FY 2020 1st Quarter Research Performance Progress Report

Project Title:	Basin-specific geochemistry to promote unconventional efficiency
Project Period:	10/01/18-9/30/21
Reporting Period:	10/1/19-12/31/19
Submission Date:	1/30/2020
Recipient:	SLAC National Accelerator Laboratory
Recipient DUNS #:	92-9824415
Address:	2575 Sand Hill Road, MS 69 Menlo Park, CA 94025
Website (if available)	www-ssrl.slac.stanford.edu
Award Number:	FWP 100211
Awarding Agency:	DOE/NETL
Principal Investigator:	Dr. John R. Bargar Senior Staff Scientist SLAC National Accelerator Laboratory Phone: 650-926-4949 Email: bargar@slac.stanford.edu
Co-Principal Investigators:	Dr. Adam Jew (SLAC National Accelerator Laboratory) Prof. Katharine Maher (Stanford University) Prof. Anthony Kovscek (Stanford University) Prof. Tiziana Vanorio (Stanford University) Prof. Gordon E. Brown, Jr. (Stanford University and SLAC National Accelerator Laboratory)
NETL Project Manager:	Dr. David Cercone

Table of Contents

Abbreviations

Ba = Barium
CT = Computed tomography
D = Darcy (unit)
Da = Damköhler number
DDI = Double de-ionized water
DM = Drilling mud
DO = Dissolved oxygen
DOE-FE = Department of Energy – Fossil Energy
EGSP = Eastern Gas Shales Project
Fe = Iron
FWP = Field work plan
FY = Fiscal Year
GTI = Gas Technology Institute
HCl = Hydrochloric acid
H_2SO_4 = Sulfuric acid
HFTS = Hydraulic fracturing test site
I.S. = Ionic strength
KM = Knowledge Management
Kr = Krypton
LBNL = Lawrence Berkeley National Laboratory
LLNL = Lawrence Livermore National Laboratory
MIP = Mercury intrusion porosimetry
MSEEL = Marcellus Shale Energy and Environment Laboratory
MXL I/S = Mixed-layer illite-smectite
NETL = National Energy Technology Laboratory
New Mexico BG = New Mexico Bureau of Geology
nm = nanometer (unit)
Pe = Péclet number
ppm = parts per million (unit)
S = Sulfur
SANS = Small angle neutron scattering
SEG = Society of Economic Geologists
SEM-EDS = Scanning electron microscopy-energy dispersion spectroscopy
SIE = Synthetic invert emulsion
SRA = Source rock analysis
SRV = Simulated rock volume
SSRL = Stanford Synchrotron Radiation Lightsource
Texas BEG = Texas Bureau of Economic Geology
TOC = Total organic carbon
μm = Micron (unit)
μ-XANES = Micro-X-ray absorption near-edge spectroscopy
URTeC = Unconventional Resources Technology Conference
XAS = X-ray absorption spectroscopy
XRF = X-ray fluorescence
XRD = X-ray diffraction

Motivation and Priority Research Needs

Fluid-shale reactions begin within seconds of injecting hydraulic fluids into unconventional reservoirs (**Figure 1**) and continue throughout shut-in and production, altering and weakening shale fracture surfaces and precipitating mineral scale. These secondary minerals frustrate attempts to recycle produced water, clog pore spaces, and inhibit escape of hydrocarbons from the resource-rich matrix. On the other hand, if we can understand and mitigate these processes, and we can provide this information to industry in the form of easily-implementable and incremental technical solutions, then we can help to improve safe and sustainable water reuse and enhance the efficiency of unconventional gas and oil production on a massive scale. Addressing these challenges strengthens U.S. energy, water, environmental, and economic security.[1] Here we focus on two strategic geochemistry-based research thrusts that will provide new knowledge in the following areas that can be used immediately by industry to improve hydrocarbon recovery: *(i)* mitigating scale precipitation in shale reservoirs; and *(ii)* improving extraction of hydrocarbons from tight matrix pore space (**Figure 2**). Additionally, we are developing a new acoustic monitoring approach that will eventually provide a way to nondestructively monitor shale alteration *in-situ* in the laboratory and subsurface.

Our industry collaborations and our previous DOE-FE-funded research have shown that unconventional oil and natural gas stimulation practices create conditions favorable for scale formation that permanently attenuate permeability and can reduce production.[2-5] Moreover, scale precipitation will intensify when operators inject reused saline water rich in dissolved solutes that can precipitate as secondary minerals, a practice that is increasing rapidly in major producing regions such as the Midland Basin. Chemical scale inhibitors designed to slow the rate of secondary mineral precipitation are largely ineffective in unconventional systems,[4, 6-8] because shut-in times far exceed the inhibition delay. Moreover, organic additives and natural organic compounds dramatically increase iron scale precipitation.[2] Thus, scale precipitation in unconventional systems remains largely unsolved and poorly understood. This project directly addresses these problems.

Basin-specific approach. This project adopts a basin-specific approach in which the fracture fluid compositions and injection schedules unique to a given shale play impact fluid-mineral and fluid-organic reactions occurring within a given basin. We will initially focus on two major unconventional basins, Marcellus (Appalachian) and Permian (West Texas), due to their economic importance and contrasting petrochemical factors (natural gas vs. oil wells) and differing complexity of fracture stimulation fluid compositions (< 10 additives for

Vision. We are on the verge of being able to use shale-fluid reaction geochemistry to solve targeted long-standing challenges in unconventional hydrocarbon production. Doing so will require that we can address three critical needs: (i) Developing predictive knowledge of geochemical reactions occurring in unconventional reservoirs when they are stimulated with water-based fluids; (ii) Identifying specific stimulation steps that enhance mineral scale formation and attenuate production, and then mitigating these problems by modifying stimulation practices through *incremental* changes that can be embraced by operators and producers; and (iii) Using this new knowledge to surgically promote the formation and connection of microscale porosity across shale-fluid interfaces to improve our ability to access hydrocarbons in matrix that are currently unreachable.

We envision that iterative experimentation, microscale observation, modeling, and development/application of novel approaches will allow us to use shale geochemistry to transform fracture stimulation. Further, by working with engaged industry partners, we will be able to provide technical solutions compatible with industry expertise.

Marcellus shale vs. >15 additives for Permian basin). Variations in pH and I.S. will be used to mimic different portions of the SRV, from those near the borehole to distal (**Figure 1**).

Goals

This project is conducting fundamental and applied R&D in four interrelated activities (Tasks 2.1, 2.2, 2.3, and Task 3, below) with the goals of: (i) identifying stimulation practices that promote mineral scale formation, and then, (ii) developing solutions to reduce or eliminate these problems by *incrementally* modifying stimulation practices in ways that can be embraced by operators and producers. Through interactions with industry collaborators and representatives, we are also (iii) promoting new best-practices based on geochemical insights from this DOE-FE-sponsored research.

The four interrelated tasks we are undertaking to achieve these goals are as follows:

Task 2.1. *Understanding the chemical parameters/reactions related to individual basins using a basin-specific approach with their respective shales and various injection recipes*

Task 2.2. *Mitigating mineral scale formation by developing new chemical formulations derived from experimental results and thermodynamic/kinetic modeling*

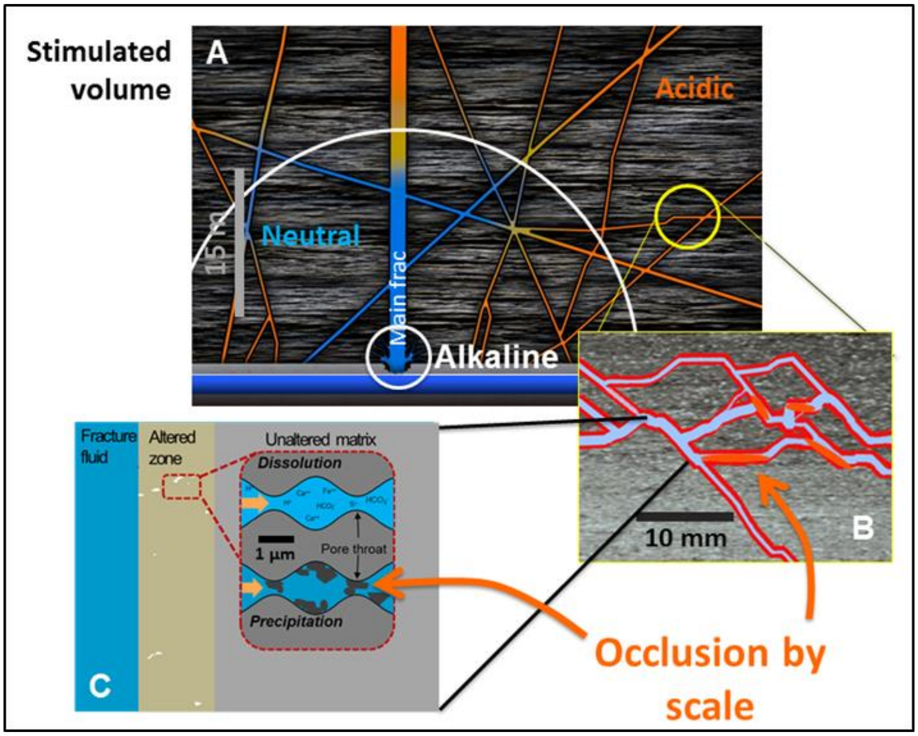


Figure 1. *Schematic of fracture system across length scales.* ***Panel A****: During stimulation, the highly acidic spearhead, which is the first injection step, is pushed out into the periphery of the fracture network where it attacks rock. In contrast, fluids near the well bore are expected to exhibit near-neutral or alkaline pHs (>7). Barium and other constituents leached from mud in the vicinity of the well bore by the acid spearhead also can be transported out into the fracture network, where they will precipitate as mineral scale, occluding porosity in fractures (****Panel B****) and in shale matrices (****Panel C****), ultimately attenuating permeability and production.* ***Panel C****: In order to be produced, gas and oil must flow through altered matrix abutting fractures. This important region of matrix is referred as the “altered zone”. It is altered by acid attack, which creates secondary porosity, and by scale precipitation, which reduces permeability.*

In these activities, we will create knowledge about scale precipitation from a basin-specific research program, and then apply it to mitigating this problem. Thermodynamic and kinetic modeling of the chemical reactions will be used to rapidly assess a large range of chemical parameters, reducing experimental time and waste.

Table 1. Synopsis of tasks

Task 1	Project management
Task 2	Scale prediction and mitigation in stimulated rock volume
2.1	**Prediction of mineral scaling in unconventional reservoirs**
2.1.1	Experimental task
2.1.2	Modeling task
2.2	**Mitigation of mineral scaling in unconventional reservoirs**
2.2.1	Modeling task
2.2.2	Experimental task
2.3	**Acoustic measurements on laboratory-reacted shales**
Task 3	**Manipulation of matrix accessibility**
3.1	Manipulate rates of mineral dissolution and precipitation
3.2	Growth and connectivity of secondary porosity
3.3	Modeling subtask
3.4	Predict and test optimal conditions

Task 2.3. *Developing a new in-situ method for monitoring secondary porosity and mineral scale generation in the field using acoustic methods*

Due to the high prevalence of mineral scale in shale systems, a new method is needed for determining secondary porosity generation and mineral scale formation in the field. This task will study changes in P- and S-wave velocities in shales reacted with fracture fluid and will identify pore-scale processes that result in alteration of rock permeability (mineral dissolution/scale formation). Laboratory experiments will evaluate the effectiveness of this method and will build a library of data that ultimately can be scaled up for field implementation.

Task 3. *Tailor the altered zone for optimal solution/gas transport through chemical manipulation of the system*

Fluid and gas exchange into/out of the shale matrix is strongly enhanced by secondary porosity created by acidification and pre-existing micro-fractures. Our recent results indicate that permeability of the altered zone (**Figure 1**) can be maintained and improved as long as mineral dissolution and scale precipitation occur concurrently in a controlled fashion. This task will perform research to determine how to tailor the altered zone to enhance dissolution/precipitation rates.

Overview of activities and results in FY 2020 Q1

Task 2.1.1. Prediction of mineral scaling in unconventional reservoirs. Experimental: Bone Spring (Permian Delaware Basin) and Marcellus (Marcellus Basin) shale experiments were conducted using their respective fracture stimulation fluid recipes. Pre-reaction imaging and characterization of Bone Spring and Marcellus shale samples and post-reaction solution analyses were completed and post-reaction solids analyses/imaging were initiated. It was determined that further experimentation using different base fluids (regional fresh water, fresh and brackish ground water, and cleaned produced water) is needed to gain a better understanding the impact of different source waters in conjunction with additives has on the different shale plays.

Task 2.1.2. Prediction of mineral scaling in unconventional reservoirs. Modeling: A manuscript on reactive transport modeling of shale matrix alterations was completed and submitted to *Energy and Fuels*.

Task 2.2.2. Mitigation of mineral scaling in unconventional reservoirs. Modeling: Our experience in Task 2.1.1 with Wolfcamp-fluid reactions showed that for the Permian Basin, Sr-bearing scale needs to be controlled downhole. This problem becomes even more of an issue as operators start using more Sr-rich

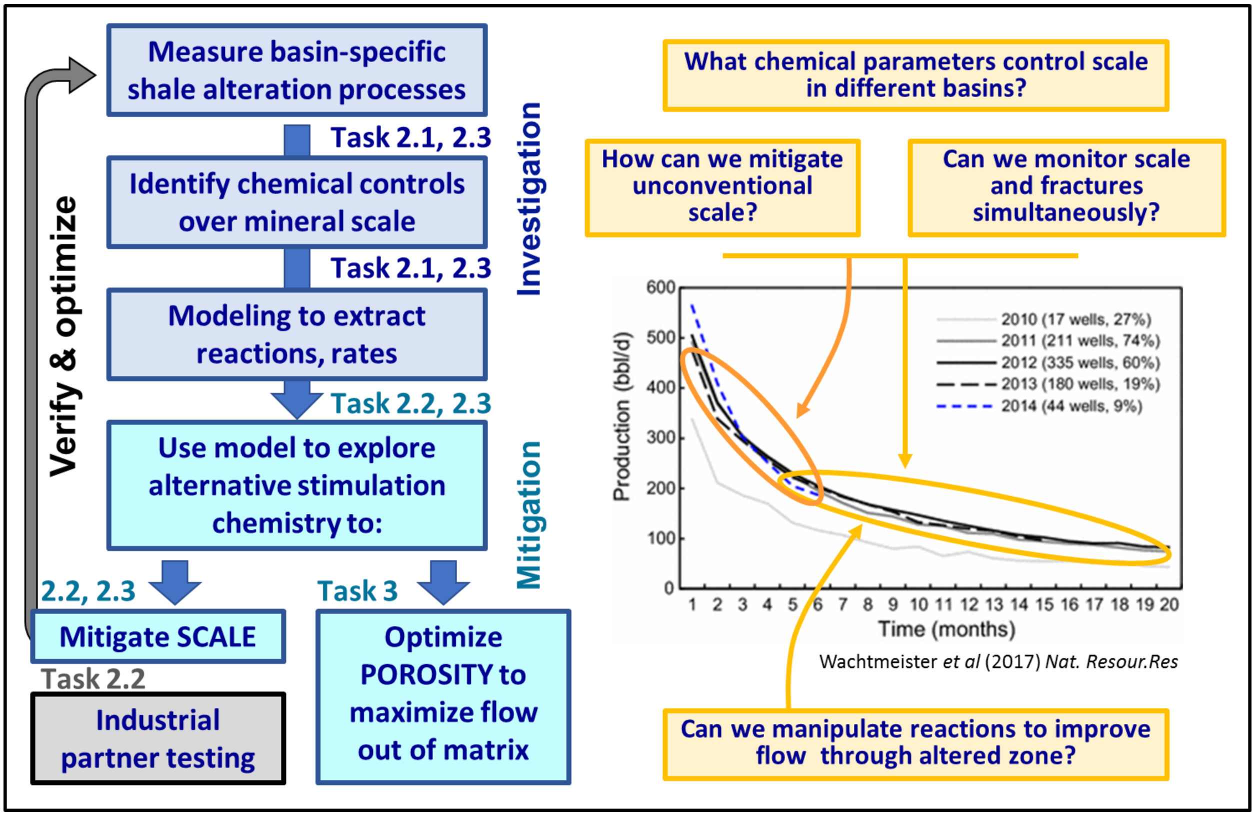


***Figure 2**. Diagrammatic representation of overall project and connection to broader context.*

cleaned brine in the base fluids for injection. Even though there is significant source of Sr in the formation water, the cleaned brine contains yet higher concentrations of dissolved Sr, which can precipitate upon injection. This issue is compounded by the fact that the clay-rich zones, highest producing zones, are the regions that take up the vast majority of Sr in the form of $SrSO_4$, $SrCl_2$, and Sr sorbed to clay. A new strategy using safe and economical $CaSO_4$ (gypsum and anhydrite) was developed to try and sorb/precipitate/swap Sr as SO_4-bearing species in the cleaned brine holding ponds. A new integrated set of experiment- modeling activities was initiated to address this problem. These new activities are fully consistent with and in fact amplify the original program goals of tasks 2.1 and 2.2.

Task 2.3. Acoustic measurements on laboratory-reacted shales: To characterize the P- and S-wave velocity signatures of acidified shale fractures, a single along-bedding fracture was created on a Marcellus well sample. The exterior surfaces of the sample were coated with an acid-resistant epoxy to restrict the reaction to the fracture surfaces alone, thereby studying the effect of fracture altered zones on rock physics properties. The pre-reaction characterization of the sample in terms of porosity, permeability, acoustic velocity, microstructure, and fracture topography has been completed. The sample is being reacted with hydrochloric acid and will be re-characterized post-reaction. Changes in acoustic velocities, and relevant storage and transport properties underlying the changes, will be analyzed to reveal how velocity signatures correlate with fracture alteration.

Task 3. Manipulation of matrix accessibility: We have made progress in conducting our core-flooding experiments. For time efficiency, our modified experimental set-up now conducts gas injection runs on two separate core holders concurrently. Crucially, both clay-rich Marcellus outcrop and MSEEL carbonate-rich Marcellus samples showed porosity/permeability was attenuated after pH 2.0 fracture fluid injection. These results clearly show that existing fracture fluid formulations *do a very poor job of promoting access* *to matrix* - instead they actually attenuate permeability in the altered zone. These findings emphasize the need to find less damaging fluid formulations that can provide engineering benefits to operators. In the next quarter, we will evaluate alternative fluid formulations based on specific shale mineralogy to specifically target formulations that can enhance permeability.

Synergies with other national laboratories

We collaborate extensively and frequently with NETL and LBNL to accomplish DOE-FE research mission needs through a twice-monthly ad-hoc shale geochemistry teleconference meeting/seminar series. This is an inclusive meeting, meant to foster collaborative interactions and accelerate discovery within the fundamental shale geochemistry research community. All interested parties from universities and other labs are welcome to participate and do so frequently. We are also collaborating extensively with LBNL, LLNL, and NETL in the DOE-FE funded HFTS multiscale research program. We have recently begun to discuss synergistic collaboration opportunities with the LANL shale geochemistry team.

Collaboration and interactions with other national laboratory programs*.* Multiple teleconferences and in-person meetings have been held each month since the start of the fiscal year with research scientists at NETL (A. Hakala, C. Lopano, M. Stuckman, B. McAdams, and W. Xiong), LLNL (J. Morris) and LBNL (H. Deng, T. Kneafsey, M. Reagan, and C. Steefel) to support the ongoing research program. On Dec. 18. 2019, we conducted a SLAC-NETL-LBNL HFTS planning meeting.

The SLAC geochemistry team is performing synergistic activities that provide unique and valuable services to the other DOE-FE research programs. Our team has deep expertise in the area of fracture fluid formulations. After expending a significant effort developing basin-specific stimulation fluid recipes for Marcellus, Midland, and Delaware basins for our research activities, we shared these recipes with collaborators at NETL, LBNL, and LLNL to help ensure that the larger DOE-FE shale research portfolio can benefit from our efforts and to be able to more readily compare experimental results from different national labs. Other key services provided recently include: (*i*) Providing new research results and data to partner labs through ad-hoc collaborations and through the formal HFTS program (*e.g.*, as documented in the HFTS project quarterly and annual reports); (*ii*) Collecting Bone Spring formation shale samples from the field and providing them to NETL and LBNL collaborators; (*iii*) Helping other projects to collect synchrotron data; (*iv*) Participating in the Knowledge Management (KM) meeting group (Jew); and (*v*) Regularly contributing questions and discussions to the KM discussion form.

Schedule for collaborative interactions*.* We are participating in the following standing meetings: (*i*) twice-monthly SLAC-NETL-LBNL fundamental shale geochemistry meeting/ seminar series; and (*ii*) twice-monthly HFTS leadership group meetings. The SLAC team will participate in two all-day HFTS project planning meetings in Berkeley, CA on Jan 15 and 16, 2020, where we will engage with research teams at NETL, LBNL and LLNL.

Details of task progress

Task 1: Project Management

J. Bargar, SLAC

Recruiting. A full-time post-doctoral fellow was on-boarded on Dec. 9, 2019.

Outreach to industry and academia. J. Bargar participated as a reviewer for the upcoming **URTeC 2020** sub-theme, "Oil/Gas/Water: Fluid-Fluid, Fluid-Rock Interactions & Chemostratigraphy". Bargar and Jew will participate as co-chairs for the same session at the URTeC 2020 conference in Denver, CO on July 20-22, 2020. Bargar co-organized a symposium on unconventional stimulation geochemistry, entitled, "Environmental Challenges and Solutions in Oil & Gas Development", to be held at the **259th ACS National Meeting and Exposition** in Philadelphia, PA on Mar 22-23, 2020.

Task 2: Scale prediction and mitigation in the stimulated rock volume

Task 2.1: Prediction of mineral scaling in unconventional reservoirs

Task 2.1.1: Experimental activity

E. Spielman-Sun, SLAC

Objectives and Approach

The primary objective for this task is to understand geochemical processes that control mineral scaling when basin-specific chemical formulations are used for the fracture stimulation fluids. By using region-specific chemical formulations, we aim to understand the formation of primary mineral scale and the major chemical reactions/parameters that are required for precipitation of mineral scale. By understanding these chemical principles, we should be able to predict the impact of new formulations on specific shale plays or predict what the new mineral scaling problems will be as new formations/plays are opened up for exploration.

Our previous work has shown the importance of fracture fluid and organics native to unconventional systems on the formation of mineral scale.[2, 3, 9] Though this body of work has resulted in several important discoveries, the fluid compositions used were specific to the Marcellus region.[10] A detailed investigation of the number of chemicals used in stimulations for various regions shows that there is a wide variety of major additive chemicals (biocides, breakers, surfactants, etc.) used in a given region. These differences necessitate a basin-specific approach in which the fracture fluid recipe for a given region is used for the corresponding shale type. This basin-specific approach will focus on Marcellus and Midland plays since they are different in mineralogy, targeted hydrocarbon (natural gas vs. oil), and fluid recipe.

Previous experiments also did not consider the injection sequence of a typical stimulation. In order to simplify kinetic modeling of the experimental systems, all of the chemicals were mixed together prior to reaction with the shale. To better simulate real-world systems, the new experiments follow the sequential addition of chemicals based on the injection schedules procured for the different shale plays. Not only will this sequential addition result in significant changes to additive concentrations at different times of the experimental process, but the different times between various stages allows varying pH's to interact with the shale depending on the dilution of the acid caused by subsequent solution additions. This sequential addition also allows for adjusting of the system in order to mimic different regions of the system (proximal to the well bore, distal to the well bore, and in-between), in which each region will have different pH conditions.

Table 2. Task 2.1.1 objectives for FY2020 Q1

Goal	**Status**
Reaction of Bone Spring and Marcellus samples with respective fracture fluids	Complete
Analysis of Bone Spring and Marcellus solutions post-reaction	Complete
Analysis of Bone Spring and Marcellus solids post-reaction	In progress

Progress in FY2020 Q1

Using previously determined basin-specific fracture fluid recipes and injection schedules (**Appendice B and C**), Bone Spring (Delaware basin; top and bottom units) and Marcellus shale (MSEEL site; outcrop sample from Oatka Creek, Le Roy NY) samples were exposed to synthetic fracture fluids. Characterization of the unreacted core (1” diameter x 1” length) and ground (150-250 µm) samples were discussed in previous reports (Bone Spring, **Quarter 3 Report, 2019**; Marcellus, **Quarter 4 Report, 2019**). One subset of ground samples was reacted in glass serum bottles to allow sampling of solution every 72 hours to evaluate solute evolution with time. The rest of the samples (ground and cores) were pressurized to 85 bar and reacted for a total of 3-weeks at 80°C, after which solution samples were collected and solid samples were rinsed with doubly de-ionized water (DDI) and dried for further analysis.

Solution analyses for Bone Spring and Marcellus have been completed, and analyses of the solids are ongoing. Synchrotron beam time for X-ray absorption spectroscopy (XAS) and X-ray fluorescence (XRF) mapping with micro-X-ray near-edge spectroscopy (µ-XANES) are scheduled for the next two quarters.

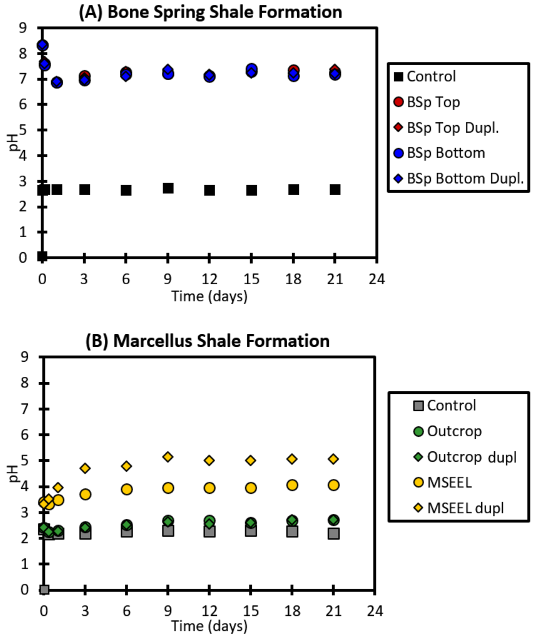


Figure 3. *pH of (**A**) Bone Spring and (**B**) Marcellus reactors with time. The initial pH is –0.3 due to the acid spearhead (15% HCl for Bone Spring, 7.5% HCl for Marcellus). Additional solution amendments of slickwater had a starting pH of 9.2 for Bone Spring and 4.5 for Marcellus. The next data point at 0.05 days is after all the fracture fluid chemicals were added and the reactors were sealed.*

Results

Changes in Solution Chemistry for Bone Spring and Marcellus Samples: The pH of the timed reactors for both Bone Spring and Marcellus shales is shown in **Figure 3**. For all shales, the initial solution pH is –0.3 due to the HCl spearhead. Subsequent additions of slickwater (pH of 9.2 for Bone Spring and 4.5 for Marcellus) caused a dramatic increase in solution pH due to a combination of dilution/neutralization by the slickwater and reaction of HCl with the calcite and dolomite the rock. This carbonate neutralization and raised pH is particularly noticeable for the MSEEL sample (19 wt.% carbonate) compared to the Marcellus Outcrop (3 wt.% carbonate). This acid neutralization, however, is much more gradual compared to Bone

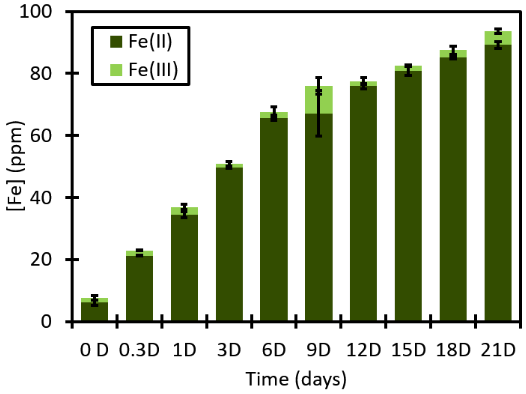


Figure 4. *Iron release from ground Marcellus Outcrop shale samples. Error bars indicate standard deviation from two samples. Iron concentrations were below detection limit for the MSEEL and Bone Spring samples.*

Spring samples with have a much higher carbonate content (>70 wt.%). The substantial change in pH for the Bone Spring samples and moderate change for the MSEEL sample is potentially very problematic because many of the solutes leached from the rock during the very low pH dissolution can precipitate as scale minerals as the pH rises.

Iron (II) and total iron concentrations solution were determined using a colorimetric ferrozine-based assay. The Bone Spring and MSEEL shale samples had no detectable iron in solution. The Marcellus Outcrop solution, which was the only shale with pyrite detectable by X-ray diffraction (XRD), showed a steady release of iron from the ground shale samples that plateaus around 90 mg/L (**Figure 4**). The high initial pyrite content of these Outcrop samples (18 wt.%) suggests that Fe(II) was released from the native pyrite as a result of reaction with the acidic fracture fluid. Majority of this iron (>95 wt.%) is reduced, which is expected at pH 2.7 given that iron (II) oxidation is generally inhibited at low pH.[11]

Changes in Bulk Solid Sample Composition for Bone Spring Samples: A list of major and selected trace elements in the Bone Spring ground shales before and after reaction is presented in **Table 3**. Small decreases in total magnesium, aluminum, calcium, titanium, and carbon were observed after reaction, likely due to carbonate and clay dissolution (XRD of the solids that will be performed in the next quarter will confirm this). This relatively small amount of dissolution is unsurprising given that the pH of the cross-linker breaker solution is so high (pH 9.2).

Plans for Next Quarter

Next quarter will be focused on completing the solids analysis of the Bone Spring and Marcellus experiments. Synchrotron-based analysis time is scheduled for the next two quarters. Wolfcamp (Midland basin) samples are scheduled for delivery this quarter, and upon arrival experiments involving Midland Basin will commence. Formulations for various types of base fluids for plays in the Permian Basin (municipal freshwater, brackish groundwater, and cleaned produced water) have been identified, and experiments focusing on the impact of these different base fluids will also commence once the Wolfcamp samples arrive. We are also still waiting for the new whole rock gas permeameter to arrive in order to conduct permeability measurements of the shale cores pre- and post-reaction.

***Table 3**. Bulk XRF measurements of selected elements for ground Bone Spring samples.*

	Na	**Mg**	**Al**	**Si**	**K**	**Ca**	**Ti**	**Fe**	**Tot C***	**Tot N***
	(%)	(%)	(%)	(%)	(%)	(%)	µg/g	µg/g	(%)	(%)
Bone Spring Top Unit										
Unreacted	0.26	0.46	0.30	4.81	0.18	35.62	313.2	2569	11.00	*BDL*
Time-Resolved Reactor	*BDL*	0.37	0.26	5.35	0.18	31.77	263.9	2711	10.84	0.32
Time-Resolved Reactor Dupl	*BDL*	0.36	0.27	5.54	0.18	32.34	249.4	2552	**	**
Pressurized Reactor	*BDL*	0.31	0.19	4.53	0.16	29.21	216.7	2337	10.30	0.49
Pressurized Reactor Dupl	*BDL*	0.28	0.05	4.24	0.15	28.10	204.7	2385	10.74	0.35
Bone Spring Bottom Unit										
Unreacted	0.22	0.38	*BDL*	0.47	0.05	39.59	72.1	1130	12.15	*BDL*
Time-Resolved Reactor	*BDL*	0.24	*BDL*	0.52	0.05	36.81	67.7	1187	**	**
Time-Resolved Reactor Dupl	*BDL*	0.32	*BDL*	0.62	0.05	36.71	71.7	1137	11.45	0.41
Pressurized Reactor	*BDL*	0.20	*BDL*	0.37	0.04	31.12	54.1	990	10.55	*BDL*
Pressurized Reactor Dupl	*BDL*	0.24	*BDL*	0.45	0.04	32.97	66.6	1309	10.98	*BDL*

* Total carbon and nitrogen were analyzed using Dumas combustion.

** Measurements will be made next quarter

BDL= below detection limit

Task 2.1.2: Modeling activity

Qingyun Li, SLAC

Task Summary

Numerical modeling of shale matrix alteration is critical for understanding the relationship between geochemical reactions and transport during shale matrix alteration. It allows experiments to be focused on critical outcome scenarios. Synergy between experiments and modeling has significantly improved the rate of discovery in this project.

To understand the reactivity of shale matrices, we built several models in FY 2017 -2019, including models on bitumen-aided Fe oxidation, shale-fluid interaction in a well-mixed reactor, and reactive transport models for shale matrices. In FY 2019, we built an efficient reactive transport model framework which features unique discretization to model shale-fluid reactions at the interface. Two models were built based on this framework to numerically simulate the experimental observations obtained in the previous FWP from post-reaction Marcellus and Eagle Ford shale sample matrices. Calibration of the models with experimental data has been helping us tremendously in understanding reactive transport processes in shale matrices upon exposure to fracturing fluids. This model framework is being adapted to experimental systems in **Task 2.1.1** in the current FWP.

Objectives and Approach

The objective in **FY2020 Q1** was to complete and submit the manuscript on shale-fluid reactive transport modeling. These objectives were accomplished (**Table 4**). During manuscript revision, the reactive transport models were further refined.

Another objective was to build a reactive transport model with a reactive network specifically for the Bone Spring samples used in **Task 2.1.1**.

Table 4. Task 2.1.2 objectives for FY2020 Q1

Goal	Status
Revise the manuscript on reactive transport in shale matrices	Complete
Submit the manuscript to *Energy & Fuels*	Complete
Test reaction networks against new experimental results from 2.1.1	Complete

Progress in FY2020 Q1

We have finished revising our manuscript on reactive transport modeling of the matrix alteration in the Marcellus and Eagle Ford core samples. The manuscript was submitted to *Energy & Fuels*. In addition, Q. Li presented a paper on this modeling work at AIChE Annual meeting (November, 2019).

Below is a list of the key findings presented in the journal manuscript:

- It takes a low-carbonate shale weeks to months to neutralize the acid imbibed into the matrix, whereas the process takes only hours to days in a high-carbonate shale.
- The pH evolution is mainly attributed to carbonate dissolution, which not only affects pH but also generates porosity.
- The spatial pH profiles can be the controlling factor for the formation of scale minerals such as barite.
- The formation of $Fe(OH)_3$ depends on both pH profiles and the presence of oxidants in the fluid and bitumen extracted from shale.

- Both the location and the overall amounts of the scale minerals are important in determining porosity and permeability of the shale matrix.
- If the precipitation rates are fast, the scale minerals tend to form in large volumes within a small space, whereas with slower precipitation rates, scale minerals are formed with lower maximum volumes in a larger space.
- Pore scale alterations other than the major dissolution and precipitation reactions may have a large impact on permeability alteration of the shale matrix.

In addition, a reactive transport model for the high-carbonate Bone Spring core samples was built. The model will be calibrated with the experimental data that is being obtained in **Task 2.1.1**. A preliminary run shows that if the imbibed fluid has a pH of 0, this acid can be completely neutralize in 3 weeks (**Figure 5a**), whereas if the imbibed fluid pH is 2, this neutralization process in the shale matrix takes less than 2 hours (**Figure 5b**).

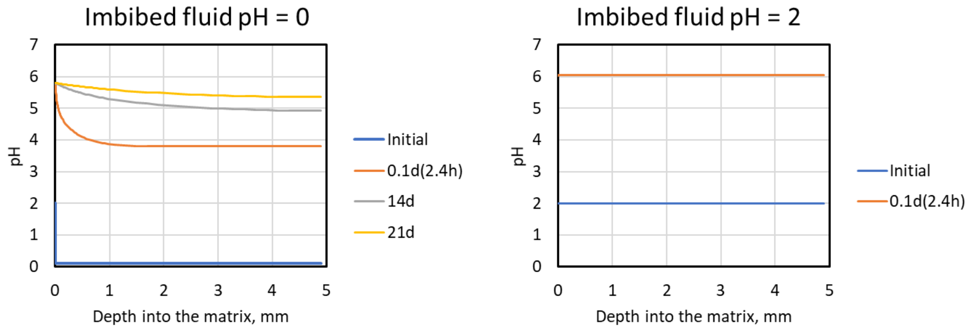


Figure 5. *Modeling results for pH profiles in the Bone Spring shale matrix. If the imbibed pH is 0, complete neutralization of the acid in the shale matrix takes 3 weeks; if the imbibed pH is 2 (where there is 100× less acid dissolved in the fluid), the complete neutralization process takes only 2 hours or less.*

Collaborative Leveraging

We are developing a collaboration with Los Alamos National Laboratory on observation of pore structure alteration due to shale-fluid interactions. In **FY2020 Q1**, pre- and post-reaction shale samples were prepared for small angle X-ray neutron scattering (SANS). These samples were sent to Hongwu Xu's group for SANS analyses.

Deliverables

Conference: Qingyun Li, Adam D. Jew, Gordon. E. Brown Jr., John R. Bargar, and Kate Maher. "Reactive Transport in Shale Matrix after Fracturing Fluid Imbibition." American Institute of Chemical Engineers (AIChE) Annual Meeting, Orlando, FL, November 10-15, 2019.

Manuscript: Qingyun Li, Adam D. Jew, Gordon E. Brown Jr, John R. Bargar, and Kate Maher. "Reactive Transport Modeling of Shale-Fluid Interactions after Imbibition of Fracturing Fluids." Submitted.

Plans for Next Quarter

The modeling activity in **Task 2.1.2** will coordinate with the experimental activity in **Task 2.1.1** to gain knowledge of shale and fluid alterations observed in **Task 2.1.1**.

A sensitivity analysis will be carried out in **FY2020 Q2**. Key input parameters such as calcite dissolution rate, effective diffusion coefficient, and solution pH will each vary separately, and the corresponding model result will be recorded. Analyzing the variation in the input parameters and the output results will allow us to gain knowledge of the importance of each input parameter.

Task 2.2: Mitigation of mineral scaling in unconventional reservoirs

Task 2.2.1: Modeling activity

Qingyun Li, SLAC

Task Summary

Our experience in **Task 2.1.1** with Wolfcamp-fluid reactions showed that for the Permian Basin, Sr-bearing scale needs to be controlled downhole. This problem becomes even more of an issue as operators start using more Sr-rich cleaned brine in the base fluids for injection. Even though there is significant source of Sr in the formation water, the cleaned brine contains yet higher concentrations of dissolved Sr, which can precipitate upon injection. This issue is compounded by the fact that the clay-rich zones, highest producing zones, are the regions that take up the vast majority of Sr in the form of SrSO4, SrCl2, and Sr sorbed to clay. A new integrated set of experiment- modeling activities was initiated to address this problem.

Building on knowledge acquired from our initial Wolfcamp-fluid experiments, we have developed a new hypothesis that will provide a central focus for integrated work between **Tasks 2.1** (Prediction of mineral scaling) and **2.2** (Mitigation of mineral scaling). This hypothesis is illustrated in **Figure 6**, where strontium sulfate scales are expected to be largely reduced with a better treatment of the base fluid used to make the fracturing fluid.

Hypothesis: removal of Sr from injected brine below a set level (to be determined) will mitigate $SrSO_4$ mineral scale precipitation in Wolfcamp shale. (**Figure 6**)

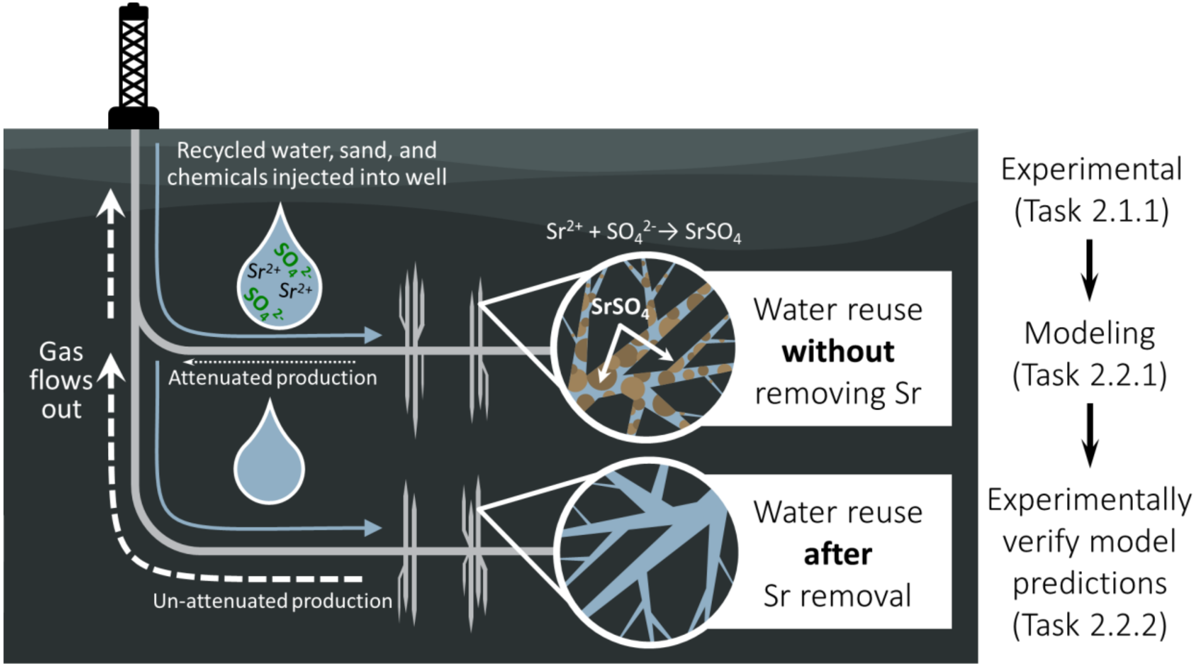


Figure 6. *Conceptual model for mitigation of strontium sulfate scale.*

In order to explore the best chemical composition of the fluid to mitigate strontium sulfate scale formation, we will build a numerical model for our Wolfcamp shale sample. Experiments data obtained from interactions between fracturing fluids and Wolfcamp shale samples (from **Task 2.1.1**) will be used to extract chemical rates using numerical modeling approaches in **Task 2.1.2**. The reaction rates will then be used to predict the amounts of scale minerals where various chemical compositions of the fracturing fluid are assumed (**Task 2.2.1**). This modeling activity can help answering the question: *How clean does the fracturing fluid need to be in order to mitigate scale mineral formation?* The best chemical composition of the fracturing fluid will be proposed (**Task 2.2.1**) for experimental tests (**Task 2.2.2**) to confirm its effectiveness in reducing strontium scale minerals.

Plans for Next Quarter

Our group will plan out the experimental conditions and modeling activity so that the experimental data and the modeling activity can best support each other. These steps will be initiated in Q2.

Task 2.2.2: Experimental activity

Adam Jew, SLAC

Objectives and Approach

As shown with regards to barite scale, the source of Ba and SO_4 appears to be coming from drilling mud as opposed to the assumption that the source is primarily from the shale and base fluid.[12] Barite in drilling mud has been shown to be destabilized through the injection of 15% HCl at the beginning of the stimulation process.[12] Once the major chemical process that resulted in Ba and SO_4 release was identified, a new acid formulation was developed in order to stabilize the barite. The process of identifying the problem through experimentation (**Task 2.1.1**) and identifying potential chemical changes using modeling prior to experimentation (**Task 2.1.2**) is invaluable and has already proven to be effective. Following the development of a new chemical formulation for mitigating different mineral scale, the new formulations will be reacted with shale in order to determine its effectiveness. Following this experimentation, formulations will be refined and re-tested in order to optimize these chemical mixtures for effectiveness, minimize cost, and to make sure that the new formulations do not interfere with other aspects of the fracture fluid (biocides, friction reducer, crosslinker, etc.).

Table 5. Task 2.2.2 objectives for FY2020 Q1

Goal	Status
Identify new mineral scale types that need to be mitigated	Ongoing
Develop a new strategy for mitigating $SrSO_4$ scaling	Complete
Test new $SrSO_4$ mitigation strategy	Ongoing

Progress in FY2020 Q1

In discussions with various operators in the Permian Basin as well as our work with Pioneer Natural Resources, it has become apparent that Sr (in the form of $SrSO_4$) is a problem that will become more pronounced as operators push towards injecting more cleaned brine into the subsurface. The work with Pioneer has shown that even though the source of the Sr in the produced water is a combination of the dissolution of the rock through stimulation and formation water. Though these sources are enriched in Sr, the Sr concentrations in the cleaned brines exceed those of the formation water and which suggest that the cleaned brine needs to be cleaned in the holding ponds for Sr (and Ba) prior to use as a base fluid. In order to provide a highly safe and more importantly extremely economical cleaning strategy for Sr, new strategies involving $CaSO_4$ species (gypsum and anhydrite) were developed.

Results

Due to the nature of the Pioneer project data, specifics can not be divulged at this moment, but overall generalizations will be presented. Experiments involving the use of cleaned brine indicates that the clay-rich portions of the shale are the primary areas in which Sr is taken up by the rock. This uptake can result in as much as a 5-fold increase Sr concentration in the solids. When a freshwater base fluid is used, Sr tends to be leached from the shale due to the acidic nature of the injection fluid. EXAFS fitting of Sr spectra for the shale samples indicate that $SrSO_4$ is the dominant Sr-bearing phase with $SrCl_2$ and Sr sorbed to clays also being present. Due to the potential of SO_4 generation through pyrite oxidation and ammonium persulfate breakdown, it is better to target Sr in the cleaned brine rather than controlling SO_4.

Plans for Next Quarter

In order to find an economical, simple solution for pre-treating the cleaned brine in the holding ponds prior to use as a base fluid experiments involving $CaSO_4$ (gypsum and anhydrite) will be conducted. The extremely high ionic strength, > 1.2M, of a typical cleaned brine solution (**Appendix C**) and poor ability to model adsorption at such high ionic strengths, experiments will be conducted using a simulated clean brine with various concentrations of ground gypsum and anhydrite. The use of these minerals is multi-fold: 1) due to the SO_4 groups on the surface of the minerals, Sr adsorption should occur, 2) at high I.S. the gypsum and anhydrite should partially dissolve supplying more SO_4 that should cause more insoluble $SrSO_4$ to precipitate, 3) partial substitution of Ca for Sr in the crystal structure should occur, and 4) due to the isostructural nature of anhydrite and celestite, epitaxial growth should occur. Following initial treatments with these minerals another set where the gypsum is dissolved using mild acid before being introduced to the synthesized base fluid will be done to provide a cheap SO_4 source for celestite precipitation.

Deliverables

A full patent was filed by Stanford University focusing on the new acid spearhead formulation. In addition, one major manuscript is planned for this Task.

Task 2.3: Acoustic Measurements on laboratory reacted shales

J. Ding, A. C. Clark, and T. Vanorio, Stanford Rock Physics Laboratory

Task Summary

The extremely low permeability of gas shale reservoirs has been requiring hydraulic and acid *fracturing* (*fracking* and *acidification*) for sustained economic productivity. This calls for an enhanced seismic characterization of reservoirs through a rock physics model that includes changes in physical properties due to chemo-mechanical processes. Having a rock physics model that includes rock-fluid interactions provides the basis for monitoring the changes *in situ* through seismic imaging. The evolution of porosity and pore connectivity during geochemical alteration of shales by fracture fluids controls permeability and hence, hydrocarbon production. Acoustic measurements offer the possibility to monitor porosity generation and scale formation in the lab and ultimately in the field. However, changes in these properties cannot be effectively monitored in the field through seismic imaging, the rock physics employed still relies on purely mechanical models. Since fracture fluid-rock interaction primarily occurs on the created fracture surfaces, it is critical to improve our understanding on the acoustic response that results from the formation of fracture altered zones. We have initiated a set of laboratory-scale experiments to examine the evolution of microstructure, porosity, and ultrasonic velocity following the acidification of artificial shale fractures. This experimental work allows us to build a rock physics model that better informs geochemistry-based strategies taken to optimize permeability within unconventional basins.

Objectives and Approach

The first objective of this task is to evaluate the shale properties (i.e., carbonate/sulfide/clay content, stress-sensitivity, bedding/fractures) that influence porosity creation and/or scale precipitation. Next, we will assess the changes in porosity and acoustic velocity, enabling the interpretation of *in situ* seismic images through the calibration of the acoustic response of altered shales in the laboratory. This will be accomplished through the following steps: (1) characterization of the microstructure, porosity, strain, and P- and S- velocities of the pre-reaction sample; (2) exposure of shale samples to specific reactive fluids; (3) re-characterization of the sample to evaluate the effects of dissolution and/or scale precipitation on porosity, permeability, and velocity; and (4) the construction of a rock physics model that incorporates the information from the experiments.

Table 6. Task 2.1.1 objectives for Quarter 5

Goal	**Status**
Prepare fractured Marcellus samples through Brazilian test	Complete
Characterize a fractured Marcellus well sample prior to reaction	Complete
React the fractured Marcellus well sample with 15% HCl	Ongoing
Data analysis of the pre-reaction characterization for the fractured Marcellus well sample	Ongoing
Characterize the fractured Marcellus well sample after reaction	Scheduled

Progress in Quarter 5

As planned in Quarter 4 of 2019, we modified our experimental protocol to better mimic the reaction geometry in the field and to facilitate collaboration with other Tasks from this project. In the new protocol, a cylindrical shale sample is split parallel or perpendicular to bedding to create an artificial fracture, and then coated with acid-resistant epoxy on the outer surfaces (**Figure 7**). With this new geometry, only the fracture surfaces remain bare, resulting in two major improvements. First, it is a direct representation of the reaction geometry in the field, which produces an altered zone at fracture surfaces adjacent to unaltered zones within intact rock. This is much preferred over previous experiments in which the reaction occurred only on the outer faces of samples (**Figure 19 and 20, Quarter 4 and Annual Report, 2019**). Second, the new protocol allows our experimental data to be more readily integrated into the results from other Tasks. The previous protocol prevented us from using samples with partial fractures caused by coring, e.g., the MSEEL clay-rich section. However, now our samples will overlap with those being studied in other Tasks, thereby enhancing collaboration and improving efficiency.

Following the new experimental protocol, a horizontal MSEEL clay-rich sample (7555’ depth) was split along a partially-fractured bedding plane (**Figure 8**). After introducing the artificial fracture, the sample was coated with epoxy on the outer surfaces and characterized by measuring porosity, permeability, acoustic velocity, microstructure, and fracture topography. Following the characterization, this sample is currently being reacted with hydrochloric acid (15 v.%) at 7.8 MPa hydrostatic pressure and 80 °C for three weeks. Data from the pre-reaction characterization of the sample are being processed and analyzed.

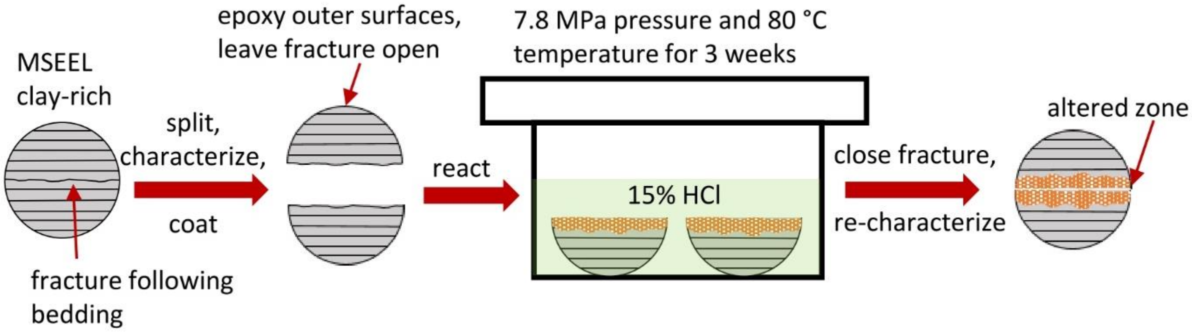


***Figure 7**. Schematic of experimental protocol using a split MSEEL clay-rich sample. This protocol will produce an altered zone at fracture surfaces adjacent to the unaltered zone. (Reproduced from Figure 22, Quarter 4 and Annual Report, 2019)*

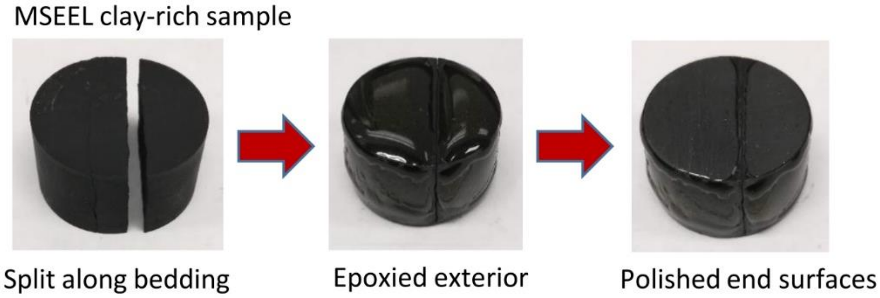


***Figure 8.** Photographs of a MSEEL sample after splitting along a bedding plane, epoxying exterior surfaces, and polishing two end surfaces. This sample is 1" in diameter and 0.6" in length*

Results

Pre-reaction permeability showed strong dependence on pressure (**Figure 9a**). As permeability was measured along the fracture, it was strongly affected by how closely the two fracture surfaces were pressed together. With regard to the pre-reaction acoustic velocity, the fast S-wave exhibited little pressure dependence, whereas the slow S-wave showed a stronger dependence, especially at lower effective pressures (a proxy for high pore fluid pressures) (**Figure 9b**). This can be explained by the oscillation modes of these two S-waves. The fast and slow S-waves propagate through the sample with a particle oscillation that is, respectively, parallel and perpendicular to fracture. Therefore, the slow S-wave is more sensitive to changes in the fracture surface contact under pressure. Since pore fluid pressure may change in the field during fracturing and/or production, the slow S-wave could be used to seismically locate fractured volumes of the subsurface kept open by pore pressure and/or proppants. Future tests are being planned to add complexity and include the role of fluids and proppants.

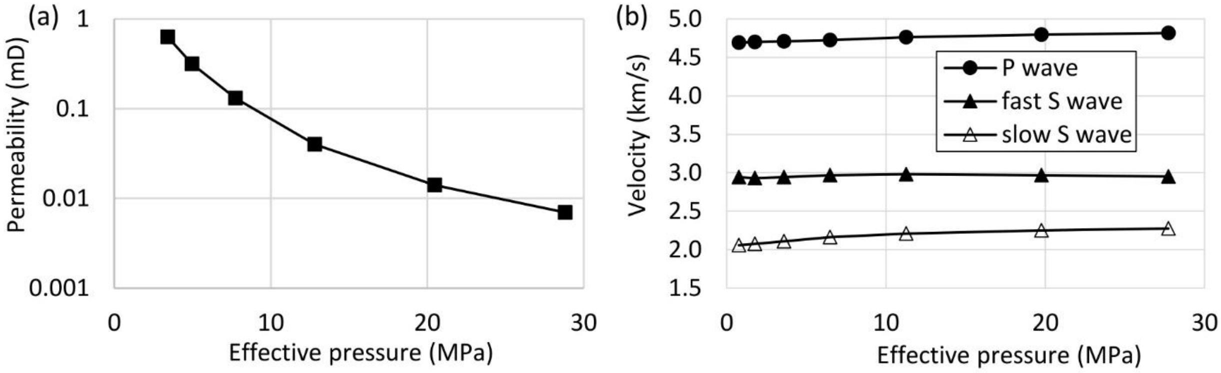


***Figure 9**. Pre-reaction (a) fracture permeability and (b) acoustic velocity of the MSEEL sample in Figure 6 after epoxying and polishing. The fast and slow S-waves propagate through sample with an oscillation that is, respectively, parallel and perpendicular to fracture.*

Deliverables

We have submitted two abstracts for URTeC 2020:

- Time-lapse acoustic monitoring of fracture alteration in Marcellus shale (Jihui Ding, Anthony C. Clark, Tiziana Vanorio, Adam Jew, and John R. Bargar)
- Time-lapse acoustic monitoring of Marcellus shale reacted with hydraulic fracturing fluid (Anthony C. Clark, Jihui Ding, Tiziana Vanorio, Adam Jew, and John R. Bargar)

Plans for Next Quarter

In **FY2020 Q2**, we will finish processing and analyzing the porosity, microstructure and fracture topography data from the pre-reaction characterization as well as bring the reaction of the MSEEL sample to completion (3-week). We will also complete the post-reaction characterization of the sample including measurements of porosity, permeability, acoustic velocity, microstructure, and fracture topography.

Task 3: Manipulation of matrix accessibility

A. Gundogar, SLAC; A. R. Kovscek, Stanford University

Task Summary

The rapid decline in recovery following hydraulic fracturing is strongly related to alteration in shale mineralogy that contributes to reductions in transport after exposure to reactive fluids in artificial and native fractures/microcracks.[3] In **Task 3**, we primarily focus on revealing the prevalent and transport-related interactions between fractured shale and fracture fluids to increase our ability to access the large volume of hydrocarbons present in shale matrices. We make use of representative core-flood experiments and multiscale imaging tools. Specifically, we investigate the alteration in size, morphology, and connectivity of shale primary and secondary porosity features ranging from core-scale (cm) to micron and nanoscales. The laboratory experiments provide the foundation for scale up to field applications.

Objectives and Approach

The objectives of **Task 3** are to evaluate systematically different stimulation fluid components, experimental practices, and the extent to which they enhance or retard flow in the altered zone. The representative flow-through experiments are important to understand how to control mineral precipitation and dissolution rates and to improve permeability of shales. The insights gained in **Task 3** aid in developing strategies to mitigate scale formation and to maximize flow through shale matrices.

In the simplified sketch of a hydraulically fractured system given in **Figure 1**, our particular interest is to maintain and improve the permeability of the altered zone (**Figure 1C**), that is, the reacted shale matrix adjacent to the major and minor fractures that are naturally or artificially created. A greater and persistent permeability in the altered zone of the shale matrix provides more efficient seepage of strongly acidic fracture fluid away from the vicinity of fracture networks (**Figure 1A**) and accordingly a greater volume of oil and gas transition from deeper layers of the shale matrix (unaltered zone in **Figure 1C**) by means of connection of microscale porosity across altered matrices. The altered zone may extend through the bulk shale matrix from a few meters to hundreds of meters depending on transport regimes, formation geomechanics, shale mineralogy, formation fluid and injected fracture fluid compositions. As reactive fracture fluid travels from the major fractures through the incipient cracks, during the soaking period of reactive fluid in the shale formation, a significant decrease commonly occurs in porosity and permeability of the reacted zone due to scale reactions such as barite, gypsum and iron precipitation as well as accumulations of fine clay or other mineral particles especially in the pore throats (**Figure 1B-C**). Pore walls may also collapse as the net affective stress changes. The reduction in altered zone permeability has a significant detrimental impact on recovery from the shale matrices with great hydrocarbon (gas or oil or both) potential.

We study the impact of rock-fluid reactions on flow properties of shales by means of three complementary experimental approaches: (i) core-flood experiments of reactive fluids in shales with (ii) multiscale and multi-instrument image analysis and (iii) chemical analysis of the pre- and post-reaction shale rocks and effluents. The representative modeling of coupled fluid flow, transport, and heterogeneous reactions on the shale samples is expected to provide better understanding of the porosity-permeability alterations observed in our experiments. In various simulation cases, the reactive transport regimes are characterized by the ratios of typical rates of reaction versus advection and diffusion - Damkohler (Da) vs Peclet (Pe) numbers. Engineers understand reactive transport as well as the extrapolation of laboratory conditions to field conditions through Pe and Da.

Table 7. Task 3 objectives for Quarter 1

Goal	Status
Pre- / Post-reaction characterization of Marcellus Outcrop, MSEEL samples	Ongoing
Perform core-flood experiments	Ongoing
Multiscale image analysis of samples	Ongoing
Multicomponent reactive transport modeling	Ongoing
Modification of experimental design for time efficiency	Ongoing

Progress in Quarter 5

In the last quarter, we finished the characterization measurements of our first set of shale samples, namely Marcellus Outcrop from Le Roy N.Y., the top and bottom layers of Bone Spring formation (Permian-Delaware Basin, TX) and carbonate- and clay-rich downhole cores from the MSEEL site (Marcellus, WV). The mineralogical, structural and petrophysical properties of the samples were gathered using quantitative XRD, source rock analysis, SEM/µCT/CT imaging, helium porosimetry, and mercury intrusion methods. The characterization data guide us for interpreting our ongoing flow through test results. We coupled core-flood experiments with in-situ dynamic CT imaging to obtain spatial and temporal evolution of porosity distribution within shales.[13] Our first core-flood experiments were conducted using the partially fractured, clay-(43%) and pyrite-rich (15%) Marcellus Outcrop sample. The preliminary workflow established for our initial scoping experiments together with the approximate timing of each step is given in **Figure 10**. The details of the experimental methodology can be found in Quarter 3 report (2019). After synthetic reactive fluid (pH 2.0 HCl solution) injection into a brine-saturated core sample, permeability reduced from 7.2 to 1.2 µD. Further, the average CT porosity decreased from 2.3 to 1.3%. From the visual examination of the reacted sample, the main fracture and smaller cracks were partially filled with fine particles of clays or other minerals. According to SEM-EDS analysis of the reacted sample, an iron-bearing mineral without sulfur had accumulated on fracture surfaces indicating iron precipitation plugging fracture spaces.

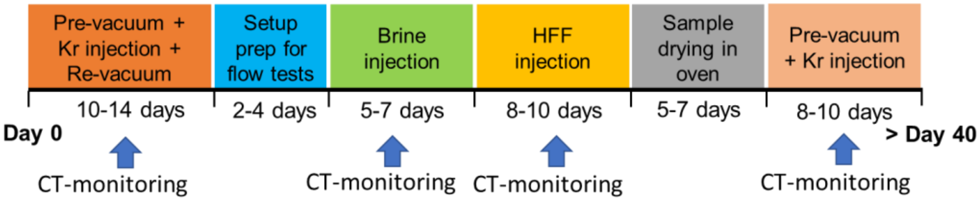


Figure 10. *The workflow of core-flooding tests in Task 3 (Kr: krypton gas, HFF: hydraulic fracturing fluid).*

In our core-flood experiments, a constant pH, synthetic basin-specific fluid solution is injected continuously from one side of the core in the parallel beddings direction under high pressure and low, representative flow rate. In field operations, once the acid spearhead with extremely high acidity (pH<1) is injected from the wellbore through the shale formations, the solution pH decreases, and the fluid composition alters during its travel across the shale matrix due to aqueous and kinetic reactions occurring in series and parallel. Likewise, our experimental conditions represent stimulated rock regions from strongly acidic (pH 2.0) to mildly/weakly acidic (pH≈3.5-5.8) intervals indicated as transitions from yellow (strongly acidic) to light blue (weakly acidic) color on the fracture system in **Figure 1A**. Because we use low flow rates and because reactions are slow relative to laboratory time scales, each-flow through experiment takes longer than a month to complete (**Figure 10**).

Results

The shale matrix of the Marcellus Outcrop after reaction was imaged using SEM and elemental analysis. We defined a grid and rasterized order across the surface to evaluate the entire cross-section. Iron (hydr)oxide was found in several places. For instance, in **Figure 11**, iron-rich dolomite in the central part of the image seems to be covered by iron without sulfur indicating iron hydr(oxide) precipitation. During image analysis, we observed no shortage or little reduction of pyrite minerals after acidic fluid exposure. It seems likely that our fracture fluid composition, pH 2.0, did not dissolve the majority of the pyrite minerals, especially those in perfect framboidal shapes.

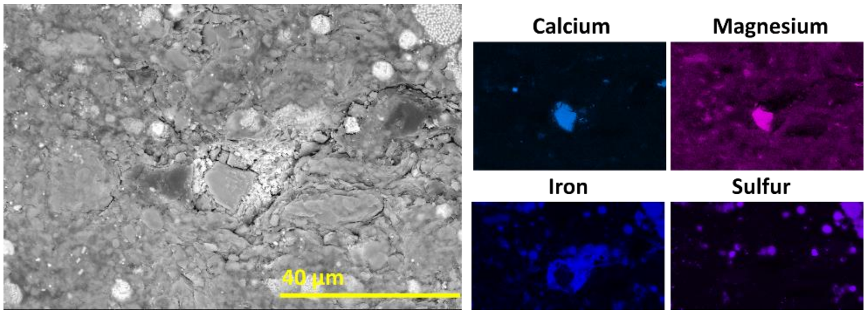


Figure 11. *SEM image (left) and elemental analysis (right) of the reacted Marcellus Outcrop matrix surface.*

Our core-flood experiments continued with the MSEEL carbonate-rich and clay-rich samples. To increase experimental efficiency (**Figure 10**), we modified our experimental set-up in such a way that two core holders were positioned in series on the CT-stage. In this way, used our dynamic core-flood system process for two separate samples concurrently. MSEEL carbonate-rich sample (90% calcite) was used for the flow experiments. During synthetic Marcellus formation brine injection,[14] the MSEEL carbonate-rich core permeability was calculated as 426 µD. During pH 2.0 HCl solution injection, permeability reduced to 212 µD. After that, the reacted MSEEL carbonate-rich sample was taken out and dried in a vacuum oven at 45°C. With our improved two core holder system, CT imaging of post-reaction MSEEL carbonate-rich and pre-reaction MSEEL clay-rich cores during Kr injection occur simultaneously.

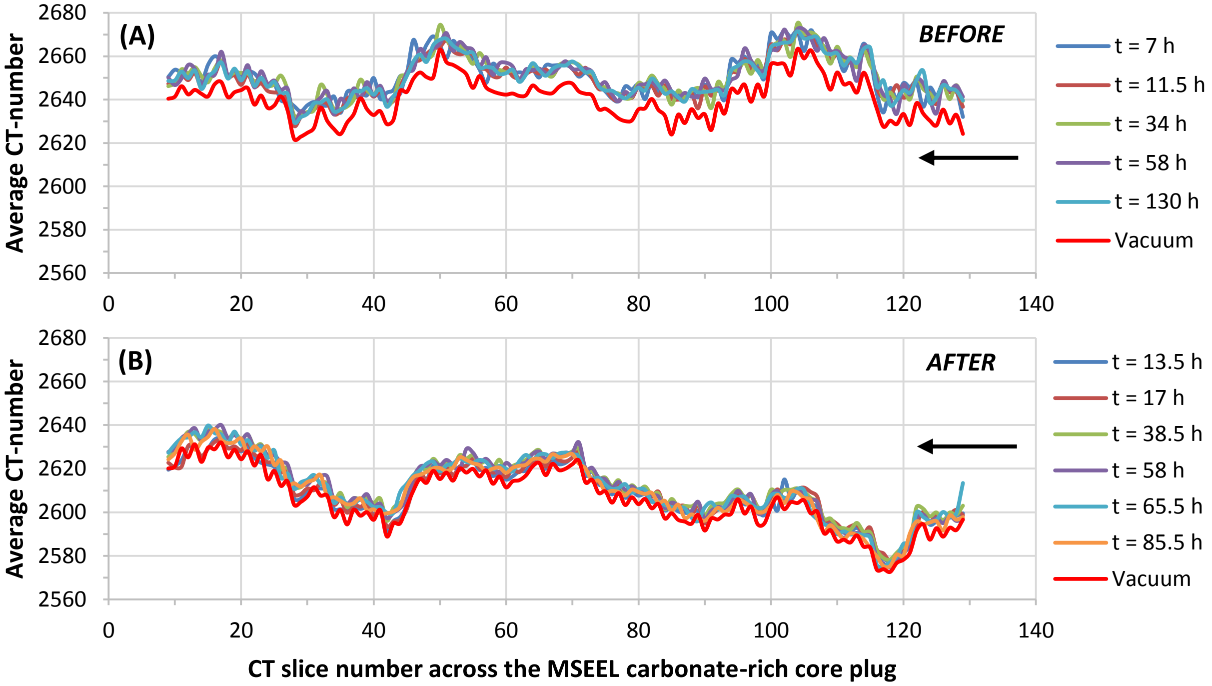


Figure 12. *CT number variation along the length of the MSEEL carbonate-rich sample with time as Kr intrudes into the matrix before (A) and after (B) reaction. The fracture fluid injection direction is shown with dark arrow.*

While the average CT-driven Kr-porosity of the unreacted MSEEL carbonate-rich sample was 2.5%, it was around 1.7% after reaction. The variations in the average CT-numbers at cross sections along the MSEEL carbonate-rich core length with time before and after reaction are given in **Figures 12A** and **12B**, respectively. As expected, the evolution of the average CT-curves with the time is in an upward direction with the greater Kr-presence in the shale fracture and pore system.[15] Based on the comparison between the CT-distributions before (**Figure 12A**) and after reaction (**Figure 12B**), the overall CT-values and accordingly porosities decrease with the reactive fluid exposure. In contrast to the shift in CT-curve from vacuum (t = 0) to Kr-saturated phases before reaction (**Figure 12A**), the porosity decreased significantly after reaction and hence Kr saturation is lower in the system. Therefore, there is not a remarkable change between CT-curves of vacuum (t = 0) and Kr-saturated cases (**Figure 12B**). The black arrows on **Figure 12** indicate that the acidic solution was injected from right to left along the core plug. Although cross-sectional CT-averages decreased following reaction, the trend of the CT-curves before and after reaction is similar in the second half of the core (from nearly the 90th slice to the outlet end at the leftmost on **Figure 12**).The greatest reduction in CT-averages after reaction is in the first part of the core (from about the 90th to the 130th slice on **Figure 12**). While there were two main maximums on **Figure 12A**, the hump on the inlet face is disappeared on **Figure 12B** after reaction. These preliminary observations indicate that, with acidic fluid introduction to the carbonate-rich MSEEL sample, the most dominant porosity reduction occurs in the region of matrix close to injection face, referred as the “altered zone” between the matrix and main fractures, i.e. reactive fluid carriers in the real field-case.

In our previous report (**Quarter 4** of 2019), the helium porosity of the MSEEL clay-rich sample was not yet measured. Recently, we measured it as 3.6% from cleaned crushed samples.

The summary of core-flood tests performed to date is given in **Table 8** for a general overview. In the light of the results of our initial flow-through experiments, mineral precipitation – in particular iron precipitation for Marcellus outcrop - is proven to play a significant role in porosity/permeability reductions of the reacted shales. These primary experimental observations coupled with multiscale and elemental image analysis point the way to manipulate fracture fluid composition based on the shale mineralogy. For our upcoming core-flood tests, we are planning to use a multicomponent fracture fluid solution with greater acidity, such as pH less than 1.0, for a more effective acid attack in the medium creating conditions suitable for micro-channeling and wormhole generation prior to pH rise. With this modification, our representative model will extend from orange (extremely acidic) to yellow (strongly acidic) to light blue (weakly acidic) intervals covering a wider and more comprehensive region on fracture system in **Figure 1A**.

Table 8: Summary of core-flood experimental results to date (The porosity and permeability measurements of the MSEEL clay-rich sample are pending and will be completed soon).

Date	**Shale sample**	**Mineral composition**	**Fracture fluid composition**	**Kr porosity**		**Permeability**	
				Pre-	**Post-**	**Brine***	**HFF†**
Q3 & Q4 of 2019	Marcellus Outcrop	Clay (43%) and pyrite-rich (15%)	1wt% NaCl, pH 2.0 HCl	2.3%	1.3%	7.2 µD	1.2 µD
Q4 of 2019 & Q1 of 2020	MSEEL Carbonate-rich	Calcite-rich (90%)	Basin specific (**Appendix C**)	2.5%	1.7%	426 µD	212 µD
Q1 of 2020	MSEEL Clay-rich	Clay (36%) and quartz-rich (43%)	Basin specific (**Appendix C**)	21%	–	–	–

* *Brine used is 0.5 M NaCl solution. †HFF is hydraulic fracture fluid.*

This quarter, we also worked on creating a realistic multicomponent reactive transport model that represents our initial experiments with clay- and iron-rich Marcellus Outcrop. The mineralogical data of the sample including its quantitative XRD and source rock properties are implemented into our new model created in CrunchFlow.[16] The formation brine and fracture fluid compositions with some additional ions required for the charge-balance of the aqueous system are defined. Eventually the model simulations are expected to mimic the temporal and spatial evolution of the shale rock and fluid properties during reactive fluid injection. The simulation results for Marcellus Outcrop sample are important to interpret the physical and geochemical processes for the induced porosity/permeability observed in laboratory experiments.

Deliverables

Gundogar, A.S.; Ross, C.M.; Li, Q.; Jew, A.D.; Bargar, J.R.; Kovscek, A.R. Multiscale imaging characterization of fracture fluid migration and reactive transport in shales, Abstract 629551 presented at 2019 Fall Meeting, AGU, 9-13 Dec 2019, San Francisco, CA.

Gundogar, A.S.; Ross, C.M.; Li, Q.; Jew, A.D.; Bargar, J.R.; Kovscek, A.R. Multiscale imaging of core flooding experiments during transport of reactive fluids in fractured unconventional shales, The 2020 SPE Western Regional Meeting, 27–30 April 2020, Bakersfield, CA (*Accepted abstract, Paper submission deadline: March 5, 2020*).

Plans for Next Quarter

In the next quarter, SEM-EDS analysis of the pre-/post-reaction MSEEL carbonate-rich samples will be done. After Kr injection, brine and reactive fluids prepared using the basin-specific recipes will be injected sequentially to the MSEEL clay-rich core. A new experimental set up is in preparation for pulse-decay tests. We will measure gas permeability and porosity of the whole core plugs before and after reactive fluid injection tests. We will improve our representative reactive transport model to evaluate the major chemical and physical parameters controlling the reacted zone flow properties.

References

1. Krauss, C., Boom in American Liquefied Natural Gas Is Shaking Up the Energy World. *The New York Times* **2017,** 16.

2. Jew, A. D.; Dustin, M. K.; Harrison, A. L.; Joe-Wong, C. M.; Thomas, D. L.; Maher, K.; Brown Jr, G. E.; Bargar, J. R., Impact of organics and carbonates on the oxidation and precipitation of iron during hydraulic fracturing of shale. *Energy & Fuels* **2017,** 31, (4), 3643-3658.

3. Jew, A.; Harrison, A.; Dustin, M.; Joe-Wong, C.; Thomas, D.; Maher, K.; Brown, G.; Cercone, D.; Bargar, J., Mineralogical and Porosity Alteration Following Fracture Fluid-Shale Reaction. In URTeC: 2017.

4. Cercone, D.; Jew, A. D.; Li, Q.; Dustin, M.; Harrison, A.; Joe-Wong, C.; Thomas, D.; Maher, K.; Brown, G. E., Jr.; Bargar, J. In *Chemical Controls on Secondary Mineral Precipitation of Fe and Ba in Hydraulic Fracturing Systems*, 2017 AIChE Annual Meeting, Minneapolis, MN, Minneapolis, MN.

5. Li, Q.; Jew, A. D.; Kiss, A. M.; Kohli, A.; Alalli, A.; Kovscek, A. R.; Zoback, M. D.; Cercone, D.; Maher, K.; Brown Jr, G. E. In *Imaging Pyrite Oxidation and Barite Precipitation in Gas and Oil Shales*, Unconventional Resources Technology Conference, Houston, Texas, 23-25 July 2018, 2018; 2018; pp 875-884.

6. Liu, Y.; Kan, A.; Zhang, Z.; Yan, C.; Yan, F.; Zhang, F.; Bhandari, N.; Dai, Z.; Ruan, G.; Wang, L., An assay method to determine mineral scale inhibitor efficiency in produced water. *Journal of Petroleum Science and Engineering* **2016,** 143, 103-112.

7. Zhang, F.; Dai, Z.; Yan, C.; Bhandari, N.; Yan, F.; Liu, Y.; Zhang, Z.; Ruan, G.; Kan, A. T.; Tomson, M. B., Barite-Scaling Risk and Inhibition at High Temperature. *SPE Journal* **2017,** 22, (01), 69-79.

8. Shen, D.; Fu, G.; Al-Saiari, H. A.; Kan, A. T.; Tomson, M. B., Barite dissolution/precipitation kinetics in porous media and in the presence and absence of a common scale inhibitor. *SPE Journal* **2009,** 14, (03), 462-471.

9. Li, Q.; Jew, A. D.; Kohli, A.; Maher, K.; Brown Jr, G. E.; Bargar, J. R., Thicknesses of Chemically Altered Zones in Shale Matrices Resulting from Interactions with Hydraulic Fracturing Fluid. *Energy & Fuels* **2019,** 33, (8), 6878-6889.

10. Hammack, R.; Harbert, W.; Sharma, S.; Stewart, B.; Capo, R.; Wall, A., An evaluation of fracture growth and gas/fluid migration as horizontal Marcellus Shale gas wells are hydraulically fractured in Greene County, Pennsylvania. *National Energy Technology Laboratory: NETL-TRS-3-2014, 76pp.* **2014**.

11. Morgan, B.; Lahav, O., The effect of pH on the kinetics of spontaneous Fe (II) oxidation by O2 in aqueous solution–basic principles and a simple heuristic description. *Chemosphere* **2007,** 68, (11), 2080-2084.

12. Jew, A. D.; Li, Q.; Cercone, D.; Maher, K.; Brown Jr, G. E.; Bargar, J. R. In *Barium Sources in Hydraulic Fracturing Systems and Chemical Controls on its Release into Solution*, Unconventional Resources Technology Conference, Houston, Texas, 23-25 July 2018, 2018; 2018; pp 863-874.

13. Aljamaan, H.; Ross, C. M.; Kovscek, A. R. In *Multiscale imaging of gas adsorption in shales*, SPE Unconventional Resources Conference, 2017; Society of Petroleum Engineers: 2017.

14. Warner, N. R.; Jackson, R. B.; Darrah, T. H.; Osborn, S. G.; Down, A.; Zhao, K.; White, A.; Vengosh, A., Geochemical evidence for possible natural migration of Marcellus Formation brine to shallow aquifers in Pennsylvania. *Proceedings of the National Academy of Sciences* **2012,** 109, (30), 11961-11966.

15. Vega, B.; Dutta, A.; Kovscek, A. R., CT imaging of low-permeability, dual-porosity systems using high X-ray contrast gas. *Transport in porous media* **2014,** 101, (1), 81-97.

16. Steefel, C. I.; Maher, K., Fluid-rock interaction: A reactive transport approach. *Reviews in mineralogy and geochemistry* **2009,** 70, (1), 485-532.

Milestone Status

Section	Title	Planned completion date	Actual completion or status
1.1	Development/Refinement of PMP	7/30/2020	
1.2	Quarterly research performance reports		
1.3	Meetings with NETL research groups	As Needed	
1.4	Annual research performance report		
1.5	Final technical report	9/30/2022	
Task 2: Scale prediction and mitigation in the stimulated rock volume			
Subtask 2.1: Prediction of mineral scaling in unconventional reservoirs			
2.1.1 Experimental subtask			
2.1.1.1	Evaluate literature/experimental design	3/31/2019	12/30/18
2.1.1.2	Complete initial scoping experiments	3/31/2019	2/28/2019
2.1.1.3	React shale with fracture fluid	9/30/2019	9/30/2019
2.1.1.4	Characterize post-reaction shale samples: laboratory-based methods	12/31/2019	
2.1.1.5	Analyze solution data from reactor experiments	12/31/2019	12/31/2019
2.1.1.6	Characterize precipitates: synchrotron-based methods	6/30/2020	
2.1.1.7	Initial manuscript for subtask 2.1.1	12/31/2020	
2.1.1.8	Submit manuscript for subtask 2.1.1	3/31/2021	
2.1.2 Modeling subtask			
2.1.2.1	Develop model framework	6/30/2019	3/31/2019
2.1.2.2	Test reaction networks against new experimental results from 2.1.1	12/31/2019	12/31/2019
2.1.2.3	Model parameter sensitivity analysis for major shale system types	3/31/2020	
2.1.2.4	Reactive transport modeling of systems in 2.1.1	9/30/2020	12/31/2019
2.1.2.5	Initial manuscript draft for subtask 2.1.2	3/30/2021	12/31/2019
2.1.2.6	Submit manuscript for subtask 2.1.2	6/30/2021	12/31/2019
Subtask 2.2: Mitigation of mineral scaling in unconventional reservoirs			
2.2.1 Modeling subtask			
2.2.1.1	Conduct numerical optimization experiments for each shale experiment	6/30/2021	
2.2.1.2	Evaluate cost/availability of constituents of optimized parameters	12/31/2020	
2.2.1.3	Develop experimental program based on optimizations	3/31/2021	
2.2.1.4	Initial manuscript draft for subtasks 2.2.1.1-3	9/30/2021	
2.2.1.5	Submit manuscript for subtasks 2.2.1.1-3	12/31/2021	
2.2.1.6	Re-evaluate/refine model as experimental data become available	6/30/2022	
2.2.1.7	Refine model-based experimental optimization procedure	3/31/2022	
2.2.1.8	Initial manuscript draft for subtasks 2.2.1.6-7	6/30/2022	

2.2.1.9	Submit manuscript for subtasks 2.2.1.6-7	9/30/2022	
2.2.2 Experimental subtask			
2.2.2.1	Formulation of new fracture fluid recipes	5/30/2020	
2.2.2.2	Testing of new formulations for various scaling conditions	9/30/2020	
2.2.2.3	React shale with optimized fracture fluid	12/31/2020	
2.2.2.4	Characterize post-reaction shale samples: laboratory-based methods (optimized fluids)	6/30/2021	
2.2.2.5	Analyze solution data from reactor experiments (optimized fluids)	6/30/2021	
2.2.2.6	Characterize precipitates: synchrotron-based methods (optimized fluids)	9/30/2021	
2.2.2.7	Initial manuscript draft for subtask 2.2.1	12/31/2021	
2.2.2.8	Submit manuscript draft for subtask 2.2.1	3/30/2022	
2.2.2.9	Optimize/reformulate fluids	9/30/2021	
2.2.2.10	Re-test new formulations (after reformulating)	12/31/2021	
2.2.2.11	Initial manuscript draft for Tasks 2.2.1.9-10	3/31/2022	
2.2.2.12	Submit manuscript for Tasks 2.2.1.9-10	5/30/2022	
Subtask 2.3: Acoustic measurements on laboratory reacted shales			
2.3.1	SEM images of top and bottom of unreacted shale	3/31/2019	3/31/2019
2.3.2	Measurement of grain density, bulk density, and porosity (pre-reacted)	9/30/2019	9/30/2019
2.3.3	React shale samples with fracture fluid	12/31/2019	12/31/2019
2.3.4	SEM images of top and bottom of reacted shale	3/31/2020	
2.3.5	Measurement of grain density, bulk density, and porosity (post-reaction)	9/30/2020	
2.3.6	Rock physics modeling	12/31/2020	
2.3.7	Post-injection stress-strain-strength curve measurement	6/30/2022	
2.3.8	Initial draft of manuscript for Task 2.3	12/31/2021	
2.3.9	Submit manuscript draft for Task 2.3	3/31/2022	
Task 3: Manipulation of matrix accessibility			
Subtask 3.1: Manipulate rates of dissolution and precipitation			
3.1.1	Evaluate literature/experimental design: stimulation conditions	3/31/2019	3/31/2019
3.1.2	Research/develop stimulation fluid recipes: Marcellus, Midland	3/31/2019	3/31/2019
3.1.3	Submit synchrotron/neutron user facility proposals	6/30/2019	6/30/2019
3.1.4	Acquire shale samples	6/30/2019	6/30/2019
3.1.5	Prepare stimulation fluids	6/30/2019	6/30/2019
3.1.6	Mineralogical characterization of shale samples	12/31/2019	12/31/2019
3.1.7	Test reactions: Initial scoping experiments	9/30/2019	9/30/2019
3.1.8	Evaluate/optimize experiment conditions	9/30/2019	9/30/2019
3.1.9	Measure permeability of unreacted cores	9/30/2019	9/30/2019
3.1.10	Collect and process µ-CT images, unreacted cores	12/30/2019	9/30/2019
3.1.11	Image processing, unreacted cores	3/31/2020	
3.1.12	Hydrostatic shale core reactions	12/31/2019	12/31/2019
3.1.13	Collect and process µ-/nano-CT images on reacted cores: macroporosity	12/31/2019	12/31/2019
3.1.14	SEM characterization: porosity evolution	12/31/2019	12/31/2019
3.1.15	XRM maps, unreacted/reacted shale cores	9/30/2020	
3.1.16	Measure permeability of reacted cores	9/30/2020	
3.1.17	Measure porosimetry of unreacted/reacted cores	3/31/2020	
3.1.18	Initial manuscript draft for subtask 3.1	12/31/2020	
3.1.19	Submit manuscript for subtask 3.1	3/31/2021	
Subtask 3.2: Growth and connectivity of secondary porosity			

3.2.1	Test reactions: Initial scoping experiments	6/30/2020	
3.2.2	Evaluate/optimize experiment conditions	9/30/2020	
3.2.3	Pre-characterize samples	9/30/2020	
3.2.4	React shale samples with fluids	3/31/2021	
3.2.5	Collect and process µ-/nano-CT images on reacted cores: macroporosity	9/30/2021	
3.2.6	Image processing, reacted shale cores	12/30/2021	
3.2.7	2D/SAXS characterization: porosity evolution	9/30/2021	
3.2.8	SEM (FIB-SEM) characterization: porosity evolution	6/30/2021	
3.2.9	Initial manuscript draft for subtask 3.2	12/31/2021	
3.2.10	Submit manuscript for subtask 3.2	3/31/2022	
Subtask 3.3: Modeling subtask			
3.3.1	Test reaction networks against new experimental data from task 3.1	12/31/2019	12/31/2019
3.3.2	Model parameter sensitivity analysis for major shale system types	3/31/2020	
3.3.3	Reactive transport modeling of systems in task 3.1	9/30/2020	
3.3.4	Initial manuscript draft for subtask 3.2	3/31/2021	
3.3.5	Submit manuscript for subtask 3.2	6/30/2021	
Subtask 3.4: Predict and test optimal conditions			
3.4.1	Predict optimal conditions from tasks 3.1, 3.2, 3.3	12/31/2021	
3.4.2	React shale samples with fluids under optimal conditions	3/31/2022	
3.4.3	Sample characterization	9/30/2022	
3.4.4	Complete initial draft of manuscript for task 3.4	Year 5	
3.4.5	Submit manuscript for task 3.4	Year 5	

Schedule Status

All milestones for this quarter have been met. As of the time of writing, the project is on-schedule.

Cost Status

Cost Plan/Status

Basesline Reporting Quarter		Year 7	Start: 10/1/18 End: 9/30/19			Year 8	Start: 10/1/19 End: 9/30/20		
		Q1	Q2	Q3	Q4	Q5	Q6	Q7	Q8
Baseline Cost Plan									
Federal Share	Task 1	$ 28,750	$ 28,750	$ 28,750	$ 28,750	$ 28,750	$ 28,750	$ 28,750	$ 28,750
	Task 2	$ 100,625	$ 100,625	$ 100,625	$ 100,625	$ 100,625	$ 100,625	$ 100,625	$ 100,625
	Task 3	$ 80,500	$ 80,500	$ 80,500	$ 80,500	$ 80,500	$ 80,500	$ 80,500	$ 80,500
	Task 4	$ 77,625	$ 77,625	$ 77,625	$ 77,625	$ 77,625	$ 77,625	$ 77,625	$ 77,625
	Task 5								
	Task 6								
Non-Federal Share									
Total Planned Costs (Federal and Non-Federal)									
Cumulative Baseline Cost		$ 287,500	$ 575,000	$ 862,500	$1,150,000	$1,437,500	$1,725,000	$2,012,500	$2,300,000
Actual Incurred Costs									
Federal Share	Task 1	$ 6,322	$ 8,227	$ 15,354	$ 34,916	$ 18,430			
	Task 2	$ 22,127	$ 28,794	$ 53,740	$ 122,207	$ 64,507			
	Task 3	$ 17,702	$ 23,035	$ 42,992	$ 97,766	$ 51,605			
	Task 4	$ 17,070	$ 22,213	$ 41,457	$ 94,274	$ 49,762			
	Task 5	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -
	Task 6	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -
Non-Federal Share									
Total Incurred Costs - Quarterly (Federal and Non-Federal)									
Cumulative Incurred Cost		$ 63,221	$ 145,490	$ 299,033	$ 648,196	$ 832,501	$ -	$ -	$ -
Variance									
Federal Share	Task 1	$ 22,428	$ 20,523	$ 13,396	$ (6,166)	$ 10,320	$ 28,750	$ 28,750	$ 28,750
	Task 2	$ 78,498	$ 71,831	$ 46,885	$ (21,582)	$ 36,118	$ 100,625	$ 100,625	$ 100,625
	Task 3	$ 62,798	$ 57,465	$ 37,508	$ (17,266)	$ 28,895	$ 80,500	$ 80,500	$ 80,500
	Task 4	$ 60,555	$ 55,412	$ 36,168	$ (16,649)	$ 27,863	$ 77,625	$ 77,625	$ 77,625
	Task 5	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -
	Task 6	$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -
Non-Federal Share		$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -
Total Variance - Quarterly (Federal and Non-Federal)		$ -	$ -	$ -	$ -	$ -	$ -	$ -	$ -
Cumulative Variance		$ 242,180	$ 447,411	$ 581,368	$ 519,705	$ 622,900	$ 910,400	$1,197,900	$1,485,400

Other Collaborative Leveraging

Collaboration on research activities is an important method to leverage the investment in this project. This project is being leveraged by the LBNL-LLNL multi-scale HFTS modeling project. Our ongoing ad-hoc collaboration with the NETL geochemistry group has been very productive and has grown into a funded partnership within the HFTS modeling project. Our collaborations with Pioneer Natural Resources and Equinor North America are providing invaluable insights into industrial fracture stimulation injection chemistry, fluid and additive sequencing, volumes, and rates that are critical in order to understand what operators are doing in highly complex unconventional oils systems. We are also collaborating with the Stanford University EFRC project led by T. Kovscek. Imaging methods developed in the EFRC project will eventually be applied to the applied NETL R&D program.

Appendix A: Deliverables

Patents.

1. Patent (2019)- Fracture Fluid Alteration to Mitigate Barite Scale Precipitation in Unconventional Oil/Gas Shale Systems. Patent ID: 16/519823

Manuscripts published, submitted, or in revision.

URTeC Extended Abstracts -

2. *Time-lapse acoustic monitoring of fracture alteration in Marcellus shale*. Jihui Ding, Anthony C. Clark, Tiziana Vanorio, Adam Jew, and John R. Bargar. Submitted
3. *Time-lapse acoustic monitoring of Marcellus shale reacted with hydraulic fracturing fluid*. Anthony C. Clark, Jihui Ding, Tiziana Vanorio, Adam Jew, and John R. Bargar Submitted
4. *A New Approach to Controlling Barite scaling in Unconventional Systems.* A.D. Jew, Q. Li, D. Cercone, G.E. Brown, Jr., J.R. Bargar. URTEC-512-MS. Extended Abstracts of the 2019 Unconventional Resources Conference 2019, DOI 10.15530/urtec-2019-512.
5. *Geochemical Modeling of Iron (Hydr)oxide Scale Formation During Hydraulic Fracturing Operations.* Q. Li, A.D. Jew, D. Cercone, J.R. Bargar, G.E. Brown, Jr., K. Maher. URTEC-612-MS. Extended Abstracts of the 2019 Unconventional Resources Conference 2019, DOI 10.15530/urtec-2019-612.
6. *Barium Sources in Hydraulic Fracturing Systems and Chemical Controls on its Release into Solution*. A.D. Jew, Q. Li, D. Cercone, K. Maher, G.E. Brown, Jr., and J.R. Bargar. URTEC-2899671-MS. Extended Abstracts of the 2018 Unconventional Resources Technology Conference 2018, 2899671, DOI doi:10.15530/URTEC-2018-2899671.
7. *Imaging Pyrite Oxidation and Barite Precipitation in Gas and Oil Shales*. Q. Li, A.D. Jew, A.M. Kiss, A. Kohli, A. Alalli, A.R. Kovscek, M.D. Zoback, D. Cercone, K. Maher, G.E. Brown, Jr., and J.R. Bargar. URTEC-2902747-MS. Extended Abstracts of the 2018 Unconventional Resources Technology Conference 2018, 2902747, DOI https://doi.org/10.15530/URTEC-2018-2902747.
8. *Effects of hydraulic fracturing fluid on shale matrix permeability*. A. Alalli, Q. Li, A.D. Jew, A. Kholi, J.R. Bargar, and M. Zoback. URTEC-2881314-MS. Extended Abstracts of the 2018 Unconventional Resources Technology Conference 2018, 2881314, DOI https://doi.org/10.15530/URTEC-2018-2881314.

Peer-reviewed Journal Papers -

9. Qingyun Li, Adam D. Jew, Gordon E. Brown Jr, John R. Bargar, and Kate Maher. “Reactive Transport Modeling of Shale-Fluid Interactions after Imbibition of Fracturing Fluids.” *Submitted*.
10. *Thicknesses of chemically altered zones in the shale matrices from interactions with hydraulic fracturing fluid.* Q. Li, A.D. Jew, A.M. Kiss, A. Kohli, A. Alalli, A.R. Kovscek, M.D. Zoback, D. Cercone, K. Maher, G.E. Brown, Jr., and J.R. Bargar. Energy & Fuels 2019, 33, 8, 6878-6889. DOI: 10.1021/acs.energyfuels.8b04527
11. *Shale Kerogen-Hydraulic Fracturing Fluid Interactions and Contaminant Release*. Megan K. Dustin, Adam D. Jew, Anna L. Harrison, Claresta Joe-Wong, Dana L. Thomas, Katharine Maher, Gordon E.

Brown, Jr., John R. Bargar, *Energy & Fuels.* Vol. 32, No. 9, 8966-8977. DOI: 10.1021/acs.energyfuels.8b01037.

12. *Organic and Inorganic Controls on Barite Precipitation in Hydraulic Fracturing Systems*. Adam D. Jew, Qingyun Li, Kate Maher, Gordon E. Brown, Jr., John R. Bargar, *Energy & Fuels*. Vol. 31, 3643-3658.
13. *Element release and reaction-induced porosity alteration during shale-hydraulic fracturing fluid interactions.* A.L. Harrison, A.D. Jew, M.K. Dustin, D.L. Thomas, C.M. Joe-Wong, J.R. Bargar, N. Johnson, G.E. Brown, Jr., K. Maher, *Applied Geochemistry*. Vol. 82, 47-62.
14. Kiss, A.M., Jew, A.D., Joe-Wong, C.M., Maher, K., Liu, Y., Brown, G.E., Jr. and Bargar, J.R., 2015, Synchrotron-based transmission X-ray microscopy for improved extraction in shale during hydraulic fracturing. SPIE Optical Engineering + Applications, v. 95920O. Available at: doi:10.1117/12.2190806

Manuscripts in preparation.

15. *The Effect of Hydraulic Fracturing Fluid on the Stability of Uranium in Unconventional Oil/Gas Shales*. Adam D. Jew, Clemence J. Besancon, Scott J. Roycroft, Vincent S. Noel, Gordon E. Brown, Jr., John R. Bargar

Presentations at National Meetings.

URTeC Conference -

16. Adam D. Jew, Qingyun Li, David Cercone, Kate Maher, Gordon E. Brown, Jr., John R. Bargar. *Barium Sources in Hydraulic Fracturing Systems and Chemical Controls on its Release into Solution*. *July 23-25, 2018, Houston, TX*
17. Qingyun Li, Adam D. Jew, Andrew M. Kiss, Arjun Kohli, Abdulgader Alalli, Anthony R. Kovscek, Mark D. Zoback, David Cercone, Katharine Maher, Gordon E. Brown, Jr., John R. Bargar. *Imaging Pyrite Oxidation and Barite Precipitation in Gas and Oil Shales. July 23-25, 2018, Houston, TX:*
18. Abdulgader Alalli, Qingyun Li, Adam Jew, Arjun Kholi, John R. Bargar, Mark Zoback. *Effects of hydraulic fracturing fluid on shale matrix permeability*. *July 23-25, 2018, Houston, TX:*
19. Qingyun Li, Adam D. Jew, David Cercone, John R. Bargar, Gordon E. Brown, Jr., and Katharine Maher. Geochemical Modeling of Iron Scale Formation during Unconventional Simulation. *July 22-24, 2019, Denver, CO:*
20. Adam D. Jew, Qingyun Li, David Cercone, Gordon E. Brown, Jr., and John R. Bargar. A New approach to controlling barium scaling in unconventional systems. *July 22-24, 2019, Denver, CO:*
21. *A. Jew* Presented at URTeC 2019 Workshop (Invited Talk), Apr. 22, Pittsburgh, PA.

Other conferences -

22. Gundogar, A.S.; Ross, C.M.; Li, Q.; Jew, A.D.; Bargar, J.R.; Kovscek, A.R. Multiscale imaging of core flooding experiments during transport of reactive fluids in fractured unconventional shales, The 2020 SPE Western Regional Meeting, 27–30 April 2020, Bakersfield, CA
23. Gundogar, A.S.; Ross, C.M.; Li, Q.; Jew, A.D.; Bargar, J.R.; Kovscek, A.R. Multiscale imaging characterization of fracture fluid migration and reactive transport in shales, Abstract 629551 presented at 2019 Fall Meeting, AGU, 9-13 Dec 2019, San Francisco, CA.

24. Qingyun Li, Adam D. Jew, Gordon. E. Brown Jr., John R. Bargar, and Kate Maher. "Reactive Transport in Shale Matrix after Fracturing Fluid Imbibition." American Institute of Chemical Engineers (AIChE) Annual Meeting, Orlando, FL, November 10-15, 2019.
25. 2019 Geological Society of America Annual Meeting: Session T29. Mineralogical Society of America (MSA) at 100: Reflections, Refractions, Diffractions, Intrusions, Subduction, Reactions, etc. from MSA Past Presidents, Phoenix, AZ, September 23, 2019. Adam D. Jew, Anna Harrison, Qingyun Li, David P. Cercome, Katharine Maher, John R. Bargar, Gordon E. Brown, Jr. *Unconventional Mineralogy: Interactions of Hydraulic Fracturing Fluids with Minerals and Organic Matter in Unconventional and Tight Oil Formations.*
26. Symposium on *shale-gas-fluid interaction for water and energy*, 2019 ACS spring meeting, March 31, 2019, Orlando, FL
27. Presented research at the NETL/DOE meeting: Mastering the subsurface through technology innovation partnerships and collaboration: carbon storage and oil and natural gas technologies review meeting. Aug. 13-16, 2018. Pittsburgh, PA
28. AIChE Annual Meeting, Oct. 29-Nov. 3, 2017, Minneapolis, MN. Adam D. Jew, David Cercone, Qingyun Li, Megan K. Dustin, Anna L. Harrison, Claresta Joe-Wong, Dana L. Thomas, Kate Maher, Gordon E. Brown, Jr., John R. Bargar. *Chemical controls on secondary mineral precipitation of Fe and Ba in hydraulic fracturing systems.*
29. AGU Fall Meeting, Dec. 11-15, 2017, New Orleans, LA. Qingyun Li, Adam D. Jew, Gordon E. Brown, Jr., John R. Bargar. *Chemical reactivity of shale matrixes and the effects of barite scale formation*
30. DOE Upstream Workshop, Feb. 14, 2018, Houston, TX. Alexandra Hakala, Joe Morris, John Bargar, Jens Birkholzer. *Fundamental Shale Interactions-DOE National Laboratory Research*
31. Adam D. Jew, Megan K. Dustin, Anna L. Harrison, Claresta Joe-Wong, Dana L. Thomas, Katharine Maher, Gordon E. Brown Jr., and John R. Bargar (2016) The Importance of pH, Oxygen, and Bitumen on the Oxidation and Precipitation of Fe(III)-(oxy)hydroxides during Hydraulic Fracturing of Oil/Gas Shales. American Geophysical Union Fall Meeting, San Francisco, USA, December 13.
32. John R. Bargar, Andrew Kiss, Arjun Kohli, Anna L. Harrison, Adam D. Jew, Jae-Hong Lim, Yijin Liu, Katherine Maher, Mark Zoback, and Gordon E. Brown, Jr., (2016) synchrotron X-ray imaging to understand porosity development in shales during exposure to hydraulic fracturing fluid. American Geophysical Union Fall Meeting, San Francisco, USA, December 12.
33. Anna L. Harrison, Katharine Maher, Adam D. Jew*, Megan K. Dustin, Andrew Kiss, Arjun Kohli, Dana L. Thomas, Claresta Joe-Wong, Gordon E. Brown Jr., and John R. Bargar (2016) H21J-04 The Impact of Mineralogy on the Geochemical Alteration of Shales During Hydraulic Fracturing Operations. American Geophysical Union Fall Meeting, San Francisco, USA, December 13.
34. John R. Bargar, Andrew Kiss, Arjun Kohli, Anna L. Harrison, Adam D. Jew, Megan Dustin, Claresta Joe-Wong, Katherine Maher, Gordon E. Brown, Jr., Mark Zoback, Yijin Liu, and David Cercone, (2016) Geochemistry of shale-fluid reactions at pore and fracture scales. 252nd American Chemical Society National Meeting, Aug 21 (invited)
35. Anna Harrison, Kate Maher, Adam Jew, Megan Dustin, Andy Kiss, Arjun Kohli, Dana Thomas, Claresta Joe-Wong, Yijin Liu, J.-H. Lim, Gordon Brown Jr., and John Bargar (2016) Physical and

chemical alteration of shales during hydraulic fracturing. Presented at the 2016 Goldschmidt Conference, Yokohama, Japan, June 29, 2016.

36. Megan K. Dustin, Adam D. Jew, Anna L. Harrison, Claresta Joe-Wong, Dana L. Thomas, Katharine Maher, Gordon E. Brown Jr., and John R. Bargar (2015) Kerogen-Hydraulic Fracture Fluid Interactions: Reactivity and Contaminant Release. American Geophysical Union Fall Meeting, San Francisco, USA, December 14-18.

37. Anna L. Harrison, Adam D. Jew, Megan K. Dustin, Claresta Joe-Wong, Dana L. Thomas, Katharine Maher, Gordon E. Brown Jr., and John R. Bargar (2015) A Geochemical Framework for Evaluating Shale-Hydraulic Fracture Fluid Interactions. American Geophysical Union Fall Meeting, San Francisco, USA, December 14-18.

38. Adam D. Jew, Claresta Joe-Wong, Anna L. Harrison, Dana L. Thomas, Megan K. Dustin, Gordon E. Brown Jr., Katharine Maher, and John R. Bargar (2015) Iron Release and Precipitation in Hydraulic Fracturing Systems. American Geophysical Union Fall Meeting, San Francisco, USA, December 14-18.

39. Claresta Joe-Wong, Anna L. Harrison, Dana L. Thomas, Megan K. Dustin, Adam D. Jew, Gordon E. Brown Jr., Katharine Maher, and John R. Bargar (2015) Coupled mineral dissolution and precipitation reactions in shale-hydraulic fracturing fluid systems. American Geophysical Union Fall Meeting, San Francisco, USA, December 14-18.

40. Megan K. Dustin, Adam D. Jew, Anna L. Harrison, Claresta Joe-Wong, Dana L. Thomas, Katharine Maher, Gordon E. Brown Jr., and John R. Bargar (2015) Kerogen-Hydraulic Fracture Fluid Interactions: Reactivity and Contaminant Release. Stanford Synchrotron Radiation Lightsource 2015 User’s Meeting, Stanford, USA, Oct 7-9.

41. Anna L. Harrison, Adam D. Jew, Megan K. Dustin, Claresta Joe-Wong, Dana L. Thomas, Katharine Maher, Gordon E. Brown Jr., and John R. Bargar (2015) A Geochemical Framework for Evaluating Shale-Hydraulic Fracture Fluid Interactions. Stanford Synchrotron Radiation Lightsource 2015 User’s Meeting, Stanford, USA, Oct 7-9.

42. John R. Bargar, Gordon E. Brown, Jr., Megan K. Dustin, Anna L. Harrison, Adam D. Jew, C.M. Joe-Wong, and Katharine Maher (2015) Geochemical control of shale fracture and matrix permeability. Shales without Scales Workshop, Santa Fe, USA, June 10. (invited)

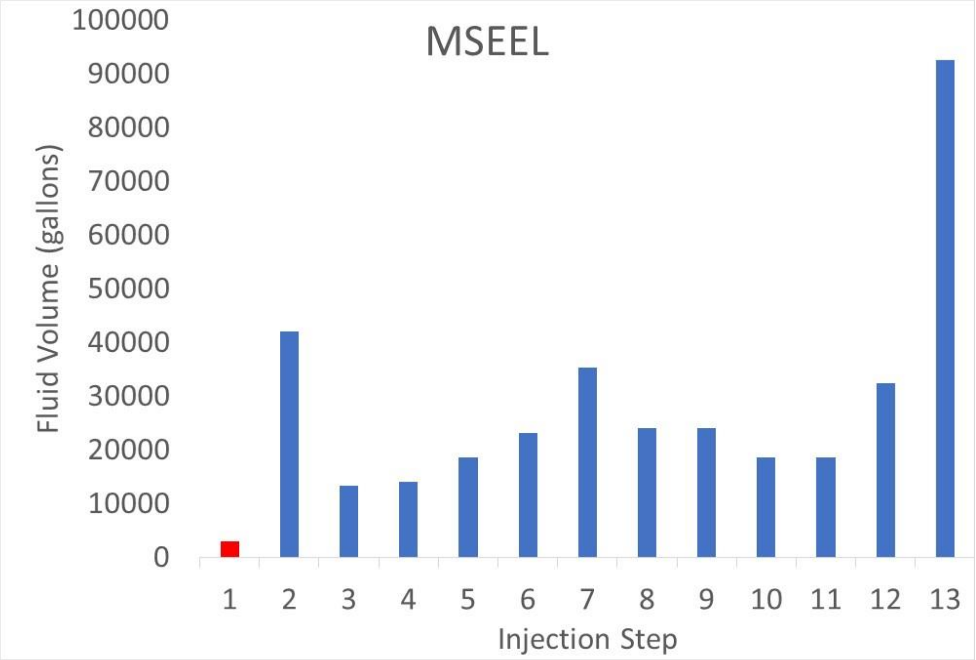
43. Anna L. Harrison, Adam D. Jew, Megan K. Dustin, Claresta Joe-Wong, Dana L. Thomas, Katharine Maher, Gordon E. Brown Jr., and John R. Bargar (2015) A Geochemical Framework for Evaluating Shale-Hydraulic Fracture Fluid Interactions. Stanford Center for Secure Carbon Storage Research Seminar, Stanford, USA, October 21.

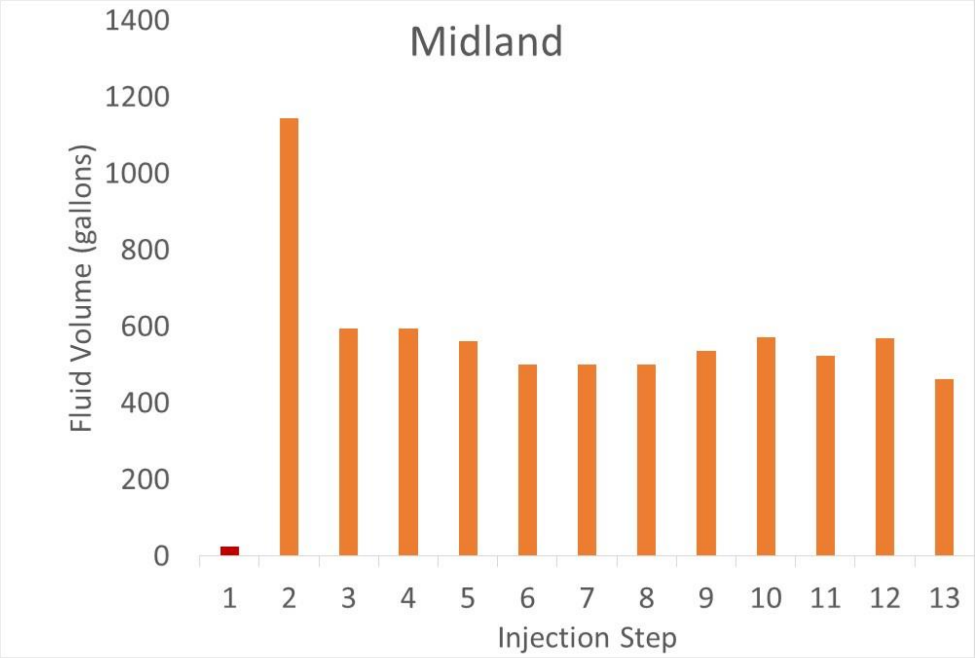
44. John R. Bargar, Gordon E. Brown, Jr., Megan K. Dustin, Anna L. Harrison, Adam D. Jew, C.M. Joe-Wong, and Katharine Maher (2015) Geochemical control of shale fracture and matrix permeability. Baker Hughes Incorporated, Tomball, USA, July 14. (invited)

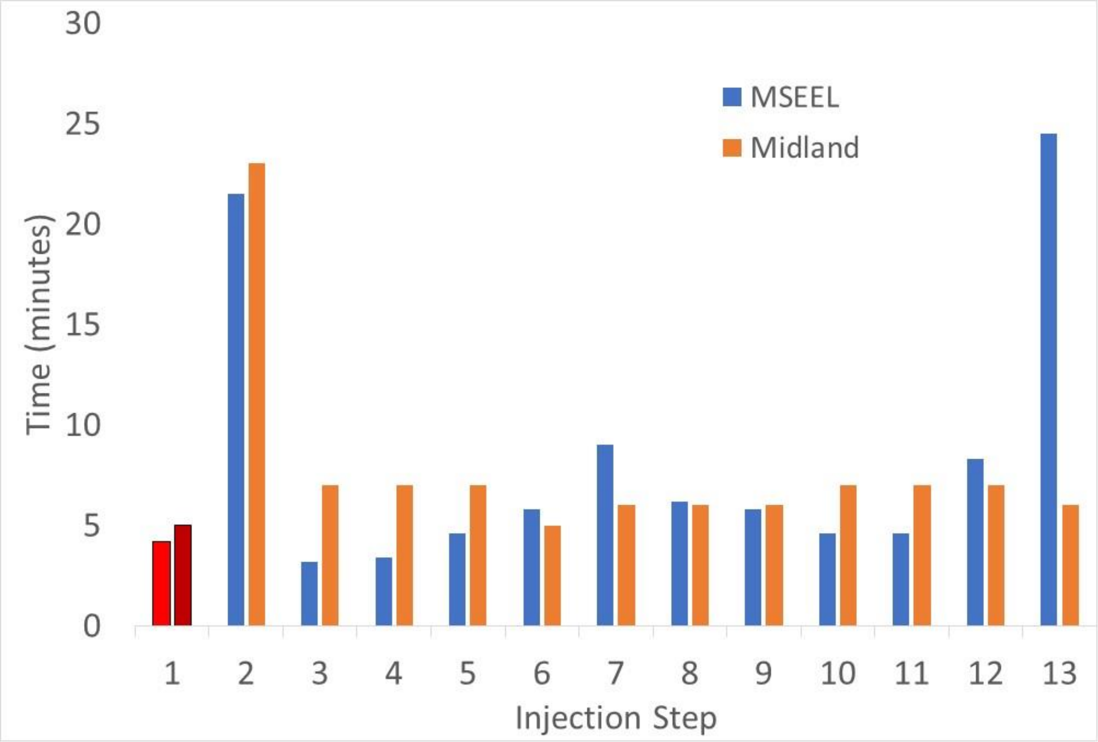
45. John R. Bargar, Adam D. Jew, Anna L. Harrison, Andrew Kiss, Arjun Kohli, Qingyun Li, Katherine Maher, and Gordon E. Brown, Jr., (2017) Geochemistry of Shale-Fluid Reactions at Pore and Fracture Scales. Goldschmidt Geochemistry conference, Aug 16. (invited)

Appendix B: Injection Volumes and Schedule

Injection volumes and injection schedule for a typical injection stage for MSEEL and Midland Basin. Red colored bars are representative of the acid spearhead for each of the wells. The lower volume per stage for Permian Basin is due to the higher number of stages for a single well versus MSEEL (~100 stages/well Permian, ~17 stages/well MSEEL). Cumulative volumes for MSEEL and Midland wells are consistent, ~300,000 gallons. Midland and Delaware Basin injection schedule/volumes are similar.

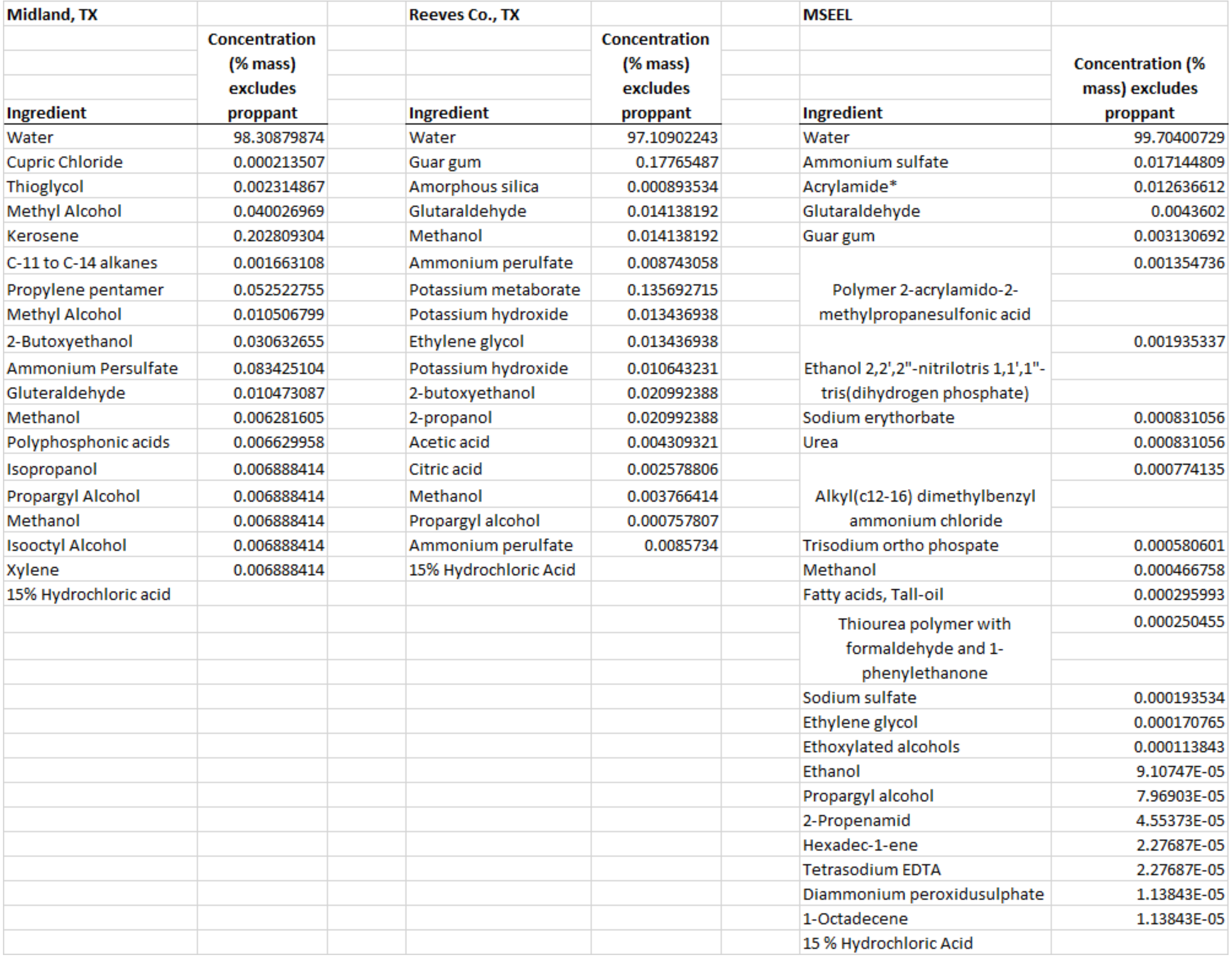





30
25
20
15
10
5
0
Time (minutes)
MSEEL
Midland
1
2
3
4
5
6
7
8
9
10
11
12
13
Injection Step

Appendix C: Stimulation Recipes

Stimulation recipes (slickwater) for three different regions Midland, TX (Midland Basin), Reeves Co., TX (Delaware Basin), and MSEEL (Marcellus). Recipes are considered to be average for each area. Chemical concentrations are normalized without silica proppant.



Midland, TX	
Ingredient	**Concentration (% mass) excludes proppant**
Water	98.30879874
Cupric Chloride	0.000213507
Thioglycol	0.002314867
Methyl Alcohol	0.040026969
Kerosene	0.202809304
C-11 to C-14 alkanes	0.001663108
Propylene pentamer	0.052522755
Methyl Alcohol	0.010506799
2-Butoxyethanol	0.030632655
Ammonium Persulfate	0.083425104
Gluteraldehyde	0.010473087
Methanol	0.006281605
Polyphosphonic acids	0.006629958
Isopropanol	0.006888414
Propargyl Alcohol	0.006888414
Methanol	0.006888414
Isooctyl Alcohol	0.006888414
Xylene	0.006888414
15% Hydrochloric acid	

Reeves Co., TX	
Ingredient	**Concentration (% mass) excludes proppant**
Water	97.10902243
Guar gum	0.17765487
Amorphous silica	0.000893534
Glutaraldehyde	0.014138192
Methanol	0.014138192
Ammonium perulfate	0.008743058
Potassium metaborate	0.135692715
Potassium hydroxide	0.013436938
Ethylene glycol	0.013436938
Potassium hydroxide	0.010643231
2-butoxyethanol	0.020992388
2-propanol	0.020992388
Acetic acid	0.004309321
Citric acid	0.002578806
Methanol	0.003766414
Propargyl alcohol	0.000757807
Ammonium perulfate	0.0085734
15% Hydrochloric Acid	

MSEEL	
Ingredient	**Concentration (% mass) excludes proppant**
Water	99.70400729
Ammonium sulfate	0.017144809
Acrylamide*	0.012636612
Glutaraldehyde	0.0043602
Guar gum	0.003130692
Polymer 2-acrylamido-2-methylpropanesulfonic acid	0.001354736
Ethanol 2,2',2"-nitrilotris 1,1',1"-tris(dihydrogen phosphate)	0.001935337
Sodium erythorbate	0.000831056
Urea	0.000831056
Alkyl(c12-16) dimethylbenzyl ammonium chloride	0.000774135
Trisodium ortho phospate	0.000580601
Methanol	0.000466758
Fatty acids, Tall-oil	0.000295993
Thiourea polymer with formaldehyde and 1-phenylethanone	0.000250455
Sodium sulfate	0.000193534
Ethylene glycol	0.000170765
Ethoxylated alcohols	0.000113843
Ethanol	9.10747E-05
Propargyl alcohol	7.96903E-05
2-Propenamid	4.55373E-05
Hexadec-1-ene	2.27687E-05
Tetrasodium EDTA	2.27687E-05
Diammonium peroxidusulphate	1.13843E-05
1-Octadecene	1.13843E-05
15 % Hydrochloric Acid	

Appendix D: Recipes for Base Fluids

Recipes for two different base fluids: Monongahela River and Clean Brine. Clean Brine is based on average values measured in Marcellus flowback water minus organics from Paukert Vankeuren, *et al*. (2017). Thermodynamic modeling of Ba and SO_4 concentrations for the Clean Brine indicates that 7% of Ba will precipitate as barite.

ION	FRESH WATER	CLEAN BRINE
	(mM)	(mM)
B^{3+}		0.7
Al^{3+}		0.01
Fe^{3+}		0.02
Ba^{2+}		2
Ca^{2+}	0.3	50
Mg^{2+}	0.4	8.7
Sr^{2+}		5.1
NH_4^+		3
K^+	0.1	2.9
Na^+	1.63	300
SO_4^{2-}	0.7	1.5
NO_3^-	0.05	1
Br^-		1.8
Cl^-	1.5	430
HCO_3^-	3	0.18
pH	7	6

Paukert Vankeuren, A. N.; Hakala, J. A.; Jarvis, K.; Moore, J. E. Mineral Reactions in Shale Gas Reservoirs: Barite Scale Formation from Reusing Produced Water As Hydraulic Fracturing Fluid. *Environ. Sci. Technol.* **2017**, *51* (16), 9391–9402.