Review

Physical, chemical, and biological characteristics of compounds used in hydraulic fracturing

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HIGHLIGHTS

- Chemical, physical, and toxicological data were identified for 81 fracturing fluid chemicals.
- Toxicity data were not available for 30 of these chemicals.
- Of the chemicals investigated, 55 were organic and 27 were biodegradable.
- Biocides were of high concern due to toxicity.
- Gelling agents contained significant chemical oxygen demand.

ARTICLE INFO

ABSTRACT

Hydraulic fracturing (HF), a method to enhance oil and gas production, has become increasingly common throughout the U.S. As such, it is important to characterize the chemicals found in HF fluids to evaluate potential environmental fate, including fate in treatment systems, and human health impacts. Eighty-one common HF chemical additives were identified and categorized according to their functions. Physical and chemical characteristics of these additives were determined using publicly available chemical information databases. Fifty-five of the compounds are organic and twenty-seven of these are considered readily or inherently biodegradable. Seventeen chemicals have high theoretical chemical oxygen demand and are used in concentrations that present potential treatment challenges. Most of the HF chemicals evaluated are non-toxic or of low toxicity and only three are classified as Category 2 oral toxins according to standards in the *Globally Harmonized System of Classification and Labeling of Chemicals*; however, toxicity information was not located for thirty of the HF chemicals evaluated. Volatilization is not expected to be a significant exposure pathway for most HF chemicals. Gaps in toxicity and other chemical properties suggest deficiencies in the current state of knowledge, highlighting the need for further assessment to understand potential issues associated with HF chemicals in the environment.

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Contents

1. Introduction

Hydraulic fracturing (HF) is a technique where fluids are pumped into wells under high pressure (e.g. up to 69,000 kPa in Marcellus Shale [1]) in order to fracture low permeability geologic formations to increase formation permeability [2,3]. HF is commonly applied to increase permeability in shale, tight sands, coal-beds, and other gas and oil-bearing strata, resulting in higher oil and gas production [2]. HF is also used in conventional oil and gas reservoirs to enhance production, improving the life cycle of previously developed oil and gas sources [3]. In addition, HF is used to develop geothermal energy resources, exposing greater surface area for heat transfer between injected fluids and thermal formations [4]. HF is also used to enhance water production in "tight" geologic formations where water is being extracted.

Extraction of hydrocarbon resources from "tight" geologic formations by the use of HF is commonly referred to as "unconventional production". Unconventional production is increasing globally as a result of technological advances in horizontal drilling, improvements in fracturing technology, and market forces which collectively have made HF an economically competitive technology for resource recovery [5,6]. In the U.S., unconventional production of natural gas from shale is projected to increase to 385 billion $m^3 \, yr^{-1}$ by 2035, up from 142 billion $m^3 \, yr^{-1}$ in 2010, an increase which would make HF extraction account for 49% of total natural gas production in the U.S. and make the U.S. a potential net exporter of natural gas by 2022 [7]. Globally, unconventional natural gas resources recovered through HF are expected to account for nearly half of newly developed gas production projects by the year 2035 [8].

In HF, the well casing is perforated at selected intervals within the targeted reservoir. Subsequent to perforating the well casing, high pressure is applied to the reservoir formation by the use of fluids, primarily water, to fracture the formation. The process is monitored at a control center, which is located at the well pad. Fracture propagation, including fracture length, is controlled based on experience working with the unique physical properties of the formation. The HF fluids are injected over a short period of time, usually within a week. Sand and other inert solids, such as ceramic beads, are injected into the formation to provide a support, or "proppant", which prevents the fractures from closing once the well pressure is released. In addition to proppant, other chemicals are added to the injected HF fluids. These chemicals are typically blended at the wellhead during, or immediately before, injection and serve various functions in the process, including preventing the growth of bacteria, facilitating the pumping of proppant down-hole and into the fractured formation, and minimizing mineral scaling of the well. Injected chemicals can include gelling and foaming agents, friction reducers, crosslinkers, breakers, pH adjusters, biocides, corrosion inhibitors, scale inhibitors, iron control chemicals, clay stabilizers, and surfactants [1,9,10]. Many of the chemicals used in HF are added to keep the proppant in suspension and deliver the proppant into the artificial fractures [2,9]. There is a wide variety of chemicals that can be used in HF and the chemical compositions of individual mixtures are commonly held as trade secrets by HF practitioners. The reticence of HF contractors to disclose the proprietary constituents in the composition of their formulations has contributed to concerns amongst the general public about the potential environmental risks associated with the chemicals used in HF treatments [11].

This paper is focused on aqueous HF treatments; however, other fluids, including gases and petroleum distillates, can be used for unconventional oil and gas production. Gas fracturing employs dinitrogen or carbon dioxide gas and is typically used in shallow, water-sensitive formations that remain self-propped after fracturing, such as in areas of western Canada [12,13]. Petroleum distillates include hydrotreated light naphthenic distillates, mineral oil, diesel fuel, and kerosene [14]. Diesel fuel has been used in some areas and in some applications instead of water because higher concentrations of polymers can be injected using non-aqueous treatments [15,16]. Petroleum distillates may also be used as carrier fluids for dissolving additives before mixing, in what are otherwise aqueous HF treatments [1]. For example, crosslinkers and pH adjusters have been dissolved or suspended in hydrophobic carrier fluids before being mixed into aqueous fracturing fluids during well-injection in order to overcome the limitations of dry chemical blending and uncontrolled premature crosslinking [17]. The U.S. EPA has worked with major HF contractors and unconventional gas producers to eliminate the use of diesel fuel in fracturing fluid due to environmental and toxicity concerns [14,16].

Following HF, fluid returns to the surface as the pressure is released from the wellhead. This fluid is generally classified as either flowback or produced water [9]. Flowback is commonly defined as the return of injected fluids and produced water is water from the formation. The distinction between flowback and produced water during operations is not clear-cut, since mixing occurs in the formation. In practice, the term flowback is used to refer to initial, higher flows in the period immediately after well stimulation and produced water refers to long-term, typically lower flows associated with commercial hydrocarbon production. After the pressure in the well is reduced, flowback water is returned to the surface at high rates for up to several weeks, and this flow is, initially, predominantly fluids that were injected, but over time the fraction of the fluid that represents formation water increases [10,18,19]. Produced water flows to the surface, along with the gas or oil, throughout the production life of the well and originates from water found in the geologic formation [10]. The volumetric recovery of injected water in the initial or flowback period varies widely and is strongly influenced by formation characteristics; while values as low as 5% and as high as 85% have been reported,

recoveries between 30% and 50% appear representative [1,5,10]. Although volumes of water used per well treatment for HF vary widely, values of approximately 7600 to 18,900 m^3 (2 to 5 million gallons) have been reported [1,5,10,20], suggesting between 1900 and 9000 m^3 (0.5 to 2.4 million gallons) of flowback will require proper management for reuse or disposal for each well. In addition to containing chemicals that were injected as part of the treatment, flowback water will also contain reaction products and constituents from the geologic formation which may include naturally occurring radioactive material (NORM); salts; heavy metals, such as mercury and lead; arsenic; and hydrocarbons, including polycyclic aromatic hydrocarbons and volatile and semi-volatile organic compounds [1,5]. Produced water is a longstanding and well-studied environmental management problem associated with both conventional and unconventional oil and gas production, and thus, was not considered in this paper, as it has been described elsewhere [21,22]. In this paper, we consider only the chemicals added to the injection well as part of unconventional production and evaluate those chemicals in the context of physical and chemical properties that affect their environmental fate, treatment potential, and toxicity.

A systematic evaluation of HF chemicals in the context of environmental impact is needed [23–27]. Recent use by HF contractors of the website FracFocus has increased the availability of information on chemicals used at well pads for HF. The most likely environmental exposure pathways for HF chemicals are expected to include the potential migration of contaminants from well pads to groundwater and surface water from accidental or operational spills, including transportation accidents and releases during treatment and disposal [10,25,28,29]. These are typical exposure pathways for industrial contaminants and in order to predict the environmental fate of HF chemicals, basic physical and chemical information needs to be compiled. Information needed for understanding environmental and health impacts of chemicals includes octanol–water partition coefficient, Henry's law constant, equilibrium constant, chemical oxygen demand (COD), melting point, boiling point, vapor pressure, aqueous solubility, biodegradability, and toxicity data for oral and inhalation exposure pathways [26]. These physical and chemical data are required for conducting environmental studies, environmental modeling, and for screening potential treatment strategies. These physical and chemical data are interpreted in the context of other variables such as soil, sediment or rock, temperature and moisture that ultimately govern the fate of chemical in the environment.

In response to concerns about the potential environmental and health impacts of HF, lists of HF chemicals have been collected over the past few years and made publicly available. Regulatory agencies in many states have established reporting requirements for unconventional production, but not all reporting requirements are mandatory [11,30,31]. Many producers have been voluntarily publishing lists of HF chemicals on their company websites or in the FracFocus Chemical Disclosure Registry [32]. The FracFocus database contains records of chemicals used at wells located throughout the U.S. [32]. Participation in the FracFocus registry is voluntary; however, participation is required by 12 state regulatory agencies to meet chemical disclosure requirements in order to receive environmental permits [32]. Contained within FracFocus are lists of HF chemicals used for development of individual wells and the quantities of the chemicals used. Reporting is done by individual producers and the data input into the registry is not standardized in terms of the information provided. FracFocus does not include physical, chemical, and toxicological information.

The objectives of this study were to clarify what chemicals are used in HF applications, compile fundamental information on the chemicals used in HF, identify data gaps concerning what is known about HF chemicals, and interpret what information is known in

the context of understanding the environmental fate of HF chemicals. In this paper, we developed a list of chemicals commonly used in HF and characterized these compounds in terms of their physical, chemical, and biological properties. Chemicals used in HF were organized by purpose and use in typical HF operations. Physical and chemical information needed for fate and transport studies, treatment technology assessments, waste management plans, risk assessments, and environmental modeling were compiled with results from standard mammalian oral and inhalation exposure tests. The compiled information was interpreted in the context of environmental releases and the challenges of developing technology for the treatment of flowback water. Hydraulic fracturing chemicals which are toxic, environmentally persistent, or for which critical physical and chemical information were not available, were identified as priority compounds for further investigation.

2. Methods

2.1. Identification of compounds used in hydraulic fracturing

Eighty-one chemical additives used in HF fluid were identified and evaluated as part of this study (Table 1). Forty-one chemicals were identified using a list of commonly used chemicals provided by the FracFocus Chemical Disclosure Registry website [33]. This list was compared to a compiled on-line database by SkyTruth that contains data on 27,000 HF operations from January 2011 through August 2012 [34]. A query was run using the SkyTruth database to verify the most commonly reported chemicals based on matching chemical names and CAS numbers. The SkyTruth database is largely based on information from the FracFocus registry and no reductions or additions to FracFocus list were needed as a result of the SkyTruth database check. The verified list was then compared to the U.S. EPA report that evaluated the potential impacts of HF on drinking water supplies [16]. After conducting an evaluation of the U.S. EPA report [16], a HF textbook [3], and published literature from industry sources [35–39], our list of commonly used fracturing chemicals grew from 41 to 81.

2.2. Physical and chemical characterization

Physical and chemical data for fracturing fluid additives was obtained from online chemical information databases [40–46], chemical reference books [47–51], materials safety data sheets [39,52,53], and a textbook [3]. In some cases, data was located in peer-reviewed scientific publications [28,54] and reports authored by the U.S. EPA [55,56], United Nations Environment Programme [57], and European Chemicals Agency [58]. Physical and chemical data are mostly based on laboratory tests using pure compounds and details of methods can be found in individual references.

Physical, chemical, and toxicological properties were selected for investigation based on their use in environmental fate and transport studies, treatability evaluations, remediation efforts, and risk assessments [59]. For example, the octanol–water partition coefficient is correlated with toxicity, soil sorption, and aquatic bioaccumulation [48]. The soil organic carbon partition coefficient (K_{OC}) is useful for determining soil sorption and contaminant transport rates [48]. Henry's constant (K_H) is an indicator of partitioning that occurs between aqueous and gaseous phases and is used in the design of air-stripping towers as well as many other design and modeling applications [48]. Chemical volatility from water was categorized as volatile, semi-volatile, or non-volatile according to K_H ranges of $x \geq 10^{-5}$, $10^{-5} > x \geq 3 \times 10^{-7}$, and $x < 3 \times 10^{-7}$ atm m^3 mol^{-1}, respectively [48]. Solubility is used in determining possible health risks. Theoretical COD was calculated using H_2O, CO_2, NO_3^-, SO_4^{2-}, and PO_4^{3-} as end products

Table 1
List of chemicals and chemical mixtures identified as being commonly used in hydraulic fracturing based on available sources.

Chemical name	CAS number	Chemical formula	Source	Chemical name	CAS number	Chemical formula	Source
Acetaldehyde	75-07-0	C_2H_4O	[33]	Formic acid	64-18-6	CH_2O_2	[16,33]
Acetic acid	64-19-7	$C_2H_4O_2$	[33,16]	Fumaric acid	110-17-8	$C_4H_4O_4$	[16]
Acetone	67-64-1	C_3H_6O	[16]	Glutaraldehyde	111-30-8	C_5H_8O	[33]
Adipic acid	124-04-9	$C_6H_{10}O_4$	[16]	Glycol ethers	Various	Various	[16]
Alkyl dimethyl benzyl ammonium chloride	68424-85-1	Various	[35]	Guar gum	9000-30-0	Various	[16,33]
Ammonium chloride	12125-02-9	ClH_4N	[33]	Hemicellulase enzyme	9012-54-8		[39]
Ammonium persulfate	7727-54-0	$(NH_4)_2S_2O_8$	[33]	Hydrochloric acid	7647-01-0	HCl	[16,33]
Ammonium sulfate	7783-20-2	$(NH_4)2SO_4$	[16]	Hydrotreated light petroleum distillate	64742-47-8	Various	[33]
Borate salts	Various	Various	[33]	Hydroxyethyl cellulose	9004-62-0	Various	[16]
Boric acid sodium salt	1333-73-9	Na_3BO_3	[16,33]	Hydroxypropyl cellulose	9004-64-2	Various	[3]
Calcium chloride	10043-52-4	$CaCl_2$	[33]	Hydroxypropyl guar	39421-75-5	$(C_{27}H_{48}O_{18})_n$	[16]
Calcium peroxide	1305-79-9	CaO_2	[3]	Isopropanol	67-63-0	C_3H_8O	[16,33]
Carbon dioxide	124-38-9	CO_2	[16]	Magnesium oxide	1309-48-4	MgO	[33]
Carboxymethyl guar	39346-76-4	Various	[16]	Magnesium peroxide	14452-57-4	MgO_2	[33]
Carboxymethyl hydroxyethyl cellulose	9004-30-2	Various	[3]	Methanol	67-56-1	CH_4O	[16,33]
Carboxymethyl hydroxypropyl guar	68130-15-4	Various	[16]	Monoethanolamine	141-43-5	C_2H_7NO	[16]
Choline chloride	67-48-1	$C_5H_{14}ClNO$	[33]	Monoethylamine	75-04-7	C_2H_7N	[16]
Citric acid	77-92-9	$C_6H_8O_7$	[33]	N,n-dimethyl formamide	68-12-2	C_3H_7NO	[37]
Copolymer of acrylamide and sodium acrylate	25987-30-8	Various	[33]	Naphthalene	91-20-3	$C_{10}H8$	[33]
Copper compounds	Various	Various	[16]	Nitrogen	7727-37-9	N_2	[16]
Didecyl dimethyl ammonium chloride	7173-51-5	$C_{22}H_{48}ClN$	[36]	Petroleum distillate	64741-85-1	Various	[33]
Diesel fuel	Various	Various	[16]	Phosphonic acid salt	Various	Various	[33]
Diethanolamine	111-42-2	$C_4H_{11}NO_2$	[16]	Polyacrylamide	9003-05-8	$(C_3H_5NO)_n$	[33]
Dimethyl dihydrogenated tallow ammonium chloride	Various	Various	[38]	Polyglycol ether	Various	Various	[16]
Potassium carbonate	584-08-7	K_2CO_3	[33]	Sodium persulfate	7775-27-1	$Na_2O_8S_2$	[3]
Potassium chloride	7447-40-7	KCl	[16]	Sodium polycarboxylate	Various	Various	[33]
Potassium hydroxide	1310-58-3	KOH	[16,33]	Sodium tetraborate decahydrate	1303-96-4	$B_4O_7\cdot2Na\cdot10H_2O$	[16,33]
Potassium metaborate	13709-94-9	BKO_2	[33]	Tetrakis hydroxymethyl-phosphonium sulfate	55566-30-8	$(C_4H_{12}O_4P)_2O_4S$	[33]
Potassium persulfate	7727-21-1	$K_2O_8S_2$	[3]	Tetramethyl ammonium chloride	75-57-0	$C_4H_{12}ClN$	[33]
Propargyl alcohol	107-19-7	C_3H_4O	[16]	Thioglycolic acid	68-11-1	$C_2H_4O_2S$	[33]
Pyridinium	16969-45-2	C_5H_6N	[16]	Thiourea	62-56-6	CH_4N_2S	[16]
Quaternary ammonium chloride	61789-71-1	Various	[33]	Tributyl tetradecyl phosphonium chloride	81741-28-8	$C_{26}H_{56}PCl$	[39]
Sodium carbonate	497-19-8	Na_2CO_3	[33]	Triethanolamine zirconate	101033-44-7	$C_{24}H_{56}N_4O_{12}Zr$	[33]
Sodium chloride	7647-14-5	NaCl	[33]	Zirconium hydroxy lactate sodium complex	113184-20-6	$C_{12}H_{19}NaO_{16}Zr$	[33]
Sodium erythorbate	6381-77-7	$C_6H_7NaO_6$	[33]	Zirconium nitrate	13746-89-9	$Zr(NO_3)_4$	[16]
Sodium hydroxide	1310-73-2	NaOH	[33]	Zirconium sulfate	14644-61-2	$Zr(SO_4)_2$	[16]
Sodium lauryl sulfate	151-21-3	$C_{12}H_{25}NaO_4S$	[33]				
1-Bromo-3-chloro-5,5-dimethylhydantoin	16079-88-2	$C_5H_6BrClN_2O_2$	[35]	Ester salt	Various	Various	[16]
2,2-Dibromo-3-nitrilopropionamide	10222-01-2	$C_3H_2Br_2N_2O$	[16]	Ethanol	64-17-5	C_2H_6O	[16,33]
2-Bromo-3-nitrilopropionamide	1113-55-9	$C_3H_3BrN_2O$	[16]	Ethyl methyl derivatives	Various	Various	[16]
2-Butoxyethanol	111-76-2	$C_6H_{14}O_2$	[33,16]	Ethylene glycol	107-21-1	$C_2H_6O_2$	[16,33]

and is valuable for determining oxygen requirements for oxidizing treatments and remediation techniques. HF chemicals were categorized as non-biodegradable, inherently biodegradable, and readily biodegradable using OECD guidelines [60]. Biodegradability is useful for determining the effectiveness of biological treatment for wastewaters and the fate of chemicals released into the environment. Toxicity was described using median lethal dose (LD_{50}) for oral and inhalation exposure in rats, mice, and rabbits. Mammalian oral and inhalation toxicity data are commonly used in environmental and health risk assessments and mammalian oral toxicity data are collected under standard conditions [61]. To standardize interpretation, chemical toxicity was categorized according to United Nations standards in the *Globally Harmonized System of Classification and Labelling of Chemicals* (GHS), which classifies acute toxicity on a scale of 1 to 5, with 5 being the least toxic (Table S2) [61]. Where chemical concentrations were reported in the literature on a volumetric basis, the chemical density data collected as part of this study was used to calculate mass-based concentrations.

3. Results and discussion

For the HF chemicals identified (Table 1), toxicity data (Tables 2 and 3) and chemical and physical data (Tables 4–9) were summarized, where such data was available. Some chemicals and mixtures for which no information was found are discussed exclusively in the text. Properties which were not relevant for the chemical or chemical mixture are denoted by "–". Information which was not located in the standard databases is identified as "Not found" in the table, and information still missing after a search of the literature was conducted is marked as "Unknown". The tables of physical, chemical, and biochemical properties are interpreted in the context of evaluating chemicals for potential environmental hazard based on persistence, mobility, and other properties such as concentration and toxicity.

3.1. Gelling and foaming components

Gelling agents are used in HF to increase fracturing fluid viscosity, allowing for better proppant suspension and transport into developed fractures. Gels can be linear, consisting of single stranded polymers, or crosslinked where individual polymer strands are chemically joined at specific functional groups to create larger molecules, further increasing fluid viscosity. Gelling agents are selected based on site-specific conditions in the well, including temperature and salinity [3]. Gelling compounds can be added to the fracturing fluid as powders or concentrates after being dissolved into a non-aqueous solvent [16]. In deep, high temperature reservoirs (above 132 °C), gel stabilizers are added to prevent premature decomposition [62]. When gel fracturing treatments are used, the concentration of the gelling agent ranges from approximately 10–1000 mg L^{-1} [1,5,10,63].

Commonly used gelling agents include guar, derivatives of guar [carboxymethyl guar (CMG), hydroxypropyl guar (HPG), and carboxymethyl hydroxypropyl guar (CMHPG)], and cellulosic compounds [hydroxyethyl cellulose (HEC), hydroxypropyl cellulose (HPC) and carboxymethyl hydroxyethyl cellulose (CMHEC)] [3,16,64]. Guar molecules are composed of β-1,4-linked mannose units with α-1,6-linked galactose units attached (Fig. 1a) [65–67], where the ratio of mannose to galactose units is typically 1.6:1 to 1.8:1 [66,67]. The cellulose derivatives HEC, HPC, and CMHEC contain a glucose sugar backbone (Fig. 1b). Guar derivatives are produced by modifying the guar hydroxyl groups to carboxymethyl and hydroxypropyl groups (O—CH$_2$—COO) (Fig. 1c and d) [68,69].

Guar and guar derivatives are commonly used as food additives and in cosmetic and health products (Table S1). Guar, guar

Table 2
Toxicity values via inhalation for frequently used additives in hydraulic fracturing fluids.

Chemical	Inhalation toxicity rat (LC$_{50}$)	Inhalation toxicity mouse (LC$_{50}$)	Reference	Chemical	Inhalation toxicity rat (LC$_{50}$)	Inhalation toxicity mouse (LC$_{50}$)	Reference
2,2-Dibromo-3-nitrilopropionamide	320 mg m^{-3}/4 h	Not found	[40]	Methanol	87,500 mg m^{-3}/6 h, 64,000 ppm/4 h, >145,000 ppm/1 h	Not found	[40]
2-Butoxyethanol	450–486 ppm/4 h	700 ppm/7 h	[40,46]	Monoethyl amine	12,600 mg m^{-3}/4 h	Not found	[40]
Acetaldehyde	37,000 mg m^{-3}/30 min	1500 ppm/4 h	[40]	N,n-dimethyl formamide	Not found	9400 mg m^{-3}/2 h	[40]
Acetic acid	11,400 mg m^{-3}/4 h	5620 ppm/1 h	[41]	Naphthalene	>100 ppm/8 h	Not found	[41]
Acetone	76,000 mg m^{-3}/4 h, 50,100 mg m^{-3}/8 h	44,000 mg m^{-3}/4 h	[40,41,46]	Potassium chloride	873 ppm/4 h	Not found	[50]
Adipic acid	>31,000 mg m^{-3}/1 h, 7700 mg m^{-3}/4 h	Not found	[41]	Propargyl alcohol	1040–1200 ppm/1 h, 873 ppm/2 h	2000 mg m^{-3}/2 h	[40,46,50]
Diammonium peroxydisulphate	520,000 mg m^{-3}/1 h, >2950 mg m^{-3}/1 h	Not found	[40]	Sodium carbonate	2300 mg m^{-3}/2 h	1200 mg m^{-3}/2 h	[40]
Ethanol	20,000 ppm/10 h	39,000 mg m^{-3}/4 h	[40,46]	Sodium lauryl sulfate	>3900 mg m^{-3}/1 h	Not found	[46]
Formic acid	15,000 mg m^{-3}/15 min	6200 mg m^{-3}/15 min, 7400 mg m^{-3}/4 h	[46,40]	Sodium tetraborate decahydrate	>2 mg m^{-3}/1 h	Not found	[40]
Glutaraldehyde	280–800 mg m^{-3}/4 h; 5000 ppm/4 h	Not found	[40]	Tetrakis hydroxymethyl-phosphonium sulfate	5500 mg m^{-3}/4 h	Not found	[40]
Hydrochloric acid	3124 ppm/1 h, 4701 ppm/30 min	1108 ppm/1 h, 2644 ppm/30 min	[40]	Thioglycolic acid	210 mg m^{-3}/4 h	Not found	[46]
Isopropanol	51,045 mg m^{-3}/8 h; 72,600 mg m^{-3}/4 h	53,000 mg m^{-3}/2 h	[40]	Thiourea	>900 mg m^{-3}/4 h	Not found	[41]

Table 3
Oral toxicity values for frequently used additives in hydraulic fracturing fluids.

Chemical	Oral toxicity (LD$_{50}$), rat (mg kg^{-1})	Oral toxicity (LD$_{50}$), mouse (mg kg^{-1})	Oral toxicity (LD$_{50}$), rabbit (mg kg^{-1})	Reference	Chemical	Oral toxicity (LD$_{50}$), rat (mg kg^{-1})	Oral toxicity (LD$_{50}$), mouse (mg kg^{-1})	Oral toxicity (LD$_{50}$), rabbit (mg kg^{-1})	Reference
Acetaldehyde	661–1930	1230	Not found	[40]	Ethylene glycol	4700	7500	Not found	[40,50]
Acetic acid	3310–3530	4960	1200	[40]	Formic acid	1100	700	Not found	[40,50]
Acetone	5800–9800	3000–5200	5340	[40]	Fumaric acid	9300–10,700	Not found	Not found	[50]
Adipic acid	>11,000	1900	>11,000	[44,50]	Glutaraldehyde	134–1470	100	1.59 mL kg^{-1} 50% aqueous solution	[40,50]
Ammonium chloride	1650	1300	LDL$_o$ = 1000	[50]	Guar gum	6770	8100	7000	[50]
Ammonium sulfate	3000	3040	Not found	[40,50]	Hydrochloric acid	238–277	Not found	900	[40]
Ammonium persulfate	689	Not found	Not found		Hydroxypropyl cellulose	10,200	>5000	Not found	[46]
Boric acid sodium salt	Not found	Not found	Not found		Hydroxypropyl guar	Not found	Not found	Not found	
Calcium chloride	1000–4179	1940–2045	100–1000	[40,50]	Isopropanol	4710–5840	3600–4475	5030–7990	[40,50]
Calcium peroxide	Not found	Not found	Not found		Magnesium oxide	3870–3990	810	Not found	[40]
Carboxymethyl guar	17,800	Not found	Not found	[46]	Magnesium peroxide	Not found	Not found	Not found	
Carboxymethyl hydroxyethyl cellulose	Not found	Not found	Not found		Methanol	5628–6970	7300	14400	[40,44]
Carboxymethyl hydroxypropyl guar	Not found	Not found	Not found		Monoethanolamine	1720–10,200	700–1475	1000	[41,50]
Choline chloride	3400–6640	3900	Not found	[40]	Monoethylamine	400–530	Not found	Not found	[40,50]
Citric acid	3000–6730	5040	7000	[50]	N,n-dimethyl formamide	2800–3000	3750	>5000	[40]
Copolymer of acrylamide and sodium acrylate	Not found	Not found	Not found		Naphthalene	490–2600	350–710	Not found	[40]
Diammonium peroxydisulphate	495–820	Not found	Not found	[40]	Sodium persulfate	Not found	Not found	Not found	
Nitrogen	Not found	Not found	Not found		Potassium carbonate	1870	2570	Not found	[50]
Petroleum distillate	Not found	Not found	Not found		Sodium polycarboxylate	Not found	Not found	Not found	
Phosphonic acid salt	Not found	Not found	Not found		Sodium lauryl sulfate	1288	Not found	Not found	[50]
Polyacrylamide	>1000	12,950	11,250	[44,50]	Sodium tetraborate decahydrate	5660	2000	Not found	[40]
Potassium chloride	2600	383–1500	Not found	[40,46,50]	Tetrakis hydroxymethyl-phosphonium sulfate	248–333	Not found	Not found	[40,50]
Potassium hydroxide	273–1230	Not found	Not found	[44,50]	Tetramethyl ammonium chloride	50	125	Not found	[46,50]
Potassium metaborate	Not found	Not found	Not found	[40]	Thioglycolic acid	114	242	119	[40,50]
Potassium persulfate	802	Not found	Not found	[50]	Thiourea	20–640	8500	10,000	[40,41]
Propargyl alcohol	20–110	50	Not found	[40,44,50]	Tributyl tetradecyl phosphonium chloride (48–50%)	1002	Not found	Not found	[53]
Pyridinium	Not found	Not found	Not found		Triethanolamine zirconate	Not found	Not found	Not found	
Sodium carbonate	2800–4090	6600	Not found	[40,46,50]	Zirconium hydroxy lactate sodium complex	Not found	Not found	Not found	
Sodium chloride	3000	4000	Not found	[40]	Zirconium nitrate	2290	Not found	Not found	[50]
Sodium erythorbate	>5000	Not found	Not found	[44]	Zirconium sulfate	3500	Not found	Not found	[50]
Sodium hydroxide	140–340	Not found	500	[40,50]	Didecyl dimethyl ammonium chloride	84–331	268	Not found	[40,44,50]
1-Bromo-3-chloro-5,5-dimethylhydantoin	578–1390	Not found	>2000	[40,44,52]	Diethanolamine	710–1820	3300	2200	[44,50]
2,2-Dibromo-3-ditrilopropionamide	178–235	Not found	118	[40,50]	Dimethyl dihydrogenated tallow ammonium chloride	Not found	Not found	Not found	
2-Bromo-3-nitrilopropionamide	Not found	Not found	Not found						
2-Butoxyethanol	470–3000	1200–1519	300–320	[40,44]	Ethanol	7060–10,600	3450	Not found	[40,50]

Table 4
Properties of gelling agents, foaming agents, and associated chemicals used in hydraulic fracturing.

Chemical	log (K_{OW})	K_H (atm m^3 mol^{-1})	K_{OC}	pK_a	COD (gO$_2$ g^{-1})	Density (g cm^{-3} at 25 °C)	Melting point (°C)	Boiling point (°C)	Vapor pressure (mmHg at 25 °C)	Solubility in water (mg L^{-1})	Biodegrad-ability	Reference
Adipic acid[a]	0.08	4.7×10^{-12}	26	4.44	1.42	1.36	152.5	337.5	3.18×10^{-7}	3.00×10^4 at 30 °C	RB	[40,42,47]
Fumaric acid[a]	0.46	8.5×10^{-14}	33.5	pK_{a1} = 3.02, pK_{a2} = 4.46	0.83	1.635	287	522	1.54×10^{-4}	7×10^{-3}	RB	[40–42,50]
Guar gum[a]	Not found	Not found	Not found	–	1.18	Not found	Not found	Not found	Not found	Not found	RB	[70,71]
Carboxymethyl guar[a]	Not found	Not found	Not found	–	Not found	Not found	Not found	Not found	Not found	Not found	RB	[70,71]
Hydroxypropyl guar[a]	Not found	Not found	Not found	–	1.45	Not found	Not found	Not found	Not found	Not found	RB	[70,71]
Carboxymethyl hydroxypropyl guar[a]	Not found	Not found	Not found	–	Not found	Not found	Not found	Not found	Not found	Not found	RB	[70,71]
Hydroxyethyl cellulose[a]	Not found	Not found	Not found	–	Not found	Not found	Not found	Not found	Not found	Not found	Not found	–
Hydroxypropyl cellulose[a]	Not found	Not found	Not found	–	Not found	Not found	Not found	Not found	Not found	Not found	Not found	–
Carboxymethyl hydroxyethyl cellulose[a]	Not found	Not found	Not found	–	Not found	Not found	Not found	Not found	Not found	Not found	Not found	–
2-Butoxyethanol[b]	0.45	2.36×10^{-6}	8	–	2.30	0.90	−74.8	168.4	0.88	Miscible	RB	[40,48,50]
Diethanolamine[b]	−1.43	3.9×10^{-11}	4	8.96	2.13	1.10	28	268.8	1.4×10^{-4}	Miscible	RB	[40,41,46]
Ethanol[c]	−0.31	5.00×10^{-6}	2.75	15.9	2.08	0.82	−114.1	78.29	59.3	Miscible	RB	[40,41,46,49,51]
Isopropanol[c]	0.05	8.10×10^{-6}	25	17.1	2.40	0.79	−87.9	82.3	45.4	Miscible	RB	[41,42,46,49,50]
Methanol[c]	−0.73	4.66×10^{-6}	2.75	15.3	1.50	0.79	−97.8	64.7	127	Miscible	RB	[40,41,46,48]
Ethylene glycol[c]	−1.36	6.00×10^{-8}	0.2	15.1	1.29	1.11	−12.7	197.3	0.092	Miscible	RB	[40,41,46,49]

COD = Theoretical chemical oxygen demand, RB = Readily biodegradable.

[a] Gelling agent.
[b] Foaming agent.
[c] Stabilizing agent used with gelling and foaming agents.

Table 5
Properties of crosslinkers used in hydraulic fracturing.

Chemical[a]	log (K_{OW})	K_H (atm m^3 mol^{-1})	K_{OC}	pK_a	COD (gO$_2$ g^{-1})	Density (g cm^{-3} at 25 °C)	Melting point (°C)	Boiling point (°C)	Vapor pressure (mmHg at 25 °C)	Solubility in water (mg L^{-1})	Biodegrad-ability	Reference
Ammonium chloride	−4.37	3.88×10^{-13}	–	–	1.20	1.52	338	520	2.42×10^{-3}	3.95×10^5	RB	[41,42]
Boric acid sodium salt	–	–	–	–	–	Not found	Not found	Not found	Not found	Not found	NB	
Potassium metaborate	–	–	–	–	–	2.3	947	Not found	Not found	Not found	NB	
Sodium tetraborate decahydrate	−1.53	–	–	–	–	1.73	75	Not found	Not found	5.93×10^4	NB	[40,50,58]
Zirconium hydroxy lactate sodium complex	Unknown	Unknown	Unknown	–	Unknown	Unknown	Unknown	Unknown	Unknown	Unknown	Unknown	
Zirconium nitrate	–	–	–	–	–	Not found	100 (decomposes)	–	Not found	Not found	Not found	
Zirconium sulfate	–	–	–	–	–	3.22	410 (decomposes)	–	Not found	5.25×10^5	Not found	
Monoethanolamine	−1.31	3.25×10^{-8}	5	9.50	2.36	1.02	10.5	171	0.40	Miscible	RB[a]	[40–42]
Monoethylamine	−0.13	1.23×10^{-5}	20	10.87	3.55	0.7	−80.5	16.5	1048	1×10^6	RB	[40–42]
Triethanolamine zirconate	Unknown	Unknown	Unknown	Unknown	1.78	Unknown	Unknown	Unknown	Unknown	Unknown	Unknown	

COD = Theoretical chemical oxygen demand, RB = Readily biodegradable, NB = Non-biodegradable.

[a] Methanol and ethylene glycol are stabilizers or winterizing agents used in conjunction with crosslinkers, and are also used with gelling and foaming agents. They are described in Table 4.

derivatives, and cellulosic compounds are derived from natural materials and are non-toxic. Guar and its derivatives are readily biodegradable; however, cellulose polymers may be more resistant to biodegradation [70,71]. Gelling agents will contribute significantly to the COD of flowback water. The COD of guar gum and HPG [$(C_{27}H_{48}O_{18})_n$] are 1.18 and 1.45 gO_2 g^{-1}, respectively, and they are used in high concentrations. The high concentrations of gelling agents may make implementation of some treatment processes, such as reverse osmosis, difficult since the organic matter will encourage microbial processes that cause fouling on membrane surfaces [72,73]. Based on criteria of persistence and toxicity, these gelling agents are not of concern, but they need to be considered in treatment design and as a source of oxygen demand during an environmental release.

In addition to guar and cellulosic derivatives, adipic acid and fumaric acid are also used as gelling agents [16]. These acids are used as thickeners in foods and are above GHS Category 5 and therefore non-toxic by our interpretation; however, one source reported adipic acid as belonging in GHS Category 4 for mice (Table 3) [50]. Like all acids, these compounds may be irritating to the eyes, nose, and throat when in powdered form [40]. Chemical and physical data indicate low volatility potential from water and high sorption potential (Table 4), suggesting low mobility in soil and groundwater. Both acids are readily biodegradable, contribute significant COD, and are used in high concentrations in HF fluids, which, as described above, can influence treatment train design and pose an environmental risk when released.

In addition to gel treatments, foamed fracturing fluids, which are created by injecting dinitrogen or carbon dioxide gas into gelled liquids, are also used to alter fracturing fluid viscosity. Foamed fluids reduce the amount of liquid required for fracturing; for example, reductions of 75% are possible when compared with linear and crosslinked gel treatments [15,16]. In low pressure reservoirs, use of foamed fracturing fluids accelerates fluid recovery, and in formations with large amounts of clay, foamed fluids reduce clay swelling [3].

Diethanolamine, 2-butoxyethanol, and related ester salts are used in foamed treatments. Diethanolamine and 2-butoxyethanol have low log K_{OW} values, suggesting they will not sorb to soils and will likely be transported with groundwater flows. 2-Butoxyethanol is semi-volatile from water, based on its Henry's constant (Table 4), and meets criteria for GHS Category 2 toxins based on rat inhalation toxicity LC_{50} values (Table 2) [61]. Both 2-butoxyethanol and diethanolamine are GHS Category 4 chemicals based on rat oral toxicity LD_{50} values [61]. These compounds are readily biodegradable (Table 4), but information on the concentrations at which these additives are used in HF was not found. Diethanolamine and 2-butoxyethanol are not expected to be persistent in the environment, but based on expected mobility, possible toxicity, and lack of available information regarding how much of these materials are used, these compounds deserve further investigation.

Gel stabilizers used to prevent decomposition include ethanol, isopropanol, methanol, ethylene glycol, and polyglycol ether [16,32]. Ethanol, isopropanol, and methanol are used extensively in industry, beverages (ethanol), and household cleaners (Table S1), and based on the Henry's constant values, all three chemicals are expected to be semi-volatile from water and are readily biodegradable (Table 4). These compounds sorb poorly to soils and are transported with groundwater. The environmental fates of ethanol and methanol have been extensively studied, due to their use as gasoline additives. Undiluted ethanol, isopropanol, and methanol are toxic by ingestion to rats between doses of 4710 and 7060 mg kg^{-1} (Table 3). These compounds used as product stabilizers are GHS Category 5 or non-toxic, are widely used in industry, are easily biodegradable, and are well characterized, and

are therefore not considered high priority compounds for further investigation.

3.2. Friction reducers

An alternative method to gel and foam treatments is "slickwater" fracturing. In slickwater treatments, chemicals are added to reduce fluid surface tension and facilitate removal of fracturing fluid from the formation. Slickwater treatments have a reputation for improving well production by reducing fracture plugging compared to gels [62]. In slickwater fracturing, up to 3785 m^3 (1 million gallons) of water may be required for each stage of production, with six to nine stages, or repeated injections, occurring per well [15]. When friction reducers are added, development of higher pressure within the formation is possible because the fluid viscosity and headloss due to friction are reduced, increasing effective static pressure [15].

A commonly used friction reducer is 2-propenamide (polyacrylamide, $(C_3H_5NO)_n$, (Fig. 1e) [32]. Reported application rates in fracturing fluids are 30–1200 mg L^{-1} [3,5,10,15,16,63]. There are three forms of polyacrylamide: anionic, cationic, and nonionic [15]. According to King [10], nearly all slickwater fracturing projects use polyacrylamide as a friction reducer.

While log K_{OW}, K_H, and K_{OC}, and physical information, such as density, melting point, vapor pressure, and solubility was not located for polyacrylamide, it is known that it is water soluble, non-volatile, and above GHS Catgeory 5, and, therefore, non-toxic (Table 3). It has been suggested that polyacrylamide can degrade through heating or exposure to ultraviolet radiation into acrylamide, which is a known human carcinogen, mutagen, and teratogen [74,75]. Polyacrylamide is biodegradable with a COD of 2.25 gO_2 g^{-1}. It has been shown that no acrylamide is produced during the aerobic biodegradation of polyacrylamide [75,76]. Based on these results, a flowback water from slickwater treatments can be expected to have a high COD, and therefore present treatment challenges, but this friction reducer is not considered a priority material for investigation based on persistance or toxicity.

3.3. Crosslinkers

Crosslinkers are added to fracturing fluids to chemically bind individual gel polymer molecules together to form larger molecules (Fig. 2), resulting in higher viscosity, more elasticity, and better proppant transport compared with linear gels that are not crosslinked. Crosslinkers frequently used in HF include borate salts; aluminum, titanium, and zirconium compounds; monoethanolamine; and monoethylamine [3,16,32]. Ammonium chloride, ethylene glycol, and potassium hydroxide are also used as crosslinkers [16]. Concentrations of crosslinkers in fracturing fluid are relatively low and range from 0.5 to 250 mg L^{-1} [1,5,10,16,63].

Available chemical and physical information for borate (Fig. 2) and zirconium compounds is limited (Table 5). These chemicals are not expected to significantly contribute to HF fluid COD. Inhalation and topical exposure to boron compounds is generally associated with upper respiratory tract, skin, and eye irritation [40]. Ingestion of 15 to 20 g of boric acid has resulted in severe toxicity or death in adults [40]. The borate salt sodium tetraborate decahydrate is a GHS Category 4 compound for mice, but is non-toxic (above GHS Category 5) for rats (Table 3). Zirconium compounds have been used to replace toxic chromium crosslinking compounds in HF treatments [77]. Zirconium is not considered a biologically reactive metal and is not expected to be a concern toxicologically [78]. Oral toxicity of zirconium nitrate and zirconium sulfate places these HF chemicals in GHS Category 5 (Table 3), although data on the toxicity of zirconium lactate complexes and triethanolamine zirconate was not found. Based on their use at low concentrations and their moderate

Table 6
Properties of breakers used in hydraulic fracturing.

Chemical	COD ($gO_2\,g^{-1}$)	Density ($g\,cm^{-3}$ at 25 °C)	Solubility in water ($mg\,L^{-1}$)	Reference
Ammonium sulfate	0.97	1.77	7.67×10^5	[40,41,43]
Ammonium persulfate	0.49	1.98	8.35×10^5	[40]
Calcium chloride	–	2.15	8.13×10^5	[40]
Calcium peroxide	–	3.34	Insoluble	[45,50]
Diammonium peroxydisulphate	0.49	1.98	8.35×10^5	[40]
Magnesium oxide	–	3.65–3.75	86	[40,50]
Magnesium peroxide	–	3	Insoluble	[40]
Potassium persulfate	–	2.48	5.2×10^4	[40,45]
Sodium chloride	–	2.16	3.57×10^5 at 0 °C	[40–42]
Sodium persulfate	–	2.4	5.49×10^3	[43]
Glycol ethers	Not Found	Not Found	Not Found	
Hemicellulase enzyme	Not Found	Not Found	Not Found	

COD = Theoretical chemical oxygen demand.

toxicity, these inorganic crosslinkers are not expected to be a major environmental concern, however environmental and toxicity data on the lactate and triethanolamine complexes are needed.

Ammonium chloride is water soluble and has a low Henry's constant at neutral pH (Table 5), indicating that the potential for volatilization from fracturing fluid is low. Ammonia is readily degradable to nitrate by bacteria and has a significant COD (Table 5), suggesting this crosslinker could contribute to the COD of flowback water. Toxicity values for ammonium chloride are in GHS Category 4 (Table 3). However, ammonium chloride is seemingly used in low concentrations, is common in the environment, and has been thoroughly studied as an environmental and health hazard, so is not considered a priority HF chemical in this context.

Monoethanolamine and monoethylamine are both readily biodegradable and soluble in water. The Henry's constant for monoethanolamine implies that this chemical will not volatilize
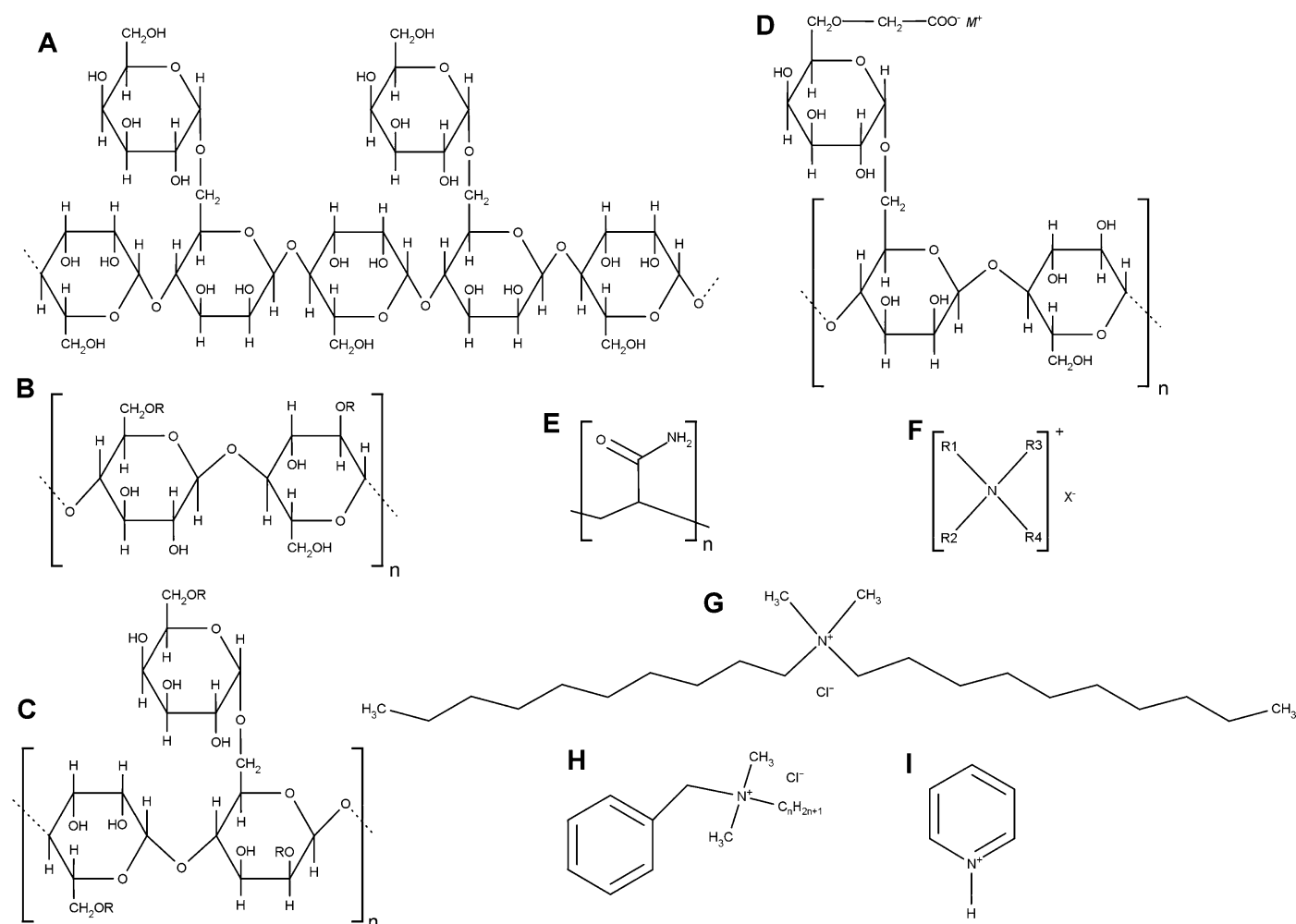

Fig. 1. Structures of commonly used chemicals in hydraulic fracturing fluids. (a) Guar, a gelling agent. The backbone has α-1,6-lined galactose side chain units attached randomly (adapted from Cheng and Prud'homme [67]); (b) hydroxyethylcellulose (HEC), a gelling agent. R = CH₂CH₂OH (adapted from Economides and Nolte [3]); (c) hydroxypropyl guar (HPG), a gelling agent. R = CH₂—CHOH—CH₃ (adapted from Economides and Nolte [3]); (d) carboxymethyl guar gum (CMG), a gelling agent (adapted from Adhikary et al. [69]); (e) polyacrylamide, a friction reducer; (f) generic quaternary ammonium compound, a biocide (adapted from Fredell [87]); (g) didecyl dimethyl ammonium chloride (DDAC), a biocide; (h) Alkyl dimethyl benzyl ammonium chloride (ADBAC), a biocide; (i) pyridinium, a corrosion inhibitor.

Table 7
Properties of pH adjusters, corrosion inhibitors, and iron controlling agents used in hydraulic fracturing.

Chemical[a]	log (K_{OW})	K_H (atm m³ mol⁻¹)	K_{OC}	pK_a	COD (gO₂ g⁻¹)	Density (g cm⁻³ at 25 °C)	Melting point (°C)	Boiling point (°C)	Vapor pressure (mmHg at 25 °C)	Solubility in Water (mg L⁻¹)	Biodegrad-ability	Reference
Acetaldehyde[b]	−0.34	6.67×10^{-5}	16	13.57	1.82	0.78	−123.4	20.1	902	1×10^6	RB	[40,41,46,49]
Acetic acid[c,d]	−0.34	1.23×10^{-3}	6.5–228	4.76	1.07	1.05	16.6	117.9	15.7	Miscible	RB	[40,48,51]
Acetone[b]	−0.24	4.26×10^{-5}	18	20	2.20	0.78	−94.7	56.1	232	Miscible	RB	[40,42,46,47]
Citric acid[d]	−1.72	8.33×10^{-18}	3.1	2.79	0.75	1.67	153	Decomposes	1.7×10^{-8}	3.83×10^5	RB	[40,49]
Ethyl methyl derivatives[b]	Various	Various	Various	–	Various	Various	Various	Various	Various	Various	Various	
Formic acid[b]	−0.54	1.67×10^{-7}	1	3.75	0.35	1.22	8.3	101	42.59	Miscible	RB	[40,41,49]
Hydrochloric acid[c]	0.25	4.9×10^{-10}	1.08	<1	–	1.18	−114.22	−85.05	35,424	6.73×105	–	[40,41]
N,n-dimethyl formamide[b]	−1.01	7.4×10^{-8}	7	0.3	2.41	0.94	−60.4	153	3.87	Miscible	RB	[40–42,46,48]
Potassium carbonate[c]	−6.19	Not Found	Not Found	–	–	2.29	899	Decomposes	2.44×10^{-17}	1.11×10^6	–	[40,42]
Potassium hydroxide[c]	Not Found	Not Found	Not Found	–	–	2.04	380	1327	1 at 714 °C	1.12×10^6	–	[40,41,50]
Propargyl alcohol[c]	−0.38	1.2×10^{-6}	14	–	2.00	0.97	−48to −52	114–115	15.6	Miscible	RB	[40–42]
Pyridinium[b]	Not found	Not found	Not found	–	3.20	Not found	Not found	Not found	Not found	Not found	Not found	
Sodium carbonate[c]	−6.19	6.1×10^{-9}	Not Found	–	–	2.54	856	Decomposes	9.92×10^{-17}	3.07×10^5	–	[40,42]
Sodium erythorbate[d]	−7.05	6.79×10^{-14}	Not found	–	0.80	Not found	168–175	Not found	2.33×10^{-18}	1.60×10^5	Not found	[40,42,43,49]
Sodium hydroxide[c]	−3.88	8.45×10^{-9}	0.22	–	–	2.13	323	1388	1.82×10^{-21}	1.11×10^6	–	[40,42]
Thioglycolic acid[d]	0.09	1.94×10^{-8}	27	3.55	1.22	1.33	−16.5	120	8.68×10^{-2}	Miscible	IB	[40,41,49]
Thiourea[b]	−1.08	2.0×10^{-9}	3–6	2.03	2.52	1.41	176–178	Sublimes	2.8×10^{-3}	1.42×10^5	IB	[40–42,46]

COD = Theoretical chemical oxygen demand, RB = Readily biodegradable, IB = Inherently biodegradable.
[a] Fumaric acid is a pH adjuster and also a gelling agent. It is described in Table 4. Isopropanol and methanol are stabilizers or winterizing agents used in conjunction corrosion inhibitors and also used with gelling and foaming agents. They are described in Table 4.
[b] Corrosion inhibitor.
[c] pH adjuster.
[d] Iron controlling agent.

Table 8
Properties of biocides used in hydraulic fracturing.

Chemical[a]	log (K_{OW})	K_H (atm m³ mol⁻¹)	K_{OC}	COD (gO₂ g⁻¹)	Density (g cm⁻³ at 25 °C)	Melting point (°C)	Boiling point (°C)	Vapor pressure (mmHg at 25 °C)	Solubility in water (mg L⁻¹)	Biodegrad-ability	Reference
1-Bromo-3-chloro-5,5-dimethylhydantoin	−0.94	8.10×10^{-7}	23	0.99	Not found	163–164	Not found	6.6×10^{-6}	8.26×10^3	Not found	[40]
2,2-Dibromo-3-nitrilopropionamide	0.8	1.91×10^{-8}	65	0.66	Not found	123–126	190 (decomposes)	9×10^{-4}	15,000	B	[40,42]
2-Bromo-3-nitrilopropionamide	Unknown	Unknown	Unknown	1.08	Not found	Not found	Not found	Not found	Not found	Not found	
Alkyl dimethyl benzyl ammonium chloride	Various	Various	6.4×10^5–6.2×10^6	Various	0.94	Various	241	3.53×10^{-12}	Various	RB	[55]
Didecyl dimethyl ammonium chloride	4.4×10^5	6.85×10^{-10}	4.4×10^5–1.6×10^6	3.09	0.92	228.81	Not found	2.33×10^{-11}	0.55	B	[40,42]
Glutaraldehyde	−0.18	1.10×10^{-7}	120–500	2.08	1.06	−14	188	0.6 at 30° C	2.2×10^5	RB	[40,41,49]
Tetrakis hydroxymethyl-phosphonium sulfate	−20.39	1.7×10^{-23}	140	0.95	1.41	−35	111	1.27×10^{-5}	1×10^6	RB	[40,42,56]
Tributyl tetradecyl phosphonium chloride	Not found	Not found	Not found	3.02	Not found	60	Not found	Not found	Not found	Not found	[54]

COD = Theoretical chemical oxygen demand, RB = Readily biodegradable, B = Biodegradable.
[a] Ammonium chloride is a biocide and also a crosslinker. It is described in Table 5.

Table 9
Properties of clay stabilizers used in hydraulic fracturing.

Chemical[a]	log(K_{OW})	K_H (atm m³ mol⁻¹)	K_{OC}	COD (gO₂ g⁻¹)	Density (g cm⁻³ at 25°C)	Melting point (°C)	Boiling point (°C)	Vapor pressure (mmHg at 25°C)	Solubility in water (mg L⁻¹)	Biodegra-dability	Reference
Potassium chloride[b]	−0.46	−	−	−	1.99	771	1420	Not found	3.55×10^5	−	[40,43]
Choline chloride[b]	−5.16	2.03×10^{-16}	2.3	2.06	1.1	305	Decomposes	4.93×10^{-10}	$>6.5 \times 10^5$	RB	[40–42,57]
Tetramethyl ammonium chloride[b]	−4.18	4.2×10^{-12}	8	2.34	1.17	402	Decomposes	1.2×10^{-8}	5.9×10^5	NB	[40]
Dimethyl dihydrogenated tallow ammonium chloride[c]	Various	Various	Various	Various	Various	Various	Various	Various	Various	Various	
Sodium lauryl sulfate[c]	1.6	Not found	10,000	2.00	Not found	206	Not found	4.7×10^{-13}	1×10^5	RB	[40,41,43,49]

COD = Theoretical chemical oxygen demand, RB = Readily biodegradable, NB = Non-biodegradable.
[a] Sodium chloride is a clay stabilizer and also a breaker. It is described in Table 6. 2-Butoxyethanol, ethanol, and isopropanol are stabilizers or winterizing agents used in conjunction with surfactants and are also used with gelling and foaming agents. They are described in Table 4.
[b] Clay stabilizer.
[c] Surfactant.

readily from solution, but the significantly higher Henry's constant of monoethylamine indicates a greater potential for volatilization (Table 5); however, inhalation toxicity for rats is moderate (Table 2). Monoethylamine has reported LD_{50} oral toxicity values for rats between 400 and 530 mg kg⁻¹ (Table 3), placing this HF chemical in GHS Category 4. The range of reported LD_{50} values for monoethanolamine is wide (Table 3), which suggests this HF chemical falls in GHS Category 4 as well. Of the crosslinkers surveyed in this study, monoethanolamine and monoethylamine appear to be the compounds of most interest and both are expected to be highly mobile in soils and groundwater based on K_{OC} values; however, neither compound is expected to be environmentally persistent.

3.4. Breakers

Following fracturing, an enzyme or inorganic breaker is introduced to reverse crosslinking, which reduces viscosity of gelled fluids and allows removal of residual polymers from newly created fractures, which would otherwise impede flow of gas and reduce well productivity [62,79]. The breaker reacts with and disrupts polymers, resulting in reduced molecular weight and fluid viscosity, allowing fracturing fluid to be recovered from wells [4]. Encapsulated or time-release breakers may be included in gels to reduce the chances of the polymer breaking prematurely [3,80,81]. Breakers are also required for slickwater fracturing fluids to degrade friction-reducing polymers. At temperatures below 66 °C, enzyme breakers can be used to break guar gels [66,82] but under higher temperature conditions (94–121 °C) and at pH above 10.5, the effectiveness of most enzymes is reduced, and inorganic breakers are used [66]. Breakers are typically used in concentrations ranging from 1 to 400 mg L⁻¹ [5,63].

Enzymes and inorganic compounds can be applied as breakers either while the fluid is being pumped into wells or after fracturing is complete. The commonly used enzyme breakers are hemicellulases; these non-toxic chemicals could contribute to COD of flowback water since they are proteins and degrade cellulose polymers into smaller, more rapidly degraded sugars. Many inorganic breakers are simple salts, such as calcium chloride, sodium chloride, and ammonium sulfate [16,32], which present no specific health hazard, but may contribute to salinity and, in the case of ammonium, COD of flowback water.

Inorganic oxidants, including ammonium, potassium, and sodium salts of peroxydisulfate [83], calcium and magnesium peroxide [3,32], and magnesium oxide [32] are used as breakers. Inorganic oxidants are well-characterized (Table 6) and present a number of chemical and physical hazards. These HF chemicals are not volatile from water, but some oxidants are GHS Category 4 toxicants and LD_{50} values were not available for several compounds (Table 3). In general, environmental contamination impacts are considered to be minor, but transportation and industrial use impacts are of interest for this group.

Glycol ethers and copper compounds are also used as breakers, though specific formulations and associated CAS numbers could not be located [16]. Exposure to low levels of glycol ethers may cause respiratory irritation, headache, and nausea, while exposure to high levels may have more severe health impacts, including liver and kidney damage, pulmonary edema, and loss of consciousness [84]. Inhalation of the dusts of copper salts may cause nasal and respiratory irritation, while contact with skin can cause itching, redness, or swelling [40]. Copper is a potent inhibitor of algae and is a toxic heavy metal that could represent a long-term environmental risk. Lack of information on specific formulations being used prevents a full assessment of breakers as a group of HF chemicals. The use of copper compounds, glycol ethers, and strong oxidants as breakers
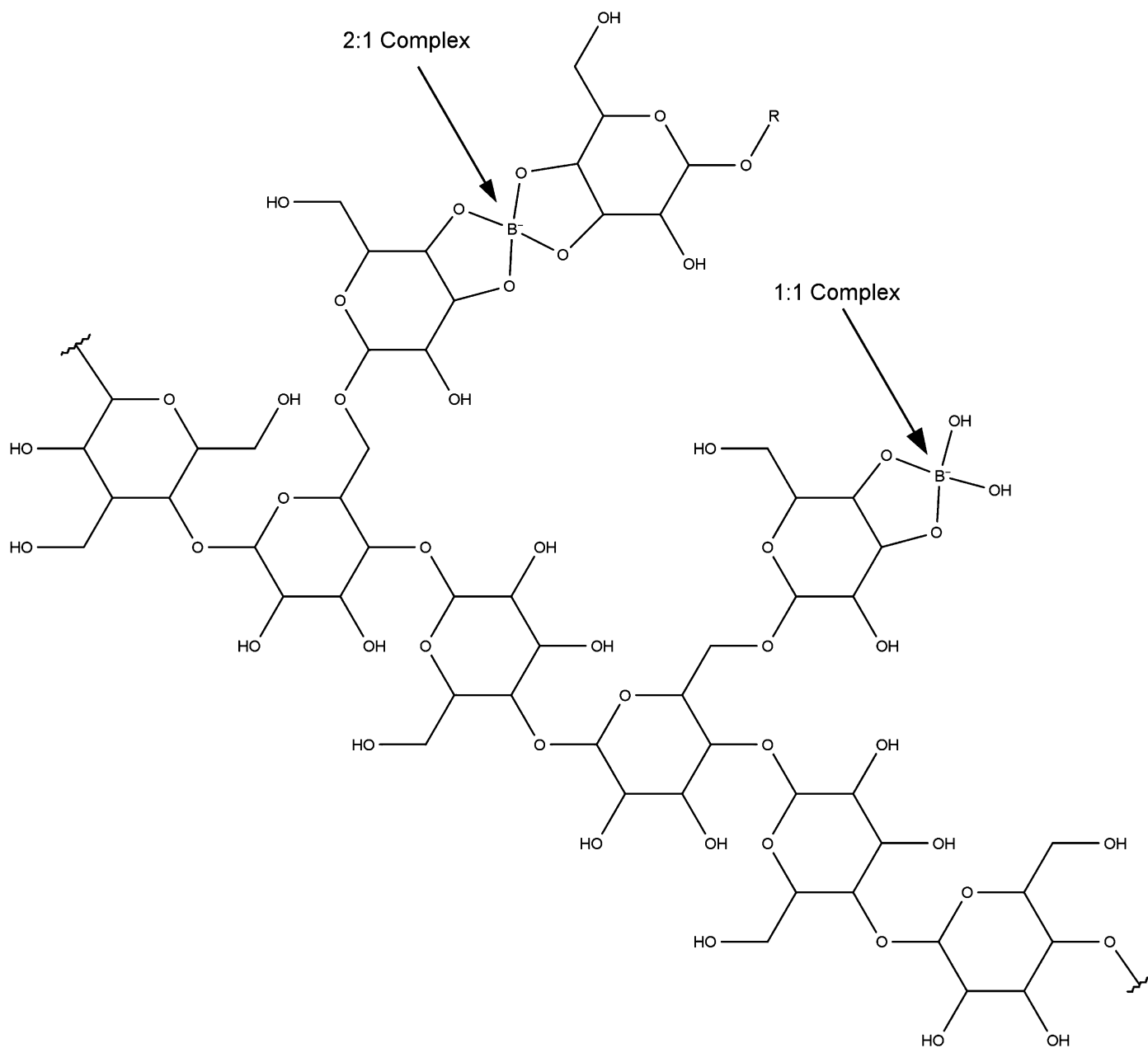
Fig. 2. Structure of guar crosslinked with borate. The R group denotes another molecule of guar (adapted from Barati et al. [80]).

suggests that further investigation of the use of these chemicals in unconventional oil and gas recovery is warranted.

3.5. pH adjusters

Acids and bases are added to fracturing fluids to adjust pH and improve effectiveness of certain chemical additives, particularly crosslinked polymer molecules. Ideal pH for a gelled treatment depends on the polymer being crosslinked and the crosslinking additive being used. Some crosslinkers perform better at high pH, such as borate crosslinking of guar and HPG, because a high pH is necessary for the crosslinking ion to dissociate from the crosslinking compound (due to high pK_a) [3]. When crosslinking HEC and HPC with zirconium, a pH between 10 and 12 is ideal; while CMHEC crosslinked with zirconium requires a pH between 4 and 6 [3].

In addition to optimizing crosslinker performance, pH control can be used as a method to manage bacterial growth in the fracturing fluid [85]. Acids are also used to clean the wellbore and dissolve formation minerals to open up flow paths for better fracturing near the wellbore [81,86]. Acids added to clean out the wellbore are typically not added directly to the fracturing fluid, but are instead used in conjunction with corrosion inhibitors and iron controllers between well perforation and HF [81]. Acid solutions used to dissolve carbonates or silicates for the purpose of increasing formation porosity (acidizing or acid-matrix treatments) are not considered in this study.

Typical pH adjusters include acetic acid, potassium hydroxide, sodium hydroxide, sodium carbonate, and potassium carbonate. Fumaric acid, previously discussed in section 3.1, is also employed as a pH adjuster. These pH adjusters are highly soluble in water and consist of biodegradable organic acids or ionic bases. Typical concentrations for pH adjusters range from 100 to 300 mg L^{-1} [5,63]. Some concentrated pH adjusters are hazardous, but many are of low toxicity (Table 3) and when diluted, they pose a minimal

risk to the environment or human health. Sodium hydroxide and potassium hydroxide are the most toxic, considered GHS Category 3 toxic chemicals with oral rat LD_{50} values of 140 and 273 mg kg^{-1}, respectively. All other pH adjusters fall under Categories 4 and 5. Fumaric and acetic acids are expected to contribute to the COD of flowback water and affect oxidative treatments (Table 7). High or low pH solutions may need to be neutralized prior to treatment, as release of untreated high or low pH solutions can have negative environmental impacts or disrupt treatment processes, especially biological treatment trains. All strongly acidic or basic solutions are potentially hazardous to the environment and to human health and are a significant disposal problem, but procedures for the safe management of these solutions are available and are standard industry practice.

3.6. Biocides

Biocides are used in HF to control bacteria that degrade fracturing chemicals and contribute to corrosion of well tubing, casings, and equipment [16,81]. Sulfate reducing and acid forming bacteria are the primary organisms targeted with the application of biocides. Biocides frequently used for HF (Table 8) include quaternary ammonium compounds (QACs), glutaraldehyde, tetrakis hydroxymethyl phosphonium sulfate (THPS), tributyl tetradecyl phosphonium chloride (TTPC), and brominated compounds including 2,2-dibromo-3-nitrilopropionamide (DBNPA) [16,32]. Ammonium chloride, discussed in Section 3.3, is also used [28]. Biocides are typically used in concentrations ranging from 10 to 800 mg L^{-1} [5,10,63,81].

Quaternary ammonium compounds (QAC) are composed of straight chained alkyls and cyclic hydrocarbons surrounding a central nitrogen atom (Fig. 1f) [87]. The type of organic group and the chain length of the tail can vary, resulting in a range of properties for different QACs, including widely varying log K_{OW} and toxicity values [88]. Each CAS number for QACs corresponds to a specific blend of QAC molecules with specific attached alkyl groups [55]. Didecyl dimethyl ammonium chloride (DDAC) and alkyl dimethyl benzyl ammonium chloride (ADBAC) are commonly used QACs (Fig. 1g and h, respectively), and the physical and chemical constants for these compounds are included in Table 8. Toxicity information was found for DDAC, but not ADBAC (Table 3). The reported mammalian LD_{50} values for DDAC vary, but this compound is likely a GHS Category 3 toxin.

The physical properties of the QACs indicate that they will not volatilize from solution, and are likely to sorb to soils and sediments and will not migrate directly with groundwater (Table 8). QACs are common ingredients of household products (Table S1) and may be found in environmental samples impacted by septic and sewage systems [88,89]. The degree of biodegradability of QACs is variable. Data suggests that biodegradation decreases as the hydrophobic alkyl chain length increases and QACs that contain a benzyl group have lower biodegradation rates [88]. However, QACs have also been measured in sediments and waters near wastewater discharge sites, suggesting that QACs are environmentally persistent [89,90]. Measurements of QACs in surface waters and sediments has confirmed preferential sorption onto sediments, although aqueous concentrations were still detectable [89].

Glutaraldehyde and the phosphonium based biocides are sometimes considered "green" alternatives to other biocides, largely because they are less persistent in the environment. Glutaraldehyde is readily biodegradable under aerobic and anaerobic conditions [91]. The estimated aerobic and anaerobic half lives in river sediments are 10.6 and 7.7 h, respectively, based on measurements of glutaraldehyde losses [92], though conditions such as concentration and acclimation of bacteria to glutaraldehyde may affect degradation rates [93]. Glutaraldehyde has a

moderate K_{OC} value, suggesting it will be mobile in soil and groundwater. Glutaraldehyde is volatile based on vapor pressure and meets criteria for GHS Category 1 toxic chemicals, according to some sources, based on rat inhalation studies (Table 2), suggesting the atmospheric contamination pathway should be considered. Glutaraldehyde is also of concern for oral toxicity (Table 3). Although glutaraldehyde is generally well-characterized and is not an environmentally persistent compound, the acute toxicity of this compound suggests that its use in HF should be further studied.

Tetrakis hydroxymethyl phosphonium sulfate (THPS) has low log K_{OW}, K_{OC}, and K_H values, suggesting that it will not sorb to soil or volatilize from solution, but will migrate with groundwater (Table 8). Under abiotic conditions, THPS has been shown to be stable at pH 5 and 7, with half-lives greater than 30 days; at pH greater than 8, THPS degrades within seven days. Under environmental conditions, THPS breaks down through hydrolysis, oxidation, and photodegradation [94] and initially degrades to trihydroxymethyl phosphine (THP), releasing two formaldehyde molecules and one sulfuric acid molecule in the process [56]. THPS is biodegradable, with carbon dioxide, water, and inorganic phosphate as the reported products [95]. Despite having rat oral LD_{50} values that place it as a GHS Category 3 toxin, THPS is considered a green alternative biocide due to its rapid biodegradation, low concentrations of harmful chemical intermediaries formed during degradation [95], low treatment dose levels, lack of halogens, and the lack of bioaccumulation potential [94,96].

Tributyl tetradecyl phosphonium chloride (TTPC) is a quaternary phosphonium biocide with a tetradecyl chain which causes the molecule to have surface-active properties [97]. Based on the oral LD_{50} for rats, TTPC at a solution concentration of 48–52% is a GHS Category 4 chemical (Table 3). Chemical and physical data as well as information regarding the environmental fate and degradation of TTPC is not readily available for this compound, indicating TTPC should be further investigated.

2,2-Dibromo-3-nitrilopropionamide (DBNPA) is of moderate concern based on oral toxicity, as it is a GHS Category 3 chemical, but meets criteria for GHS Category 1 toxic chemicals based on rat inhalation LD_{50} values. However, DBNPA is unlikely to significantly volatilize from water, based on the Henry's constant, but it may volatilize from dry soils based on the vapor pressure. DBNPA has low log K_{OW}, and K_{OC}, suggesting that it will not sorb to soil and may migrate with groundwater (Table 8). Through hydrolysis, DBNPA degrades to dibromoacetonitrile, followed by dibromoacetomide, dibromoacetic acid, glyoxylic acid, and oxalic acid. The most stable of these products is dibromoacetic acid, with a half-life of approximately 300 days at 25 °C and pH 7.4 [98]. Degradation through contact with sunlight or reaction with nucleophiles results in formation of cyanoacetamide and ultimately cyanoacetic acid, malonic acid, and oxalic acid [98]. Biocide mixtures containing DBNPA typically contain a small percentage of 2-bromo-3-nitrilopropionamide, a known degradation product of DBNPA [98–100]. Only limited chemical and physical information for 2-bromo-3-nitrilopropionamide is available.

1-Bromo-3-chloro-5,5-dimethylhydantoin has a broad range of reported mammalian oral LD_{50} values, generally in GHS Category 3 (Table 3), suggesting it is less toxic that DBNPA. Moderate volatilization from water is expected and it may be highly mobile in soils and groundwater based on a K_{OC} value of 23. When exposed to water, 1-bromo-3-chloro-5,5-dimethylhydantoin dissociates into dimethylhydantoin (DMH) and hypohalite ions [101]. The production of hypohalite ions has led to the use of 1-bromo-3-chloro-5,5-dimethylhydantoin for disinfection in water purification plants and cooling water systems, as well as residential applications such as swimming pools and hot tubs [101,102]. However, DMH may be of concern for environmental contamination due to its hydrolytic and photolytic stability [101].

The presence of biocides in HF wastewater may limit the treatment options by interfering with biological treatment methods or limit co-disposal of HF flowback with municipal wastewater. Studies have shown that QACs are not completely removed in wastewater treatment plants, and that at influent concentrations between 0.5 and 1 mg L^{-1} for benzalkonium chloride and 5 mg L^{-1} for dodecyl dialkyl ammonium chloride, these QACs can inhibit basic carbon respiration processes. Above 10 mg L^{-1} of either QAC, sludge nitrification can be inhibited [89]. In a study of the chemicals used in leather tanning, glutaraldehyde concentrations of 0.125–2.5 mg L^{-1} inhibited the activated sludge treatment process, with increasing inhibition occurring as the concentration increased, with nearly complete inhibition occurring at a concentration of 2.5 mg L^{-1} [103]. Given the wide use of biocides in HF, their diverse chemistry, their toxicity, and the lack of complete information on toxicology and use, biocides warrant additional investigation. More research is needed to determine the environmental fate and toxicity of QACs and other biocides, including biocides marketed as green alternatives.

3.7. Corrosion inhibitors

Corrosion inhibitors are added to acid treatments and to fracturing fluids to form a protective layer on metal well components, preventing corrosion by acids, salts, and corrosive gasses [104–106]. Selection of corrosion inhibitors and corresponding doses is dependent on well temperature, formation minerals, flow regime, and contact time. Typical doses of corrosion inhibitors range in concentrations from 10 to 7000 mg L^{-1} [5,10,63,81]. A variety of proprietary blends of chemicals are used; however, corrosion inhibitor mixtures often include acetaldehyde, acetone, ethyl methyl derivatives, formic acid, *n,n*-dimethyl formamide, propargyl alcohol, pyridinium, and thiourea (Table 7) [16,32,105]. Isopropanol and methanol are also used as corrosion inhibitors and are discussed in Section 3.1.

In general, corrosion inhibitors are highly soluble and biodegradable (Table 7). The low log K_{OW} and K_{OC} values indicate that these chemicals are not likely to sorb to soils, but that there is potential for these chemicals to migrate into surface and groundwater if released into the environment. Chemical data for ethyl methyl derivatives was not found because the specific compounds used and CAS numbers were not available [16]. Data for pyridinium (Fig. 1i) was also not available, and further investigation is recommended.

Corrosion inhibitors include chemicals that are toxic and carcinogenic. Acetaldehyde and thiourea are "reasonably anticipated to be a human carcinogen[s]" according to the U.S. Department of Health and Human Services National Toxicology Program [107]. Median lethal doses for corrosion inhibitors range from 20 to 9800 mg kg^{-1} via the oral route in rats (Table 3). Of the compounds for which toxicity data was found, propargyl alcohol and thiourea are GHS Category 2 chemicals, making them among the most toxic chemicals used in HF. Propargyl alcohol is considered readily biodegradable and although it is highly mobile in soil and groundwater, it is not expected to be environmentally persistent. Thiourea is only considered inherently biodegradable and is expected to be highly mobile in soil and groundwater, increasing its potential for environmental impacts. Due to environmental regulations and concerns about toxicity, development is underway for new oxygen-based corrosion inhibitors and other substitutes that are biodegradable, less toxic, and non-bioaccumulating [108]. Corrosion inhibitors are widely used in industry, and as a group they are not well characterized (Table 7), and they deserve further investigation based on their toxicity.

3.8. Scale inhibitors

Scale inhibitors, including phosphonic acid salts, sodium polycarboxylate, and copolymers of acrylamide and sodium acrylate, are added to fracturing fluids to protect piping and prevent formation plugging [32,109,110]. Scaling reduces well production by blocking formation pores, reducing permeability, and by blocking flow in piping and tubing. Scale inhibitors are typically used in low concentrations, ranging from 75 to 400 mg L^{-1} in fracturing fluid [5,10,63,81]. Most scale inhibitors work by blocking nucleation sites on growing mineral crystals, preventing further growth [109]. Polycarboxylates and acrylate polymers are the most commonly used additives, as phosphonate compounds are often incompatible with other fracturing fluid additives [81]. To our knowledge, no public chemical data is available on the identified scale inhibitors or could not be found due to the lack of CAS numbers or chemical forumlas reported in the FracFocus database, thus, further investigation of these chemicals is recommended.

3.9. Iron control

Chemicals may be added to fracturing fluids to control iron precipitates that block flow paths within the formation, reducing reservoir rock permeability, well productivity, and fluid recovery [111,112]. Ferric iron (Fe^{3+}) can also inadvertently act as a crosslinker in fracturing fluids containing gelling agents, changing the viscosity of the fluid [111]. Iron precipitation is prevented through the use of iron controlling agents such as thioglycolic acid, citric acid, acetic acid, and sodium erythorbate [9]. Iron controlling agents are typically used in a concentration of 50–200 mg L^{-1} [5,10,63]. These chemicals work by acting as chelating agents, forming complexes with ferrous iron (Fe^{2+}) to prevent the iron from precipitating [81,113]. The use of iron control agents depends on the shale characteristics; Marcellus shale usually does not contain enough iron to warrant iron controlling agents, while the Fayetteville shale does contain high quantities of iron [9].

Acetic acid, citric acid, and sodium erythorbate are common food additives, and as a result, they are of low toxicity to humans. Acetic acid and citric acid are readily biodegradable; however, no data concerning the biodegradability of sodium erythorbate was found. Thioglycolic acid is commonly used in hair care products and leather processing, and while biodegradable, poses a greater toxicity risk due to an oral LD$_{50}$ value of 114 mg kg^{-1} in rats, classifying it as a GHS Category 3 toxic chemical.

All four iron-controlling agents investigated are highly soluble in water and are expected to contribute to the COD of flowback water (Table 7). With the exception of acetic acid, the chemicals are not expected to volatilize from fracturing fluid based on Henry's constants (Table 7). The low K_{OC} values of citric acid and thioglycolic acid indicate that these chemicals will not sorb extensively to soils, but will be mobile in surface and groundwater (Table 7). The K_{OC} of acetic acid is higher and is pH dependent, with a range from 6.5 to 228, but is still relatively low (Table 7). Of the iron control agents, thioglycolic acid appears to be the most problematic as a potential environmental contaminant, although all are generally readily degraded and not persistent.

3.10. Clay stabilizers

Clay stabilizers are used to prevent the swelling of clays found in gas shale layers, particularly smectite. Some gas-containing shales can contain up to 50% clays by volume [15]. Clay swelling and migration can cause borehole instability and can reduce reservoir rock permeability by up to 90%, reducing well productivity and contributing to complications such as sticking of the drill-pipe in the borehole [114,115]. The degree of clay swelling is dependent

on the salinity of the fracturing fluid and the species of cations present, with higher salinities generally reducing swelling [114]. Among cations, divalent cations generally result in less swelling than monovalent cations, and potassium and ammonium salts contain the preferred monovalent cations [114]. Clay migration is also an issue, as clays can become suspended and dispersed by produced water or fracturing fluid, clogging pores and reducing productivity [116]. Clay stabilizers work via ion exchange, replacing the cations (such as sodium) in the clay with other cations (such as divalent cations) that have a lesser tendency to become hydrated and swell the clay. Fracturing fluid that is in contact with clay must maintain a minimum concentration of clay stabilizers to prevent a reversal in cation exchange and clay swelling [114].

Clay stabilizers typically comprise 0.05–0.2% of the total fracturing fluid by volume and concentrations range from 500 to 2000 mg L^{-1} [5,10,63,81]. Clay stabilizers include choline chloride, tetramethyl ammonium chloride, potassium chloride, and sodium chloride [32]. Potassium chloride and sodium chloride are widely used in industry and are well known, and are therefore not considered high priority compounds for concern, however saline wastewaters can present significant management challenges.

Tetramethyl ammonium chloride, a QAC used as a clay stabilizer rather than as a biocide, is a GHS Category 2 oral toxin (Table 3) and one of the most toxic chemicals identified in this study. Tetramethyl ammonium chloride poses an environmental risk as it has been deemed non-biodegradable in aerobic studies and is expected to be highly mobile in soils based on K_{OC} values (Table 9). Although, tetramethyl ammonium chloride is not expected to volatilize from water, if dispersed into the air, any volatile fraction will rapidly degrade via hydroxyl radicals [40]. Although tetramethyl ammonium chloride is expected to contribute to fracturing fluid COD, it is not necessarily biodegradable. Tetramethyl ammonium chloride is also used as a catalyst for organic synthesis and polymerase chain reaction [117], though reports of other uses are limited. Due to the fact that tetramethyl ammonium chloride is one of the few GHS Class 2 toxins identified as being used in HF and it is in the same chemical group as QAC biocides, this compound should be further investigated and its use in HF applications better understood.

Choline is readily biodegradable and generally poses minor or no health risk to humans, as it is falls in GHS Category 5. Choline chloride is used as a food additive and choline is considered an essential nutrient in humans [118]. Choline chloride is expected to be non-volatile from water and a contributor to fracturing fluid COD (Table 9). Choline chloride is compatible with most fracturing fluids, breakers, and crosslinkers, making it an attractive clay stabilizer [119]. Current trends towards the use of choline chloride, as opposed to ammonium salts and the historically used sodium chloride and potassium chloride, are meant to reduce environmental impacts through increased biodegradability, lower toxicity, and lower concentrations in fracturing fluid, as choline chloride is more effective at reducing clay swelling at lower concentrations [81,86,114].

3.11. Surfactants

Surfactants are used in HF fluid to control for optimal viscosity of fracturing fluids, reduce surface tension between the shale formations and the HF fluid, and assist fluid recovery after fracturing [3,81]. In some instances, surfactants may also act as biocides or clay stabilizers [3]. Surfactants are important in emulsion-based fracturing fluids that contain both hydrocarbon and aqueous phases, ensuring proper viscosity and transport properties [3]. Surfactants also reduce the wetting of shale interfaces, allowing for increased gas flow through channels in the formation.

Surfactants, more specifically viscoelastic surfactants, can also be used in place of crosslinkers and gelling agents and foaming agents in high temperature and pressure formations to maintain fluid viscosity while reducing formation damage and increasing fluid recovery [120]. Viscoelastic surfactants form rod-shaped micelles that associate with each other in fracturing fluids containing proper concentrations of salts, resulting in high viscosity and elasticity [3,86]. However, when viscoelastic surfactants come into contact with formation water or hydrocarbons their structure is disrupted, lowering viscosity without the need for breakers while leaving minimal residue in the formation [3].

Surfactants can vary greatly, consisting of amphoteric, anionic, or non-ionic compounds [81]. Typical surfactants include sodium lauryl sulfate and dimethyl dihydrogenated tallow ammonium chloride. Product stabilizers and winterizing agents, mistakenly identified as surfactants in FracFocus, including ethanol, 2-butoxyethanol, and isopropanol are discussed above [32]. Depending on their intended purpose, surfactants are typically used in concentrations ranging from 500 to 1800 mg L^{-1} in fracturing fluid [5,10,63,81]. No chemical data concerning dimethyl dihydrogenated tallow ammonium chloride was available in the databases surveyed due to the lack of a CAS number and exact chemical composition, and thus, further investigation on this compound is recommended. Generally, the surfactants investigated are highly soluble in water, readily biodegradable, and are expected to contribute to flowback COD. Sodium lauryl sulfate has a moderately high K_{OC} value, and is expected to have moderate to low mobility in soil and groundwater [40,41]. Sodium lauryl sulfate is found in household products and is not anticipated to be a health risk due to its LD$_{50}$ value.

4. Conclusions

Eighty-one commonly used HF fluid additives were identified from the FracFocus database and other sources and examined. The chemicals used in HF treatments function as gelling and foaming agents, friction reducers, crosslinkers, breakers, pH adjusters, biocides, corrosion inhibitors, scale inhibitors, iron control chemicals, clay stabilizers, and surfactants. Not all compounds are used in all treatments; for example, gels are not typically used with friction reducers. Within each functional category there are choices of chemicals that can be used; for example, there are several classes of biocides that could potentially be used interchangeably.

Fifty-five of the HF chemicals identified were organic, with 27 of these considered readily or inherently biodegradable according to OECD guidelines [60]. Four chemicals had high CODs (>3 gO$_2$ g^{-1}) (monoethyl amine, pyridinium, didecyl dimethyl ammonium chloride, tributyl tetradecyl phosphonium chloride), while another 13 had moderate CODs (>2 gO$_2$ g^{-1}), and many of these compounds are used at significant concentrations in HF treatments. Using data from Tables 4–9 and the reported concentrations at which HF chemicals are used in HF treatments [5,10,63], we estimate that the COD of HF fluids will be in the range of 5000 mg L^{-1} or more, with potential values ranging four times higher if high concentrations of corrosion inhibitors are used (Table S4). These calculated values correspond reasonably well with reported values for flowback water [1,18,19], and it can be concluded that flowback will be a high COD wastewater, but there are very few studies characterizing flowback and further investigation of flowback water quality is needed. High COD industrial wastes present significant treatment challenges. Further study of individual chemicals, chemical mixtures, and actual flowback are needed to determine what treatment technologies, including aerobic and anaerobic biological treatment, are appropriate for HF wastewaters. The use of some membrane

treatment technology may be problematic given the high COD and high expected biodegradability of HF waste waters.

Overall, volatility of the chemicals examined was not a major concern, as only 12 chemicals were considered volatile or semivolatile from water based on Henry's constants (Tables 4–9). However, given that some HF chemicals meet criteria for GHS Category 1 and 2 inhalation toxins (Table 2), the potential significance of the volatile exposure pathway cannot be ignored and should be further investigated.

Overall, most of the chemicals that had available toxicity data are of moderate or little concern based on mammalian acute oral toxicity. None of the HF chemicals were classified as GHS Category 1 oral toxins; however, three chemicals were classified as GHS Category 2 oral toxins (propargyl alcohol, thiourea, tetramethyl ammonium chloride) and ten were classified as GHS Category 3 oral toxins (Table 3). Importantly, there remains a significant gap in toxicity information, as no mammalian toxicity data was found for approximately one-third of the 81 chemicals examined. Poorly characterized compounds include biocides, corrosions inhibitors (e.g. pyridinium), scale inhibitors, and iron control agents which are widely used in industry. Biocides as a group are of concern, as they contain the highest number of toxic compounds. Other identified chemicals of concern, based on inhalation toxicity, are glutaraldehyde and thioglycolic acid (Table 2). Furthermore, at least five chemicals are confirmed or suspected carcinogens (ethanol, naphthalene, diethanolamine, acetaldehyde, thiourea).

While increased chemical disclosure by companies that perform HF is an important step towards understanding the potential risks associated with contamination events, organization of that information is still required for a more comprehensive understanding of potential environmental and health hazards of chemicals used in unconventional oil and gas extraction processes. HF contractors and companies conducting these operations should continue to disclose information to databases such as FracFocus, but more information about the compositions of proprietary additives and chemical derivatives used in fracturing processes, concentrations at which chemical are used, and mass amounts of chemicals used would be useful for environmental risk assessment.

All of the chemicals used in unconventional production are widely used in industry and data gaps concerning toxicity, biodegradability, physical constants, and concentrations of use should be addressed so that accurate and informed environmental and health assessments can be made. It is recommended that log K_{ow}, Henry's law constant, and other fundamental physical and chemical properties be determined and reported for each compound [59]. In order to understand the environmental fate of HF chemicals during accidental or deliberate releases, tests on biodegradability of pure compounds and mixtures, under both aerobic and anaerobic conditions, should be conducted [60]. At a minimum, acute mammalian oral toxicity, using rats or mice and protocols consistent with international standards [61,121], should be measured and reported for each compound. Environmental toxicity information, using tests on standard fish, crustacean, and plant or algae species [121], is recommended to support complete environmental assessments of industrial chemicals.

Finally, there is a crucial need for more field studies, including characterization of HF fluids before injection and characterization of flowback after injection. Studies need to be conducted to examine the fate of HF chemicals in complex environmental systems with the objective of more completely understanding environmental hazards associated with HF chemicals and chemical mixtures. These studies need to include an evaluation of complex mixtures and examine how the interactions between chemicals found in HF fluids influences the environmental fate of individual components.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jhazmat.2014.04.040.

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