



# Degradation of hydraulic fracturing additive 2-butoxyethanol using heat activated persulfate in the presence of shale rock

Katherine E. Manz <sup>a, b</sup>, Kimberly E. Carter <sup>a, b, \*</sup>

<sup>a</sup> University of Tennessee/Oak Ridge National Laboratory Bredeesen Center, University of Tennessee, Knoxville, TN 37996, USA

<sup>b</sup> Department of Civil and Environmental Engineering, University of Tennessee, Knoxville, TN 37996, USA



## HIGHLIGHTS

- 2-BE (HF chemical) rapidly oxidizes via heat activated persulfate with iron present.
- Shale rock addition slows 2-BE degradation, despite increasing iron concentrations.
- During 2-BE degradation, persulfate may react with shale causing metal dissolution.

## ARTICLE INFO

### Article history:

Received 7 February 2018

Received in revised form

18 April 2018

Accepted 1 May 2018

Available online 4 May 2018

Handling Editor: Keith Maruya

### Keywords:

2-Butoxyethanol

Hydraulic fracturing

Shale rock

Persulfate

TDS

## ABSTRACT

Changes in fluid composition during hydraulic fracturing (HF) for natural gas production can impact well productivity and the water quality of the fluids returning to the surface during productivity. Shale formation conditions can influence the extent of fluid transformation. Oxidizers, such as sodium persulfate, likely play a strong role in fluid transformation. This study investigates the oxidation of 2-butoxyethanol (2-BE), a surfactant used in HF, by sodium persulfate in the presence of heat, pH changes, Fe(II), and shale rock. Increasing temperature and Fe(II) concentrations sped up 2-BE oxidation, while pH played little to no role in 2-BE degradation. The presence of shale rock impeded 2-BE oxidation with increasing shale concentrations causing decreasing pseudo-first-order reaction rate constant to be observed. Over the course of reactions containing shales, dissolved solids were tracked to better understand how reactions with minerals in the shale impact water quality.

© 2018 Elsevier Ltd. All rights reserved.

## 1. Introduction

Extracting oil and natural gas from unconventional shale reservoirs requires HF with high volumes of water mixed with chemical additives (Gregory et al., 2011; Chen and Carter, 2016). Chemical additives include surfactants and oxidizing breakers that likely transform during the fracturing process (Thurman et al., 2014; Kahrilas et al., 2016). Transformation of additives and shale may impact the flowback and produced water quality that returns to the surface during natural gas production.

HF wastewater spills are a concern due to potential contamination of water aquifers. While many chemicals have been

identified in hydraulic fracturing flowback and produced fluids, the transformed fluids are the source of pollution when spills occur. Surfactants are consistently found in HF waters (Kahrilas et al., 2016). 2-BE is a commonly identified surfactant found in HF additives including the foaming agent, Revert Flow (Stringfellow et al., 2014; Lewellyn et al., 2015; Rogers et al., 2015, 2017; DiGiulio and Jackson, 2016; Manz and Carter, 2016; Manz et al., 2016; Marcon et al., 2017). Revert Flow improves production by decreasing surface tension, thus preventing water blocking during the HF process. While the harsh physical conditions downhole may stimulate organic additive transformation, HF operators also use strong oxidizing agents such as persulfate salts (Gaillard et al., 2013; Stringfellow et al., 2014; Paukert Vankeuren et al., 2017). Persulfate has the potential to speed up and enhance transformations, therefore; persulfate is a key component to understanding how additives transform during the HF treatment of a well.

\* Corresponding author. University of Tennessee/Oak Ridge National Laboratory Bredeesen Center, University of Tennessee, Knoxville, TN 37996, USA.

E-mail address: [kcarte46@utk.edu](mailto:kcarte46@utk.edu) (K.E. Carter).

Addition of shale to persulfate reactions in the HF environment has not been previously investigated. Persulfate activation through increased formation temperatures and pressures has been previously investigated by the authors (Manz and Carter, 2017). As persulfate activation was observed under HF conditions (Manz and Carter, 2017), the shale constituents may impede or enhance the activation. For example, shale contains minerals that contain iron, which may activate persulfate (Ahmad et al., 2010) and enhance oxidation of additives. Minerals found in shale include pyrite, hematite, goethite, and limonite (Grim and Rowland, 1944; Marcon et al., 2017). Shale also contains minerals, such as chlorite and gypsum (Phan et al., 2018; Marcon et al., 2017), which may prevent oxidation of additives because these minerals contain carbonates (Liang et al., 2006).

The objective of this study is to address the potential persulfate activation using shale rock and the impact it has on 2-BE degradation and water quality. Fluid conditions that mimic those used during a fracture, including temperature, pH, iron, and shale rock, are systematically introduced. Further impacts persulfate usage has on HF water quality are evaluated through quantification of metals leached into solution during shale-activated reactions. Determination of 2-BE oxidation reactions with persulfate in the presence of shale will enable a better understanding of the impacts persulfate utilization has on flowback and produced water quality.

## 2. Experimental

### 2.1. Chemicals

Solutions were prepared using deionized water (Milli-Q Plus purification system, Darmstadt, Germany). Chemical used, including 2-BE (95%), Optima grade dichloromethane, ferrous sulfate (>99%), hydrochloric acid (35–38%), sodium persulfate (>98%), TraceMetal™ grade nitric acid, sodium persulfate (>98%), sodium bicarbonate (>99%), potassium iodide (>99%), and SPEX CertiPrep™ calibration standard 2 without mercury (5% nitric acid), were purchased from Fisher Scientific (Pittsburgh, PA 15275, USA). Revert Flow (RF) was received from Weatherford International (Houston, Texas, USA).

### 2.2. Shale rock

WV-7 shale rock used in this study was obtained from the Marcellus shale play at a depth of 6621.1 m (West Virginia Geological Survey, Morgantown, WV 26508, USA). The shale was crushed with a mortar and pestle and sieved to a mean diameter of 1.00–2.00 mm using No. 10 and 18 sized meshes. Bulk shale mineralogy was determined using X-Ray diffraction (XRD) and verified using acid digestion and inductively coupled plasma optical emission spectrometry (ICP-OES) analysis. Diffraction patterns were collected using a Panalytical Empyrean XRD with Cu source (Almelo, Netherlands) and ICP-OES data was collected with a ThermoFisher Scientific iCAP DUO 7400 (Waltham, MA 02451). Fig. S1 in the supporting information (SI) displays the resulting diffractogram of the unreacted WV7 shale and Fig. S2 displays the ICP digestions results. Bulk mineralogy of the shale is listed in Table 1 and contained calcite, dolomite, muscovite-2M1, rubidium zinc silicon oxide, pyrite, and quartz. Microscope observations were made using a Zeiss scanning electron microscope (SEM) (model EVO-MA15) equipped with an Energy-dispersive X-ray (EDS) detector (Bruker, model X Flash 6130).

### 2.3. Batch oxidation experiments

In HF practices, surfactants are used in total concentrations

ranging from 500 to 1800 mg L<sup>-1</sup> (Stringfellow et al., 2014), while the HF additive supplier suggested RF concentration of 1 gallon RF per 1000 gallons water (Manz and Carter, 2016). RF was determined to be 1.0328 g mL<sup>-1</sup> and contained 3.31 wt% 2-BE (Manz and Carter, 2016). Therefore, the 2-BE concentration in HF fluids may be as low as 34 mg L<sup>-1</sup>. Solutions in this study contained 120 mg L<sup>-1</sup> 2-BE for ease of measurement and were prepared 12 h prior to experiments, which allowed for overnight mixing in amber jars. Fe(II) concentrations used to activate persulfate ranged from 0 to 100 mg L<sup>-1</sup>. Fe (II) was used because 2 + is the same oxidation state as the pyrite found in the WV7 shale rock. Acidic conditions such as those used in the industry, 0.012–15% (Ferrer and Thurman, 2015; Kekacs et al., 2015; Torres et al., 2016; Marcon et al., 2017), were achieved using 0.07% hydrochloric acid as listed by FracFocus (Manz and Carter, 2017). pH was measured with a Fisher Scientific Accumet XL600 benchtop pH meter (Pittsburgh, PA 15275, USA). Experiments were performed in triplicate using 250-mL volumes in capped 1-L amber borosilicate jars. The jars were placed in a shaking water bath (New Brunswick Scientific Co, Inc, Model G76, Edison, NJ USA) 12 h prior to experiment start at temperatures of 20, 35, 45, 55, and 65 °C. Experiments were spiked with a concentrated solution of stock sodium persulfate to a final concentration of 21 mmol L<sup>-1</sup> to initiate experiments. Fracing fluids can return to the surface of the well from the first day after fluids are injected and may continue to flow out for several years following injection (Mouser et al., 2016). However, 2-BE was degraded much faster than this time frame. Therefore, experiments were carried out for 8 h, with the exception of experiments performed at 20, 35, and 45 °C because persulfate activation was slower at these temperatures than at higher temperatures. Samples were taken at designated times between 0 and 480 min in 10-mL volumes. Samples were immediately extracted for 2-BE (Manz and Carter, 2016) and analyzed for pH, TOC, and persulfate concentration. Mass balance calculations were performed to minimize sampling effects. Control experiments were performed without persulfate to account for the 2-BE oxidation at high temperatures and possible 2-BE absorption onto shale.

### 2.4. Sample analysis

2-BE concentration was determined using an Agilent 7890B gas chromatograph (GC) (Santa Clara, CA 95051) equipped with a splitter that connected to a 5977 A Mass Selective spectrometer (MS) and a flame ionization detector (FID), allowing simultaneous MS and FID analysis. The liquid-liquid extraction procedure and GC parameters have been previously described (Manz and Carter, 2016). In short, 3-mL of sample was pipetted into a scintillation vial containing 3-mL of methylene chloride and vortexed using a 115 V Mini Vortex Mixer (Fisher Scientific, Pittsburgh, PA 15275). The solution was separated using a 6-mL polypropylene syringe (Fisher Scientific, Pittsburgh, PA 15275) and the methylene chloride was collected in a separate vial. The extraction procedure was repeated three times. Calibration curves were made using known 2-BE concentration dissolved in methylene chloride. Extractions were repeated with hexane and chloroform to detect additional reaction byproducts as different compounds have different affinities for different solvents. The GC-MS-FID was operated in splitless mode and equipped with an Agilent 7963 auto-sampler and an Agilent J&W DB-1 (30-m x 0.25-mm ID x 0.25-μm film thickness) capillary column. Ultra-high purity helium (Airgas Corporation, Knoxville, TN 37921) was used as the carrier gas and maintained at 2.5 mL min<sup>-1</sup>. Samples (2.5-μL injection volume) were analyzed in triplicate. The GC was held at an initial temperature of 40 °C for 4 min, and the temperature was ramped up 10 °C min<sup>-1</sup> to 180 °C, and held at 180 °C for 3 min before ramping back down. The limit of detection of this method is 0.957 mg L<sup>-1</sup> 2-BE

Download English Version:

<https://daneshyari.com/en/article/8850856>

Download Persian Version:

<https://daneshyari.com/article/8850856>

[Daneshyari.com](https://daneshyari.com)