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Laboratory-Scale Studies on Chemical Reactions Between Fracturing Fluid and Shale Core from the Marcellus Shale Energy and Environmental Laboratory (MSEEL) Site

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Abstract

Injection of fracturing fluids into shales during hydraulic stimulation can result in various chemical reactions involving the injected fluid and host shale rock. Differences in chemical composition between the injected fluids and fractured rock can result in mineral precipitation along shale fractures and within the shale matrix, potentially affecting long-term gas recovery from the shale. Our prior research showed that mineral precipitation and dissolution occur along freshly-generated fractures, and within the shale matrix, during core flood experiments in which laboratory-fractured Marcellus Shale was exposed to simulated hydraulic fracturing fluids. Many of the mineral precipitation reactions were hypothesized to occur due to the inability for antiscaling compounds in the fracturing fluids to control mineral precipitation at elevated temperature and pressure. In some locations along the fracture, proppant was cemented to shale surfaces through secondary mineral precipitates. The present study focuses on core flood experiments using fresh core and site hydraulic fracturing fluid from the Marcellus Shale Energy and Environmental Laboratory site (MSEEL; Morgantown, WV) at reservoir pressure and temperature conditions. The objectives of this study are to evaluate the reproducibility of the earlier experiments using fresh core, and to identify causes for any observed differences with the prior outcrop-based experiments.

Introduction

Introduction of fracturing chemicals into shale formations can initiate chemical reactions that result in shale mineral dissolution and precipitation of secondary minerals within the shale matrix and along newly-generated fractures. These reactions can affect matrix and fracture permeability by generating new flow pathways in the case of mineral dissolution. Secondary mineral precipitation could be both beneficial and detrimental to gas flow within the reservoir, as depending on the mineral morphology and location, precipitation could result in additional propping of fractures, or could reduce matrix and fracture permeabilities. Recent attention to fracturing chemical-mineral reactions that could affect gas production have shown that both the formation mineralogy and injected fluid chemistry have a significant influence on the overall chemical changes during hydraulic fracturing. Barite has been of interest in the Marcellus Shale due to elevated concentrations of barium measured in produced waters and the shale. Barite scale in the wrong locations within the system can present a significant challenge for sustained long-term production as barite dissolution and removal are difficult and potentially costly.

Prior batch experimental studies focused on reactions between Marcellus Shale and fracturing fluids showed that, in the presence of elevated barium and fracturing chemicals, barite precipitation was either directly observed or predicted based on saturation indices calculations from experimental fluid chemistries (Dieterich et al., 2015; Marcon et al., 2017). In core flood experiments performed with laboratory-generated fracturing chemicals and core plugs derived from Marcellus Shale outcrop, barite precipitation was observed by computed tomography (CT) and scanning electron microscopy (SEM). Barite is also predicted based on saturation indices calculations with fluid chemistry, for fracturing fluids generated with both freshwater and recycled produced water compositions as the carrier fluid (Vankeuren et al., under review). In these experiments, barium was either leached from the shale (in the case of freshwater-based fracturing fluid) or present in the initial fracturing fluid (in the case of produced water-based fracturing fluids). Sulfate was generated through reaction of the ammonium persulfate breaker, and to a lesser extent, oxidation of pyrite in the shale. Replicate experiments designed to verify the Vankeuren (under review) study, and the integrity of the experimental system used for the present study, showed similar results (Moore et al., 2017)

The Marcellus Shale Energy and Environmental Laboratory (MSEEL) is a gas-producing research well located in Morgantown, West Virginia operated by North Northeast Energy (NNE) and managed by West Virginia University (WVU) as one of the National Energy Technology Laboratory/U.S. Department of Energy (NETL/DOE) hydraulically-fractured shale field sites. The site includes a production well that was vertically cored (MIP 3H) and hydraulically stimulated during November 2015. Samples from MSEEL include fresh core and fracturing chemical mixtures actually used on site, which can provide a new perspective on potential mineral reactions during hydraulic fracturing, as our prior studies were performed with a lab-generated fracturing fluid and Marcellus Shale core plugs extracted from outcrop samples. The focus for this study was to evaluate mineral dissolution and precipitation in MSEEL 3H core samples reacted with a sample of the hydraulic fracturing fluid developed for fracturing of the MIP 3H well (November 2015).

Methods

Experimental Design and Apparatus

Experiments were designed to represent diffusive flow and reaction of hydraulic fracturing fluids with the shale reservoir rock over a simulated four-day shut in period. The apparatus consisted of a dual core holder system, with an inlet reservoir leading to an injection pump (Figure 1). Fluids were introduced into a Hassler type core holder, which contained shale cored from MSEEL 3H samples for evaluating fluid-rock interactions, or remained empty for procedural blank tests. Injection was performed with a solvent pump at a constant rate, overburden pressure was maintained with a confining pump, and a back-pressure pump controlled system pressure and acted as the effluent reservoir. Fluids were sampled from the influent and effluent reservoirs for evaluating changes to fluid chemistry from the experimental apparatus (in the case of the system blank test) and fluid-rock interactions (in experiments containing MSEEL core). The confining reservoir chemistry was sampled and monitored to ensure a no flow boundary was maintained between the core sleeve and end plugs. Experiments and blank tests were performed at 150°F, 3000 psi confining pressure, 2800 psi pore pressure, and a fluid flow rate of 0.03 ml/min. Injected fluid was chilled to 5°C for the duration of the test to avoid microbial growth. Two core flood experiments were performed with MSEEL core, and one experiment was performed where 3H injection fluid was circulated through the experimental apparatus in the absence of core (referred to as the “blank experiment” in the results and discussion).

Core Selection, Preparation, and Hydraulic Fracturing Fluid

Two depths of the MSEEL 3H core were selected based on location associated with hydraulic fracturing of the 3H well, and based on the ability to sub-core from the existing slabs: 7498.4 ft, and 7504.6 ft. These samples were chosen because they were the most competent sections of core near the lateral kick off point, which was slightly lower at approximately 7500 ft. Samples were cut from 2/3 slab and core was drilled bedding concordant. Drilling performed perpendicularly to the bedding plane resulted in core disking. The 1.5 inch diameter samples were cored with at least 4 inches total length and fractured by a modified Brazilian method (Atkinson et al., 1982); the cores were in two 2” long sections each as even the concordant cores tended to break. Fractures were filled with less than a single monolayer of 40/70 mesh >99% quartz Innoprop proppant, and loaded into core sleeves. Hydraulic fracturing fluid used for the experiments was sampled from the batch of fracturing fluid injected into the MIP 3H well during fracturing (date range 11/6/2015 through 11/15/2015). The composition of the fracturing fluid is presented in Table 1. A pump malfunction occurred at 24 h for the 7498.4 ft experiment resulting in a higher flow rate through the experimental apparatus, which resulted in a higher volume accumulation in the effluent reservoir and may result in some differences of fluid chemistry measured at 24 and 48 h for this experiment.

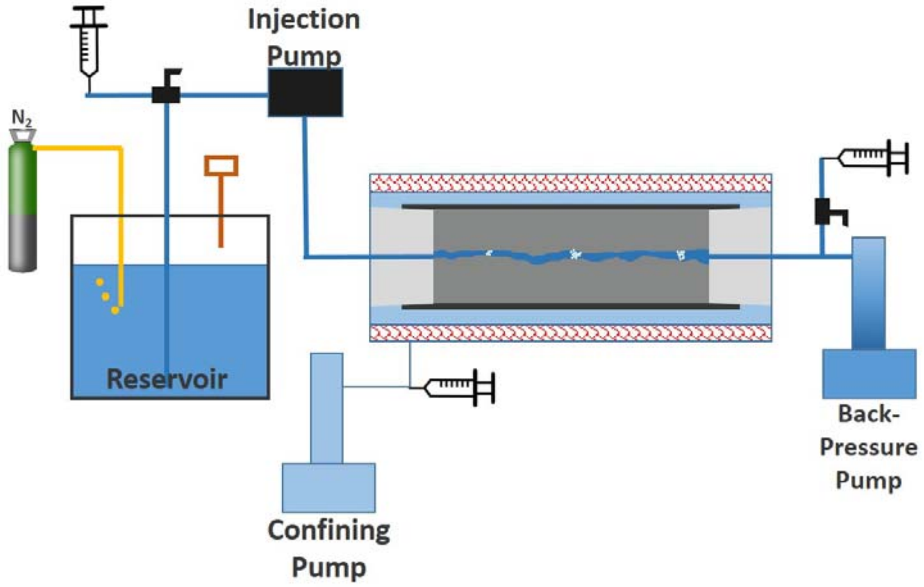

Figure 1: Schematic of experimental apparatus

Fluid Chemistry Analysis

Fluid sample analysis was performed by ion chromatography (IC), inductively coupled plasma mass spectrometry (ICP-MS), and inductively coupled plasma optical emission spectroscopy (ICP-OES). Influent and effluent reservoir fluids were sampled according to the following schedule after introduction of fluids into the experimental apparatus: 2, 24, 48, 72, and 96 h. Samples for IC analysis were filtered through 0.2 µm membrane and not-acidified, and samples for ICP-MS and ICP-OES samples were unfiltered and acidified with ultrapure nitric acid (Thermo Fisher, Optima grade) prior to analysis. The pH of the influent and effluent reservoir fluids were monitored during sampling. The temperature of fluids when sampled from the collection reservoir ranged from 21.25 ± 2.42 °C for the blank and both core-containing experimental runs.

Computed Tomography Scanning and Image Processing

The 3H cores were scanned before and after exposure with a North-Star Imaging M-5000 Industrial Computed Tomography (CT) scanner. Voxel resolution was 25.4 µm. Image processing was performed using ImageJ$^{©}$ and ilastik$^{®}$. No discernable features of interest, which included reacted zones and precipitate, were detected using traditional or advanced techniques. Thus, post-processing of the images was not performed in a quantitative fashion.

Table 1: Hydraulic Fracturing Fluid Product Component Disclosure for MIP 3H Well from FracFocus.org

Trade name	Supplier	Purpose	Ingredients	Chemical Abstract Service Number (CAS #)	Maximum Ingredient Concentration in Additive (% by mass)	Maximum Ingredient Concentration in HF Fluid (% by mass)
Proppant Transport	Schlumberger	Corrosion Inhibitor, Scale Inhibitor, Biocide, AntiFoam Agent, Acid, Breaker, Gelling Agent, Friction Reducer, Iron Control Agent, Fluid Loss Additive				
			Water (Including Mix Water Supplied by Client)	N/A		87.63568
			Quartz, Crystalline silica	14808-60-7	99.06784	12.21724
			Hydrochloric acid	7647-01-0	0.66726	0.08228
			Ammonium sulfate	7783-20-2	0.06845	0.00844
			Guar gum	9000-30-0	0.05865	0.00724
			Acrylamide, 2-acrylamido-2-methylpropanesulfonic acid, sodium salt polymer	38193-60-1	0.05052	0.00623
			Glutaraldehyde	111-30-8	0.02831	0.00349
			Ethanol, 2,2’,2”-nitrolis-1,1’,1”-tris(dihydrogen phosphate), sodium salt	68171-29-9	0.00971	0.00120
			Diammonium peroxidisulphate	7727-54-0	0.00601	0.00074
			Polymer of 2-acryalmido-2-methylpropanesulfonic acid sodium salt and methyl acrylate	136793-29-8	0.00541	0.00067
			Alkyl(c12-16) dimethylbenzyl ammonium chloride	68424-85-1	0.00506	0.00062

Table 1, continued

Trade name	Supplier	Purpose	Ingredients	Chemical Abstract Service Number (CAS #)	Maximum Ingredient Concentration in Additive (% by mass)	Maximum Ingredient Concentration in HF Fluid (% by mass)
			Sodium erythorbate	6381-77-7	0.00436	0.00054
			Trisodium ortho phosphate	7601-54-9	0.00427	0.00053
			Urea	57-13-6	0.00332	0.00041
			Polypropylene glycol	25322-69-4	0.00294	0.00036
			Methanol	67-56-1	0.00252	0.00031
			Fatty acids, tall-oil	61790-12-3	0.00156	0.00019
			Thiourea, polymer with formaldehyde and 1-phenylethanone	68527-49-1	0.00129	0.00016
			Ethylene glycol	107-21-1	0.00121	0.00015
			Non-crystalline silica (impurity)	7631-86-9	0.00084	0.00010
			Vinylidene chloride/methylacrylate copolymer	25038-72-6	0.00080	0.00010
			Sodium sulfate	7757-82-6	0.00078	0.00010
			Alcohols, C14-15, ethoxylated (7EO)	68951-67-7	0.00061	0.00008
			Ethanol	64-17-5	0.00061	0.00007
			Propargyl alcohol	107-19-7	0.00041	0.00005
			2-Propenamid (impurity)	79-06-1	0.00017	0.00002
			Hexadec-1-ene	629-73-2	0.00014	0.00002
			1-Octadecene (C18)	112-88-9	0.00007	0.00001
			Dimethyl siloxanes and silicones	63148-62-9	0.00005	0.00001
			Tetrasodium ethylenediaminetatraacetate	64-02-8	0.00009	0.00001
			Dodecamethylcyclohexasiloxane	540-97-6		
			Poly(tetrafluoroethylene)	9002-84-0	0.00001	
			Formaldehyde	50-00-0	0.00001	
			Copper(II) sulfate	7758-98-7		
			Decamethyl cyclopentasiloxane	541-02-6		
			Magnesium silicate hydrate (talc)	14807-96-6	0.00002	
FR Pro 150	ECM	Friction Reduction				
			Water	7732-18-5	50.00000	0.01575

Table 1, continued:

			Polyacrylamide-co-acrylic acid	9003-06-9	32.00000	0.01008
			Sodium chloride	7647-14-5	15.00000	0.00472
			Alcohol ethoxylate surfactants	Trade	5.00000	0.00157
			Petroleum distillate	64742-47-8	25.00000	

Results

Calcium shows an increase in the MSEEL 7504.6 ft and 7498.4 ft core flood experiments relative to the influent and blank effluent Ca concentrations (Figure 2A,C). The effluent pH value for the MSEEL 7504.6 ft experiment was consistently lower compared to the pH of the influent and blank effluent, and the pH of the influent and effluents for the blank and MSEEL 7498.4 ft experiment remained within the same range (Figure 2B,D). The influent pH remained between 7.56 ± 0.37. The blank effluent pH ranged from 7.30 ± 0.06, the MSEEL 7504.6 ft effluent pH ranged between 6.89 ± 0.06, and the MSEEL 7498.4 ft effluent pH ranged from pH: 7.09 ± 0.12. Elevated Ca in effluent from the MSEEL core flood experiments, along with lower pH, suggests that Ca-bearing mineral dissolution (likely calcite) occurred during the experiments concurrently with chemical reactions that caused a pH decrease.

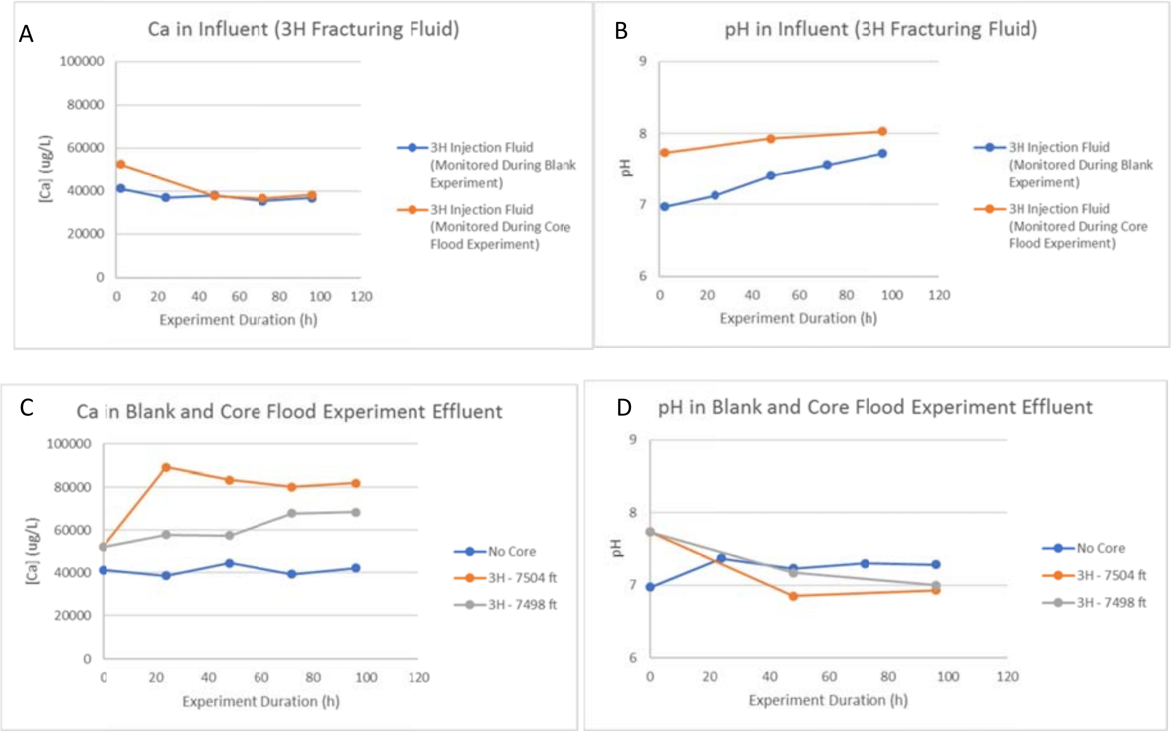

Figure 2: Calcium (A,C) and pH (B,D) for the influent, blank, and core flood experiments with MSEEL 7504.6 ft and 7498.4 ft cores. Lines are included to show the data trend and do not constitue a fit of the data. The influent data show changes to the 3H injection fluid over the time frame of the experiment, prior to introduction into the experimental system (A,B). The blank and core flood panels show changes in effluents for experiments with and without core (C,D). The 0 hour time point in plots C and D represents the value for the influent for more direct comparison of changes in fluid chemistry detected in the effluent.

Barium and strontium are both present in the fracturing fluid and do not vary significantly in the influent during the course of the experiment (Figure 3A,B). Barium concentrations during the MSEEL 7504.6 ft experiment were similar to the core-free blank experiment, suggesting that Ba behavior in the system was mainly influenced by existing Ba within the experimental apparatus. This likely is residual barite precipitate that was difficult to remove during cleaning of the apparatus after prior experiments (Figure 3C). The elevated initial Ba concentrations in the MSEEL 7498.4 ft experiment reflect influences of the pump malfunction on the solution composition (Figure 3C). Strontium exhibits similar trends in the MSEEL core flood effluents as with the blank effluent, which may result from chemical memory effects in the experimental system (Figure 3B,D).

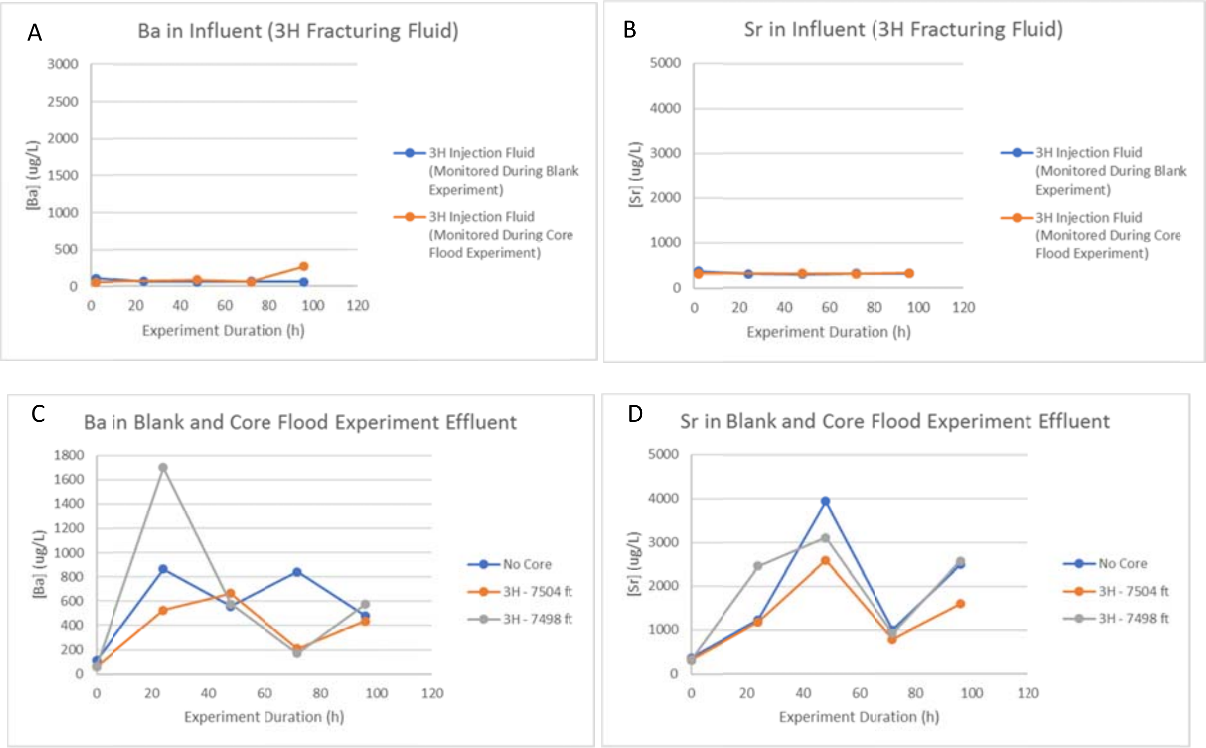

Figure 3: Barium and strontium chemistry for the influent (A,B) and the blank and core flood experiments with MSEEL 7504.6 ft and 7498.4 ft cores (C,D). Lines are included to show the data trend and do not constitue a fit of the data. The influent data show changes to the 3H injection fluid over the time frame of the experiment, prior to introduction into the experimental system (A,B). The blank and core flood panels show changes in effluents for experiments with and without core (C,D). The 0 hour time point in plots C and D represents the value for the influent for more direct comparison of changes in fluid chemistry detected in the effluent.

Sulfate concentrations for both MSEEL core flood effluents are elevated relative to the blank, and show similar trends over time (Figure 4A,B). The control experiment sulfate concentrations remain similar to the influent concentration, suggesting minimal contribution of sulfate from the experimental apparatus to the fluid chemistry (Figure 4A,B).

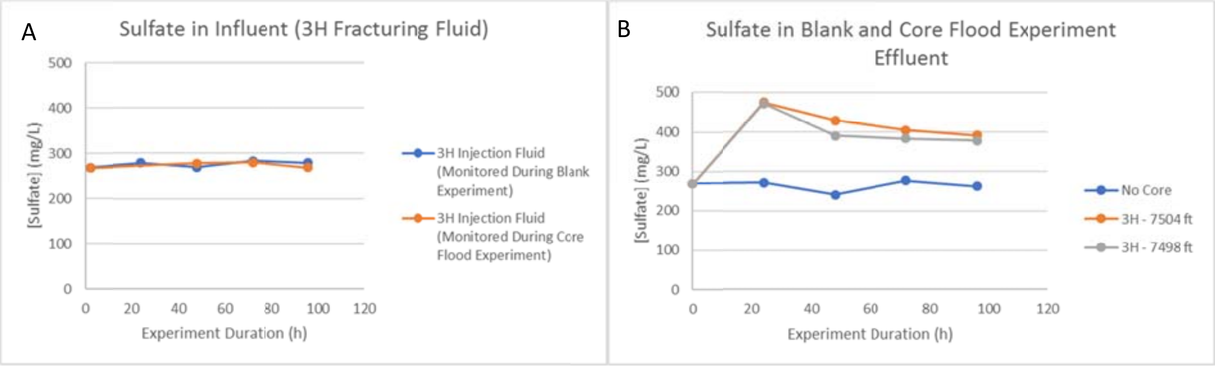

Figure 4: Sulfate concentrations for the influent (A) and blank and core flood effluents (B). Lines are included to show the data trend and do not constitue a fit of the data. The influent data show changes to the 3H injection fluid over the time frame of the experiment, prior to introduction into the experimental system (A). The blank and core flood panels show changes in effluents for experiments with and without core (B). The 0 hour time point in plot B represents the value for the influent for more direct comparison of changes in fluid chemistry detected in the effluent.

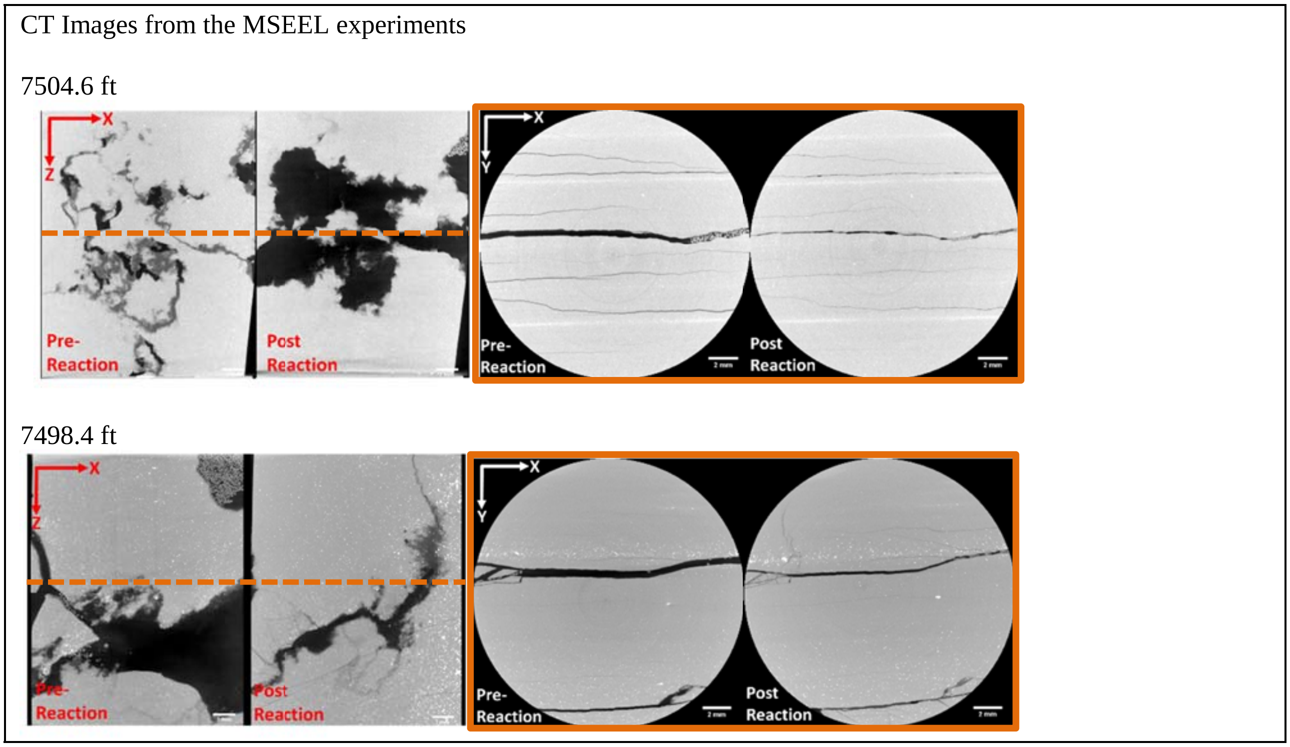

Figure 5: CT grayscale images of the rock cores before and after reaction. Images on the left are looking perpendicular to the fracture plane while images on the right are looking parallel to the fracture or along flow direction. Apertures variation is a result of the pre-reaction scans being done before confining pressure and post reaction scans after confining pressure was applied and then released. Brighter elements within the images are proxies for highly attentuating minerals whileas dark sections are filled with air or water.

Discussion

Evidence for barite precipitation was not observed, either in the fluid chemistry or the CT images of the experiments with the MSEEL MIP 3H core. CT images did not show any variation in matrix attenuation (grayscale) nor did it show any additional mass gained along the fracture margin as was observed in previous experiments.

Influence from memory effects of Ba and Sr within the experimental apparatus prevents further interpretation of Ba and Sr mineral scale chemistry resulting from fracturing fluid-shale reactions in the MSEEL experiments presented here. This differs significantly from prior experiments with Marcellus Shale outcrop core reacted with lab-generated fracturing fluids, where barite and Sr-bearing carbonate secondary precipitation was observed within the core (Vankeuren et al., under review). However, precipitation at the core inlet also was observed (Vankeuren et al., under review), and a check of barite saturation indices with MINTEQ for the 2h time point of the 3H injection fluid and blank effluent show that both fluids are saturated with barite.

The blank and MSEEL core flood experiments do show elevated solution-phase Ba and sulfate. Although mineral scale is expected to form in the presence of elevated solution-phase Ba and sulfate, other fluid-phase species may affect barite solubility. Examples include the concentration of total dissolved solids present in solution, and the presence of organic acids and antiscalant compounds, which can increase barite solubility. Similar interpretations were presented in prior studies performed with Marcellus Shale in batch experiments (Marcon et al., 2017) and in barite solubility studies (Edenborn et al., 2016; He and Vidic, 2016: Hakala et al., 2017).

Differences in the influent fluid chemistry between the MSEEL experiments in this study, and prior experiments performed with Marcellus Shale outcrop, also may explain differences in the experimental results. A Schlumberger chemical treatment was applied to the MIP 3H well, while the prior experiments applied a fracturing fluid design based on results from a review of FracFocus data, and generated with fracturing chemicals supplied by a different service company (Vankeuren et al., in review; Moore et al., 2017). The fracturing fluid mixtures between the MSEEL and prior experiments therefore contained different fracturing chemicals, and different concentrations of fracturing chemicals where similarities existed. For example, ammonium persulfate, considered to significantly control sulfate generation and resulting barite precipitation in the prior experiments, is present in different concentrations in the lab-generated solution from prior experiments and the MIP 3H fracturing fluid. Ammonium persulfate was 0.02% of solution in the experiments performed by Vankeuren et al (under review) and Moore et al. (2017). In the experiments reported here, the maximum amount of ammonium persulfate in solution is 0.00074% by mass, and likely was lower during our MSEEL core flood experiments (performed during March 2017) due to oxidant degradation during storage after the November 2015 preparation of fracturing fluid at the well pad.

Sulfate is present in the influent due to existing concentrations in the make-up water, and due to addition of fracturing chemicals (such as ammonium persulfate, and copper sulfate; Table 1). Sulfate increases in both MSEEL core flood experiments, and does not change in the blank experiment relative to the influent concentration (Figure 4A,B), indicating that reaction between the influent and cores resulted in sulfate generation. Sulfate can be generated from the fracturing fluid and from reactions with minerals in the shale. Shale mineral reactions likely to generate sulfate concentrations observed in the MSEEL experiments include ion exchange, gypsum dissolution and pyrite oxidation. Sulfate release via ion exchange was observed in ultrapure water extracts of MIP 3H sidewall cores (Hakala et al., 2017). Because of the slight pH decrease observed in the MSEEL core flood effluents, pyrite oxidation is also a potential contributor to sulfate in the system as the reaction produces sulfate and lowers the solution pH. Pyrite may oxidize due to the presence of oxygen (Eq. 1) or Fe^{3+} (Eq. 2) in solution (Rimstidt and Vaughan, 2003).

$$FeS_2 + 3.5O_2 + H_2O = Fe^{2+} + 2H^+ + 2SO_4^{2-} \qquad \text{Equation 1}$$

$$FeS_2 + 14Fe^{3+} + 8H_2O = 15Fe^{2+} + 16H^+ + 2SO_4^{2-} \qquad \text{Equation 2}$$

Lowering of the pH concurrent with increases in Ca concentrations in the MSEEL core flood effluents provides evidence for calcite dissolution, which has been observed in prior batch and core flood experiments with Marcellus Shale (Dieterich et al., 2016; Marcon et al., 2017; Vankeuren et al., under review). Concurrent calcite dissolution during pyrite oxidation within shales has been observed in other studies focused on shale-fracturing fluid interactions (Wilke et al., 2015).

Conclusions

Composition of the hydraulic fracturing fluid will affect observed secondary mineral precipitates that form in newly-generated fractures and the shale matrix. The presence of oxidants, especially persulfate-based compounds, can have a significant effect on scale mineral precipitation; certain reactions may not be observed if the oxidant isn't as active, or in a low concentration. Concurrent pyrite oxidation and calcite dissolution occur in the MSEEL core flood experiments. The MSEEL core flood experiments showed no change between the pre- and post-reaction CT scans, indicating a difference in fracturing fluid-shale reactions that result in mineral scale formation, compared to prior studies. Further characterization of the shale post-reaction is planned. Additional studies exploring interactions between fracturing fluids and shale involving a range of concentrations of specific fracturing chemicals will provide information on how to best control mineral scale formation during hydraulic fracturing of shale gas reservoirs.

Acknowledgements

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