Optimization of Well Stimulation Fluids in the Marcellus Shale Gas Development Using Integrated Technologies

EME 580: FINAL REPORT

By

Olawoyin, Richard; rzo5017@psu.edu	York, Jason; jcy127@psu.edu
Madu, Christian; ccm5180@psu.edu	Li, Hang; hil5131@psu.edu
Ahn Chong Hyun; cza5010@psu.edu	Enab, Khalid; kae5168@psu.edu

MAY 1, 2011

TABLE OF CONTENT

LIST OF FIGURES

LIST OF TABLES

PROBLEM STATEMENT

It is important to increase the economic attractiveness of the unconventional gas sources to the private sector by;

- decreasing risks,
- increasing reliability,
- help operators substantially lower operational costs
- meet increasingly stringent environmental regulations,
- recycle water to reduce demand on local supplies.

A solution that lessens the environmental impact of gas drilling and reduces the current treatment cost to service providers.

Our Integrated Planning Approach reveals synergies that;

- reduced life-cycle costs of infrastructure,
- reduced greenhouse gas emissions,
- reduced energy usage from conventional sources,
- enhance other environmental benefits,
- reduced environmental impact without sacrificing performance.

NOVELTY

1. New waste water treatment integrated technology
2. Drilling fluid and fracturing fluids optimum design to facilitate higher load recovery
3. Energy generation from flow back fluid treatment
4. Innovative membrane selection for forward osmosis
5. Pioneering economic analysis of the integrated system

Executive Summary

This integrative design project placed an enormous emphasis on the unconventional gas development in the Marcellus Shale, which the Bradford County as the center focus. The need for an effective control of flow back waters, which are derived as byproducts of well stimulation in an attempt to improve the economic viability of a tight gas well, was deemed necessary in curtailing the challenges of pollution and negative image/perception in which operators are viewed. A complete assessment of the shale origin, deposition, constituent, mineralogy, stratigraphy, paleo-environmental significance, and economical potential was carried out to aid in understanding the composition of the rocks found along the route of exploration and production. The Bradford county is a prolific area with vast gas production potentials, which also signals challenges such as the operational fluid management. A typical well was designed in the Springfield township of Bradford using CMG software to analyze the production potential in the area over 40 years, and a fracture design was done using the FracPro software. The simulation demonstrates that hydraulic fracture can appreciably increase cumulative production and production rate in the well. An estimated amount of water needed to fracture open the formation for the free flow of gas was 3.6 Million gallons per day (approximately 85, 714 barrels) and due to the efficient well design and stimulation design, a load recovery of approximately 86% of the injected fluid is achievable which amount to 73,714 barrels of waste water to be treated.

The system capacity of the Forward Osmosis process, operating on a hydraulic fracturing flow-back water will treat; 14, 400 Barrels = 604, 800 gallons per day with an “average” chemical composition of; 4,300 mg/l barium, 21,850 mg/l calcium, 14,000 mg/l magnesium, and 3,400 mg/l strontium. These would produce, at 40% solids sludge cake, 67,000 lb of barium sludge and 281,815 lb of calcium/strontium/magnesium sludge per day. Exclusive of the incoming hydraulic fracture flowback water and treated water storage tanks, we have estimated that a 604, 800 gpd FO process system would require a hydro-pneumatic tank and a vessel for the FO system.

The novel design takes into consideration the flowback recovery per hour in our system, which is 600bbl/hr for the centralized system, but 150bbl/hr for a single well pad. The tank size required would be a 25,000 gallon tank, covering approximately 1,202 square feet and cost $52,255. In

other to prevent corrosion, an epoxy lining was installed which increased the cost to $64,610 with a design working pressure of 125# ASME.

The system components composed of the following in summary;

- 4 inch by 4 inch, 17 bbl/min centrifugal transfer pump to pump water from wells into
- A elevated 25,000 gallon hydro pneumatic tank
- A 40ft x 8ft x 8ft dual insulated dry goods shipping container will be used to house our Forward Osmosis Unit
- A low pressure recirculation vessel will house the 120 1m^2 Spiral Wound TFC MP Membrane Modules and Ammonium Bicarbonate Draw Solution
- The dissolved solids will be removed from into120 gal Excalibur ®intermediate bulk container (IBC)
- The dilute draw solution flows through a 1.2 kW turbine generating the power for our system. Energy will be stored in a minimum 1.2 kW capacitor.
- The dilute draw solution then flows into a single vacuum distillation column and reboiler for separation of reclaim water from ammonium and carbon dioxide gases.
- Reclaim passes into a storage container to be reused for future well fracturing

The draw solution composition and control system;

- The 36% NH_4CO_3 draw solution is pumped into the low pressure recirculation vessel, using a ½ to ¾ horsepower, 1.8 bbl/min centrifugal transfer pump.
- Ammonium Bicarbonate used because of its effective high osmotic efficiency and easy separation from water at low temperatures (68^{0}F)
- SCADA monitoring will allow the system to generate the ideal concentration of Ammonium Bicarbonate to achieve our optimal flow rate of 10bbls/min. This will be achieved be controlling the amount of Ammonium Bicarbonate dissolved in water in main Draw Solution Storage tank.

The forward osmosis system uses a a membrane system which separates the solutes from the water effectively. The choice of membrane was made with efficiency and power generation in mind, the TFC membrane was selected. The membrane parameters are as follows;

- Water permeability coefficient (A) = 5.81L/m^{2}hbar
- Salt or solute permeability coefficient (B) = 0.61L/m^{2}h

- Structural parameter *(S)* = 370μm
- Power density *(W)* = 10W/m^2
- Water flux (J_w) = 30 L/m^2h
- Osmotic pressure differential *(Δπ)* = 25bars
- Hydraulic pressure differential *(ΔP)* = 12.5bars

Using the forward osmosis filtration to recycle waste water into a high quality fluid for use in fracturing jobs, on each well, over 80% of the waste water can be recycled to provide approximately 25% of the water required for hydraulic fracturing. The capital cost of each system is about $100,000. The annual operating cost of the FO system would be about $0.60/kgal of produced water. This relatively high cost results from the low value assumed for flux across the membrane. If guarantee a constant driving force across the membrane, the FO flux may increase 70%, the unit water costs will drop by 36% to about only $0.38/kgal. A cost estimate savings of over one million dollars ($1,000,000) is expected if the integrated forward osmosis sytem is implemented. Aside cost savings, there is zero to none emission generated from the system which makes it considerably environmentally friendly compared to other types of treatments.

Other benefits include;

- Save about three-quarters of a billion gallons of fresh water per year.
- Eliminates 66,600 bbls of waste water per horizontal well of trucking related road damages and emission, leading to reduction in the carbon footprint of the industry.
- Approximately 175 truck loads can be eliminated per fracture job
- 4,375 gallons of diesel emissions eliminated per 66,600 bbls of waste water reclaimed.
- Save approximately 6.2 million gallons of diesel use each year.

Considering the fact that there are many more known shale basins in the United States and around the world where the forward osmosis technology alongside the power generation can be employed. On the other hand, the forward osmosis technology is not restricted to shale development in unconventional reservoirs, but is applicable in conventional oil and gas plays also.

The naturally low permeability shale must be fractured to guarantee higher productivity and the fracturing process involves the use of millions of gallons of water that must be recovered as flow back or produced waste water. Public and regulatory pressure is demanding that operators in the oil and gas industry improve water management practices.

Exploring several results of laboratory and field testing from early commercial jobs indicate that, flexible, portable and scalable Forward Osmosis units are applicable to resourcefully and efficiently reclaim water-based waste for valuable reuse as a high quality completion fluid.

It is recommended that future design and development of the forward osmosis blue energy integrated system (FOBES) for waste water treatment should consider improved material use and better energy generation methodologies from the chemical potential energy between waste water and an improved draw solution.

Additional improvement on the selected membrane would be helpful in enhancing the efficiency of the integrated process. Investments into the development of forward osmosis membranes with higher solute rejection and higher water flux are highly recommended.

CHAPTER 1: LITERATURE REVIEW

1.1. Introduction

Due to the enormous natural gas deposits discovered in the Marcellus Shale formation, there has been an increase in gas extraction activities in the Marcellus area. A huge investment is being made in developing extraction technologies to adequately recover natural gas from formations of very low permeability, which necessitated the use of the horizontal drilling and hydraulic fracturing techniques. These methods are very helpful in reaching the pay zone and also creating fractures or connecting natural fractures in the formation, after which the gas can be extractable and optimum recovery attainable. The use of hydraulic fracturing method in the stimulation of reservoirs of tight formations in the Marcellus area is gaining more momentum as energy demand across the region, and/or over the world increases. Recent advances in directional drilling made shale formations, very accessible and more prolific. It has been estimated by The United States Geological Survey (USGS) that there is a technical possibility of recovering up to 200 TCF (trillion cubic feet) of natural gas from shale gas formations. Towards this end, there has been a huge capital intense investment in the Marcellus Shale by some International Energy firms in developing productive fields, providing advanced technology and in the exploration of the natural resource of interest (Gas).

These events are new to many towns that never experienced drilling and production activities and are intensified in regions that previously experienced little petroleum development activities. Inasmuch as the production of natural gas for the purpose of meeting current energy consumption requirement is quintessential to the prosperity of the human population at large, it may also damage the environment if not with careful operations. There has been a growing concern over the stimulation of the Marcellus Shale, ranging from contamination of drinkable well water, to excessive water withdrawal from the watersheds and other related environmental/ psycho-social effects of both drilling operations and the disposal of flow back fracture fluids. Wastewater is usually produced alongside the gas and they contain total dissolved solids in high concentrations and the chemical additives added to the hydraulic fracturing fluid. Data provided by the Pennsylvania Department of Environmental Protections (DEP) confirm the various violations by the operators in the Marcellus Shale area. It is evident that in some areas of the commonwealth, these fluids (wastewater and undiluted fracturing chemicals) were either accidentally spilled to the waters of the commonwealth or in some cases, were discharged into water bodies due to the unavailability of proxy treatment plants.

The goal of the research is to provide an effective waste water management in the Marcellus Shale area (Figure 1) and their impacts on the gas exploration and production industry as a means of providing responsiveness to environmental risks, highlighting the need for the industry's sustainability when controllable risk are mitigated or minimized. Statistical facts are presented to show the different interactions of risk factors and how they trend in response to environmental concerns, also pollution prevention methods. The sources of pollution of high interest in industrial operations are hazardous air pollutants, waste water, spills and operational waste materials. Fortunately, technological advancements have led to improvements in reducing the effects of these pollutants to the environment, such as the integrated forward osmosis system design which is the focus of this study. Technology improvement positively impacts cost savings in the oil and gas industry, such as implementing innovative technology for exploration, production, processing, transportation and storage operations, leading to a better scenario of environmental protection and compliance.

1.2 MARCELLUS SHALE

In 1836, Henry Darwin Rogers classified the Marcellus as "Cadent Lower Black Slate" in the first Pennsylvania Geological Survey, while in 1839 Professor James Hall established the term "Marcellus Shale" in his 1839 report (New York State Geological Survey) titled "Marcellus Shale due to distinctive outcropping near the village of Marcellus, New York, just to the west of Syracuse in Seneca County. The Marcellus Shale was deposited as marine sedimentary rock in mid-Devonian (400 mil years ago) (Figure 2), due to sea level variation and at depth devoid of oxygen. It extends across much of the Appalachian basin and contains largely untapped natural gas reserves making it attractive for energy development in the United States.

The gas in the Marcellus Shale is a result of its contained organic contents; the more organic material contained in the rock the greater its ability to yield gas. John Harper of the PA

Geological Survey suggests that the areas with the greatest production potential might be where the net thickness of organic-rich shale within the Marcellus Formation is greatest.

Maximum thickness of the Marcellus ranges from 890 ft in New Jersey,(*White, Ron W.; Monteverde, Donald H. 2006*) to 40 ft in Canada *(Singer, S.N. et al 2003).* In West Virginia, the Marcellus Formation is as much as 200 ft thick *(Boughton, Carol J.; McCoy, Kurt J. (2006).* In extreme eastern Pennsylvania, it is 790 ft thick, *(White, I.C.; Chance, H.M. (1882)* thinning to the west, becoming only 49 ft thick along the Ohio River and only a few feet in Licking County, Ohio *(Mayhood, Kevin 2008).*

Stratigraphic convergence or thinning from east to west is caused by decrease in grain size of the clastic deposits, which entered the basin from the east *(Dennison, J.M.; Hasson, K.O. (1976).* Northeastern PA is where the thick organic-rich shale intervals are located.

The latest data estimates gas reserves in the Marcellus Shale to be up to 500 Tcf *(Engelder & Lash,2008)* compared to the yearly average of total natural gas consumption in the United States which is roughly 23 Tcf *(Soeder & Kappel, 2009).*

1.2.1 Waste Water Management in The Marcellus Shale Play

The management of water resources poses considerable challenges to the Pennsylvania Gas extraction Industry as it begins to expand the development of the Marcellus Shale. Currently, the drilling, completion, and stimulation of each horizontal shale well consumes up to 10 million gallons (gal) of fresh water, roughly equal to daily indoor water usage of 125,000 people *(U.S. Department of the Interior March 2010)*

Many of the logistical problems associated with the development of shale gas stem from the large amounts of water associated with the completion and operation of shale gas wells that must be transported, stored and disposed of in a manner that is protective of human health and the environment.

The challenge ahead for Marcellus Shale gas developers is to identify techniques to deliver the water required for drilling and completion and to develop methods for the disposal of brines represented by flowback and produced water that comply with applicable environmental regulations.

This rapid decline in operational brine water treatment plants affected nearby Marcellus Shale gas drilling activity immensely (Litvak, 2008) (Figure 3). Some drillers found it necessary to cut down to operating one rig a day instead of two (Litvak, 2008).

The Appalachian Shale Water Conservation Management Committee (ASWCMC) recently conducted a survey; The survey forecasts a growth in rig activity from 64 rigs drilling 857 wells in 2009 to 171 rigs drilling 2,243 wells in 2013. The daily water consumption associated with drilling and completions activity is projected to increase from 6.1 mil gpd to 18.7 mi gpd over the same period. Multi-stage hydraulic fracturing was identified as the main consumptive use activity accounting for nearly 95% of all water used in drilling and completions operations.

Surface waters are identified as the main source of waters planned for this purpose comprising 60-70% of the total water demand with groundwater serving as a very minor source for well completions (less than 4% of the total water demand) (ASWCMC,2008). The remaining portions of source water are municipal supplied and forecasted recycling efforts.

1.2.2 Water Quality

The composition of the fluid varies widely depending on the type of operation, location, and geology. The combination of these makes almost every situation unique. While existing technologies offer a wide selection of treatment options, cost remains the determining factor.

Two of the major water quality concerns with the concept of reusing reserve pit water as base fluid for hydraulic fracturing are the high concentration of total suspended solids and the high concentration of undesirable solutes such as calcium, barium, and heavy metals. Rieb, Allen, and Hogan March 2009; Geehan, July 2009.

1.2.3 Wastewater generation:

The most common sources of wastewater in E&P operations were identified as shown below.

A. Drilling

1. Spent mud or water from mud dewatering
2. Rig runoff
3. Rainwater catch

4. Rig wash
5. Grey water and black water from the drilling camp

B. Completion

1. Diluted completion and drill-in fluids
2. Acidizing and chemical stimulation waste fluids
3. Frac flowback – In hydraulic fracturing operations,

C. Production solids are solids that float on the surface, are suspended as a colloid, or are suspended due to the motion of the water (not in solution).

1. Produced water (Produced Water Facts; *citation - Produced Water Society*)

1.2.4 Contaminants

Organics category includes liquids, solids, and semisolids insoluble in water (hydrophobic) or partially insoluble in water: This category includes volatile organic compounds (VOCs), which are legally defined in the various laws and are regulated in the US by the U.S. EPA in the air, water and land (Veil, Puder, Elcock, & Redveik, January 2004).

1.2.4.1 Suspended Dissolved solids

Dissolved Solids are inorganic and organic substances molecularly dispersed in water; they are reported as Total Dissolved Solids (TDS).

1.2.4.2 Bio-contaminants

Bio-contaminants are essentially microorganisms present in water – including algae, fungi, and bacteria (sulfur reducing bacteria, acid producing bacteria, and aerobic bacteria). Bio-contaminants can cause microbial influenced corrosion (MIC), create toxic substances such as hydrogen sulfide gas, plug the pores of the hydrocarbon-bearing formation, and damage or render equipment ineffective.

1.2.4.3 NATURALLY OCCURRING RADIOACTIVE MATERIALS (NORM)

These include materials such as Strontium, Radium (Radium 226, Radium 228), and Uranium. The sources of most of the radioactivity are isotopes of uranium-238 (U-238) and thorium-232 (Th-232), which are naturally present in subsurface formations from which oil and gas are produced. NORM is regulated by U.S. states regarding admissible levels, licensing, equipment contamination, worker protection, and waste disposal (Arthur, Bohm, Coughlin, & Layne, 2008).

1.2.4.4 Chemistry of Produced water

The general nature of produced water production, composition, environmental issues and current practices associated with the management of produced water streams associated with conventional gas production are covered in several recent reviews *(Veil, et al., 2004; Boysen, et al., 2002; Doran and Leong, 2000).*

The soluble salt content (TDS) levels in flowback water can range from a few thousand mg/l to over 200,000 mg/l (>20% salt content) in the Marcellus Shale. The wide range of salt concentrations in flowback water may be due to; natural variation of formation conditions, the tendency of flowback water to increase in salt content as it flows from the well after fracturing (Figure 4).

Chapter Two: Treatment Methods

Physical and chemical treatment can provide "*Engineered Water*" for all levels of operations.

2.1 Current Practice

The primary conventional method for disposing of gas field waste water is through pre-treatment facilities which use clarification and filtration processes coupled with direct discharge to surface waters or sewage treatment plants.

There are 8 permitted disposal wells in the state of Pennsylvania. The average injection rate of these wells is less than 1,000 bpd. The US Environmental Protection Agency (EPA) administers the permitting and operating of disposal wells in Pennsylvania.

2.2 Projections

For any given shale gas play, this category of brine generation will increase over a finite time period, will plateau over a finite period and will decline as well completions in that play are diminished in number each year.

The nature of the brine water disposal challenge is temporal in nature and is closely related to the annual rate of well completions in the shale gas fields.

Pre-Treatment Process under National Pollutant Discharge Elimination System (NPDES) permits:

Deep well injection:

Brines from gas operations can be disposed of using Class II wells, a category of well disposal reserved for the oil and gas industry.

Demineralization Systems:

Consist of pretreatment often involving filtration, followed by a demineralization step to concentrate the salts into a small volume of brine, followed by disposal of the concentrated brines, usually by deepwell injection.

Thermal Evaporation/Condensation

Several commercial designs rely on mechanical vapor compression. The challenge in applying thermal systems to brine demineralization includes heat exchanger fouling with organic deposits.

Natural Evaporation

The Appalachian Region does not have the land area or the climate (i.e. temperature/ humidity) conditions necessary to support the rapid evaporation of flowback waters (Figure 5).

Crystallization

A process of precipitating salts in a water stream has been combined with falling film evaporators and mechanical vapor recompression (MVR) technology to achieve a further concentration of brines beyond the capability of conventional thermal evaporators, thereby allowing the recovery of near-solid salts or highly concentrated brine suspensions that can be recycled for other uses. But the challenge is large sizes of equipment required for the handling of modest flows which limit the ability to modularize this technology to the extent of making it mobile.

Filtration

An essential pretreatment for nearly any demineralization step will include filtration. These filtration processes will remove suspended solids, oils and grease but will not achieve concentration of soluble salts as is achieved in demineralization (Figure 6).

Ozone

The addition of ozone has been proposed to enhance the removal of soluble organics, oils, greases, and heavy metals when coupled with the above-mentioned filtration. One factor that may determine the economic feasibility of this approach is the cost of ozone delivered to the process.

Freeze Thaw

Freeze thaw evaporation (FTE) technology is a water treatment process in which water is sprayed under freezing conditions onto a freezing pad to create an ice pile. Freeze thaw evaporation has been commercially introduced at sites where conventional produced waters are treated for brine reduction *(Boysen, et al., 2002).* Limitation of this technology; must be deployed in the areas with sufficient days of freezing weather, also requires very large land area.

Membrane distillation is arguably a future valid and efficient way of obtaining clean water out of wastewater. (Walton, Lu, Turner, Solis, & Hein, 2004) (Bolto, Tran, & Hoang, 2007). Warm wastewater and cooler pure water are circulated one side and the other of a hydrophobic membrane which will permit only vapors of water to pass through the nano-sized pores from the contaminated side to the clean side under vapor pressure influence.

Reverse Osmosis (hyper-filtration)

This process is capable of demineralizing brines. RO uses high pressure (600-900 psig) to force brine through a membrane that retains salts on one side and allows demineralized water to flow through to the other side. As of 1997, there were approximately 2,000 RO plants in the world treating a total of 800 million gallons of water per day (MGD).

Most of these plants treat brackish water and seawater to supplement water supplies for municipalities and industry. many operational problems involving membrane fouling have surfaced in the initial attempts in the field to deploy the technology (Lawrence, et al., 1995; Doran and Leong,2000).

These operational problems arise from the complex composition of the produced water & the effects of certain constituents on the membrane material. These fouling problems are largely responsible for the lack of deployment success of RO in the oil and gas industry.

Forward osmosis is nature's way of transporting fluid through membranes; the "draw" solution a solute creates a big enough osmotic pressure gradient to trigger the transfer of water. The solute needs to be either usable with the water, such as the NaCl, which produces clear brine; or it has to be relatively easily removable, such as the NH_3 and CO_2 gas mixture *(Bruno, 2009; McCutcheon, McGinnis., & Elimelech, 2005).*

The suspended and dissolved solute rejection efficacy of the FO membranes used in the unit has been well established in several scientific literatures. The FO membranes have been proven to reject 100% of *bacteria, viruses, and colloidal solids* in addition to removing over 97-99% of the *heavy metals and salt* .

[Cath, Childress, & Elimelech September 2006; Mi & Elimelech, July 2008; Mi & Elimelech, February 2010; Cornelissen, Harmsen, de Korte, Ruiken, Qin, Oo, & Wessels July 2008].

3.0 Drilling and Completion

Drilling and completion Is a very important step in producing gas and oil so that we have to focus on the drilling and completion to increase the recovery.

3.1 Drilling

There are three drilling techniques has been used in the petroleum and natural gas industry. The first technique is the vertical wells. The second technique is the horizontal wells. The Third one is the multilateral wells but this has not been used in the Marcellus yet.

3.1.1 Vertical wells

Vertical wells technique is the first technique has been used in the petroleum engineering industry. The vertical well starts from the surface by 90 degree angle with the surface going all the way through the formation. Vertical wells are much cheaper than the horizontal wells but it gave much more recovery. Also the vertical wells use much more surface area than the horizontal wells.

3.1.2 Horizontal wells

Horizontal wells start as a vertical well then at the kick off point starts to go horizontal which can be 2000 – 6000 ft. long. Horizontal wells recover much more than the vertical well because it drains more area of the reservoir. The horizontal wells Provide greater access with a smaller footprint as from one hole on the surface we can have up to 6 horizontal wells comparing to 12 - 14 vertical wells each well needs a separate hole.

Choosing the technique which will be used depend on many issues like the reservoir geology, fractures and the permeability. According to our objective which is decreasing the environmental impact we prefer to go with the horizontal wells to decrease the environmental impact and increase the recovery.

3.2 Drilling fluids

Drilling fluids been used during the drilling process to Remove cuttings from well, Suspend and release cuttings, Control formation pressures, Seal permeable formations, Maintain wellbore stability, Minimizing formation damage, Cool, lubricate, and support the bit and drilling assembly and Transmit hydraulic energy to tools and bit Ensure adequate formation evaluation.

There are some additives to the drilling fluid to make it more efficient and functional like Viscosifiers, Filtration Control Materials, Rheology Control Materials, Alkalinity and pH Control Materials, Lost Circulation Control Materials, Lubricating Materials and Shale Stabilizing Materials. These materials gave the drilling fluid the needed properties to make the drilling process much easier.

R. James, ConocoPhillips Norge present the drilling fluids types in “Occupational Exposure Hazards Related to the Use of Drilling Fluids Presented with Remedial Risk Management Guidelines”. Drilling fluids divided to two groups, water based fluid (WBF) and Non-aqueous fluids. The water based fluid (WBF) consisted of 76% of brine/water, 14% of Barite, 6% of Clay/polymer and 4% of other. Non-aqueous fluids consisted of 46% of non-aqueous, 33% fluid Barite, 18% Brine, 2% Emulsifiers and 1% Gellants /other.

Non-aqueous fluids can be split into three groups based on their aromatic hydrocarbon content high-aromatic content fluids, medium-aromatic content, and low/negligible aromatic. As we can see the drilling fluid has a lot of water and our main goal is to decrease the waste water so that we will focus on the treatment of the drilling fluid.

3.3 Drilling Fluids Contamination

Hydrocarbon-based contaminants can be found because the formations drilled through to the reservoir contain hydrocarbons. Gases from formations are primarily composed of methane. Non-hydrocarbon gases can be founded because the formations can contain hydrogen sulphide (H_2S) gases and H_2S-containing water samples. Other gases like Carbon monoxide can be present particularly when coal beds are drilled but this occurrence is extremely rare.

3.4 Completion

Well completion commonly refers to the process of finishing a well so that it is ready to produce oil or natural gas. There are a number of types of completions like Open Hole Completion, Conventional Perforated Completion, Sand Exclusion Completion, Permanent Completion, Multiple Zone Completion and Drain-hole Completion.

3.4.1 Open-hole Completion

Open-hole completions are the most basic type and are used in formations that are unlikely to cave in. An open-hole completion consists of simply running the casing directly down into the formation, leaving the end of the piping open without any other protective filter. Very often, this type of completion is used on formations that have been ‘acidized’ or ‘fractured.’

3.4.2 Conventional Perforated Completion

Conventional perforated completions consist of production casing being run through the formation. The sides of this casing are perforated, with tiny holes along the sides facing the formation, which allows for the flow of hydrocarbons into the well hole, but still provides a suitable amount of support and protection for the well hole. The process of perforating the casing involves the use of specialized equipment designed to make tiny holes through the casing, cementing, and any other barrier between the formation and the open well. In the past, 'bullet perforators' were used, which were essentially small guns lowered into the well. The guns, when fired from the surface, sent off small bullets that penetrated the casing and cement. Today, 'jet perforating' is preferred. This consists of small, electrically-ignited charges, lowered into the well. When ignited, these charges poke tiny holes through to the formation, in the same manner as bullet perforating.

3.4.3 Sand Exclusion Completion

Sand exclusion completions are designed for production in an area that contains a large amount of loose sand. These completions are designed to allow for the flow of natural gas and oil into the well, but at the same time prevent sand from entering the well. Sand inside the well hole can cause many complications, including erosion of casing and other equipment. The most common methods of keeping sand out of the well hole are screening or filtering systems. These include analyzing the sand experienced in the formation and installing a screen or filter to keep sand particles out. The filter may be either a type of screen hung inside the casing, or a layer of specially-sized gravel outside the casing to filter out the sand. Both types of sand barriers can be used in open holes and perforated completions.

3.4.4 Permanent Completion

Permanent completions are those in which the components are assembled and installed only once. Installing the casing, cementing, perforating, and other completion work is done with small diameter tools to ensure the permanent nature of the completion. Completing a well in this manner can lead to significant cost savings compared to other types.

3.4.5 Multiple Zone Completion

Multiple zone completion is the practice of completing a well so that hydrocarbons from two or more formations may be produced simultaneously, yet separately. For example, a well may be drilled that passes through a number of formations as it descends; alternately, it may be more effective in a horizontal well to add multiple completions to drain the formation efficiently. Although it is common to separate multiple completions so that the fluids from the different formations do not intermingle, the complexity of achieving complete separation can present a barrier. In some instances, the different formations being drilled are close enough to allow fluids to intermingle in the well hole. When it is necessary to prevent this intermingling, hard rubber 'packing' instruments are used to maintain separation among different completions.

3.4.6 Drain-hole Completion

Drainhole completions are a form of horizontal or slant drilling. This type of completion consists of drilling out horizontally into the formation from a vertical well, providing a 'drain' for the hydrocarbons to empty into the well. In certain formations, drilling a drainhole completion may allow for more efficient, and balanced extraction of the targeted hydrocarbons. Drainhole completions are more commonly associated with oil wells than with natural gas wells.

In the Marcellus shale we use Conventional Perforated Completion and Drainhole Completion.

3.5 Casing

Conductor casing is usually no more than 20 to 50 feet long. It is installed to prevent the top of the well from caving in and to help in the process of circulating the drilling fluid up from the bottom of the well. The conductor casing is cemented into place before drilling begins.

Surface Casing is usually few hundred to 2,000 feet long, and is smaller in diameter than the conductor casing. The primary purpose of surface casing is to protect fresh water deposits near the surface of the well from being contaminated by leaking hydrocarbons or salt water from deeper underground. The Surface Casing is cemented into place too.

Intermediate Casing Used for deeper wells that penetrate over-pressured formations, lost circulation zones, unstable shale sections or salt sections

Production Casing is the casing that provides a conduit from the surface of the well to the petroleum-producing formation.

Cementing

Well cementing is the process of mixing and placing cement slurry in the annular space between casing and the open hole.

Chapter 4: Well Stimulation

4.1 Stimulation techniques

Stimulation techniques have evolved with the exploitation of unconventional gas reservoirs since the economic viability of unconventional-gas developments relies on effective stimulation of extremely low permeability rock, typically 10 to 100 nanodarcies (Cipolla L. Craig). As shale gas has grown to be one of the largest resource potential, stimulation process has shown continual innovation throughout the days. However, the most common method of well stimulation hydraulic fracturing is at the heart of controversy since it wastes huge amount of chemically treated water resource underground. Therefore, reducing the use of water resource and improving recovery rate of injected fluid while improving economic production is critical issue in developing unconventional gas reservoir.

4.2 The Hydraulic Fracturing

Hydraulic Fracturing involves the injection of pressurized water or has into the well, which creates new fractures in the shale and enlarges existing ones. The primary purpose of hydraulic fractured shale reservoirs is the extension of the drainage radius via creation of a long fracture sand pack that interconnects with natural fractures thereby establishing a flow channel network to the wellbore (J. Paktinat et al, 2007). This creates additional permeability so that improves production of gas. Fractures are created by pumping fracture fluid into the reservoir and slickwater and carbon dioxide are most well known fracture fluids. Among these fracture fluids, slickwater works best in low-permeability reservoirs, and have been the primary instrument in opening up unconventional plays if there is competitive water availability (T. Palisch et al, 2008). In the Appalachian area with its precipitation of approximately 43 inches receives 10 inches more per year than the average for the continental United Sates (Administration, National Oceanic and Atsompheric, 2005). In addition, there are many accessible consumptive water resources including lakes, rivers, private water sources, and municipal water near Marcellus shale thus slickwater hydraulic fracture treatment can be considered as the best fracture fluid in Marcellus shale reservoir.

4.3 Slickwater

Slickwater combines water with a friction-reducing additive allowing the water to be pumped faster into the formation. In addition to the cost advantage, slickwater treatments require less clueanup, provide longer fractures, and carry proppant further into the fracture network (J. Daniel, Brian Bohm, and Davd Cornue, 2009). Water is the primary component of slickwater fracture fluid. Generally, more than 90 percent of the fracture fluid is water. Figure 1 graphically demonstrates the relative amounts of the components in a fracture fluid used recently in the Fayettevill Shale; this fluid is 99.5 percent water with less than 0.5 percent other compounds (J. Daniel, Brian Bohm, and Davd Cornue, 2009). During the hydraulic fracturing process, after slug of slickwater with a friction-reducing chemical additive is pumped, the operator begins the fracturing process by pumping a large volume of slickwater with fine sand at low volume. Subsquent steps include the application of slickwater volumes with coarser sand proppant which keeps fractures closer to the wellbore open and a flush to remove proppant from equipment and wellbore (J. Daniel, Brian Bohm, and Davd Cornue, 2009). In those stages of slickwater process, a typical horizontal shale gas well is estimated to require between 3,000,000 and 4,000,000 gallons of water (J. Daniel, Brian Bohm, and Davd Cornue, 2009). *Figure 7* shows volumetric composition of typical fracture fluid slickwater. The process of developing Marcellus shale gas wells typically requires larger volumes of water than is necessary for conventional gas wells. Therefore, reducing required amount of water for fracturing treatment would provide great economical benefit.

4.4 Flowback Water

After a hydraulic fracture treatment, when the pumping pressure has been relieved from the well, the water-based fracturing fluids begin to flow back through the well casing to the wellhead (J. Daniel, Brian Bohm, and Davd Cornue, 2009). This water is referred to as flowback water and consists of spent fracturing fluids and, in some cases, dissolved constituents from the formation itself (minerals present in the shale as well as brine waters that may be present within any natural pore space contained in the shale). In various basins and shale gas plays, extent of this volume of flowback water may account for less than 30 percent to more than 70 percent of the original fracture fluid volume (J. Daniel, Brian Bohm, and David Cornue, 2009). In the most of

Marcellus sites, this flowback rate is estimated at 35 percent so that it draws major economical loss by re-supplying volume of fresh water for subsequent fracturing stages (A.W. Gaudlip and L.O. Paugh, 2008). Unrecovered fracture fluid which remains underground with hazardous chemical treatment also brings environmental challenges because it could flow into drinking water source. If we can improve flowback rate, this recovered fluid can be treated further for recycling. Therefore, enlarging recovery rate during flowback would increase positive impact while reducing negative effect.

4.5 Microemulsion (ME)

The primary purpose of surfactants used in stimulating sandstone reservoirs is to reduce surface tension of the fracturing fluid, decrease interfacial tension between injected fluid and reservoir rock and increase post-fracturing fluid recovery. The interfacial tension balance can be characterized as capillary pressure, which defined as

$$P_c = \frac{2\pi r \sigma Cos\,\theta}{\pi r^2} = \frac{2\sigma Cos\,\theta}{r} \qquad (1)$$

The term σ is the injected fluid/gas interfacial tension of the treating fluid in dynes/cm, or surface tension. θ is the contact angle of the fluid at the rock/fluid/gas interface and r is the pore throat radius (Penny, G. and J.T. Pursely, 2005). However, conventional surfactants when injected at high pressures adsorb rapidly into the sandstone formation, reducing their effectiveness in recovery of flowback water. Due to this problem, surfactants alone do not provide adequate water recovery properties for the reservoir in the Appalachian Basin which has low temperature, pressure and permeability (J. Paktinat et al, 2005). In addition, as illustrated in *figure 8,* it is possible that large quantities of injected fracturing fluid could be trapped in the area near the fractured proppant pack (Penny, G. and J.T. Pursely, 2005). This condition provides negative impact on gas production since it lowers relative permeability. However, when a microemulsion system is applied within fracturing fluids it minimizes the interfacial tension between the injected fluid and reservoir rock, overcoming the capillary forces that have trapped gas into the formation because microemulsion structures are carried to the interface faster and deeper into the proppant pack than a common surfactant (J. Paktinat et al, 2005). It in fact pentrates and disrupts the water structure on the rock surface. According to G. Penny, it has been observed that the contact angle is on the order of 60 degree or more (Penny, G. and J.T. Pursely, 2005). Since capillary pressure is a cosine θ function, the cosine of 60 degrees is 0.5. The benefit of this is that capillary pressure is reduced by 50% over any reduction associated with surface tension reduction. This means the injected fluid can be mobilized at half of the pressure. Figure 9 illustrates the fluid recovery data for the wells tested during case studies done at Appalachian Basin wells with the application of microemulsion technology (J. Paktinat et al, 2005). Recent field results also show that fluid recovery without microemulsion is from 15 to 30 percent while using the microemulsion resulted in 50 to 100 percent increase in load recovery in the Barnett shale (Penny, G. and J.T. Pursely, 2005). With this increased recovery rate, the micro emulsion treatments enables to use previous stage flowback fluids thereby reducing costs associated with transporting unnecessary fluids to job sites and the amount of polluted water remaining underground.

4.6 Proppant Transportation Modifier (PTM)

Another innovative technology beside microemulsion is proopant transportation modifier (PTM). Slickwater shale fracturing uses proppant transportation that depends on turbulent flow, sand banking and/or bed transport. Theses result in the majority of the proppant being deposited on the bottom of the created fracture, close to the wellbore, leaving a large portion of the created fracture length unpropped (N. Kostenuk, 2010). As seen in *figure 10 and 11*, this bed load transportation has very little proppant distribution outside the main fracture and leave large portion of the created fracture geometry remain unpropped (Cipolla C. et al, 2009). Since the majority of the reservoir's productivity comes from the propped portions of the created fracture, those unpropped portion remains to be potential loss. However, the use of a proppant transportation modifier (PTM) additive to the slickwater fluid has great performance in proppant distribution. As illustrated in figure 12 the PTM changes the proppant to an airphilic state, which creates a layer of micro-bubbles around each proppant grain and change the buoyancy of the proppant, allowing it to be transported in slick water without the use of viscosity or turbulent flow (N. Kostenuk, 2010). Since sand settling is drastically reduced by PTM, less proppant is required for the process thereby required amount of fluid which carries proppant can also be reduced. Also faster fracture fluid (lower completion cost) and increased production are achieved because PTM results in increase of conductivity and permeability as shown in *Figure 12* (N. Kostenuk, 2010).

Chapter 5: Osmotic Treatment

5.1 Reverse Osmosis

Reverse Osmosis is one of the most widely used water treatment and wastewater reclamation methods used in the industry. Reverse Osmosis is an engineered osmotic process, which uses hydraulic pressure to drive the transfer of water across a semi-permeable membrane. [Cath] Some of the limitations of Reverse Osmosis, that are the driving forces for research and development of Forward Osmosis processes, are the increasing costs associated with the energy needed to apply the hydraulic pressure and cost of membrane replacement due to fouling.

5.2 Forward Osmosis

The need to find a viable and economical water treatment and wastewater reclamation method, has led to the intensified research and development of Forward Osmosis. The majority of the literature focuses upon the utilization of Forward Osmosis to produce potable water from seawater. The focus of this literature review is to study the research and development advancements in Forward Osmosis to find a viable and efficient means for treating flow-back fracturing water from lateral gas wells from the Marcellus Shale in Bradford County PA. Forward Osmosis has garnered much recent research and development since the high costs of energy is making Reverse Osmosis increasingly less economical. The main driving force of Reverse Osmosis is the use of hydraulic pressure to increase the osmotic pressure and thus increase the mass transfer of water across a semi-permeable membrane. [Cath] This hydraulic pressure is driven by pumps that draw a significant amount of energy. The membranes used in Reverse Osmosis have to be designed to withstand the applied pressure yet, this design also makes the membranes more susceptible to membrane fouling. Membrane fouling reduces the life-span of the membrane, replacing the membrane before its life-span also adds to the increases costs associated with Reverse Osmosis.

Forward Osmosis is an appealing alternative for water treatment and wastewater reclamation. Chung et al. define why Forward Osmosis is appealing: Forward Osmosis is one of the unique and emerging technologies that can produce both clean energy and water drive by the osmotic pressure difference across a semi-permeable membrane." Forward Osmosis operates with no applied hydraulic pressures, it has a high rejection rate of contaminates, and it has a lower propensity for membrane fouling, in comparison to applied pressure driven osmotic processes. [Cath, Bamaga2011] Forward Osmosis is a engineered osmotic process that transports water across a semi-permeable membrane. Forward Osmosis uses an osmotic pressure gradient to induce the mass transfer of water across the membrane. The pressure gradient is generated by using a draw solution of one side of the membrane to create a higher osmotic pressure than the impacted water feed stream on the other side of the membrane. [McGinnis 2007] The osmotic energy intensity, P, which is the rate of energy responsible for establishing water flow can be expressed as:

$$\mathrm{P} = \mathrm{q}\Delta\pi \qquad (1)$$

where q is the water flux through a membrane and $\Delta\pi$ is the pressure difference across the membrane [Bamaga 2011] Bamagea et al. [2011] define how to determine the pressure difference, $\Delta\pi$ across a Forward Osmosis membrane as:

$$\Delta\pi = \pi_{\mathrm{DS}} - \pi_{\mathrm{feed}} \qquad (2)$$

where π_{DS} is the osmosis pressure of the draw solution in Pa and π_{feed} is the osmosis pressure of the feed water in Pa. “The general equation for explain water transport in osmotic processes is defined as:

$$\mathrm{Jw} = \mathrm{A}(\sigma\Delta\pi - \Delta\mathrm{P}) \qquad (3)$$

where Jw is water flux, A the water permeability constant of the membrane, σ is the reflection coefficient, and ΔP is the applied pressure.” [Lee 1981] Figure 13 which was adapted from Lee et al. by Cath et al.[Cath] showing the flux directions and driving forces of three osmotic processes: forward Osmosis, reserve osmosis and the pressure retarded osmosis.

5.3 Pressure-retarded osmosis and Reverse Osmosis.

Direction and magnitude of water flux as a function of applied pressure in FO, PRO, and RO. FO takes place when the hydraulic pressure difference is zero. The PRO zone is where the applied pressure difference is between zero and the flux reversal point, and the RO zone is where the applied pressure difference is greater than the osmotic pressure difference. Figure adapted from [Lee 1981]

5.4 Draw Solution

The driving forces for Forward Osmosis is the concentrated draw solution on the permeate side of the membrane. [Cath] Early draw solutions and membranes used for draw solutions have been varied from salt water, to sugars to dissolved gases and salts. Kravath and Davis [McCutcheon 2007] used glucose as draw solutions for Forward Osmosis. Stache [McCutcheon 2007] experimented with draw solutions sucrose. Those who designed experimental Forward Osmosis experiments during the late 1990s and early 2000s utilized draw solutions involving salt solutions (NaCl and MgCl2)[McCutcheon 2007] Glew [McCutcheon 2007] and McGinnis [McCutcheon 2007] experimented with draw solutions by mixing gas SO2 with alcohols and potassium, respectively. Elimelech et al. [McCutcheon 2007] designed a draw solution utilizing the water-soluble mixture of ammonium bicarbonate. Ng et al.[McCutcheon 2007] also experimented with the ammonium bicarbonate draw solution. Yen et all [2006] experimented with organic compounds as draw solutions. Achilli et all. [2010] studied inorganic based draw solutions for possible use in Forward Osmosis applications. [McCutcheon 2007] shows some of the historical researches regarding the experimental design of Forward Osmosis processes. Table 1 [Achilli 2010] shows some of the more widely used draw solutions and the costs of those draw solutions. Figure 14 [Achilli 2010] depicts a schematic flow chart of how to select an inorganic compound for use as a draw solution that is suitable for Forward Osmosis application. This flow chart could be reworked to help someone select a draw solution applicable for a specific Forward Osmosis application, since this flow chart contains selection biases based upon all of the desirable characteristics for a Forward Osmosis application. McCluthceon et all. [McGinnis 2007] and McGinnis [McGinnis 2007] outlined the necessary characteristics of a draw solution to be used in a Forward Osmosis application. The draw solution must have high osmotic efficiency, must have a low molecular weight in order to generate high osmotic pressure, zero-liquid discharge, non-toxic, chemically compatible with the membrane, must be easily separated from potable water, and must be recyclable to be used over again. Ammonium bicarbonate is a novel draw solution for Forward Osmosis process for treatment of brackish water. [McGinnis 2007] Ammonia (NH3) and carbon dioxide (CO2) are two highly soluble gases that meet the criteria for an idea draw solution. This draw solution is also easily and economically separated from potable water using moderate heating distillation [McGinnis 2007] McClutcheon et al. [McGinnis 2007] Figure shows the results reported by with the recovery rates and generated osmotic pressure obtained by using ammonia- bicarbonate as a draw solution. An overview of researchers on the forward osmosis process with different recovery methods by using cellulose acetate type membranes is presented in Figure 15[McCutcheon 2007]

McGinnis [2007] explained the draw solute recovery method used by McCluthcehon et. al.[2006] in their novel ammonia-bicarbonate draw solution in Forward Osmosis along with other methods that could be used to recovery draw solutions. Table 2 allows for a comparison of energy requirements of current seawater desalination technologies to the ammonia-carbon dioxide forward osmosis process, also a quick overview of potential recovery methods and the costs associated with each method were analyzed.

5.5 Membrane Selection

One of the most limiting features of Forward Osmosis is that of the membrane. The majority of membranes used in Forward Osmosis applications and experimental designs were originally designed for Reverse Osmosis applications. [Wong 2010] Membranes designed for Reverse Osmosis applications are designed with a thin selective active layer which is supported by thick layers made of polymers and fabric [Wong 2010]. Currently there are only two companies that manufacture membranes specifically for Forward Osmosis operations - Hydration Technologies Inc. (HTI) [Wong 2010] and Catalyx Inc. [Wong 2010]. The HTI membrane is composed of cellulose triacetate supported by embedded polyester screens. [Wong 2010] SEM images of the HTI Forward Osmosis Membrane. Experimental research has shown lower Forward Osmosis flux than expected and this is due to concentration polarization (internal(ICP) and external(ECP)) Some of the key factors for designing an effective Forward Osmosis membrane are: producing a membrane that minimizes internal concentration polarization [Wong 2010], the chemistry and structural of the membrane [Bamga 2011],and membrane configuration, with respect to feed and draw streams [Bamga 2011] When Forward Osmosis tests were conducted using a HTI membrane, flux performance significantly greater than that of conventional Reverse Osmosis membranes [4,38,39,40] The increase in flux is due to the reduction of internal concentration polarization (ICP) since the thick fabric layers that are seen in Reverse Osmosis membranes are not present in the HTI membrane. Even with this increased flux with the RTI membrane, there still needs to be further advancements in Forward Osmosis membrane design. The desired attributes for a membrane to be used in Forward Osmosis processes are: dense ultra-thin active layer with high water permeability and low solute permeability , a thin and porous support layer to reduce internal concentration polarization, reduce the chance of membrane fouling by designing the membrane to be hydrophilic and to increase the lifetime of the membrane, ensure that the membrane has high mechanical strength [Wong 2010] Current literature shows two experimental design Forward Osmosis membranes [Wong 2010] Both of these membranes are designed hollow fiber membranes. Wong et al. [2010] have designed two hollow fiber thin film composite membranes for use in Forward Osmosis processes. Figure 17 shows SEM photographs of their two membranes. Wong et al. [2010] data have show that their #B-FO membrane achieves high water flux of 32.2 L/m2, according to open literature this membrane is the best Forward Osmosis membrane design. Wang et al. [2010] have also designed a hollow fiber membrane that utilizes Polybenzimidazole(PBI) nanofiltration for Forward Osmosis applications. Figure 18 shows the PBI nanofiltration hollow fiber membrane. Wang et al. [2010] data have shown that this membrane has high water flux and salt selectivity, and thus another promising candidate for effective Forward Osmosis commercially manufactured membranes. Figure 19 illustrates SEM photographs of various FO Membranes.

Research by Gray et. Al. has shown the importance of membrane orientation for decreasing internal concentration polarization, increasing water flux, and thus increasing the efficiency of Forward Osmosis membranes. Figure 20 shows how the flux varies with the same membrane, but having the draw solution fixed on different portions of the membrane. Membrane orientation is show to have significant impact upon the performance of the membrane. [Wang 2010] Table 3 [Gray 2006] shows the results of different draw solutions and different membrane orientation, which leads to the conclusion that the membrane orientation should be dependent upon the Forward Osmosis application [Gray 2006] Another important consideration to Forward Osmosis design is that which Membrane Module to utilize. There are three current designs to consider: Plate and Frame which is the simplest device for packing and sizing flat sheet membranes for forward osmosis applications; Spiral-wound, mainly seen in Reverse Osmosis operations where only one stream is flowing tangential to the membrane; and Tubular, which is the most desirable membrane module for three reasons. Tubular membranes are the most desirable membrane module for Forward Osmosis applications since the process will be run continuously, the tubular membranes are self-supporting and finally because it allows liquids to flow freely upon both sides of the membrane (a necessary flow pattern for Forward Osmosis)

The focus of this design is to apply Forward Osmosis to waste fracture water reclamation. It is important to analyze the current Forward Osmosis applications so that a system can be designed and executed. There are limited commercial applications of Forward Osmosis, but those applications are across diverse fields of study. Forward Osmosis has been used in industrial wastewater treatment. The goal of Forward Osmosis was to provide a low energy means of removing heavy metals from potable water [Cath 2007] One of the drawbacks of this application, is the use of Reverse Osmosis membranes in this Forward Osmosis design. Forward Osmosis is used to treat the brackish landfill leachate. Forward Osmosis has shown an affinity to capture a wide variety of materials from the leachate [Cath 2007] Table 4 show the general contaminates found in landfill leachate and how effective was the Forward Osmosis process. NASA is studying the feasibility of a FO/RO process for long-term human space missions. Since the astronauts have a limited amount of potable water, it is important to have an economic and effective means of wastewater treatment. [Cath 2007] The food industry uses Forward Osmosis for the concentration of liquid beverages [Cath 2007]. The pharmaceutical industry uses forward osmosis in osmotic pumps as a means of delivering medications when the oral route is not effective. [Cath 2007] Figure 21 shows a osmotic pump used in the pharmaceutical industry [Cath 2007]

A polyurethane membrane covers one end of the reservoir. The osmotic engine (i.e., the draw solution) occupies a portion of the cylinder behind the membrane. An elastomeric piston separates the draw solution from the drug formulation in the drug reservoir. Upon diffusion of water into the osmotic engine, the piston is pushed and the drug is released through the drug outlet orifice

5.6 Hybrid method: Forward Osmosis/Reverse Osmosis.

Since membrane technology for Forward Osmosis is limited and the increasing costs of Reverse Osmosis, has led to feasibility studies of the potential of using a hybrid FO/RO process for the treatment of seawater and wastewater. The goal of this process is to reduce the amount of cost associated with reverse osmosis, by using Forward Osmosis to concentration the feed stream prior to Reverse Osmosis. [Bamga 2011] This process would reduce the costs associated with the pressure required by Reverse Osmosis, because the pretreatment with Forward Osmosis requires no applied hydraulic power [Bamga 2011] show schematic drawing for experimental FO/RO designs [Bamga 2011] Advances in Forward Osmosis membrane technology will not only increase the effectiveness of Forward Osmosis process but also the FO/RO processes. The FO/RO hybrid process is aimed at reducing the costs of desalination for seawater, and by NASA for wastewater treatment for long space missions.

Chapter 6: Renewable Energy Generation

Renewable energy refers to energy that is inexhaustible and can be replenished naturally over a relatively short period of time. Renewable energy can be generated from a large variety of sources and the major sources for renewable energy include the wind, rain, tides, waste (water), sunlight, geothermal heat, and biomass.

6.1 History

Looking as far back as the early age of the human race, it is quite evident that renewable energy resources were already in use. Besides generating and controlling the use of fire, early humans clearly utilized the abundance of natural energy resources: water, wind, sun, and even geothermal heat. A lot has been documented over the past years on various events that clearly indicated the use of these natural resources to generate energy. The use of sunlight for making fire is indicated in the writings of Lucian of Samosa in the 2nd century AD. He wrote that Archimedes resisted the Roman attack with a burning-glass during the Seige of Syracuse (3rd century BC). Even solar architecture has been in used as far as 2500 years ago by most early civilizations. These ancient civilizations made use of solar, wind and water energy to condition their living areas, making them more conducive for living, especially during adverse weather conditions. The ancient Greeks developed techniques that utilized solar energy to stay warm during the winter season, reducing their dependence on firewood, and to cool their homes in hot summers respectively. One of the most ancient and sophisticated examples of ancient solar architecture can be found at the Pueblo Indian city of Acoma in North America. Wind has been used for centuries for propelling ships and to operate windmills. Rivers have turned water wheels for millennia-the Romans even used geothermal energy for water heating- and water energy has also been used for water-mills. Two basic kinds of water mills were known in medieval Europe; one was simple and portable but inefficient (Figure 22) while the other was complex, not portable, and far more efficient. The complex (vertical) mill (Figure 23) was more common England, northern France and Germany, and by Domesday Book in 1086, it had completely replaced the simple (horizontal) mills.

6.1.1 Renewable Energy Today

Modern renewable energy technology dates from the second half of the 19th century, although some early research breakthroughs in the 18th century greatly set a foundation for present day technologies. Horace de Saussure, a noted Swiss naturalist, observed in the 1760s, "It is a known fact, and a fact that has probably been known for a long time, that a room, a carriage, or any other place is hotter when the rays of the sun pass through glass. To determine the effectiveness of trapping heat with glass covers, de Saussure built a rectangular box out of half-inch pine, insulated the inside, and had the top covered with glass, and had two smaller boxes placed inside. When exposed to the sun, the bottom box heated to 228 degrees F (109 degrees C) or 16 degrees F (9 degrees C) above the boiling point of water (Figure 24).

de Saussure was unable to explain how this heat was generated. Today this technology is better explained, whereby sun rays that penetrated the glass covers got absorbed by the black inner lining and converted it into heat. Clear glass allows sun rays to easily penetrate through it, but prevents heat from doing same, as such the trapped sunlight in the box heated up. And today, indeed, the hot box has become the prototype for the solar collectors that have provided sun-heated water to millions since 1892.

With the present high demand for energy all over the world, new technologies have focused on techniques to capture and store dispersed renewable energy potential into more concentrated and efficient forms. A lot of breakthrough has been made in almost all sources of renewable energy. Sophisticated technologies have made it possible for engineers to generate large amounts of energy (geothermal energy) from the very c enter of the earth. Wastes have also been used to generate large amounts of energy; in California today the three primary sources of biomass energy are agricultural wastes, forestry wastes, and municipal wastes. In the August issue of the Journal of Energy Engineering, it was published according to University of Toronto research, that the energy stored in Toronto's municipal wastewater could be harnessed to run water treatment facilities and contribute power to the city grid. In Pennsylvania, the Susquehanna River and several smaller river basins offer considerable hydropower resources and the Appalachian and Allegheny mountain ranges are areas of high wind power potential.

To solve our present energy needs, big energy companies as well as government agencies have directed a percentage of their resources towards developing the renewable energy sector. KGRA Energy Corporation has received a $750,000.00 grant from the State of Pennsylvania's

Department of Environmental Protection towards the construction of waste heat-to-power project. The new cogeneration facility will be located in Bradford County, Pa. and will harvest the heat from reciprocating engines at a natural gas compression station currently under construction by a major US natural gas company. It will produce approximately 1.26MW of clean renewable electricity from a generator linked to an organic Rankine cycle power system. At least 83 countries have some type of policy to promote renewable power generation. The most common policy is the feed-in tariff, which has been enacted in many new countries and regions in recent years. By early 2010, at least 50 countries and 25 states/provinces had feed-in tariffs, more than half of these adopted only since 2005. Strong momentum for feed-in tariffs continues around the world as countries continue to establish or revise policies. States and provinces have been adopting feed-in tariffs in increasing numbers as well. Renewable energy has an important role in providing modern energy access to the billions of people in developing countries that continue to depend on more traditional sources of energy, both for households and small industries. The number of rural households served by renewable energy is difficult to estimate, but runs into the tens of millions considering all forms of renewables. Micro-hydro configured into village-scale or county-scale mini-grids serves many of these. More than 30 million households get lighting and cooking from biogas made in household-scale digesters. An estimated 3 million households get power from small solar PV systems. Biomass cookstoves are used by 40 percent of the world’s population.

In the US in 2008, renewable energy sources accounted for about 7% of all energy consumed, and this accounted for about 9% of the country’s total electric power production. In this same year the consumption of renewable energy in the US could be broken down as follows:

• Hydropower	34%
• Biomass Wood	28%
• Biomass Waste	6%
• Biomass Biofuels	19%
• Wind	7%
• Others	6%

From this analysis we can clearly see that hydropower is the most exploited renewable energy resource in the US. Globally, the use of hydroelectricity and other grid-connected renewable energy sources should gradually increase over the years, at a rate of 3.0% per year until 2030, according to the EIA (Energy Information Administration).

Looking at all the renewable energy resources, it is quite evident that these resources have been exploited over the years-even in the early age- for one major reason; to meet our energy demands. But unlike in the early age, in present times, exploiting renewable energy resources has become almost imperative, considering the deadly human and environmental impacts present day activities on non-renewable energy generation has caused to the earth. The earth now experiences harsh climates as well as a disastrous rate of pollution, which has greatly disrupted the ecosystem, and even destroyed the ozone layer. Climate change concerns, coupled with high oil prices, peak oil, and increasing government support, are driving increasing renewable energy legislation, incentives and commercialization. New government spending, regulation and policies helped the industry weather the global financial crisis better than many other sectors.

The traditional design elements for maintaining comfort in hot and humid climate such as screens, water sprinklers, ventilators, skylights, chowks, verandas and windows that could aid night radiation, cooling and control thermal mass have been discarded with the availability of cheap fossil fuels that could provide artificial control of the built environment. A return to a more natural lifestyle is the need of the hour.

Until the middle of the 18th century and the discovery of fossil fuels, renewable sources were the only sources of energy available to man.

Excessive use of fossil fuels has caused global climate change which has became obvious in the last few decades and has forced people and governments throughout the world to seriously reconsider the replacement of fossil fuels with renewable energy sources.

6.2 Blue Energy

Blue energy is a term used for describing the energy or electricity generated from the chemical processes that occur when both fresh and salt water converge. Due to the chemical processes involved, blue energy is also referred to as osmotic energy or salinity gradient energy. The term salinity-gradient energy indicates the theoretical non-expansion work that can be produced from mixing two salt solutions with different concentrations. The term osmotic energy is derived from the osmosis process. Osmosis means passage of water from a region of low solute concentration (high water concentration) to a region of high solute concentration (low water concentration) through a semi-permeable membrane. This semi-permeable membrane only lets water molecules pass, while salt molecules, sand, silt and other contaminants are prevented to do so. Several physiological processes use this osmotic effect. For instance, our body uses it to bring water back from the kidneys, and plants use osmosis to keep the water pressure inside the plant at a fixed level. Blue energy is a type of water energy which capitalizes on osmotic processes or salinity-gradient effects. It is also referred to as ocean energy since it can be extracted through a variety of ocean supported activities such as tidal power, current power, wave power, and even wind power associated with the body of water.

6.3 Literature

The need for new and more efficient energy sources has led to a number of alternatives. In order to tackle the harmful effects of energy generation and utilization, energy supply research and advancements have been made based on the following perspectives; a renewable energy source and an environmental-friendly non-combustion energy conversion. With this primary goal, blue energy emerged, since it completely fulfils this objective.

Salinity-gradient energy is a renewable energy source that only dates back to the first half of the 20th century. It was mentioned that besides the gravitational potential, the natural runoff in coastal areas possess an excessive physical-chemical potential. This excessive potential was a result of salinity-gradient between the mainly-fresh runoff waters (at river mouths) and the receiving mainly-saline reservoirs such as seas and oceans. This natural occurrence is irreversible and no work is attained. From this process, if some reversibility is partly implemented, work can be obtained from the mixing process, hence producing energy. In literature, it was assumed that from each cubic meter of river water 2.3 MJ of work could be extracted. In 1954 Pattle suggested the use of the osmotic pressure differential between river water and sea water to generate power and actually constructed an apparatus that produced power. According to Norman: “The tremendous energy flux available in the natural salination of fresh water is graphically illustrated, if one imagines that every stream and river in the world is terminated at its mouth by a waterfall 225 m high”. As an example, keeping in mind the words of Norman, Westus researchers ,at the Westus Dutch research institute, believe the 30-km long Afsluitdijk that dams up the river mouth of the river IJssel (a distributary of river Rhine) becomes comparable to a huge power dam of over 200 m high (Figure 25). The 1,100-km2 Lake IJssel (the artificial estuarine reservoir of river IJssel) becomes comparable to an enormous energy reservoir with over a billion cubic meter storage capacity (assuming a level difference of only 1 m) (J.W. Post 2009).

From available literature, relatively minimal research has been done on this very promising source of energy. The present constraints in membrane technologies, and the excessive cost in building a blue energy plant, have greatly discouraged investors. Cost-effectiveness has also been a major concern to Hans de Wit, professor of electrochemistry at the Delft University of Technology. In 2007, De Wit and other scientists wrote an energy report for the Royal Dutch Academy of Science entitled "Sustainability Lasts Longest." The report was critical of blue energy. "An enormous effort is required to get [blue energy] to work effectively," the authors stated. "Such a huge effort for such a small contribution simply makes no sense." One major factor why blue energy still stands strong as the future of clean energy is the that globally available power in form of salinity gradients has been estimated in the 1970s (on the basis of average ocean salinity and annual global river discharges) to be between 1.4 and 2.6 TW . 1.4 TW (12,279 TWh/y) should be able to satisfy over 80% of the current global electricity demand (which is over 15,746 TWh/y)(Isaacs, J.D. and W.R. Schmitt 1980)

But over the years some optimistic researchers kept up their work in making blue energy a reality. Jan Willem Post greatly did some breakthrough research in his 2009 PhD thesis work; ‘Blue Energy: electricity production from salinity gradients by reverse electrodialysis’. From his work, Post clearly visualizes the promising prospects in blue energy, especially for Netherlands where salinity gradients could can become a significant source of energy, lead to a strong recommendation to policy makers, captains of industry, and principal scientists to proceed with research and development of reverse electrodialysis. Post and his colleagues prospect that within a decade or so, they hope blue energy will produce a significant share of the Netherlands' electricity. Theoretically, the amount of energy available from mixing 1 cubic meter of sea water (comparable to 0.5 mol/L NaCl) and 1 cubic meter of river water (comparable to 0.01 mol/L NaCl) both at a temperature of 293 K, is 1.4 MJ (J.W. Post 2009).

With the breakthrough in research, such as that of Post, De Wit sees potentials in blue energy. "It presents real opportunities," he says. "My only point is, let's not make it more than it is. I see very interesting, small-scale applications, primarily in areas where there are no power plants nearby." On that, De Wit and Post agree. "Our motto is, 'Use it where you can,'" Post says. "If blue energy can be used with existing infrastructure, or if the necessary infrastructure can be relatively easily built, it's a great supplement to other sustainable energy sources." Many other big companies as well as governments have already commenced large scale developments of blue energy. In Ostend, in Belgium, a cooperative agreement was signed by the University of Ghent and six Flemish enterprises, signalling the start of the FlanSea project – a so-called "blue energy" project that, in the future, is meant to ensure the sustainable and reliable production of electrical power based on wave energy. In support of its endeavours, the FlanSea research project has received a subsidy from the IWT in the amount of EUR 2.4 million.

6.4 Methods of Blue Energy generation

There are three major methods to generate blue energy and these methods are:

- The Salinity Gradient Solar Pond Method (SGSP)
- The Reverse Electrodialysis Method (RED)
- The Pressure Retarded Osmosis Method (PRO)

6.4.1 The Salinity Gradient Solar Pond Method (SGSP)

This is a technology, whereby a man-made pond collects and stores thermal energy due to density differences between the three layers that make up the pond (as illustrated in the figure 26. The upper convection zone is the uppermost zone, followed by the stable gradient zone, then the bottom thermal zone. The stable gradient zone is the most important. Water in this layer cannot rise to the higher zone because the water above has lower salinity and is therefore lighter and it cannot sink to the lower level because this water is denser. This middle zone, the stable gradient zone, becomes an insulator for the bottom layer. Sunlight is absorbed by the salty water and lining, heating the lower layers of the pond. This water from the lower layer, the storage zone, is pumped out and the heat is used to produce energy, usually by turbine. This method has already been implemented commercially in the Eddy Potash Mine in New Mexico that utilizes this technology to provide the energy needed by the mine.

The technology behind this method is not very complex and makes it very easy to build. When it comes to the disadvantage, one major limitation is the viability of this method in just very hot areas such as deserts. This factor makes this method very selective considering the fact that water -which is the major requirement for blue energy generation- is usually not available in very hot areas. Another major consideration of this method is the possibility of salt water leaching into fresh ground water. For this reason, solar ponds should not be built above moving ground water that is close to the surface. In many cases, a liner is necessary to contain the brine. These disadvantages make this method unfavorable for our system since our location (the Bradford County) is not in a desert or very hot region and the possibility of salt water leaching becomes very realistic due to the presence of a lot of fresh ground water.

6.4.2 The Reverse Electrodialysis Method (RED)

This method is centered on the theory of electrodialysis whereby salt ions are transported from one solution through ion-exchange membranes to another solution under the influence of an applied electric potential difference. The ion exchange membranes are of two types; the cation exchange membrane (CEM) and the anion exchange membrane (AEM), and these membranes are the most important component of this technology. A salt solution and fresh water are let through a stack of alternating cathode and anode exchange membranes. Salt water separated from fresh water between two such membranes will lose both positive ions and negative ions. This is shown in the figure 27.

This charge separation produces a potential difference and as a result, electrons can be transferred from anode to cathode via an external electric circuit. This electrical current and the potential difference over the electrodes can be used to generate electrical power, when an external load or energy consumer (e.g., a light bulb) is included in the circuit. The driving force for the migration of ion is a difference in free energy between the concentrated and the diluted solution side and the voltage obtained depends directly on the number of membranes in the stack. This is the method being investigated in the Netherlands, and Westus-a Dutch water technology research institute- has been working on harnessing blue energy by means of RED.

Over the years, very little breakthrough has been done on this method. This method design is very complex, and its high dependence on the number of membrane (Joost Veerman, 2010) creates a major size constraint, considering the little power that can be generated from a 1 cubic meter of membrane. Another major concern of this method to our design is the salinity concentration of the waste water. There is a limit on applicable salt concentrations in the concentrated brines, which is in accordance with the observation that the power density has a non-linear response to increasing electrochemical potential (which is the result of a decreasing permselectivity with increasing salt concentrations)(Post et al, 2007). As such the very high salt concentrations of the waste water will not be favorable for this method.

6.4.3 Pressure Retarded Osmosis (PRO)

This method unlike the others, centers on the pressurization of water. Two solutions of different salinity are brought into contact by a semi-permeable membrane. This membrane allows the solvent (i.e., water) to permeate and retains the solute (i.e., dissolved salts). The chemical potential difference between the solutions causes transport of water from the diluted salt solution to the more concentrated salt solution (Figure 28). If hydrostatic pressure is applied to the concentrated solution, the water transport will be partly retarded. The transport of water from the low-pressure diluted solution to the high-pressure concentrated solution results in a pressurization of the volume of transported water which can be used to generate electrical power in a turbine. The figure below illustrates this technology.

Norway (State-owned utility Statkraft's prototype plant) opened on Tuesday the 24th of November 2009, the world's first osmotic power plant, which produces emissions-free electricity by mixing fresh water and sea water through a special membrane.

Just like the other methods, the principal driving force in this method is salinity gradient. This is a very practical method and the design is very much less complex when compared to the other methods. The comparatively vast implementation of this technology (especially in the desalinity industry) is an indication of its relative viability. The major concern of this method is the membrane technology. Our water treatment section of this design focuses on the osmosis theory and osmosis membrane technology and as such makes the PRO method very viable for our design.

6.5 The theory of the Osmotic process

Osmosis is the transport of water across a semipermeable membrane from a solution of higher water concentration (lower osmotic pressure) to a solution of lower water concentration (higher osmotic pressure). This movement across this membrane is driven by a difference in solute molar concentrations across a membrane that allows passage of water, but rejects most solute molecules and ions. There are 3 major osmotic processes and they are Forward Osmosis (FO), Reverse Osmosis (RO) and PRO –which we are implementing in our blue energy system.

The osmotic pressure differential ($\Delta\pi$) is the pressure which, if applied as a hydraulic pressure (ΔP) to the more concentrated solution, would prevent net transport of water across the membrane. FO uses the $\Delta\pi$ across the membrane, rather than a ΔP (as in RO), as the driving force for transport of water through the membrane. The FO process results in concentration of a feed stream (which in the case of our system is the less salty water) and dilution of a highly concentrated stream usually referred to as the draw solution (which in the case of our blue energy system is the waste water). Flux in FO is in the opposite direction of RO. PRO can be viewed as an intermediate process between FO and RO, whereby hydraulic pressure is applied to the draw solution but the net water flux is still in the direction of the concentrated draw solution. The general equation describing water transport in forward osmosis (FO), reverse osmosis (RO), and PRO is:

$$J_w = AJ_w(\Delta\pi - \Delta P) \tag{1}$$

(where J_w is the water flux and A is the water permeability coefficient of the membrane)

For FO, ΔP is zero; for RO, $\Delta P > \Delta\pi$; and for PRO, $\Delta P < \Delta\pi$.

The flux directions of the permeating water in FO, PRO, and RO are illustrated in the figure 29. The orientation of an asymmetric membrane is also indicated; in FO, the dense layer of the membrane faces the feed solution and in RO and PRO, the dense layer faces the draw solution.

In PRO, the power that can be generated per unit membrane area (i.e., the power density) is equal to the product of the water flux and the hydraulic pressure differential across the membrane:

$$W = J_w \Delta P = \mathrm{A}(\Delta\pi - \Delta P)\Delta P \tag{2}$$

By differentiating Eq. (2) with respect to ΔP, it can be shown that W reaches a maximum when $\Delta P = \Delta\pi/2$. Substituting this value for ΔP in Eq. (2) yields:

$$W_{max} = \mathrm{A}\,\frac{\Delta\pi^2}{4} \tag{3}$$

J_w as a function of ΔP is illustrated in the figure below for both real and ideal conditions. The FO point (at $\Delta P = 0$), the PRO zone (where $\Delta P < \Delta\pi$), and the RO zone (where $\Delta P > \Delta\pi$) are indicated. The flux reversal point occurs where $\Delta P = \Delta\pi$. W and W_{max} in the PRO zone are also illustrated in Figure 30.

7.0 ECONOMIC ANALYSIS

According to estimates generated by Deutsche Bank, the range of internal rate of return (IRR) for the Marcellus Shale is 72–100%. IRR is a capital budgeting metric used by firms to decide whether they should make investments. It is an indicator of the efficiency or quality of an investment, as opposed to net present value (NPV), which indicates value or magnitude. The IRR is greater for the Marcellus than for other US shales, they concluded, because of premium natural gas pricing due to location and relatively low royalties in Appalachia. In addition, the Marcellus is estimated to have the lowest break-even price ($3.17) when compared to the Haynesville, Barnett, Fayetteville and Woodford Shales. The next-closest break-even price was $4.73 in the Haynesville. These break-even prices come from the NYMEX natural gas prices required to drive the individual plays' returns down to a 10% weighted average cost of capital. Notably, this study states that the five plays analyzed represent the "best of breed" among US shale plays, and one would not expect most other shale and tight gas plays to compare to these strong metrics. Woodford, Fayetteville and Haynesville gas production is currently increasing greatly while the Marcellus Shale is not predicted to really take off until about 2011. The slower transition in the Marcellus is due to the difficult terrain, uncertain regulatory environment and lack of infrastructure and proper equipment. The problem with typical Marcellus Shale wells is the lack of gathered information and information that is commercially available to the public (Rohan Belvalkar,2009).

A study was conducted using a reservoir modeling software package to investigate the gas production from the Marcellus Shale. The objective was to compare and contrast the gas production in vertical and horizontal wells with varying fracture half-lengths and horizontal lateral lengths. The reservoir modeling and simulation were conducted using Marcellus Shale properties to calculate gas production rates to determine economic feasibility. Once all of the production data was simulated, an economic analysis was conducted to determine the optimal designs for the parameters studied. A cash flow model was constructed for all of the simulated runs. Once the cash flow charts were constructed, NPVs were calculated along with IRRs. These two values were used to analyze the economic feasibility of the design parameters considered. The main parameters needed were capital and operating expenses, interest rate and gas price. The results of the economic analysis for all $3/Mcf wells showed 18 of the 74 cases studied to be economic designs. The final results showed that no single-fracture-treated horizontal or vertical wells were economic. Only the 1,000-ft fracture half-length with three fracture stages was economic regardless of lateral length or spacing. The same was true with five fracture stages, except that, in those cases, 750-ft and 1,000-ft half-lengths were economic regardless of lateral length and spacing. As for seven and nine fractures, 500-, 750- and 1,000-ft half-lengths were economic regardless of lateral lengths. Wells with larger numbers of fracture stages had higher IRRs. In addition, well designs with the same number of fracture stages had higher IRRs with longer fracture half-lengths; yet, when the different lateral lengths were considered, the shorter lateral lengths actually had higher IRRs with the same number of fracture stages. The results for all $6/Mcf cases differ quite a bit from the $3 gas pricing results (A. Agrawal,2010).Due to the price change, 24 more of the original well and fracture designs became economical. Now vertical wells become economical with 750- and 1,000-ft fracture half-lengths regardless of the number of stages. Also, three- and five-stage fracture treatments now become economical in all fracture half-lengths except 250 ft. Once again, the well designs with larger numbers of fracture stages had higher IRRs. Also, for well designs with the same number of fractures, higher IRRs were found with longer fracture half-lengths. Yet, when analyzing the different lateral lengths, the shorter lateral lengths actually had higher IRRs. When the number of fracture treatments increases, and for each number of fracture treatments, the half-length increases from left to right. It can easily be seen that the larger the number of fracture stages and the greater the fracture half-length, the larger the profit and the more economical the well. The red bars indicate wells studied at the $3/Mcf gas price, and the blue bars indicate $6/Mcf. For wells with seven fracture stages, the only economical results were with half-lengths of either 500, 750 or 1,000 ft regardless of length of the wellbore for $3 gas pricing. All of the wells with seven fracture treatments were economical at $6/Mcf. As the number of fractures and half-length increase, the IRR increases as well. As for the difference in lateral lengths, it is very small, but it actually doesn’t pay to drill the extra 1,000 ft of wellbore if you are not going to add additional fracture stages. This actually made the shorter wellbores more cost-efficient over the time period studied. Horizontal wells were found to be more economic when compared to vertical wells. Vertical wells were found to be economic in the higher gas pricing scenario. In general, the optimal designs had a fractured half-length of 1,000 ft and the maximum number of fracture stages .As far as the lateral length was concerned, it was not cost-efficient to drill longer laterals if the number of fracture stages was not going to be increased, but it was cost-efficient if more fracture stages were added

(TABLE 5). As expected, much higher IRRs were found with the higher gas pricing. Higher gas prices allow more exploration in vertical wells or smaller-scale horizontal wells due to the lower initial cost. There was no direct trend, but some IRRs increased dramatically due to the gas price change (R. Schweitzer,2009). Ultimately, in the Marcellus Shale, the more money spent up front with larger fracture jobs, the more economic the results appear to be (TABLE 6).

After acquiring approvals from SRBC, we can submit the drilling permit application, which was discussed in the literature review. This application has also a fee associated with it. Prior to February 2009 it was only $100 per well regardless of the specification of the well, however since then it has changed and now it is calculated based on the depth and length of the well. In this project with D=6000 ft and L= 4000 ft the application fee was calculated to be $2150 (Armstrong Agbaji, 2009).

In Bradford County, the depth is 5,500 ~ 6,500 feet with 4000 ft - long lateral length. The average cost for making a horizontal well is 3.5 million ~ 4.0 million. This single well cost includes rigs leasing cost which is around $22,000 per day. Also, this cost includes pad construction, water truck traffic, infrastructure building, gas pipelines and local hiring. It should be noted at this point that this cost does not contain the cost of leasing land in Susquehanna County. Completing a well is a very expensive process. This cost is different from one company to another. Generally, a vertical well in Marcellus costs around $810,000, whereas a horizontal one costs approximately 3 - 5 million dollars. One can estimate the cost range of completing wells in Marcellus Shale. There is a report from Range Resources who has performed a lot of drilling operation in PA. The average cost of making horizontal wells in 10 years in Bradford County is $4.0 million (Byungtark Lee,2009).

The supply of high pressure pumping services (for well stimulation and hydraulic fracturing) account for 30% to 35% of the costs of a typical unconventional gas well. There have been many failures and uneconomic wells stimulated and completed in each of the gas shale play, but as technology improves and we gain more experience, the success ratio and quality of the well completions continues to improve. Failures can include anything from losing a wellbore to ending up with a sub-economical well. This objective of this work has been to review the literature to determine the best practices for completing and stimulating well in our case. While existing technologies offer a wide selection of treatment options, cost remains the determining factor. Ultimately, all treatment methods must compete with the cost of disposal. Then what are the most economically viable treatment methods to obtain the quality desired? The answer to this dilemma seems to be the use of an array of methods, in a customizable, interchangeable setup that would fit better with the needs of the Operator.

During the process of fracturing, large quantities of water are pumped into the Marcellus formation 5,000 to 8,000 feet below, which makes the management of freshwater and wastewater produced is an equally important issue. On one hand, in certain locations within the Marcellus Play and in other shale gas development regions in Appalachia, the delivery of water supplies to the wellhead may encounter the constraints of long distances from suitable surface water sources or inadequate aquifers to support a useful water delivery flow of 50 gpm or more. Because of the logistical likelihood of these problems, it is necessary to find acceptable alternative water sources; Municipal water suppliers, for instance, are an expedient source of fresh water. The cost associated with municipal supplied water can vary greatly from one municipality to another. The current rates quoted in Pennsylvania range from $1 to $14 per 1000 gal. In the case that the water is hauled the total cost of municipal supplied water per well can be considered negligible in comparison to the cost of trucking. (A.W. Gaudlip and L.O. Paugh,2008)

The used fracture water that is a by-product of the operation was once thought to be a major rail commodity. Since the entire state of Pennsylvania has a total of seven disposal wells, compared to more than 50,000 found in Texas (Saltwater Distposal Wells FAQ, 2010). The geology of this area cannot accommodate the amounts of wastewater necessary for the industry. For lack of local disposal options, operators often find themselves hauling wastewater as far as Ohio and West Virginia to be injected into disposal wells. The cost per barrel of water trucked in this manner can be as high as $15, without taking in consideration the wear and tear on road infrastructure (Clark & Veil, 2009). After realizing the fact that hauling both fresh and by-product water by truck is an expensive matter, this project is aiming economical ways to recycle the wastewater water.

Drillers are taking their fracwater to municipal wastewater treatment plants; however because of the high level of dissolved solids (heavy metals and salt) those plants cannot treat the wastewater properly, since they do not have the adequate industrial wastewater treatment facilities. After a test, resulted higher - than - expected level of total dissolved solid in the Monongahela, the DEP warned municipal sewage plants to get state approval before accepting gas well wastewater. Basically, fracwater needs to be treated at specialized wastewater treatment plants, which can take heavy metal and salt out of fracwater. Unfortunately not many (less than 10) of these plants exist in the Pennsylvania. This shortage in wastewater facility treatment plant has created a big challenge to drillers and authorities. Some drillers have started to recycle and reuse the fracwater onsite and send it for treatment after multiple usages. In addition, the SRBC is working with industry personnel to determine best management practices for hydrofracing water reuse. Also with a contact, made with DEP office in Harrisburg, we were told that there is a very significant interest in building these treatment plants, due to this wave(Hemant Kumar,2009).

Lease cost involves the expense, incurred by a company to use land for exploration, drilling and production involved in oil and gas operations. As the land records date back to 1700s, the leasing process becomes complicated and may take three to six months. Land - owner, Mineral right - owner and coal mining right - owner can be three different people. In addition to Mineral right, permission is required from other two owners. It involves a complicated process of getting approval from the surface land owners to set up the equipment, needed and also the permission to drill through the coal seam. The latter is easier because it is impossible for a person with the coal mining rights to stop a company from drilling through it. Securing the lease and starting the planned activities usually take anywhere between 3 to 6 months in Pennsylvania. Usually, Lease cost is stated per acre per year. However, this is a mutual consent between the surface land owner and the lessee. For example, when a company leases 100 acres at $750 for 5 years it means that the lease owner will get $75000 one time and the company can use its land for operation for 5 years. Lease cost for a specific location varies with the price of natural gas. Before the potential of the Marcellus as an economic play was fully understood, lease prices were at a premium of $500. When gas prices touched 15$/MMBTU, the lease cost increased to as high as $3000.Lease cost also varies from county to county, depending mainly on the gas in place and other factors. The lease cost basically reflects the profit making of a certain area. As stated earlier lease cost mainly goes up with time. So the earlier a company gets into a play the more money it makes. Lease agreements are generally renewed at the ongoing price at that particular time. Big players have a team of lawyers and real‐estate specialists to deal with leasing terms and conditions. Lease costs for each counties are easily available (Michael Godec,2009).

Royalty paid by the company to the lease owner is about 1/8th the total revenue the company earns from gas production. This is almost the same for any location in Pennsylvania. This is often the major source of revenue for a lease owner. Also along with this, some land owners ask for a tap from the pipelines on their land without paying for the gas, they use from this source. They are also paid for the pipelines that pass through their land. This cost is in addition to the lease cost and the royalty, paid to the lease owner. Sometimes companies give signing on bonuses, given as royalty starting only when production begins (Armstrong Agbaji,2009).

In summary, the best technology or service delivery does little good if it does not compete financially. Through performing the literature review, we found some solution competes favorably with the costs of the marketplace and the performance, standard-based unit fee (per barrel) requires no customer capital expense. Possible recovery of natural gas condensate, methanol, and 10# brine, plus reduction in trucking, disposal and many other factors yields a more than competitive net value benefit.

In some cases, experience indicates that the complete cost of water management is elusive without a comprehensive and detailed view of costs often buried in a variety of company operating categories. Companies have spent significant effort, in concert with major operating companies and drilling management experts, to create an interactive model to enable our prospective customers to accurately evaluate their current costs in light of services fee to determine whether or not a true benefit exists. In our project, *Net Value Calculator* (NVC)(Fig 31) costing model will be used to better understand real costs through comparison (212 Resources， 2009).

Chapter 8: Analysis and Project Design

8.0 Background:

The enormous Marcellus black shale deposit, located at the northern Appalachia, which holds an estimated 168 trillion cubic feet of natural gas is found at extensive depth and very compact. The formation is developed using the horizontal drilling and the hydraulic fracturing of the formation for eeconomic gas production. The Bradford County is the area of study and it has over 286 wells drilled till date (Figure 32).

Up to 3.6 million gallons of hydraulic fracture water, mixed with various additives, is needed to completely fracture each horizontal deep well in the Marcellus Shale play. The spent water is usually highly contaminated and must be removed from the well, this research work achieved a recovery of about 70 to 86%, and this is normally referred to as "flowback" water. Table 7 shows the fracture schedule design and Figure 33 illustrates the slurry volume per fracturing stages. The fracture geometry is shown in Figure 34-36.

8.1 Reservoir Simulation

Well simulation

According to the government regulation on the Marcellus shale drilling area the company are not allowed to drill more than one will on every 640 acre feet unless the company shows that It need more than one well to drain the whole area. Most of the companies have one well at every 16 acre feet which mean 40 wells on every 640 acre feet. According to our goal which decreasing the environmental impact on the Marcellus shale drilling area we have studied implementing the multi-lateral wells in drilling the Marcellus shale to increase the recovery and decrease the environmental impact. Our goal was to have just one well on every 640 acre feet. We have used CMG to help us to find the best drilling technique to give us the highest recovery with the minimum environmental impact.

The reservoir properties

Our reservoir is at the Bradford County and we can the properties of the reservoir at Table 7b. Our reservoir is 8620 feet depth and the reservoir thickness is about 180 feet. As we have mentioned that our goal is to draining 640 acre feet so that our reservoir is going 5280 feet in I axes and 5280 in J axes which is 640 acre feet. As we have mentioned that the permeability is very low at the marcels shale so that we can find that our vertical permeability is 0.001 md and the horizontal permeability is 0.01 md.

We had many drilling techniques ideas to drain the 640 acre feet .We will show the results for this techniques which include the horizontal well, dual horizontal well at the same distance from the top, dual horizontal well with a distance between them, two dual horizontal wells with distance and multilateral well.

Horizontal well

We have tried one horizontal well which is going 8710 feet vertically from the surface (90 feet vertically in the reservoir) and 1440 feet horizontally. We run CMG for 40 years and the well recovery starts at ($3.5*10^6$) ft^3/day and the cumulative gas come up to ($6.2 * 10^9 ft^3$) As we can see in Figure 37 and figure 38. When we see the pressure distribution Figure 38 after the 40 years we can find that one well is not enough to drain the whole 640 acre feet.

As we can see on the figure 39 that on horizontal well cannot drain the whole 640 acre feet so that To drain the 640 acre feet we will need more than one well so that we have tried the dual horizontal well.

Dual horizontal well at the same depth

On the dual horizontal well as shown below the well will be drilled 8710 feet vertically from the surface (90 ft. vertically in the reservoir) and will go 1440 feet horizontally in both directions which mean 2880 feet total in horizontally. As we can see at figure (40) that the gas rate for the dual horizontal well is ($5.1*10^{6\ ft3}$/day) which is much more than one horizontal well but it is not the best. The cumulative gas is $9.7*10^9$ ft^3 as we can see in figure (41). Also if we look at figure (42) which presents the pressure distribution after 40 year we can see that dual horizontal gave much better results than the one horizontal well but it still need more wells to drain the aimed area.

Dual horizontal with distance

The difference between the dual horizontal and the dual horizontal with distance is the distance between the two horizontal wells as at the dual horizontal we have the two wells at the same distance from the surface. As we can see in figure (43) the dual horizontal with distance we have the well is drilled 8670 feet vertically then at the depth of 50 feet in the reservoir we drill the first horizontal branch which extends to 1440 feet. After drilling the first branch we continue drilling the vertical part 80 feet more before we drill the second horizontal branch to the other direction and this branch is extended to 1440 feet too. As we can see in the figure (44) the gas rate starts at ($6*10^6$ ft^3/day) which is higher than the dual horizontal. Also the cumulative gas rate is higher than the dual horizontal as it is $9.9*10^9$ ft^3 as we can see in figure (45). The difference in the total recovery and the drained area between the dual horizontal well and the dual horizontal well with distance is not big as we could see but this because the thickness of the reservoir but if we are has a thicker reservoir it would give much better results.

Two dual horizontal wells in the 640 acre ft

As we can see in the figure (46) that the dual distance is the best technique over the previous ones but if we look at the pressure distribution we can find that this well can drain half of the area so that we tried to put two dual horizontal wells with distance in the 640 acre ft. As we can see in the figures (47), (48) below the gas rate for the first well and the second well is ($9.3*10^6$ ft^3/day). As we can see in figure (49),(50) the cumulative gas for the first and the second well is $1.92*10^{10}$ ft^3. As we can see in figure (51) the pressure distribution after 40 years two dual horizontal almost drain the whole area and gave better results.

Multilateral well

On the multilateral well we used the dual horizontal with 80 feet distance and added to lateral to each horizontal branch. As we can see in the figure (52) that the will is drilled 2670 feet horizontally then at the depth of 50 feet in the reservoir we drill the first horizontal branch which extends to 1440 feet and two laterals extended from the main horizontal branch for 2037 feet and the same on the second horizontal branch. This technique gave us the best recovery as we can see in figure (53) the gas rate starts at ($1.18*10^7$ ft^3/day) comparing to all the techniques we have presented before. Also this technique gives the best cumulative which is $2.6*10^{10}$ ft3 as in figure (54).And this technique gave us very good results because it drain the whole 640 acre feet which achieve our goal in decreasing the wells number and drain the same area as we can see in in figure (55) the pressure distribution for the multi-lateral well.

As we can see in the figure (56) that the multilateral well give the best recover over all the other techniques and as we can see the difference in cumulative gas between the regular horizontal well and the multilateral is almost $1.98*10^{10}ft^3$. We can also see that we have tried to put two dual horizontals in the 640 acre feet but as we can see the one multilateral still give best results as the difference in cumulative gas is $6.8*10^9ft^3$.

But according to our forward osmosis design for water treatment we will use on horizontal well because it is the simplest technique which we can apply our project and then as a future work we have to determine how we can use the multilateral efficiently with the forward osmosis system.

Drilling fluid

We decided to use a water based mud in our drilling. Water based mud does not give as good results as oil based mud or synthetic. We decided to use the silicate based drilling mud in our system because it gave the best results in drilling.

The silicate drilling fluid advantages:

- Optimum inhibition characteristics.
- High penetration rates.
- Reduced trouble time and superior wellbore integrity.
- Optimum solids removal performance.
- Minimal environment impact.

There are three factors which making the silicate drilling mud giving optimum inhibition. The first factor is the chemical bonding of silica oligomers on the cutting and formation surface. The second factor is the precipitation of the silicate with divalent ions. The third factor is the inorganic polymer which forms a protective layer on the surface.

The formation of the silicate based mud:

Potassium carbonate (40 kg/m3), sodium chloride, sodium silicate liquid (8%), xanthan gum (YP 25 lb./100ft2), poly anionic cellulose (8 kg/m3), starch (API-FL < 5ml/30 min), biocide (1kg/m3), calcium carbonate fine (25 kg/m3) and calcium carbonate med (25 kg/m3).

Tomislav (2004), have studied this formation in drilling 450 wells and approved that this formation gave the best results in inhibition the formation, solid removal and the environmental impact. They mentioned also that this formation gave better results than the oil based mud.

Casing

In our design we will have a conductor casing which will be 50 feet long (24 inches) which is used in preventing the top of the will from caving and help in the process circulating the drilling fluid up from the bottom of the well. Then we will have a 500 feet long (20 inches) connecting the conductor casing and this part is to protect and isolate the near surface ground water. Then we will connect a surface casing to the conductor casing which will be 2000 feet (14inches) which protect the fresh water deposits near the surface of the well from the contamination which can happen by leaking of hydrocarbon or salt water. As long as our reservoir is 8620 feet depths so we will use an intermediate casing which will be 5070 feet long (6inches) to connect the production casing with the surface. In the pay zone we will have the production casing.

Cementing

We decide to use the bentonite cementing. The addition of the bentonite to the cement lowers the slurry density because it has a lower specific gravity. Bentonite concentrations are as high as 25 % of the cement. There are two ways to mix the bentonite with the cement. The first one is mixing the cement with the bentonite before mixing it with the water. The second is using prehydrated in the mixing water. In our design we will use the first mixing which is the dry way because it decreases the water content. The ratio of the dry bentonite and the prehydrated is about 3.6:1 for comparable slurry properties. Using the bentonite does not just decrease the slurry cost it also causing reduction in the cement strength and thickening time.

Conclusion

According to the government regulation which is having just one well in every 649 acre feet and to satisfy our goal which is draining the whole 640 acre feet we have found that the best drilling technique is to drill the multilateral well in the middle of the 640 acre feet. As the results show that the whole 640 acre feet has been depleted in the 40 years which we used as our project life time. By using the multilateral drilling technique the results showed that we were able to recover up to $2.6*10^{10}$ ft3.

As we can see in the figure (57) that the multilateral well give the best recover over all the other techniques and as we can see the difference in cumulative gas between the regular horizontal well and the multilateral is almost $1.98*10^{10}ft^3$. We can also see that we have tried to put two dual horizontals in the 640 acre feet but as we can see the one multilateral still give best results as the difference in cumulative gas is $6.8*10^9ft^3$. But according to our forward design for water treatment we will use on horizontal well because it is the simplest technique which we can apply our project and then as a future work we have to determine how we can use the multilateral efficiently with the forward osmosis system.

silicate drilling fluid gave a very good results as a water based drilling mud which encourages us to use it in our project because it give Optimum inhibition characteristics, High penetration rates, Reduced trouble time and superior wellbore integrity, Optimum solids removal performance, Minimal environment impact.

Bentonite cement is gave a good results in the Marcellus shale as Using the bentonite does not just decrease the slurry cost it also causing reduction in the cement strength and thickening time.

8.2 Hydraulic Fracturing

8.2.1 Introduction

Due to environmental concerns and fresh water availability, recovering as much as flowback water has become one of the greatest concerns for hydraulic fracturing. Hydraulic fracturing is a formation stimulation technique used to create additional permeability in a producing formation. By creating additional permeability, hydraulic fracturing facilitates the migration of fluids to the wellbore for purpose of production (Veach, et al, 1986). The purpose of this part of work is to examine water treatment techniques and critically design fracturing fluid that are employed in slickwater fractures of shale reservoirs at the Bradford Field and enhance fluid recovery used for fracturing.

8.2.2 Fracture Design

Since we are focusing mainly on fracturing fluid, mechanical design of fracturing will follow typical method commonly used for Marcellus shale. In this way, it is possible to save tremendous of time and cost which would occur from applying risky techniques to the formation. Comments will be made on the topic of proppant selection. *Figure 58* show typical fracturing process of shale gas.

8.2.3 Fluid Design

Slickwater fracturing has increased over the past decade with the advent of shale gas plays. Horizontal wells are now the standard with up to 1 million gallons of water in as many as 6 to 9 frac stages per well. With fracture treatments requiring tens of thousands of barrels of water per stage to stimulate fractures, massive amount of fracture fluid loss occurs due to the water based fluid creating interfacial tension between the injected fluid and the reservoir rock. Therefore, the goal of this fluid design is to achieve facture fluid which could increase flowback water recovery. Commonly used additives for frac-fluid is shown at *Table 7c.* However, in this design innovative microemulsion type surfactant would be added as a flowback enhancer. Proppant transportation modifier (PTM) would not be added since PTM costs significant amount of money and not yet applicable to commercial reservoir.

8.2.3.1 Additive Selection

(1) Thickening agent – Hydrozypropylguar gels (HPG) without breaker

The typical HPG gel treatment uses a 40-pund crosslinked gel containing gel breaker. However, reservoir temperature at the Bradford site is relatively low around 70-100F such that HPG without breaker is suitable for our target site. Furthermore, porosity (0.005), thickness (200ft), permeability (0.0001~0.01md) and pressure (3,000~4,000psi) of targeted site also allows HPG as best thickening agent.

(2) Friction Reducer – salt tolerant (up to 12% NaCl) Anionic Polycrylamide

Polyacrylamide is a polymer of acrylamide subunits that can be readily cross-linked. Considering relatively low reservoir temperature and PH of 6 to 8, anionic polyacrylamide is an economic choice for the Bradford site. However, high concentration of salt which can decrease the capability of friction reducer is found over the Marcellus Shale including out site. Therefore, the most effective friction reducer exhibits in the Marcellus shale is anionic polycrylamide with up to 12% salt tolerance. *Figure 59* shows a comparison effect of this friction reducer (Houston et al, 2009) .

(3) Biocide - 20% active dibrominated nitrilopropionamide (DBNPA)

DBNPA is a common pesticide used as an algicide, bactericide and fungicide (slime forming algae, bacteria and fungi; preservative (additive); fungicide (mold and mildew) (Houston et al, 2009). Since target field located at Bradford County contains high level of sulfate-reducing bacteria (SRB), the liquid 20% active DBNPA is highly effective, easy to apply and considered one of the safest biocides for the environment. *Figure 60* illustrated the capability of DBNPA to reduce the level of SRB (Houston et al, 2009).

(4) Iron Control – Iron control agent (ICA)

Iron-reducing and chelating agents consist of acidic chemicals such as citric acid, acetic acid, and ethylenediaminetrataacetic acid (EDTA) leeps the iron in formation in a soluble or reduced form. If iron is not controlled it could cause polymer degradation which could lead to damage of the formation.

(5) Clay Stabilizer – 2% Potassium chloride + 2gpt clay stabilizing agent (CS)

An analysis of the shale in the Marcellus in *Table 7d* clearly shows clay abundance (P. Kauman and G.S. Penny, 2008). Thus, without clay stabilizers would cause permeability decrease of the formation. Higher concentration of KCL show better performance but cost then becomes issue. Therefore, 2% KCL + 2gpt CS is our choice of clay stabilizer.

(6) Scale ingibitor – anionic phosponates

Calcium sulfate, calcium carbonate and barium sulfate can cause scale problems if the concentration is high enough. Most common scale inhibitor is anionic phosponates. This is known to be compatible with chosen friction reducer and clay stabilizer.

(7) Corrosion inhibitor – N,n,dimethyl formamide

Corrosion inhibitor is used to hinder the corrosion of steel tubing, well casing, tools and tanks (J. Daniel, Brian Bohm, and Bobbi Jo Coughlin, 2009). Considering the temperature of our site relatively small amount of this additive is sufficient.

(8) Breaker – peroxydisulfate

The temperature of our site does not lead thermal breaking of the polymer gel. However, a breaker is added to the fracture fluid in later stages of the process to break down the viscosity of the gelling agent to aid in releasing the proppant and enhance the volume of flowback water after completion (J. Daniel, Brian Bohm, and Bobbi Jo Coughlin, 2009).

(9) Sulfactant – nonionic microemulsion containing linier and branched alcohol ethoxylates + 2% ethoxylated alcohol fluorosurfactant

The major use of surfactant in shale treatment is to lower interfacial tension. Flowback recovery rate can be drastically enhanced with the application of ME + 2% FS system. *Figure 61 and 62* shows laboratory experiments done by using chosen surfactant. Field study performed at the Bradford formation which has almost identical reservoir property also shows post-fracture recovery rate of 70%-86% with the application of microemulsion technology (P. Kauman and G.S. Penny, 2008).

(10) Proppant Transportation modifier (PTM) – not in use.

Tiorco Chemical Co. and Stephan Chemical Co. both went under research of PTM or buoyancy changing proppant transportation. However, according to senior research Mr. Yang at Tiorco company "currently developed technology regarding PTM is not applicable anywhere due to extremely high price of PTM." Since there is no massive production facility of the surfactant used for PTM, PTM itself costs very high which make impossible to keep payzone. He also recommended use of ceramic proppant whose technology has been developed for decades now becoming popular for new developing shale reservoir.

Table 7e shows final additives concentration designed for this project.

8.2.3.2 Proppant selection

Widely used proppant these days around Marcellus shale is CarboProp (40/70). It is frequently selected for moderate depth oil and gas wells and has excellent crush resistance in a broad range of applications. Effective at closure stresses to 14,000 psi. In order to enhance proppant distribution, the use of lightweight CarboLite (20/40) with CarboProp is our choice of proppant. *Figure 63 and 64* show typical property of CarboProp and CarboLite. Once ceramic proppant was expensive to use for fracturing huge shale reservoir but constant development and extension of ceramic industry recently provides cost effective high performance proppants. *Figure 65* illustrates benefits of ceramic proppants (CARBO ceramics, 2010).

8.3 Characterization of Post-Fracture Flow-back water

Conversion factor

1 Barrel = 42 Gallons

1 Gallon = 0.023809523809523808 Barrels

3,600,000 Gallons of hydraulic fracture fluids used for a single horizontal well fracture job = 85714.28571428571, approximately 85, 714 barrels

A load recovery of approximately 86 % of the injected fluid is achievable due to the fracture design (fluid type, fluid viscosity, proppant type and pump volume) which amount to 73,714 bbl (Fig. 66)

It is important to note that;

1. The amount of dissolved components increased as flowback advanced (Fig. 67). Both sodium and calcium exhibit analogous trends in the developed wells.
2. Sodium and calcium are the most common cations (Fig. 68).
3. Alkalinity and pH decreased as flowback progressed, potentially explaining the rise of calcium levels.
4. This is prone to sulfate scaling as the amount of calcium rises while sulfate is drops (Figs. 68 and 69).
5. A mono-valent ion trend is illustrated in Fig. 70 while Fig. 71 shows a divalent cation trend.
6. Fig. 72 shows a sharp increase in barium levels in the latter stages of flow back (at about 30% load recovery) suggests possible barium sulfate scale development as the flow back progresses. The solubility of barium sulfate is very low and it can be a very aggressive scale.
7. Iron content in the flowback increased as flowback progressed (Table 8).
8. Chemical composition of these waters can be classified as highly saline.
9. With cations such as Magnesium, Strontium, and Barium, chemical signatures of the waters are consistent with carbonate-rich and evaporite sources.

Table 9 presents analytical data from the Marcellus Shale Well in Bradford county flowback waters taken over a period of 20 days. Barium is significantly high, reaching a maximum value of 3100 mg/L. Strontium levels reached a maximum value of 4,310 mg/L on the twentieth day. It was observed that Sr values are as high as 15,000 mg/L in flowback waters from other

Appalachian Basin Marcellus wells at later times. Potassium levels are more to the other of 496mg/L at 20 days. Also present are less common metal ions, including boron, cobalt and lithium. Magnesium and manganese are often found to correlate well with calcium levels.

As the chemical composition of Marcellus flowback water varies (Table 10) dependent upon the well location and elapsed time since the fracture was completed, the following test results are typical of the results obtained (Table 11 and 12).

8.4 Engineering Considerations:

Waste water treatment and water reclamation processes implemented for treating hydraulic fracture flowback must take into consideration the disposal of the large amount of sludge solids produced by the process. The Forward Osmosis process, operating on a hydraulic fracturing flow-back water to treat 14, 400 Barrels = 604, 800 gpd with an “average” chemical composition of barium 4,300 mg/l, 21,850 mg/l calcium, 1,300 mg/l, magnesium, and 3,400 mg/l strontium, would produce, at 40% solids sludge cake, 67,000 lb of barium sludge and 281,815 lb of calcium/strontium/magnesium sludge per day. Pennsylvania Department of Environmental Protection residual waste permitting requirements and the cost of moving large quantities of flowback water, hydraulic fracture makeup water, and produced sludge solids shows the need for a number of dedicated FO flowback treatment systems sited across the area under laid by Marcellus shale formation.

Exclusive of the incoming hydraulic fracture flowback water and treated water storage tanks, we have estimated that a 604, 800 gpd FO process system would require a hydro-pneumatic tank and a vessel for the FO system Figure 73.

8.5 Hydropneumatic Tanks

Vessels that contain both water and air under pressure can be called a hydropneumatic tank. The captive compressed air acts as a cushion which can exert or absorb pressure as required. Our design takes into consideration the flowback recovery per hour in our system, which is 600bbl/hr for the centralized system, but 150bbl/hr for a single well pad. The tank size required would be a 25,000 gallon tank, covering approximately 1,202 square feet and cost $52,255. In other to prevent corrosion, we would install an epoxy lining which wpould increase the cost to $64.610 and it would have a design working pressure of 125# ASME.

8.6 Concept of Forward Osmosis

FO is a membrane-based separation method that utilizes the energy from an osmotic gradient across the membrane to pull or 'draw' the water through the selectively permeable membrane. This is in contrast to reverse osmosis (RO) which utilizes mechanical energy to force the water through the membrane. The draw solution used to pull the water in the forward osmosis system is typically a highly concentrated, homogenous salt or sugar solution, and the resulting produced water is therefore a diluted version of the draw solution. The undesirable solids and solutes are denied access through the FO membrane, resulting in a concentrated waste stream on the waste water side of the membrane and also we have a nano-pure diluted draw solution on the effluent side of the membrane which is later separated simply by heating. The draw solution for our design is the ammonia carbonate solution, and the issue of membrane fouling is reduced using the forward osmosis since there is no pressure applied on the membrane by the osmosis process. The salt concentration provide the chemical energy that operates the system, in the forward osmosis system, there is no need for pre treatment and also there is no substantial electrical or power consumption within the system thus making the carbon footprint of the process very small. Forward osmosis has the smallest carbon footprint of the available water reclamation processes.

The forward osmosis reclamation process satisfies the following conditions for practical and cost-effective waste reclamation process:

- ➢ the amount or volume of 'new' freshwater required for completion fluid is greatly reduced,
- ➢ no new waste streams are created,
- ➢ the volume of drilling waste to be disposed of is reduced,
- ➢ an otherwise wasted chemical energy source is utilized to reclaim the reserve pit waste water, and
- ➢ the system is operated on the well location without disrupting normal operational practices, which reduces the operator's overall logistical concerns and environmental exposure.

The FO units design are flexible, scalable and portable to facilitate the waste water to be treated on location, thereby doing away with the trucking costs and environmental exposure associated with hauling the wastewater to disposal sites. The complete unit would be mounted on a 53-foot trailer pulled by 10-wheel Class 8 tractors. The reclaimed water from the forward osmosis unit would be stored in fracture water tanks located on the well sites which are reused for other fracturing jobs or the the reclaimed water could be stored in lined pits.

8.7 Field Applicability of the Forward Osmosis Unit:

The forward osmosis unit design, for the approximately 10 bbl/min unit would consist of a large TFC membrane 16 inch by 40 inch spiral-wound elements in one low pressure recirculation vessel. The FO unit design can effectively reclaim in excess of 90% of the water from typical flow back water tanks. The total suspended and total dissolved solute rejection effectiveness of the forward osmosis membranes used in the unit has been well established in the scientific literature. The FO membranes have been proven to reject 100% of bacteria, viruses, and colloidal solids in addition to removing over 97-99% of the heavy metals and salts
A 4 inch by 4 inch, 17 bbl/min centrifugal transfer pump would be used to recirculate the water from the tanks into the unit for processing. 36% NH_4CO_3 draw solution is pumped into the unit using a ½ to ¾ horsepower, 1.8 bbl/min centrifugal transfer pump. The entire system which consists of pumps and ancillary equipment (lights, trailer house, etc) would be powered by a 25 kilowatt diesel generator, but in our case, we would generate this needed power from the system. It is important to note that the pumps do not push the water through the membranes but only supply source water to the unit, the osmotic gradient 'pulls' the water all the way through the membrane. The 10 bbl/min FO unit can be effectively operated by a single person, or for efficiency, two operators (each taking a 12 hour shift) will be on location.

8.8 Forward Osmosis and Blue Energy Combination System

Initial designs proposed had utilizing the Forward Osmosis and Blue Energy aspects of our IPA as separate entities. These initial designs aimed at increasing the efficiency of the independent systems and then the efficiency of the overall design. After intensive review of the engineering attributes of these previous designs, combining the two systems to work simultaneously together proved to be a more efficient and cost effective system design. The goal of the Blue Energy in this system is to provide the energy required to pump flow back water from the drilled well and to power the Supervisory Control and Data Acquisition (SCADA) system. The osmotic gradient generated by the TFC-MP membrane and Ammonium Bicarbonate draw solution theoretically allows for sufficient energy generation for our system needs. This integrated system will decrease the energy costs, increase the effectiveness of our system, and decrease environmental concerns.

System Overview

The proposed design is a novel semi-portable centralized flow back water treatment facility. This system will be semi-portable to reduce the costs and environment impacts associated with current methods of flow back water treatment for gas wells in Bradford county Pennsylvania. This system will be scaled to treat 604,800gpd (gallons per day) A Supervisory Control and Data Acquisition (SCADA) system will be utilized to maintain the optimal flow rate of 10bbl/min of treated water. The solids separated from the reclaim water will be contained in a separate tank that can be transported for storage until it is to be sold. The treated water will be housed in a separate area. This treated water then can be used in future well fracture operations, sold or can be returned to the environment since it will meet/exceed standards enacted by the Environmental Protection Agency (EPA). Figure 74 shows a general overview of the most important features of the system. Forward Osmosis is the most effective flow back water treatment method since, there is no need for pre treatment of the flow back water and also there is no substantial electrical or power consumption within the system thus making the carbon footprint of the process very small. Forward osmosis has the smallest carbon footprint of the available flow back water reclamation processes that were considered for our flow back water treatment facility.

8.9 Goal of the Integrated System

The proposed design aims to provide a portable and effective flow back water treatment system that additionally generates the power necessary to run the system. A portable shipping container will be modified to house both the Forward Osmosis and Blue Energy portions of the system. An elevated tanker trailer will be used to house the flow back water that will be introduced into the treatment system. This system will be designed to effectively treat 604,800 gallons of flow back water per day. The reclaimed water from the forward osmosis unit would be stored in fracture water tanks located on the well sites which are reused for other fracturing jobs or the reclaimed water could be stored in lined pits. The goal of this system is to provide a portable and effective flow back water treatment system that eliminates the limitations of currently used techniques.

8.10 System Housing Selection

A steel portable shipping container will be used to house the Forward Osmosis Unit, Blue Energy generation components and Supervisory Control and Data Acquisition (SCADA) systems. This proposed design will utilize a 40 foot Dual Insulated Dry Goods Shipping Cargo Container with the dimensions 40ft L x 8ft H x 8ft W. A Dual Insulated Dry Goods Shipping Cargo Container was the ideal housing unit since modified containers are readily available. The estimated price for the 40ft shipping container Figure 75 and chassis Figure 76 is $7,000 USD including modifications. The Forward Osmosis and Blue Energy systems would be housed within 30-36ft of the available 40ft of the Dual Insulated Dry Goods Shipping Cargo Container. The reaming 4-10ft of available length will be used to house the main components of the Supervisory Control and Data Acquisition (SCADA) system and other miscellaneous components. The container will need separate insulation considerations for the Forward Osmosis process and for Supervisory Control and Data Acquisition (SCADA) system. The Forward Osmosis system section of the container must be insulated to prevent the liquids in the system from freezing and to reduce the costs associated with heating required for the separation of the draw solute from the treated water. The Supervisory Control and Data Acquisition (SCADA) section of the container must be insulated and vented to prevent the computer components from overheating in the warmer periods of operation. During the cooler periods, the computer components will generate enough heat to prevent failure. Anti-Slip mats will be installed within the Dual Insulated Dry Goods Shipping Cargo Container to reduce the likelihood that any human operator would slip due to liquids on the floor. Shatterproof fluorescent lights will be installed in both the Forward Osmosis section and Supervisory Control and Data Acquisition (SCADA) section of the container. The lights will be installed mainly for maintenance operations. This container will be housed upon a trailer designed to house and haul shipping containers by Semi Trucks. This elevation also allows for housing a container to collect and house the dissolved solutes separated out of the flow back water by the forward osmosis membrane. This collection method will be directly connected to the system to prevent spillage of the dissolved components into the environment. An Excalibur ®intermediate bulk container

(IBC) Figure 77 manufactured by Snyder will be used. A plastic intermediate bulk container (IBC) be used since it is lightweight, durable and resists corrosion better than an steel intermediate bulk container (IBC) .

8.11 Flow Back Water Storage Selection.

In order to better control the flow of flow back water entering the Forward Osmosis system a liquid storage tank will be used. This liquid storage tank will also be elevated off of the ground. It is necessary to increase the pressure of the flow back water entering the forward osmosis system. By elevating the flow back water storage tank above the level of the forward osmosis system, gravity can be used to increase the pressure of the flow back water entering the system. This tank would additionally be outfitted with a trailer chassis to make it portable.

8.12 Draw Solution Selection

The draw solution is the driving force for movement of water out of the flow back water through the semi-permeable membrane. An ideal draw solution must have a high a high osmotic efficiency, low molecular weight, zero-liquid discharge, non-toxic, chemical compatibility to the membrane, easy separation from water and recyclable. [McGinnis 2007] The proposed forward osmosis design uses Ammonia bicarbonate (NH_4HCO_3). Ammonia bicarbonate meets all of the desired characteristics of an ideal draw solution for forward osmosis. Experimental design has show separation of water from wastewater will low concentrations of Ammonia bicarbonate. This is an additional reason why Ammonia bicarbonate has been selected as a draw solution. Since the concentration of the flow back water varies at different stages of well fracturing, a draw solution that can separate water at low concentrations is desirable. The draw solution can also increase the concentration to help increase the osmotic efficiency to increase the effectiveness of Blue Energy generation. 36% Ammonia Bicarbonate draw solution is pumped into the system using centrifugal transfer pump. Since the one of the goals of the forward osmosis is to treat flow back water economically, Ammonia bicarbonate can be easily separated from water, by increasing the temperature of the mixture to moderate temperature of 60 degrees Fahrenheit.

8.13 Forward Osmosis Membrane Selection.

The membrane is the main limiting factor of the forward osmosis system. The membrane must have a low concentration polarization both internal(ICP) and external concentration polarization(ECP), chemically compatible to draw solution, reduce the propensity for fouling, membrane configuration and strength, membrane capacity, increase flux and increase osmotic pressure. By incorporating Blue Energy into the flow back water treatment system, increased osmotic pressure; increased flux and membrane capacity carry even more weight than normal forward osmotic applications. The Thin-Film Composite Medium Performance membrane developed by Yin Yip at Yale University (Yip, 2011) will be used for this proposed design. Analytical grade Polysulfone beads, N,N-dimethylformamide, 1,3-phenylenedianmine and 1,3,5-benzenetricarbonyl trichloride to construct the membrane. The backing support layer for the Plysulfone Beads is a thin (40 μm) open-structure polyester nonwoven fabric. This membrane has show sustainable power generation from salinity gradients, the driving force for Blue Energy. This membrane also satisfies the necessary attributes for a forward osmosis membrane. This membrane consists of a thin active layer supported by a polymer layer that is highly permeable to water and has a high propensity to reject dissolved solutes. The thickness of the active layer and support layer are 125 micrometers. Due to the polyamide chemistry this membrane will be stable up to a pH of 11. The membrane has an intrinsic water permeability is 5.81 ($L\ m^{-2}h^{-1}bar^{-1}$); solute permeability coefficient of 0.61 ($L\ m^{-2}\ h^{-1}$) ; a structural parameter of 370(μm); has a peak power density of 10 ($W/m^{2.}$); water flux of 30 (L/m2h) and can create a osmotic pressure differential of 25bars. (Yip, 2011) This membrane was soaked in a 1.5 M ammonia bicarbonate solution for seven days and showed no visual changes and the flux remained constant. Since the pH concentration will fall within the acceptable range, we do not predict a high propensity for membrane fouling, thus reducing the costs since the membrane will not need to be continually changed. Thus, under normal operating conditions an estimated life span of five years should be achieved. The TFC membrane would be housed in several spiral - wound membrane modules. The use of several simultaneous spiral-wound membrane modules will be used to increase efficiency of the flow back water treatment and reach our optimum reclaim water flow rate of 10bbls/min.

8.14 Supervisory Control and Data Acquisition (SCADA)

A SCADA system was developed and utilized to control draw solution concentration and temperature in the forward osmosis system. Also, the SCADA receives signals from conductivity, pH, temperature, and pressure sensors, as well as readings from an analytical balance were acquired and recorded by the SCADA system in an attempt to maintain a constant draw solution concentration, the forward osmosis system.

The SCADA system monitors and controls the concentration of salt in the draw solution by adjusting the pressure gradient of the system; it monitors the concentration of the draw solution and corrects the conductivity by sporadically operating a peristaltic pump that distributes concentrated salt solution into the draw solution tank several times per minute as needed. A screen capture of the SCADA system is presented in Figure 78.

8.15 System Design

A 4 inch by 4 inch, 17 bbl/min centrifugal transfer pump, powered by a 25 kilowatt diesel generator, will be used to pump the flow back water from the wells into the 25,000 gallon hydropneumatic tank. A. A SCADA monitoring sensor would be placed here to control the flow rate of flow back water into the Forward Osmosis Unit. The flow back storage tank is connected to the Forward Osmosis unit through a 10ft long 3in pipe at a 45-degree angle. The flow back water flows from the entrance into the system to the low pressure recirculation vessel via two feet of 2in pipe at zero angle. A SCADA monitoring sensor will be placed in this area of pipe to measure pH and concentration used to determine the concentration of the ammonium bicarbonate necessary to achieve proper separation. In the low pressure recirculation vessel the TFC membrane in housed in a spiral-wound membrane module that will house a 1 meter TFC membrane. The unit will consist of multiple spiral-wound membrane modules so that the optimum membrane surface area can be achieved. The flow back water and draw solution run tangential in a cross flow mode this allows the liquids to flow freely on both sides and for the dissolved solids to drop out . The 36% NH_4CO_3 draw solution is pumped into the low pressure recirculation vessel, using a ½ to ¾ horsepower, 1.8 bbl/min centrifugal transfer pump. A SCADA monitoring sensor and valve will be placed at the inlet to the recirculation vessel from the draw solution storage tank to control the amount and concentration of the draw solution released. The dissolved solutes drop from the surface of the membrane element to pass through the container into a 120 gallon plastic Excalibur IBC via a 4" to 6" piping.

The osmotic pressure gradient created by the ammonium bicarbonate draw solution draws the reclaimed water through the membrane and through the turbine (generating the energy necessary to power our system) via a 1" one foot long pipe. The water flux capacity for the system will be 3600 L/m^{2}h. The Power density of the system will be 1200 W/m^{2}The dilute draw solution and reclaim water then are introduced into a single vacuum distillation column at the top of the column and moves downward in a counter-current flow. The heat from the rising vapor (approx 60 degrees Celsius) from the fired reboiler to the falling liquid causes the separation of the more volatile ammonia and carbon dioxide from the reclaim water. The volatile ammonia and carbon dioxide gases pass from the single vacuum distillation column back into the draw solution storage tank. The water that passes through the bottom of the single vacuum distillation column is then passed thought the fired reboiler (which causes the water vapor necessary to separate the draw solution from the reclaim water) to the fracture water tanks located on the well sites which are reused for other fracturing jobs or the reclaimed water could be stored in lined pits through a 2" pipe of various lengths depending on where the reclaim water will be housed. A SCADA monitoring sensor will be placed here to monitor the flow rate and report to other monitor to adjust their settings or to remain the same. Figure 79 shows a schematic drawing of our Novel Semi-Portable Centralized Forward Osmosis Water Treatment Facility. Figure 80 illustrates a generalized footprint of our Novel Semi-Portable Centralized Forward Osmosis Water Treatment Facility. It is important to note that since this will be set up at either a single well or as a centralized system. The pipe lengths to the hydropneumatic tank will vary. It will also be important to incorporate a feed-back loop system that can be directly monitored by our SCADA system to monitor pressure through these pipes. This is important in detecting a leak and rapidly implementing our Spill Containment procedures. The Forward Osmosis and hydropneumatic tank need to be placed upon a lined gravel pad. This will prevent potential spill liquids from entering the ground. Calculations need to be performed onsite to determine the distance that the berm should be to prevent liquid from the hydropneumatic tank if punctured or knocked over from exceeding the lined gravel pad.

Chapter 9: Osmotic Energy Generation (Blue Energy) System Design

9.1 The Principle Of Pressure Retarded Osmosis (Pro)

The two major methods of osmotic power generation are the Reverse Electrodialysis (RED) and Pressure Retarded Osmosis (PRO) methods (Post, et al., 2007). This system adopts the PRO method, and this section will explain how power is generated by this means and how this method can be incorporated in our blue energy system. This method is a viable source of renewable energy, and its theory is embedded in the osmosis theory where water from a solution of lower salinity – also known as feed solution- passes through a semi-permeable membrane into a solution of higher salinity – also known as draw solution. But the major difference in this process from a traditional osmosis process is the application of pressure on the side of the draw solution, which assists in pressurizing it and when this pressurized solution flows through a water turbine, power is generated (Leob, 1976).

The major factors that affect the PRO method are the osmotic pressure differential (Δπ), the hydraulic pressure differential (Δ*P*), and the semi-permeable membrane parameters. The general water transport equation is given by:

$$\boldsymbol{J_w} = \boldsymbol{A}(\Delta\pi - \Delta P) \qquad (L/m^2h) \qquad (1)$$

Where J_w is the water flux and A is the water permeability coefficient of the membrane (also referred to as the intrinsic permeability)

The direction of the water flux is shown in figure 81.

The salt permeability coefficient (B) is another important factor, and this coefficient is a measure of a semi-permeable membrane to allow small amounts of salt diffusion across the membrane from the draw solution to the feed solution as a result of concentration gradients. This effect will reduce the osmotic pressure differential hence is not healthy for the system. The B coefficient is inversely proportional to the efficiency of the system, as such the smaller the better. The equation is given by:

$$\boldsymbol{B} = \frac{\boldsymbol{A(1-R)(\Delta P-\Delta\pi)}}{\boldsymbol{R}} \qquad (L/m^2h) \qquad (2)$$

Where R is the salt rejection

The salt rejection (R) is given by:

$$R = 1 - \frac{C_{D,M}}{C_{F,M}} \tag{3}$$

Where $C_{D,M}$ is the salt concentration of the draw solution at the membrane surface and $C_{F,M}$ is the salt concentration of the feed solution at the membrane

Concentration polarization is another important parameter that affects the osmotic pressure differential negatively. It is defined as the accumulation or depletion of solutes near the membrane boundaries as a result of the water flow through the membranes, and in effect there are two types; external concentration polarization (ECP) and internal concentration polarization (ICP) (Achilli et al., 2009). The ECP results from the reduction of the concentration of the solute on the draw solution side of the membrane, and this effect can be calculated using the ECP($\frac{\pi_{D,M}}{\pi_{D,b}}$) modulus given by:

$$\frac{\pi_{D,M}}{\pi_{D,b}} = exp\left(-\frac{J_w}{k}\right) \tag{4}$$

Where $\pi_{D,M}$ *is the osmotic pressure at the membrane surface ;* $\pi_{D,b}$ *is the bulk osmotic pressure of the draw solution and k is the mass transfer coefficient*

The water flux is in the direction of the draw souliton as such J_w is negative and the polarization effect is dilutive i.e. $\pi_{D,M} < \pi_{D,b}$.

The ICP is the concentration polarization that is brought about as a result of the solute being concentrated in the support layer of the membrane.Illustration of osmotic driving forces profiles across a semi-permeable membrane and the effects of the ICP and ECP is shown in figure 82 (Achilli, Cath, & Childress, 2009)

Taking into considerations the ICP and ECP effects, and assuming that $\frac{C_{F,b}}{C_{D,M}} = \frac{\pi_{F,b}}{\pi_{D,M}}$ the water flux equation will be given by:

$$J_w = A\left[\pi_{D,b} exp\left(-\frac{J_w}{k}\right)\frac{1-\frac{\pi_{F,b}}{\pi_{D,b}}exp(J_w K)exp\frac{J_w}{k}}{1+\frac{B}{J_w}[exp(J_w K)-1]} - \Delta P\right] \tag{5}$$

And K is the solute resistivity for diffusion with the porous layer, and it is given by:

$$K = \frac{t\tau}{D\epsilon} \tag{6}$$

Where t is the support layer thickness, τ *is tortuosity,* ϵ *is the porosity of the support layer, and D is the bulk diffusion coefficient.*

The K term is also a very important parameter, and its magnitude affects the membrane performance indirectly; the smaller the K term, the more effective the membrane (Leob, 2002).
The membrane structural parameter (S) is another very important parameter and is given by:

$$S = KD = \frac{t\tau}{\epsilon} \qquad (\mu m) \qquad (7)$$

9.2 Power Density In PRO

Water flux through the membrane and the hydraulic pressure differential across the membrane are the major variables for power density (W) calculation. The power density equation is given by:

$$W = J_w \Delta P \qquad (W/m^2) \qquad (8)$$

Substituting the equation (1) into equation (7) will give us a power density equation of:

$$W = A(\Delta\pi - \Delta P)\,\Delta P \qquad (9)$$

Differentiating equation (8) with respect to ΔP, it can be shown that the maximum power density (W_{max}) is obtained when $\Delta P = \frac{\Delta\pi}{2}$ and the governing power density equation will now be given by:

$$\boldsymbol{W_{max} = A\frac{\Delta\pi^2}{4}} \qquad (10)$$

9.3 Forward Osmosis (FO)

The term forward osmosis is used to refer to normal osmotic processes, so as not confuse it with PRO or reverse osmosis (RO). Forward osmosis is illustrated in figure 83.
The Forward osmosis process is a process that will occur on its own, without any form of external pressure or push. Our system adapts the FO theory and the advantages include:

- Elimination of external pressure
- Reduce cost by eliminating large pressure pumps and pressure exchanger systems
- Pressure generated in draw solution can be utilized in place of external pressure
- Supports the objective of small-scale power generation
- Availability of FO membranes that can be used to develop PRO situations

In an FO system, as the water flows towards the draw solution, through the semi-permeable membrane, the hydraulic pressure obviously increases on the side of the draw solution (hypertonic solution) due to the increase in volume as shown in Figure 84.

9.4 Blue Energy Generation from the Waste Water Using Forward Osmosis

In designing a blue energy system, one of the major difficulties over the year has been the choice of membrane since most of the available membranes are not commercially efficient and usually require large surface areas to be able to generate any reasonable amount of energy. Our system incorporates a thin-film composite membrane (TFC) and the TFC-PRO membrane (Yip, et al., 2011) is the type of TFC membrane used for our system. This is an assymetric membrane and the micrograph is shown in Figure 85.

There are three major TFC-PRO membranes; the Low permeability (LP), medium permeability (MP), and high permeability (HP) TFC-PRO membranes. Their properties are shown in Figure 86:

From the plots it can be observed that the highest power density is obtained from the MP TFC-PRO membrane, and the B term is comparatively low too. This is the most favorable for our system.

The feed solution and draw solution also equally affect tremendously the performance of the FO system. In our system the feed solution is the waste water and the draw solution is Ammonium bicarbonate (NH_4HCO_3). The concentrations of the draw and feed solutions both affect the osmotic pressure differential of the system and will therefore affect the power density of the system as shown in the equations above.

The experimental values of the membrane parameters are:

Water permeability coefficient (A) = 5.81L/m^{2}hbar

Salt or solute permeability coefficient (B) = 0.61L/m^{2}h

Structural parameter *(S)* = 370µm

Power density *(W)* = 10W/m^2

Water flux (J_w) = 30 L/m^{2}h

Osmotic pressure differential ($\Delta\pi$) = 25bars

Hydraulic pressure differential (ΔP) = 12.5bars

Our membranes are arranged in a cylindrical pack which maximizes space, allowing better portability. The membrane system is designed to occupy a space of 4m by 1.91m by 1.6m (*length by width by height*) and as such can accommodate 120 membrane units of a 1m^2 TFC-

PRO membrane. Therefore the total expected water flux capacity and power density will be 3,600 L/m^{2}h and 1,200W/m^2 respectively. Taking into considerations the effects of osmotic pressure on the water flux, and since this a controllable parameter, our system is designed to attain a water flux capacity of over 17,000 L/m^{2}h (approximately 150bbl/h) by increasing the osmotic pressure of the system.

9.5 Turbine and Power Storage Considerations

As earlier mentioned the power capacity of the system is only when the water from the pressurized draw solution side of the membrane flows though a water turbine, which in turn generates power. Taking into consideration the expected power density of our system, a comparatively small, high efficiency turbine of minimum capacity of 1.2kW is incorporated in our system. This turbine is going to depend mainly on the flow of the pressurized thermolytic mixture (mixture of the draw solution and water) and not on depth.

Our storage system adapts a capacitor system, with the ability to store power for years. This storage system is connected to a step-up transformer, when required, to raise the power supplied to system equipments. The power storage system also has a minimum power capacity of 1.2 kW.

9.6 Osmotic Power Generation System Design Assumptions and Contingency Plan

A lot of assumptions were made in the design of this system and these assumptions include:

Concentrations of feed solution and draw solution are maintained at considerably stable values.

The ICP and ECP effects are negligible.

Osmotic pressures remain the same during the desalination and power generation processes.

The SCADA takes care of any unwanted changes in solution properties.

- The system is 100% efficient.
- The experimental parameters are suitable for the entire system.
- The draw solution can attain the required hydraulic pressure for maximum power generation.
- The design also adapts the following contingency plan:
- The membranes are arranged in a way that they are easily replaceable in the event of any malfunctioning whatsoever.
- The osmotic concentration of the system is maintained by the control of the concentration of the draw solution.

In order to meet other power demands that might exceed the expected supply, a step-up transformer can be installed.

Unused capacitors are available at the site, to take care of any excess power produced.

In the case of unwanted rise in temperature in the container, a ventilation system is provided to maintain the temperature in the container.

All the components of this system are maintained on a regular basis to ensure that they are all functioning at their expected capacities.

Chapter 10: Associated Costs Evaluation

The total costs of this project associated with above mentioned activities are obtained. Some of these data have not been published in any literature work. They have been obtained by personal interview of company representatives.

Exploration Cost

The initial phase in petroleum operations that includes generation of a prospect or play or both, and drilling of an exploration well is called 'Exploration'. Cost belonging to these activities comes under exploration cost. There are several kinds of Exploration, namely, Geochemical, Geophysical and Seismic. This cost has been taken as \$20% of total expenses for this study.

Administration Cost

Expense incurred in controlling and directing an organization, but not directly identifiable with financing, marketing, or production operations. Salaries (Accountants, Engineers, and Laymen) and costs of general services fall under this heading. Administrative costs are related to the organization as a whole. This was considered as 10% of total expenses for this study. (Byungtark Lee,2009)

Royalty

A payment made for the use of property, especially natural resource. The amount is usually a percentage of revenues obtained through its use. This amount is calculated as certain percentage of revenue (before tax) generated from the production sale. It was considered as 12.5% for this project.

Lease Cost

Lease cost involves the expense, incurred by a company to use land for exploration, drilling and production involved in oil and gas operations. As the land records date back to 1700s, the leasing process becomes complicated and may take three to six months. In addition to Mineral right, permission is required from other two owners. It involves a complicated process of getting approval from the surface land owners to set up the equipment, needed and also the permission to drill through the coal seam. The latter is easier because it is impossible for a person with the coal mining rights to stop a company from drilling through it. Securing the lease and starting the planned activities usually take anywhere between 3 to 6 months in Pennsylvania (Rohan Belvalkar,2009). Usually, Lease cost is stated per acre per year. However, this is a mutual consent between the surface land owner and the lessee. Lease cost for a specific location varies with the price of natural gas. Before the potential of the Marcellus as an economic play was fully understood, lease prices were at a premium of \$500. When gas prices touched 15\$/MMBTU, the lease cost increased to as high as \$3000 (Rogers, 2008). Lease cost also varies from county to county, depending mainly on the gas in place and other factors. The lease cost basically reflects the profit making of a certain area. As stated earlier lease cost mainly goes up with time. So the earlier a company gets into a play the more money it makes. Lease agreements are generally renewed at the ongoing price at that particular time. Big players have a team of lawyers and real-estate specialists to deal with leasing terms and conditions. Lease costs for each county are easily available. In Bradford country, this cost varies (\$500-\$2500/acre) with market price of the gas. It was taken as \$1500/acre Table 13.

Infrastructure Cost

This cost is associated with the money spent on facilities viz. Offices, Site, Roads, Gathering station, Processing Plant, and Pipelines. In an interview, this cost was reported in \$/Mcf by Rex Energy. It was not possible to get the further break-up of cost related with each component. This was \$1/Mcf.

10.1 Drilling and Completion Cost

10.1.1 Drilling Permit Fee

There are more than 350,000 drilled wells since 1859 in PA. Oil and gas laws (all or in part) have regulated exploration and drilling for oil and gas. They are ‘The Clean Streams Law’, ‘The Dam Safety’ and ‘Encroachments Act’ etc. There are several agencies like Pennsylvania Fish and Boat Commission, Susquehanna and Delaware River basin commissions that oversee the quality of water and aquatic life in Pennsylvania. Oil and Gas Act of 1984 requires oil and gas companies to acquire a drilling permit, through an extensive permit application process. The application fee has changed from the flat rate of \$100 to at least \$250. It increases with depth and type of drilling. This permit is submitted to Pennsylvania Department of Environment Protection (DEP), who enforces the regulations.(Hemant Kumar,2009)

Prior to February 2009 it was only \$100 per well regardless of the specification of the well, however since then it has changed and now it is calculated based on the depth and length of the well. In this project with D=6000 ft and L= 4000 ft the application fee was calculated to be \$2150 for a single well.(Armstrong Agbaji,2009)

Vertical Drilling:

$$C_V = \begin{cases} 200 & D \leq 1500 \\ 250 & 1500 < D \leq 2000 \\ 250 + 50\left(\frac{D-2000}{500}\right) & 2000 < D \leq 5000 \\ 550 + 100\left(\frac{D-5000}{500}\right) & D \geq 5000 \end{cases}$$

$$D = 6000 \qquad C_V = 550 + 100\left(\frac{D-5000}{500}\right) = 550 + 100\left(\frac{6000-5000}{500}\right) = 750$$

Horizontal Drilling:

$$C_H = \begin{cases} 900 & L \leq 1500 \\ 900 + 100\left(\frac{L-1500}{500}\right) & L > 1500 \end{cases}$$

$$L = 4000 \qquad C_H = 900 + 100\left(\frac{4000-1500}{500}\right) = 1400$$

Total Cost of Drilling permit:

$$C_{T=}\ C_{V+}\ C_H = 750+1400=2150$$

10.1.2 Drilling and Completion cost

A horizontal well can better exploit the shale in case of the presence of a vertical natural fracture system. The Marcellus Shale is heavily jointed by cross cutting vertical natural fractures. So, a vertical drilling would be expected to intersect not more than two fractures at a given location. The average cost for making a horizontal well is 3.5 million ~ 4.0 million. This single well cost includes fracturing services, rigs leasing cost which is around \$22,000 per day. Also, this cost includes pad construction, gas pipelines and local hiring. It should be noted at this point that this cost does not contain the cost of leasing land in Bradford County Table 13.(Davidson, John.2009)

Completing a well is a very expensive process. This cost is different from one company to another. Generally, a vertical well in Marcellus costs around $810,000, whereas a horizontal one costs approximately 1.8 million dollars.

According to Range Resources, who has performed a lot of drilling operation in PA. The average cost of making horizontal wells in 10 years in Bradford County is $4.0 million Table 14.

Water management cost

Fresh Water source

SRBC limits water withdrawal from surface water, groundwater, or a combination of the two to 100,000 gpd/30-day average (3,000,000 gallons). Any further water withdrawal beyond this limit requires permission from SRBC. Each application has a fee associated with it. It can be derived from the Fee Resolution 98-19 from SRBC website and is to be submitted at the application submission time. This fee must be paid in advance and is a non-refundable fee (John A. Veil,2010).To avoid such expense and to insure adequate and dependable supply of water to support well drilling and well stimulation activities, we consider municipal water supply as the fresh water source, the cost can vary greatly from one municipality to another. The current rates quoted in Bradford county range from $5 to $14 per 1000 gallons, but it can be considered negligible in comparison to the cost of trucking. On the other hand, our self-designed mobile forward osmosis filtration system is able to recycle waste water into a high quality completion fluid for use in fracture jobs. On each well, over 80% of the waste water can be recycled to provide approximately 25% of the water required for hydraulic fracturing. As a result, the fresh water consumption cost, on each well, can be reduced from $35,000 to $26000.

10.1.3 Wastewater Treatment

10.2 Conventional methods and challenges

Drillers are taking their wastewater to municipal wastewater treatment plants; however because of the high level of dissolved solids (heavy metals and salt) those plants cannot treat the wastewater properly, since they do not have the adequate industrial wastewater treatment facilities. After a test, resulted higher-than-expected level of total dissolved solid in the

Monongahela, the DEP warned municipal sewage plants to get state approval before accepting gas well wastewater. Basically, wastewater needs to be treated at specialized wastewater treatment plants, which can take heavy metal and salt out of wastewater. Unfortunately not many (less than 10) of these plants exist in the Pennsylvania. This shortage in wastewater facility treatment plant has created a big challenge to drillers and authorities. On the other hand, the high cost of trucking and treatment also bring out another problem, usually the trucking cost ranges from $1 up to $10 per barrel and the average disposal cost quoted from four treatment plants is around $0.05 per gallon(Table 15).

10.3 Recycle and reuse the wastewater onsite

Based on the problems and limits mentioned above, this project is interested in finding water to use in fracture jobs and in managing the subsequent flowback and produced water from those wells in ways that minimize costs and environmental impacts. Our suggested method to accomplish this goal is to establishing a mobile onsite wastewater filtration system, using forward osmosis (FO) technology (Figure 87). Using FO system to recycle drilling waste into completion fluid not only reduces a significant portion of the need for additional fresh water, but also greatly reduces the amount of heavy truck traffic required to move the waste and source water in and out of the well-site, respectively. This portable system is able to provide highest water quality: rejects 100% of virus, bacteria, solids, >90% of undesirable solutes including iron, calcium, metals, barium. Furthermore, the system is energy-saving, driven by alternative energy – osmotic gradient, to reduce the electricity usage. Commercial scale units are trailer mounted systems capable of recycling up to 4 barrels per minute; 168 gallons per minute - 242,000 gallons per day. (McGraw-Hill, 2010)

10.4 Design Economic Analysis

10.4.1 The Cost of design and operating FO system

An initial cost estimate for this application was developed to provide the most meaningful estimate, using the Water Treatment Estimation Routine (WaTER) developed by the United States Department of the Interior, Bureau of Reclamation. (EPA-600/2-09-1626, 2009.)

As mentioned above, Commercial scale units are trailer mounted systems capable of recycling up to 4 barrels per minute; 168 gallons per minute - 242,000 gallons per day. The portable FO system only contains 280 cylinder shaped membrane elements placed in 6 pressure vessels at a capital cost of about $50,000.which reduces physical space requirements but maintains large membrane surface area up to 4000m^2.（Figure 88）

The annual operating cost of the FO system would be about $0.60/kgal of produced water. This relatively high cost results from the low value assumed for flux across the membrane. If guarantee a constant driving force across the membrane, the FO flux may increase 70%, the unit water costs will drop by 36% to about only $0.38/kgal. It is, therefore, economically attractive comparing to the cost of trucking and disposal that discussed previously.

10.5 Total Cost Comparison

The final step of the cost evaluation for this study is to integrate the cost of every aspect, in order to get a total cost estimate. The final calculation includes the cost of exploration, administration, royalty, lease, infrastructure, drilling, completion, hydraulic fracture services, pad construction, gas pipelines and local hiring. It shows that, using the forward osmosis technology, the self designed mobile wastewater reclamation system can significantly reduce the cost of water management up to $1 million. Therefore the total cost is reduced to around $5.33 million for a single well per year, instead of $ 6.41 million traditionally. (EMERALDSURF,2008)

Chapter 11: Environmental Impact of Forward Osmosis Technology

The extensive use of the forward osmosis technology to reclaim drilling and fracturing waste water would have some environmental impact as well. But this is minimal and less impacting than other known methods, considering the fact that the energy required to run the system is produced by the system. If the reserve waste water tank contains 74,000 bbls (3.1 mmbbls), and the forward osmosis unit reclaims 90% of the waste water, then 66,600 bbls of waste water will be reclaimed and 8,000 bbls will be left for recirculation. To reclaim this 66,600 bbls of waste water, the forward osmosis system will use approximately 6000 bbls of 36% NH_4CO_3, resulting in a final produced volume of approximately 72,600 bbls.

Widespread usage of forward osmosis technology to reclaim drilling and fracturing waste water in the Marcellus Shale would save about three-quarters of a billion gallons of fresh water per year. Aside this benefit, the forward osmosis model also eliminates 66,600 bbls of waste water per horizontal well of trucking related road damage and emissions due to reserve pit waste water haul off represents a significant reduction in the carbon footprint of the industry. Approximately 175 truck loads can be eliminate per reserve pit from conventional practice. An average of 4 mpg for a typical 18-wheeler and a 100 mile average load distance per truck represents approximately 25 gallons of fuel emissions eliminated per load, or 4,375 gallons of diesel emissions eliminated per 66,600 bbls of waste water reclaimed. Based on the assumptions above, widespread usage of FO technology to reclaim drilling and fracturing waste could save approximately 6.2 million gallons of diesel emissions each year. Considering the fact that there are about 25 known shale basins in the United States where the forward osmosis technology alongside the power generation can be employed. Conversely, the forward osmosis technology is not limited to shale development but is applicable in conventional oil and gas plays also.

Chapter 12 Regulations:

12.1 The Pennsylvania's **Oil and Gas Act, 1984 (Act 223),** Title 58. Sec. 601.101

This tates the authority of the Department of Environmental Resources in protecting land owners, regulate the drilling and operation of oil and gas wells, for gas storage reservoirs, for various reporting requirements, including certain requirements as it pertains to the operation of coal mines, for well permits, for well registration, for distance requirements, for well casing requirements, for safety device requirements, for storage reservoir obligations, for well bonding requirements, for a Well Plugging Restricted Revenue Account to enforce oil and gas well plugging requirements, for the creation of an Oil and Gas Technical Advisory Board, for oil and gas well inspections, for enforcement and for penalties. While Sec. 601.102 clearly states the following;

- ✓ Permit the optimal development of the oil and gas resources of Pennsylvania consistent with the protection of the health, safety, environment and property of the citizens of the Commonwealth.
- ✓ Protect the safety of personnel and facilities employed in the exploration, development, storage and production of natural gas or oil or the mining of coal.
- ✓ Protect the safety and property rights of persons residing in areas where such exploration, development, storage or production occurs.
- ✓ Protect the natural resources, environmental rights and values secured by the Pennsylvania Constitution.

12.2 **The Clean Streams Law** P.L 1987, Act 394 of 1937, as amended:

The purpose of the aforementioned Act is to "conserve and improve the purity of the waters of the Commonwealth for the protection of public health, animal and aquatic life, and for industrial consumption, and recreation; empowering and directing the creation of indebtedness or the issuing of non-debt revenue bonds by political subdivisions to provide works to abate pollution; providing protection of water supply and water quality; providing for the jurisdiction of courts in the enforcement thereof; providing additional remedies for abating pollution of waters; imposing certain penalties; repealing certain acts; regulating discharges of sewage and industrial wastes; regulating the operation of mines and regulating the impact of mining upon water quality, supply and quantity; placing responsibilities upon landowners and land occupiers and to maintain primary jurisdiction over surface coal mining in Pennsylvania".

Section 4 emphasized on the Declaration of Policy, which are as follows;

- ✓ Clean, unpolluted streams are absolutely essential if Pennsylvania is to attract new manufacturing industries and to develop Pennsylvania's full share of the tourist industry;
- ✓ Clean, unpolluted water is absolutely essential if Pennsylvanians are to have adequate out of door recreational facilities in the decades ahead;
- ✓ It is the objective of the Clean Streams Law not only to prevent further pollution of the waters of the Commonwealth, but also to reclaim and restore to a clean, unpolluted condition every stream in Pennsylvania that is presently polluted;
- ✓ The prevention and elimination of water pollution is recognized as being directly related to the economic future of the Commonwealth; and
- ✓ The achievement of the objective herein set forth requires a comprehensive program of watershed management and control.

Chapter 13: Conclusion

The advent of shale gas development in the quest of meeting the world's energy demands, did not come only with benefits but also some challenges. The natural low permeability shale must be fractured to guarantee higher productivity and the fracturing process involves the use of millions of gallons of water that must be recovered as flow back or produced waste water. Public and regulatory pressure is demanding that operators in the oil and gas industry improve water management practices. Exploring several results of laboratory and field testing from early commercial jobs indicate that, flexible, portable and scalable Forward Osmosis units are applicable to resourcefully and efficiently reclaim water-based waste for valuable reuse as a high quality completion fluid. In addition to reducing the required quantity of fresh water drawdown and reducing the amount of waste water generated in the development process, the results confirms that forward osmosis can significantly lessen the carbon footprint of exploration and production in the oil and gas industry. Waste water reclamation represents one piece of the overall water management puzzle. Additional technologies and applications can further enhance the oil and gas industry's overall impact on fresh water resource conservation.

Chapter 14 RECOMMENDATIONS

Forward osmosis is a simple and spontaneous process that was recently engineered and adapted to various water treatment applications mostly in industrial water management. For the purpose of this design project, it was successfully established that forward osmosis can be coupled with power generation processes to simultaneously recover purified water from a broad range of impaired waters, and to provide power from the waste water- draw solution contact, which lowers the energy required for the total project economics.

Future work should include proper flow modeling, testing the process at a larger scale with the aim of generating energy from other sources besides waste water such as sea water, run off and industrial waste. The system designed in this project can be easily used for several kinds of water reclamation and energy production.

It is recommended that future design and development of the forward osmosis blue energy integrated system for waste water treatment should consider improved material use and better energy generation methodologies from the chemical potential energy between waste water and an improved draw solution. Additional improvement on the selected membrane would be helpful in enhancing the efficiency of the integrated process. Investments into the development of forward osmosis membranes with higher solute rejection and higher water flux are highly recommended.

APPENDIX

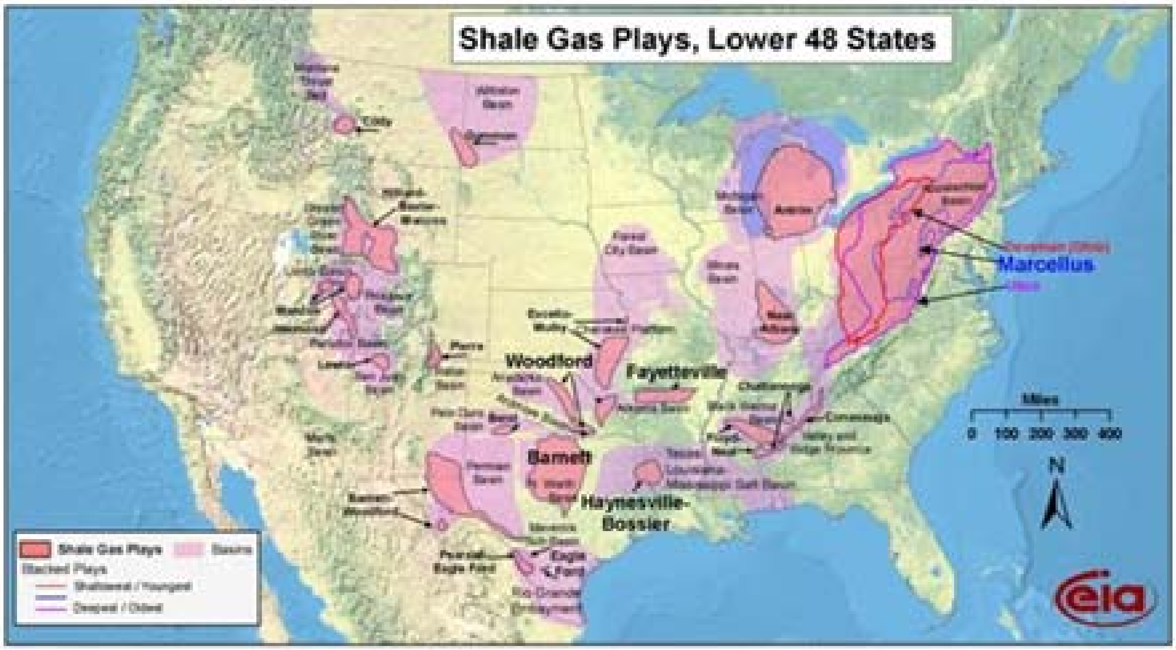


Figure 1 - Shale Play in the US: Courtesy: EIA

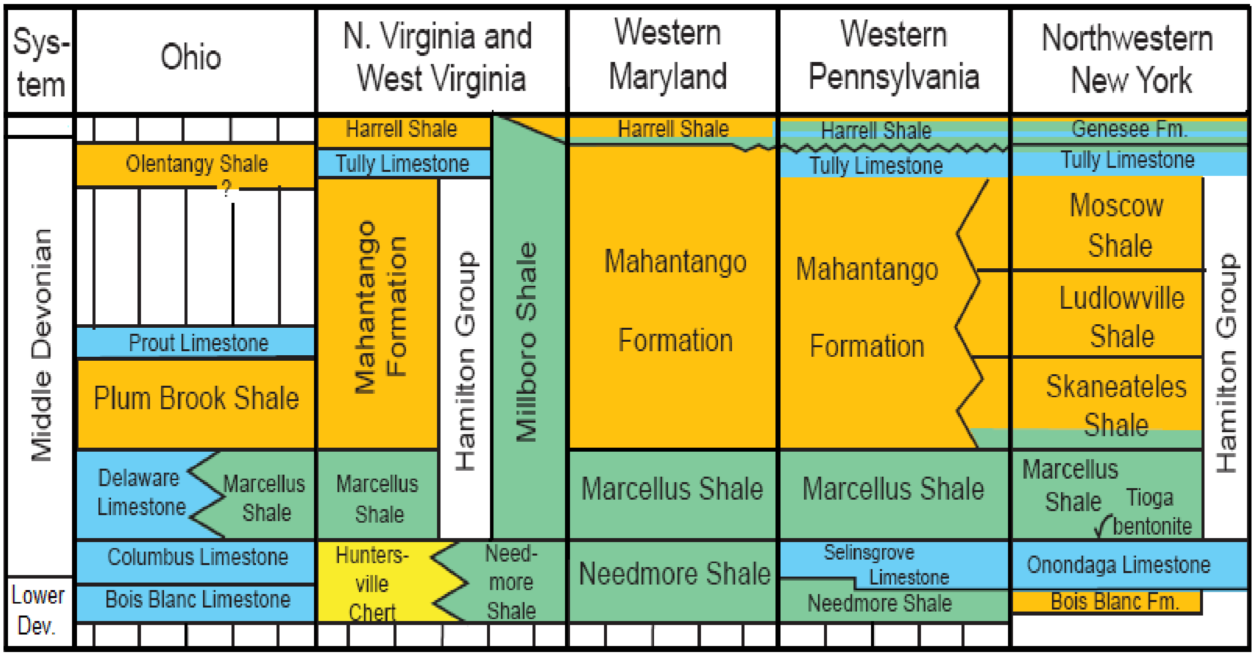


Figure 2 - Stratigraphic Column Showing The Marcellus Shale

Figure 3 - Drilling by a public water reservoir Beaver Run Reservoir, (marcellus-shale.us)

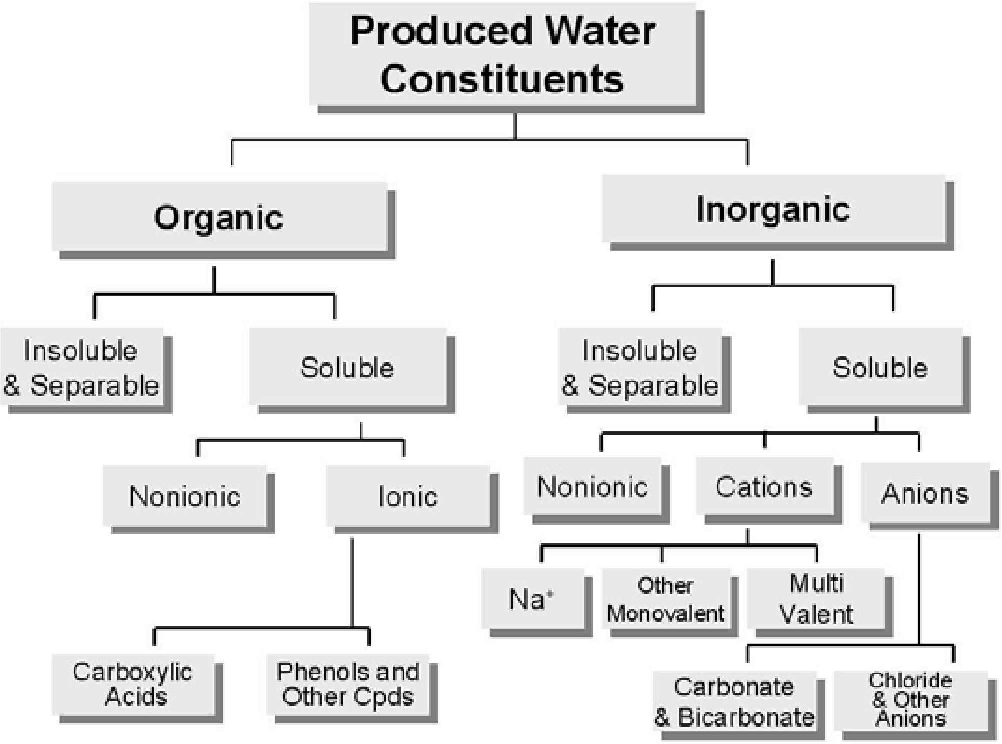


Figure 4 - Breakdown of Produced Water Chemical Constituents.

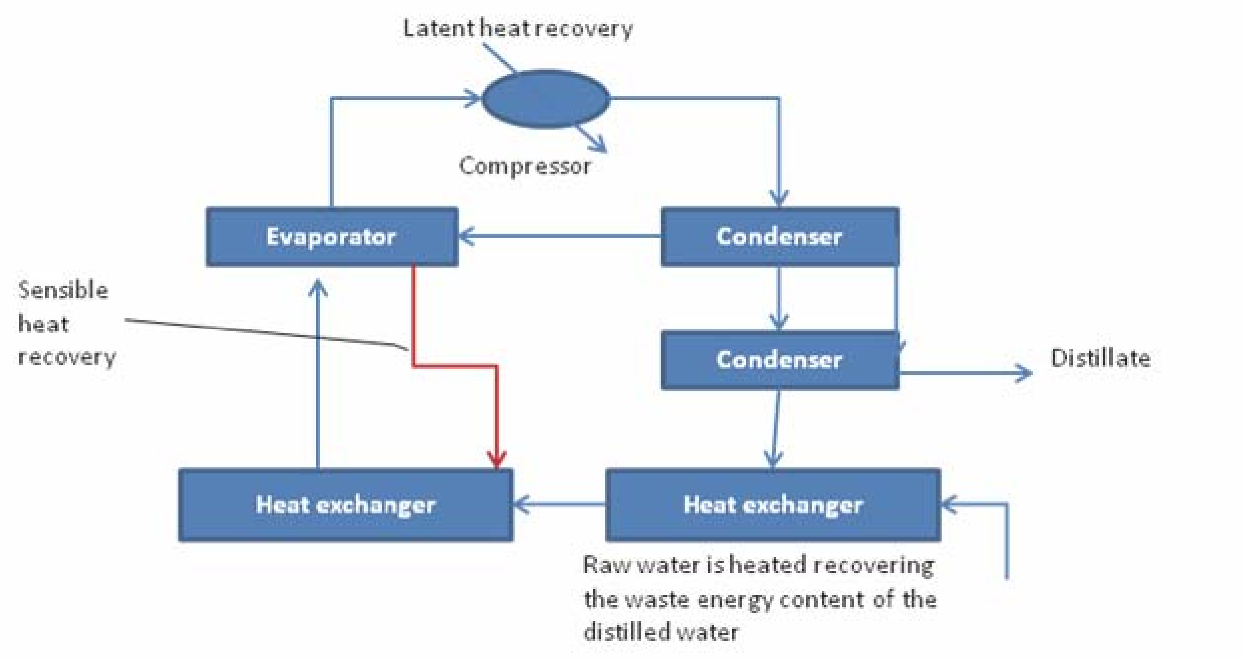


Figure 5 - Vapor compression evaporation process, Pierce D.A. 2010

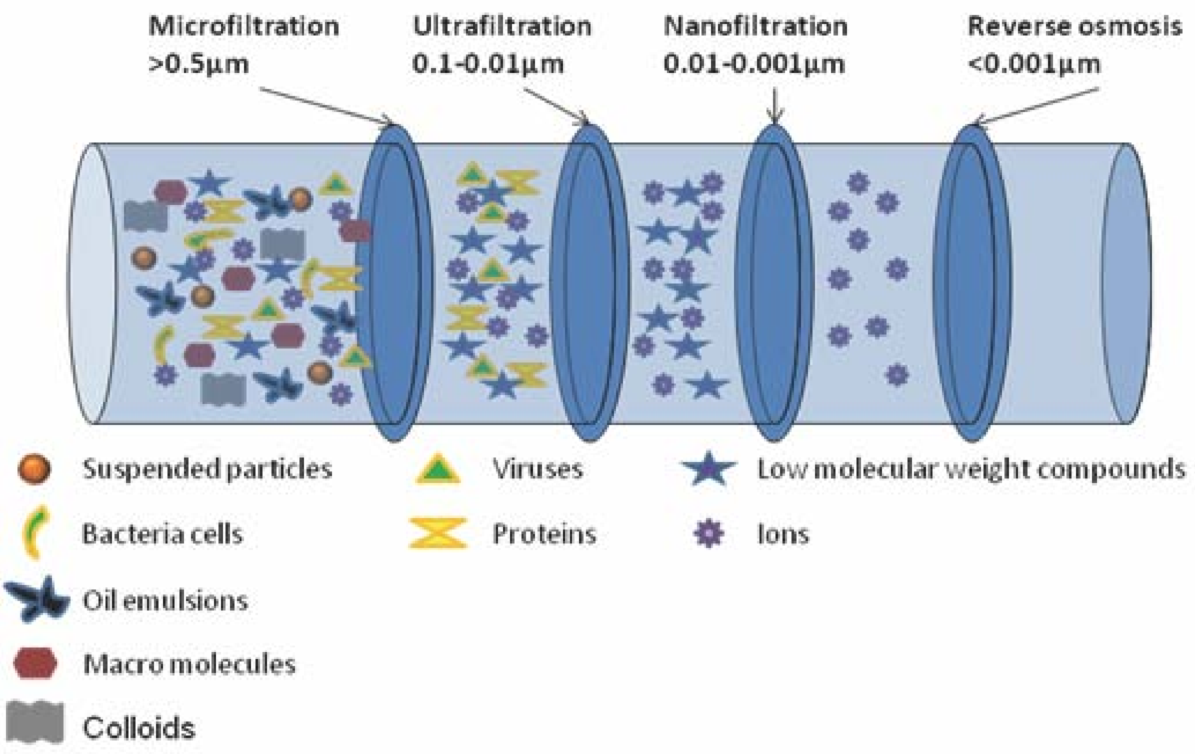


Figure 6 - Separation via filtration Pierce D.A. 2010

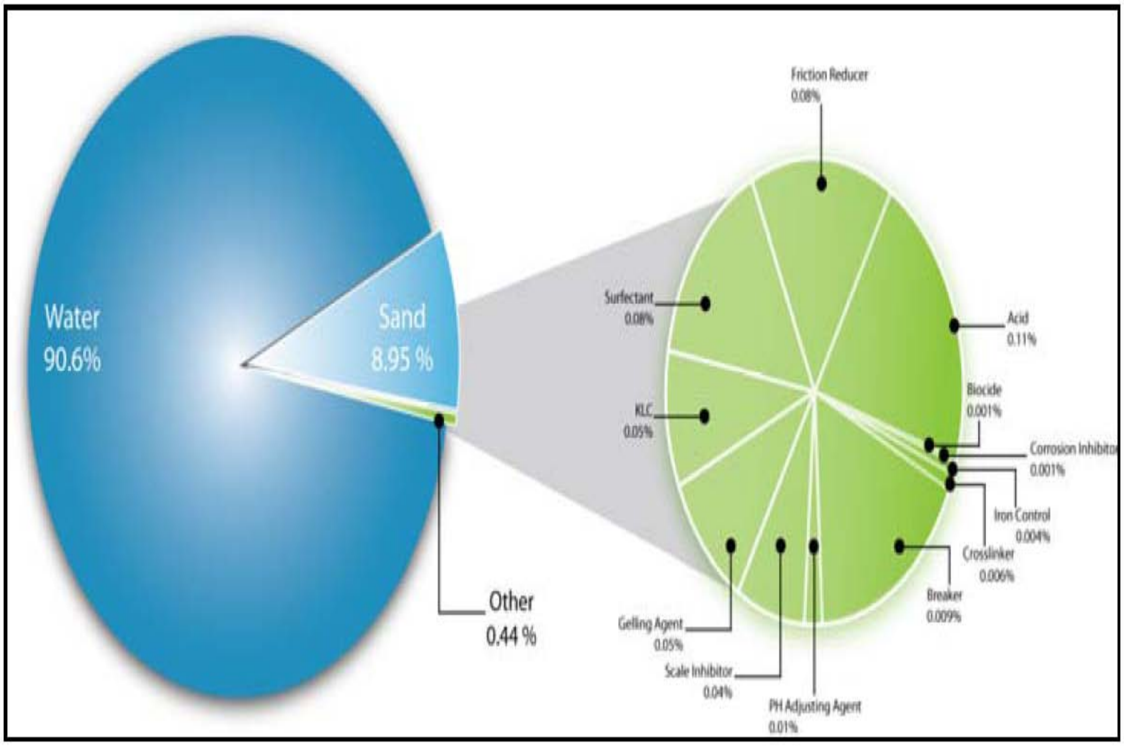
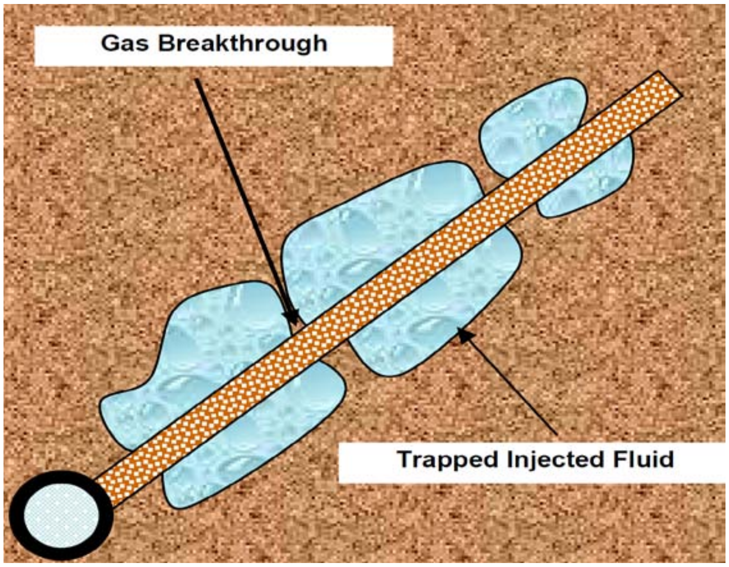


Figure 7: Volumetric Composition of a Shale Gas Fracture Fluid (Source: J. Daniel, Brian Bohm, and Davd Cornue, 2009)



Firgure 8. Representation of injected fracturing fluid being trapped near the proppant pack (Penny G.S., 2005)

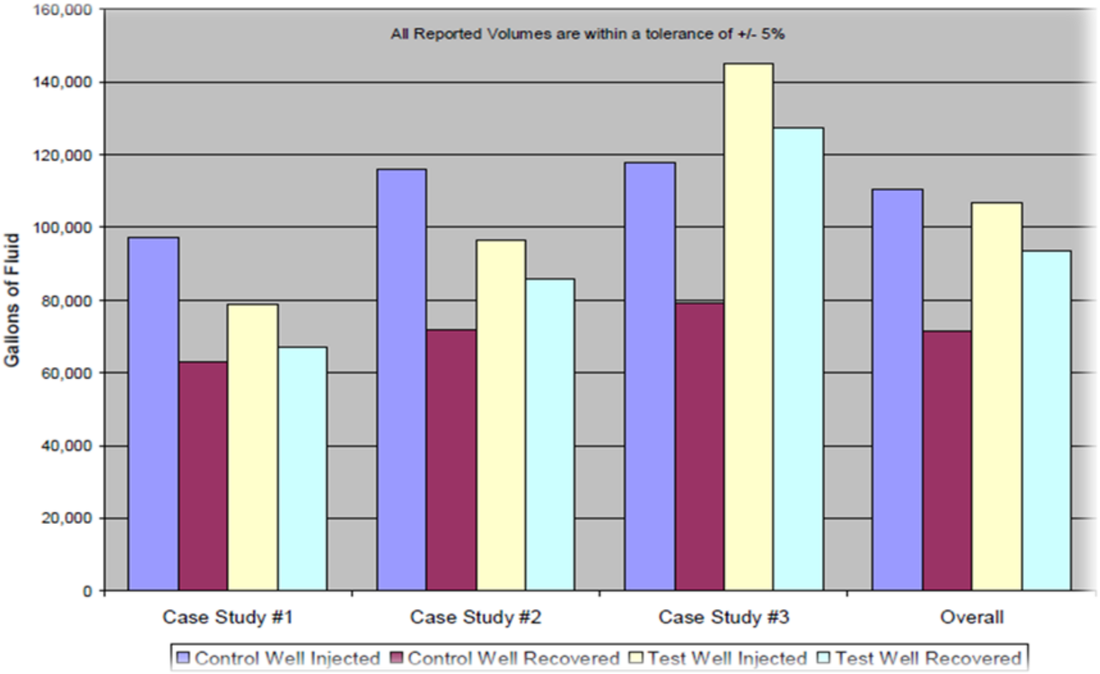


Figure 9. Fluid Recover Data for Case Studies

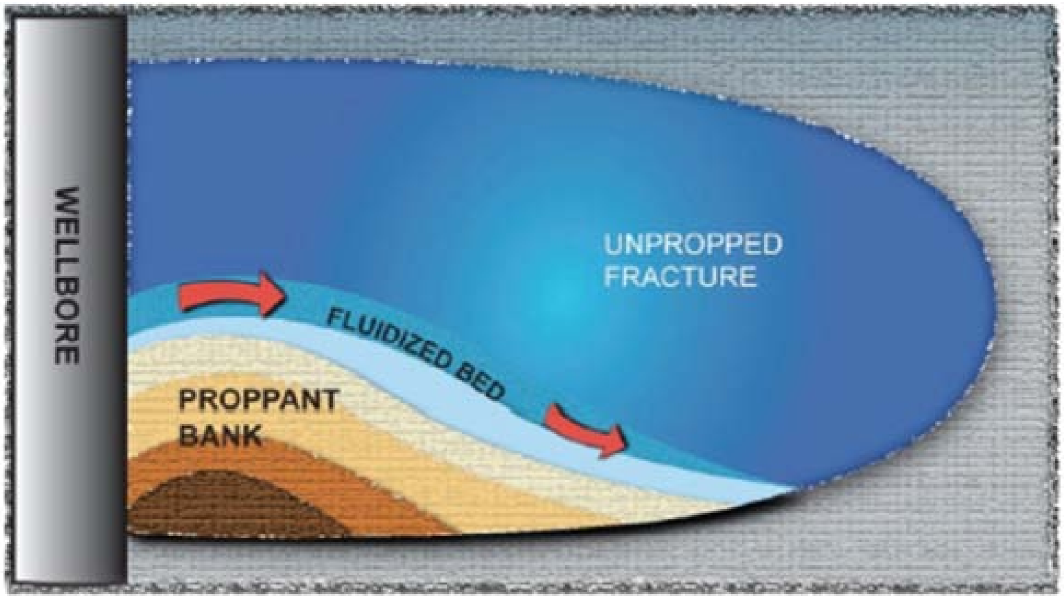


Figure 10. Slickwater bed load proppant transport(N. Kostenuk, 2010)

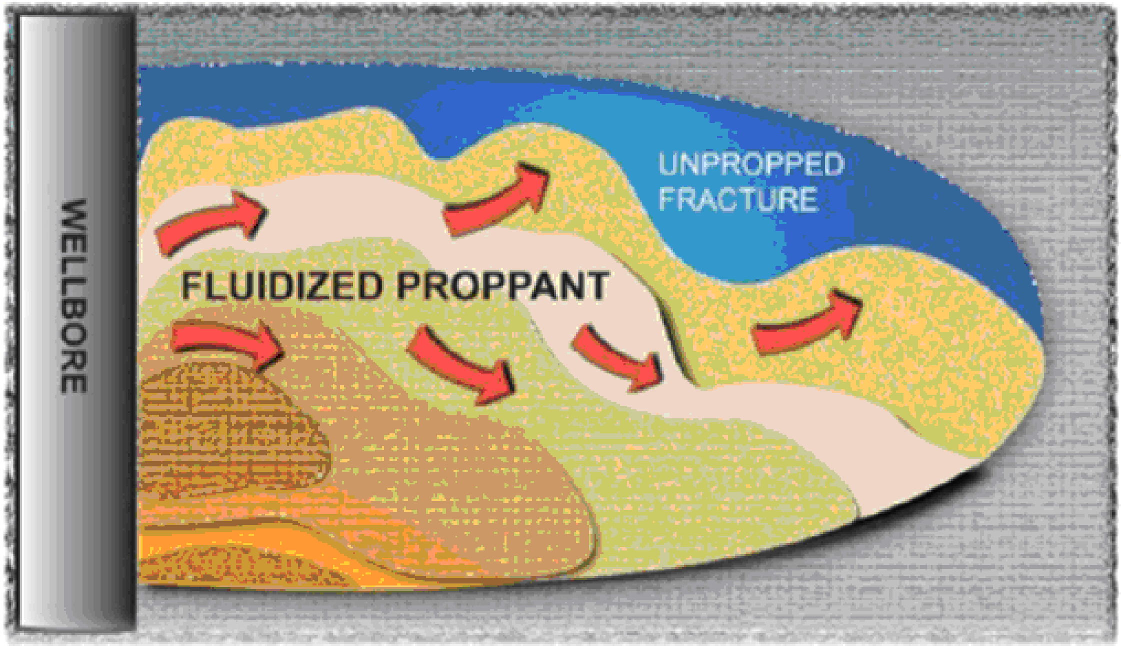


Figure 11. Slickwater with proppant transportation modifier (N. Kostenuk, 2010).

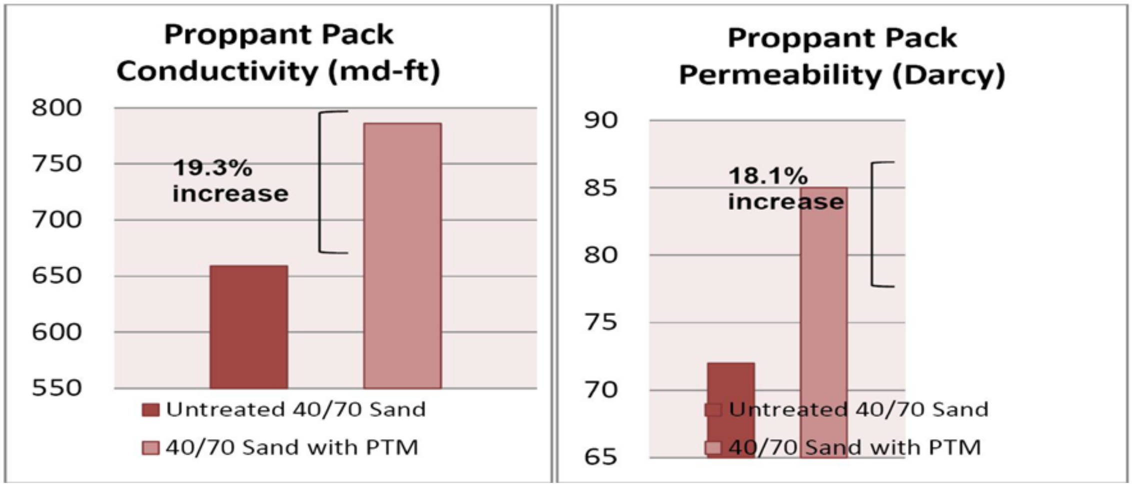


Figure 12. Comparison of Proppant Conductivity and Permeability (N. Kostenuk, 2010).

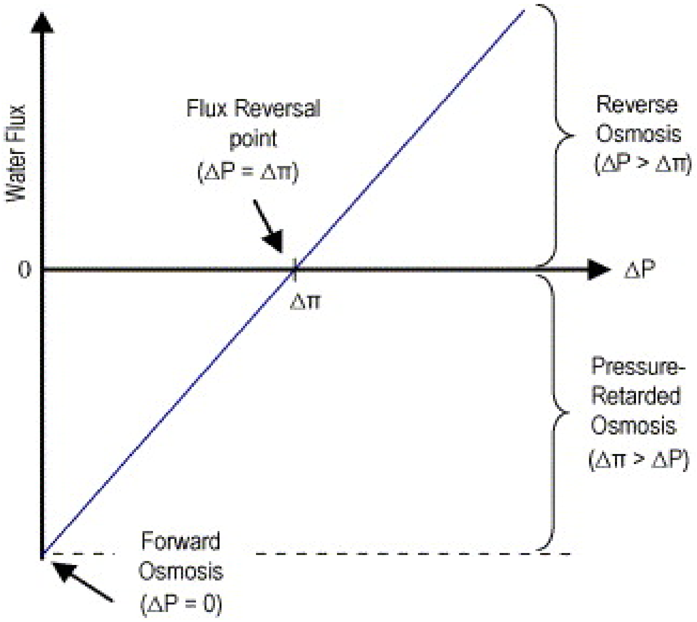


Figure 13: Osmotic Pressure Gradient

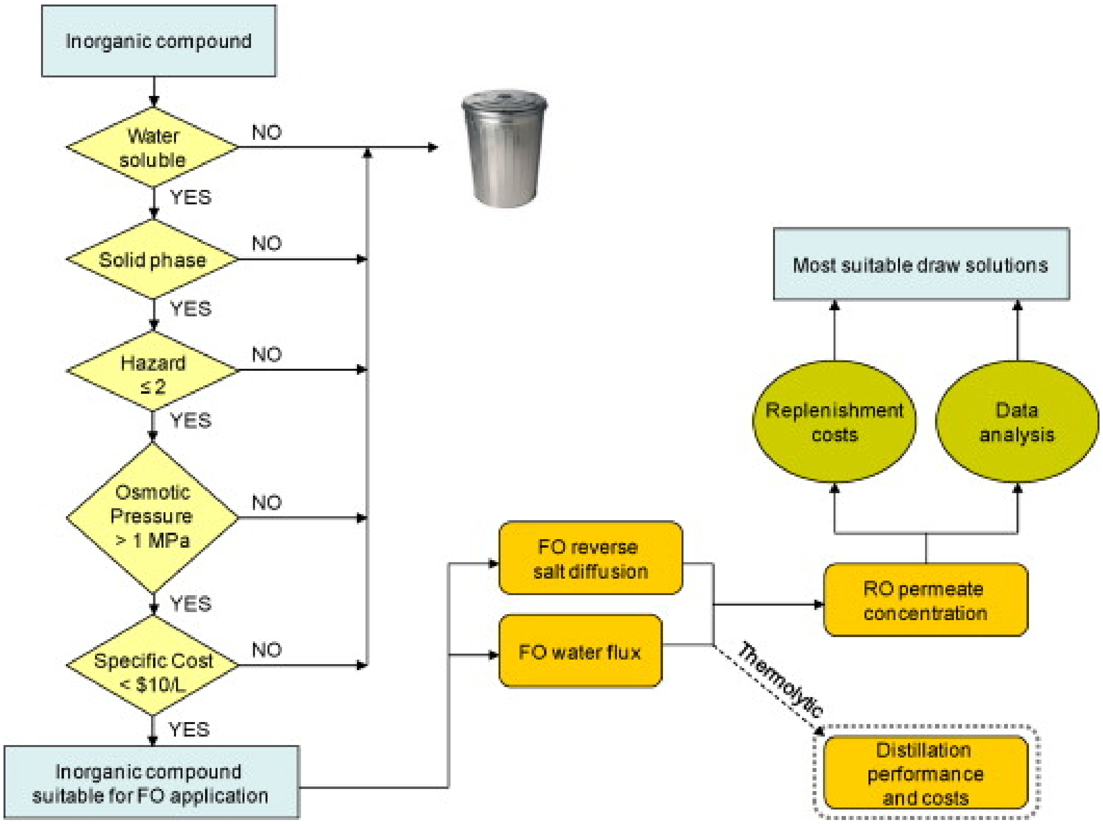


Figure 14 - Illustration of flow diagram for draw solution selection.

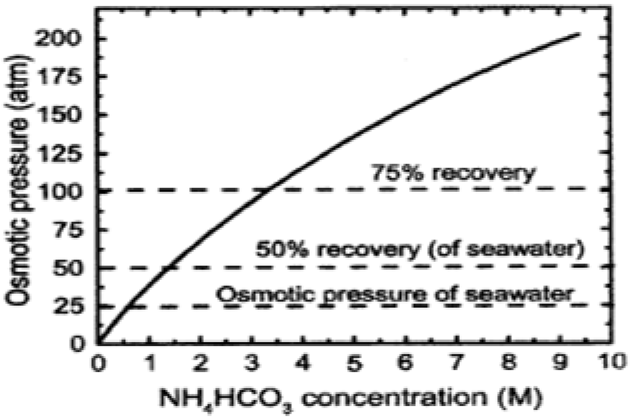


Fig 15 Osmotic pressure generated by ammonium bicarbonate solution at 50°C. Calculations were carried out with a software package from OLI Systems, Inc. (Morris Plains, NJ). The horizontal dashed lines represent osmotic pressures of the following feed waters: seawater and seawater undergoing 50% and 75% recovery.

Figure 15 - Osmotic Pressure with NH_4HCO_3 as Draw Solution (McGinnis, 2007)

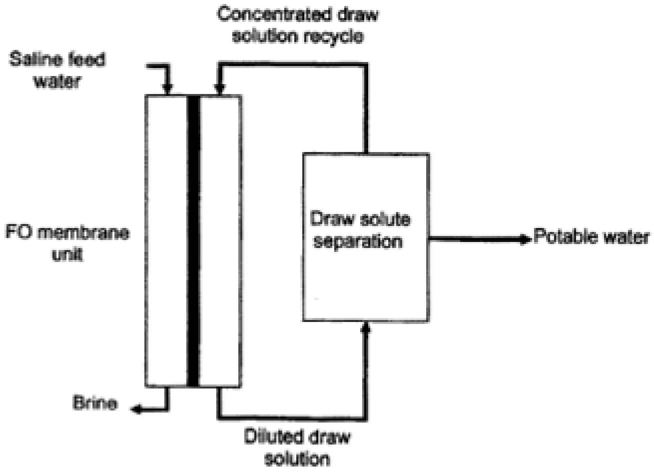


Fig 16 Schematic diagram of the novel ammonia-carbon dioxide forward osmosis desalination process.

Figure 16 - Box Diagram of Experimental Forward Osmosis Design. (McClutcheon 2006)

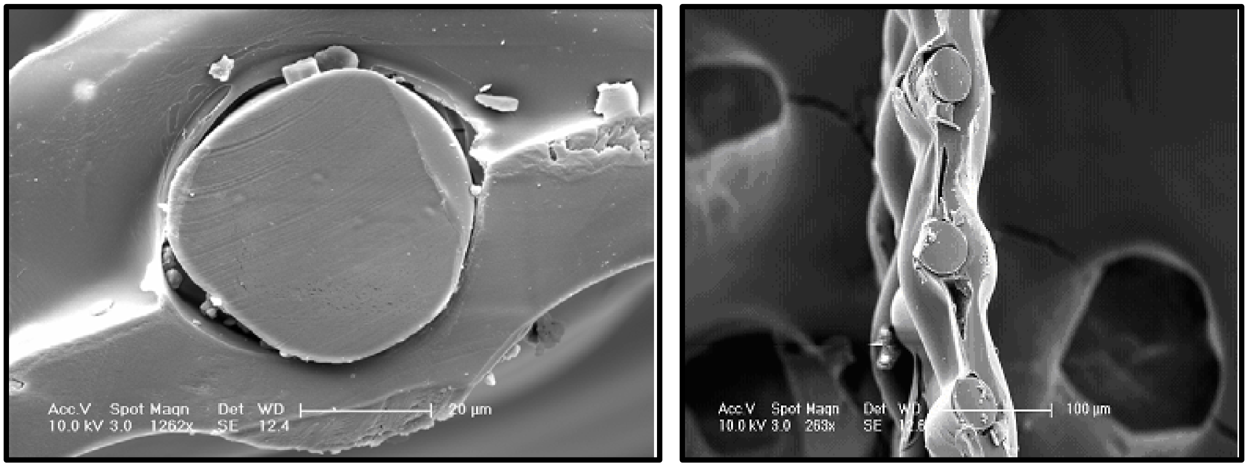


Figure 17. Shows SEM Photograms of Two Hollow Fiber Forward Osmosis Membranes Developed by Wong et. Al. 2010

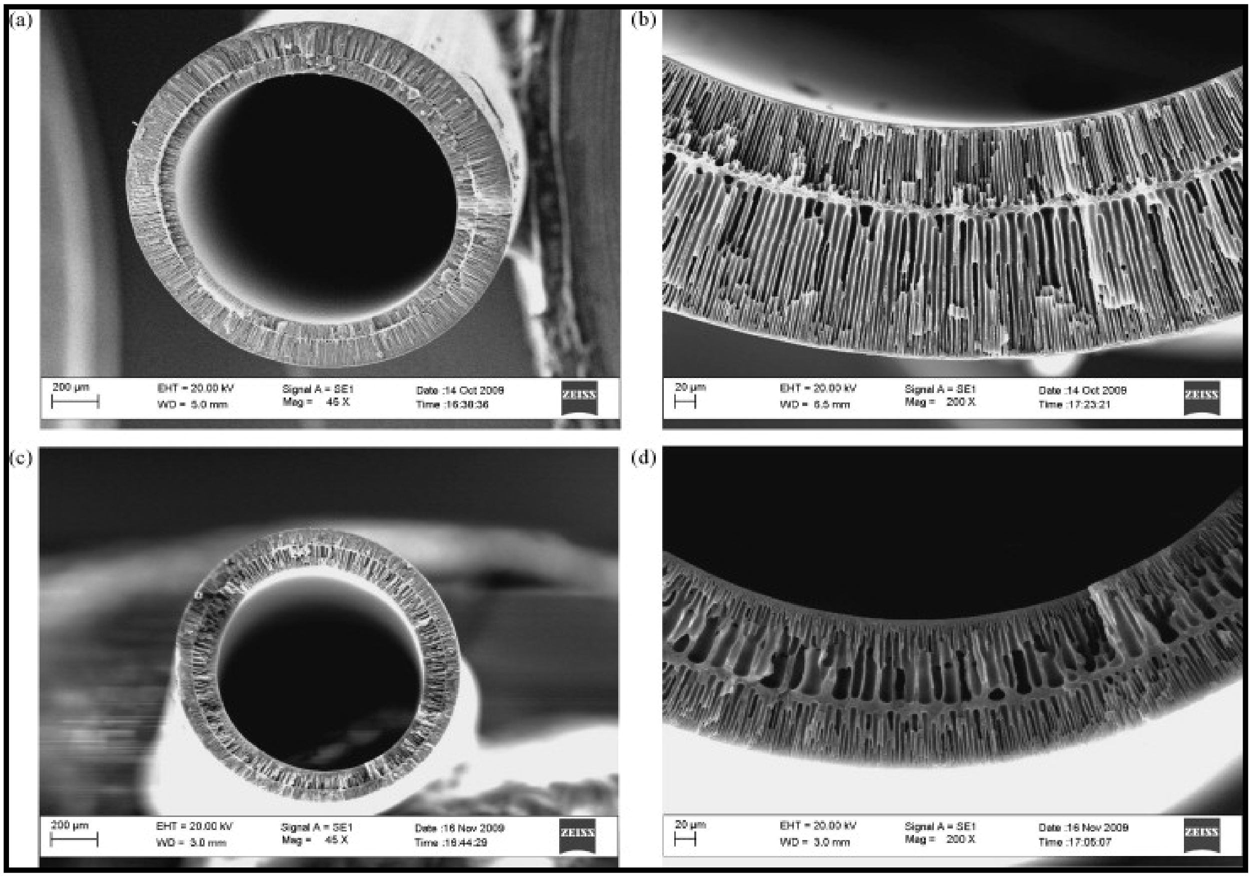


Figure 18. Morphology of PES FO hollow fiber substrates. (a) #A cross-section at 45×, (b) #A enlarged at 200×, (c) #B cross-section at 45×, and (d) #B enlarged at 200×.[Wong,2010]

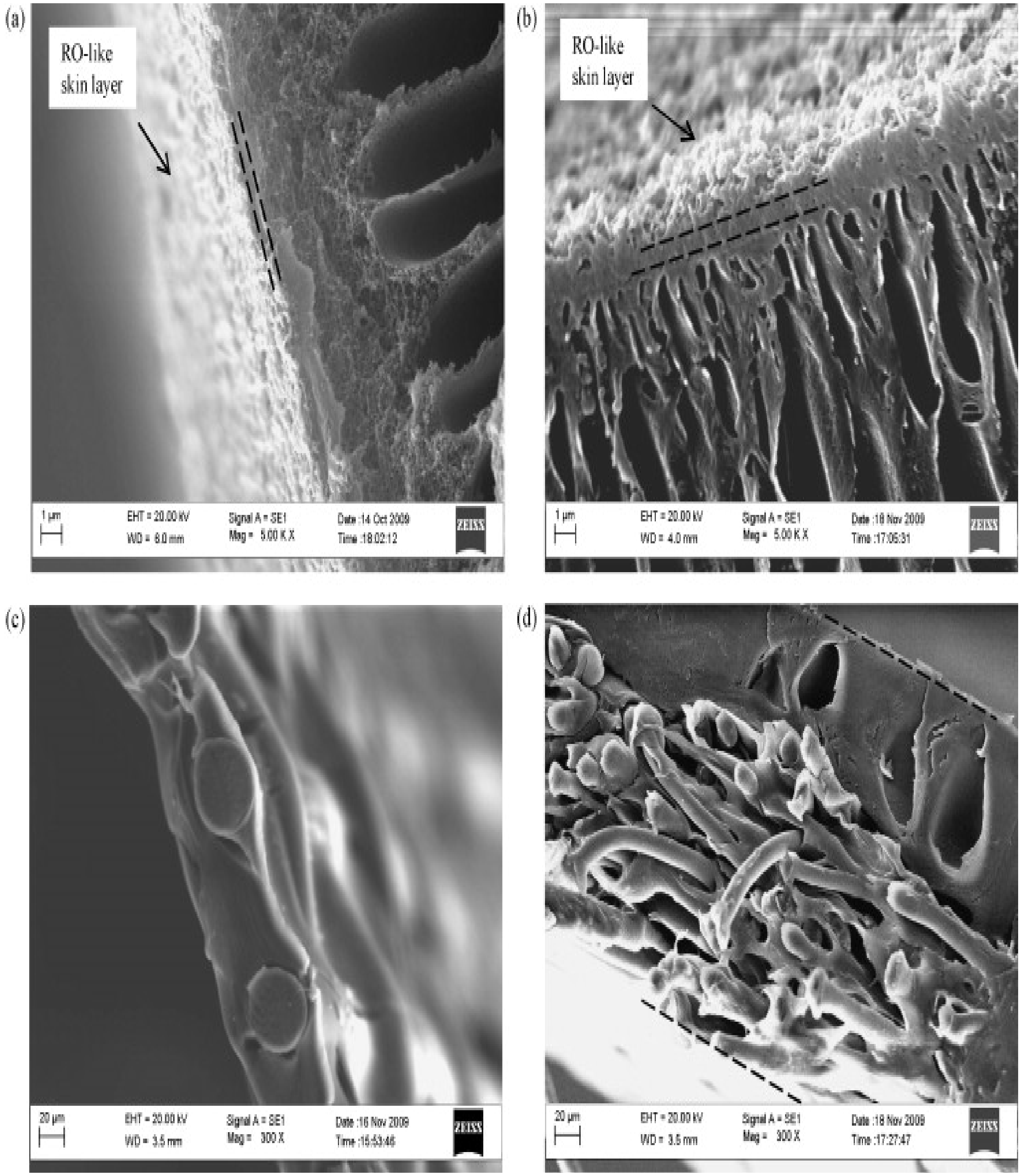


Figure 19. Cross-section morphologies of FO membranes. (a) #A-FO hollow fiber at 5000×; (b) #B-FO hollow fiber at 5000×; (c) Cartridge-type HIT flat sheet at 300×; (d) Pouch-type HIT flat sheet at 300×.(Wong,2010)

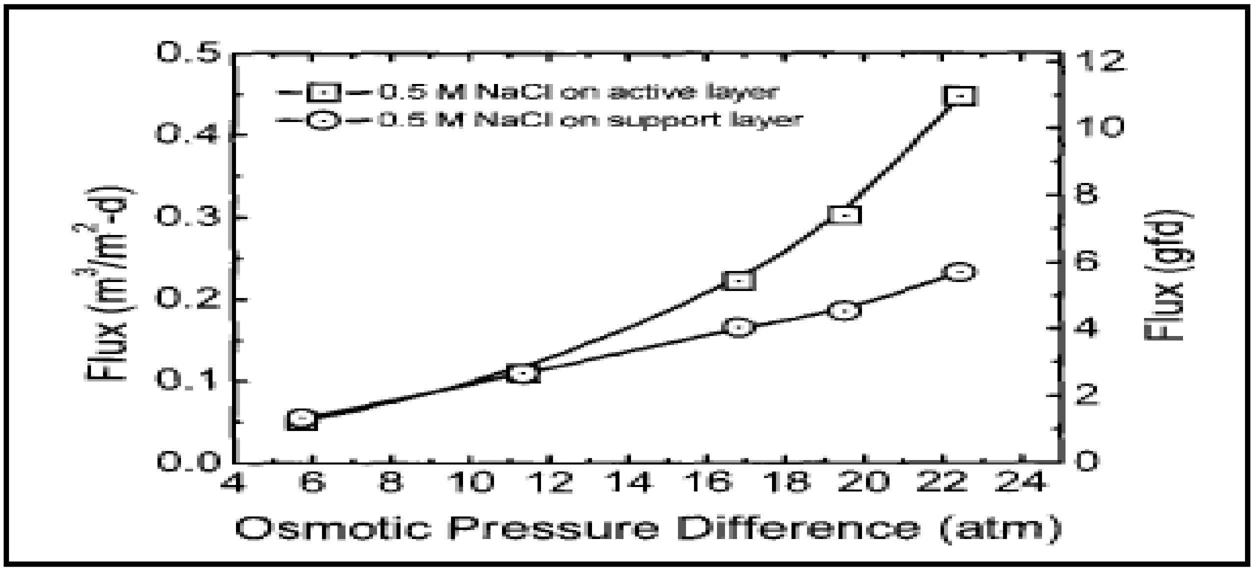


Figure 20 - Water flux data for 0.5 M NaC1 draw solution and a variety of NaC1 feed solutions ranging from deionized water to 0.375 M. (Gray, 2006)

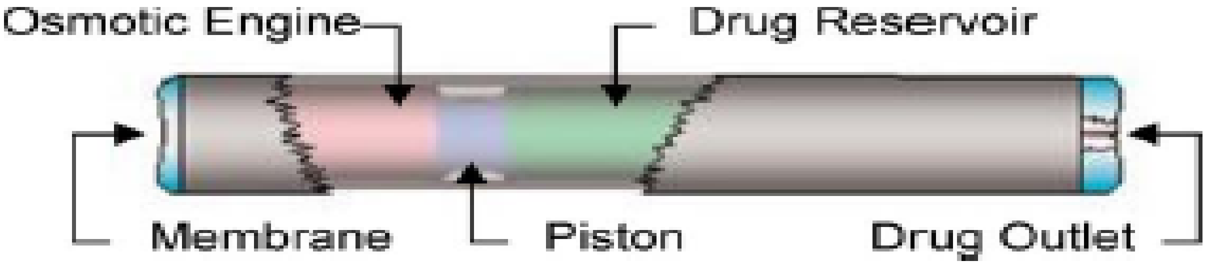
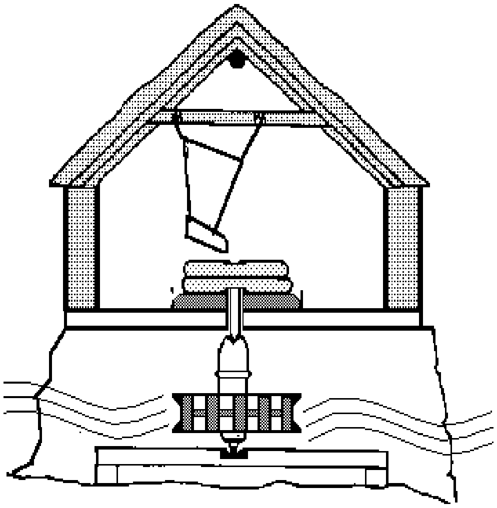


Figure 21. Cross-section of the implanted DUROS® System. (Ng,2006)



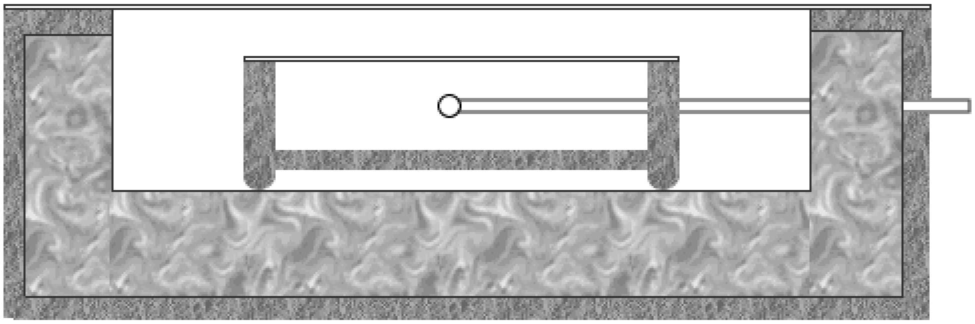
Norse mill was widely used in Scandanavian, Irish and Scottish settlements far from feudal centers of power, and also in the Mediterranean. This was simple, low-tech, small and not very efficient mill running at approximately 1/2 hp. But the technology was decentralized, easy to build and maintain, and not useful for collecting grain as a taxes, and therefore preferred by family groups and small farmers.

Figure 22 - Simple water mill - horizonal or Norse mill

High-tech, efficient, expensive, complex vertical mills had a centralizing tendency, and were the type used to collect “soke” taxes for feudal lords. This vertical is an "overshot" mill, and would have developed about 3 hp.

There were over 6,000 in England at the time of Domesday survey 1088, while at the same time, virtually no Norse mills.

Figure 23 - Complex vertical water mills



Cross section of Langley's hot box, which was based on de Saussure's later models. A thermometer was used to measure the air temperature inside the inner box.

Figure 24 - A cross-section of a hot box. Eighteenth- and nineteenth-century scientists used the hot box to test how much sunheat glass-covered enclosures could trap.

Figure 25: The salinity-gradient energy potential makes the 30-km long Afsluitdijk in The Netherlands comparable to the 221 m high Hoover Dam in Nevada and Arizona (USA).

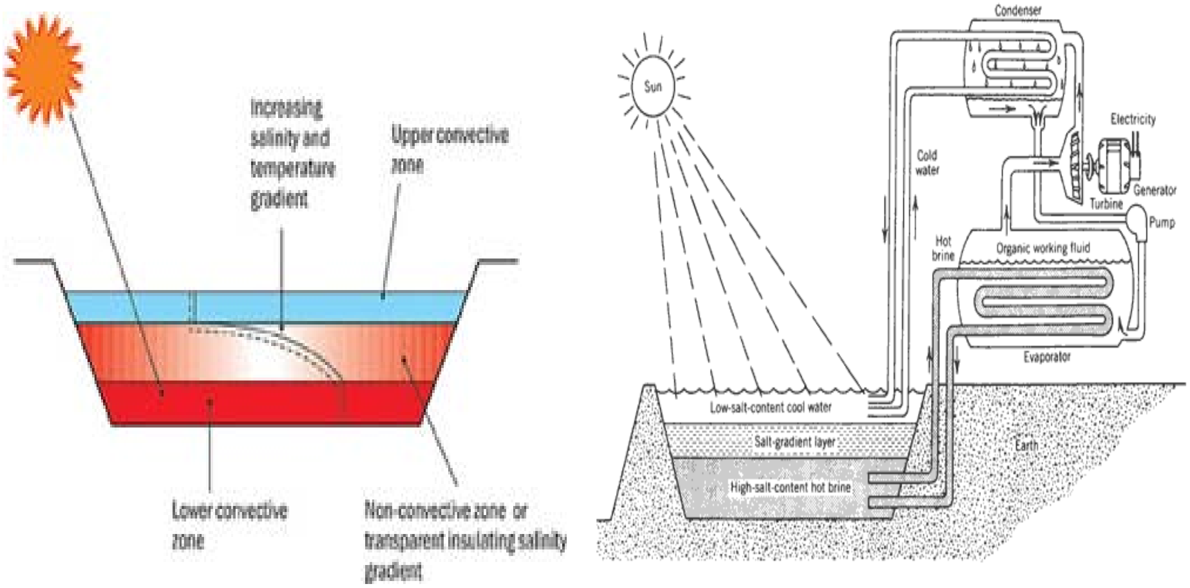


Figure 26 - A visual demonstration of how a solar pond is used to generate electricity

Source: www.powerfromthesun.net/Chapter6/Chapter6.htm. Author: unknown. Permission: www.powerfromthesun.net/Chapter6/Chapter6.htm.

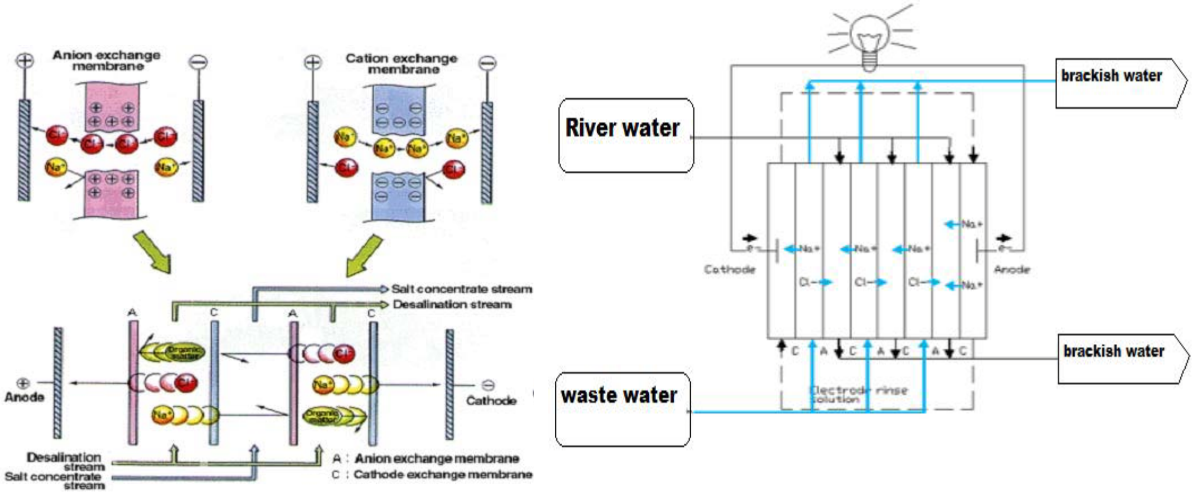


Figure 27 - Schematic representation of reverse electrodialysis; C is a cation exchange membrane and A is an anion exchange membrane.

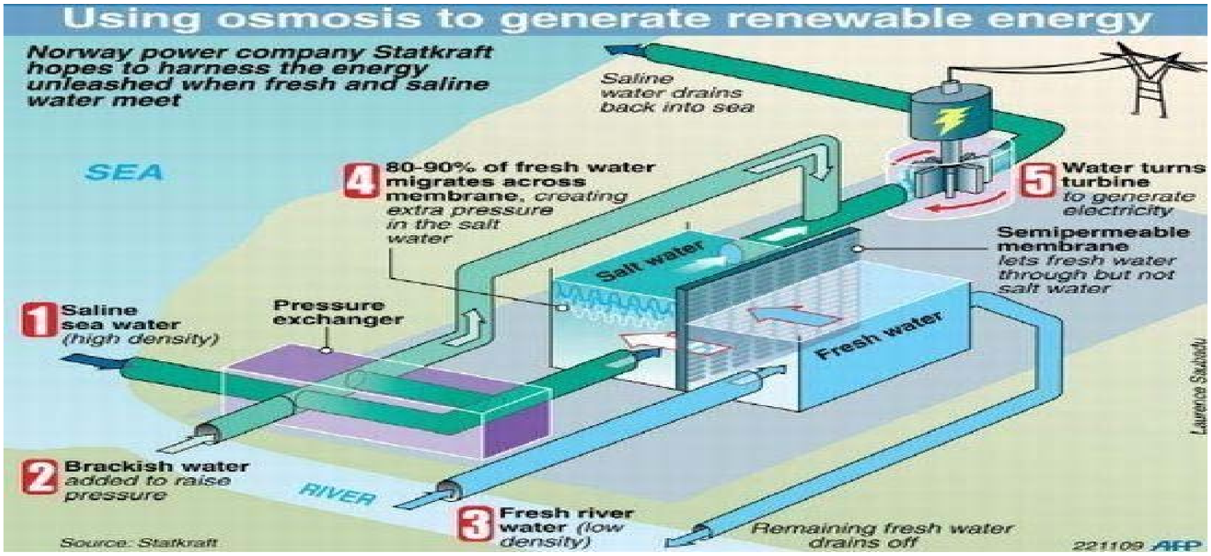


Figure 28 - Generation of energy by Pressure retarded osmosis method by Statkraft's prototype plant

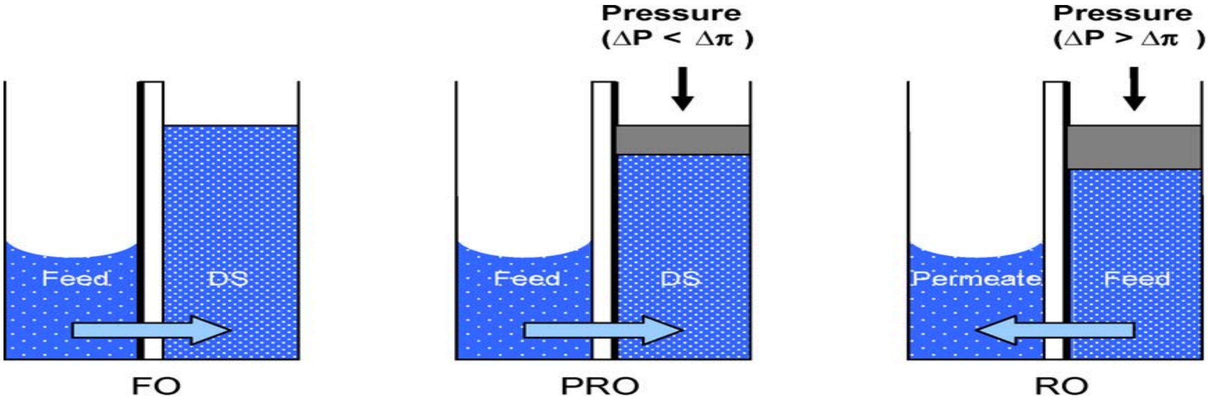


Figure 29 - Representation of solvent flow in FO, PRO, and RO. Membrane orientation is indicated in each system by the thick black line representing the membrane dense layer.

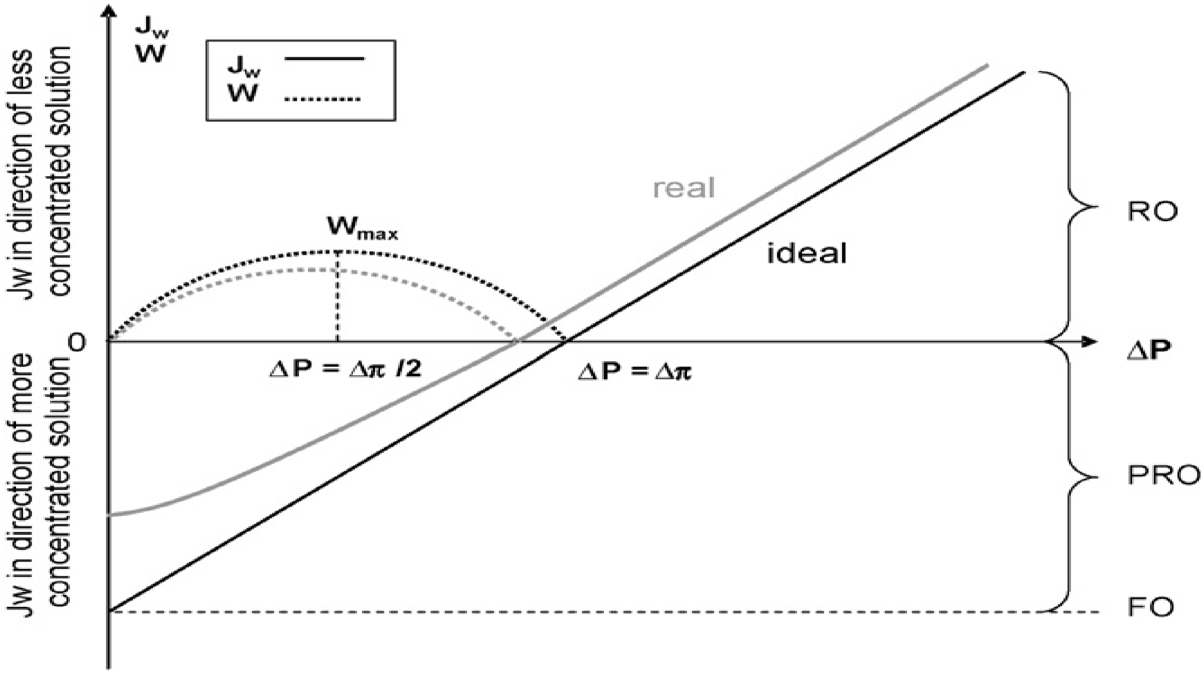
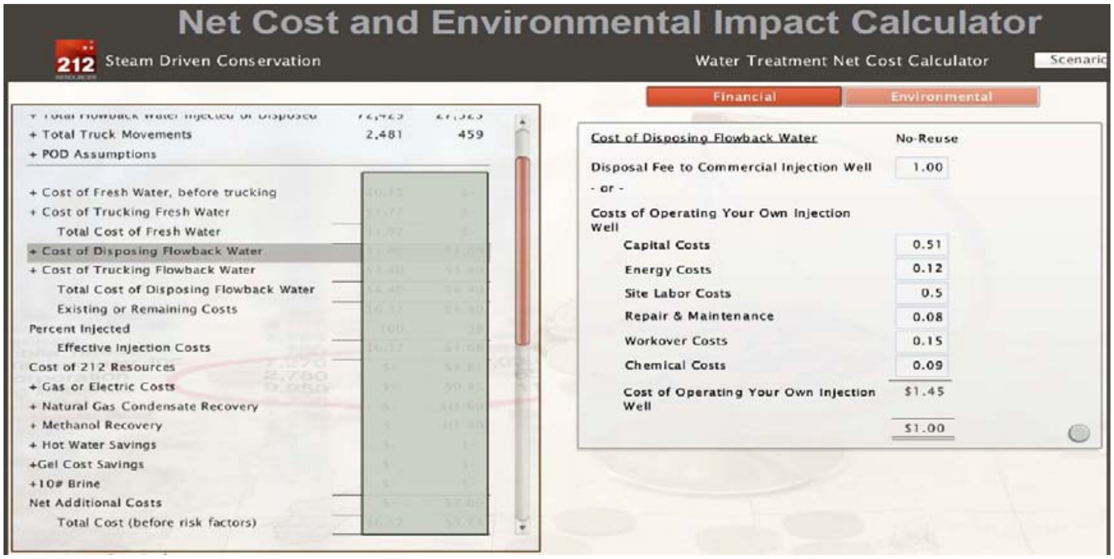


Figure 30 - Magnitude and direction of Jw for FO, PRO, and RO and magnitude of W for PRO is shown. Figure adapted from (K. L. Lee et al)



+ Total Truck Movements	2,481	459
+ POD Assumptions		
+ Cost of Fresh Water, before trucking		
+ Cost of Trucking Fresh Water		
Total Cost of Fresh Water		
+ Cost of Disposing Flowback Water		
+ Cost of Trucking Flowback Water		
Total Cost of Disposing Flowback Water		
Existing or Remaining Costs		
Percent Injected		
Effective Injection Costs		
Cost of 212 Resources		
+ Gas or Electric Costs		
+ Natural Gas Condensate Recovery		
+ Methanol Recovery		
+ Hot Water Savings		
+Gel Cost Savings		
+10# Brine		
Net Additional Costs		
Total Cost (before risk factors)		

Cost of Disposing Flowback Water	No-Reuse
Disposal Fee to Commercial Injection Well	1.00
- or -	
Costs of Operating Your Own Injection Well	
Capital Costs	0.51
Energy Costs	0.12
Site Labor Costs	0.5
Repair & Maintenance	0.08
Workover Costs	0.15
Chemical Costs	0.09
Cost of Operating Your Own Injection Well	$1.45
	$1.00

Fig 31- Net Cost Calculator (212 Resources, 2009)

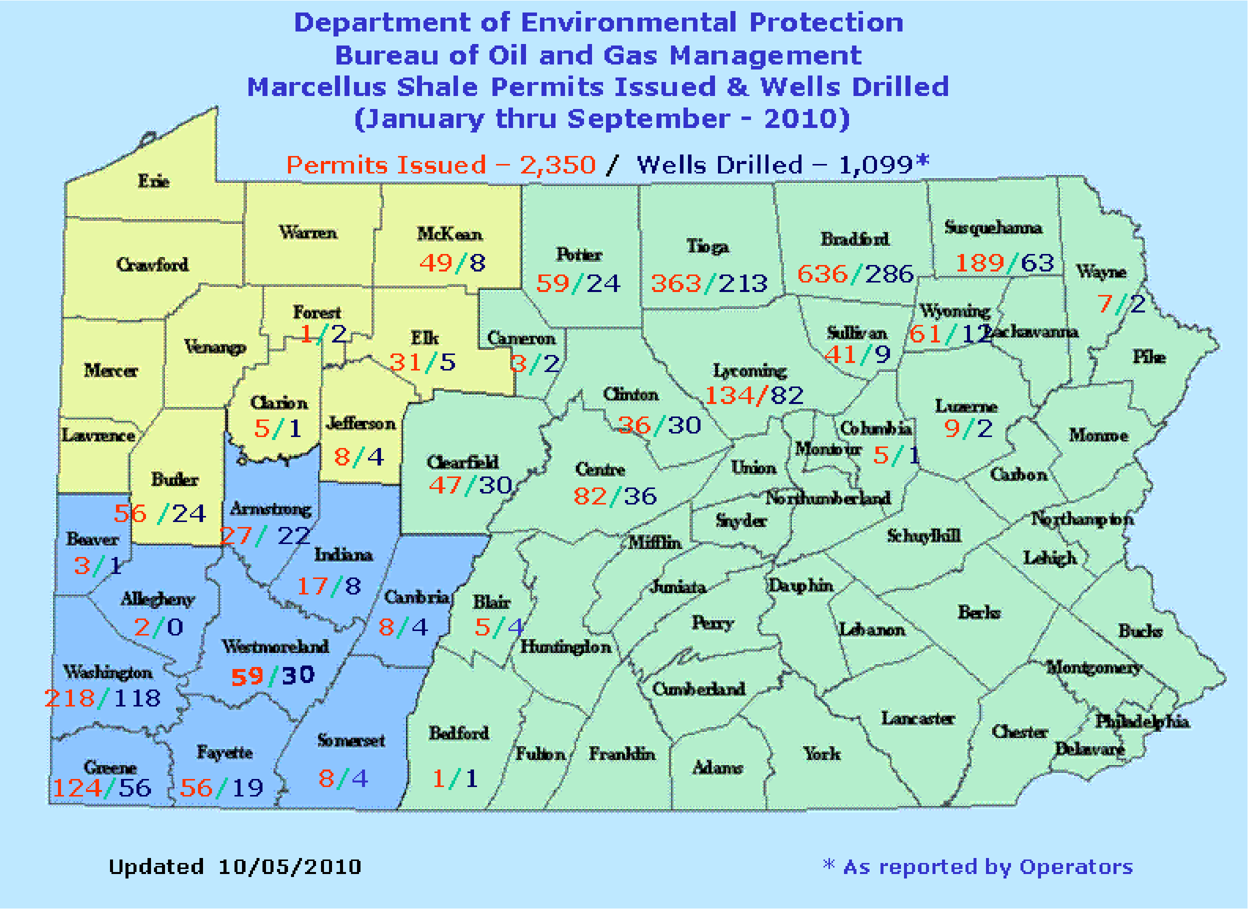


Figure 32- Number of wells drilled in the PA section of the Marcellus Shale

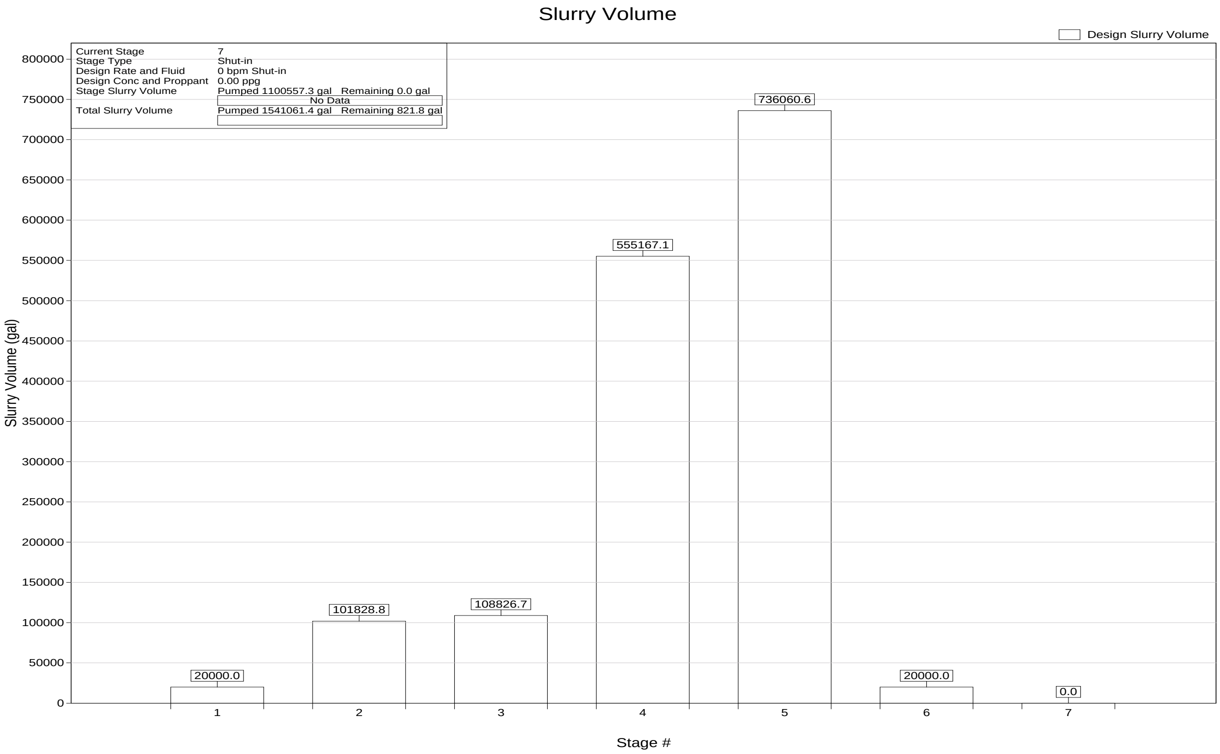
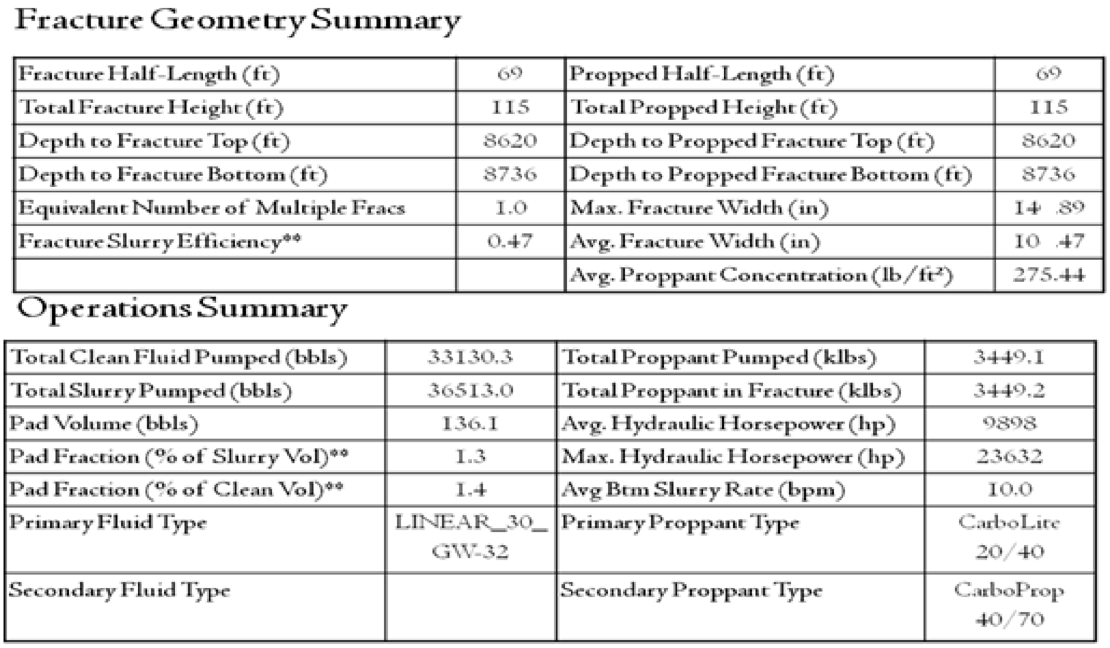


Figure 33: Slurry Volume at different stages



Fracture Geometry Summary

Fracture Half-Length (ft)	69	Propped Half-Length (ft)	69
Total Fracture Height (ft)	115	Total Propped Height (ft)	115
Depth to Fracture Top (ft)	8620	Depth to Propped Fracture Top (ft)	8620
Depth to Fracture Bottom (ft)	8736	Depth to Propped Fracture Bottom (ft)	8736
Equivalent Number of Multiple Fracs	1.0	Max. Fracture Width (in)	14 .89
Fracture Slurry Efficiency**	0.47	Avg. Fracture Width (in)	10 .47
		Avg. Proppant Concentration (lb/ft²)	275.44

Operations Summary

Total Clean Fluid Pumped (bbls)	33130.3	Total Proppant Pumped (klbs)	3449.1
Total Slurry Pumped (bbls)	36513.0	Total Proppant in Fracture (klbs)	3449.2
Pad Volume (bbls)	136.1	Avg. Hydraulic Horsepower (hp)	9898
Pad Fraction (% of Slurry Vol)**	1.3	Max. Hydraulic Horsepower (hp)	23632
Pad Fraction (% of Clean Vol)**	1.4	Avg Btm Slurry Rate (bpm)	10.0
Primary Fluid Type	LINEAR_30_ GW-32	Primary Proppant Type	CarboLite 20/40
Secondary Fluid Type		Secondary Proppant Type	CarboProp 40/70

Figure 34: Facture Geometry

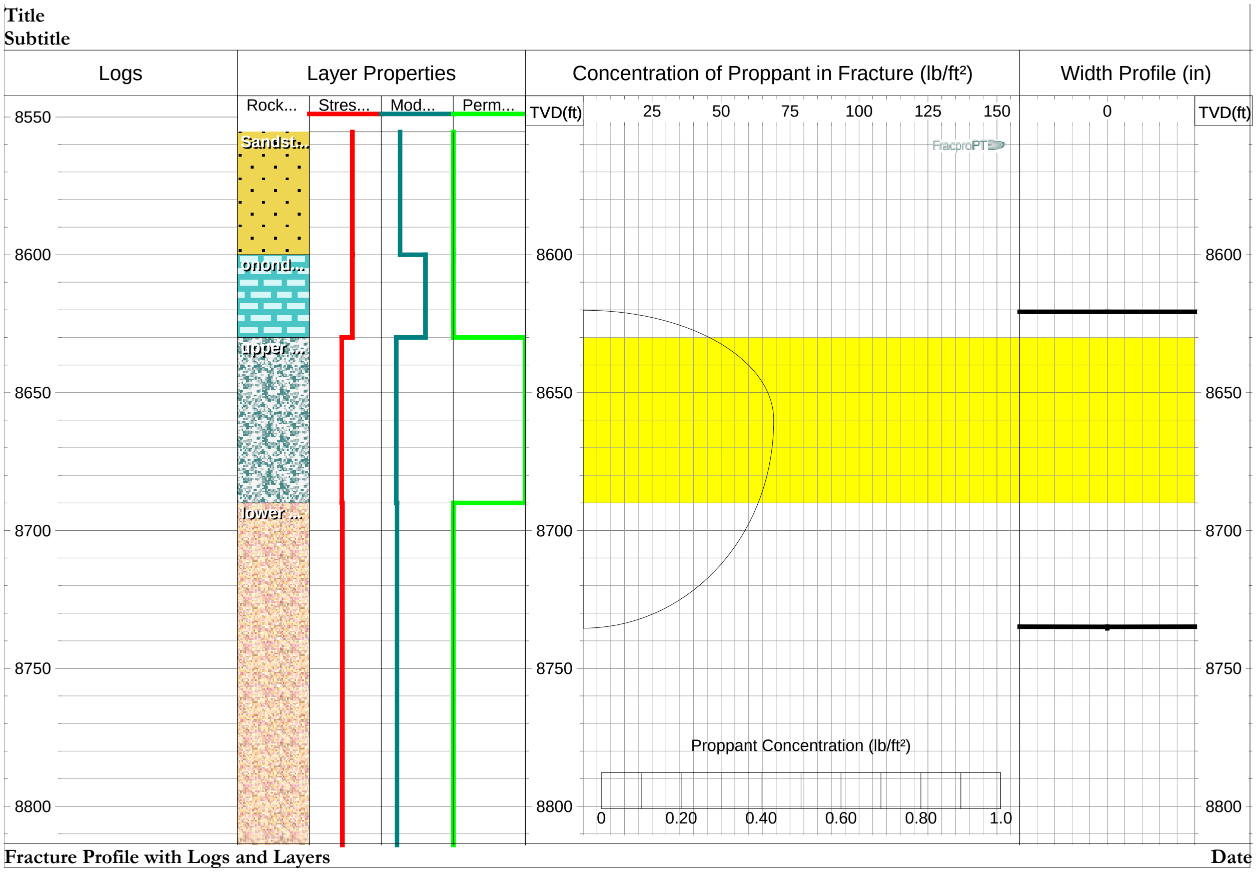


Figure 35: Fracture Profile in the Marcellus Shale Bradford County

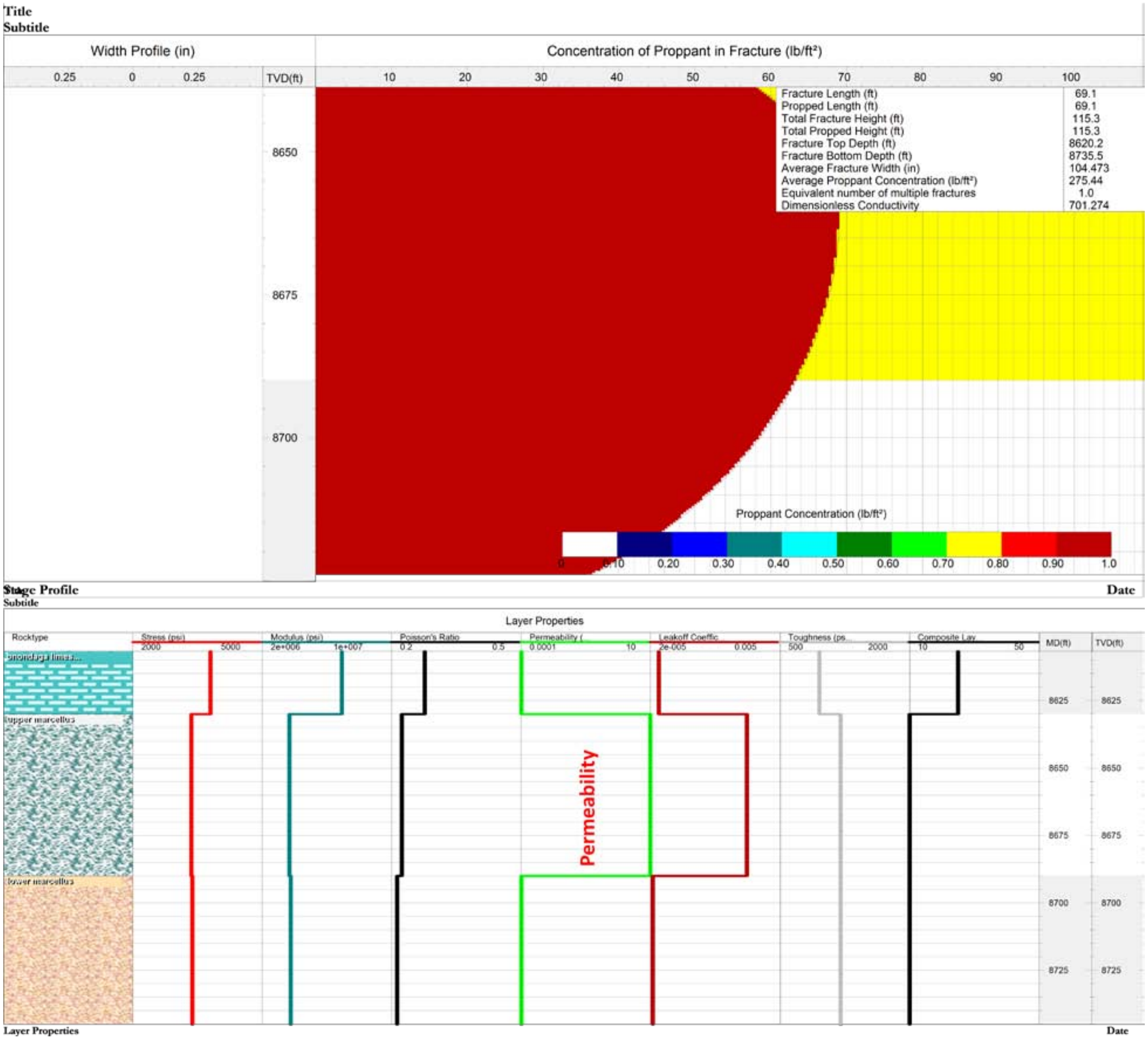


Figure 36: Fracture extension in the Shale formation

From the simulation of the fracture propagation and orientation, the total number of water needed to achieve a half length of 69ft into the shale and increase the permeability by more than 100mD is 85,000 lbs.

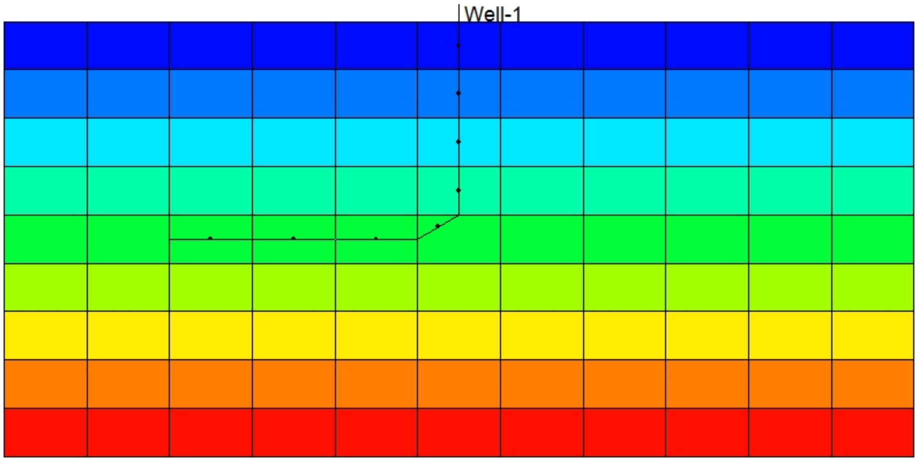


Figure 37 (horizontal well)

\

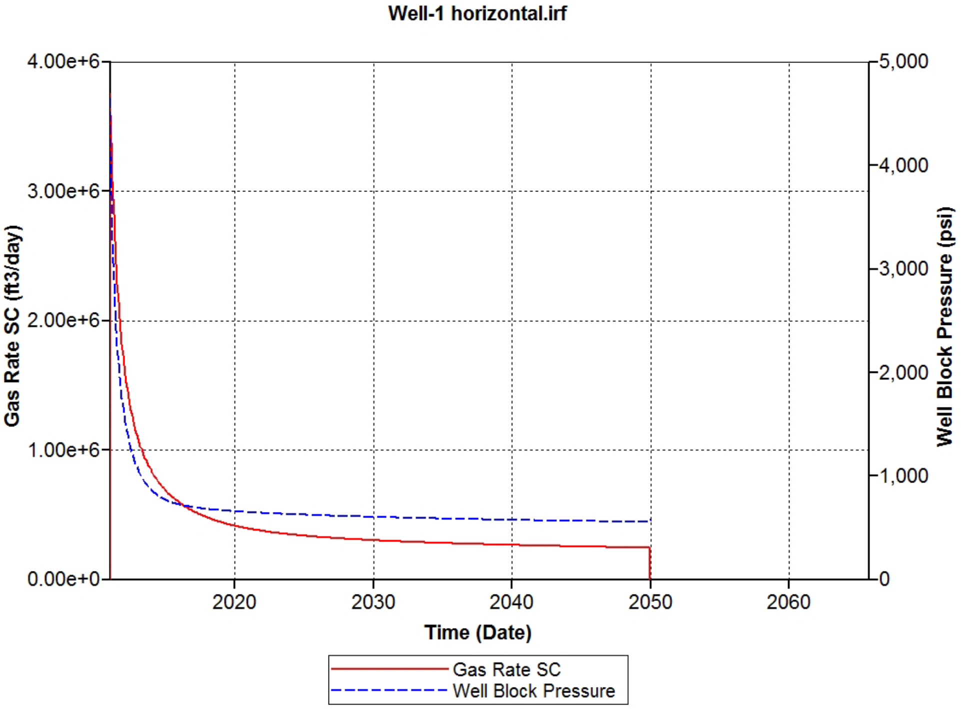


Figure 38 (Gas rate vs. Time for horizontal well in 40 years)

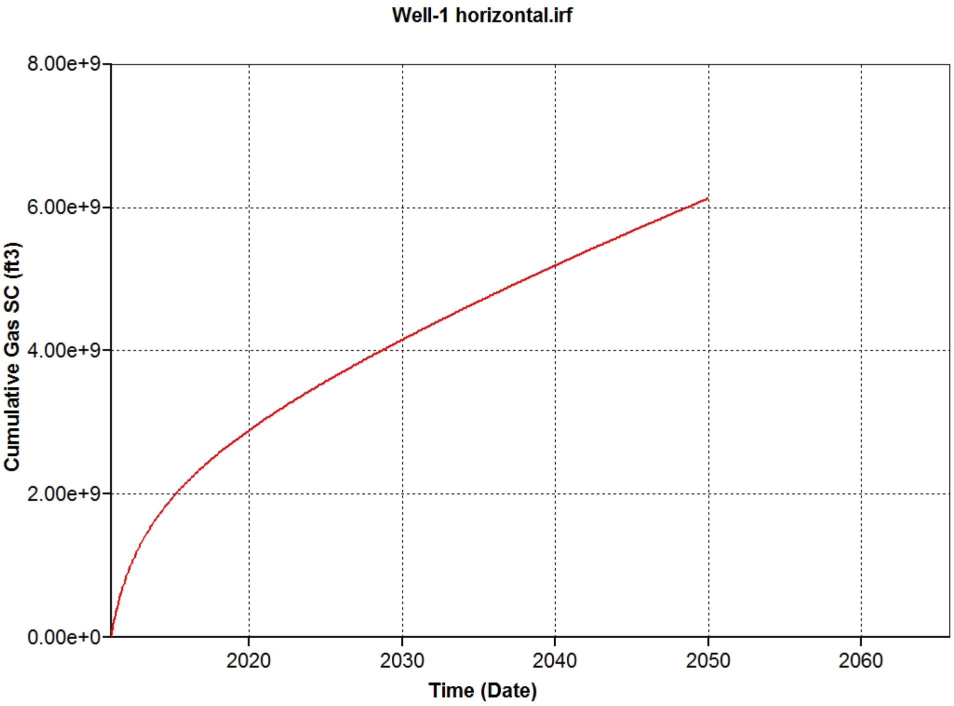


Figure 39 (Cumulative gas vs. tome for horizontal well in 40 years)

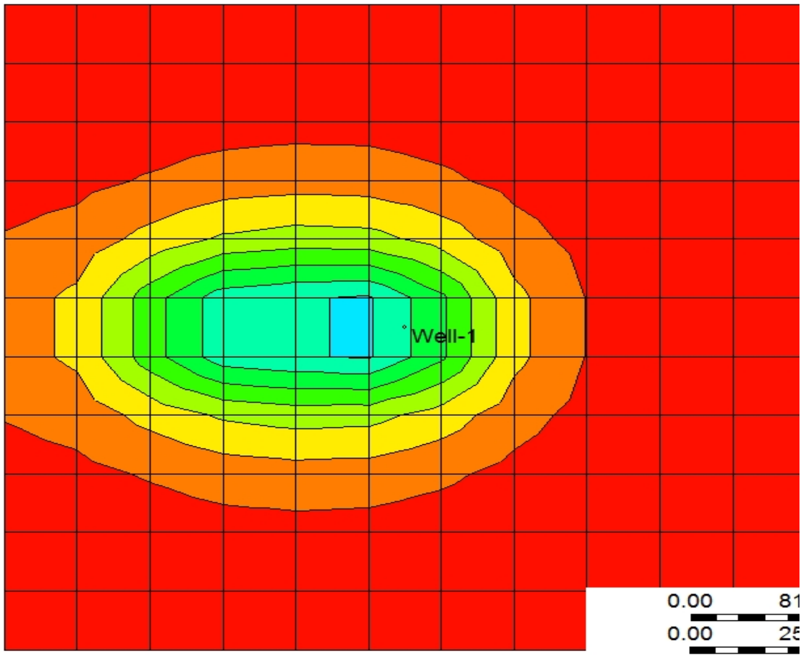


Figure 40 (Pressure distribution after 40 years for one horizontal well)

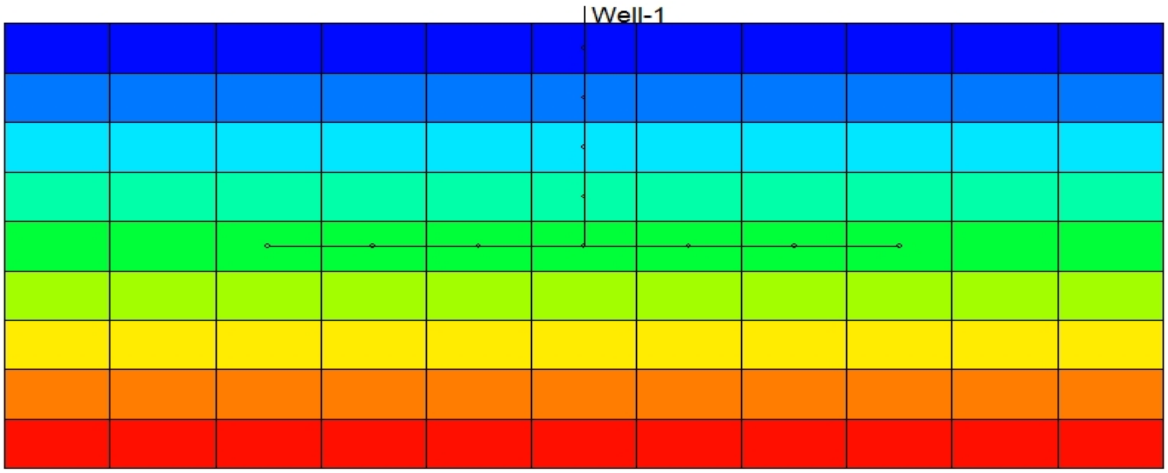


Figure 41 (Dual horizontal well)

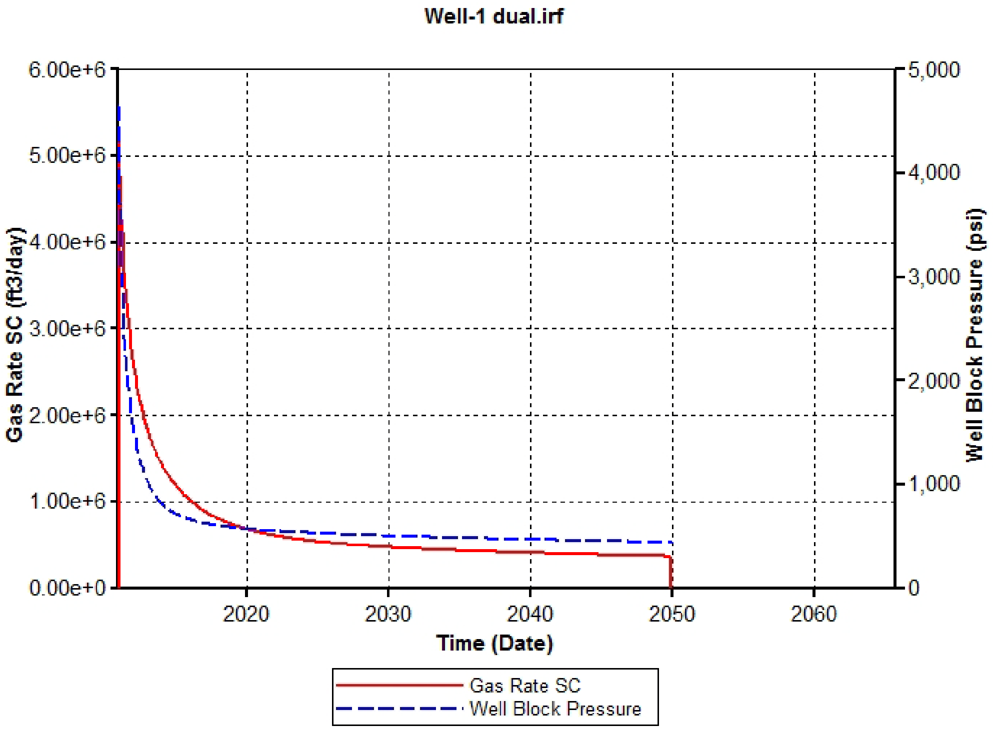


Figure 42 (Gas rate vs. Time for dual horizontal well in 40 years)

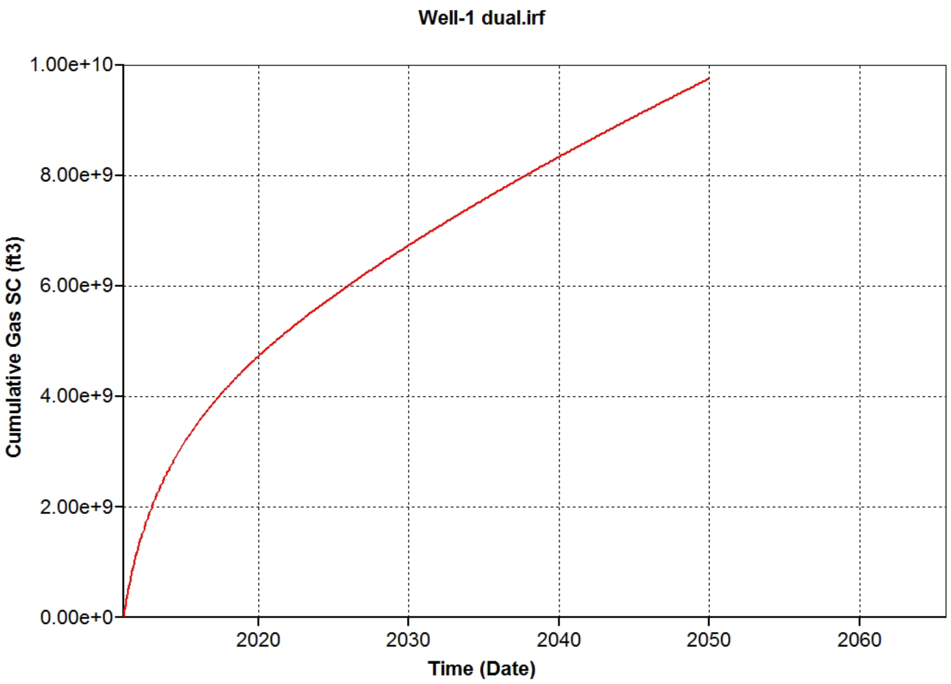


Figure 43 (Cumulative gas vs. tome for dual horizontal well in 40 years)

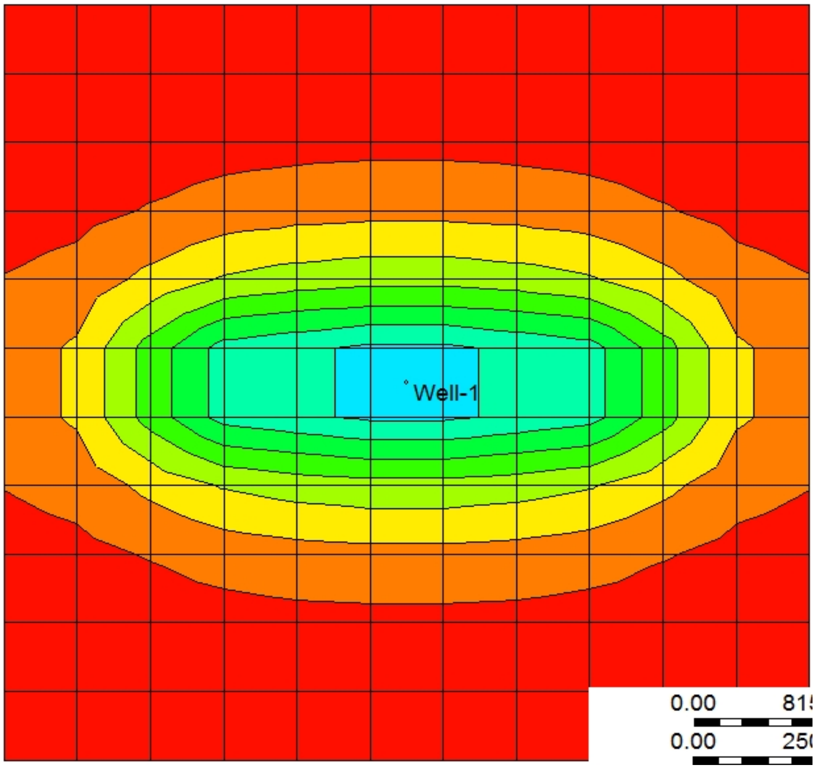


Figure 44 (Pressure distribution after 40 years for dual horizontal well)

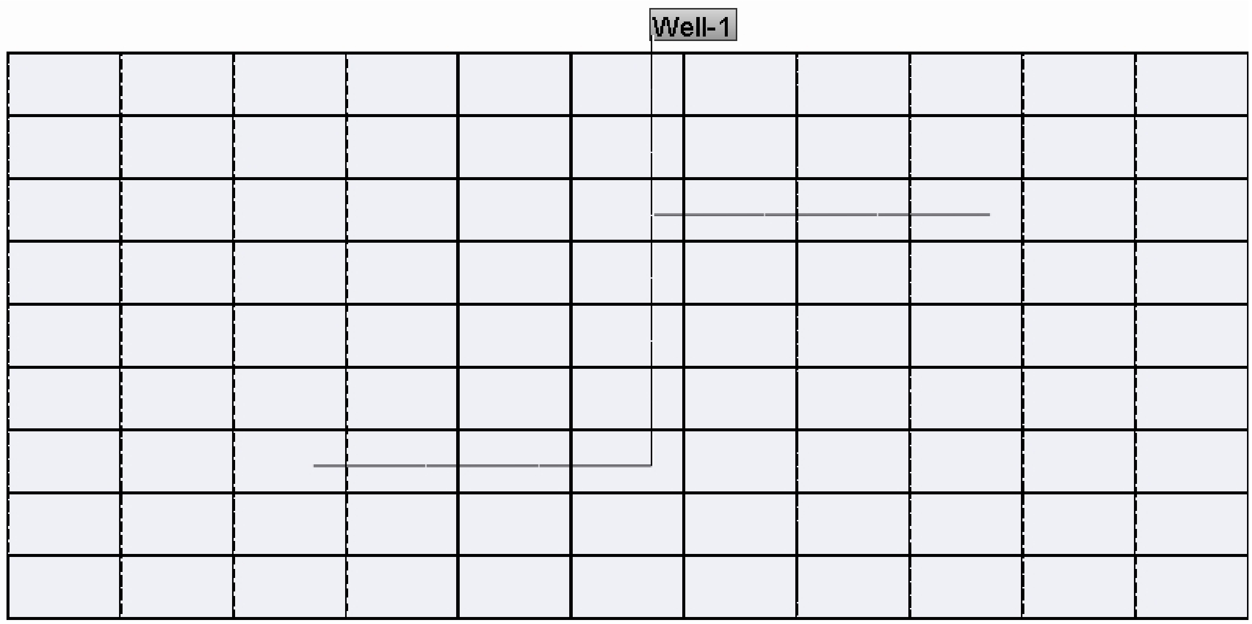


Figure 45 (Dual horizontal well with distance)

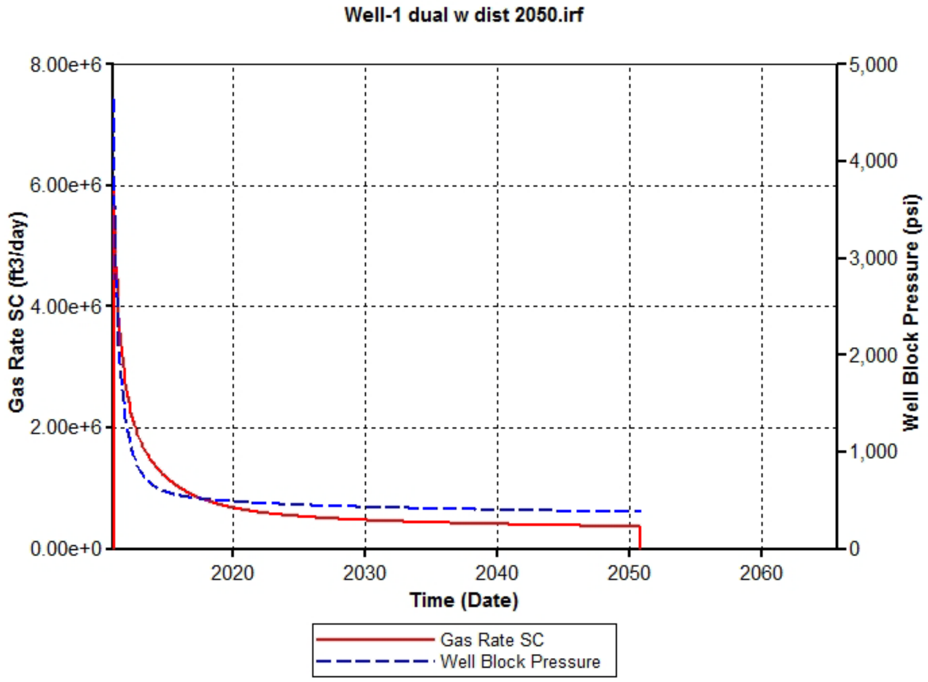


Figure 46 (Gas rate vs. Time for dual horizontal with distance well in 40 years)

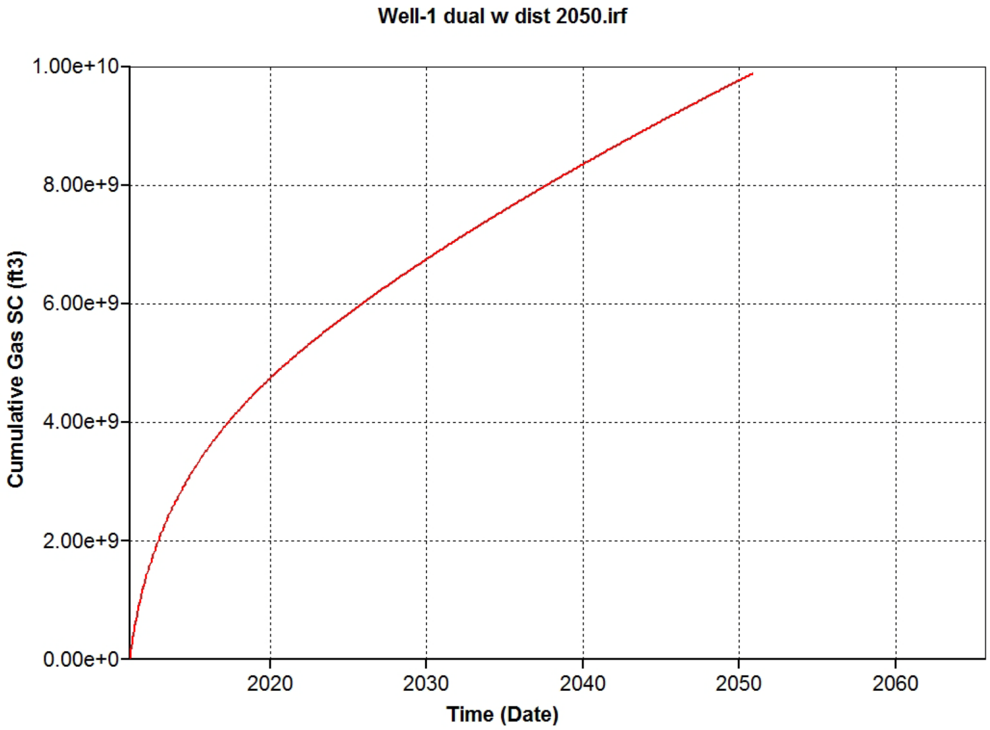


Figure 47 (Cumulative gas vs. tome for dual horizontal with distance well in 40 years)

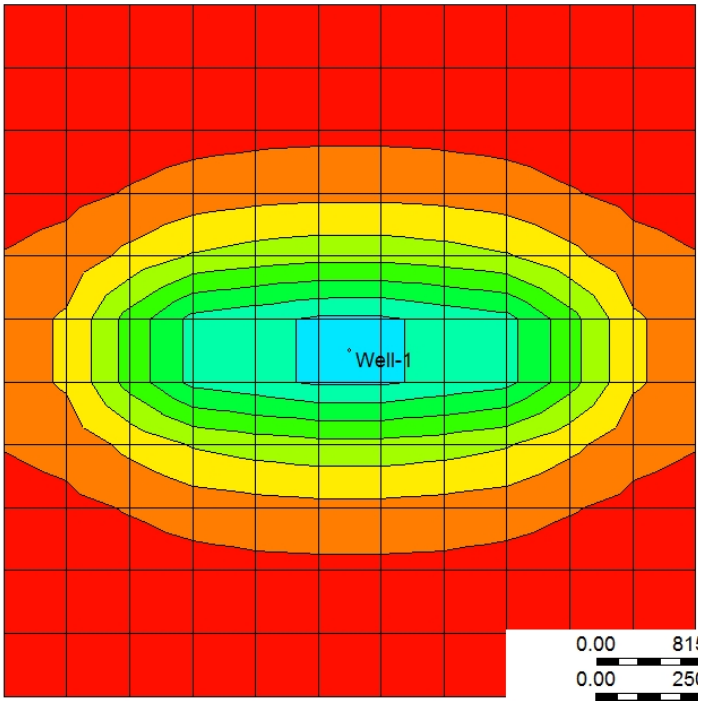


Figure 48 (Pressure distribution after 40 years for dual horizontal wit distance well)

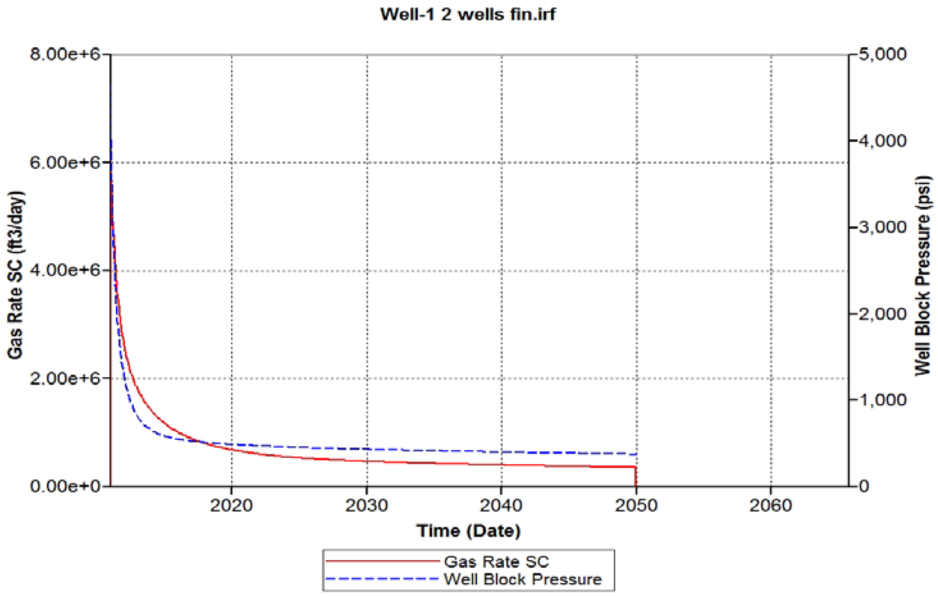


Figure 49 (Gas rate vs. Time for well 1 of two dual horizontal with distance well in 40 years)

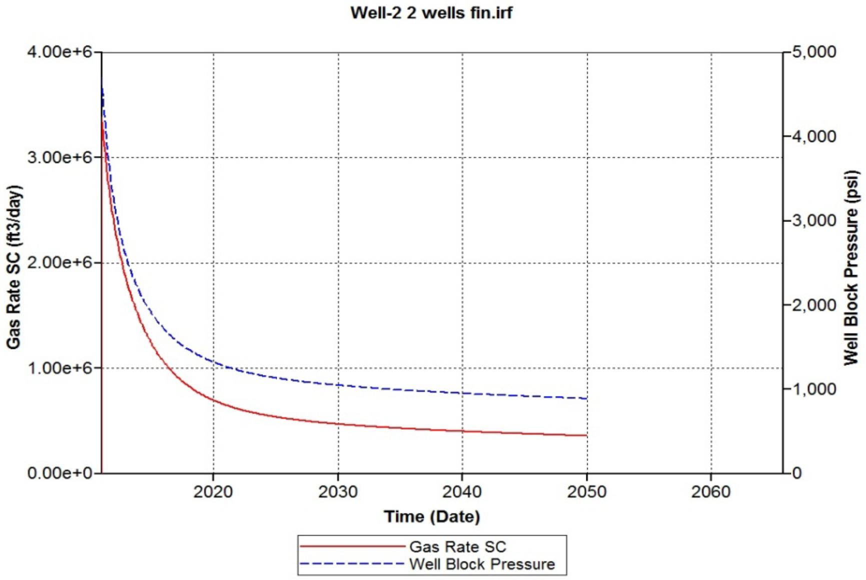


Figure 50 (Gas rate vs. Time for well 2 of two dual horizontal with distance well in 40 years)

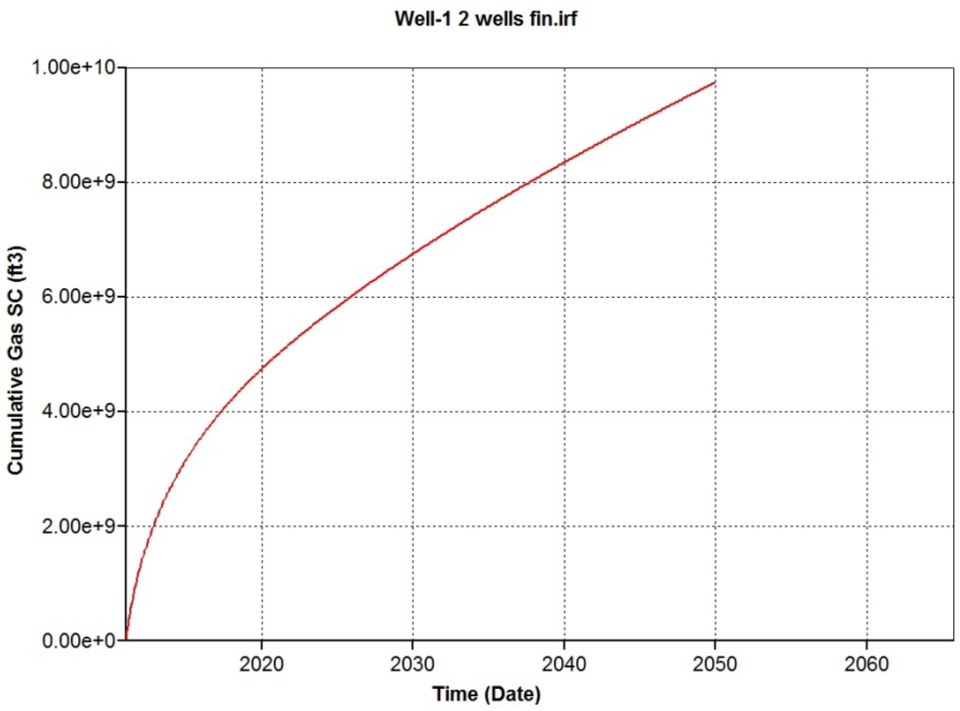


Figure 51 (Cumulative gas vs. tome for well 1 dual horizontal with distance well in 40 years)

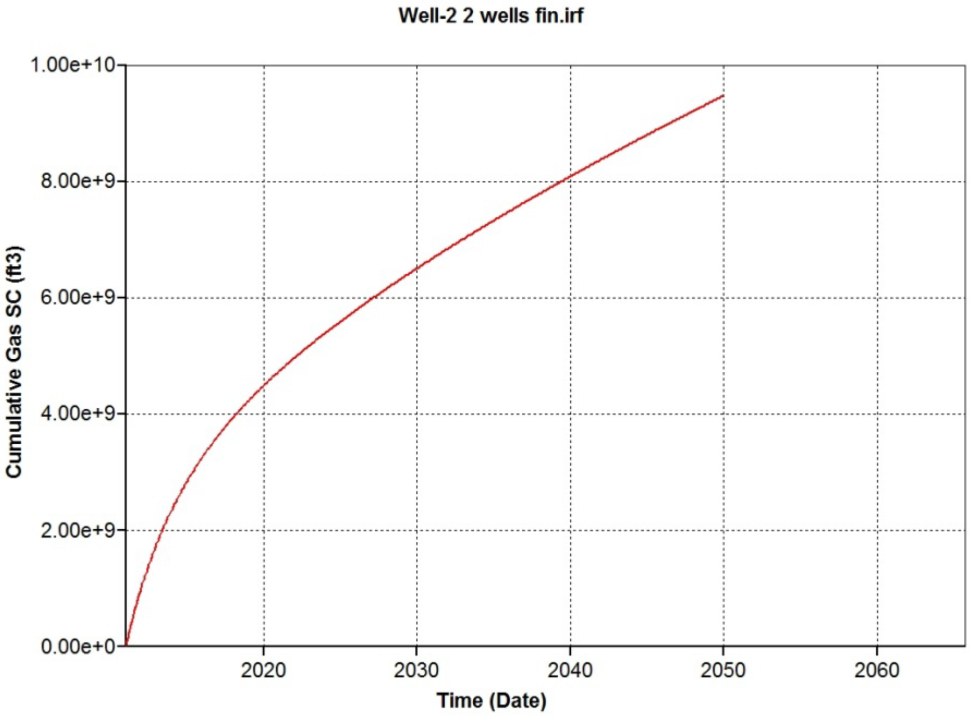


Figure 52 (Cumulative gas vs. tome for well 2 dual horizontal with distance well in 40 years)

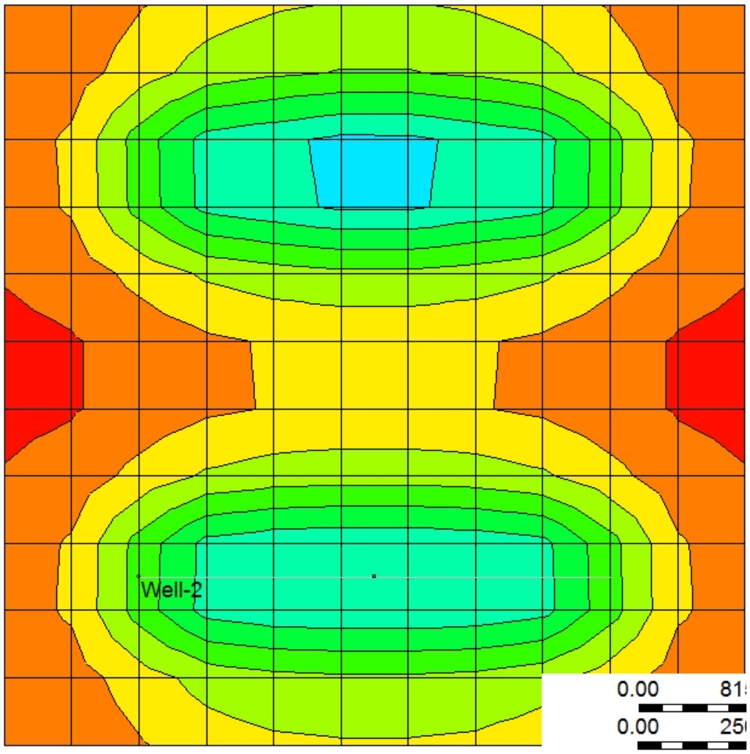
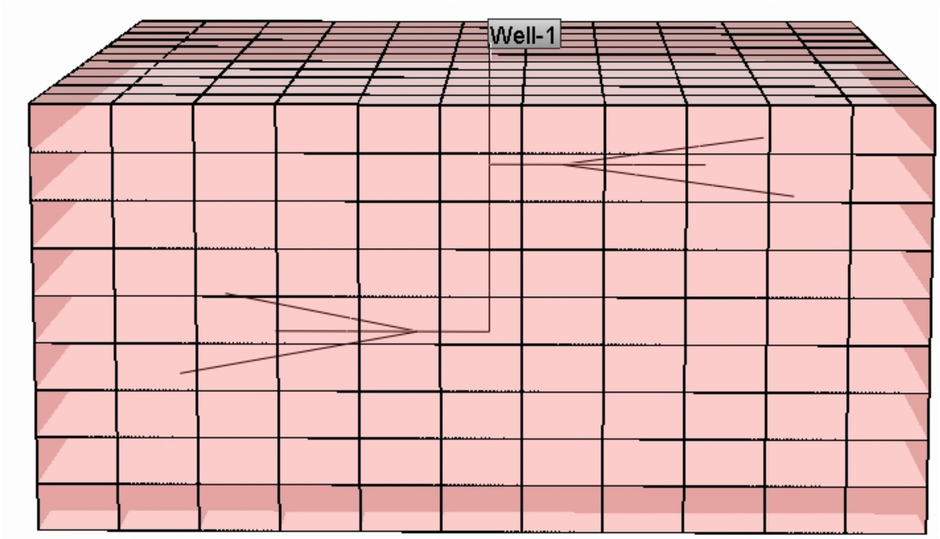


Figure 53 (Pressure distribution after 40 years for two dual horizontal wit distance well)



Top look for the multi-lateral well

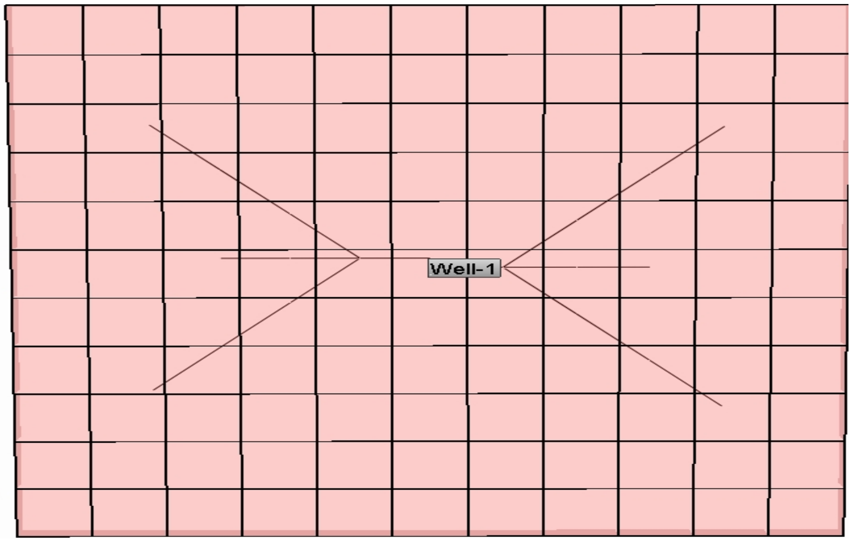


Figure 54 (Multi-lateral well)

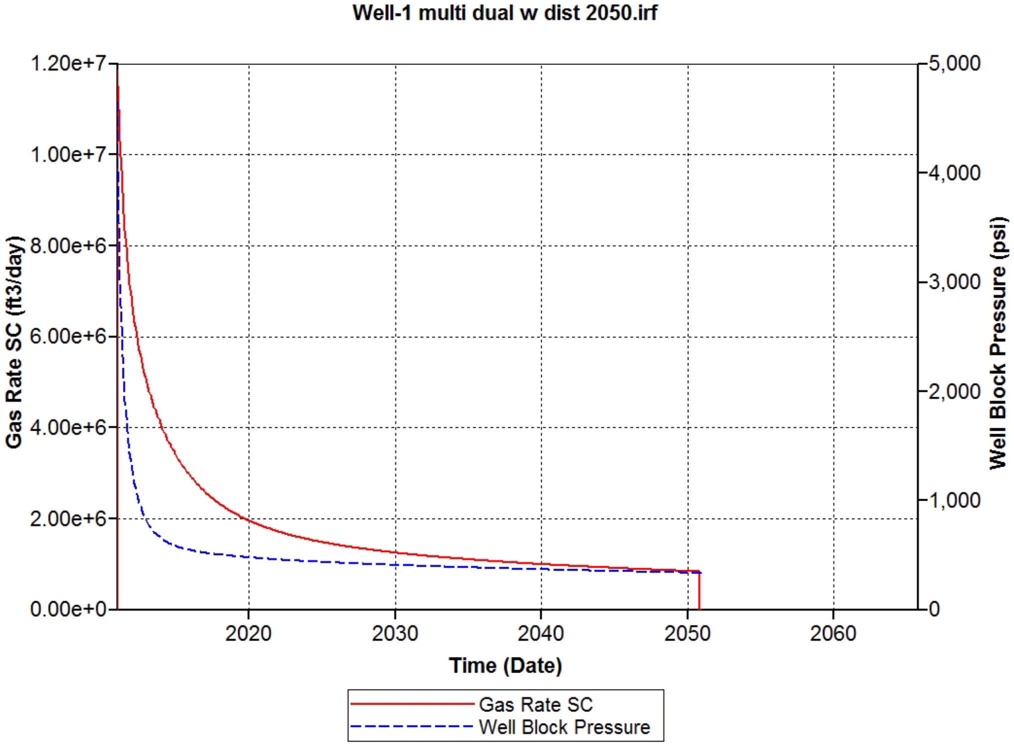


Figure 55 (Gas rate vs. Time for well 2 of multi-lateral)

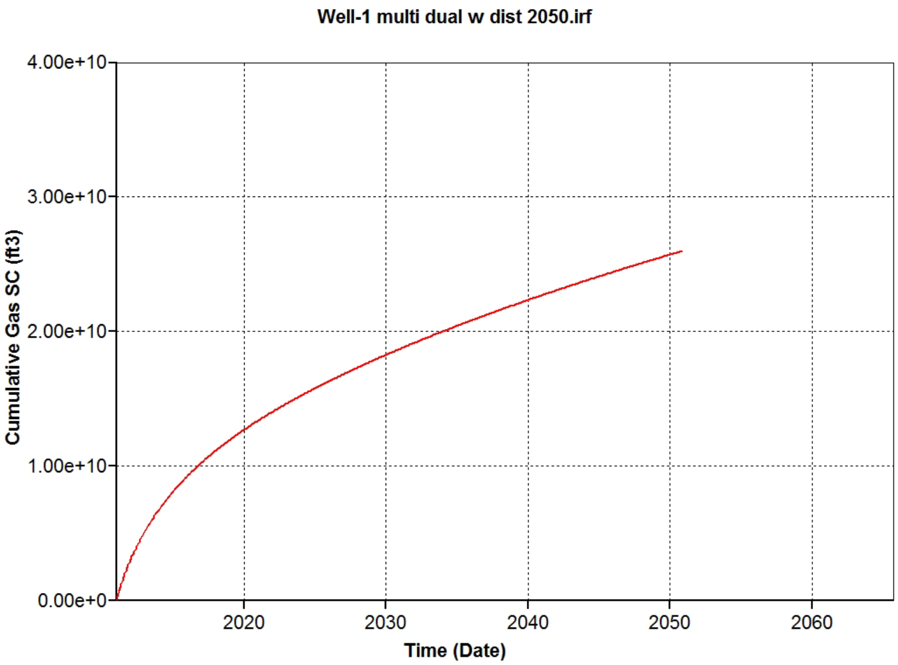
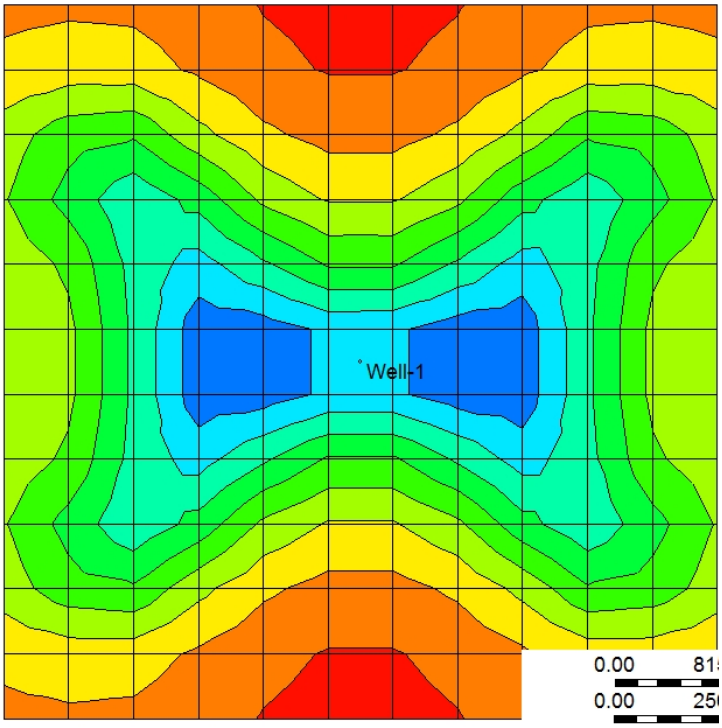


Figure 56 (Cumulative gas vs. tome for multi-lateral)



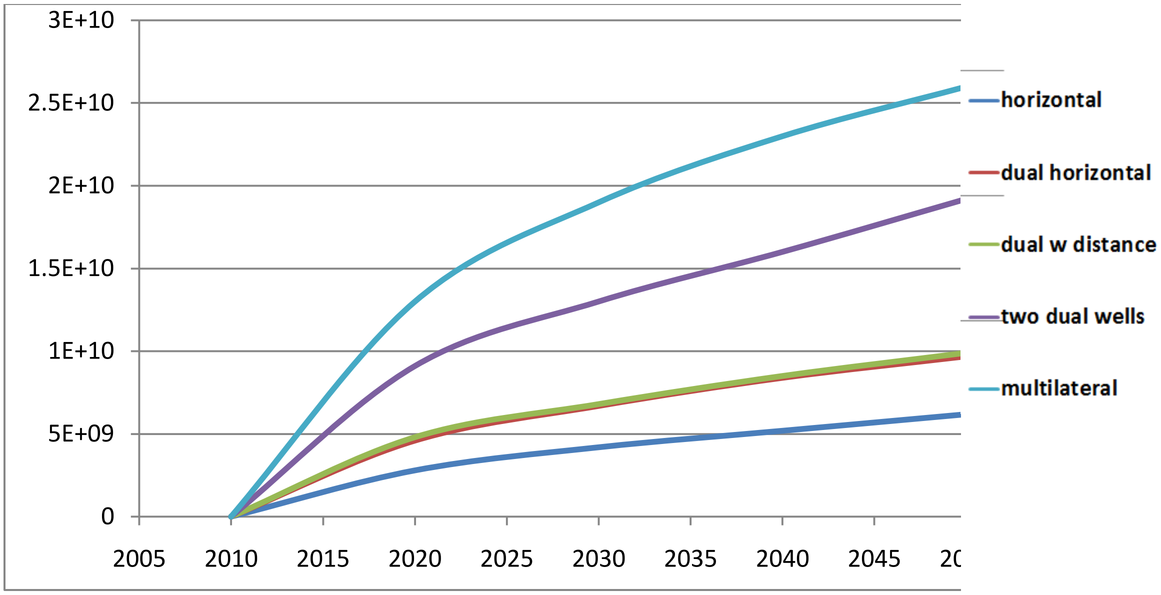
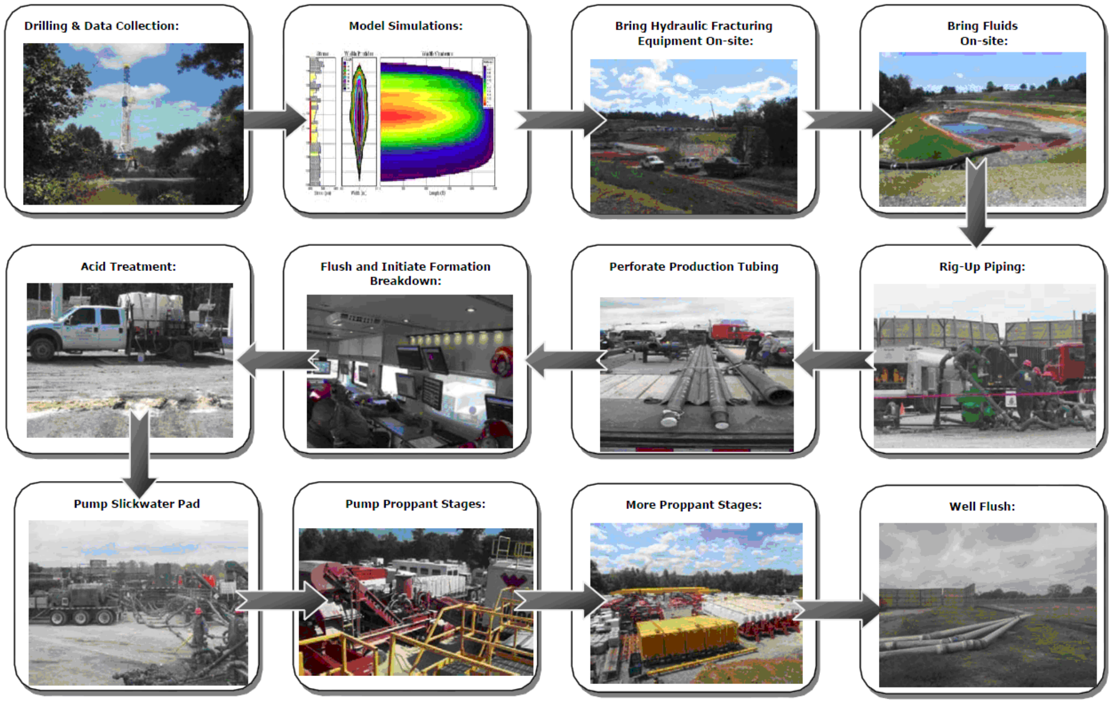


Figure 57 (The cumulative gas for all drilling techniques we have tried)



(Source: Evaluating Implications of Hydraulic Fracturing in Shale Gas Reservoirs, SPE 121038)

Figure 58.Fracturing activities

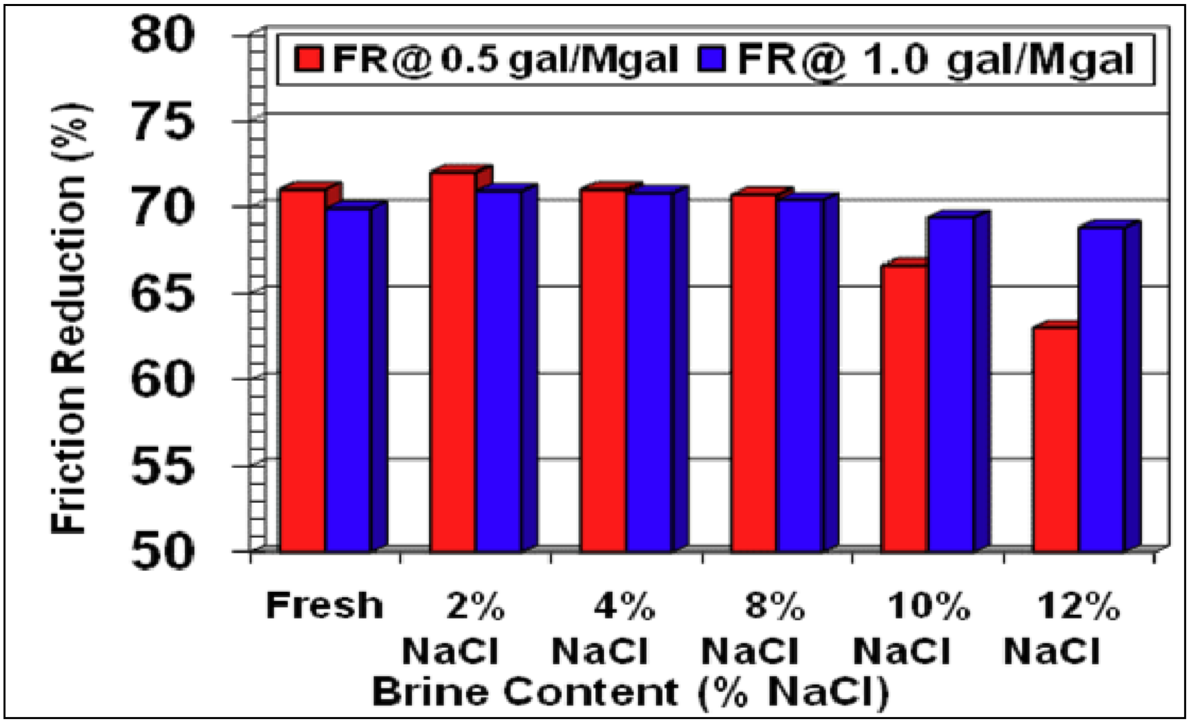


Figure 59. The percentage of friction reduction caused by adding salt-toerlant friction reducer.

Source: SPE 125987

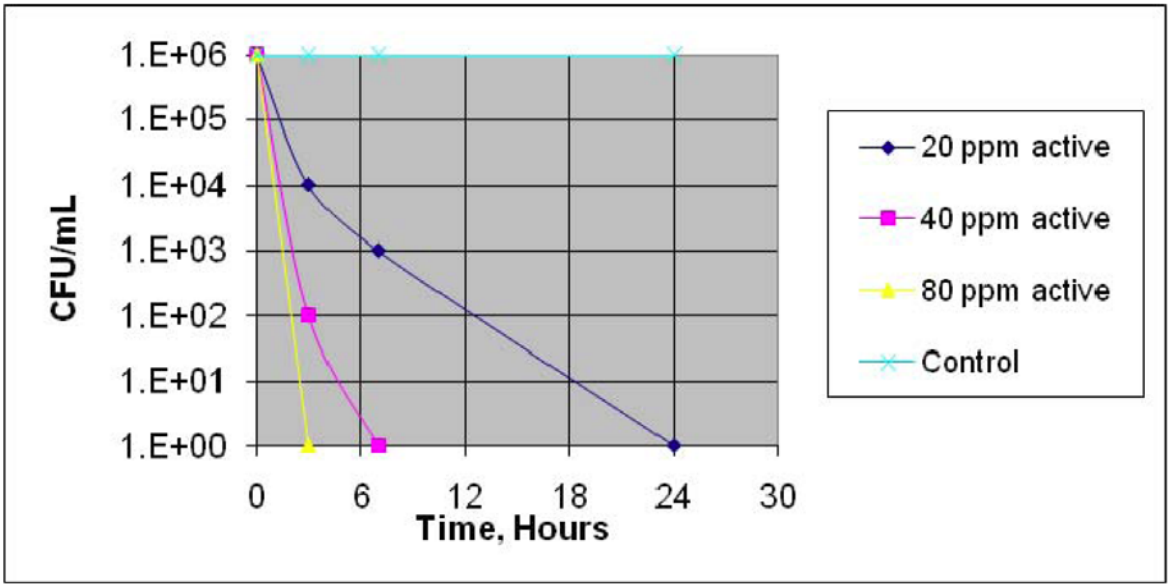


Figure 60. Effctiveness of 20% active DBNPA biocide against SRB

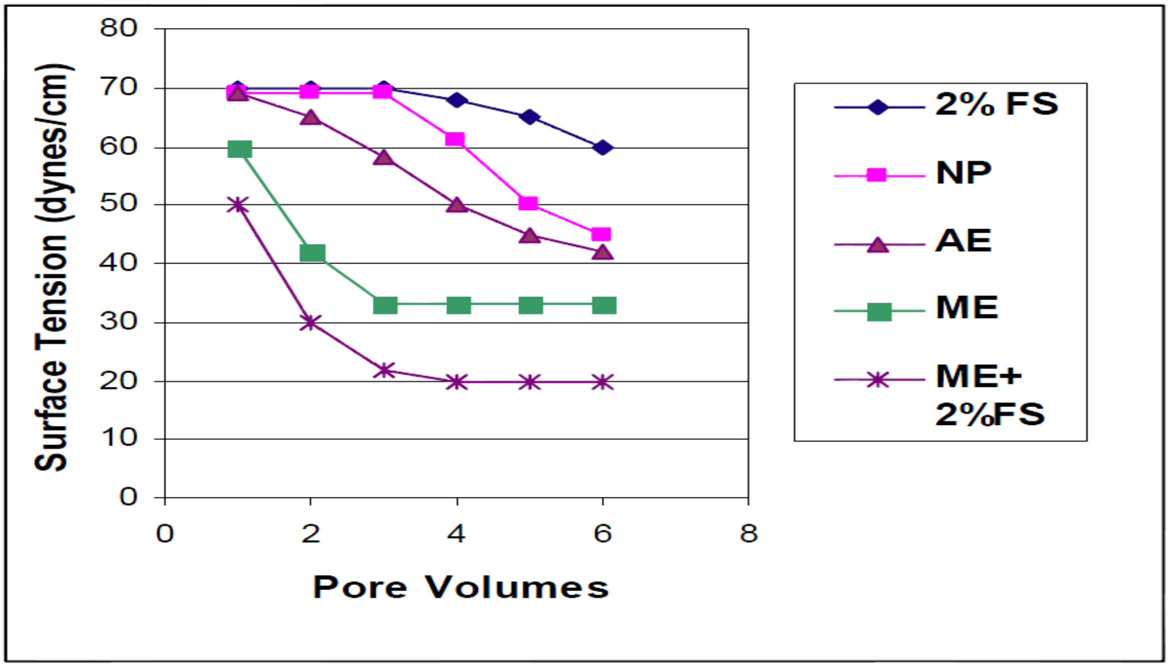


Figure 61. surface tension test

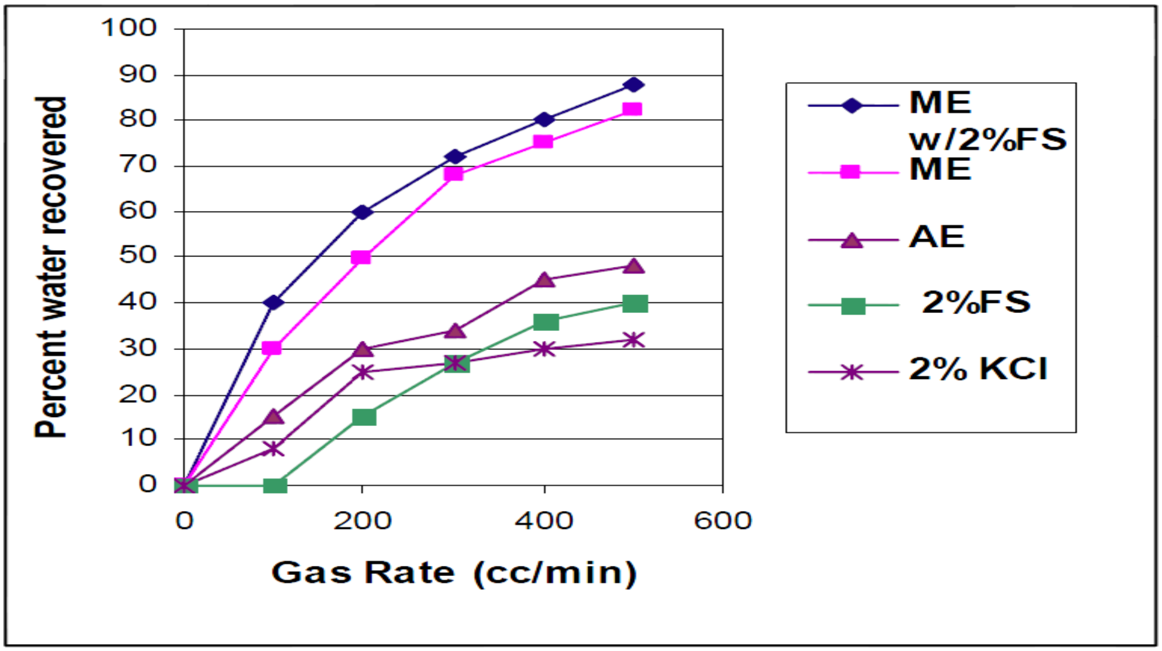
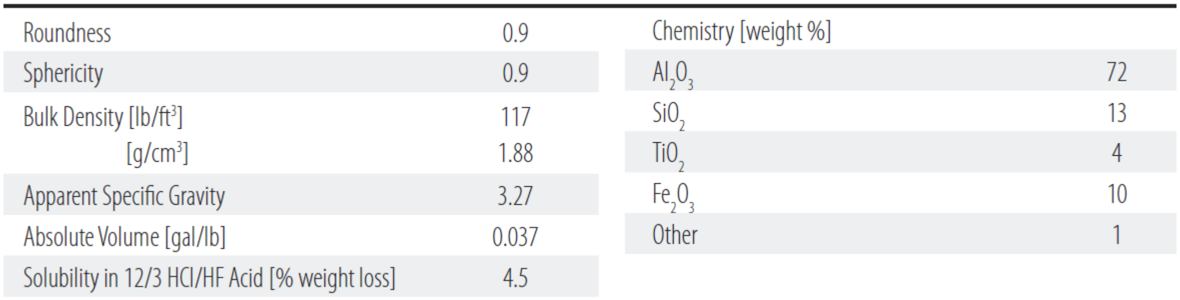


Figure 62. Water recovery test

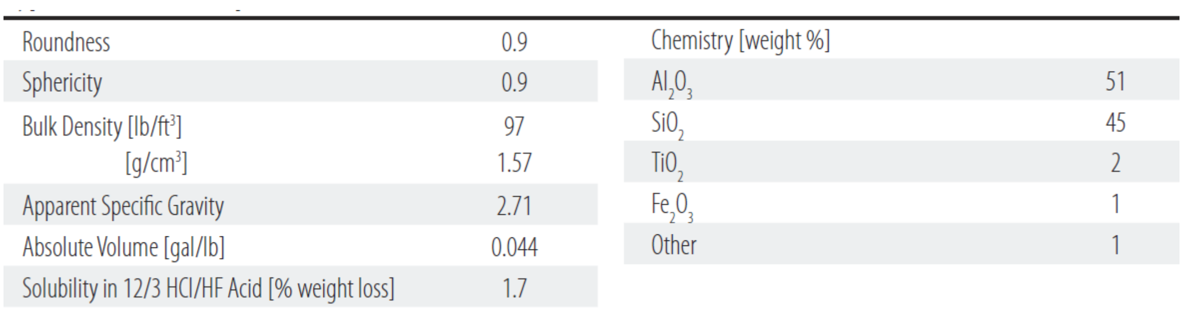
Figure 63. CarboProp



Roundness	0.9
Sphericity	0.9
Bulk Density [lb/ft^3]	117
[g/cm^3]	1.88
Apparent Specific Gravity	3.27
Absolute Volume [gal/lb]	0.037
Solubility in 12/3 HCl/HF Acid [% weight loss]	4.5

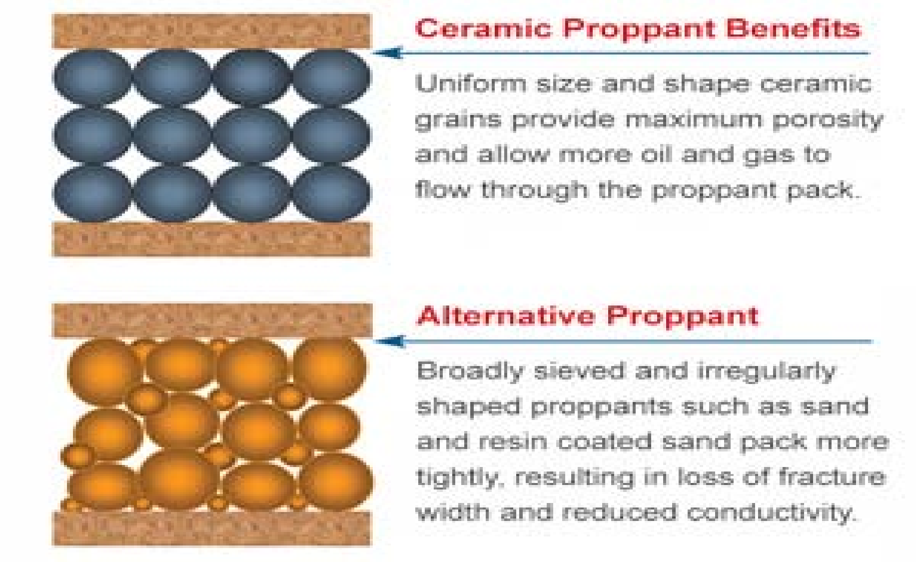
Chemistry [weight %]	
Al_2O_3	72
SiO_2	13
TiO_2	4
Fe_2O_3	10
Other	1

Firgure 64. CarboLite



Roundness	0.9
Sphericity	0.9
Bulk Density [lb/ft^3]	97
[g/cm^3]	1.57
Apparent Specific Gravity	2.71
Absolute Volume [gal/lb]	0.044
Solubility in 12/3 HCl/HF Acid [% weight loss]	1.7

Chemistry [weight %]	
Al_2O_3	51
SiO_2	45
TiO_2	2
Fe_2O_3	1
Other	1



Ceramic Proppant Benefits

Uniform size and shape ceramic grains provide maximum porosity and allow more oil and gas to flow through the proppant pack.

Alternative Proppant

Broadly sieved and irregularly shaped proppants such as sand and resin coated sand pack more tightly, resulting in loss of fracture width and reduced conductivity.

Figure 65. Ceramic Proppant

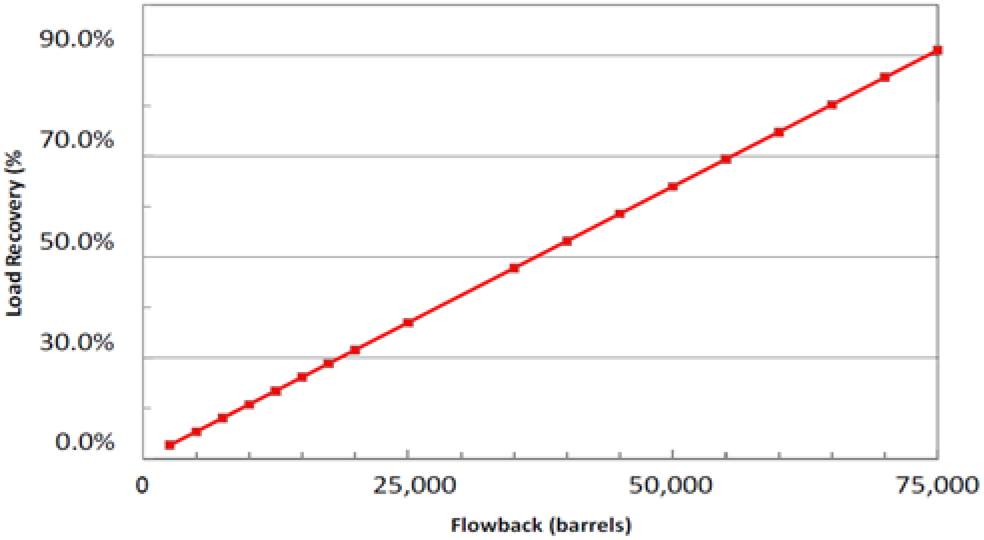


Fig 66 —Marcellus Shale Well flowback–load volume percent recovery vs. flowback volume.

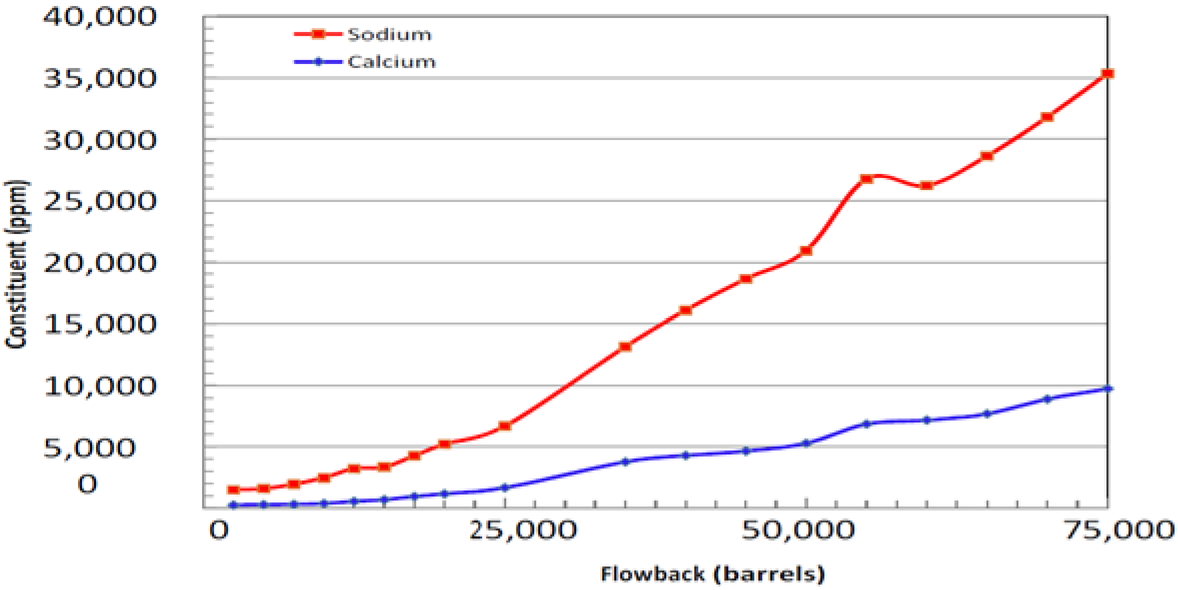


Fig 67 –Marcellus Shale Well flowback analysis–major cation trend.

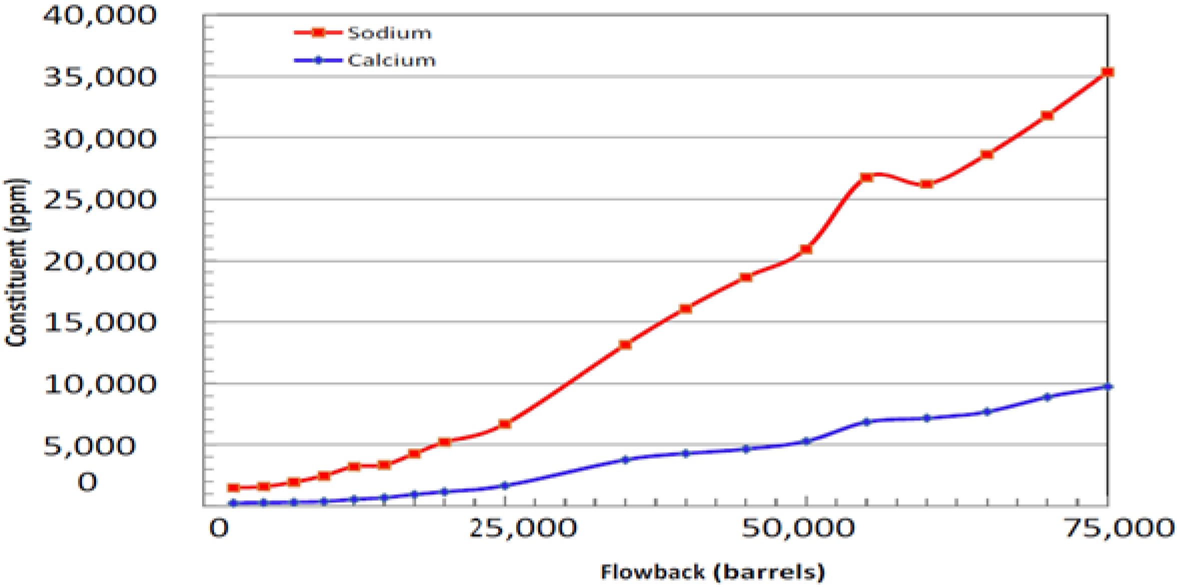


Fig 68 –Marcellus Shale Well flowback analysis–major cation trend.

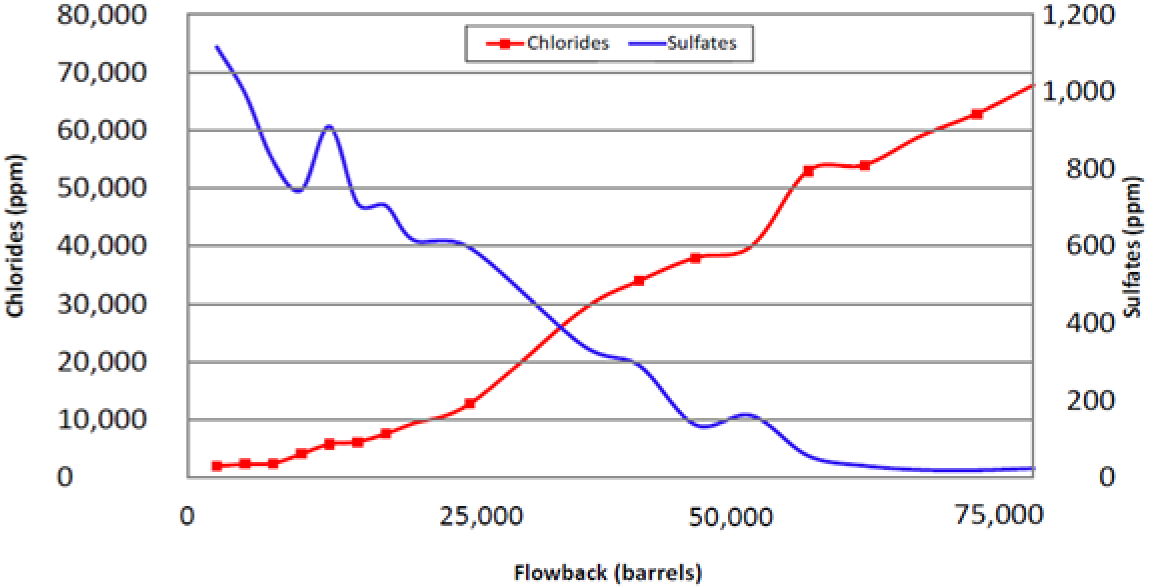


Fig. 69 -Marcellus Shale Well flowback analysis–anion trend.

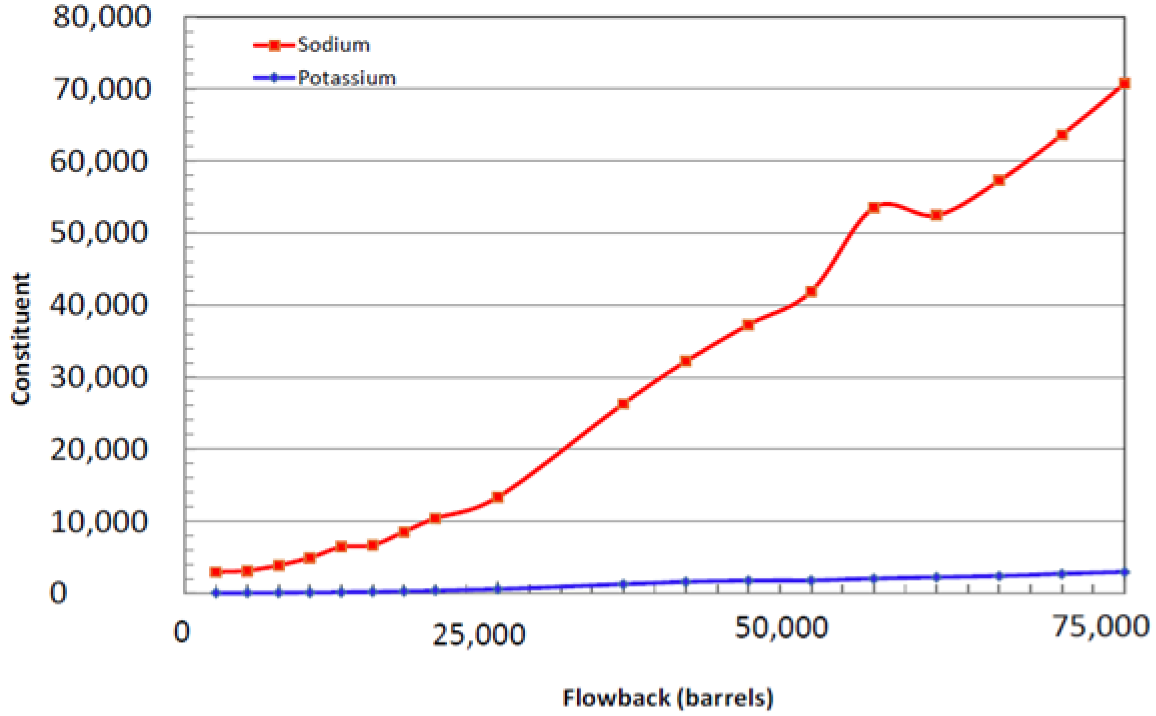


Fig. 70 —Marcellus Shale Well flowback– monovalent ion trend.

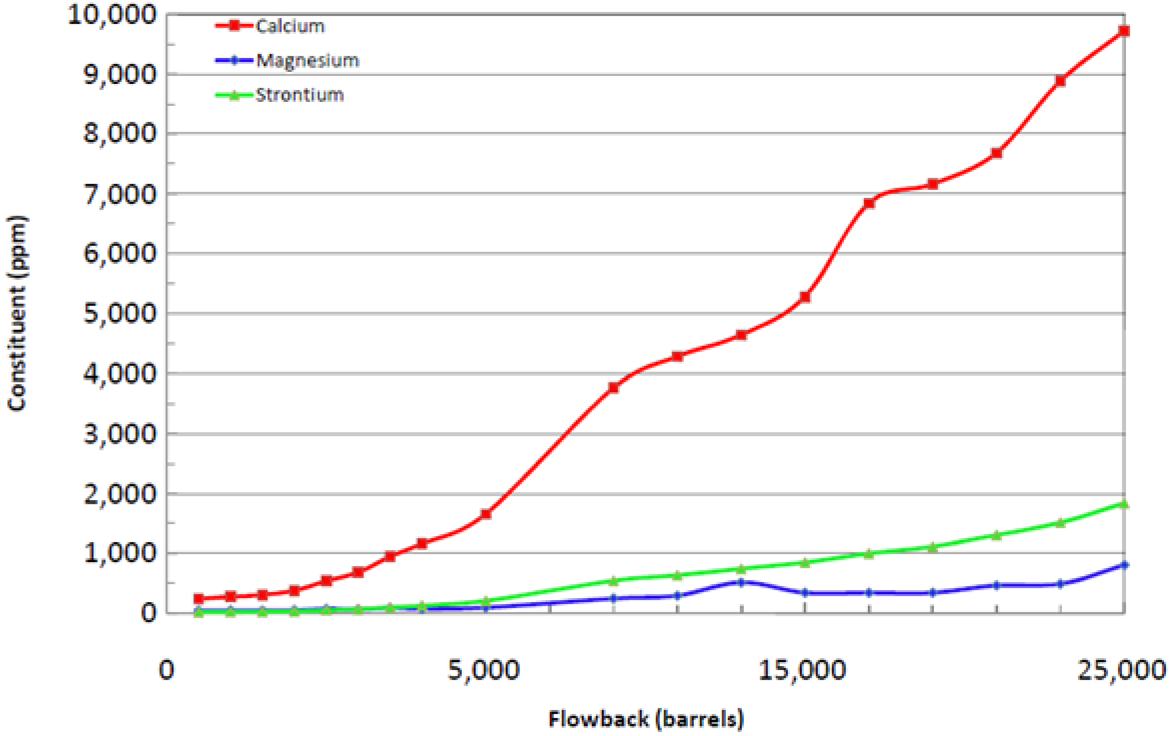


Fig. 71 —Marcellus Shale Well flowback–divalent cation trend.

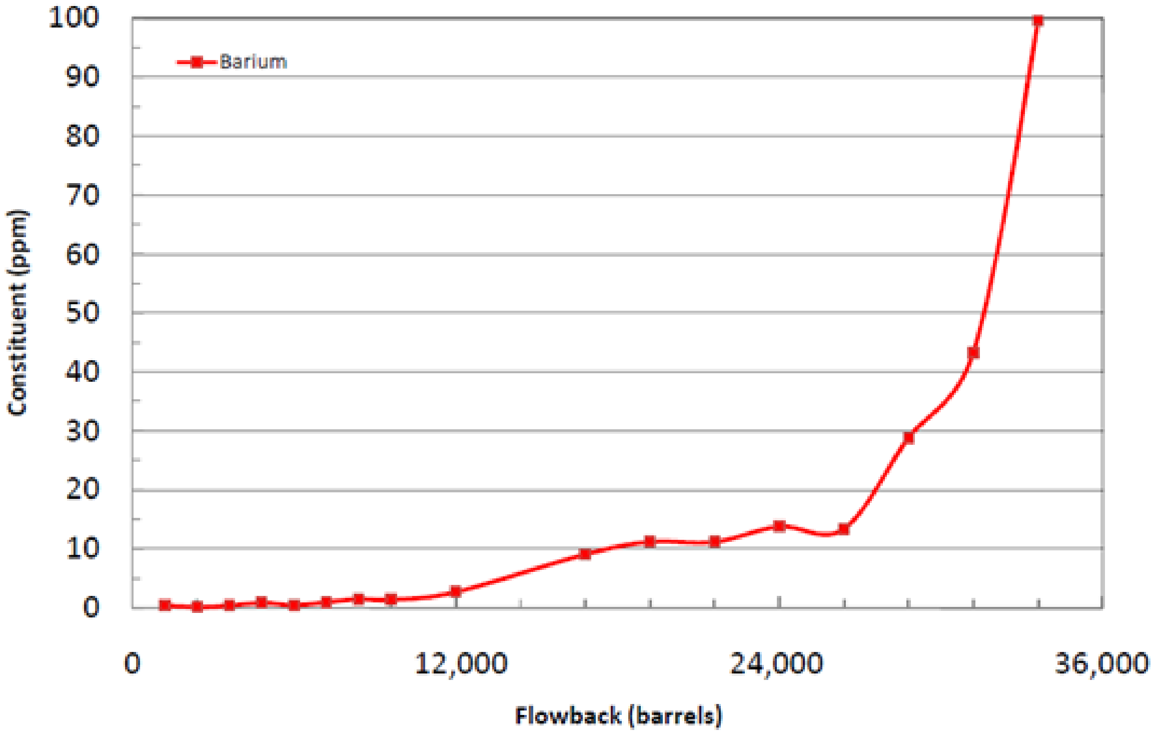
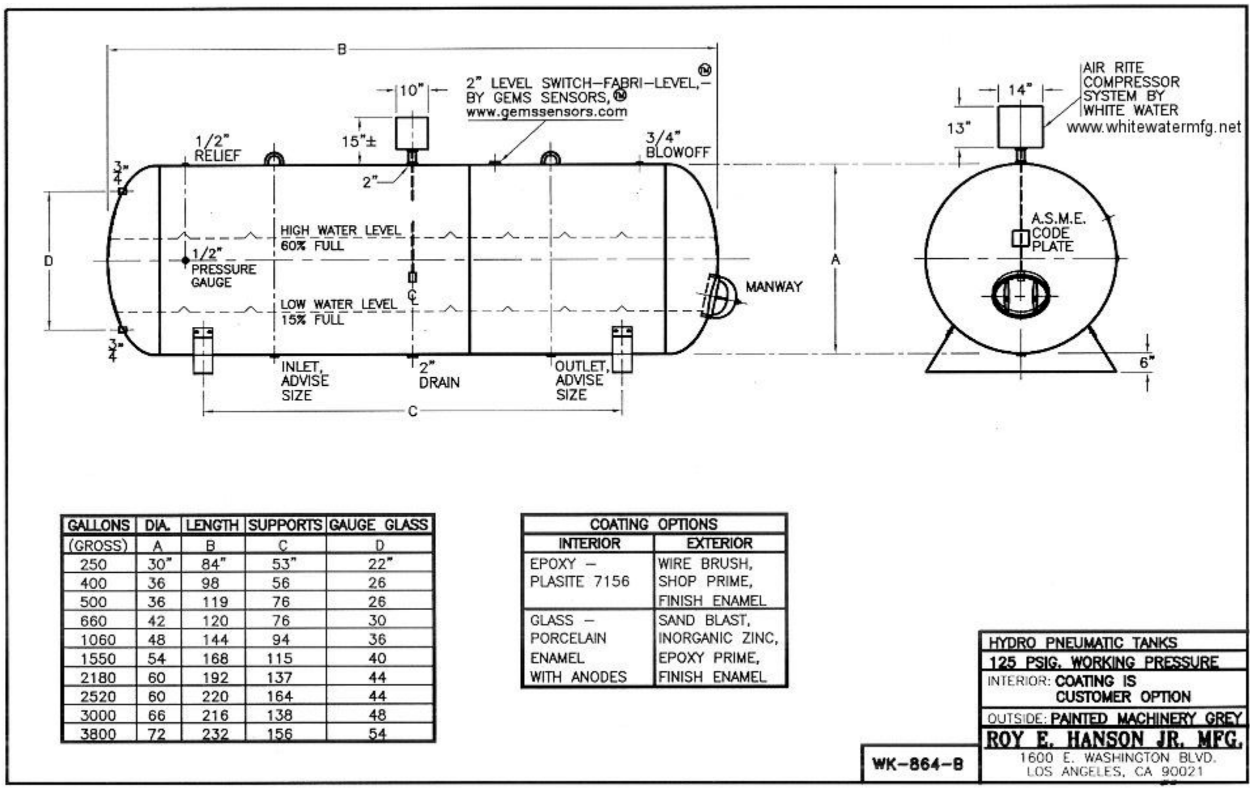


Fig 72 — Marcellus Shale Well flowback–barium trend.



GALLONS	DIA.	LENGTH	SUPPORTS	GAUGE GLASS
(GROSS)	A	B	C	D
250	30"	84"	53"	22"
400	36	98	56	26
500	36	119	76	26
660	42	120	76	30
1060	48	144	94	36
1550	54	168	115	40
2180	60	192	137	44
2520	60	220	164	44
3000	66	216	138	48
3800	72	232	156	54

COATING OPTIONS	
INTERIOR	EXTERIOR
EPOXY – PLASITE 7156	WIRE BRUSH, SHOP PRIME, FINISH ENAMEL
GLASS – PORCELAIN ENAMEL WITH ANODES	SAND BLAST, INORGANIC ZINC, EPOXY PRIME, FINISH ENAMEL

HYDRO PNEUMATIC TANKS
125 PSIG. WORKING PRESSURE
INTERIOR: COATING IS CUSTOMER OPTION
OUTSIDE: PAINTED MACHINERY GREY
ROY E. HANSON JR. MFG.
1600 E. WASHINGTON BLVD.
LOS ANGELES, CA 90021

Figure 73: Schematic diagram of hydro-pneumatic tank (tankdrawing.com)

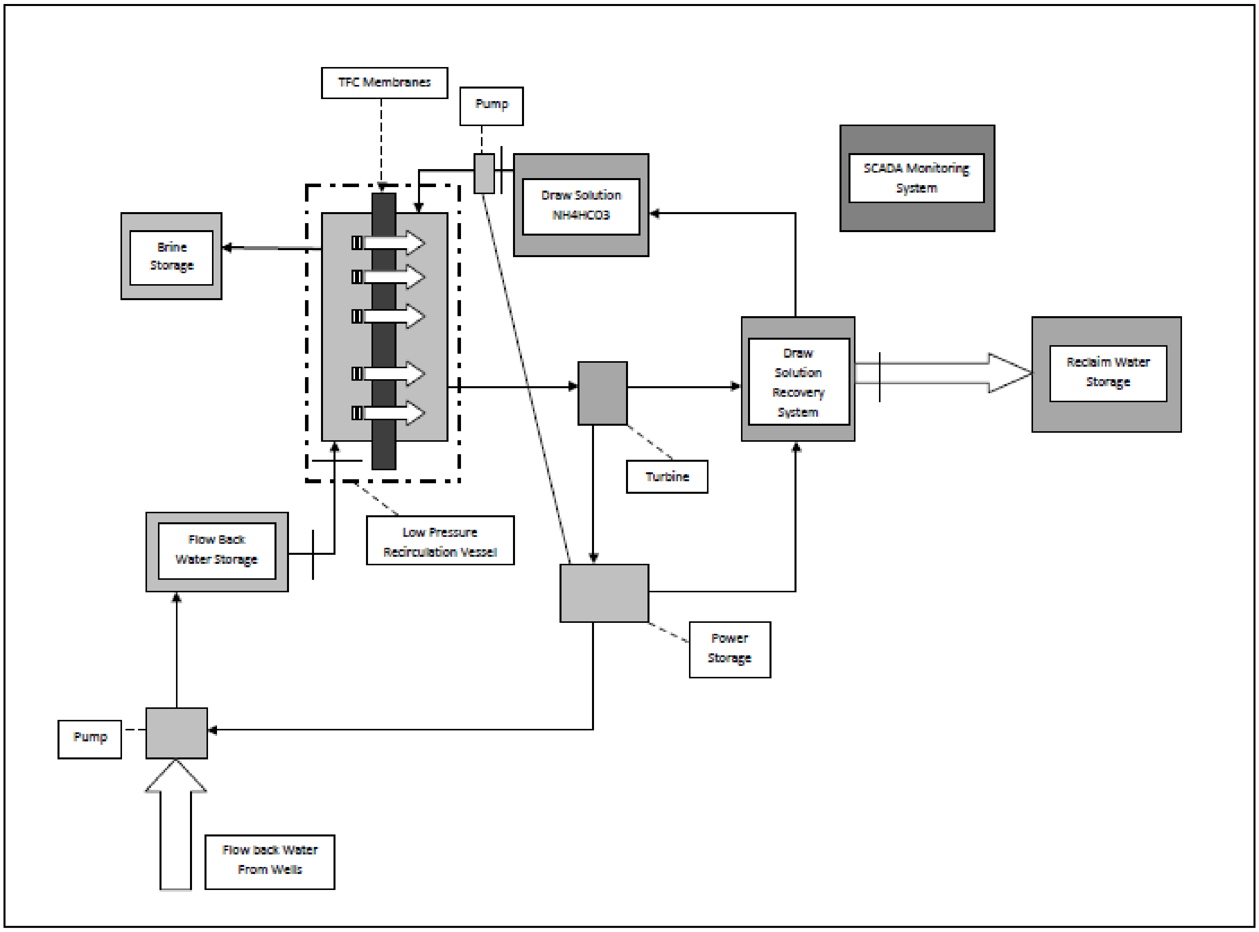


Figure 74. Box Diagram Illustrating the Components and Flow Process through Novel Semi-Portable Centralized Water Treatment Facility.

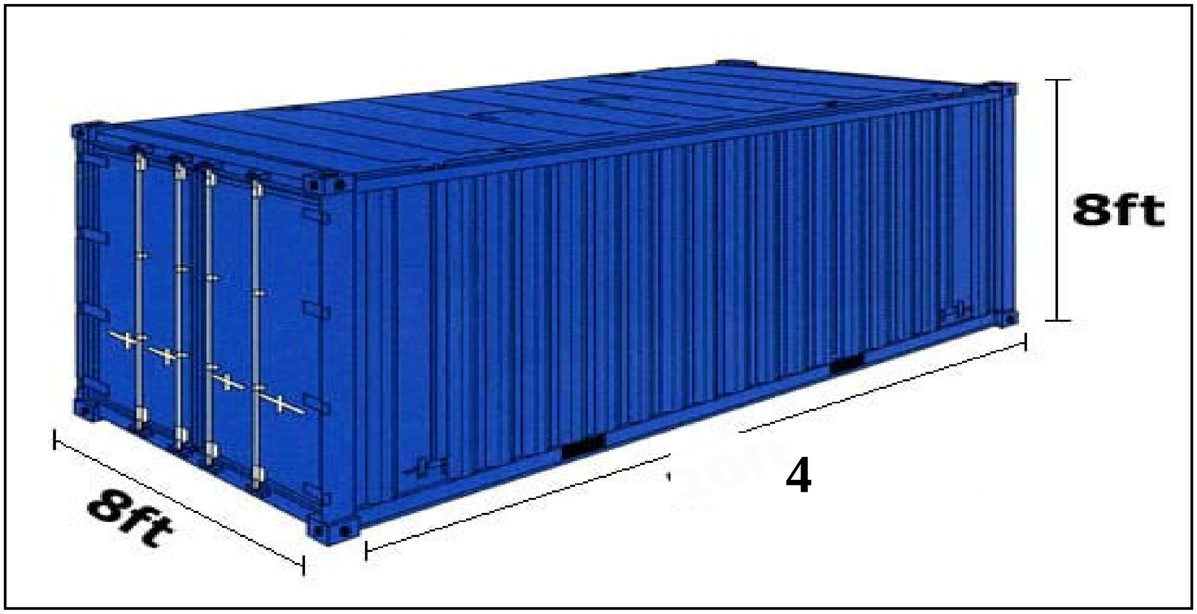


Figure 75 - The Dimensions of the Dual Insulated Dry Goods Shipping Cargo Container to House Forward Osmosis and Blue Energy Unit.

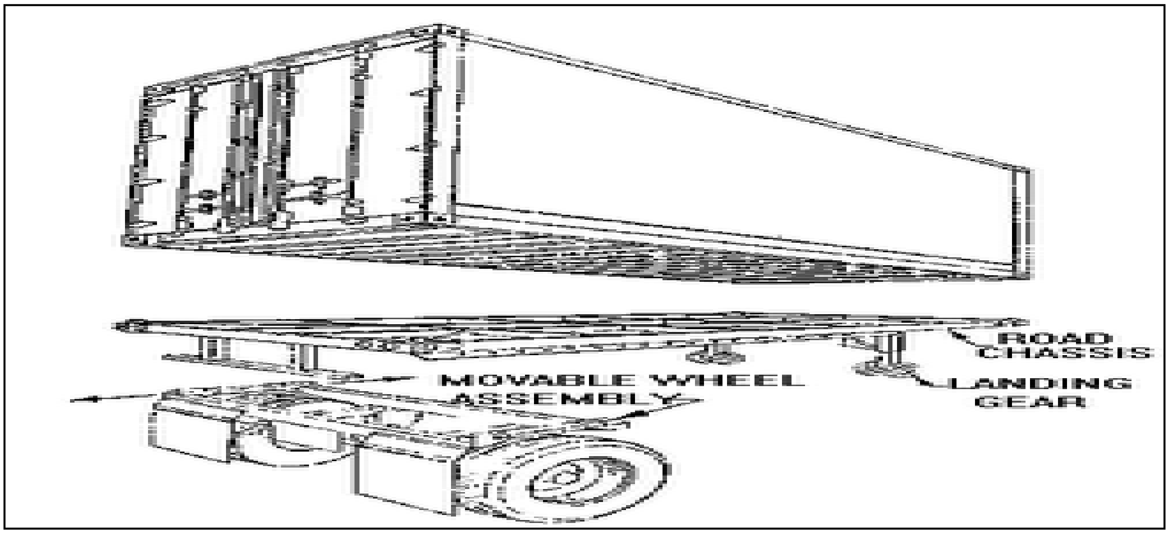


Figure 76 - The Dual Insulated Dry Goods Shipping Cargo Container and Chassis.

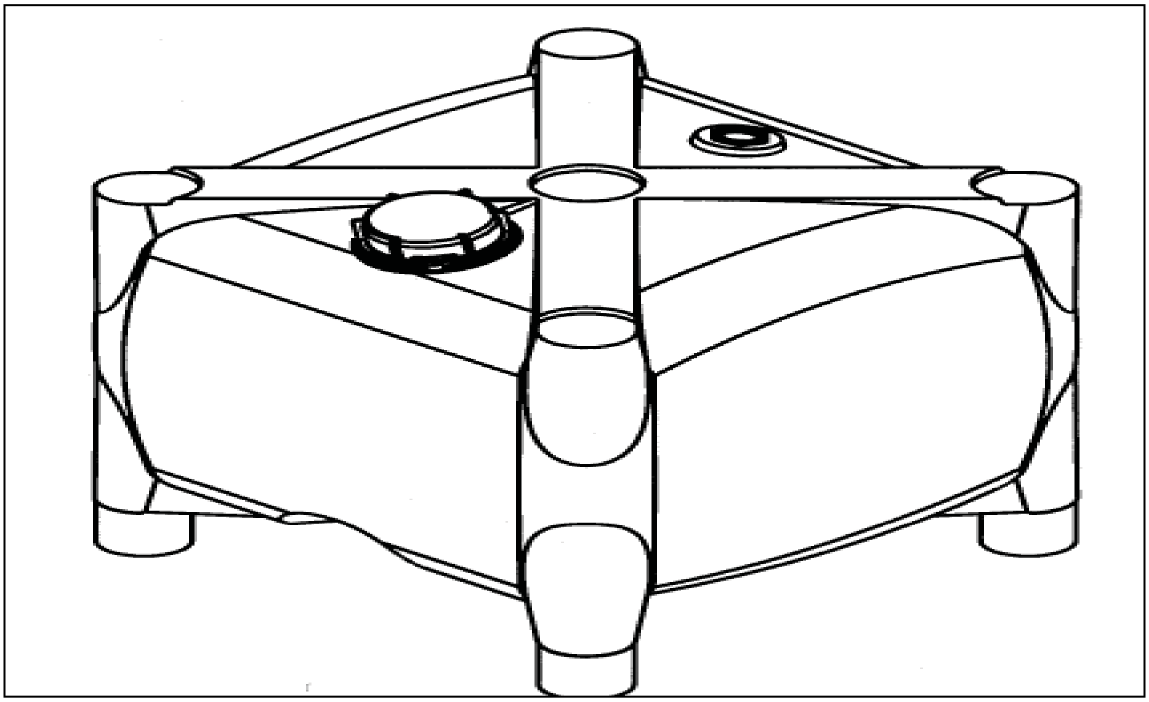
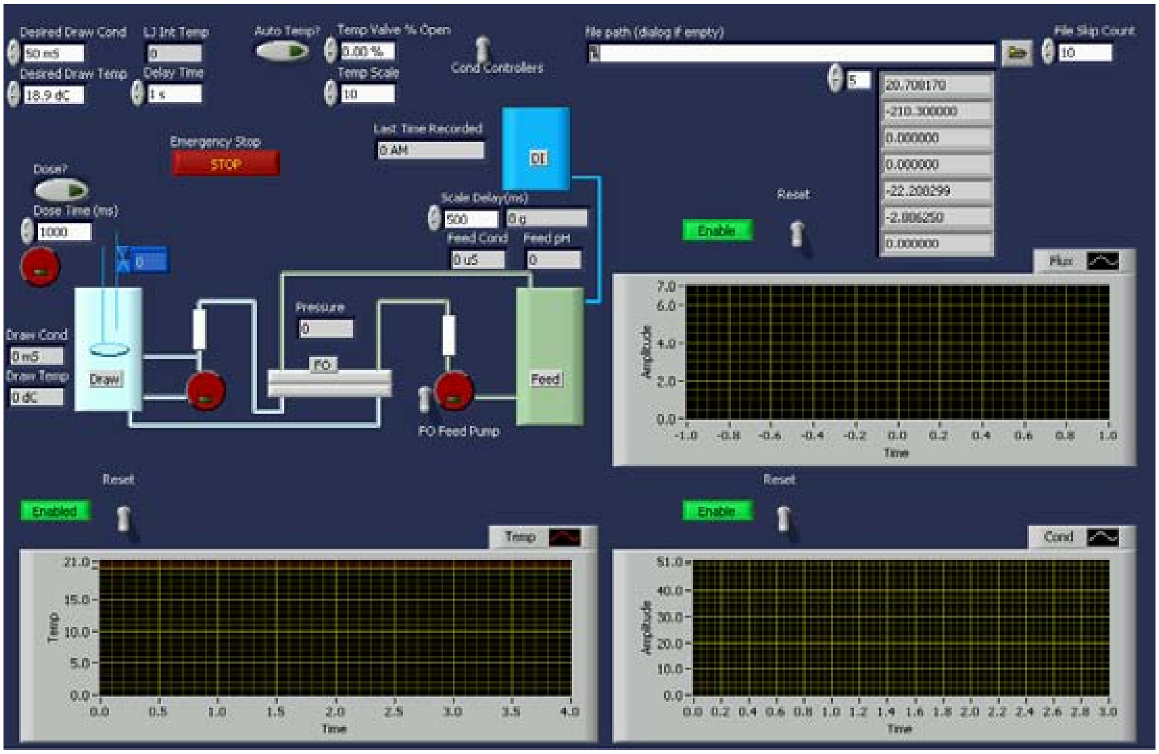


Figure 77 - 120 Gallon Excalibur ®intermediate bulk container (IBC)



Desired Draw Cond 50 mS
LJ Int Temp 0
Temp Valve % Open 0.00 %
Desired Draw Temp 18.9 dC
Delay Time 1 s
Temp Scale 10
File Skip Count 10
5
20.708170
-210.300000
0.000000
0.000000
-22.200299
-2.006250
0.000000
Last Time Recorded 0 AM
Dose Time (ms) 1000
Scale Delay(ms) 500
0 g
Feed Cond 0 uS
Feed pH 0
Pressure 0
Draw Cond 0 mS
Draw Temp 0 dC

Figure 78 - Control panel of the SCADA system used to maintain draw solution concentration and temperature, and record experimental data

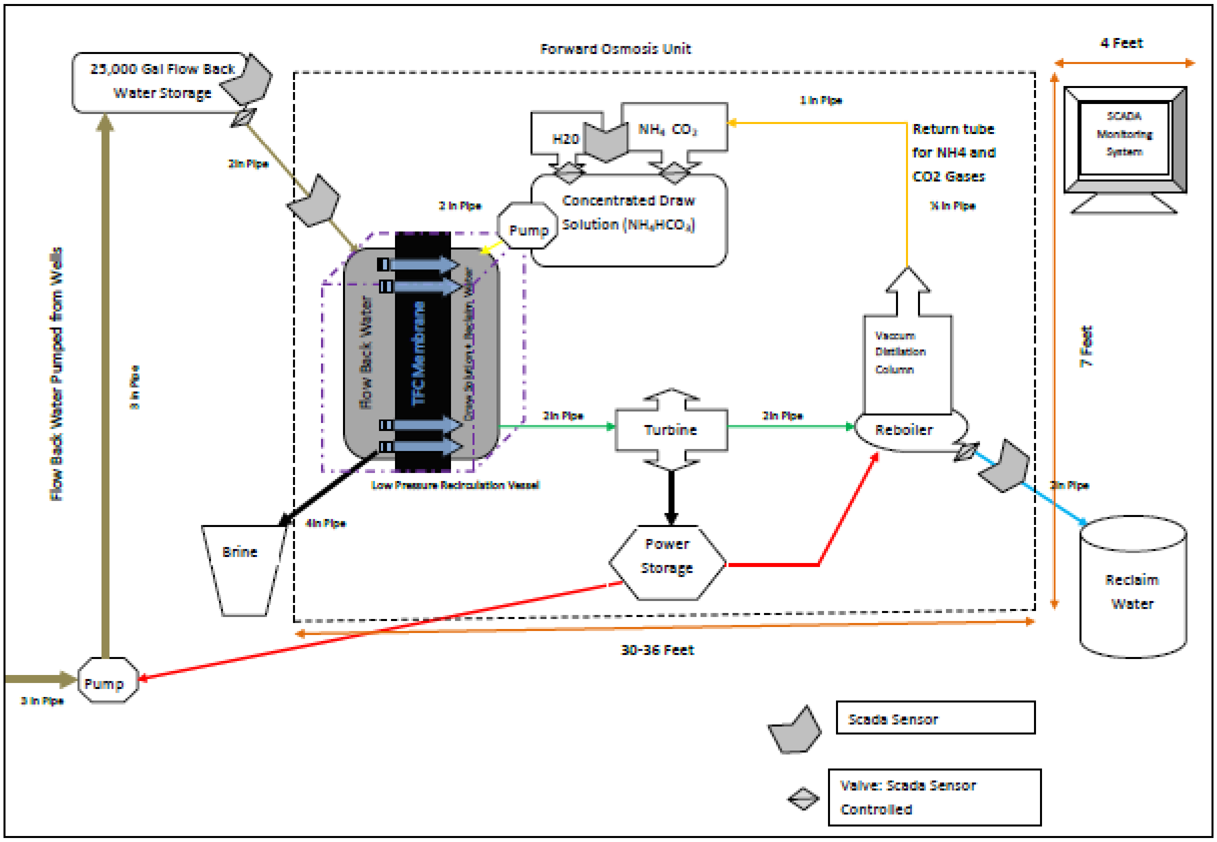


Figure 79 - Schematic Drawing -Novel Semi-Portable Centralized Forward Osmosis Water Treatment Facility

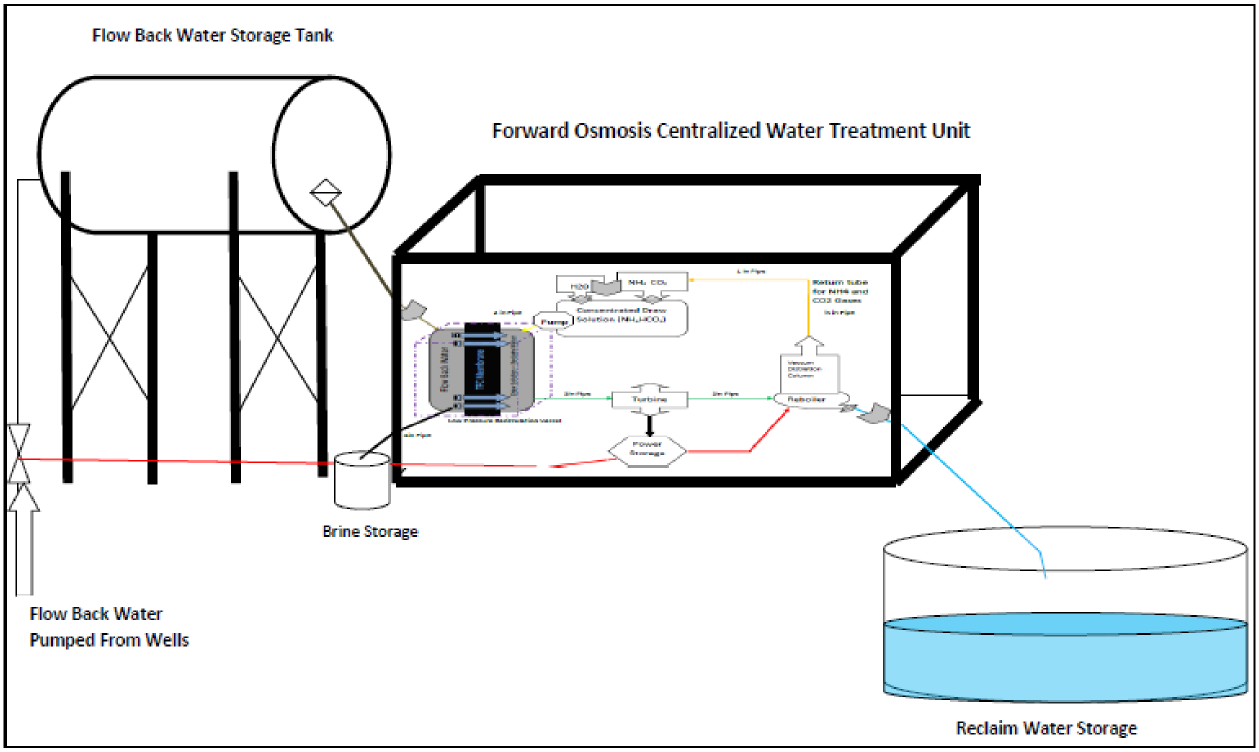


Figure 80 - Generalized Footprint - Novel Semi-Portable Centralized Forward Osmosis Water Treatment Facility.

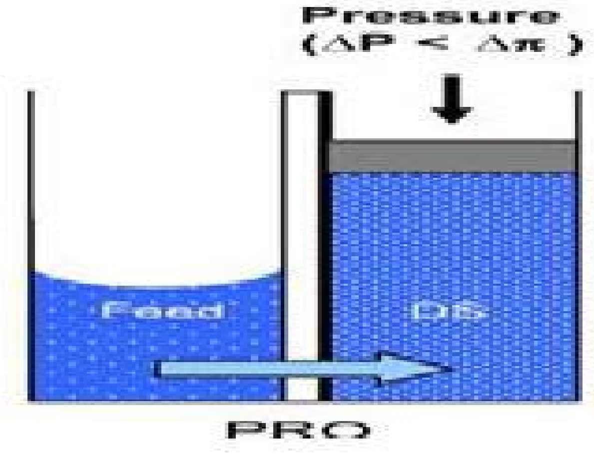


Figure 81: Direction of water flux in the PRO method

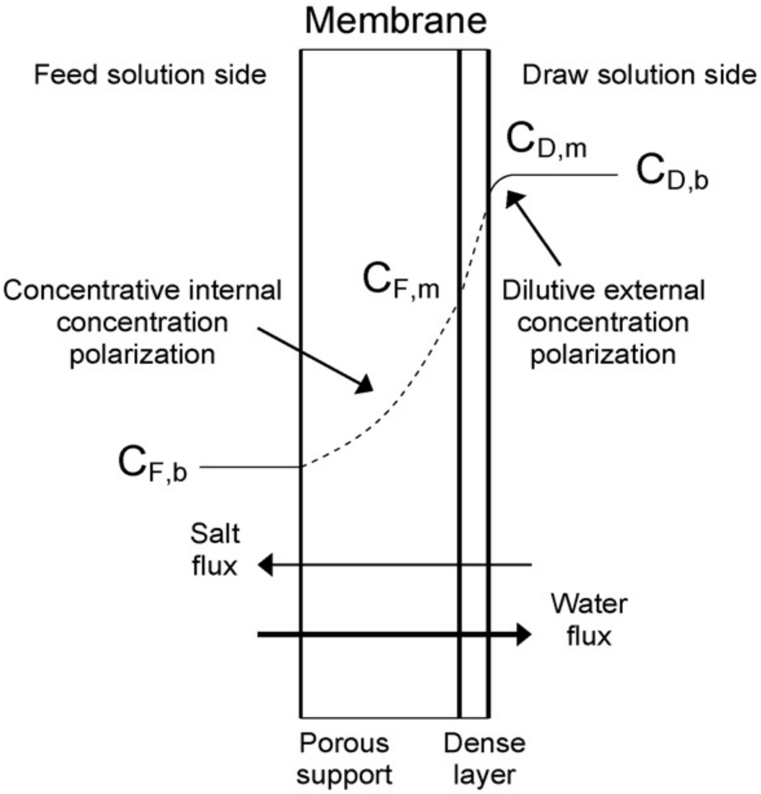


Figure 82: Illustration of osmotic driving forces profiles across a semi-permeable membrane, and the effects of the ICP and ECP

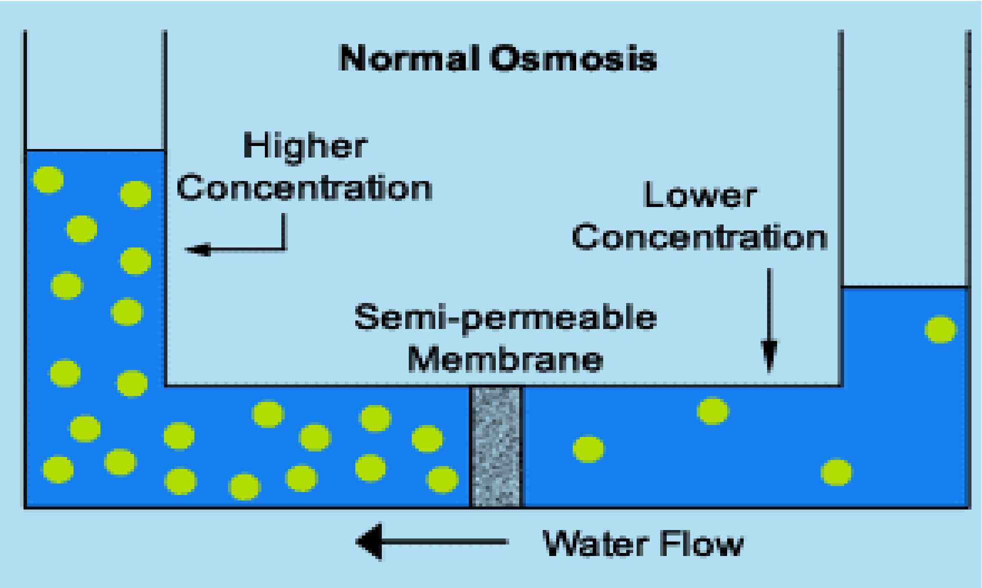
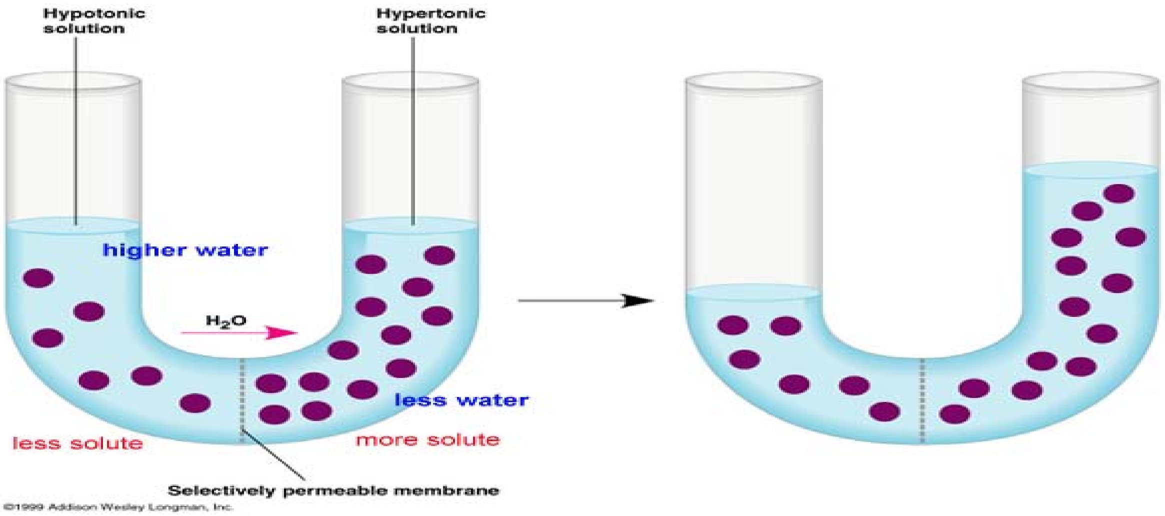


Figure 83: The forward osmosis (FO) process



©1999 Addison Wesley Longman, Inc.

Figure 84: Illustration of change in volume in FO

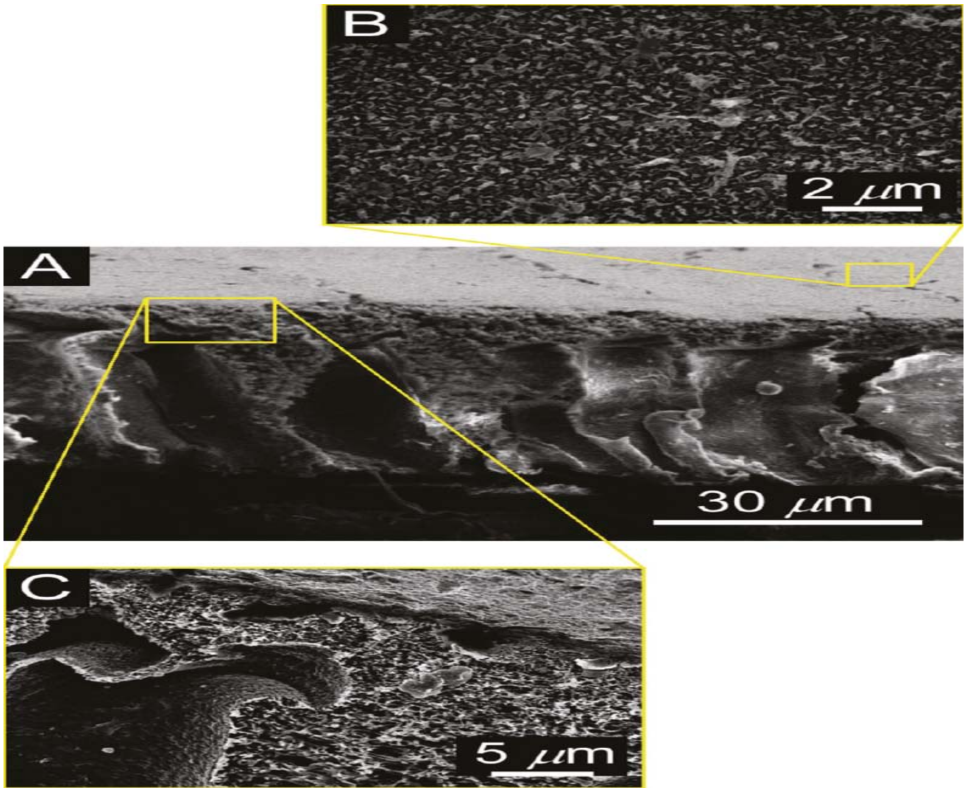


Figure 85: SEM micrographs of a TFC-PRO membrane: (A) cross section with a fingerlike macrovoid structure (B) magnified view of thepolyamide active layer surface, and (C) magnified view of the skin layer at the top of the porous support with dense, spongelike morphology.

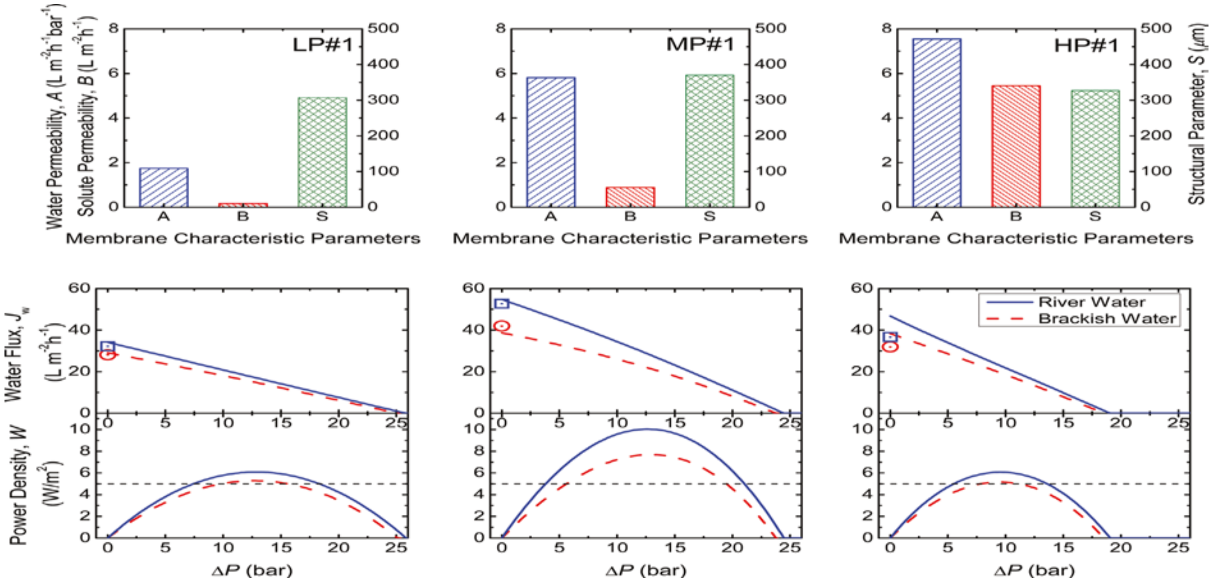


Figure 86: Plots of modeled water flux, Jw, and power density, W, (bottom) as a function of applied hydraulic pressure, ΔP, for TFC-PRO LP#1 (left),MP#1 (center), and HP#1 (right) membranes and their respective characteristic parameters (top): intrinsic water permeability, A; solute permeability coefficient, B; and support layer structural parameter, S. Osmotic pressure of synthetic seawater is 26.14 bar, as determined by OLI Stream Analyzer software, and osmotic pressures of synthetic river water and 1,000 ppm TDS brackish water are 0.045 and 0.789 bar respectively (Yin et al, 2011) .

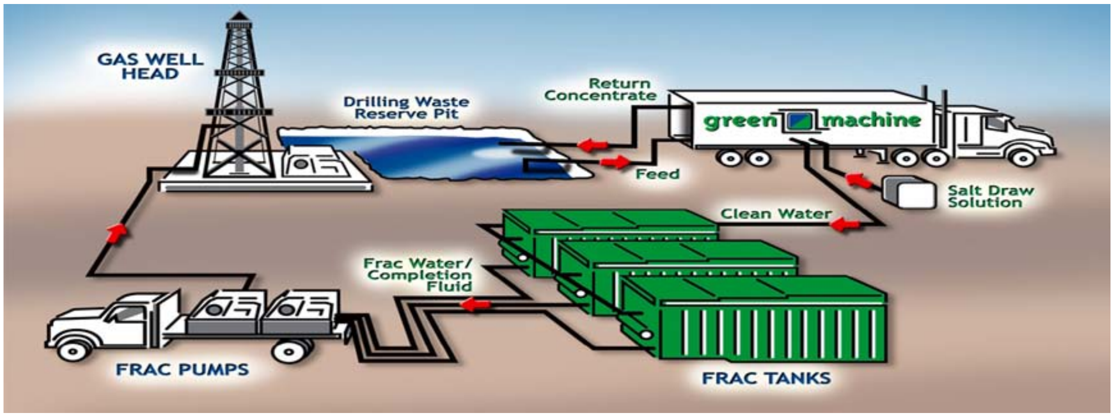
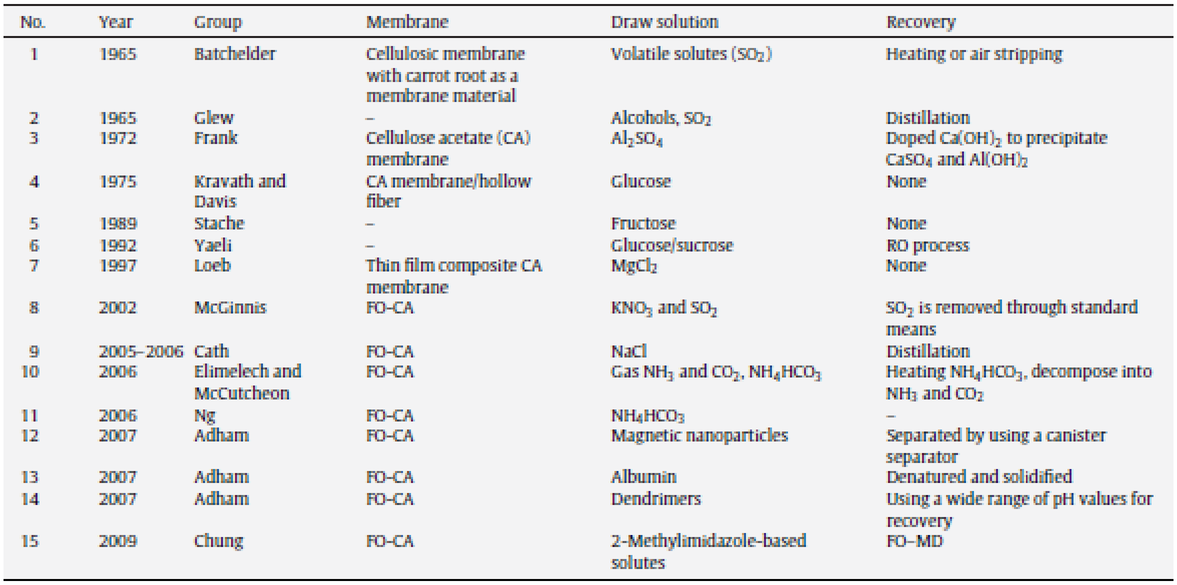


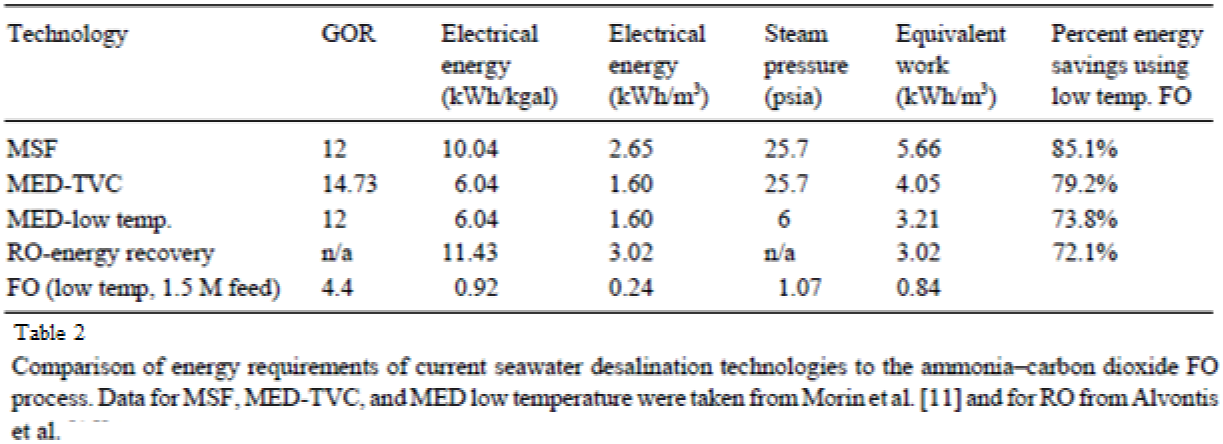
Figure - 87 Mobile FO onsite system (EMERALDSURF,2008)

Figure 88 - Trailer mounted FO filtration system (EMERALDSURF,2008)



No.	Year	Group	Membrane	Draw solution	Recovery
1	1965	Batchelder	Cellulosic membrane with carrot root as a membrane material	Volatile solutes (SO_2)	Heating or air stripping
2	1965	Glew	–	Alcohols, SO_2	Distillation
3	1972	Frank	Cellulose acetate (CA) membrane	Al_2SO_4	Doped $Ca(OH)_2$ to precipitate $CaSO_4$ and $Al(OH)_2$
4	1975	Kravath and Davis	CA membrane/hollow fiber	Glucose	None
5	1989	Stache	–	Fructose	None
6	1992	Yaeli	–	Glucose/sucrose	RO process
7	1997	Loeb	Thin film composite CA membrane	$MgCl_2$	None
8	2002	McGinnis	FO-CA	KNO_3 and SO_2	SO_2 is removed through standard means
9	2005–2006	Cath	FO-CA	NaCl	Distillation
10	2006	Elimelech and McCutcheon	FO-CA	Gas NH_3 and CO_2, NH_4HCO_3	Heating NH_4HCO_3, decompose into NH_3 and CO_2
11	2006	Ng	FO-CA	NH_4HCO_3	–
12	2007	Adham	FO-CA	Magnetic nanoparticles	Separated by using a canister separator
13	2007	Adham	FO-CA	Albumin	Denatured and solidified
14	2007	Adham	FO-CA	Dendrimers	Using a wide range of pH values for recovery
15	2009	Chung	FO-CA	2-Methylimidazole-based solutes	FO–MD

Table 1 - Aqueous solution osmotic pressure (πDS), concentration (CDS), solubility, and diffusion coefficient (D). [Achilli 2010]

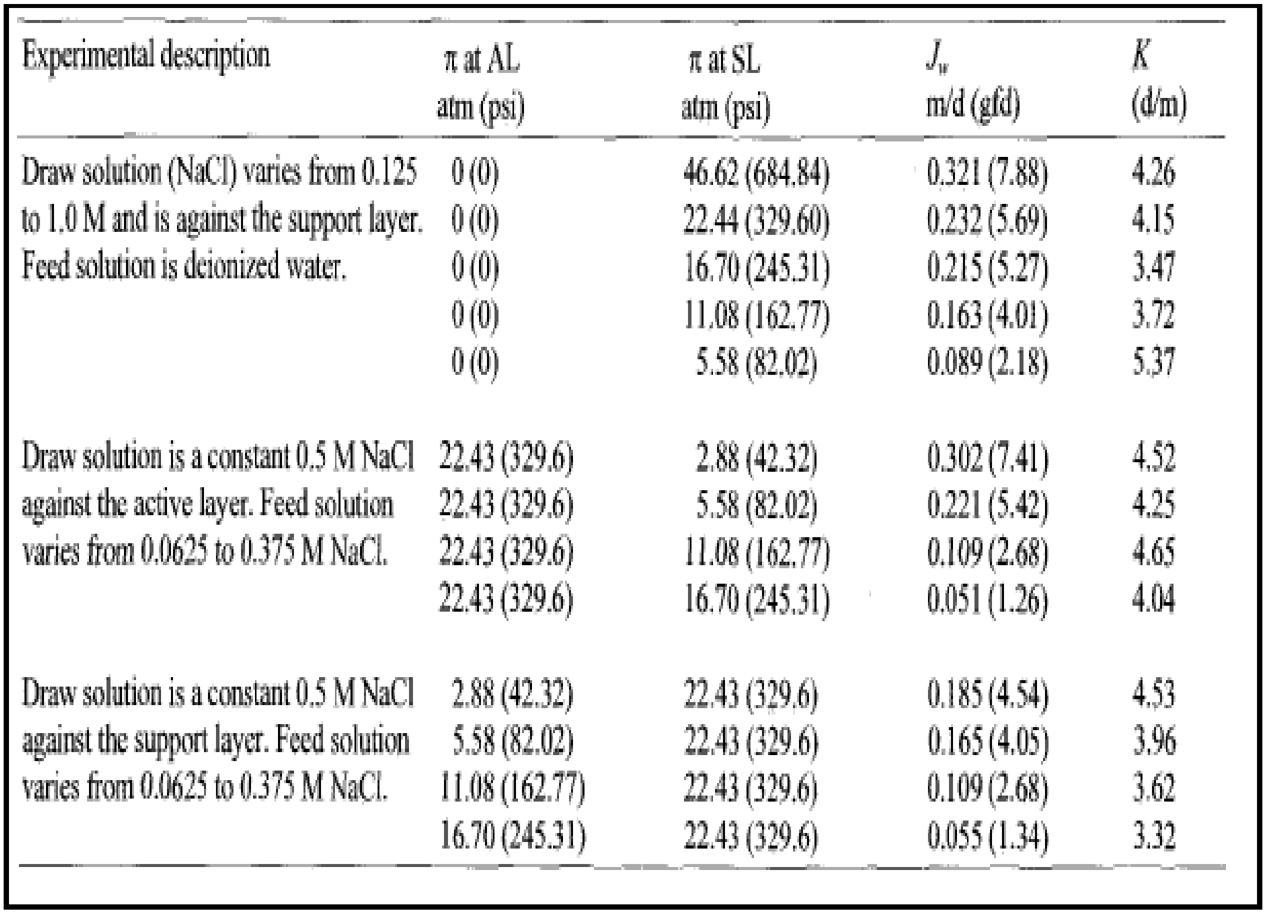


Technology	GOR	Electrical energy (kWh/kgal)	Electrical energy (kWh/m^3)	Steam pressure (psia)	Equivalent work (kWh/m^3)	Percent energy savings using low temp. FO
MSF	12	10.04	2.65	25.7	5.66	85.1%
MED-TVC	14.73	6.04	1.60	25.7	4.05	79.2%
MED-low temp.	12	6.04	1.60	6	3.21	73.8%
RO-energy recovery	n/a	11.43	3.02	n/a	3.02	72.1%
FO (low temp, 1.5 M feed)	4.4	0.92	0.24	1.07	0.84	

Table 2

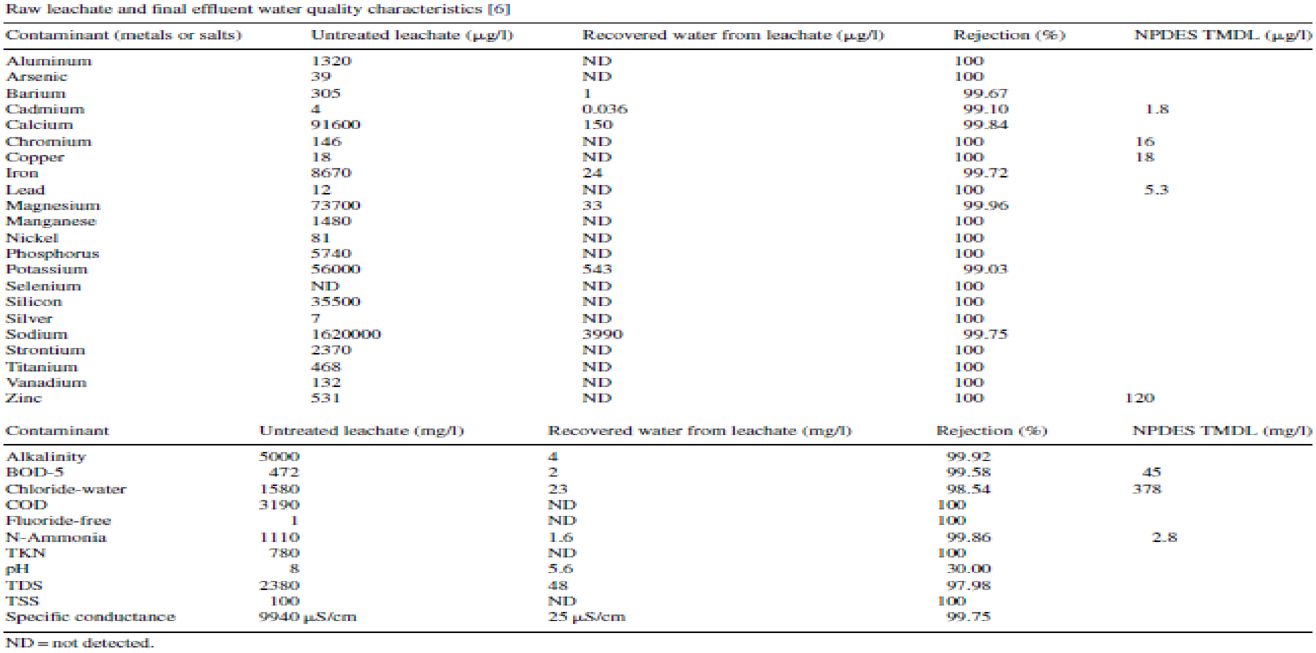
Comparison of energy requirements of current seawater desalination technologies to the ammonia–carbon dioxide FO process. Data for MSF, MED-TVC, and MED low temperature were taken from Morin et al. [11] and for RO from Alvontis et al.

Table 3. Summary of experimental flux data, corresponding bulk osmotic pressures (Tt), and calculated K values for the experiments with NaC1 depicted in Figs 1, 3, and 4. Note that"AL" refers to the membrane active layer while "SL" refers to the membrane support layer. (Wanling 2006)



Experimental description	π at AL atm (psi)	π at SL atm (psi)	J_w m/d (gfd)	K (d/m)
Draw solution (NaCl) varies from 0.125 to 1.0 M and is against the support layer. Feed solution is deionized water.	0 (0)	46.62 (684.84)	0.321 (7.88)	4.26
	0 (0)	22.44 (329.60)	0.232 (5.69)	4.15
	0 (0)	16.70 (245.31)	0.215 (5.27)	3.47
	0 (0)	11.08 (162.77)	0.163 (4.01)	3.72
	0 (0)	5.58 (82.02)	0.089 (2.18)	5.37
Draw solution is a constant 0.5 M NaCl against the active layer. Feed solution varies from 0.0625 to 0.375 M NaCl.	22.43 (329.6)	2.88 (42.32)	0.302 (7.41)	4.52
	22.43 (329.6)	5.58 (82.02)	0.221 (5.42)	4.25
	22.43 (329.6)	11.08 (162.77)	0.109 (2.68)	4.65
	22.43 (329.6)	16.70 (245.31)	0.051 (1.26)	4.04
Draw solution is a constant 0.5 M NaCl against the support layer. Feed solution varies from 0.0625 to 0.375 M NaCl.	2.88 (42.32)	22.43 (329.6)	0.185 (4.54)	4.53
	5.58 (82.02)	22.43 (329.6)	0.165 (4.05)	3.96
	11.08 (162.77)	22.43 (329.6)	0.109 (2.68)	3.62
	16.70 (245.31)	22.43 (329.6)	0.055 (1.34)	3.32

Table 4. Effectiveness of Forward Osmosis on Various Landfill Leachate Contaminants. (Cath, 2007)

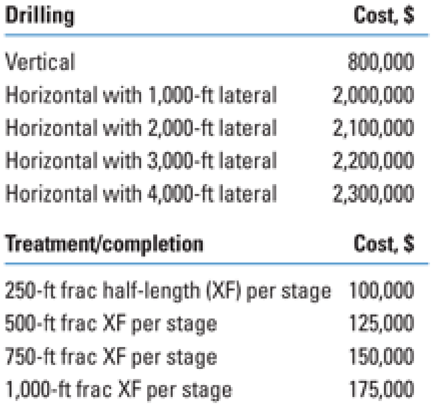


Raw leachate and final effluent water quality characteristics [6]

Contaminant (metals or salts)	Untreated leachate (μg/l)	Recovered water from leachate (μg/l)	Rejection (%)	NPDES TMDL (μg/l)
Aluminum	1320	ND	100	
Arsenic	39	ND	100	
Barium	305	1	99.67	
Cadmium	4	0.036	99.10	1.8
Calcium	91600	150	99.84	
Chromium	146	ND	100	16
Copper	18	ND	100	18
Iron	8670	24	99.72	
Lead	12	ND	100	5.3
Magnesium	73700	33	99.96	
Manganese	1480	ND	100	
Nickel	81	ND	100	
Phosphorus	5740	ND	100	
Potassium	56000	543	99.03	
Selenium	ND	ND	100	
Silicon	35500	ND	100	
Silver	7	ND	100	
Sodium	1620000	3990	99.75	
Strontium	2370	ND	100	
Titanium	468	ND	100	
Vanadium	132	ND	100	
Zinc	531	ND	100	120

Contaminant	Untreated leachate (mg/l)	Recovered water from leachate (mg/l)	Rejection (%)	NPDES TMDL (mg/l)
Alkalinity	5000	4	99.92	
BOD-5	472	2	99.58	45
Chloride-water	1580	23	98.54	378
COD	3190	ND	100	
Fluoride-free	1	ND	100	
N-Ammonia	1110	1.6	99.86	2.8
TKN	780	ND	100	
pH	8	5.6	30.00	
TDS	2380	48	97.98	
TSS	100	ND	100	
Specific conductance	9940 μS/cm	25 μS/cm	99.75	

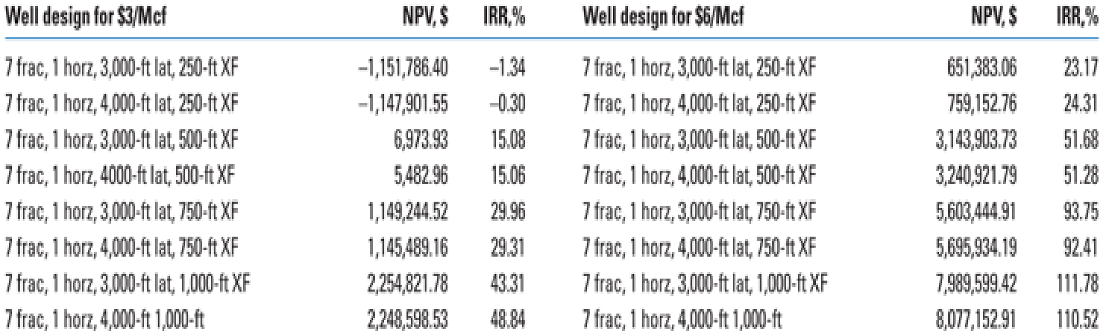
ND = not detected.



Drilling	Cost, $
Vertical	800,000
Horizontal with 1,000-ft lateral	2,000,000
Horizontal with 2,000-ft lateral	2,100,000
Horizontal with 3,000-ft lateral	2,200,000
Horizontal with 4,000-ft lateral	2,300,000

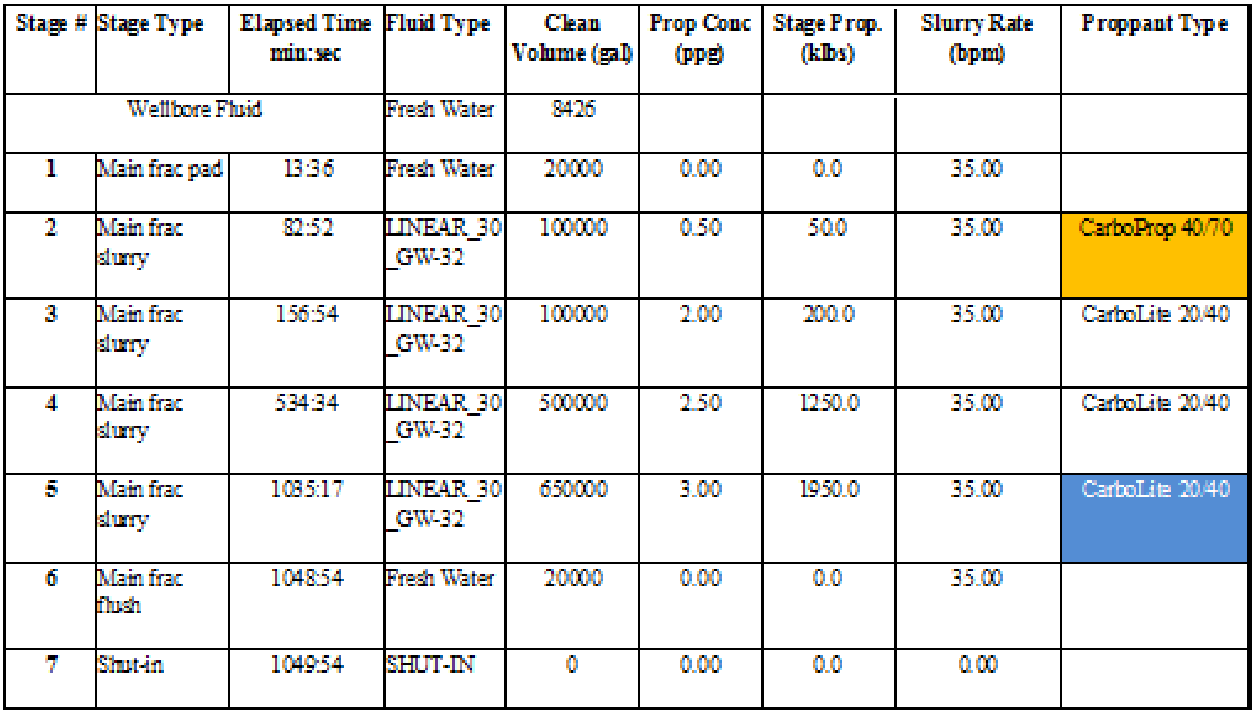
Treatment/completion	Cost, $
250-ft frac half-length (XF) per stage	100,000
500-ft frac XF per stage	125,000
750-ft frac XF per stage	150,000
1,000-ft frac XF per stage	175,000

Table 5. Drilling and completion costs (J., Pletcher,2009)



Well design for $3/Mcf	NPV, $	IRR,%	Well design for $6/Mcf	NPV, $	IRR,%
7 frac, 1 horz, 3,000-ft lat, 250-ft XF	–1,151,786.40	–1.34	7 frac, 1 horz, 3,000-ft lat, 250-ft XF	651,383.06	23.17
7 frac, 1 horz, 4,000-ft lat, 250-ft XF	–1,147,901.55	–0.30	7 frac, 1 horz, 4,000-ft lat, 250-ft XF	759,152.76	24.31
7 frac, 1 horz, 3,000-ft lat, 500-ft XF	6,973.93	15.08	7 frac, 1 horz, 3,000-ft lat, 500-ft XF	3,143,903.73	51.68
7 frac, 1 horz, 4000-ft lat, 500-ft XF	5,482.96	15.06	7 frac, 1 horz, 4,000-ft lat, 500-ft XF	3,240,921.79	51.28
7 frac, 1 horz, 3,000-ft lat, 750-ft XF	1,149,244.52	29.96	7 frac, 1 horz, 3,000-ft lat, 750-ft XF	5,603,444.91	93.75
7 frac, 1 horz, 4,000-ft lat, 750-ft XF	1,145,489.16	29.31	7 frac, 1 horz, 4,000-ft lat, 750-ft XF	5,695,934.19	92.41
7 frac, 1 horz, 3,000-ft lat, 1,000-ft XF	2,254,821.78	43.31	7 frac, 1 horz, 3,000-ft lat, 1,000-ft XF	7,989,599.42	111.78
7 frac, 1 horz, 4,000-ft 1,000-ft	2,248,598.53	48.84	7 frac, 1 horz, 4,000-ft 1,000-ft	8,077,152.91	110.52

Table 6: Seven-fracture economics for $3 and $6 per Mcf gas pricing (J., Pletcher,2009)



Stage #	Stage Type	Elapsed Time min:sec	Fluid Type	Clean Volume (gal)	Prop Conc (ppg)	Stage Prop. (klbs)	Slurry Rate (bpm)	Proppant Type
Wellbore Fluid			Fresh Water	8426				
1	Main frac pad	13:36	Fresh Water	20000	0.00	0.0	35.00	
2	Main frac slurry	82:52	LINEAR_30_GW-32	100000	0.50	50.0	35.00	CarboProp 40/70
3	Main frac slurry	156:54	LINEAR_30_GW-32	100000	2.00	200.0	35.00	CarboLite 20/40
4	Main frac slurry	534:34	LINEAR_30_GW-32	500000	2.50	1250.0	35.00	CarboLite 20/40
5	Main frac slurry	1035:17	LINEAR_30_GW-32	650000	3.00	1950.0	35.00	CarboLite 20/40
6	Main frac flush	1048:54	Fresh Water	20000	0.00	0.0	35.00	
7	Shut-in	1049:54	SHUT-IN	0	0.00	0.0	0.00	

Table 7: Fracture Design Treatment Schedule

Design clean volume (bbls)	33095.2	Design proppant pumped (klbs)	3450.0
Design slurry volume (bbls)	36711.5		

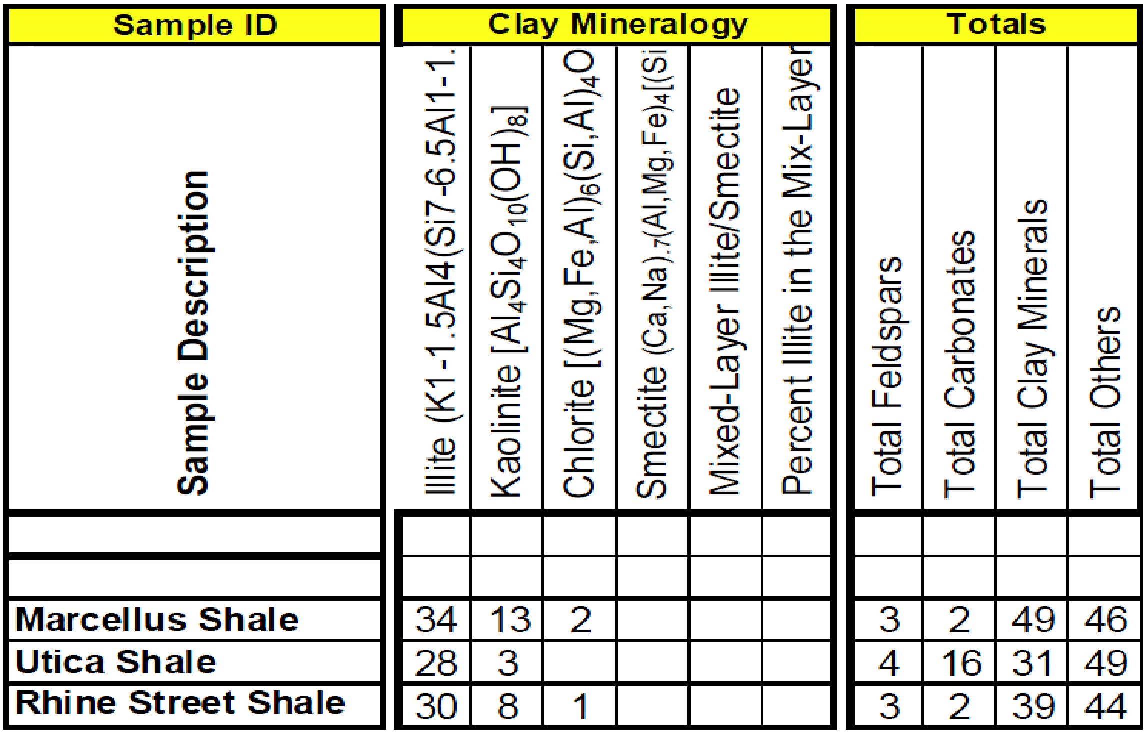
Table 7b (The reservoir properties)

DEPTH	**8620 Ft**
Thickness	180 Ft
I	5280 Ft
J	5280 Ft
Permeability (horizontal)	.01 md
Permeability(vertical)	.001
Porosity	5 %
Temperature	210 F
Initial Pressure	4000 psi
Rock compressibility	.000001

Table 7c. Fracturing fluid additives, main compounds and common uses

Additive Type	Main Compound	Common Usue of Main Compund
Acid	Hydrochloric acid or muriatic acid	Swimming pool chemical and cleaner
Biocide	Glutaraldehyde	Cold sterilant in health care industry
Breaker	Sodium Chloride	Food preservative
Corrosion inhibitor	N,n-dimethyl formamide	Used as a crystallization medium in Pharmaceutical Industry
Friction Reducer	Petroleum distillate	Cosmetics including hair, make-up, nail and skin products
Gel	Guar gum or hydroxyethyl cellulose	Thickener used in cosmetics, sauces and salad dressings.

Table 7d. Clay and mineralogy of three shales

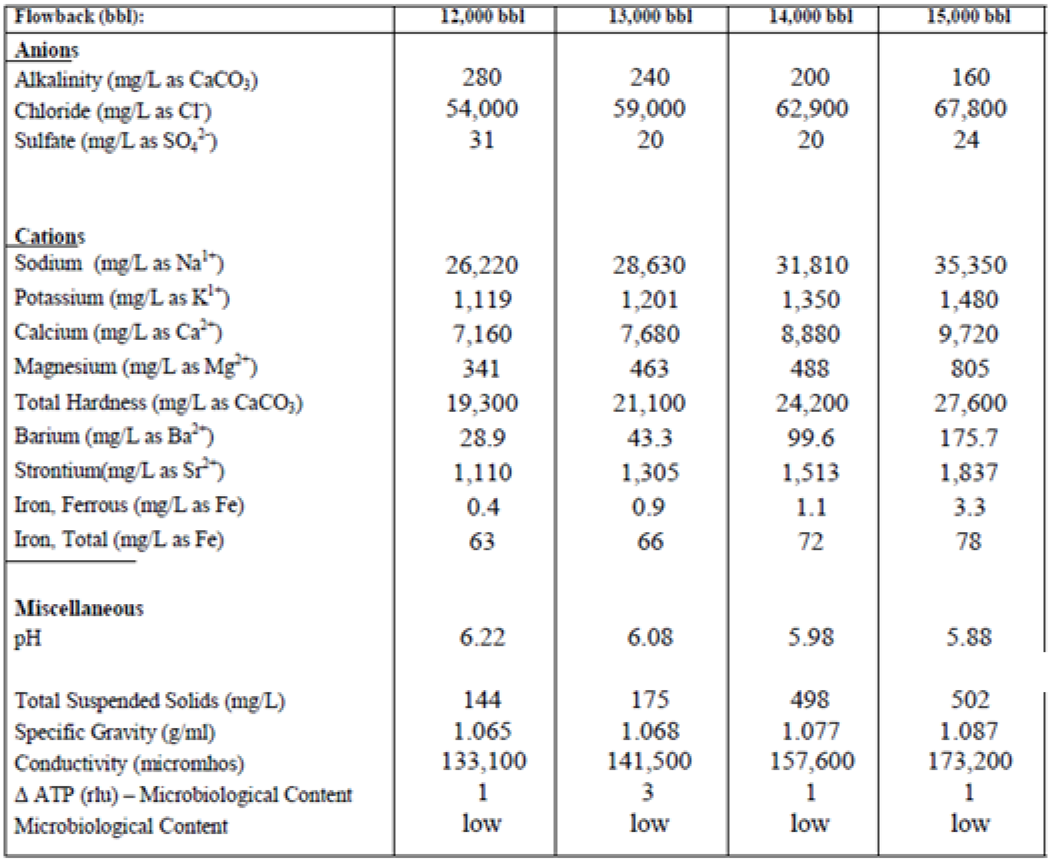


Sample ID	Clay Mineralogy						Totals			
Sample Description	Illite (K1-1.5Al4(Si7-6.5Al1-1.	Kaolinite [$Al_4Si_4O_{10}(OH)_8$]	Chlorite [$(Mg,Fe,Al)_6(Si,Al)_4O$	Smectite $(Ca,Na)_{.7}(Al,Mg,Fe)_4[(Si$	Mixed-Layer Illite/Smectite	Percent Illite in the Mix-Layer	Total Feldspars	Total Carbonates	Total Clay Minerals	Total Others
Marcellus Shale	34	13	2				3	2	49	46
Utica Shale	28	3					4	16	31	49
Rhine Street Shale	30	8	1				3	2	39	44

Table 7e. Final additive concentration

Type	Concentration (%)
HPG	0.05
Friction reducers	0.06
Surfactant	0.085
Breaker	0.009
Clay stabilizers	0.005
Scale inhibitor	0.013
Iron Controller	0.005
Biocides	0.03
Corrosion Inhibitors	0.001

TABLE 8: MARCELLUS SHALE WELL LATE STAGE FLOWBACK WATER CHEMICAL CHARACTERIZATION DATA



Flowback (bbl):	12,000 bbl	13,000 bbl	14,000 bbl	15,000 bbl
Anions				
Alkalinity (mg/L as $CaCO_3$)	280	240	200	160
Chloride (mg/L as Cl^-)	54,000	59,000	62,900	67,800
Sulfate (mg/L as SO_4^{2-})	31	20	20	24
Cations				
Sodium (mg/L as Na^{1+})	26,220	28,630	31,810	35,350
Potassium (mg/L as K^{1+})	1,119	1,201	1,350	1,480
Calcium (mg/L as Ca^{2+})	7,160	7,680	8,880	9,720
Magnesium (mg/L as Mg^{2+})	341	463	488	805
Total Hardness (mg/L as $CaCO_3$)	19,300	21,100	24,200	27,600
Barium (mg/L as Ba^{2+})	28.9	43.3	99.6	175.7
Strontium(mg/L as Sr^{2+})	1,110	1,305	1,513	1,837
Iron, Ferrous (mg/L as Fe)	0.4	0.9	1.1	3.3
Iron, Total (mg/L as Fe)	63	66	72	78
Miscellaneous				
pH	6.22	6.08	5.98	5.88
Total Suspended Solids (mg/L)	144	175	498	502
Specific Gravity (g/ml)	1.065	1.068	1.077	1.087
Conductivity (micromhos)	133,100	141,500	157,600	173,200
Δ ATP (rlu) – Microbiological Content	1	3	1	1
Microbiological Content	low	low	low	low

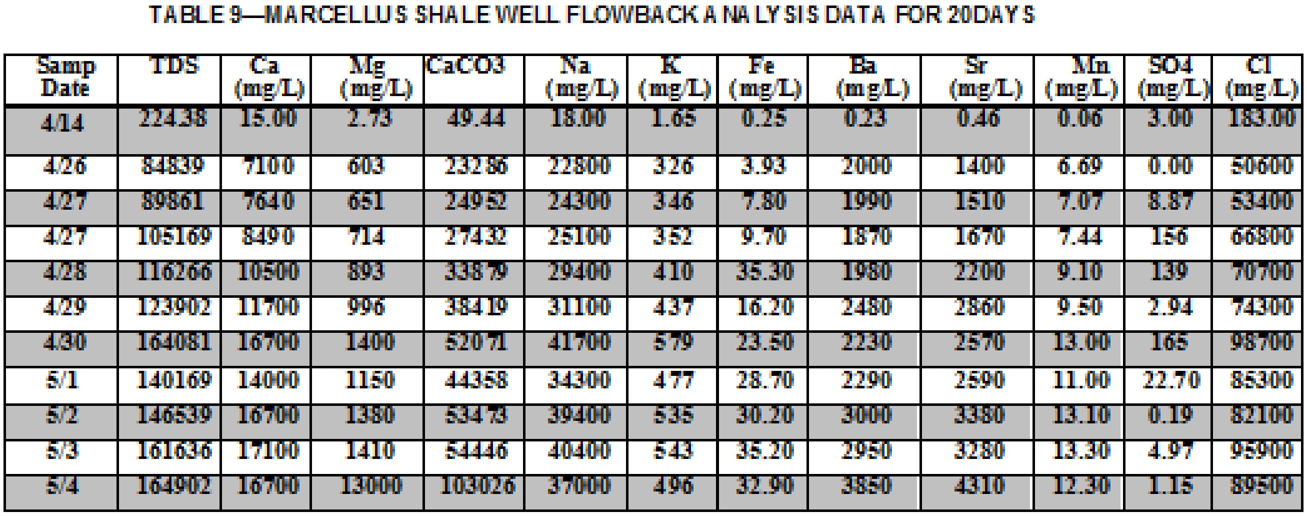


TABLE 9—MARCELLUS SHALE WELL FLOWBACK ANALYSIS DATA FOR 20DAYS

Samp Date	TDS	Ca (mg/L)	Mg (mg/L)	CaCO3	Na (mg/L)	K (mg/L)	Fe (mg/L)	Ba (mg/L)	Sr (mg/L)	Mn (mg/L)	SO4 (mg/L)	Cl (mg/L)
4/14	224.38	15.00	2.73	49.44	18.00	1.65	0.25	0.23	0.46	0.06	3.00	183.00
4/26	84839	7100	603	23286	22800	326	3.93	2000	1400	6.69	0.00	50600
4/27	89861	7640	651	24952	24300	346	7.80	1990	1510	7.07	8.87	53400
4/27	105169	8490	714	27432	25100	352	9.70	1870	1670	7.44	156	66800
4/28	116266	10500	893	33879	29400	410	35.30	1980	2200	9.10	139	70700
4/29	123902	11700	996	38419	31100	437	16.20	2480	2860	9.50	2.94	74300
4/30	164081	16700	1400	52071	41700	579	23.50	2230	2570	13.00	165	98700
5/1	140169	14000	1150	44358	34300	477	28.70	2290	2590	11.00	22.70	85300
5/2	146539	16700	1380	53473	39400	535	30.20	3000	3380	13.10	0.19	82100
5/3	161636	17100	1410	54446	40400	543	35.20	2950	3280	13.30	4.97	95900
5/4	164902	16700	13000	103026	37000	496	32.90	3850	4310	12.30	1.15	89500

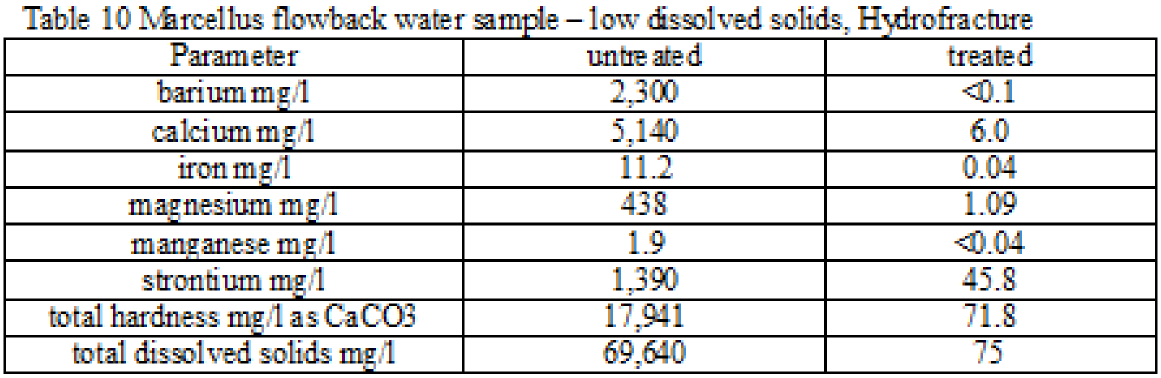
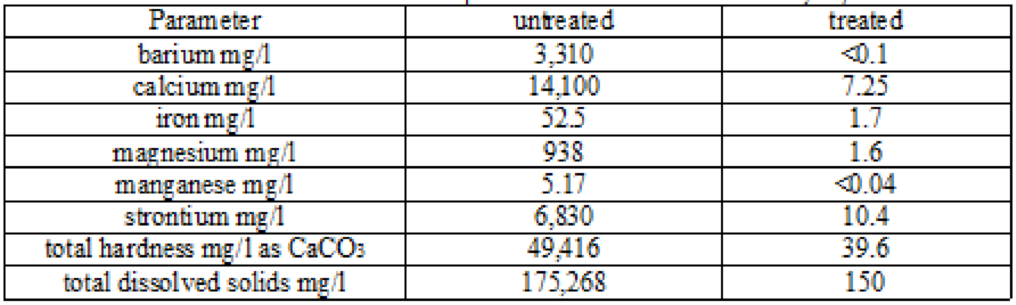


Table 10 Marcellus flowback water sample – low dissolved solids, Hydrofracture

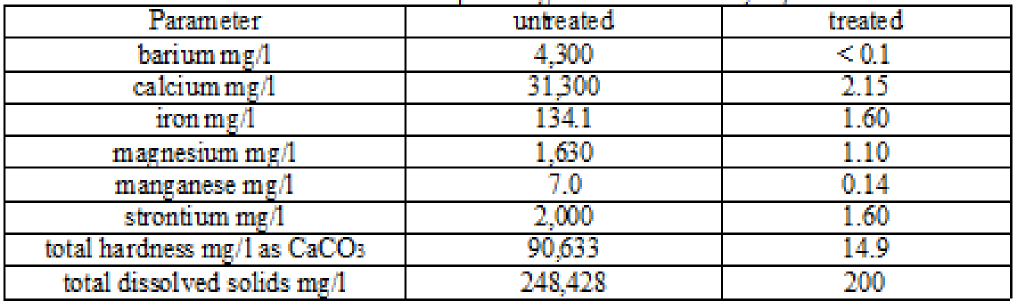
Parameter	untreated	treated
barium mg/l	2,300	<0.1
calcium mg/l	5,140	6.0
iron mg/l	11.2	0.04
magnesium mg/l	438	1.09
manganese mg/l	1.9	<0.04
strontium mg/l	1,390	45.8
total hardness mg/l as CaCO3	17,941	71.8
total dissolved solids mg/l	69,640	75

Table 11 Marcellus flowback water sample – moderate dissolved solids, Hydrofracture 1



Parameter	untreated	treated
barium mg/l	3,310	<0.1
calcium mg/l	14,100	7.25
iron mg/l	52.5	1.7
magnesium mg/l	938	1.6
manganese mg/l	5.17	<0.04
strontium mg/l	6,830	10.4
total hardness mg/l as $CaCO_3$	49,416	39.6
total dissolved solids mg/l	175,268	150

Table 12 Marcellus flowback water sample – high dissolved solids, Hydrofracture 4



Parameter	untreated	treated
barium mg/l	4,300	< 0.1
calcium mg/l	31,300	2.15
iron mg/l	134.1	1.60
magnesium mg/l	1,630	1.10
manganese mg/l	7.0	0.14
strontium mg/l	2,000	1.60
total hardness mg/l as $CaCO_3$	90,633	14.9
total dissolved solids mg/l	248,428	200

County Name	Lease Cost ($/acre)
Bradford	1500
Fayette	1150
Susquehanna	2500
Greene	3000
Clearfield	2500

Table.13 Lease cost for the counties in 2010

REFERENCES

Achilli, A., Cath, T. Y., & Childress, A. E. (2009). Power generation with pressure retarded osmosis: An experimental and theoretical investigation, 343 (2009) 42–52. Journal of Membrane Science , 343, 42-52.

Achilli, A.; Childress, A. E. Pressure retarded osmosis: From the vision of Sidney Loeb to the first prototype installation—Review Desalination 2010, 261 (3) 205– 211

Adam T bourgoyne. Martin E. chenveret and Keith K. millheim, Applied Drilling Engineering.

Adham S., Oppenheimer J., Liu L., Kumar M. Dewatering reverse osmosis concentrate from water reuse using forward osmosis, Water Reuse Foundation Research Report, Product No. 05-009-01, 2007, pp. 1–52.

Administration, National Oceanic and Atmospheric. Annual Summary. 2005.

Agrawal,: "A Technical and Economic Study of Completion Techniques in Five Emerging US Gas Shales" paper SPE 135396-MS, 2010

Andrea Achilli, Tzahi Y. Cath, Amy E. Childress, Selection of inorganic-based draw solutions for forward osmosis applications, Journal of Membrane Science, Volume 364, Issues 1-2, 15 November 2010, Pages 233-241

Ang, W. S.; Elimelech, M.Protein (BSA) fouling of reverse osmosis membranes: Implications for wastewater reclamation J. Membr. Sci. 2007, 296 (1–2) 83– 92

Appalachian Shale Water Conservation and Management Committee. 2008. Spreadsheet Survey of 13 ASWCMC Companies, August 2009.

Arnold, K., Stewart, M. Surface Production Operations: Design of Gas Handling Systems and Facilities 2 ed, Vol 2. s.l. : Gulf Publishing Compagny, 1999.

Arthur, J. Daniel, Bohm, Brian and Layne, Mark. Hydraulic Fracturing Considerations for Natural Gas Wells of the Marcellus Shale. Cincinnati : ALL Consulting, 2008.

Arthur, J. Daniel, et al. Evaluating the Environemtal Implications of Hydraulic Fracturing in Shale Gas Reservoirs. s.l. : ALL Consulting , 2008.

Arthur, J. Daniel. West Virginia Surface Owners' Rights Organization. [Online] Sep. 21th,2008. http://www.wvgs.wvnet.edu/www/datastat/GWPC_092008_Marcellus_Frac_Arthur_et_al.pdf.

Baker, R. W. Membrane Technology and Applications, 2nd ed.; J. Wiley: New York, 2004; p x, 538

Bamaga O.A., Yokochi A., Zabara B., Babaqi A.S. Hybrid FO/RO desalination system: Preliminary assessment of osmotic energy recovery and designs of new FO membrane module configurations, Desalination, Volume 268, Issues 1-3, 1 March 2011, Pages 163-169.

Barnes, Dustin. North East Mud Services Company L.L.C. [Online] 2009. http://www.nemud.com/.

Baoxia Mi, Menachem Elimelech, Chemical and physical aspects of organic fouling of forward osmosis membranes, Journal of Membrane Science, Volume 320, Issues 1-2, 15 July 2008, Pages 292-302

Bill Grieser and Jim Bray, Halliburton "Identification of Production Potential in Unconventional Reservoirs "SPE 106623-MS 2007

Boysen, J.E., Boysen, D., Larson, T., and J. Sorenson, "Topical Report: Field Application of the Freeze/Thaw Evaporation (FTE) Process for the Treatment of natural Gas Produced Water in Wyoming," Available from the Gas Research Institute, Des Plaines, IL GRI Report Number GRI-02/0221 (2002).

Bullin, Keith. Processing Possibilities for Shale Gas Plays. s.l. : Bryan Research and Engineering, 2008.

Cabot Oil & Gas. [Online] Cabot Oil & Gas Corporation, Dec. 8th, 2008. http://phx.corporateir.net/phoenix.zhtml?c=116492&p=irol-newsArticle&ID=1233344&highlight

CARBO Ceramics. 2010. "Why ceramic proppant?" http://www.carboceramics.com/

Cardona, E.; Piacentino, A.; Marchese, F.; Energy saving in two-stage reverse osmosis systems coupled with ultrafiltration processes, Desalination, Volume 184, Issues 1-3, Desalination and the Environment, 1 November 2005, Pages 125-137

Cath, T. Y.; Childress, A. E.; Elimelech, M.Forward osmosis: Principles, applications, and recent developments J. Membr. Sci. 2006, 281 (1–2) 70– 87

Cipolla, C., Warpinski, N., Mayerhofer, M., Lolan, E. and Vincent, M. "The relationship Between Fracture Comlexity, Reservoir Properties, and Fracture Treatment Design," SPE 115769, 2009.

Charpentier, R.R. Estimates of Unconventional Natural Gas Resources Resources of the Devonian Shales of the Appalachian Basin. s.l. : US GEOLOGICAL SURVEY BULLETIN 1909 , 1993.

Chung T.S., et al., Forward osmosis processes: Yesterday, today and tomorrow, Desalination (2010), doi:10.1016/j.desal.2010.12.019

Cipolla, L. Craig. “Modeling Production and Evaluating Fracture Performance in Unconventional Gas Reservoir,” SPE 118536

Claudel and Boulamri L., A new model of gas solid kinetics — the case of ammonium carbamate formation and decomposition. Thermochimica Acta 126 (1988), pp. 129–148.

CONSOL Energy. [Online] CNX Gas Corporation, 2008. http://www.consolenergy.com/AboutUs/QuickFacts.aspx.

Dale, A. Pierce,: “Water Recycling Helps with Sustainability” paper SPE 134137-MS, 2010

Daniel J., Bohm Brian, and Cornue Davd Cornue. “Enviromental Considerations of Modern Shale Gas Development,” SPE 122931, 2009.

Daniel J., Bohm Brian, and Bobbi Jo Coughlin. “Evaluating Implications of Hydraulic Fracturing in Shale Gas Reservoirs.” SPE 121038, 2009.

Davidson, John. keystoneedge. [Online] Cabot Oil & Gas Corporation, Dec. 11th, 2008. http://www.keystoneedge.com/innovationnews/cabotoilgas1211.aspx.

Developments”. Journal of Membrane Science, Volume 281, Issues 1-2, Pages 70-87

Doran, G. and Leong, L.Y.C., "Developing a Cost Effective Solution for Produced Water and Creating a 'New' Water Resource," DOE Report DOE/MT/95008-4 (2000).

Durham, L.S. "Appalachian Basin’s Marcellus – the new target". s.l. : American Association of Petroleum Geologists, March, 2008.

“Emission Facts - Average Carbon Dioxide Emissions Resulting from Gasoline and Diesel Fuel”. (February 2005), U.S. Environmental

Eric Maidla, Marc Haci, and Daniel Wright, Slider LLC “Case History Summary: Horizontal Drilling Performance Improvement Due to Torque Rocking on 800 Horizontal Land Wells Drilled for Unconventional Gas Resources “SPE 133647-MS 2010

Evans, A.; Strezov, V.; Evans, T. J.Assessment of sustainability indicators for renewable energy technologies Renewable Sustainable Energy Rev. 2009, 13 (5) 1082–1088

Fresh Water / Salt Water‖ by Geotechnical, Rock, Water Resource Library. http://www.grow.arizona.edu/water/freshsaltwater.shtml

Gaudlip A.W. and Paugh L.O. “Marcellus Shale Water Management Challenges in Pennsylvania,” SPE 119898, 2008.

Geehan, T. (July 2009). “Water Treatment Processes Make Strides”. E&P.

Geise, G. M.; Park, H. B.; Sagle, A. C.; Freeman, B. D.; McGrath, B. E.Water Permeability and Water/Salt Selectivity Tradeoff in Polymers for Desalination J. Membr. Sci. 2011, 369,130– 138

Ghosh, A. K.; Hoek, E. M. V.Impacts of support membrane structure and chemistry on polyamide–polysulfone interfacial composite membranes J. Membr. Sci. 2009, 336 (1–2)140– 148

Glater, J.; Zachariah, M. R.; A Mechanistic study of halogen interaction with polyamide reverse-osmosis membranes ACS Symp. Ser. 1985, 281, 345– 358

Glater, J.; Zachariah, M. R.; Mccray, S. B.; Mccutchan, J. W.Reverse-osmosis membrane sensitivity to ozone and halogen disinfectants Desalination 1983, 48 (1) 1– 16

Glew D.N., Process for liquid recovery and solution concentration, US Patent 3,216,930 (1965).

Gordon T. Gray, Jeffrey R. McCutcheon, Menachem Elimelech, Internal concentration polarization in forward osmosis: role of membrane orientation, Desalination, Volume 197, Issues 1-3, 2 October 2006, Pages 1-8

Gray G.T., McCutcheon J.R. and Elimelech M., Internal concentration polarization in forward osmosis: role of membrane orientation, Desalination 197 (2006), pp. 1–8

Hale A.H. and Mody F.K., * Shell Development Co” Mechanism for Wellbore Stabilization With Lime-Based Muds” SPEIIADC 25706

Hayes, T. and A. Arthur. 2004. “Overview of Emerging Produced Water Treatment Technologies.” Proceedings of the 11th Annual International Petroleum Environmental Conference. October 12-15.

“Haynesville Shale Overview”. (1 March 2010). Louisiana Department of Natural Resources.

Hemant Kumar. Sustainable Development and Design of Marcellus Shale Play in Susquehanna, PA, 2009.

Herron J.R., Beaudry E.G., Jochums C.E., Medina L.E., Apparatus for direct osmotic concentration of fruit juices, US Patent 5,281,430 (1994). New Product Developments. Filtration Industry Analyst, 2008 (2008) 14.

Holdich, R., Kosvintsev, S., Cumming, I., & Zhdanov, S. (2006). Pore Design and Engineering for Filters and Membranes. Philosophical Transactions: Mathematical, Physical and Engineering Sciences , 364 (1838), 161-174.

Houston, Nathan, Matt Blauch, and Dalton Weaver. “Fracture-Stimulation in the Marcellus Shale-Lessons Learned in Fluid Selection and Execution,” http://www.naturalgas.org/naturalgas/well_completion.asp#completion

Isaacs, I. J., & Seymour, R. (1973). The ocean as a power resource. International of Environmental Studies , 4 (1), 201-205.

Isaacs, J. D., & Schmitt, W. R. (1980). Ocean Energy: Forms and Prospects. Science , 207 (4428), 265-273.

James R., ConocoPhillips Norge; A. Nistov, Statoil; C. Smulders, Shell Intl.; K. Walker, M-I Swaco; T. Schei, ConocoPhillips Norway; N. LeBlond, Total Fluides; M. Sopko, Nexen; and T. Fonneland, Norsk Hydro “Occupational Exposure Hazards Related To The Use Of Drilling Fluids Presented With Remedial Risk Management Guidelines” SPE 108514-MS 2007 .

James R., SPE, P. Navestad, and T. Schei, Phillips Petroleum Co. Norway, T. Geddes, G. Nelson, SPE, and D. Webster, Carless Refining & Marketing Ltd “Improving the Working Environment and Drilling Economics Through Better Understanding of Oil Based Drilling Fluid Chemistry” SPE/IADC 57551.

Kai Yu Wang, Tai-Shung Chung, Jian-Jun Qin, Polybenzimidazole (PBI) nanofiltration hollow fiber membranes applied in forward osmosis process, Journal of Membrane Science, Volume 300, Issues 1-2, 15 August 2007, Pages 6-12

Kauman P. and Penny G.S. “Critical Evaluations of Additives Used in Shale Slickwater Fracs,” SPE 119900, 2008.

Kawaguchi, T.; Tamura, H.Chlorine-resistant membrane for reverse-osmosis. 1. Correlation between chemical structures and chlorine resistance of polyamides J. Appl. Polym. Sci.1984, 29 (11) 3359– 3367

Kostenuk N. and Browne D.J. “Improved Proppant Transport System for Slickwater Shale Fracturing,” CSUG/SPE 137818, 2010.

Kravath R.E. and Davis J.A. Desalination of seawater by direct osmosis, Desalination 16 (1975), pp. 151–155.

Kwon, Y. N.; Leckie, J. O.Hypochlorite degradation of crosslinked polyamide membranes—II. Changes in hydrogen bonding behavior and performance J. Membr. Sci. 2006, 282 (1–2)456– 464

Lee, Dae Sung., Herman, Jonathan D, Elsworth, Derek "A Critical Evaluation of Unconventional Gas Recovery from the Marcellus Shale, Northeastern United States"

Lee, K., Baker, R., & Lonsdale, H. (1981). Membrane for power generation by pressure retarded osmosis. Journal of Membrane Science , 8, 141-171.

Lind, M. L.; Ghosh, A. K.; Jawor, A.; Huang, X. F.; Hou, W.; Yang, Y.; Hoek, E. M. V.Influence of zeolite crystal size on zeolite–polyamide thin film nanocomposite membranes Langmuir 2009, 25 (17) 10139– 10145

Leob, S. (2002). Large-scale power production by pressure-retarded osmosis, using river water and sea water passing through spiral modules. Desalination , 143 (2), 115-122.

Leob, S. (1976). Production of energy from concentrated brines by pressure retarded osmosis. Journal of Membrane Science , 1 (1), 49-63.

Leob, S., & Norman, R. S. (1975). Osmotic Power Plants. Science , 189 (4203), 654-655.

Leob, S.; Titelman, L.; Korngold, E.; Freiman, J.Effect of porous support fabric on osmosis through a Loeb–Sourirajan type asymmetric membrane J. Membr. Sci. 1997, 129 (2) 243–249

Lynn W B. Drilling companies looking for natural gas in county. [Online] 2008. http://www.theprogressnews.com/default.asp?read=12052.

Marcellusshales. [Online] Equitable Resources, 2008. http://www.marcellusshales.com/marcellusshalecompanies.html.

McCutcheon, Jeffrey R. & Elimelech Menachem (2006). Influence of concentrative and dilutive internal concentration polarization on flux behavior in forward osmosis. Journal of Membrane Science, 284(1-2), 237-247.

McCutcheon, Jeffrey R. & Elimelech Menachem (2007). Modeling water flux in forward osmosis: implications for improved membrane design. AICHE J., 53, 1736.

McCutcheon, Jeffrey R., McGinnis R.L. & Elimelech M. (2006). Desalination by ammonia–carbon dioxide forward osmosis: Influence of draw and feed solution concentrations on process performance. Journal of Membrane Science, 278, 114–123.

McCutcheon, Jeffrey R.; McGinnis, R. L.; Elimelech, M.A novel ammonia–carbon dioxide forward (direct) osmosis desalination process Desalination 2005, 174 (1) 1– 11

McGinnis, R. L.; McCutcheon, J. R.; Elimelech, M.A novel ammonia–carbon dioxide osmotic heat engine for power generation J. Membr. Sci. 2007, 305 (1–2) 13– 19

McGinnis R.L. Osmotic desalination process, US Patent 6,391,205 B1 (2002).

McKelvey, S. A.; Koros, W. J.Phase separation, vitrification, and the manifestation of macrovoids in polymeric asymmetric membranes J. Membr. Sci. 1996, 112 (1) 29–39

Mehta, A.; Zydney, A. L.Permeability and selectivity analysis for ultrafiltration membranesJ. Membr. Sci. 2005, 249 (1–2) 245– 249

Mehta, G. D.; Loeb, S.Internal polarization in the porous substructure of a semipermeable membrane under pressure-retarded osmosis J. Membr. Sci. 1978, 4 (2) 261–265

Mi, Baoxia, Elimelech, Menachem. (15 July 2008). "Chemical and Physical Aspects of Organic Fouling of Forward Osmosis Membranes". Journal of Membrane Science, Volume 320, Issues 1-2, Pages 292-302.

Mi, Baoxia, Elimelech, Menachem. (15 February 2010). "Organic Fouling of Forward Osmosis Membranes: Fouling Reversibility and Cleaning

Michael, Brownell. Gas Well Drilling and Development Marcellus Shale. New York: Susquehanna River Basin Commission, 2008

Michael Godec,: "Economics of Unconventional Gas" OGJ Unconventional Gas Article #5, 2009

Modern Shale Gas Development in the United States: A Primer". (April 2009). U.S. Department of Energy, Office of Fossil Energy, National Energy Technology

Mulder, M. Basic Principles of Membrane Technology, 2nd ed.; Kluwer Academic:Dordrecht, 1996; p 564.

Mulder, M. H. V.; Hendrikman, J. O.; Wijmans, J. G.; Smolders, C. A. ARationale for the preparation of asymmetric pervaporation membranes J. Appl. Polym. Sci. 1985, 30 (7)2805– 2820

Nemeth E. Julia, Innovative system designs to optimize performance of ultra-low pressure reverse osmosis membranes, Desalination, Volume 118, Issues 1-3, Conference Membranes in Drinking and Industrial Water Production, 20 September 1998, Pages 63-71.

Ng H.Y., Tang W. and Wong W.S., Performance of forward (direct) osmosis process; membrane structure and transport phenomenon, Environ. Sci. Technol. 40 (2006), pp. 2408–2413.

Niemi, H., & Palosaari, S. (1993). Calculation of permeate flux and rejection in simulation of ultrafiltration and reverse osmosis processes. Journal of Membrane Science , 84 (1-2), 123-137.

Paktinat J., Pinkgouse J.A., and Fontaine J. “Investigation of Methods To Improve Utica Shale Hydraulic Fracturing in the Appalachian Basin,” SPE 111063, 2007.

Paktinat J., Pinkgouse J.A., Stoner W.P., Williams C., and Carder G.A. “Case Histories: Post-Frac Fluid Recovery Improvements of Appalachian Basin Gas Reservoirs,” SPE 97365, 2005.

Palisch T., Vincent M., and Handren P., “Sliwater Fracturing - Food for Thought,” SPE 115766, 2008.

Penny, G. and J.T. Pursely. “The Application of Microemulsion Additives in Drilling and Stimulation Result in Enhanced Gas Production” SPE 94274, 2005.

Percival, Pamela. (May, 2009). “Oil and Gas Wastewater Recycling Continues to Increase, But is Affected by Current Economy”. Fort Worth Basin Oil & GasMagazine.

Petersen, R. J.Composite reverse-osmosis and nanofiltration membranes J. Membr. Sci.1993, 83 (1) 81– 150

Phillip, W. A.; Yong, J. S.; Elimelech, M.Reverse draw solute permeation in forward osmosis: Modeling and experiments Environ. Sci. Technol. 2010, 44 (13) 5170– 5176

Pletcher, J. Drillers access mile ‑ deep gas deposits in what may be new 'gold rush'. s.l. : Herald Standard, May 19, 2008.

Post, J. W. (2009). Blue Energy: Electricity production from salinity gradients by reverse electrodialysis. Wageningen University, Socio-Economic and Natural Sciences of the Environment.

Post, J. W., Veerman, J., Hamelers, H., Euverink, G., Metz, S., Nymeijer, D., et al. (2007). Salinity-gradient power: Evaluation of pressure-retarded osmosis and reverse electrodialysis. Journal of Membrane Science , 288, 218-230.

Piquepaile, Roland. ZDNet. [Online] Jan. 20th, 2008.http://blogs.zdnet.com/emergingtech/?p=809.

Performance of Forward Osmosis Membranes on Activated Sludge”. Journal of Membrane Science, Volume 319, Issues 1-2, Pages 158-168.

Protection Agency, Office of Transportation and Air Quality, Publication EPA420-F-05-001, Page 2

R.S., N. (1974). Water salination - source of energy. Science , 186 (4161), 350-352.

Robert L. McGinnis, Jeffrey R. McCutcheon, Menachem Elimelech, A novel ammonia-carbon dioxide osmotic heat engine for power generation, Journal of Membrane Science, Volume 305, Issues 1-2, 15 November 2007, Pages 13-19

Robeson, L.M. Correlation of separation factor versus permeability for polymeric membranes J. Membr. Sci. 1991, 62 (2) 165– 185

Rong Wang, Lei Shi, Chuyang Y. Tang, Shuren Chou, Changquan Qiu, Anthony G. Fane, Characterization of novel forward osmosis hollow fiber membranes, Journal of Membrane Science, Volume 355, Issues 1-2, 15 June 2010, Pages 158-167

Russell T. Ewy and E. Keith Morton, Chevron Energy Technology Company "Wellbore Stability Performance of Water Base Mud Additives" SPE 116139-MS 2008.

Rieb, B., Allen, S., and Hogan, J. (March 2009). "The Benefits of Recycle-Produced Water for Fracs". E & P.

Sada, D. Joshi. Horizontal Well Technology. 1991.

Sairam M., et al., Method for the preparation of cellulose acetate flat sheet composite membranes for forward osmosis—Desalination using MgSO4 draw solution, Desalination (2011).

Sandra RodrÃguez, ECOPETROL, and Ricardo Arenas, Humberto Sierra, Carlos Montoya, and Mario Serrano, SPE, Halliburton "Breaking Old Paradigms With the Use of High-Performance Water-Based Mud Systems "SPE 138809-MS 2010.

Schweitzer, R.: "The Role of Economics on Well and Fracture Design Completions of Marcellus Shale Wells" paper SPE 125975-MS, 2009

Shuren Chou, Lei Shi, Rong Wang, Chuyang Y. Tang, Changquan Qiu, Anthony G. Fane, Characteristics and potential applications of a novel forward osmosis hollow fiber membrane, Desalination, Volume 261, Issue 3, Special Issue in memory of Sidney Loeb (1917-2008), 31 October 2010, Pages 365-372

Skilhagen, S. E.Osmotic power—A new, renewable energy source Desalination Water Treat. 2010, 15 (1–3) 271– 278

Smolders, C. A.; Reuvers, A. J.; Boom, R. M.; Wienk, I. M.Microstructures in phase-inversion membranes. 1. Formation of macrovoids J. Membr. Sci. 1992, 73 (2–3) 259–275

Stache K., Apparatus for transforming seawater, brackish water, polluted water or the like into a nutrious drink by means of osmosis, US Patent 4,879,030 (1989).

State, EMV. Pennsylvania. Driver and Vehicle Services. Pennsylvania Department of Transportation. [Online] 02 2009. http://www.dmv.state.pa.us/pdotforms/stats/Pennsylvania%20Motor%20Vehicle%20Registrations.pdf.

Stutts, K. J.; Ferritto, M. S.; Mickols, W. E.Treatment of composite polyamide membrane to improve performance. Patent 5876602, 1999.

Tang C.Y., kwon Y.N. and Leckie J.O., Probing the nano- and micro-scales of reverse osmosis membranes—a comprehensive characterization of physiochemical properties of uncoated and coated membranes by XPS, TEM, ATR-FTIR, and streaming potential measurements, J. Membr. Sci. 287 (2007), p. 146

Thorsen, T.; Holt, T. The potential for power production from salinity gradients by pressure retarded osmosis J. Membr. Sci. 2009, 335 (1–2) 103– 110

Tiraferri, A.; Yip, N. Y.; Phillip, W. A.; Schiffman, J. D.; Elimelech, M.Relating performance of thin-film composite forward osmosis membranes to support layer formation and structure J. Membr. Sci. 2011, 367 (1–2) 340– 352

Tomislav Soric, INA Naftaplin and Pavel Marinescu, Silicate-Based Drilling Fluids Deliver Optimum Shale Inhibition and Wellbore Stability, IADC/SPE 87133. MARCH 2004.

Trypuc M. and Kiełkowska U., Solubility in the NH4HCO3 + NaHCO3 + H2O system, J. Chem. Eng. Data 43 (1998), p. 210-204.

Tzahi Y. Cath, Childress A.E. and Elimelech M., Forward osmosis: principles, applications, and recent developments, J. Membr. Sci. 281 (2006), p. 70.

Tzahi Y. Cath, Sherwin Gormly, Edward G. Beaudry, Michael T. Flynn, V. Dean Adams, Amy E. Childress, Membrane contactor processes for wastewater reclamation in space: Part I. Direct osmotic concentration as pretreatment for reverse osmosis, Journal of Membrane Science, Volume 257, Issues 1-2, Membrane Contactors, 15 July 2005, Pages 85-98

U.S. Department of the Interior | U.S. Geological Survey. (29 March 2010).

Van de Witte, P.; Dijkstra, P. J.; van den Berg, J. W. A.; Feijen, J.Phase separation processes in polymer solutions in relation to membrane formation J. Membr. Sci. 1996,117 (1–2) 1– 31

Veerman, J. (2010). Reverse Electrodialysis design and optimization, modeling and experimentation.

Veil, J.A., Puder, M.G., Elcock, D., and Redweik, R.J., "A White Paper Describing Produced Water from Production of Crude Oil, Natural Gas, and Coal Bed Methane," ANL Report under DOE (NETL) Contract W-31-109-Eng-38 (2004).

Vos, K. D.; Burris, F. O.; Riley, R. L.Kinetic study of hydrolysis of cellulose acetate in pH range of 2–10 J. Appl. Polym. Sci. 1966, 10 (5) 825– 832

Wanling Tang, How Yong Ng, Concentration of brine by forward osmosis: Performance and influence of membrane structure, Desalination, Volume 224, Issues 1-3, Issues 1 and 2: 11th Aachener Membran Kolloquium, 28-29 March 2007, Aachen, Germany - Issue 3: Aqua 2006, 2nd International Conference on Water Science and Ttechnology - Integrated Management of Water Resources, November 2006, Athens, Greece, 15 April 2008, Pages 143-153

Wick, G., & Schmitt, W. (1977). Prospects for renewable energy from sea. Marine Technology Society Journal , 11 (5-6), 16-21.

Wijmans, J. G.; Kant, J.; Mulder, M. H. V.; Smolders, C. A.Phase-separation phenomena in solutions of polysulfone in mixtures of a solvent and a nonsolvent—Relationship with membrane formation Polymer 1985, 26 (10) 1539– 1545

Without Chemical Reagents". Journal of Membrane Science, Volume 348, Issues 1-2, Pages 337-345.

Yanagishita, H.; Nakane, T.; Yoshitome, H.Selection criteria for solvent and gelation medium in the phase inversion process J. Membr. Sci. 1994, 89 (3) 215– 221

Yip, N. Y., Tiraferri, A., Phillip, W. A., Schiffman, J. D., & Elimelech, M. (2010, April 21). High Performance Thin-Film Composite Forward Osmosis Membrane. 44 (10), pp. 3812-3818.

Yip, N. Y., Tiraferri, A., Phillip, W. A., Schiffman, J. D., Hoover, L. A., Kim, Y. C., et al. (2011, April 14). Thin-Film Composite Pressure Retarded Osmosis Membranes for Sustainable Power Generation from Salinity Gradients. Environmental Science & technology , A-J.

Yanagishita, H.; Nakane, T.; Yoshitome, H. Selection criteria for solvent and gelation medium in the phase inversion process J. Membr. Sci. 1994, 89 (3) 215– 221

Xu Y., Peng X., Tang C.Y., Fu Q.S. and Nie S., Effect of draw solution concentration and operating conditions on forward osmosis and pressure retarded osmosis performance in a spiral wound module, J. Membr. Sci. 348 (2010), pp. 298–309.