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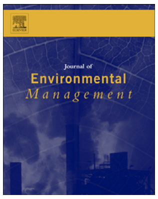

Review

Physical-chemical evaluation of hydraulic fracturing chemicals in the context of produced water treatment

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ABSTRACT

Produced water is a significant waste stream that can be treated and reused; however, the removal of production chemicals—such as those added in hydraulic fracturing—must be addressed. One motivation for treating and reusing produced water is that current disposal methods—typically consisting of deep well injection and percolation in infiltration pits—are being limited. Furthermore, oil and gas production often occurs in arid regions where there is demand for new water sources. In this paper, hydraulic fracturing chemical additive data from California are used as a case study where physical-chemical and biodegradation data are summarized and used to screen for appropriate produced water treatment technologies. The data indicate that hydraulic fracturing chemicals are largely treatable; however, data are missing for 24 of the 193 chemical additives identified. More than one-third of organic chemicals have data indicating biodegradability, suggesting biological treatment would be effective. Adsorption-based methods and partitioning of chemicals into oil for subsequent separation is expected to be effective for approximately one-third of chemicals. Volatilization-based treatment methods (e.g. air stripping) will only be effective for approximately 10% of chemicals. Reverse osmosis is a good catch-all with over 70% of organic chemicals expected to be removed efficiently. Other technologies such as electrocoagulation and advanced oxidation are promising but lack demonstration. Chemicals of most concern due to prevalence, toxicity, and lack of data include propargyl alcohol, 2-mercaptoethyl alcohol, tetrakis hydroxymethyl-phosphonium sulfate, thioglycolic acid, 2-bromo-3-nitrilopropionamide, formaldehyde polymers, polymers of acrylic acid, quaternary ammonium compounds, and surfactants (e.g. ethoxylated alcohols). Future studies should examine the fate of hydraulic fracturing chemicals in produced water treatment trains to demonstrate removal and clarify interactions between upstream and downstream processes.

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1. Introduction

During the extraction of oil and gas (O&G) from geological reservoirs, water is also extracted, often in quantities that far exceed the volumes of O&G produced (Clark and Veil, 2009; Veil, 2015). Water is the O&G industry's largest volume waste stream and the volume of water produced is expected to rise from current estimated levels of approximately 13 billion gallons per day to more than 15 billion gallons per day by 2017 (BCC Research LLC, 2012). The United States alone generates approximately one trillion gallons of produced water per year (Veil, 2015). Produced water volumes tend to increase dramatically as mature fields pass peak production levels and for crude wells nearing the end of their productive existence; water production can exceed oil production by more than ten times (BCC Research LLC, 2012; Clark and Veil, 2009; Veil, 2015).

Produced water is often reused on-field for purposes such as maintaining reservoir pressure, water flooding, cyclic steam injection, and other secondary and tertiary production processes (Clark and Veil, 2009; Veil, 2015). Other beneficial uses for produced water include power plant cooling fluid, dust and ice control, and irrigated agriculture, particularly where the salt content of the produced water is naturally low (Clark and Veil, 2009; Dallbauman and Sirivedhin, 2005; Guerra et al., 2011; Veil, 2015). However, almost 50% of produced water is not reused and must be disposed, most commonly by well injection, but also by methods that could potentially contaminate surface waters and shallow aquifers (Clark and Veil, 2009; Veil, 2015).

In the face of continuing drought in the Western USA and the expanding recognition that water is an undervalued resource, there is growing interest in reclaiming produced water for beneficial reuse, particularly in arid areas where agriculture and O&G production coincide geographically. O&G production activities are under increasing regulatory scrutiny and there is mounting pressure for the industry to change water management practices and lessen potential environmental impacts from inadequately treated wastewaters. In order for produced water to be diverted to beneficial reuse in agriculture, it is important to ensure that adequate safeguards are in place.

The increased regulation and public scrutiny surrounding unconventional O&G production activities, particularly hydraulic fracturing, is an important aspect of produced water beneficial reuse. Recent studies have shown that a wide array of anthropogenic chemicals are used in O&G fields and that these chemicals and their degradation products can occur in produced water (Ferrer and Thurman, 2015a, b; Lester et al., 2015; Stringfellow et al., 2014). Since typical produced water treatment trains are designed for the separation and recovery of gaseous or hydrophobic hydrocarbons, the question rises whether commonly used treatment systems will remove hydraulic fracturing chemicals and other O&G field chemicals (M-I SWACO, 2012; Shaffer et al., 2013).

The amount of treatment produced water receives varies. Minimally, produced water is treated using gravity settling (e.g. oil-water separation) to recover oil product, separate gas, and remove particulate matter (Arthur et al., 2005; Fakhru'l-Razi et al., 2009). Additional treatment may consist of dissolved air/gas flotation or coagulation-flocculation (Arthur et al., 2005). Nut shell filters are used as coalescing media to remove residual oil (Liu and Liu, 2016; Srinivasan and Viraraghavan, 2008). Water softening is often used to reduce scale-forming minerals that are problematic in enhanced oil recovery and disposal (Fakhru'l-Razi et al., 2009). The most advanced systems use multimedia filtration (anthracite, sand, and garnet), ion exchange softening (weak acid cation softening), and cartridge filtration followed by a two-pass RO system (Liske and Leong, 2006; Orr, 2011). Although some degree of trace contaminant removal likely occurs in even the most basic treatment processes via capture onto particle surfaces and into small oil droplets (Faksness et al., 2004), produced water treatment systems have not been designed to remove hydraulic fracturing chemicals specifically.

The use of hydraulic fracturing in O&G production contributes organic content, toxicity, and salinity that can interfere with produced water treatment (Abualfaraj et al., 2014; Barbot et al., 2013; Chapman et al., 2012; Haluszczak et al., 2013; Thacker et al., 2015). The presence of salinity, trace toxins, and recalcitrant organics present unique challenges that require a comprehensive treatment strategy (Gregory and Mohan, 2015; Shaffer et al., 2013). Produced waters from fractured wells contain high oxygen demand (Lester et al., 2015; NYS DEC, 2011; Stringfellow et al., 2014) that can interfere with physical-chemical treatment and cause fouling in membranes (Evans et al., 2014; He et al., 2014). Produced water from fractured wells appears biodegradable (Kekacs et al., 2015; Strong et al., 2014), and treatable using biological (Lester et al., 2015) and physical-chemical treatment methods (He et al., 2014; Jiang et al., 2013; Walsh, 2013). However, verification of removal of hydraulic fracturing chemicals in produced water treatment trains is needed.

Here, we use fundamental physical and chemical properties and biodegradability test results to examine treatability of hydraulic fracturing chemicals in conventionally used and widely available treatment processes. We evaluate whether technologies and processes developed for the treatment of naturally occurring hydrocarbons and salts can remove anthropogenic chemicals. Conventional produced water treatment is described elsewhere (Arthur et al., 2005; Clark and Veil, 2009; Colorado School of Mines, 2009; Fakhru'l-Razi et al., 2009; Igunnu and Chen, 2012). Here, we

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