracture treatments has been slickwater with low concentrations of proppant, that usually use 20/40 or finer sand.

The bulk of proppants that do not settle in the fractures created by the fracturing job are removed during the post-fracturing flush. These tend to settle in the tank on the surface, with lesser amounts entrained in the friction reducer that is carried back to the surface with the flowback. Commonly, aggressive flowback procedures may result in erosion of the fracturing sand from the near-wellbore formation.

1.3 Gelling Agents

Due to its low viscosity, water is not always suitable for fracturing certain formations because of its limited ability to transport proppant. To overcome this, industry developed linear and crosslinked fluids, which contain water gellants or thickeners and thus have a higher viscosity.

The following formation characteristics are considered when selecting gelling agents:

- Pressure.
- Temperature.
- Permeability.
- Porosity.
- Zone thickness.

A substantial number of fracturing treatments use thickened, water-base linear gels. Typical gelling agents used in fracturing fluids are guar gum, guar derivatives such as hydroxypropyl guar (HPG) and carboxymethyl hydroxypropyl guar (CMHPG), or cellulose derivatives such as carboxymethyl guar or hydroxyethylcellulose (HEC). Generally 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. Compared to starch, it has up to eight times the thickening power [6].

Water-soluble polymers composed of guar or guar derivatives are used in most fracturing systems. Other additives are used to optimize the fluid characteristics of the application, and also to degrade the water-soluble polymer in order to make it easier to recover from the well prior to production.

Guar gums are preferred thickeners in enhanced oil recovery, and guar gum and its derivatives are used in most of the gelled fracturing fluids. One of the benefits of guar gum is that it is more water-soluble than others. Another benefit is that it is a better emulsifier because it has more galactose branch points. Guar gum is strongly shear shinning, has high low-shear viscosity and is not affected by ionic strength or pH, but it does degrade at low pH, even at moderate temperatures (pH 3, 50°C).

Guar derivatives, however, demonstrate stability at high temperatures and pH levels. Guar use creates exceptionally high viscosity, which improves the ability of the fracturing liquid to transport proppant. Guar hydrates fairly rapidly in cold water, creating highly viscous pseudoplastic solutions, which generally have greater low-shear viscosity than other hydrocolloids. The colloidal solids present in guar make fluids more efficient because they create less filter cake.

Hydroxypropyl Guar (HPG)

Guar gum is derived from the endosperm, or seed, of guar beans. The process used to produce guar powder does not completely separate the guar gum 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 causes slight changes to its properties. These properties include increased solubility in water-alcohol mixtures, decreased hydrogen bonding, and improved electrolyte compatibility. These changes allow the product to be used in a variety of fields, such as textile printing, explosives, and oil-water fracturing applications.

Guar can be derivatized with propylene oxide to produce hydroxypropyl guar (HPG), which is more stable than guar at high temperatures, and is thus better suited for use in high-temperature (> 150°C) wells. Additional processing and washing removes much of the plant material from the polymer, so HPG typically contains only about 2 - 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. Hydroxypropyl guar substitution makes HPG more stable than guar at elevated temperatures; therefore, HPG is better suited for use in high-temperature wells. The addition of less-hydrophilic hydroxypropyl substituents also makes HPG more soluble in alcohol.

1.4 Crosslinker

Crosslinking agents enable the individual polymeric molecules to form a complex network of entangled polymer with the associated water molecules. 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 combined with guar and HPG to produce viscous gels that can be stable above 150°C. At a pH above 8, borate ions and guar form a 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 - 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 boric acid (H_3BO_3) concentration can cause over-crosslinking of the gel.

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 and heat are removed. Typically, borate crosslinking is reversible; crosslinks form, break, and reform. If the polymer is not thermally degraded, this reversible behavior continues to accommodate changes in shear rate or temperature.

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 and monitored during onsite preparation. To obtain the best possible performance from a crosslinked fluid, the following issues must be addressed.

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 viscosity development will be lower than anticipated. If too much crosslinker is used, the crosslinking rate will be faster than anticipated and the final viscosity may be much lower because of syneresis. Syneresis 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 syneresis in delayed crosslinked fluids usually requires heating the fluid to the anticipated downhole temperature to fully react all the crosslinker.

Crosslinkers and 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 the pH variation in crosslinked fluid, buffers are included. 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; the levels must be monitored diligently.

Crosslinkers and Chemical Contamination

A variety of common compounds and oilfield products can interfere with the performance of crosslinker compounds. Typically, these contaminants reduce or eliminate crosslinking, producing a fluid with a slow rate of viscosity development (i.e., long crosslink time) and significantly lower viscosity. In the most obvious cases, the crosslinker may produce no viscosity increase at all. Naturally occurring compounds that can be present in mix water include bicarbonate, phosphate and silicates. In addition, many surfactants, clay stabilizers and foaming agents can interfere with crosslinked fluid performance as well. 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).

1.5 Friction Reducers

To optimize the fracturing process, fluids must be injected at maximum pressures and pumped at maximum rates; however, increasing flow velocity and pressure in this manner can lead to undesirable levels of friction in the injection well and in the fracture itself. To minimize friction, friction reducers are added to water-base fracturing fluids. The friction reducers are typically latex polymers or copolymers of acrylamides. They are added to slick water treatments (water with solvent) at concentrations of 0.03 - 0.25 kg per m^3. Some examples of friction reducers are oil-soluble anionic liquid, cationic polyacrylate liquid, and cationic friction reducer [6].

Friction Reducers for Water

Polymers are high-molecular-weight molecules that have an affinity for water molecules. They deter turbulence by controlling migration of the individual water molecules. Low concentrations (1 - 2 kg/1000 L) of guar or HPG polymers and copolymers of polyacrylamide are the most efficient friction reducers for water.

In water, the pH affects the polymer hydration rate. If the pH is low, hydration may be rapid, resulting in lumping of the gel. If the water pH is too high, the gel hydrates too slowly. Water temperature also affects the hydration rate - the higher the water temperature, the faster the polymer hydration (viscosity development). To determine the optimal water temperature and pH, a sample of polymer from location should be used to prepare a linear (pre-crosslink) gel with the water from the fracture tanks. Careful testing should ensure that proper dispersion (no lumps) and hydration (viscosity development) are obtained on location.

With the success of slickwater fracturing operations, friction reducers have grown in popularity. Friction pressure is reduced with the addition of friction reducers which allows higher pumping pressures from the same number of trucks. Common friction reducers are polyacrylamide-based and have a typical loading range of 0.25 - 1.0 L of friction reducer per 1000 L of water.

There are three types of polyacrylamide friction reducers:

- Anionic.
- Cationic.

- Nonionic.

They are thermally stable up to about 200°C, and readily decompose after 300°C. Chemical and thermal degradation of the polymer lowers its effectiveness.

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. This will ensure the selection of the most cost-effective and efficient product.

The practice in the field today is “rule of thumb” adjustment of the friction reducer, a process that can be highly inefficient. Approaching the problem more scientifically can produce significant cost savings. It is clear from the data that adding more than about 0.5 gram per tonne (g/t) of currently available commercial materials yields little increase in friction reduction. Indeed, higher concentrations may increase interactions between the different additives that reduce their effectiveness.

As shown earlier, some friction reducers are more salt-tolerant than others, and the operator must ensure that the correct type of product is used. If the wrong friction reducer is used, a higher concentration is required to achieve the same effect. This can cause formation damage, or require the use of greater quantities of breaker, resulting in higher costs [11].

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 cause minimal damage to the formation [12].

There are several kinds of polyacrylamides - anionic, cationic and nonionic - used under different conditions. These can be used in a variety of water types, from fresh water to produced brines.

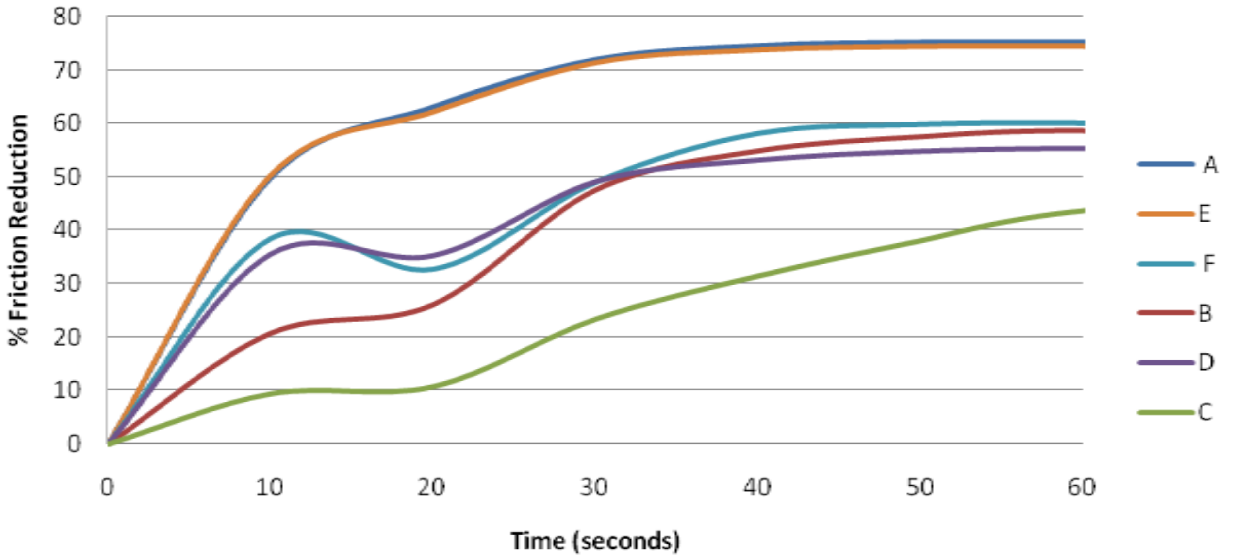

Figure 1.2 Comparison of commercially available friction reducers 60 seconds after injection into the flow loop [11].

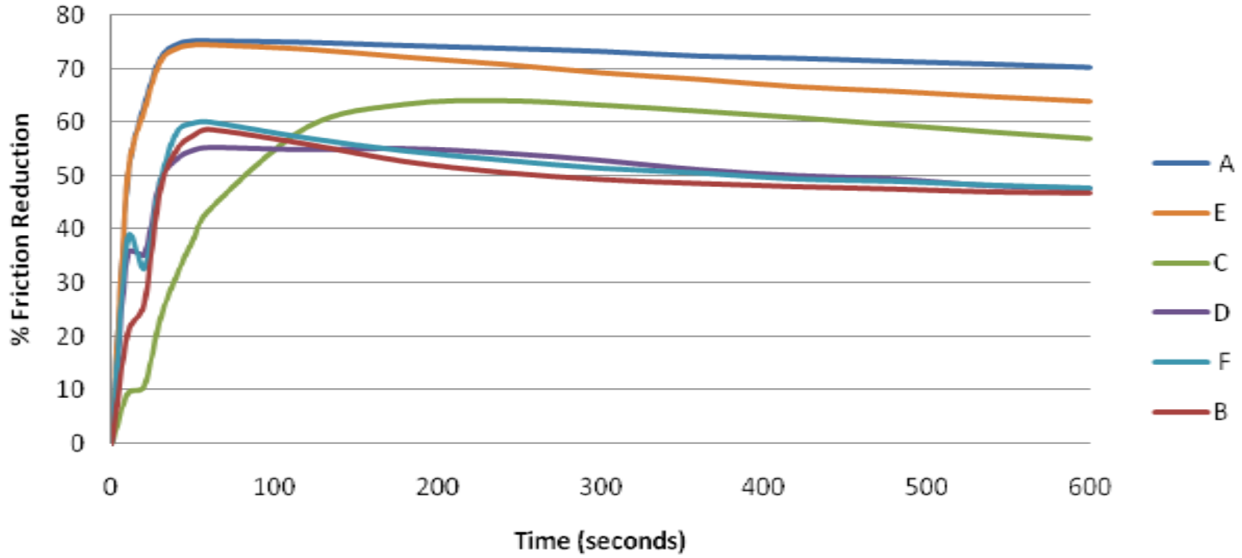

Figure 1.3 Comparison of commercially available friction reducers 10 minutes after injection into the flow loop [11].

Care must be taken when selecting a friction reducer since different polymers hydrate at different rates. Figures 1.2 and 1.3 illustrate the variations in commercially available friction reducers. Six products were supplied by a major operating company for independent evaluations in a friction test loop with 15 meters of tubing.

At 20 seconds, the tested polymers hydrated at different rates; the difference in friction reduction between the lowest and highest values was roughly 50%. At 20 seconds, the polymer has made two complete passes through the loop. At ten minutes (600 seconds), or 60 passes through a progressive cavity pump, the difference between the lowest and highest values is roughly 20% [11].

Some friction reducers can cause formation damage. Such damage may require a breaker, the use of which is sometimes delayed to allow the friction to be reduced in the tubing where it is most effective. Once past the perforations, the breaker will break up polymer build-up to reduce damage and encourage polymer flowback. Carman et al tested oxidative breakers on a fresh-water and brine-based polyacrylamide friction reducer used in slickwater fracture treatments. All breakers tested worked at 80°C to some extent [6].

The results, generated using a technique called Molecular Weight Cut Off, showed that persulfate breakers worked best at 80°C, and were effective at 40°C at concentrations of 5 - 10 parts per thousand (ppt) of water. Flow loop data showed no degradation of polymer at a persulfate concentration of 1 g/t up to 40°C, nor did the breaker have a detrimental effect on polymer hydration [11].

Anionic Friction Reducers

In balancing 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 therefore have a high molecular weight. Polyacrylamide 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 lowers their drag reduction. This is why anionic polyacrylamides give greater friction 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 fresh water [8].

Cationic Friction Reducers

Typically, oilfield cationic friction reducers are used in acidizing or with heavy brines. These polymers can work well in fracturing treatments and are compatible with cationic biocides; however, they cost far more than the more common anionic friction reducers. Another option is polysaccharides, which are also compatible with cationic biocides, but achieving the same drag reduction as an anionic polyacrylamide friction reducer would require 10 times as much polysaccharide. Therefore, the use of these alternative materials becomes an economic issue.

Care must be taken to ensure enough friction reducer is used. The amount required depends on whether the cations are monovalent or divalent, on the salt concentration in the water, and on whether the water is fresh or produced [11].

Fluids such as water and low-viscosity oil achieve turbulence when pumped through small tubulars at high rates, creating high-friction pressure. Adding polymers (friction reducers) to the turbulent fluid can produce dramatic decreases in friction pressure.

High turbulence must be a factor before friction reducers are effective.

Friction reducers offer no advantage unless the fluid is in turbulent flow. An already viscosified water or oil-based fracturing fluid will not benefit from the addition of friction reducers. Similarly, when a viscous oil is pumped through casing or large-diameter tubing at a low rate, adding friction reducers has little effect.

Salt Sensitivity

As the theories predict, anionic polyacrylamide friction reducers are affected by salts in the treatment water. This is a serious problem, as the industry is using more and more produced water in fracturing treatments. It is also worth noting that there is little improvement in drag reduction once the polymer concentration exceeds 0.5 g/t. Adding more polymer does not improve the result.

Slickwater pumped at high rates with low sand concentration has been effective at treating shale gas formations. One type of liquid-polymer emulsion has proven to be an ideal slickwater additive: a salt-tolerant friction reducer (STFR) designed especially for compatibility with the specific shale lithology. This product can be used with brine liquids at NaCl concentrations of 2 - 12%. Salt tolerance allows fracturing fluid with high salt concentration to be reused repeatedly provided that other geochemical properties are controlled [14].

Temperature Sensitivity

Polyacrylamides have good thermal stability up to 200°C; however, they do begin to break down between 200°C and 300°C at the amide group. Above 300°C, decomposition of the main chain and other bonds will occur.

Friction Reducers for Oil

Friction reducers for oil include acrylonitrile copolymers, as well as aluminum phosphate ester gelling agents used in low concentrations with an activator. An oil-friction reducing agent can reduce friction by up to 55% in crude oil, and as much as 70% in refined oil. The oil's viscosity is unaffected by friction reducers.

Summary

The friction loop used to collect the data depicted in Figures 1.2 and 1.3 is an invaluable tool for comparing friction-reducer effectiveness in fracture waters of varying composition. Figures 1.4 and 1.5 below show that the performance of a friction reducer can vary widely based on the contents of the base fluid.

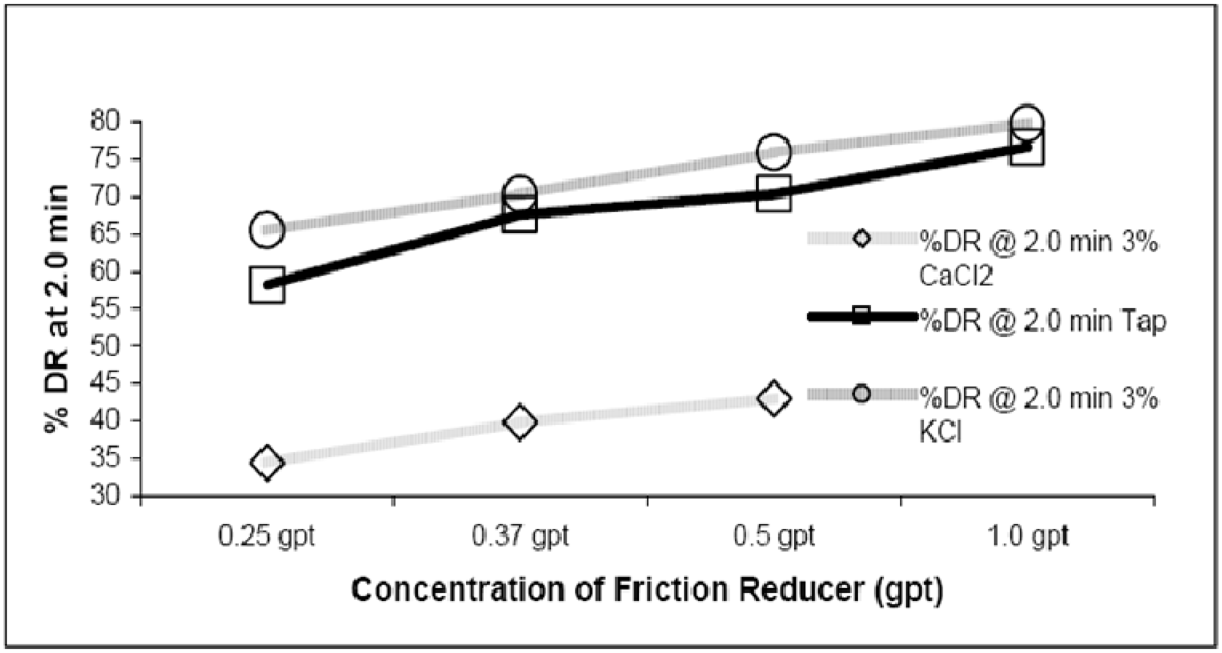

Figure 1.4 Effect of Ions on Friction Reducer Performance [8].

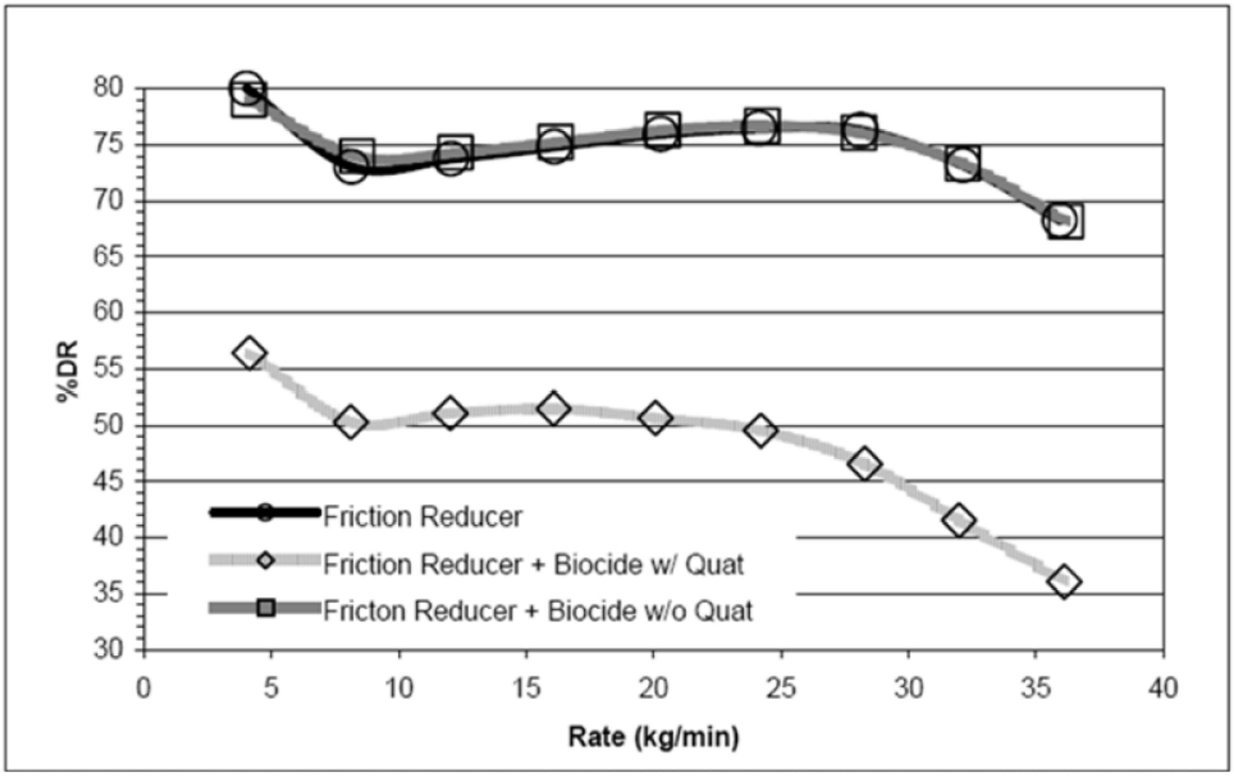

Figure 1.5 Effect of Incompatible Additives on Friction Reduction [8].

As freshwater scarcity increases and government agencies tighten regulations concerning water use and disposal, a growing number of shale-gas wells will be stimulated with produced water. This will escalate the importance of developing more robust and versatile friction reducers, as well as 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, and with the base fluid, to ensure that they will function as expected [15].

1.6 Breakers

Breaker fluids are used to degrade the viscosity of the fracturing fluid, which helps enhance post-fracturing fluid recovery, or flowback. Breakers can be mixed with the fracturing fluid during pumping, or introduced later as an independent fluid. There is a variety of breaker types, including time-release and temperature-dependent varieties. Most breakers are typically acids, oxidizers or enzymes [6].

Thermal breaking of the polymer backbone generally occurs in wells with bottomhole temperatures higher than 107°C, so a breaker should be added when the bottomhole temperature is lower than that. Breakers are added for two reasons:

- Reduce the fluid viscosity so that the fracturing fluid can be cleaned up quickly following a treatment.
- 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 molecular weight of the polymer decreases.

Enzyme breakers and oxidative breakers are both used in water-base fluids. Enzyme breakers such as hemicellulase 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. At temperatures lower than 50°C thermal decomposition is slow, but these breakers can be used at 16°C - 52°C if an amine is concurrently added to catalyze the reaction. Oxidative breakers are effective over a wide pH range (3 - 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.

Performance at High Temperature

Oxidizers are considered superior for high-temperature applications. Current enzymes are active up to 110°C, but higher-temperature versions will most likely be identified in the future.

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 lifespan of the enzyme. Under ideal conditions (less than 80°C, pH 5 - 8) enzymes break the polymer into smaller fragments than oxidizers do, but there is no information in the literature to document that this process produces significant amounts of simple sugars.

Length of Breaking Process

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

Fast Break

A fast break, which allows quick turnaround of the well, is accomplished much better with oxidizers.

Chemical Sensitivity

Enzymes are highly sensitive to pH changes. The presence of curable-resin-coated proppants will not affect the performance of enzymes, but will affect oxidizer performance.

pH-Adjusting Agents

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 when extra acid or base is introduced (for example, through contaminated water or proppant).

pH is critical, for example, in the following fracturing fluid additive functions:

- Enzyme breakers. The optimum pH range for enzyme breakers is 3.5 - 5.0. Enzyme breakers are deactivated when the fluid pH value is greater than 9.0.
- Crosslinking rate and polymer stability. Crosslinked fluids are generally formulated to work best in a narrow pH range (±0.25 units from the optimum); guar and hydroxypropyl guar can be crosslinked at a pH range of 3 - 10, depending on the type of crosslinker used.
- Hydration of the polymer. Guar and hydroxypropyl guar are treated to be dispersible and non-hydrating 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 use of acid as a fracturing breakdown aid has been demonstrated in most shales, even when there was little or no acid reactivity in the formation. It is common practice to use acid in areas where there is calcite cementation or fill in the fractures, but if excessive amounts of calcite cement and acid are used, plugging problems can result.

(It is a commonly-known rock-mechanics fact that wet rock is weaker than dry rock, so injecting any aqueous fluid into a rock, but especially an acid (e.g. 10 - 15% HCl) can lower its strength and promote fracturing. Although most shales have at least moderate water saturation, adding water, regardless of salt content, seems to reduce rock strength.) HCl is commonly used as a breakdown tool because it is inexpensive, effective and works gradually on acid-soluble material. However, acid may not be needed in all cases.

The leading edge of an otherwise effective mutual solvent and acid system can be contaminated with debris cleaned off the walls of the tanks and tubing. For this reason, the leading edge of the acid job is usually circulated out of the well using a process called pickling the tubing. In this treatment, acid and solvents are injected into the tubing to dissolve and disperse iron, pipe dope, mud and other debris, and are then circulated or reversed out of the well without being injected into formation. This technique is effective when the tubing has not been cleaned or its condition is unknown.

Volumes of both acids and additive treatments range from one to two tubing volumes depending on the condition of the tubular. 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.

In general, most flowback and produced waters have pH values between 6 and 8. Produced waters, either stored or handled, will have pH values remain neutral unless caustics or acids are added for 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 (precrosslink) 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.

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

1.7 Surfactant

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 an appropriate molecule.

A surfactant is a material that at low concentration adsorbs at the interface between two immiscible substances. These immiscible substances may be two liquids, such as oil and water, a liquid and a gas, or a liquid and a solid. They can help promote the flowback of injected fluids to restore the relative permeability of the fracture gas. Some bactericides and clay control agents are surfactants.

Common surfactants are adsorbed rapidly onto a shale matrix. The formulation of the surfactants into a microemulsion allows the surfactant to travel further into the matrix and to remain with the leading edge of the penetrating fluid. The addition of microemulsions to fracture treatments has resulted in a 50 - 100% increase in load recovery and gas production [11].

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 in 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 treatment process.

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 but linked by a strong covalent chemical bond. The molecules are classified into four groups according to the ionic charge carried by the water-soluble group:

- Anionic.
- Cationic.
- Nonionic.
- Amphoteric.

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. Examples of anionic surfactants include:

- Sulfates.
- Sulfonates.
- Phosphates.
- Phosphonates.

Of these, the most common are sulfates and sulfonates. Anionic surfactants are sensitive to the multivalent ions Ca^{2+} and Mg^{2+}. These ions 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 non-emulsifying 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 consists of long-chain primary, secondary and tertiary amines, which are soluble only in acidic solutions, where they ionize to form a long chained cation and simple anion salt.

The second category is quaternary ammonium compounds. These ionize to form long-chained cations with a wide range of solution pH. Cationic surfactants exhibit 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. When cationic and anionic surfactants are mixed they tend to precipitate in aqueous solutions and are generally considered incompatible.

Nonionic Surfactants

Nonionic surfactants have no charge at all in the hydrophilic group and a long-chain organic for the lipophylic 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.

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 hydrophilic group is usually a polyhydric alcohol or an alkyd oxide polymer. These surfactants are used as non-emulsifiers and foaming agents.

Amphoteric Surfactants

Amphoteric 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. Amphoteric surfactants are usually either amine sulphonates or amine phosphates.

Temperature Stabilizers

Stabilizers are used to prevent the degradation of water-base fracturing fluids at temperatures greater than 100°C. The temperature stability of a fracturing fluid is dependent on the following:

- **Stability of the Polymer:** for example, guar is less stable than hydroxypropyl guar. It is desirable for injected polymers to remain in their functional state for as long as possible, while still being biodegradable and harmless when the operation finishes.
- **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, though there are circumstances, as described elsewhere, that require more acidic conditions.

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 [6].

Fluid-loss additives of the past and present include:

- **Bridging Materials** such as 100 mesh sand, 100 mesh soluble resin, silica flour.
- **Plastering Materials** such as starch blends, talc silica flour, and clay [6].

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 the fracture. More flowback means less new water needed, which is environmentally and financially efficient.

2.0 Hydraulic Fracturing Fluids and Flowback

2.1 General Considerations for Fracturing Fluid Selection

The design engineer must identify the most appropriate fluid for any set of conditions. Reservoirs vary significantly in **temperature, permeability, rock composition,** and **pore pressure.**

The fracturing fluid used in any operation significantly impacts treatment effectiveness and cost. The main fracturing fluid categories are aqueous, oil, and foam. All have appropriate uses, but aqueous fluids are preferred for oil and gas fracturing operations due to low cost, high performance, high suspending power, environmental acceptability, and handling ease.

Several broad principles are critical in choosing a fracturing fluid. The fluid must:

- Open and propagate a fracture efficiently.
- Transport a proppant (usually sand) throughout the fracture’s length.
- Leave most proppant in the fracture while flowing as much fluid as possible back out.
- Minimize polymer-induced proppant-pack damage.
- Minimize pumping and treatment pressure requirements by reducing frictional pressure drop.
- Provide good fluid-loss control.
- Clean up rapidly after pumping.
- Be cost effective in use.

Beyond these broad principles are other important issues to address:

- Minimizing fracture-face damage from unavoidable leakoff.
- Ensuring compatibility between the fracturing fluid, the reservoir fluids, and the formation.
- Meeting expectations about post-treatment cleanup and environmental concerns.

Balancing considerations when choosing a fracturing fluid:

- Foam fluids have superior cleanup properties.
- Very high proppant concentrations can exceed mixing and blending equipment capabilities, and be more difficult to clean up.
- Foam fluids are added to the fracturing fluid's liquid portion, making their use impractical when super-high proppant concentrations are required.
- Foam fluids may be more appropriate in very tight formations where fracture conductivity is less important.

Fluid Viscosity and Rheology

It should be possible to pump a fracturing fluid with a viscosity of 100 ± 25 cp at a shear rate of 170 s^{-1}. At these values, the fluid will suspend almost all of the propping agents. **To meet this design requirement, reservoir temperatures must be known:** the pad fluid and half of the slurry will be exposed to the bottom hole static temperature (BHST).

Fracturing fluid viscosity decreases with:

- Increasing temperature.
- Time exposed to critically high temperatures.

Example:

For reservoir temperatures above 150°C, increase the polymer concentration in the pad fluid and early treating fluid to compensate for lower viscosity at high temperature levels. As treatment proceeds, shorter bottom hole static temperature (BHST) exposures permit polymer concentrations to be reduced.

Fluid viscosity at the fracture entrance must not create a blockage (or "proppant bridge"). To admit the proppant effectively, the fracture must have some minimum width. The minimum width is a function of proppant size, proppant concentration, and volume injected.

A bridge at the wellbore has serious consequences. A large near-well-bore restriction requires a more viscous fluid to create adequate width and force fluids into the fracture. Fracture width is a function of the fracturing fluid viscosity and the Young modulus. In soft formations, characterized by low Young modulus ($< 1 \times 10^6$ psi), the viscosity level required to suspend the proppant typically avoids proppant bridging. Formations with high Young Modulus ($> 5 \times 10^6$ psi) may need a high viscosity fluid to create adequate fracture width and avoid any wellbore restriction. Tortuosity and/or parallel fractures near the wellbore cause additional pressure drops. Very viscous fracturing fluids can compensate if needed.

Accurate rheological analysis is a key to treatment success.

Calculate frictional losses to improve the accuracy of surface treating pressure and injection rate predictions.

Assess turbulence levels, which change as fracturing fluid moves through the formation. Flow is typically turbulent in the well bore and perforations; laminar in the fracture.

The rheological properties of both clean and proppant-laden fluid impact fracture geometry and extension during treatment. Consider laminar flow behavior within the fracture in the proppant transport and fracture geometry designs.

Fluid Frictional Pressure

The surface pressure during a fracturing treatment depends on the:

- Fracture gradient.
- Net pressure.
- Hydrostatic pressure of the fracturing fluid.

- Friction pressure in the tubulars of the fracturing fluid.
- Perforations.
- Near-wellbore friction.

Hydrostatic pressure and friction in the tubulars are important fluid selection parameters. Fluid friction pressure in tubulars, through the perforations, and along the fracture all influence fluid viscosity:

- Hydrostatic pressure is a function of fluid density.
- On deep wells, ensure that the fluid density will maintain a low treating pressure at ground level.
- The polymer used, and its concentration, control a fluid's viscosity (and thus its frictional pressure).
- Polymer concentrations must be engineered to reach adequate, but not excessive, levels.
- Do not ignore frictional pressures that you assume will remain low (e.g., through the perforations and along the fracture). Polymer concentrations can rise, causing a significant fluid friction increase at low flow rates in small diameter openings.
- Lower density fluid flows back more rapidly at low reservoir pressure. This can be a good reason for choosing foamed or energized systems or, in some cases, gelled oil.
- Reducing the pressure at ground level provides cost advantages and minimizes fracturing equipment wear.

- Foam fluids, with less hydrostatic head, cause higher ground level pressures than aqueous fluids.
- Oil-base fluids have lower density than water-base fluids.
- When friction pressure in the tubulars is high, surface pressure must increase to achieve the same fracture gradient (or bottom hole pressure).

Fracturing Fluid Compatibility with Reservoir Fluid and Rock

Always consider aqueous fluids first. They are cost effective, safe to use, and offer the widest additive range. Many operators choose a fracturing fluid base according to the water sensitivity of the reservoir rock. This can lead to inappropriate fluid selections and sub-optimal results.

Several studies contradict the common belief that oil base fluids are inherently more compatible with oil reservoir fluids, and make rock damage less likely. They show that fluid leakoff and permeability-induced damage rarely cause severe problems. Fracture conductivity considerations should always take precedence over the possibility of fracture face damage.

- Oil-base fluids generally cost more than aqueous fluids due to the cost of the oil.
- Oil-base fluids need extra hydraulic horsepower to compensate for frictional pressure losses.
- Flammable oils pose extra safety concerns, including an extreme fire hazard risk from fluid leakage.

The literature largely agrees that clay swelling and clay particle migration (separately or in combination) lead to water sensitivity, depending on rock composition. Sandstone is especially sensitive; its permeability decreases rapidly and significantly on contact with water contact.

While clay dispersion may impact unfractured wells strongly, its impact on fractured wells, under normal conditions, is slight:

- A rock’s surface contact area is directly related to its fracture face damage tolerance.
- As its surface contact increases, a rock will tolerate additional fracture face damage with little impact on the productivity of a well.
- A very small fracture can increase the surface contact area in a wellbore more than 300 times.
- Given adequate fracture conductivity, studies show that shallow damaged zones around a fracture do not materially affect well production (Analytical and reservoir simulations, explained later in cleanup section).
- Migrating clay particles can bridge across pore throats near the fracture face region; fluid flows through the formation, changing salinity levels can alter a clays volume.
- The most common migratory clay is kaolinite; the most common swelling clay is smectite.

- Traditionally, clay swelling and migration have been controlled by using aqueous fluids containing salts. The most common salts used today are potassium chloride, amine, and polymeric amine compounds.

Fluid Leakoff

It is impossible to demonstrate 100% fracturing fluid recovery or to differentiate flowback fluids from natural formation water.

Some fracturing fluid may flow from the created fractures to other areas within the gas-containing formation during the fracturing process. This “fluid leakoff” may flow into micro- or macro-pore spaces within the formation, existing natural fractures in the formation, or small fractures opened into the formation by pressure in the induced fracture.

The fluid leakoff rate is a critical component of the fracture geometry calculations for any treatment design. The volume of fluid lost during the treatment determines the fracturing fluid efficiency (the ratio of the fracturing fluid volume to the volume pumped).

Fluid loss to the formation is a filtration process controlled by the fracturing fluid composition, the differential pressure between the fracture and the reservoir, and the reservoir’s transmissibility and diffusivity.

When you select or engineer a fracturing fluid, remember that every fluid type and polymer concentration has a different leakoff coefficient (even for the same rock conditions).

A test is the best way to determine the leakoff coefficient of any fracturing fluid in a given reservoir rock.

Fracturing fluids are forced into the subsurface under high pressure to enlarge and propagate existing fractures, and many factors can combine prevent their full recovery:

- The hydraulic gradients that cause fluids to flow away from the well during injection are much greater than the hydraulic gradients that occur during fluid recovery. As a result, some of the fracturing fluids will travel beyond the “capture zone” of the production well [6].

- The capture zone of a production well is the water-contributing portion of its aquifer. The zone’s size is affected by regional groundwater gradients and by the drawdown caused by the well. Fluids that flow beyond the capture zone are rarely recovered as flowback.
- Fracturing may change the fine scale structure of the rock and alter the fluid flow properties of the formation.

Fracturing with Slickwater Fluids

Slickwater, a low-viscosity aqueous fluid and proppant, is the most common hydraulic fracturing method used for shale gas.

Slickwater Description

The objective of a slickwater treatment is to create maximum surface area, with minimal fluid damage, at the lowest cost. Slickwater treatments are pumped at high rates with relatively low proppant concentrations due to the poor proppant transport characteristics of the low viscosity fluid. Fluids are kept simple to keep costs low and rarely contain more than three additives. Viscosity additives are used in small amounts, if at all.

Slickwater is used in formations with low to very low permeability. It is effective for mature shales with adequate organic content, in which the contact area correlates strongly with production.

It is also appropriate for formations with significant secondary porosity and where operators can create a large amount of complexity. This is seen in brittle rock with low stress anisotropy, present in many in many shale plays.

Slickwater Fluid Volumes

Slickwater treatments typically have many stages and use very high volumes of fluid. They aim to produce a large fracture and massive fairways, using low proppant concentrations in a low-conductivity rock.

Polymers Used in Slickwater

Friction reducing polymers are used in slickwater at much lower concentrations relative to polymer additives in other fracturing fluids. Each polymer has a different capacity for drag reduction with respect to water, depending on the ionic strength of the mix water used to blend the fluid. Friction reducers are synthetic polymers that resist bacterial degradation.

Source water, produced water, and flowback water, alone or in combination, are commonly used for high rate fracturing in tight gas formations. Salts or scales in these waters may cause fluid performance issues (e.g. flocculation of solids) and reduce friction reducer effectiveness. Divalent ions such as calcium and magnesium are especially detrimental.

Increased salt concentration reduces the effectiveness of friction reducer. Compensate by adding extra friction reducer to the fluid.

Bactericides Used in Slickwater

Biocides prevent bacterial growth, but may alter physical characteristics of a fluid (such as its viscosity) by degrading the polymer. Since free radicals (usually from oxygen) can cause polymers to degrade, a potential compatibility issue exists between oxygen scavengers and biocides. Biocides must be compatible with corrosion inhibitors, scale inhibitors, polymers, and other well treatment fluids.

Oilfield operations are typically concerned with these bacteria types:

- Sulfate reducing bacteria (SRB) bacteria,
- General heterotrophic bacteria (GHB),
- Acid producing bacteria (APB).

SRB, anaerobic bacteria that can sour a well, are an oilfield’s greatest bacterial threat; GHB and APB are aerobic bacteria that can cause corrosion and viscosity loss in biopolymer fluids.

Scale Inhibitors used in Slickwater

Produced water may contain solids and/or salts that can precipitate. Treatment options include water filtration and flocculant use. Add a scale inhibitor to the fracture treatment to prevent precipitation or scale formation when mixing different source waters.

Recyclability of Slickwater

Slickwater is the most forgiving fracture treatment in terms of reusability. Many additives are available to address a wide range of fluid engineering issues.

Table 2.1 Slickwater Sensitivities

Slickwater			
Water Quality	Range	Problem	Remedial Options
Temperature (°C)	3°C - 40°C	Temperatures above 40°C present a challenge for safe handling of fluid at surface Lower temperatures may cause freezing problems	Passive cooling in tanks or ponds Heat exchanger Use a hydration unit for mixing of water and friction reducer
pH	5.0 - 8.0	pH < 5 may cause prolonged hydration of friction reducer	NaOH or HCl
Chloride (mg/L)	< 90,000	Chlorides inhibit friction reducer hydration Greater amounts of friction reducer may be required	Reverse osmosis, mechanical vapour recompression
Hardness (mg/L $CaCO_3$)	< 15,000	Divalent cations inhibit hydration	Lime softening, ion exchange
Concentration Factor for Residual Additive	2	There is a concern that friction reducer impacts the formation and interferes with fresh additive	Breaker

Ingredients			
Suspended Solids (mg/L)	50 (< 100 um)	Suspended solids can damage the formation	Settling, filtration, hydrocyclones, electrocoagulation

Concerns about Slickwater

Slickwater, a low viscosity fluid, provides poor proppant transport. This necessitates high pump rates, low proppant concentrations, and very high volumes to create the desired large fracture extents:

- The proppant transport issues can impact the efficiency of propped height as a function of total fracturing geometry created.
- The high pumping volumes and large surface contact areas of a typical slickwater operation can produce a very high amount of dissolved ions.
- When selecting a saline tolerant biocide the impact of the biocide on friction reducer performance must be considered (refer to Figure 2.2).
- The potentially high ion content of slickwater flowback must be addressed, whether reuse or disposal is planned. Excessive divalent cations can inhibit friction reducer performance (refer to Figure 2.1).
- H_2S, with its wide-ranging health, safety, and environmental implications, is of particular concern.
- While slickwater fracturing jobs have difficult fluid volume, horsepower, surface footprint, and sand volume logistics, the slickwater process has proved itself often in many shales.

2.2 Fracturing with Linear Gel Fluids

Linear Gel Fluid Description

Linear (non-crosslinked) gel-based fluids use fresh water, seawater, or potassium chloride brines are efficient, economical fracturing fluids. Linear fracturing fluids perform best in the following applications:

- Depleted or under-pressured wells.
- Low-permeability gas wells.
- Fracture treatments where leakoff control is not critical.
- Fracture geometries where height growth is a concern.
- Budget-constrained projects.
- Low temperature applications.
- As a slickwater substitute for better proppant transporting large fracturing operations.

Linear Gel Fluid Volumes

Linear gel treatments can use much lower volumes than slickwater and require fewer stages.

Polymers used in Linear Gels

Water soluble, high molecular weight polymers are used in linear gels to increase fracturing solution viscosity. Greater viscosity increases the proppant concentration that the solution can support. The most common polymers used in linear gels are types are guar gum and hydroxypropyl guar (HPG).

Guar Gum

Guar is a polysaccharide, a long-chain polymer of mannose and galactose sugars with a very high affinity for water. When added to water, guar particles “swell” and “hydrate” (e.g. the polymer molecules associate themselves with water molecules, unfold, and extend into the solution).

At the molecular level, a guar solution resembles long, bloated strands suspended in water. The strands tend to overlap and hinder motion, causing the solution’s viscosity to increase.

Hydroxypropyl Guar (HPG)

Guar gum comes from the endosperm of the guar bean and contains up to 10% of insoluble plant material. It can be derivatized with propylene oxide to produce hydroxypropyl guar (HPG) containing 2 - 4% insoluble residue.

HPG is more stable than guar at elevated temperatures, making it more suitable than guar for high-temperature wells. Less hydrophilic than guar, HPG is more soluble in alcohol.

While once considered less damaging than guar to the formation face and proppant pack, recent studies show pack damage to be similar.

Hydroxyethylcellulose

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

Xanthan Gum

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 under 10 sec^{-1}, xanthan solutions suspend proppants better than HPG.

Xanthan, more expensive than guar or cellulose derivatives, is used less frequently.

Carboxymethyl Hydroxypropyl Guar

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

Recyclability of Linear Gels

Linear gel can be reused, but there are limitations, as follows:

- Residual bacteria can metabolize the gel, affecting fluid viscosity and performance.
- Bacteria can also sour or damage the reservoir where flowback fluid is stored.
- Residual polymers in fluid can accumulate and concentrate, becoming difficult to handle. This can potentially cause damage when they are reintroduced into the well.
- Recycled water must be able to hydrate newly added polymers. Many parameters, such as fluid pH and salinity, can inhibit hydration.

Table 2.2 Gel Sensitivities.

Linear Gels			
Water Quality	Range	Problem	Remedial Options
Temperature (°C)	15°C - 40°C	Temperatures above 40°C present a challenge for safe handling of fluid at surface Lower temperatures may prolong the hydration of gel polymers	Passive cooling in tanks or ponds Heat exchanger
pH	6.0 - 8.0	A pH < 6 may cause prolonged hydration of gel A pH > 8 may result in inadequate gelling	NaOH or HCl
Chloride (mg/L)	< 50,000	Chlorides inhibit friction reducer hydration and can destabilize the gel fluid	Reverse osmosis, mechanical vapor recompression
Iron (mg/L)	< 25	Iron degrades and breaks polymers in gels, causing premature breaking or crosslinking	Iron sequestration, oxidization
Sodium (mg/L)	< 1000	Excess sodium destabilizes the fluid	ion exchange, mechanical vapor recompression,

			reverse osmosis
Bacteria (CFU)	0	Bacteria feed on the gel which reduces the gel viscosity	Biocide, ultraviolet, electrocoagulation
Concentration Factor for Residual Additive Ingredients	2	There is a concern that polymers impact the formation and interfere with fresh additive	Breaker
Suspended Solids (mg/L)	50 (< 100 um)	Suspended solids can damage the formation	Settling, filtration, hydrocyclones, electrocoagulation

Concerns about Linear Gels

Linear gel fluids have a relatively low viscosity and increasing temperatures will reduce fluid viscosity even more. The only way to increase viscosity with a linear gel is to add more polymer. Polymer concentrations must be engineered to reach adequate, but not excessive, levels that balance performance, cost, and proppant pack damage.

2.3 Fracturing with Crosslinked Gel Fluids

Polymers produce viscous solutions at ambient temperature, but thin significantly as the temperature rises. While increasing the polymer concentration will offset the thermal effects, this is expensive and may damage the proppant pack.

Crosslinking agents dramatically increase a polymer’s effective molecular weight by binding polymer chains. This can produce high fluid viscosities at relatively low polymer concentrations. Inorganic species such as borate salts and organometallic complexes react with guar and hydroxypropyl guar.

In a very concentrated polymer solution, the molecules will overlap (for HPG, at least 0.25% wt/wt). The complex can react with an overlapping polymer, linking them together. This creates a new species with twice the molecular weight of the polymer alone.

Since each polymer chain can crosslink at more than one site, very high-molecular-weight networks can develop, especially under static conditions resulting in a highly viscous solution.

Crosslinked fluids perform best in the following applications:

- Normally pressured wells.
- Low rate fracturing operations 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.

Crosslinked Gel Fluid Volumes

Crosslinked gels are typically used at much lower volumes than slickwater. However, in a hybrid treatment, the fluid volumes may reach, or exceed, the volumes typical of a standard slickwater design.

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 above 8, an extremely viscous fluid forms in seconds.

Crosslinked fluid stability requires high pH values, with 9 - 12 the optimum range. Viscosity can be controlled by adjusting the polymer or crosslinker concentration.

Organometallic Crosslinked Fluids

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 200°C can be fractured with these fluids if the treatment is designed to provide adequate cooldown.

The organometallic-polymer bond is very sensitive to shear. High shear irreversibly degrades organometallic crosslinked fluids. 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 Crosslinked 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 80°C.

Conductivity fluid dynamics and post-closure polymer concentrations should be used as guidelines to determine conductivity-limited fracturing treatments. Factors that can adversely affect conductivity fluid dynamics 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 6 kg/m^3.

Recyclability of Crosslinked Fluids

Crosslinked gels are the most difficult fluids to reuse. They present all the same concerns as linear gels for hydration and bacteria. They can be reused, but with limitations. Of particular concern are residual bacteria, which can metabolize the gel to affect the viscosity and performance. 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.

Table 2.3 Crosslinked Fluid Sensitivities

Crosslink Fluids			
Water Quality	Range	Problem	Remedial Options
Temperature (°C)	15°C - 40°C	Temperatures above 40°C present a challenge for safe handling of fluid at surface Lower temperatures may prolong the hydration of gel polymers	Passive cooling in tanks or ponds Heat exchanger
pH	6.0 - 8.0	pH < 6 may cause prolonged hydration of gel polymers pH > 8 may result in inadequate gelling	NaOH or HCl
Chloride (mg/L)	< 30,000	Chlorides destabilize the fluid and create problems with crosslinking	Reverse osmosis, mechanical vapor recompression

Iron (mg/L)	< 25	Iron degrades and breaks polymers in gels, causing premature breaking or crosslinking	Iron sequestration, oxidization
Alkalinity (mg/L $CaCO_3$)	< 600	Alkalinity acts as a pH buffer and high concentrations of crosslinking activator may be needed	pH adjustment, lime addition
Sodium (mg/L)	< 1000	Excess sodium destabilizes the fluid	Reverse osmosis, mechanical vapor recompression
Silica (mg/L)	< 35	Excess silica may inhibit the crosslinking of polymer gels	
Bacteria (CFU)	0	Bacteria feed on the gel which reduces the gel viscosity	Biocide, ozone, electrocoagulation
Concentration Factor for Residual Additive Ingredients	Field Tests Required	Borate impacts the control of crosslinking	Disposal of flowback or physical/chemical water treatment for dissolved solids
	2	There is concern that polymers impact the formation and interfere with fresh additive	Breaker
	Field Tests Required	Buffers impact the control of crosslinking	Disposal of flowback or physical/chemical water treatment for dissolved solids
Suspended Solids (mg/L)	50 (< 100 um)	Suspended solids can damage the formation	Settling, filtration, hydrocyclones, electrocoagulation

2.4 Fracturing with Foam

Schlumberger reports that slickwater is used most frequently for deep, high-pressure shale, while nitrogen-foamed fracturing fluids are commonly pumped into shallower shales and shales with low reservoir pressures.

Description of 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).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.

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. N_2 and CO_2 gases can be used to produce foams.

The stability of a foam is normally measured under static conditions at low temperature and pressure. The following 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.

Three conditions are necessary to create a 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.

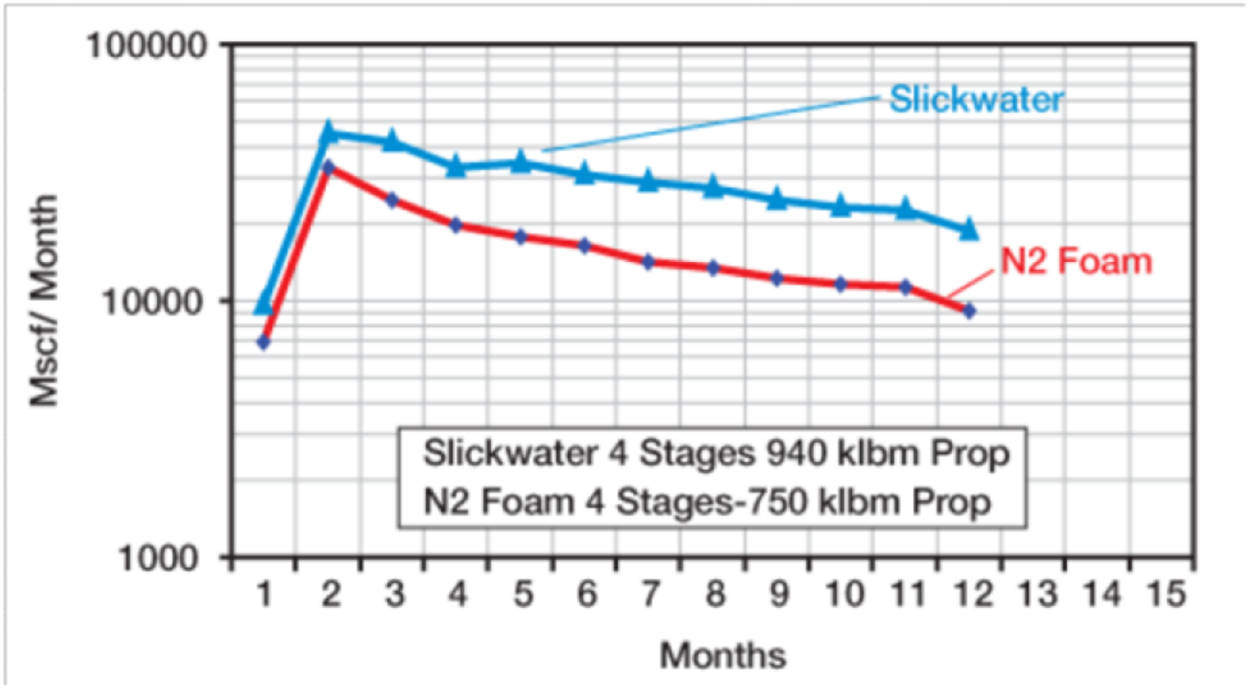

Figure 2.3 Performance of N_2 Foam vs. Slickwater.

Cleanup

Post-treatment cleanup is a large industry concern with foam fractures, and this 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.

Table 2.4 Comparison of Nitrogen and Carbon Dioxide Foam Fluids.

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)

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.

Foam Fluid Volumes

The volumes for foamed fluids tend to be generally much lower than slickwater operations. Foams use a reduced amount of water because only 30% is water and the rest is N_2 or CO_2. Foamed fluids are the best way to minimize water usage (apart from fracturing with hydrocarbons).

Recyclability of Foam

The recyclability of a foamed fluid 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-based 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.

2.5 Fracturing with Viscoelastic Fluids

Description of VES Fluids

VES stimulation fluids are polymer-free, water-based fluids prepared by diluting a viscoelastic surfactant (VES) in brine.

Unique features of VES fluid are:

- No polymer hydration is necessary, and there is no need to add crosslinker or breakers.
- The breaker for ClearFRAC fluid is the produced hydrocarbon, or dilution by other formation fluids.
- VES is a solids-free fluid. Consequently, the retained permeabilities of proppant packs placed with ClearFRAC 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 can be used in oil, gas, and condensate reservoirs with bottomhole temperatures up to 135ºC.

VES Fluid Volumes

The volumes for VES fluids tend to be generally about one half lower than slickwater operations 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 of VES Fluid Volumes

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.

Table 2.5 Sensitivity of VES Fluids.

Viscoelastic Fluids			
Water Quality	Range	Problem	Remedial Options
Temperature (°C)	20°C - 40°C	Temperatures above 40°C present a challenge for safe handling of fluid at surface	Passive cooling in tanks or ponds Heat exchanger
pH	5 - 12	pH outside this range can affect surfactant properties Testing required	
Chloride (mg/L)	< 33,000	High chloride concentration could affect the fluid quality and performance of some additives	Reverse osmosis, mechanical vapor recompression
Suspended Solids (mg/L)	50 (< 100 um)	Suspended solids can damage the formation	Settling, filtration, hydrocyclones, electrocoagulation

3.0 General Principles of Fracturing Fluid (Flowback) Cleanup

When a hydraulic fracture stimulation completes, flowback fluids return to the surface in 7 - 28 days. The flowback may contain both dissolved constituents from the formation itself and constituents of the fracturing fluid pumped into the well.

Flowback was initially considered an oilfield waste. Disposal was typically done offsite using underground injection. In some regions, such as the Montney Shale in British Columbia, the availability of injection wells is limited and disposal by injection is expensive. With water volumes of approximately 1000 m^3 per stage, and up to 40 stages per horizontal well in a typical slickwater hydraulic fracture treatment, offsite disposal costs can be extremely high.

To minimize this expense, the industry introduced laboratory testing and chemical treatment of flowback fluids. Onsite flowback recycling for reuse in subsequent fracturing operations brings major cost savings and reduces the environmental impact of the fracturing process.

Fracturing fluid cleanup attempts to retrieve, or “flowback”, all components of the fracturing fluid. Experience shows that there is not 100% fracturing fluid recovery. It is also difficult to differentiate flowback fluids from natural formation water.

Many factors affect flowback at every fracturing operation:

- Unrecovered fracturing fluids typically remain within the target formations. They may occupy macro-porosity (typically natural fracture porosity) spaces in the shale formation or the micro-pore spaces vacated by escaping gas.
- Fluids may become stranded in reservoir rock fractures that heal (which blocks fluid flowback to the well). Small amounts of this stranded fluid can flowback to the well over an extended period of time. Extended contact with the formation alters the fluid chemistry through increased mineral dissolution, eventually making the flowback similar to the natural formation water.
- Delayed flowback after fracturing may increase the total dissolved solids concentration in the flowback water. Any resulting salinity can increase treatment costs.

- A “check-valve” effect can trap fracturing fluid on one side (the upgradient) of a collapsed or narrowed fracture, preventing flowback to the production well. This can occur in both natural and induced fractures, which narrow when fluid injection ceases, formation pressure decreases, and the extraction of methane and groundwater begins.
- Gel damage, relative permeability effects, the complexity of the fracture system, fracturing behaviors that strand fluids (fracture closure), and many other factors cause flowback load returns to vary.

3.1 Gel Flowback Considerations

Gel base fracturing fluids have very different properties from water and from the highly soluble constituents of slickwater fracturing fluids. These substances are much more difficult to recover. One EPA reviewed study described evidence of gel clumps within fractures. Undissolved gel may attach to the sides of a fracture. It can also become trapped within smaller fractures or pores in formations surrounding the coalbed. These fluids are not likely to flow with groundwater during production, but may add gel constituents to flowing groundwater subsequent to fluid recovery.

3.2 Polymeric Fluid Flowback Considerations

Polymeric fracturing fluids leave residues in the near-fracture-face region and in the proppant pack, thus decreasing the productivity of the well.

VES fluids are a free-polymer fluid that leave very little residue in the fracture, resulting in high conductivity fractures.

During a fracture treatment, the fracturing fluid starts creating the fracture and as the fracture progressively grows, 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 such a 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 viscosity fluid with a high concentration of polymer.
- A fracture face with a polymer filter cake.
- A near-fracture-face region (around the fracture) of the formation with a high saturation of fracturing fluid filtrate; this filtrate will have a viscosity value very close to the water at reservoir temperature.
- When a non-wall-building fluid is used, the following scenario is obtained at the end of the job.
- Proppant pack in the fracture full of the non-wall building fluid.
- A near-fracture-face region (around the fracture) of the formation with a high saturation of the non-wall building fracturing fluid.

In considering the suggested limits for the common fracturing types applied in hydraulic fracturing of shales, it is important to recognize that the limits suggested are gradational. Furthermore, the exceedance of a suggested constituent limit does not preclude the use of that source water as a fracturing fluid, nor does it preclude the fracturing type under consideration. Rather, if a sensitive constituent requires an amount in excess of the indicated limits, this indicates the need to apply a more complex fracturing fluid design criteria, which requires the input of a hydraulic fracturing design specialist.

3.3 Flowback Duration

Fractures with a long reach and minimum complexity tend to flow back quickly, while complex fractures and mildly reactive shale have longer fluid recovery times. The initial flowback flow rate can be relatively high (e.g. > 400 m^3 per day), but it diminishes rapidly with time to the normal rate of produced water flow from a natural gas well (e.g. about 0.2 m^3 per day).

The flowback period in shale gas reservoirs is typically several weeks. Limited time-series data show that about 60% percent of flowback occurs within four days after fracturing. The daily flowback rate then declines sharply to 2 - 5% of the total flowback over a two-week period.

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Fracturing Fluid
Flowback Reuse Project

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Fund

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