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The geochemistry of hydraulic fracturing fluids

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Abstract

The inorganic geochemistry of hydraulic fracturing fluids is reviewed with new insights on the role of entrapped formation waters in unconventional shale gas and tight sand formations on the quality of flowback and produced waters that are extracted with hydrocarbons. The rapid increase of the salinity of flowback fluids during production, combined with geochemical and isotopic changes, indicate mixing of the highly saline formation water with the injected water. The salinity increase suggests that the volume of the injected water that is returned to the surface with the flowback water is much smaller than previous estimates, and thus the majority of the injected water is retained within the shale formations. The high salinity of the flowback and produced water is associated with high concentrations of halides, ammonium, metals, metalloids, and radium nuclides that pose environmental and human health risks upon the release of the hydraulic fracturing fluids to the environment.

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1. Introduction

During the last decade the rapid rise of unconventional shale gas and tight sand oil development through horizontal drilling and high volume hydraulic fracturing has expanded the extraction of hydrocarbon resources in the U.S., Canada, South America, and soon more broadly in China and other parts of the world. Nonetheless, the rapid development of unconventional energy extraction has triggered an intense public debate regarding the potential environmental and human health impacts from hydraulic fracturing, resulting

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in banning of hydraulic fracturing in some U.S. states (e.g., New York) and several countries in Europe (e.g., France). The environmental concerns include fugitive emissions of methane to the atmosphere and contamination of water resources[1,2]. Previous research has shown that hydraulic fracturing can impact water resources through: (1) contamination of shallow aquifers by fugitive hydrocarbon gases (i.e., stray gas contamination)[3-5], (2) contamination of surface water and shallow groundwater from spills, leaks, and/or the disposal of inadequately treated oil and gas wastewater[6,7], (3)accumulation of toxic and radioactive elements in soil or stream sediments near disposal or spill sites[6,7], and (4) the over-extraction of water resources for high-volume hydraulic fracturing, particularly in water-scarce areas[8,9].

2. Results and Discussion

2.1. Volume of flowback and produced waters

The production volume of flowback fluids vary among the different unconventional plays, and typically follow the oil and gas production rates. In the U.S., the typical volume of flowback and produced waters vary from $5.2x10^6$ to $25.9x10^6$ L per shale gas well and $8x10^6$ to $22.8\ x10^6$ L for unconventional oil well[8]. Parallel to the sharp decrease in the production rates in time of hydrocarbons from unconventional oil and gas wells, the flow rates of flowback and produced waters decrease by 2- to 10-fold[2,8]. Over the lifetime of production an unconventional oil or gas well (up to ~10 years to date), the accumulated volume of produced water will become much more significant relative to the short-term and high production rates of flowback water[8]. Based on available data, we estimate that flowback water constitutes only 5 to 10% of the total wastewater that is generated from a shale-gas well during the well's decade-long production of hydrocarbon extraction. By comparison to flowback water, produced water dominates the volume of water accumulated at the surface and based on the chemical constituents of these fluids, produced waters may have a higher potential to affect the environment over the lifetime of unconventional oil and gas wells.

2.2. Sources of flowback and produced water from unconventional oil and gas wells

Most of the injected water that is used for hydraulic fracturing is retained within the shale or the tight sand formations and thus the volume of the returned (flowback) water is significantly lower than the volume of the injected water[8,10-14]. Data from the Marcellus Shale indicate that only 25% of the injected hydraulic fracturing fluids are returned to the surface as flowback water over 90 days following hydraulic fracturing[10]. The flowback water is characterized by a rapid change in chemistry, with a typically fast increase in salinity during the first few days (Figure 1A)[10,14-16]. The cause for the rise of the salinity of flowback water is debated and three major explanations have been proposed: (1) dissolution of halite and other salts in the shale formation[17]; (2) imbibition of the injected water to the shale formation and diffusional osmosis of ions from the shale to the flowback water[11,13]; and (3) imbibition of the injected water to the shale rocks and exchange with evaporated paleoseawater entrapped in the shale formation complex[14,16,18,19]. This evidence includes (1) the similarity of the chemical composition of Marcellus brines to the composition of evaporated seawater (e.g., high Br/Cl, low Na/Cl)[15,16], (2) the similarity of the Marcellus brines to the composition of formation waters from other geological formations in the Appalachian Basin, (3) the increase of $\delta^{18}O$ with salinity[14] (Figure 1B), which suggests mixing between injected water with low $\delta^{18}O$ and saline end-member with high $\delta^{18}O$, and (4) the difference in the $^{87}Sr/^{86}Sr$ ratios of exchangeable Sr from "dry" shale relative to the Marcellus produced water[18,19]. Consequently, the rise in salinity reflects mixing between the injected water (fresh water or recycled oil and gas wastewater) and the formation water entrapped in the shale.

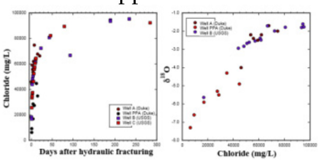

Fig. 1. (a) Changes in salinity (chloride content) of flowback water following hydraulic fracturing in 4 wells from the Marcellus Formation; (b) Correlation between stable isotopes of oxygen and chloride contents in flowback waters from the Marcellus Formation. Data from Duke University and USGS[14].

The notion that flowback water is a blend of two water sources and that the salinity increase over time reflects a progressive increase of the fraction of the entrapped formation water and indicates that the return of the injected water to the surface is even smaller than previously estimated. For example, the rapid rise of chloride content up to 50,000 mg/L after 10 days (for a well that was using fresh water for hydraulic fracturing; Figure 1A) indicates that only 50% of the flowback water is composed of injected water, assuming a saline end-member with Cl~100,000 mg/L, and the actual volume of the returned injected water is smaller. Using this mass-balance calculation for chloride, combined with the differences in volume between injected water and flowback from the Marcellus wells[10] indicates that only 10 to 20% of the injected water is returned to the surface, much smaller than estimates made by volume alone.

2.3. Contaminants in flowback and produced waters

The man-made chemicals that are added to the injected water as part of the hydraulic fracturing process have been a point of contention between environmentalists and industry. Some authors[20] recently reviewed over 1000 reported additives substances and identified both nontoxic chemicals as well as highly toxic contaminants. Possible release of these contaminants to the environment was demonstrated in a study of shallow groundwater in Pennsylvania where diesel range organic compounds (DRO), including bis (2-ethylhexyl) phthalate, which is a disclosed hydraulic fracturing additive, were found in some wells in areas of shale gas development[21]. In addition to the organic chemicals, inorganic contaminants constitute an important potential source of contamination. As shown in Figures 1 and 2, the rise in salinity of flowback with time indicates higher contributions of the saline entrapped formation water, which controls the quality of flowback and produced waters. We identified three major groups of inorganic elements that control the water quality. The first is the salinity of the formation water. Figure 2 presents a map of the shale gas and tight sand oil plays in the U.S., sorted by the salinity of the formation water. Our analysis shows a wide range of salinity, with high TDS in the Bakken and Marcellus Formations. High correlations have been observed between bromide, ammonium, and to lesser extent, iodide with chloride in the formation waters from different geological units in the Appalachian Basin[22]. The high concentrations of salts and ammonium (up to 2,500 mg/L in the Bakken brines)[7] could directly contaminate surface waters from spills or wastewater disposal[6,7,22]. As demonstrated at several wastewater treatment facilities in Pennsylvania, regular treatment systems are ineffective in removing halides from oil and gas wastewater, which are directly released to the environment with the treated oil and gas wastewater[6,22]. The high levels of bromide, iodide and ammonium in oil and gas wastewater could also induce the formation of highly toxic disinfection byproducts in drinking water systems located downstream from spills or treatment facilities[23].

Fig. 2. A map of the unconventional shale gas and tight sand oil basins in the U.S., sorted by the salinity of the produced water.

The second group of contaminants encompasses toxic metals and metalloids. Flowback and produced waters from the Marcellus and Bakken Formations are characterized high levels of Ba, Sr, Se, B, Mn, V, Cu, Zn, Cd, and Pb that exceed the threshold levels of ecological and drinking water standards[7,24]. Concentrations of many contaminants such as Ba, Sr, Mn, and Se, increase with salinity, and the higher contribution of formation water relative to injected water contributes higher concentrations of toxic metals and metalloids. The third group is radioactive elements known as naturally occurring radioactive materials (NORMs) that are present in flowback and produced water. The high salinity and reducing conditions in oil and gas reservoirs enhance differential mobilization of NORMs from the uranium-rich shale rocks, with high abundances of ^{228}Ra and ^{226}Ra relative to low concentrations of U and Th in formation waters[6,14]. Since radium adsorption decreases with salinity, radium nuclides are typically correlated with salinity[14]. As shown for other inorganic contaminants, the higher salinity of the formation waters, particularly those form the Marcellus and Bakken Formations, is associated with higher activities of radium nuclides in produced water. Disposal of oil and gas wastewater to streams[6] or leaks to the environment[7] results in accumulation of radium in stream sediments and soil, generating radioactivity legacies at the impacted sites.

3. Conclusions

Analysis of the volume of the injected water that is returned to the surface following hydraulic fracturing relative to the contribution of the formation water, which is released as flowback and produced water together with the extracted hydrocarbons, shows a much higher contribution of the naturally occurring saline water. Thus, the inorganic contaminants that are associated with formation waters constitute a much larger environmental risk over the lifetime of an unconventional oil or gas well. We identified three types of contaminants in formation water including halides, metals and metalloids, and NORMs. In many cases, the concentrations of these contaminants are highly correlated with the salinity for the formation water.

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