

**ANALYZING AQUEOUS SOLUTION IMBIBITION INTO SHALE AND
THE EFFECTS OF OPTIMIZING CRITICAL CHEMICAL ADDITIVES**

An Undergraduate Research Scholars Thesis

by

MATTHEW WIESE, SAMMAZO PLAMIN and MAHA QURESHI

Submitted to Honors and Undergraduate Research
Texas A&M University
in partial fulfillment of the requirements for the designation as

UNDERGRADUATE RESEARCH SCHOLAR

Approved by
Research Advisor:

Dr. Robert Lane

May 2014

Major: Petroleum Engineering

TABLE OF CONTENTS

	Page
ABSTRACT.....	1
ACKNOWLEDGEMENTS.....	2
CHAPTER	
I. INTRODUCTION.....	3
Interactions between shale and water.....	3
II. METHOD.....	6
Project objectives.....	6
Experimental procedure.....	7
III. BARNETT SHALE.....	11
Tests with Barnett shale and multiple additives.....	11
IV. CURRENT AND FUTURE WORK.....	15
Shale comparison and continued additive evaluation.....	15
V. CONCLUSIONS.....	19
Accomplishments and determinations from current data sets.....	19
REFERENCES.....	21
APPENDIX A.....	22

ABSTRACT

Analyzing Aqueous Solution Imbibition into Shale and the Effects of Optimizing Critical Chemical Additives. (May 2014)

Matthew Wiese, Sammazo Plamin and Maha Qureshi
Department of Petroleum Engineering
Texas A&M University

Research Advisor: Dr. Robert Lane
Department of Petroleum Engineering

Two methods of hydraulic fracturing most widely utilized on unconventional shale gas and oil reservoirs are “gelled fracturing” and “slick-water fracturing”. Both methods utilize up to several million gallons of water-based fluid per well in a series of stages pumped into direct contact with subsurface rock. Shale can absorb water through a process called capillary imbibition when the two come in contact. Additionally, since a common component of shale rock is clay, water may intercalate into clay structures in the shale causing them to swell and/or break off from a fracture face, potentially plugging the desired fluid conductivity of the created fractures. Currently the extent of water-based fluid imbibition and intercalation in major shale plays is not known; however it is not uncommon for only 15 – 30% of pumped fracture fluid to return to the surface during production from a well. How these issues affect fracture conductivity and thus production from unconventional oil and natural gas wells is poorly understood. Additionally, it is not known how various fracturing fluid additives affect the magnitude of water-based fluid imbibition and/or intercalation into shale. The work our group is conducting seeks to quantify the effects of pertinent chemical additives on fluid imbibition and intercalation into shale samples. We do this with the hope that we will eventually be able to determine how natural phenomena and additives affect long term resource production from unconventional oil and natural gas wells.

ACKNOWLEDGEMENTS

Our group of undergraduates would like to thank Dr. Robert Lane for giving us the opportunity to develop this project. Without his guidance, insight and support we would have never been able to complete the work outlined in this thesis. Additionally, we would like to thank all our industry partners for their support of this project from the beginning and their continued interest in our results.

CHAPTER I

INTRODUCTION

Interactions between shale and water

The abundance of natural gas that has recently begun entering the US market has created a stir throughout the energy industry. The reason for the recent increased supply has been the development of upstream operations that give oil and gas operators the ability to produce resources from previously inaccessible reservoirs made up of a rock called shale.

The two primary technologies that have made exploitation of shale reservoirs economic are horizontal drilling and hydraulic fracturing. When accessing shale resources, wellbores are drilled vertically to near the top of the target interval, then re-directed to follow horizontally along the length of rock formations underground. Hydraulic fracturing techniques are then utilized to provide flow pathways for previously untapped reserves of petroleum. Two primary hydraulic fracturing methods, singly or in combination, are used on unconventional oil and gas wells. These are “gelled” fracturing and “slick-water” fracturing. Fracturing is initiated by pumping enormous volumes of water into the subsurface at high pressures. This cracks reservoir rock and creates flow paths known as fractures that are fractions of an inch wide and hundreds of feet long and high. Propping materials carried in the fracture fluid prevent the created fractures from completely closing after pumping ceases. After fracturing petroleum liquids and gases that were previously trapped in rock can migrate through the propped fractures to a well where they can be produced.^[1]

Through previous research primarily in drilling applications it is widely documented that water based fluid interacts with shale in two main ways.^[2] First, because much of the shale pore structure is water wet (the mineral surfaces are polar or ionic) water is absorbed into its pore matrix when the two come in contact through a process called capillary imbibition. Second, if layered clays are present in the shale, water can intercalate into clay structures causing the clay structures to swell and lose structural integrity. During drilling operations companies have historically attempted to limit imbibition and intercalation as much as possible using chemical additives to preserve wellbore integrity. However, to produce gas from shale wells industry operators are pumping large volumes of water into direct contact with subsurface formations, without using sophisticated shale stabilization technology. Considering the well documented fact that interactions between shale and water based fluid occur, it is highly likely that imbibition and intercalation affect induced fractures, potentially having an adverse impact on natural gas or liquids production and estimated ultimate recovery from unconventional wells.

Field observations indicate that interaction between shale reservoirs and fracturing fluid is definitely occurring. The amount of fracture fluid returned to the surface when wells are brought on production, known as load recoveries, are low industry-wide; recovery of only 15 – 30% of the total fluid volumes pumped is typical.^[3, 4] Thus massive volumes of water are now being forced into rock formations that are known to react in possibly adverse ways when the two come in contact. Water-based fluid may be drawn into the reservoir rock matrix through capillary forces and/or clay intercalation or it may be trapped in un-propped fractures created during fracturing where it remains due to limited available permeability pathways as these fractures close when pressure is no longer applied to the formation. What is yet to be determined is the

extent of each of these processes and their impact on water losses and fracture performance impairment.

There are currently two primary schools of thought related to fracturing fluid imbibition and intercalation in shale-gas reservoirs. Some believe that preventing or minimizing fluid absorption by subsurface shale is the proper course of action. These operators believe that returning the most fracturing fluid possible minimizes fluid volumes absorbed by shale formations and decreases any productivity damage from the water used in a fracturing operation. A decrease in fluid absorption by subsurface rock post-fracturing could be a significant effort in the future that delivers more production with less water loss from the hydrologic cycle.^[5] While decreased absorption appeals to a more environmentally friendly viewpoint, the impact of increased water return on long-term natural gas production from a well is not presently known.

Others hypothesize that water-based fracturing fluid is not causing any harm to productivity when it is absorbed by shale in the subsurface. These operators have now begun attempting to increase the amount of fluid absorbed by shale after hydraulic fracturing operations.^[6] By doing so, they can decrease water disposal costs and theoretically increase the initial production of natural gas from their wells by removing water that could lead to liquid loading of a well. This being said, a decrease in returned fluid also signifies a loss of surface water to the subsurface and could potentially harm long term production. These general viewpoints have provided the basis for a large amount of industry and academic research currently being conducted.

CHAPTER II

METHOD

Project objectives

Based on the criteria outlined in chapter one, we have determined primary and supplementary objectives in order to highlight the direction for our work.

Our plan includes development of a method for testing aqueous solution imbibition and intercalation into shale in order to determine impacts on load flowback. This can be used to test effects of various potential additives that could minimize load water losses to source rock formations and improve water returns from hydraulic fracturing processes. We believe limiting imbibition could have a positive effect on production flows by minimizing formation and/or propped fracture blockages; helping to answer the question of where water goes when it is injected during fracturing; and lessen the amount of water that is being removed from the surface hydrologic cycle. Objectives supportive of that end are included in the bulleted list below.

- Determine the rate of deionized water imbibition into shale samples from different plays of interest.
 - Shale outcrop samples currently being tested:
 - Barnett
 - Marcellus
 - Eagle Ford
 - Cylindrical Core Sample Dimensions:

- 1.5” Diameter
 - 1.0” Length
- Identify chemical additives that have the potential to affect water-rock interactions through a literature review or by using accepted industry conventions.
 - Chemicals presently identified for testing:
 - Potassium Chloride
 - Dodecylbenzenesulfonic Acid (Anionic Surfactant)
 - Dodecyltrimethyl – Ammonium Bromide (Cationic Surfactant)
 - Arquad 2NT – 32EUN (Oil Wetting Surfactant)
 - Proprietary chemical from AkzoNobel
 - Surface Modified Silica Nanoparticles (5 nm)
 - Proprietary material from 3M
 - Offered with varying degrees of surface modification
 - Three levels of modification currently available for testing
 - Unmodified Silica Nanoparticles (5nm)

Experimental procedure

To begin we developed have developed a way to test imbibition and intercalation under ambient laboratory conditions. The experimental procedure we have developed in conjunction with our advisor to complete our work is included the bulleted listed below.

- 1) Dry cylindrical shale core plugs (1.5” diameter, 1.0” length) in a drying oven at 250 degrees Fahrenheit for 24 hours to remove residual water.

- 2) Weigh cores after drying using an analytical balance and record their mass.
- 3) Prepare deionized water or the desired solution with the correct concentration of chemical additive.
 - a. Additive concentrations are based on accepted industry convention or determined from literature review. Experimental results are then interpreted and concentrations are adjusted as necessary.
 - b. Currently Tested Chemicals and Concentrations:
 - i. Potassium Chloride (KCl): 4 wt. % and 6 wt. %
 - ii. Dodecylbenzenesulfonic Acid (Anionic Surfactant): 0.1 wt. %
 - iii. Dodecyltrimethyl – Ammonium Bromide (Cationic Surfactant): 0.1 wt. %
 - iv. Arquad 2NT – 32EUN (Oil Wetting Surfactant): 0.1 wt. %
 - v. Unmodified and Three Levels of Surface Modified Silica Nanoparticles (5nm): 2 wt. % and 0.5 wt. %
 - c. Use 200 mL of deionized water when preparing solutions or completing experiments with water alone.
- 4) Reweigh the core right before starting an experimental trial to determine how much water vapor from the air has been absorbed
- 5) Wrap the side and top of the core with Teflon tape, leaving the bottom open to contact the solution of interest. This is done to decrease the amount of fluid evaporated from sample pore spaces throughout the trial and to minimize the volumes of fluid lost when it imbibes out the top and sides of the sample.
- 6) Attach a hanging apparatus made of string and a cable tie to the sample.

- 7) In a purpose-built chamber that minimizes air movement and solution evaporation, hang the core from the bottom of an elevated balance using a weighing hook and position the prepared solution on a laboratory scissors jack below the hanging shale sample. See **Figure 1** in **Appendix A** for an example of an experiment in progress.
- 8) Raise the beaker using the jack until the surface of the solution comes into contact with the uncovered face of the shale core.
- 9) As soon as the surface of the solution reaches the bottom of the core start a data collection program to record sample weight over time.
- 10) A data collection program is set to record the weight of the sample every second for the first five minutes. This is done to get a better snapshot of how the sample's mass is affected right as it comes in contact with the water.
- 11) After five minutes, pause the experiment and change the settings on the program so that it records sample mass every minute for the remaining.
- 12) Close the chamber door to prevent fluid evaporation and other interference that could cause skewed mass readings.
- 13) Resume the data collection program.
- 14) Leave to sit for the enough time to allow the imbibition rate to stabilize (12-24 hours) while the mass is periodically recorded on an Excel spreadsheet.
- 15) Return, lower the beaker of solution and remove the core after the desired amount of time have passed.
- 16) Remove Teflon wrapping from the core.
- 17) Re-weigh and record the new mass of the core for reference.

- 18) Return the core to the oven and dry for 24 hours at 250 degree Fahrenheit to determine if it returns to its original mass.
- 19) Plot core sample mass vs. time to determine the magnitude of imbibition and intercalation of the fluid.
- 20) Use a linear trend line to analyze data and determine how fluid additives effect fluid uptake rate by each sample based on comparison to trials conducted with pure water.
- 21) Report findings so that promising candidate fluid additives can be used in further investigations.

CHAPTER III

BARNETT SHALE

Tests with Barnett shale and multiple additives

Upon developing our methodology and acquiring the necessary materials we began testing the magnitude and rate of imbibition for pure, deionized water into Barnett shale samples. Early experiments indicated that a twenty four hour time window for each trial was sufficient. A one day trial time allows for a reasonable amount of experiments to be completed in a given amount of time while still providing adequate data from each experiment. All the following data is the result of experiments on Barnett shale samples.

Data from our first group of experiments using deionized water as a test fluid are displayed in **Figure 2 in Appendix A. Figure 2** indicates that results from nearly every trial using pure water show a relatively constant rate of sample mass increase over the course of each experiment and a final mass change of between 1.8 g and 2.6 g. Also, in nearly every case a positive mass change is seen at close to 3 hours. A surprising trend is that in all cases except one, sample mass decreased for close to an hour before it began to increase, returning to its original mass after close to 3 hours of exposure. This initial mass decrease is a phenomenon we have observed in varying magnitudes after nearly every experiment we have conducted where the sample only has one exposed face in contact with fluid. Some degree of sample mass decrease for the first hour of nearly every experiment has been present regardless of shale type or the presence of additives in solution. We are still attempting to determine the cause of the observed mass loss and anticipate

it is related to experimental design as opposed to an actual significant decrease in the bulk mass of each sample.

To date, we have completed experiments with 4.0 and 6.0 weight percent Potassium Chloride (KCl) solution, cationic surfactant, anionic surfactant, proprietary oil-wetting surfactant and two different concentrations of surface modified silica nanoparticles. Trials with results that were indicative of those seen for each additive are listed in **Table 1** in **Appendix A** for comparison. Imbibition rate was calculated using a trend line for each data set. Our control, deionized water, had a solution uptake rate of 0.116 g/hr.

Trial 10 was completed with a 4 percent weight Potassium Chloride (KCl) solution and yielded an uptake rate 0.027 g/hr less than pure deionized water. The observed decrease in imbibition rate was expected in KCl experiments because Potassium Chloride is already an accepted industry convention for clay stabilization in drilling fluid applications.^[6] Comparison of 4 and 6 percent weight KCl solution experiments indicates that a 2 percent increase in additive concentration only decreased imbibition rate by 0.001 g/hr. The small rate decrease observed indicates that increasing the concentration of KCl past a certain point could have a diminishing effect on imbibition inhibition in our application. Further tests at higher concentrations of KCl and smaller concentration intervals must be completed in the future to support or refute this assertion.

The initial focus of our additive research was three surfactants we identified for testing through literature review and recommendation. Currently, we have tested two surfactants that had

previously been used in a group of experiments related to shale fracture behavior.^[7] One of the surfactants is anionic and one is cationic. Also, we have tested a proprietary, oil-wetting surfactant manufactured by AkzoNobel. The anionic surfactant displayed a minimal decrease in imbibition rate (0.016 g/hr) relative to deionized water. Experiments with cationic and oil-wetting surfactants displayed small rate increases of 0.010 g/hr and 0.004 g/hr relative to water. None of the rate effects from any of the surfactants is considered substantial. Additionally, trials with oil-wetting surfactant required modification to our experimental method in order to achieve adequate additive dissolution. The addition of a magnetic stirrer was necessary to achieve sustained additive dissolution and could have possibly affected results.

Recently, we have identified nanoparticles as additives of interest due to current research on their application as imbibition inhibitors in drilling fluids.^[8] To date, we have tested surface modified silica nanoparticles (5 nanometers diameter) at concentrations of 0.5 and 2 percent weight on Barnett shale samples. Trial 25 in **Table 1** was completed with a 0.5 percent weight concentration and displays an imbibition rate much lower than the control. The nanoparticle induced rate decrease is also 0.016 g/hr lower than KCl which marks them as the only additives that have been able to decrease imbibition rate more than the test industry convention. The relatively large decrease in uptake rate induced by nanoparticles indicates that these additives might be a viable way to decrease fluid uptake by shale.

Additionally, further results have indicated that the any imbibition impeding effects nanoparticles have could be heavily dependent on additive concentration and level of surface modification. When nanoparticle concentration was increased from 0.5 to 2.0 percent weight, the

rate of imbibition increased from 0.073 g/hr to 0.087 g/hr. The observed rate increase was contrary to what was expected and the cause is currently unclear. Iterative experimentation with nanoparticles at different concentrations and levels of surface modification will allow us to examine observations about this group of additives further.

One final observation that can be made based on our preliminary data is related to the drying of each Barnett sample. Each sample we use is dried before and after testing. In every case, the mass of a shale sample at the beginning of a trial is more than it is right after it is pulled from the oven. This can be attributed to samples absorbing residual water from the air between when all the samples are first dried and when they are individually selected for experimentation. Each sample is dried individually after experimentation to determine if it returns to its original mass. In every case where a sample has been dried after an experiment its mass has been less than it was right after the first cycle of drying. This indicates that some form of mass loss is occurring during each trial possibly due to the dissolution of one or more compounds in the rock. We have begun saving water samples from each trial for testing in the future shed light on this observation.

CHAPTER IV

CURRENT AND FUTURE WORK

Barnett and Marcellus shale comparison

Immediately after finishing our original set of experiments with Barnett shale we moved to complete the same battery of tests on Marcellus shale cores for comparison to one another. Initially, we set about changing any steps of the experiment there was trouble with. Also, graph and chart formatting began being consistently updated at the beginning of each experiment to help ensure the consistency of results.

On the topic of data collection, we began displaying our results in a way that reflects the average distance an amount of fluid has imbibed into a rock and not just the rate at which that fluid is absorbed. While this is simply another way of looking at the same results, it works as an effective form of data normalization, making results comparison from experiments with different types of shale more accurate. Shale is, by its nature, extremely heterogeneous. Shale samples from different geologic formations and even different parts of the same formation can have variable petrophysical properties that affect a number of the rock's hydrocarbon bearing characteristics. Since our calculations for imbibition length include porosity and core dimensions we believe distance, as opposed to rate, will offer a more consistent representation of the data we have and will be collecting. By studying the distance an imbibition front moves into a rock sample we can begin to establish a basis for the fate of fracturing fluid as it moves from the fracture to the matrix of a reservoir. Also, knowing imbibition distance allows for more accurate

analysis when comparing results from different trials. In the future, it is our group's hope that a law or empirical representation can be derived that can universally describe average imbibition distance as a function of time and rock/chemical properties. By using length of imbibition in this way, it would be theoretically possible to determine the extent of fluid imbibition in previously fractured wells using information about the fracturing fluid and properties of a shale formation in a specific area.^[7] Calculations could then be used to help determine total imbibition and its effect on petroleum production. **Figure 3** in **Appendix A** shows how the final length of imbibition for each trial was calculated.

Also, it was at this point that we chose to modify our experimental design further. We no longer just touch the face of the shale sample to the surface of the fluid we are testing. Now, one quarter inch of the Teflon wrapped sample is submerged with the rest remaining out of the solution. We have determined that submerging the sample face in this way removes the initial mass decrease we had consistently observed in previous trials believed to result from displaced air that was trapped under the face of the shale. Also, in an effort to complete more experiments, we have adopted a twelve hour trial period. Twelve hours allows for twice as many experiments to be completed while still allowing for imbibition rate stabilization. These two modifications have allowed for us to collect results with more speed and accuracy.

Twelve hour trials have now been repeated with Barnett shale and compared to our previous twenty four hour tests. Results from these trials are similar but not exactly the same because of the modification to how far we dip our samples in the solution being tested. As a result, we are

now using our modified experimental method to re-do trials with Barnett shale and our most promising additives from previous experiments. Currently, we are also testing Marcellus shale for comparison to Barnett. Additionally, we are completing a more comprehensive analysis with our most promising additives to better determine their range of imbibition inhibition effectiveness. Preliminary results from these trials are listed in **Table 2** in **Appendix A**.

Table 2 shows the effect of low coverage nanoparticles and Potassium Chloride on imbibition rate in Barnett and Marcellus shale samples using our modified experimental method. Overall, the Marcellus shale cores show a noticeably lower imbibition rate compared to Barnett. We believe the reason for this noticeable decrease is the difference in geologic and petrophysical properties in the two samples. As previously noted, shale is extremely heterogeneous from formation to formation. Some of this heterogeneity is highlighted in **Table 3** and **Table 4** in **Appendix A** which list common mineralogical compositions and porosities for Barnett and Marcellus shale in comparison with one another.

The difference in imbibition rates between the two formations seen in our experiment was expected and is the reason we've cited a need to test rock samples from a multitude of different shale plays. We believe that the reason for this particular rate discrepancy stems from a higher presence of what are called "swelling" clays in Barnett. These clays imbibe water very quickly and swell, creating structural integrity issues in the rock when drilling through shale using water based mud. That being said these, clays direct effect on petroleum production from unconventional shale gas and oil resources still currently remains to be seen and will hopefully come to light as industry research moves forward.

For experiments in the near future, we have obtained four different types of nanoparticles (unmodified, low-coverage, mid-coverage and high coverage) and plan on completing an iterative evaluation of each different particle's effect on imbibition. We do this with the hope that we can identify the nanoparticle that melds noticeable imbibition inhibition characteristics with potential cost effectiveness.

CHAPTER V

CONCLUSIONS

Accomplishments and determinations from current data sets

- Developed an experimental methodology that is effective at determining the mass of fluid imbibed into a sample of shale after a given period of time under ambient conditions.
- A 12 hour trial window allows for a reasonable amount of experiments to be completed in a given amount of time while still providing adequate data for analysis.
- Deionized water imbibes into Barnett shale samples at a relatively constant rate under ambient conditions.
- The imbibition of water-based fluid might be due to two potential mechanisms: Capillary imbibition and clay intercalation/swelling.
- As expected, Potassium Chloride (KCl) decreases the uptake rate of water-based fluid into Barnett shale. KCl effectiveness as a shale stabilizer is believed to be due to the inhibition of clays which inhibits fluid uptake by clay intercalation.
- Equal increases of KCl concentration do not have equal impact on imbibition rate.
- Identified anionic, cationic and oil-wetting surfactants do not have a substantial effect on imbibition rate.
- Surface modified silica nanoparticles have shown to be more effective than KCl as uptake inhibitors at a concentration of 0.5 percent weight. We are not yet certain of its mechanism, but hypothesize that it inhibits capillary imbibition rather than clay intercalation.

- A 2.0 percent weight concentration of surface modified nanoparticles increased as opposed to decreased imbibition rate relative to a 0.5 percent weight concentration.
- Cores dried after each trial at the same temperature and for the same amount of time consistently record masses below their initial dry mass, indicating dissolution of minerals into the bulk fluid.
- Depth of imbibition into a shale sample as opposed to total mass gain offers an interesting representation of our data and could play a part in developing imbibition prediction models.
- Marcellus shale absorbs fluid at half the rate of Barnett which is believed to be a result of the presence of swelling clays in Barnett.

REFERENCES

1. King, G.E., SPE, Apache Corporation. 2012. Hydraulic Fracturing 101: What Every Representative, Environmentalist, Regulator, Reporter, Investor, University Researcher, Neighbor and Engineer Should Know About Estimating Frac Risk and Improving Frac Performance in Unconventional Gas and Oil Wells. Presented at the SPE Hydraulic Fracturing Technology Conference. SPE-152596-MS.
2. Civan, Faruk, SPE, University of Oklahoma. 2001. Water Sensitivity and Swelling Characteristics of Petroleum-Bearing Formations: Kinetics and Correlation. Presented at the SPE Production and Operations Symposium. SPE-67293-MS.
3. Rick Gdanski and Harold Walters, SPE, Halliburton. 2010. Impact of Fracture Conductivity and Matrix Relative Permeability on Load Recovery. Presented at the SPE Annual Technical Conference and Exhibition. SPE-133057-MS.
4. T.T. Palisch, SPE, CARBO Ceramics; M.C. Vincent, SPE, Insight Consulting; P.J. Handren, SPE, Denbury Resources. 2010. Slickwater Fracturing: Food for Thought. Presented at the SPE Annual Technical Conference and Exhibition. SPE-115766-MS.
5. Brannon, H.D., Daulton, D.J., Hudson, H.G. et al. 2012. The Quest to Exclusive Use of Environmentally Responsible Fracturing Products and Systems. Presented at the SPE Hydraulic Fracturing Technology Conference. SPE-152068-MS.
6. Penny, G.S., Dobkins, T.A., and Kuru, E. 2006. Field Study of Completion Fluids to Enhance Gas Production in the Barnett Shale. Presented at the SPE Gas Technology Symposium. SPE-100434-MS.
7. Makhanov, K., Dehghanpour, H., and Pursley, J.T. 2012. An Experimental Study of Spontaneous Imbibition in Horn River Shales. Presented at the SPE Canadian Unconventional Resources Conference. SPE-162650-MS.

APPENDIX A



Figure 1: Experimental setup including computer for collection, balance, chamber, scissors jack, and sample in contact with a solution of interest.

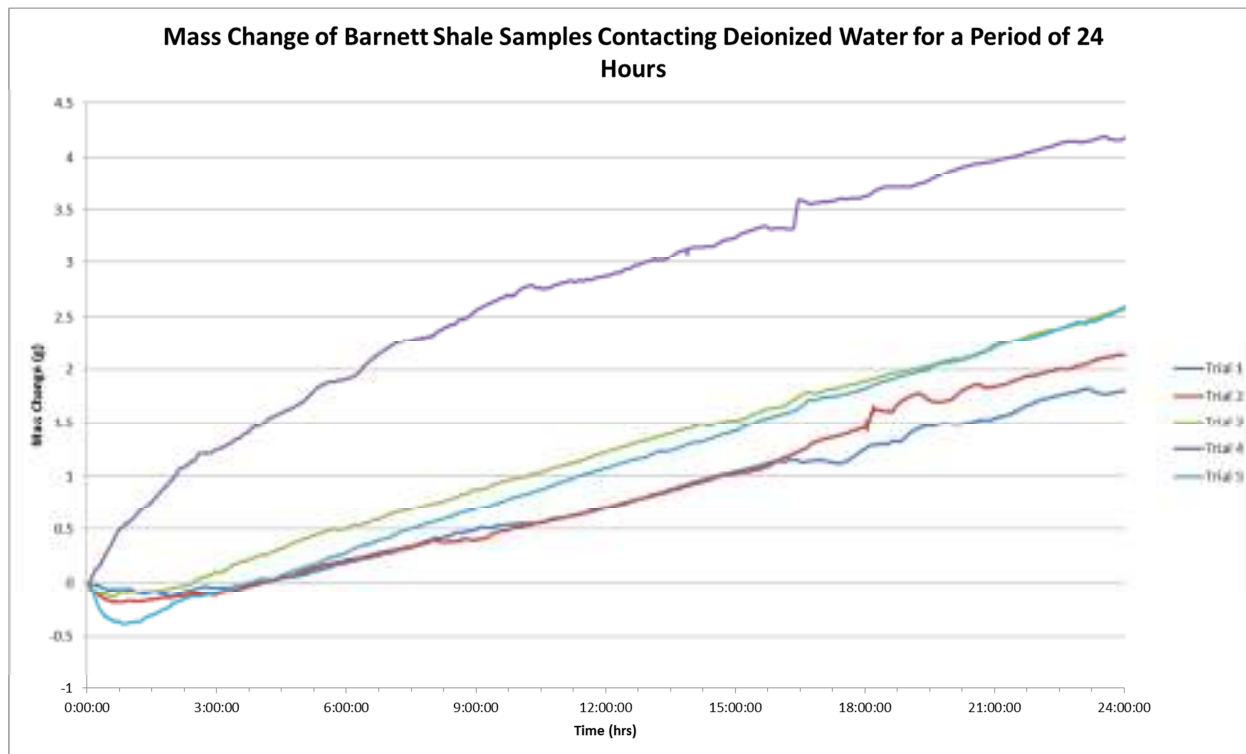


Figure 2: Mass change of cylindrical 1.5” diameter, 1.0” length Barnett shale cores contacting deionized water for a period of 24 hours.

<i>Composition of Imbibition Solution</i>	<i>Trial Number</i>	<i>Weight of Dried Core Sample Before Trial (g)</i>	<i>Rate of Solution Uptake (g/hr)</i>
Deionized Water, No Additives	3	54.814	0.116
4% wt. KCl	10	54.614	0.089
6% wt. KCl	44	58.140	0.088
0.1% wt. Anionic Surfactant	22	55.730	0.100
0.1% wt. Cationic Surfactant	13	55.631	0.126
0.1% wt. Oil-Wetting Surfactant	36 and 37	---	0.120
0.5% wt. Surface Modified Nanoparticles	25	54.510	0.073
2.0% wt. Surface Modified Nanoparticles	24	55.250	0.087

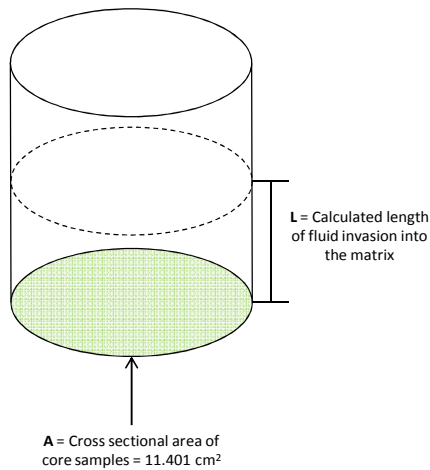
Table 1: Initial mass and rate of Solution uptake for Barnett shale samples in the presence of different chemical additives dissolved in deionized water.

Composition of Imbibition Solution	Marcellus Shale Rate of Solution Uptake (g/hr)	Barnett Shale Rate of Solution Uptake (g/hr)
Deionized Water, No Additives	0.26	0.54
4% wt. KCl	0.275	0.344
0.5% wt. Surface Modified Nanoparticles	0.234	0.383

Table 2: Rates of pure water and additive solution uptake for Barnett and Marcellus shale samples in comparison to one another

Length of Fluid Invasion into a Sample During Experimentation

- Δm = Mass change of the a sample over the course of a trial
- V_f = Volume of fluid imbibed into the sample during a trial
- ρ_f = Density of fluid being tested
- ϕ = Shale sample porosity (Barnett: ~7.00%)



$$V_f = L * A * \phi \quad \text{and} \quad V_f = \frac{\Delta m}{\rho_f}$$

therefore

$$\frac{\Delta m}{\rho_f} = L * A * \phi$$

and

$$L = \frac{\frac{\Delta m}{\rho_f}}{A * \phi}$$

Example Calculation: Freshwater Trial 1

$$L = \frac{(1.808g) \left(\frac{cc}{1.0g} \right)}{(11.401cm^2)(0.07)} = 2.265 \text{ cm}$$

Figure 3: How to turn observed rate (dSo/dL) into an implied average distance (L) away from a fracture face an imbibition front has traveled in an unconventional resource for a given value of time.

<i>Porosity, φ</i>	<i>Barnett Shale</i>	<i>Marcellus Shale</i>
	0.01 – 0.07	0.06 – 0.10

Table 3: Common Barnett and Marcellus shale porosity ranges

<i>Mineral</i>	<i>Barnett (%)</i>	<i>Marcellus (%)</i>
Quartz	35-50	10-60
Clays (primarily Illite)	10-50	10-35
Calcite (Dolomite, Siderite)	0-30	3-50
Feldspars	7	0-4
Pyrite	5	5-13
Phosphate (Gypsum)	Trace	Trace
Mica	0	0-30

Table 4: Typical Barnett and Marcellus shale mineralogy