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Role of Organic Acids in Controlling Mineral Scale Formation During Hydraulic Fracturing at the Marcellus Shale Energy and Environmental Laboratory (MSEEL) Site

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Abstract

Gas production from hydraulically-fractured shales requires an ability to recover gas stored in tight shale matrices through newly-generated fractures. We previously found that geochemical reactions between hydraulic fracturing fluids and Marcellus Shale may result in the precipitation of scale-forming minerals along primary fractures. Organic acids present within fractured shale, either naturally-present in the shale or from reaction of injected frac chemicals, can affect scale-forming mineral solubility. To date limited information exists on water-soluble organic acids present in the Marcellus Shale that can affect the solubility of minerals such as barite. This study investigates which water-soluble organic substances are present in Marcellus Shale core collected from the Marcellus Shale Energy and Environmental Laboratory site (MSEEL; Morgantown, WV), and how these organic substances affect barite scale formation. Results to date suggest that the water-soluble component of shale minerals likely contributes organic acids to the produced water. On-going work is focused on using measured organic acid concentrations, along with measured dissolved solutes in MSEEL produced waters, to estimate the potential for barite and other mineral scales to form in hydraulically-fractured Marcellus Shale.

Introduction

Organic acid composition and concentrations measured in produced waters from hydraulically-fractured Marcellus Shale wells varies (Akob et al., 2015). This is a result of organic variability across the Marcellus Shale formation, chemicals and procedures applied during fracturing treatments for gas recovery, and sample handling and analytical approaches for produced waters (Orem et al., 2014; Akob et al., 2015).

Barite and other mineral scales are an issue in oil and gas wells due to their potential to affect hydrocarbon recovery flow pathways (He and Vidic, 2015). Ba^{2+} and sulfate co-exist in Marcellus Shale produced waters (Haluszczak et al., 2013), and have been observed to co-exist in experimental fluids associated with fracturing fluid-shale reactions involving Marcellus Shale (Dieterich et al., 2016; Marcon et al., 2017; Vankeuren et al., under review). Both field and experimental data suggest that organic acids affect barite solubility in hydraulically-fractured Marcellus Shale, and their presence was noted as a cause for increased concentrations of Ba and sulfate in produced waters (He et al., 2014).

In this study, we measured organic acid concentrations from ultrapure water extracts of Marcellus Shale side wall cores collected from the Marcellus Shale Energy and Environmental Laboratory MIP 3H well (Sharma et al., 2017). These values, along with produced water chemistry data collected during flowback of the MIP 3H well, were used to model the effect of organic acids on mineral saturation indices. The primary focus was on barite as a potential mineral scale in hydraulically-fractured Marcellus Shale, however results for other sulfate-bearing scale minerals (gypsum, celestine) and halite are presented for comparison.

Methods

Produced waters were collected from the MSEEL MIP 3H well gas-water separator during flowback and transported to the Sharma Isotope Laboratory at West Virginia University for filtration (0.45 µm) and preservation. For ion chromatography (IC) measurements, no additional preservation was performed prior to analysis at NETL Pittsburgh. Samples were preserved with ultrapure nitric acid after filtration for the inductively coupled plasma mass spectrometry (ICP-MS) and optical emission spectroscopy (ICP-OES) measurements performed at NETL Pittsburgh. Data presented are from direct measurements, except for sulfate. Because sulfate in MIP 3H produced water was not measured by IC, total sulfur values from ICP-OES measurements were used to calculate moles of total sulfur, which then were converted to sulfate. This approach results in an over-estimation of sulfate relative to actual concentrations in the produced water, which are anticipated to be lower than the total sulfur concentration. However, the values calculated are within the range of sulfate extracted from 3H sidewall cores (described below), and represent an upper limit of the possible total sulfate in the MIP 3H produced waters.

MIP 3H sidewall cores were recovered from the Union Springs member of the Marcellus Shale, with depths from 7521.22 ft (2292 m) to 7552.95 ft (2302 m), at the MSEEL site in Morgantown, WV, USA. Rock chips were crushed using a ball mill mixer prior to extraction for water soluble components using ultrapure water (18.2 MΩ.cm) at 20:1 (water:rock) ratio. Slurry mixture of water and rock powder was centrifuged and syringe filtered through a 0.2 µm membrane filter. The water leachates were measured for cation and anion concentrations, including organic acids, by ion chromatography (Thermo Scientific Dionex ICS-5000+) and additional cation concentrations were measured by ICP-MS (NexION 300X).

Visual MINTEQ v. 3.1 (Gustaffson, 2013) was used to calculate saturation indices in MIP 3H produced waters with solution chemistries from the MIP 3H field data (days 1, 5, 10, and 56 after flowback). Modeling was performed with and without organic acids to evaluate the effect of organic acids on mineral saturation indices. Organic acid concentrations for acetate, formate, and butyrate were from measurements of the ultrapure water leachates from the MIP 3H sidewall cores.

Results and Discussion

Produced waters collected from the MIP 3H well show an increase in most dissolved solutes during the first 56 days after initiation of flowback (Table 1).

The ultrapure water extracts of MSEEL MIP 3H sidewall cores show that acetate, formate, and butyrate are extracted by ultrapure water, along with Ba and sulfate (Table 2). Ultrapure water leachates of Marcellus Shale contain relatively high sulfate in comparison to chloride. This easily water soluble component of Marcellus Shale could release sulfate into frac fluid that leads to enhancement of barite scaling, consistent with low sulfate concentrations in produced waters from the gas-water separator. Ba release from exchange sites of clays and organic matter (Phan et al., 2015; Renock et al., 2016) are a source for Ba in produced water, in addition to being present in existing formation water.

Saturation indices for Ba, Ca, and Sr sulfate scales, and halite for comparison, are shown in Figure 1, with values reported in Table 3. Saturation indices in the absence of organic acids are greater compared to calculations performed with organic acids present. This shows that organic acids present in concentrations that are water-leachable from the shale can affect the solubility of potential scaling minerals in the system. Barite is the only mineral with saturation indices that show precipitation can occur in the system, and the value increases during the course of flowback (Figure 1; Table 3). The fraction of free cations is reduced in the presence of organic acids (Figure 2). Saturation indices of barite, gypsum, and celestine in produced water are lower in the presence of organic acids because the organic acids form complexes with Ba^{2+}, Ca^{2+}, and Sr^{2+}, resulting in a decrease in the fraction of free cations.

Table 1: Produced water chemistry data for MIP 3H.

		Day 1[a]	Day 5[a]	Day 10[a]	Day 56[a]
Ag[b]	**µg/L**	746	746	746	746
Al[b]	**µg/L**	41	41	41	41
B	**µg/L**	8870	10220	10980	9916
Ba	**µg/L**	226193	649893	1101993	2945993
Ca	**µg/L**	1615584	2772584	4027584	8291584
Fe	**µg/L**	39650	40910	60950	193500
K	**µg/L**	101370	93017	114421	137998
Li	**µg/L**	19524	34573	42993	68374
Mg	**µg/L**	197783	328583	452083	897683
Mn	**µg/L**	2751	5148	6478	12484
Na	**µg/L**	7307495	10979495	14469495	22939495
H_4SiO_4	**µg/L**	32698	65444	69987	62212
Sr	**µg/L**	238392	475692	708592	1580992
Ti[b]	**µg/L**	83	83	83	83
Zr	**µg/L**	101	116	57	119
Fluoride	**mg/l**	10	6	9	3
Chloride	**mg/l**	15592	25496	33207	59619
Nitrite	**mg/l**	NM	NM	NM	NM
Bromide	**mg/l**	159	287	363	646
Nitrate	**mg/l**	3	3	1	3
Sulfate[c]	**µg/L**	8880	21192	32534	85351
Phosphate	**µg/L**	69395	117961	83626	53483

[a] Column headers indicate number of days after flowback when the water sample was collected.
[b] Value reported is the detection limit; analyte was present however not quantifiable because it was below the detection limit.
[c] Calculated from total sulfur measured by ICP-OES. Actual sulfate values were not measured due to being below the 2.5 mg/L detection limit in prior samples.

Table 2: Ultrapure water extracts of MSEEL MIP 3H Marcellus Shale sidewall cores (n=11)

Constituents	Unit	Min	Max	Average
Acetate	mg/kg	1.8	6.5	3.0
Formate*	mg/kg	0.5	1.0	0.8
Butyrate	mg/kg	1.9	14.3	6.3
Sulfate	mg/kg	116	1465	878
Ba^{2+}	mg/kg	2.7	5.1	3.5

*values are below the method detection limit of 5.7 mg/kg

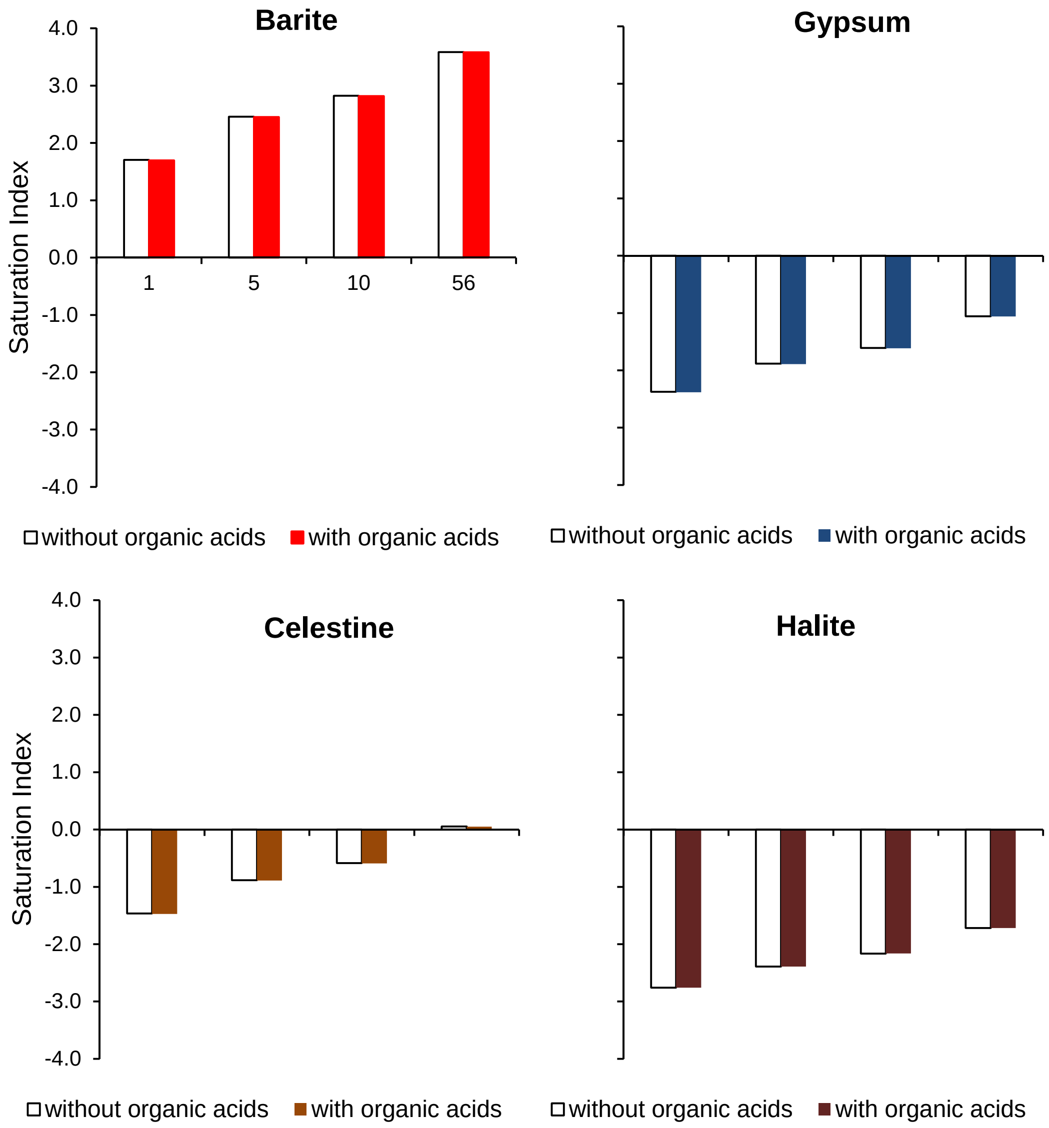

Figure 1: Effect of organic acids on the saturation indices of some minerals in MIP 3H produced water collected on day 1, day 5, day 10, and day 56 (numbers on the X axis) after flowback. Organic acids form complexes with divalent cations (Ba^{2+}, Ca^{2+}, and Sr^{2+}) resulting in a decrease in the fractions of free divalent cations, lowering the saturation indices of barite, gypsum, and celestine. However, organic acids show little effect on the saturation index of halite (Table 3).

Table 3: Effect of organic acids on the saturation indices, log(Q/K), of some minerals in MSEEL MIP 3H produced water calculated by Visual MINTEQ 3.1

Minerals	Time after flowback	Without organic acids	With organic acids*
Barite	1	1.704	1.696
	5	2.459	2.453
	10	2.824	2.819
	56	3.586	3.582
Gypsum	1	-2.373	-2.383
	5	-1.884	-1.891
	10	-1.609	-1.615
	56	-1.056	-1.060
Celestine	1	-1.465	-1.474
	5	-0.884	-0.89
	10	-0.587	-0.592
	56	0.054	0.051
Halite	1	-2.760	-2.760
	5	-2.390	-2.390
	10	-2.164	-2.163
	56	-1.719	-1.719

*Assuming water:rock ratio of 0.01 during hydraulic fracturing, predicted concentrations of acetate, formate, and butyrate in produced water attributed by water soluble components of Marcellus Shale are 300, 80, and 630 mg/L, respectively.

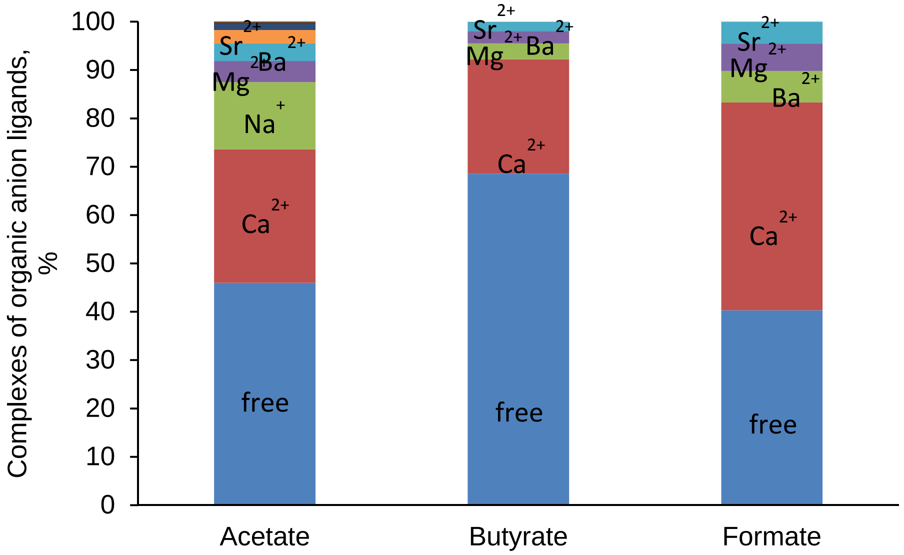

Figure 2: Complexes of acetate, butyrate, and formate in MIP 3H produced water collected on day 56 after flow back. Complexes of organic acids with Ba+, Sr^{2+}, Ca^{2+}, and Mg^{2+} result in a decrease of free ions, thus, suppress the scaling potential of sulfate scales containing these divalent cations.

Conclusions

Organic acids measured in the water-soluble leachate of Marcellus Shale include acetate, butyrate, and formate. These organic acids, along with dissolved mineral-forming solutes such as Ba^{2+} and sulfate, may be present in fractured shale formations after interaction between hydraulic fracturing fluids and the shale. Mineral saturation indices calculated in the presence of acetate, butyrate, and formate show a decrease relative to those calculated in the absence of organic acids. This study showed that organic acids are present in water-extractable fractions of Marcellus Shale, and that their presence could affect the precipitation of mineral scale within the shale.

Acknowledgements

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