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Full Length Article

Characterization of Marcellus Shale and Huntersville Chert before and after exposure to hydraulic fracturing fluid via feature relocation using field-emission scanning electron microscopy

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ABSTRACT

Two sets of experimental *in situ* fluid–rock interaction studies were implemented to understand the interactions between hydraulic fracturing fluid and rocks of the Marcellus Shale gas play. Marcellus Shale and Huntersville Chert core samples were exposed to synthetically prepared fracturing fluid and recycled fracturing fluid from the field, respectively, and examined before and after *in situ* exposure using surface relocation techniques via high-resolution field-emission scanning electron microscopy (FE-SEM) to investigate chemical or physical alterations.

Results indicate that *in situ* pressure promoted fracture growth along the sedimentological (horizontal) bedding plane of the Marcellus Shale samples. Moreover, calcium carbonate ($CaCO_3$) dissolution was observed and gypsum ($CaSO_4 * 2H_2O$) appeared to precipitate both on the surface and in the numerous fractures. Barite ($BaSO_4$), strontianite ($SrCO_3$), celestine ($SrSO_4$), and apatite ($CaPO_4$) formed a unique pattern of precipitates on the surface of the Huntersville Chert samples. Additionally, Rhenium and rare earth element (REE) Europium were identified in minerals which precipitated on the Huntersville Chert surface identified by FE-SEM spectral analysis.

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1. Introduction

The Appalachian Basin covers numerous states in eastern North America including New York, Pennsylvania, Ohio, Maryland, West Virginia, Kentucky, Tennessee, and Alabama. Overall, the Appalachian Basin as a whole covers an aerial extent of 185,500^2 miles, is 1075 miles long, and ranges from 20 to 310 miles wide [22]. The hydrocarbon bearing Marcellus Shale Formation located within the Appalachian Basin spans 600 linear miles [6]. The less laterally extensive Huntersville Chert formation is located in west-central Pennsylvania within the Appalachian Basin and underlies the Marcellus Shale Formation [11]. In order to access the hydrocarbons stored in the Marcellus Shale directional drilling and hydraulic fracturing is implemented.

Hydrocarbon exploration of the Marcellus Shale has resulted in over 12,000 permitted wells in Pennsylvania between 2005 and 2012 [27]. According to Vidic et al. [27] these 12,000 wells produced between <0.1 and >20 million cubic ft/day of natural gas. Importantly, the Marcellus Shale can sustain the United States natural gas demand for approximately 15 years if usage remains the same at 23 trillion cubic ft/year [23]. Due to the increase in drilled wells and high volumes of fluid utilized during hydraulic fracturing, experimental studies are required to determine whether chemical and physical alteration of Marcellus Shale and confining geologic formations occurs as residual fracturing fluid remains in the subsurface. Marcellus Shale well stimulation which utilizes a component of recycled flowback water can benefit from understanding the chemical and physical effects of fluid–rock interactions. For instance, determining alterations caused by the stimulation process with a recycled fluid component in Marcellus Shale production may improve fracturing fluid recipes based upon well-specific geochemistry to maximize hydrocarbon production.

Hydraulic fracturing of geologic formations has been utilized for the production of hydrocarbons across the United States since the 1940s [15]. Modern hydraulic fracturing techniques are applied to both vertical and horizontal wells, with the majority being unconventional horizontal wells in tight organic-rich shale formations such as the Marcellus and Utica Shales of the Appalachian Basin in the northeastern United States. In order to successfully hydraulically fracture one horizontal Marcellus Shale well for hydrocarbon production, between 2 and 7 million gallons of water is required [12].

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Horizontal well stimulation of the hydrocarbon bearing Appalachian Basin Middle Devonian Marcellus Shale involves large volumes of hydraulic fracturing fluid that interacts with formation water and mineral surfaces within the subsurface [19,9]. During stimulation, between 47% and 91% of the fracturing fluid remains in the subsurface while 9–53% returns out of the wellbore as flowback water [8,27]. Fracturing fluid remaining in the subsurface can possibly alter petrophysical characteristics including surface area, porosity, and mineralogy of the host formation that may inhibit hydrocarbon permeability [19]. Captured flowback water is typically recycled into additional fracturing fluid for well stimulation [21,2]. Fracturing fluid is created by mixing high volumes of water with additives such as biocides, friction reducers, and proppants. The fluid is subsequently forced downhole under high pressure and into the target geologic formation. Once the target formation has been hydraulically stimulated, the fracturing fluid can return to the Earth's surface as flowback water for containment, but a portion of the fracturing fluid remains in the subsurface. On average 10% of the fracturing fluid used to stimulate a horizontal Marcellus Shale well returns as flowback [27], which means millions of gallons of fluid remain in the subsurface. The chemical and physical effects of the fracturing fluid remaining in the subsurface is uncertain, although shale absorption of the fluid through imbibition is one proposed hypothesis [19,9].

Flowback water from Marcellus Shale wells represents an environmental concern due to high salinity, total dissolved solids (TDS), and leachates from naturally occurring radioactive material (NORM) [12,7,1,5,10,3,24]. As a result of the complex chemistry and environmentally hazardous nature of flowback water, costly treatment was previously conducted via transportation to waste water facilities capable of handling high TDS fluids. Currently, service companies are recycling the flowback water for subsequent well stimulation [21,2]. This process of utilizing recycled fluid for hydraulic fracturing requires additional research to understand the effect of elevated TDS fluids on the target formation.

The objective of this study was to identify chemical and physical alterations of solid core from the Marcellus Shale and Huntersville Chert (Onondaga Limestone) after interaction with fracturing fluid, as determined via feature relocation using field emission-scanning electron microscopy (FE-SEM). Both short-term (effects of fracturing fluid initially entering the subsurface) and long-term (effects of fracturing fluid remaining in the subsurface) scenarios were examined. Investigating fluid impact on Huntersville Chert in addition to the Marcellus was performed because Marcellus Shale wells in Pennsylvania are commonly drilled through a segment of the underlying chert/limestone in order to acquire "conservation well" status. Therefore, Huntersville Chert underlying the Marcellus Shale can be exposed to hydraulic fracturing fluid during well stimulation. Experiments were conducted to determine whether the rock structure changes upon interaction with fracturing fluid via mineral dissolution, precipitation, or chemical etching. This study also aimed to characterize chemical precipitates which formed during fluid contact.

2. Materials and methods

2.1. Rock

Rock core utilized during this experiment was retrieved in September 2008 from a well site located in Greene County, Pennsylvania [4]. The main core sample was stored under atmospheric conditions until 2014. Subset samples of Marcellus Shale and Huntersville Chert were collected from the middle of the core in order to remove material directly in contact with the atmosphere. The samples were then immediately placed inside a nitrogen desiccator to prevent atmospheric alteration. Throughout the experiments utmost care was taken to limit atmospheric exposure of the rock samples.

2.1.1. Marcellus Shale

The Marcellus Shale sample was obtained from a depth of 7801 ft (2378 m) and is classified as a grayish black shale. The shale was split into two pieces with a Buehler IsoMet low speed rock saw with a diamond blade. The samples were only exposed to the atmosphere long enough for cutting and analysis to take place. For storage between analyses the samples were placed in a nitrogen desiccator. One piece of the core was cut parallel to the sedimentary bedding plane denoted as "Marcellus Shale parallel cut" (Fig. 1), and the second piece was cut transverse to the sedimentary bedding plane to expose an edge-on facies denoted as "Marcellus Shale transverse cut" (Fig. 2). Cutting the core sample into two bedding planes allowed detailed electron microscopy studies to be conducted for both mineralogical surface orientations which encounter fracturing fluid during stimulation. Both Marcellus Shale samples had the internal rock face polished to allow for higher resolution FE-SEM images. For the parallel and transverse samples, 5 locations were captured per sample via FE-SEM (10 sites in total).

2.1.2. Huntersville Chert (Onondaga Limestone)

The Huntersville Chert sample (Fig. 3) was obtained from a depth of 7909.7 ft (2410 m) and is classified as a dark gray calcareous/argillaceous chert. The chert was split into two pieces with a Buehler IsoMet low speed rock saw with a diamond blade. The samples were only exposed to the atmosphere long enough for cutting and analysis to take place. For storage between analyses the samples were placed in a nitrogen desiccator. One piece of the core was cut parallel to the sedimentary bedding plane and the second piece was cut transverse to the sedimentary bedding plane to expose an edge-on facies. Cutting the core sample into two bedding planes allowed detailed electron microscopy studies to be conducted for both mineralogical surface orientations. Both Huntersville Chert samples had the internal rock face polished to allow for higher resolution FE-SEM images and 5 locations per sample were captured via FE-SEM (10 sites in total).

2.2. Fracturing fluids

Two fracturing fluids were used during this study (1) a synthetic fracturing fluid for the Marcellus Shale experiments and (2) a field collected recycled fracturing fluid for the Huntersville Chert experiments. The Huntersville Chert experiments were conducted first and resulted in a layer of sulfate precipitate the rock surface, which obscured FE-SEM re-analysis. As our study aimed to investigate physical changes to the rock surface before and after fluid contact, we created a synthetic fracturing fluid leaving out sulfate and barium in order to leave the Marcellus Shale's rock surface unobscured for FE-SEM analysis.

2.2.1. Synthetic fracturing fluid

Synthetic fracturing fluid was used for Marcellus Shale fluid–rock interaction. The recipe is detailed in Table 1. The chemical composition of the synthetic fracturing fluid was modeled by Liu [18] after analyzing samples of fracturing fluids collected from a well site in Greene County, Pennsylvania (samples were collected by the U.S. Department of Energy) seen in Table 2. Three separate fracturing sites were sampled from the well-pad to provide average elemental concentrations for the synthetic fluid after inductively coupled plasma-optical emission spectroscopic (ICP-OES) and ion chromatographic (IC) analysis by Liu [18].