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# Temporal analysis of flowback and produced water composition from shale oil and gas operations: Impact of frac fluid characteristics



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## ABSTRACT

Flowback/produced water reuse cannot be optimized without a thorough understanding of the quality of the water that needs to be treated for reuse, including the temporal variability. Samples for flowback/produced water were collected over a 200-day period (day 0 refers to when flowback began) from two wells. One of the frac fluids had an initial pH greater than 10 and used a guar-based gel and the second fluid contained a non-guar polysaccharide based polymer with an initial pH of less than 6. Total dissolved solids (TDS) and total organic carbon (TOC) were used as macro-indicators and key ions (barium, calcium, chloride, magnesium, sodium, strontium, boron and iron) were compared to TDS with the different frac fluids and there were significant positive correlations observed between the key ions and TDS with relatively high values of the coefficient of determinant (over 0.85). The concentrations of calcium, chloride, sodium and strontium are statistically equivalent between the two fluids. A mass balance approach was applied to evaluate the quantity of mass of injected additives that was recovered over the 200-day period. Recoveries of zirconium, potassium and aluminum ranged from 3% to 33% after 200 days, and notable differences were observed between frac fluids.

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## 1. Introduction

Energy demand is estimated to increase at an annual rate of 0.2% from 2010 through 2035, and electricity demand will grow by 0.8% per year (AEO, 2012). The successful development of the shale gas industry in the United States is expected to meet an increasing fraction of the energy demand and has spurred an interest in its potential in other parts of the world (Geopolitics and Natural Gas, 2012). In the U.S, the technically recoverable reserves of shale gas are greater than 1452 trillion cubic feet (USEIA, 2013), a supply that could potentially power this country for up to 100 years.

The primary advantages of utilization of natural gas are its widespread accessibility, easy transport and relative to coal, clean combustion (Gregory et al., 2011; Jaramillo et al., 2007). However, the hydraulic fracturing process, used to enable economical production from low permeability unconventional reservoirs such as shale oil and shale gas formations, can place increased pressure on the use of finite natural resources such as fresh water, raising social concerns in the community. Even though statewide estimates of water withdrawal for hydraulic fracturing has been estimated to be less than 0.1% of total water usage in Colorado (COGCC, 2012),

there have been local issues related to water sourcing and competition. Recycling of flowback and produced water for beneficial use is being pursued in many parts of the country and this trend is expected to minimize concerns related to hydraulic fracturing and regional water depletion.

The water demands for drilling and hydraulic fracturing are different depending on the formation depth, formation permeability, in-situ stress in the pay zone, in-situ stresses in the surrounding layers, reservoir pressure, formation porosity, formation compressibility, and the thickness of the reservoir (USDOE, 2004). In addition, fracturing fluid formulations may influence the volume of water required for a particular fracturing treatment. On average, water consumption to complete horizontal wells is between 2–5 million gallons of water (Goodwin et al., 2012; Hick-enbottom et al., 2013; Lee et al., 2011; Nicot and Scanlon, 2012; Rahm, 2011; Stephenson et al., 2011; Suarez, 2012).

The flowback/produced water recovered from fracturing operations during the completion of the well vary greatly in character depending on location of the wells due to different formations (spatial variation), the time the water is collected after well completion (temporal variation) (Barbot et al., 2013). The injected different frac fluid might also be expected to affect flowback/produced water quality. However, there is no study investigating the flowback/produced water quality based on different frac fluid with temporal variation in Wattenberg field in Colorado. Reusing

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of flowback/produced water cannot be performed without understanding the water quality characterization. Flowback/produced water reusing varies based on factors, involving regulations, availability of injection, scale of development and accessibility of water treatment infrastructure (Rahm et al., 2013).

The objective of this study was to characterize the variation in organic and inorganic constituents in the flowback/produced water with respect to time and frac fluid composition. To understand the temporal variation, the samples were collected for a 200-day period from two co-located wells that were completed using significantly different frac fluids.

The characteristics of produced water from conventional and unconventional oil and gas reservoirs and the possible treatment guidelines for produced water have been published (Andrew et al., 2005; Fakhru'l-Razi et al., 2009; Sirivedhin and Dallbauman, 2004). This study focused not on the produced water treatment but how the produced water quality changes with well age and two representative frac fluids.

## 2. Materials and methods

### 2.1. Composition of frac fluids

Oil and gas service companies have been working on developing the most effective hydraulic frac fluid composition to achieve a higher conductivity of the proppant pack placed during the fracturing operation in order to increase the production rate of oil and gas wells. The well performance depends largely on how well the proppant is transported down the wellbore into the reservoir and how long the proppant remain suspended in the frac fluid (FFCF, 2000). The main considerations for the frac fluid are the fracture conductivity, proppant transport, and the mitigation of potential formation permeability damage (Dusterhoft et al., 2009) that may be induced during frac operation.

For this study, the flowback water quality characteristics from wells completed with two different frac fluids that are used in the Wattenberg field in northeastern Colorado are compared. The components of Frac Fluid A and Frac Fluid B are summarized in Table 1. The main differences between the frac fluids are the use of either a residue-free polysaccharide or derivatized guar as gelling agents and the initial pH value. Zirconium (Zr) is used as the polymer cross-linker for both fluids. In addition, EDTA was only used in Frac Fluid B as an activator.

### 2.2. Sample collection

The flowback/produced water samples were collected from two horizontal wells located in Northeast Colorado. The flowback water sampling began on March 21, 2013 which is time when flowback began. Samples were collected at 2 h intervals from 0 to 1 d, at 6 h intervals from 1 to 3 days, at 12 h intervals from 3 to 5 days and at 24 h intervals from 6 to 12 days. More samples were collected at 30 days, 70 days, 102 days, 145 days and 203 days from the Frac Fluid B well, and at 20 days, 70 days, 102 days, 146 days and 202 days for the Frac Fluid A well. The wells were on the same pad, located 100 yards apart at the same depth within 50 feet and therefore minimal formation variability was assumed.

### 2.3. Analytical methods

Sodium, calcium, magnesium, potassium, iron, zirconium, silicon, strontium, barium, boron, and aluminum were quantified using USEPA method 6010C (ICP-AES); chloride and sulfate were measured with USEPA Method 300 (IC); carbonate and bicarbonate were measured with USEPA Method 310. A Shimadzu TOC-

**Table 1**

Summary of frac fluid components (Frac Focus Chemical Disclosure Registry).

Component	Ingredients	
	Frac Fluid A (pH=5.0)	Frac Fluid B – High pH=10.2
Proppant	Crystalline silica, quartz	Crystalline silica, quartz
Friction Reducer	Hydrotreated light petroleum distillate	Hydrotreated light petroleum distillate
Crosslinker	Ammonium chloride Zirconium, acetate lactate ammonium complex Inorganic salt	Ammonium chloride Zirconium, acetate lactate ammonium complex Glycerin, propanol Triethanolamine zirconate
Additive Breaker	Ammonium salt Chlorous acid Sodium chloride Ammonium persulfate Crystalline silica, quartz Sodium persulfate	Ammonium salt Chlorous acid Sodium chloride
Biocide	4,4-Dimethyloxazolidine 3,4,4-Trimethyloxazolidine 2-Amino-2-methyl-1-propanol	4,4-Dimethyloxazolidine 3,4,4-Trimethyloxazolidine 2-Amino-2-methyl-1-propanol
Buffer	Glutaraldehyde Acetic acid Ammonium acetate	Acetone, glutaraldehyde Potassium carbonate
Non-ionic Surfactant	1,2,4-Trimethylbenzene Ethanol Aromatic petroleum naphtha Naphthalene91-20-3 Poly(oxy-1,2-ethanediyl), alpha-(4-nonylphenyl)-omega-hydroxy	Ethanol Methanol Terpenes and terpenoids
Gelling agent Surfactant	Residue-free polysaccharide Proprietary component Isopropanol67-63-0 Terpenes and terpenoids	Guar gum derivative –
Activator	–	EDTA/copper chelate Diethylenetriamine
Scale inhibitor	–	Ethylene glycol Substituted carboxylate

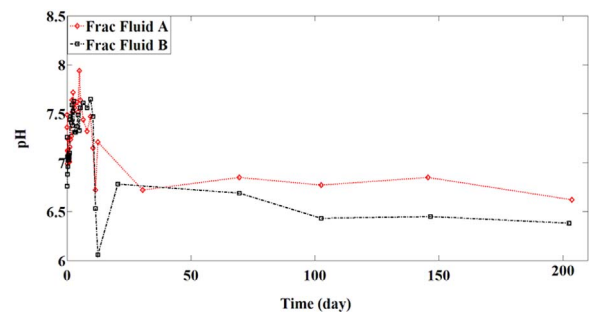
VCSH analyzer with a detection limit of 5µg/L was used to measure the TOC concentrations in the flowback/produced water samples.

## 3. Results and discussion

### 3.1. Impacts of temporal variation on flowback water quality

A summary of pH from Frac Fluid A and B wells with well age is shown in Fig. 1.

The range of pH was between 6.62 and 7.94 with 7.22 of average from Frac Fluid A (initial pH=5) and between 6.06 and 7.65 with 7.13 of average from Frac Fluid B (initial pH=10). The pH value were fluctuated about until 30 days and were stable after 30



**Fig. 1.** pH in flowback from both Frac Fluid A and B.

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