White Paper 71116

Hydraulic Fracturing Wastewaters

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Executive Summary

Wastewater produced from hydraulic fracturing (fracking) contains salts (anions and cations), metals, and radioisotopes that have been mobilized from the hydrocarbon-rich shale layer. When high-pressure is used to crack the shale, wastewater flows to the surface where it is subject to different fates. Fracking wastewater can be disposed of into injection wells if no further use is required. If the wastewater will be used in subsequent fracking events, the water is first desalinated prior to mixing with additives. Lastly, wastewater can be sent to publicly owned treatment works (POTWs) to be treated prior to surface water discharge. Due to health and environmental safety concerns, anions, cations and organic acids found in fracking wastewaters that will not be directly disposed of should be monitored. Reagent-Free™ Ion Chromatography (RFIC™) systems can be used to determine the concentrations of anions, cations, and organic acids that are commonly found in fracking waters.

Keywords

Fracking, flowback water, produced water, Reagent-Free Ion Chromatography, publicly owned treatment works (POTW)

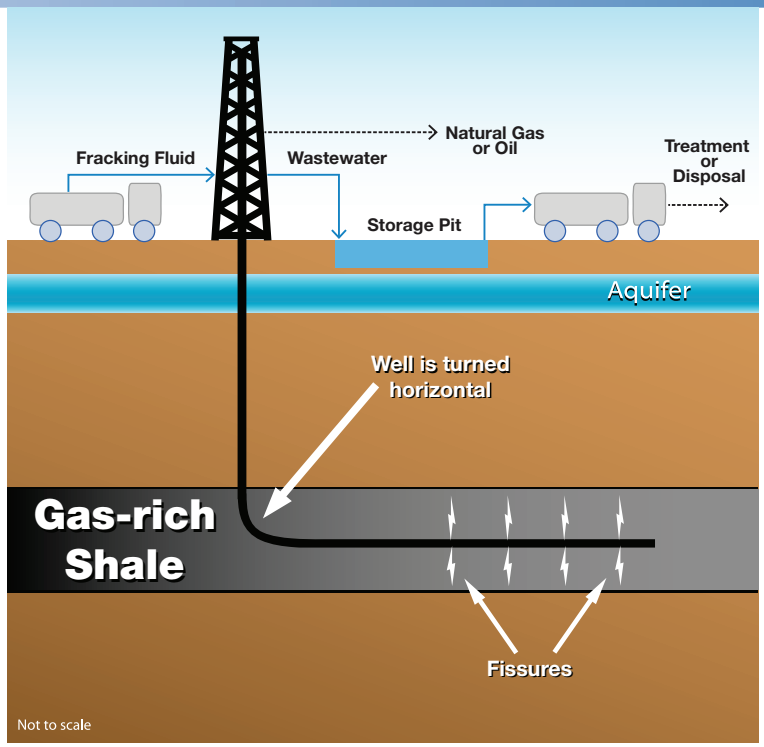

Figure 1. Fracking overview.

Introduction

Hydraulic fracturing (or fracking) extracts hard-to-reach natural gas and oil from deep underground deposits by drilling a well into bedrock (primarily shale) and then injecting fluid under high-pressure causing cracks to form. These cracks release trapped hydrocarbons that can be captured. Fracking fluid contains approximately 90% water which can be sourced from ground water, surface water, or treated wastewater.[1] The remainder of the fluid includes sand and chemical additives such as friction reducers, anti-bacterial agents, and corrosion inhibitors.[2] Sand is used to prop open cracks, facilitating the flow of hydrocarbons.

Upon relieving the injection pressure, the fracking fluid's direction of flow reverses which returns fracking wastewater to the surface. The percent of fracking wastewater that returns can range from 10–70%, depending on the nature of rock layers present.

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Fracking Wastewater

There are two types of fracking wastewater: flowback and produced. Flowback water refers to the fluid that returns to the surface upon completion of a hydraulic fracturing event prior to production. Produced water refers to the fluid that returns to the surface once the well starts producing natural gas and oil. Both types of water can contain liquid that was resident in the shale layer (formation brine); however flowback water is primarily composed of fracking fluid and its associated chemicals.

Figure 2 depicts a typical hydraulic fracturing workflow. Fracking wastewater is either disposed of by pumping into injection wells, partially treated by desalination, or discharged to surface water post-treatment. The above disposal and transfer processes do run the risk of unintentional spills during transport which can impact water sources in the immediate vicinity.

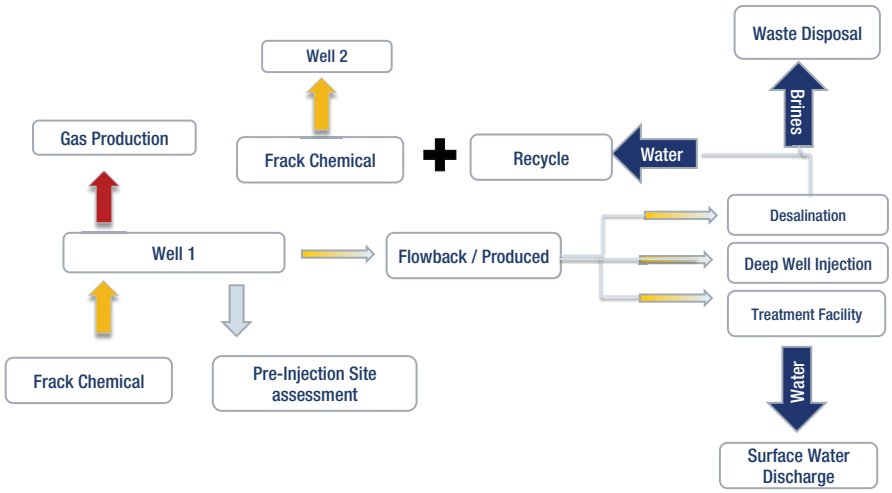


Figure 2. Hydraulic fracturing workflow.

Reuse of Fracking Wastewater

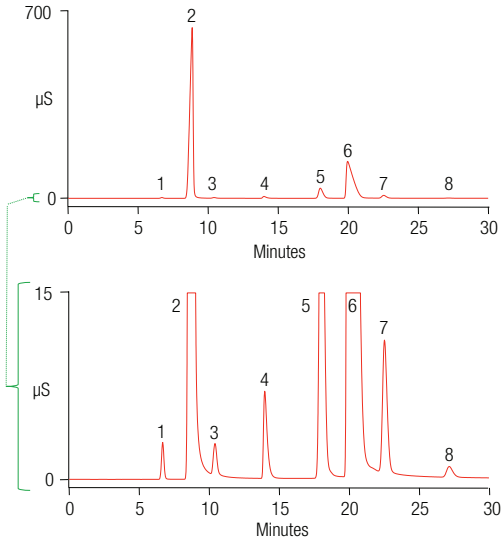
Due to the scarcity and cost of water, fracking wastewaters are reused for additional fracking events in the same proximity. Prior to reuse, these waters are desalinated to remove salts, which can inhibit the effectiveness of additives and are known to cause scaling. For example, cations such as calcium, barium, and strontium may cause scale formation in water pumps, pipes, etc., reducing extraction efficiency. To counter this, additional anti-scaling agents would need to be added to the fracking fluid prior to reuse.[3] Occasionally organic acids such as formate and acetate are added to control pH. These organic acids are sources of carbon for bacterial growth. Bacterial growth in hydraulic fracturing wastewaters can result in the production of hydrogen sulfide which is very toxic and may cause corrosion. Biocides are added to prevent bacterial growth.[4]

Discharge of Fracking Wastewater into Surface Water

Another option is the treatment of fracking wastewaters onsite or at POTWs prior to discharge. If not properly treated, these wastewaters will have a negative impact on downstream drinking water sources. For example, significant concentrations of chloride and bromide can be found in hydraulic fracturing wastewaters. If ozonation is used during the drinking water purification process, chloride and bromide react with ozone to produce chlorite and bromate. The National Primary Drinking Water Regulations regulate both bromate and chlorite, as the former is carcinogenic and the latter can lead to nervous system damage.[5] Sulfate, which is regulated under the National Secondary Drinking Water Regulations, can make drinking water unpalatable and have a laxative effect.[6]

Ion Analysis of Fracking Wastewater

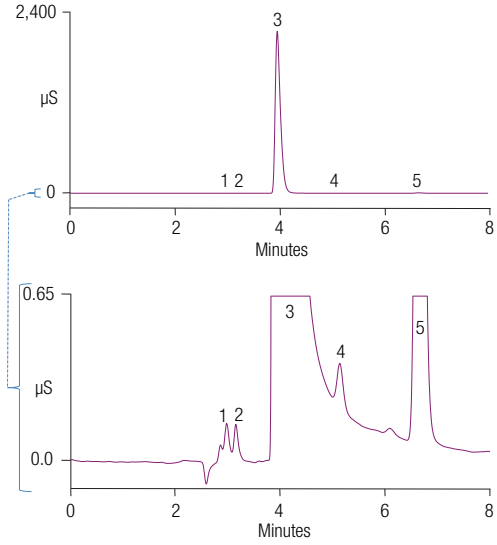
The anions, cations, and organic acids mentioned above can be easily determined in hydraulic fracturing wastewater using Thermo Scientific™ Dionex™ RFIC systems which electrolytically create the precise amount of eluent required for ion chromatography (IC) applications. This capability eliminates the need to handle the acids and bases required for the preparation of IC eluents, allowing chromatographers to run a full range of gradient and isocratic separations more effectively than with hand-made eluents. These systems allow for a simpler and more reliable way to deliver superior results while simultaneously saving time and labor. Furthermore, because the instrument pump seals and pistons only come into contact with deionized water, overall pump maintenance is significantly reduced.[7] Figure 3 a, b shows examples of cation, anion, and organic acid determinations in flowback water using RFIC systems.



Column: Thermo Scientific™ Dionex™ IonPac™ CG16/CS16, 0.5 mm i.d.
Eluent Source: Thermo Scientific Dionex EGC-MSA (capillary) cartridge
Gradient: 20–30 mM MSA (0–10 min)
30–55 mM MSA (10–18 min)
55 mM MSA (18–30 min)
20 mM MSA (30–36 min)
Flow Rate: 0.01 mL/min
Inj. Volume: 0.4 µL
Col. Temp.: 40 °C
Detection: Suppressed conductivity, Thermo Scientific™ Dionex™ CCES™ 300 Cation Capillary Electrolytic Suppressor, recycle mode
Sample: 100-fold diluted flowback water, filtered, 0.2 µm

Peaks:	Measured	Undiluted
1. Lithium	0.34 mg/L	34 mg/L
2. Sodium	320.0	32,000
3. Ammonium	1.8	180
4. Potassium	5.8	580
5. Magnesium	13.0	1,300
6. Calcium	120.0	12,000
7. Strontium	13.0	1,300
8. Barium	2.3	230

Figure 3a. Determination of cations in fracking flowback water using capillary IC.[8]



Columns: Dionex IonPac AG18/AS18, 4 mm
Eluent Source: Dionex EGC III KOH cartridge
Eluent: 39 mM KOH
Flow Rate: 1 mL/min
Inj. Volume: 25 µL
Col. Temp.: 30 °C
Detection: Suppressed conductivity, Thermo Scientific™ Dionex™ ASRS™ Anion Self-Regenerating 300 Suppressor, recycle mode
Sample: 100-fold fracking flowback, filtered, 0.2 µm

Peaks:	Measured	Undiluted
1. Acetate	< 0.05 mg/L	< 5 mg/L
2. Formate	< 0.05	< 5
3. Chloride	940.0	94,000
4. Sulfate	0.12	12
5. Bromide	8.90	890

Figure 3b. Determination of inorganic anions and organic acids in fracking flowback.

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