



Project Acronym and Title:
**M4ShaleGas - Measuring, monitoring, mitigating and managing the
environmental impact of shale gas**

**REVIEW OF THE COMPOSITION OF OPERATIONAL FLUIDS AND
FLOWBACK WATER IN HYDRAULIC FRACTURING**

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Project deliverable number: D11.1
Status: Definitive

Disclaimer

This report is part of a project that has received funding by the *European Union's Horizon 2020 research and innovation programme* under grant agreement number 640715.

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Public introduction

M4ShaleGas stands for *Measuring, monitoring, mitigating and managing the environmental impact of shale gas* and is funded by the *European Union's Horizon 2020 Research and Innovation Programme*. The main goal of the M4ShaleGas project is to study and evaluate potential risks and impacts of shale gas exploration and exploitation. The focus lies on four main areas of potential impact: the subsurface, the surface, the atmosphere, and social impacts.

The European Commission's Energy Roadmap 2050 identifies gas as a critical fuel for the transformation of the energy system in the direction of lower CO₂ emissions and more renewable energy. Shale gas may contribute to this transformation.

Shale gas is – by definition – a natural gas found trapped in shale, a fine grained sedimentary rock composed of mud. There are several concerns related to shale gas exploration and production, many of them being associated with hydraulic fracturing operations that are performed to stimulate gas flow in the shales. Potential risks and concerns include for example the fate of chemical compounds in the used hydraulic fracturing and drilling fluids and their potential impact on shallow ground water. The fracturing process may also induce small magnitude earthquakes. There is also an ongoing debate on greenhouse gas emissions of shale gas (CO₂ and methane) and its energy efficiency compared to other energy sources. There is a strong need for a better European knowledge base on shale gas operations and their environmental impacts particularly, if shale gas shall play a role in Europe's energy mix in the coming decennia. M4ShaleGas' main goal is to build such a knowledge base, including an inventory of best practices that minimise risks and impacts of shale gas exploration and production in Europe, as well as best practices for public engagement.

The M4ShaleGas project is carried out by 18 European research institutions and is coordinated by TNO-Netherlands Organization for Applied Scientific Research.

Executive Report Summary

With this report, available information on the chemical composition of fracturing fluids as well as flowback and produced waters from different shale gas plays in the US, Canada and Europe is summarized. It becomes obvious that selection of chemical additives in fracturing fluids is highly variable and not only dependent on the reservoir conditions. Flowback water composition is dependent on the composition of the injected fracturing fluid but also represents a mixture with natural formation water and other chemical constituents derived from the shale or fluid-rock interactions during hydraulic fracturing operation. With respect to this complex situation and the obvious knowledge gaps, future research aims are presented.



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1 INTRODUCTION

1.1 Context of M4ShaleGas

Shale gas source rocks are widely distributed around the world and many countries have now started to investigate their shale gas potential. Some argue that shale gas has already proved to be a game changer in the U.S. energy market (EIA 2015¹). The European Commission's Energy Roadmap 2050 identifies gas as a critical energy source for the transformation of the energy system to a system with lower CO₂ emissions that combines gas with increasing contributions of renewable energy and increasing energy efficiency. It may be argued that in Europe, natural gas replacing coal and oil will contribute to emissions reduction on the short and medium terms.

There are, however, several concerns related to shale gas exploration and production, many of them being associated with the process of hydraulic fracturing. There is also a debate on the greenhouse gas emissions of shale gas (CO₂ and methane) and its energy return on investment compared to other energy sources. Questions are raised about the specific environmental footprint of shale gas in Europe as a whole as well as in individual Member States. Shale gas basins are unevenly distributed among the European Member States and are not restricted within national borders, which makes close cooperation between the involved Member States essential. There is relatively little knowledge on the footprint in regions with a variety of geological and geopolitical settings as are present in Europe. Concerns and risks are clustered in the following four areas: subsurface, surface, atmosphere and society. As the European continent is densely populated, it is most certainly of vital importance to understand public perceptions of shale gas and for European publics to be fully engaged in the debate about its potential development.

Accordingly, Europe has a strong need for a comprehensive knowledge base on potential environmental, societal and economic consequences of shale gas exploration and exploitation. Knowledge needs to be science-based, needs to be developed by research institutes with a strong track record in shale gas studies, and needs to cover the different attitudes and approaches to shale gas exploration and exploitation in Europe. The M4ShaleGas project is seeking to provide such a scientific knowledge base, integrating the scientific outcome of 18 research institutes across Europe. It addresses the issues raised in the Horizon 2020 call LCE 16 – 2014 on *Understanding, preventing and mitigating the potential environmental risks and impacts of shale gas exploration and exploitation*.

¹ EIA (2015). Annual Energy Outlook 2015 with projections to 2040. U.S. Energy Information Administration (www.eia.gov).



1.2 Study objectives for this report

With this report, available literature and information on fluid compositions in hydraulic fracturing activities will be reviewed. Starting with a short introduction on the chemicals applied in high-volume hydraulic fracturing of horizontal wells in shale environments, available data on the composition of these fracturing fluids will be provided, based on the available literature for hydraulic fracturing activities in the US, Canada and Europe. In the second part of this report, available literature on studying composition of flowback and produced waters from shale gas exploitation will be summarized. With this background information, knowledge gaps and further research needs and questions will be elucidated.

1.3 Aims of this report

The aim of this report is to provide information on the current status in chemical composition of fracturing fluids as well as flowback and produced waters from hydraulic fracturing of shales and with this to provide recommendations for future research work. This work summarizes available data from shale gas exploration in the US, Canada and Europe.

2 COMPOSITION OF FRACTURING FLUIDS

2.1 Hydraulic Fracturing

The growing importance of exploring gas and oil from unconventional reservoirs by hydraulic fracturing (HF) also raises public concerns about the potential impacts on human health and the environment. Beside others, concerns are related to the enormous water demand for this technique as well as the application of tons of chemicals in the applied fracturing fluids and the composition of the resulting flowback and produced waters. On the one hand, provision of these huge amounts of water may provide problems to natural environments and drinking water supplies but on the other hand fracturing fluid and flowback waters with unknown composition are feared to be contaminants and handling of these fluids as well as proper treatment are evaluated as still unsolved problems.

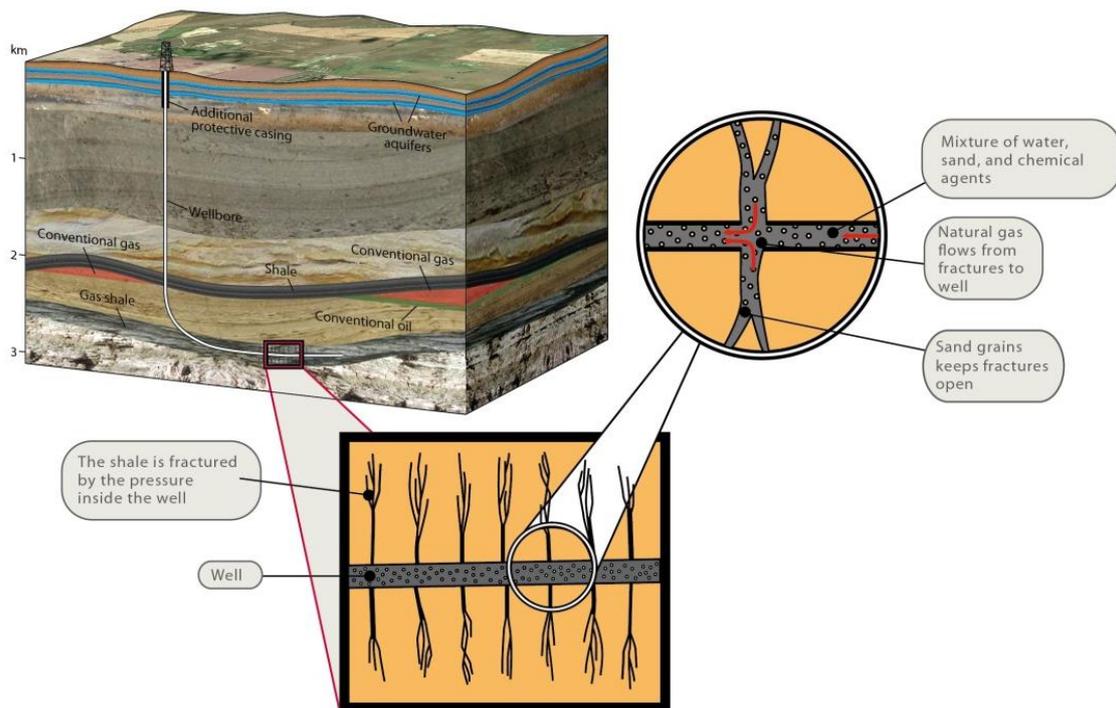


Figure 1: Schematic cross-section of general types of oil and gas resources and the orientations of production wells used in HF (taken from SHIP, 2015).

HF is a stimulation technique used to increase production of oil and gas and involves the injection of fluids under pressures great enough to fracture the oil- and gas-containing formations (US-EPA 2015b). With HF permeability in shale, tight sands, coal-beds, and other gas and oil-bearing strata is increased (Stringfellow et al., 2014). HF is used in conventional oil and gas reservoirs, but also to develop geothermal energy



resources and unconventional oil and gas reservoirs (Figure 1). HF has been used since the late 1940s and for the first almost 50 years HF was used in vertical wells in conventional hydrocarbon reservoirs. HF is still used in these settings, but the process has evolved. Technological developments have led to its use in low-permeability (unconventional) hydrocarbon reservoirs. Wells stimulated by HF may be vertical, deviated, or horizontal in orientation, and they may be newly drilled or older at the time the fracturing is done (US-EPA 2015b).

Water-based fracturing fluids are the most common, but other fluid types can be used for fracturing also. Foams or emulsions are composed of material that is not miscible with water, like nitrogen, carbon dioxide, or hydrocarbons (Montgomery, 2013; US-EPA 2015b). The most common water-based fluid systems are slickwater formulations, which are typically used in very low permeability reservoirs, and gelled fracturing fluids, which can be used in reservoirs with higher permeability (Barati & Liang, 2014).

The fracturing fluids generally consist of three parts: 1) the base fluid (i.e. water), 2) the additives and 3) the proppant. Each additive is a mixture of various chemicals with the main ingredient serving a specific purpose during HF (e.g. friction reducer, gelling agent, crosslinker, breakers, biocide, stabilizer) (Spellman, 2012; Carter et al., 2013;). The particular composition of the fracturing fluid is selected by a design engineer based on empirical experience, the geological setting, reservoir geochemistry, economics, availability of chemicals and preference of the service company or operator (Montgomery 2013; US-EPA 2015b). The largest constituent of a typical fracturing fluid is water (>90%), followed by proppants (<10%) and additives (0.5 – 2%) (Figure 2).

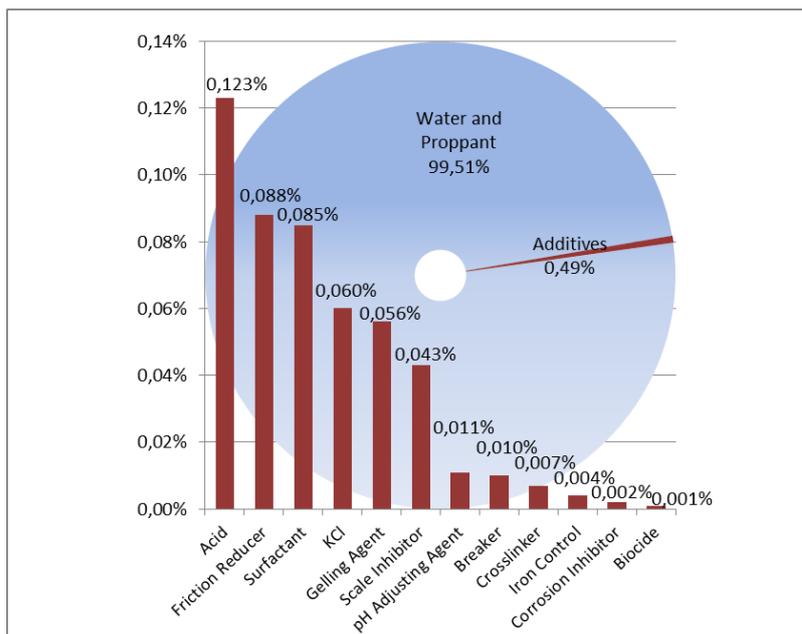


Figure 2: Volumetric composition of a fracturing fluid (data taken from ALL Consulting 2008).



Prior to fracturing, the well needs to be cleaned and prepared. Typically, an acid package will be injected first to adjust pH, clean any cement left inside the well and dissolve any pieces of rock that may remain in the well and could block the perforations (US-EPA 2015b). Then the fracturing fluid will be pumped down the wellbore to create fractures in the formation. The chemical additives are introduced at different times and amounts (Carter et al., 2013). Typically this fluid consists of a mixture of water and friction reducer, but also other additives may be added like e.g. gelling agents, biocides and scale inhibitors. The fluid generates numerous small fissures in the shale. The proppant keeps the fissure open to increase the gas flow. Additional chemicals may be added to gelled fluids, initially to maintain viscosity and later to break the gel down into a more readily removable fluid (Spellman 2012, Carter et al., 2013, US-EPA 2015b). Toward the end of the treatment, a final flush or clean-up phase may be conducted, with the primary purpose of maximizing well productivity (Carter et al., 2013). After the formation has been fractured the pressure is released from the well which causes the fluid mixture to flowback to the surface. This fluid is generally classified as either flowback or produced water (Stringfellow et al., 2014). Flowback water is commonly defined as the water that is released within the initial two weeks following the completion of the HF process (Abualfaraj et al., 2014). Produced water, however, is the naturally occurring water within the shale formation (Stringfellow et al., 2014) (see Chapter 3 for more details).

2.2 Chemical additives used in hydraulic fracturing

Chemical additives for fracturing fluids are quite often described based on the function they fulfill during HF. Descriptions of the individual functions and listings of the chemicals that are used for the specific purposes are found elsewhere (Montgomery, 2013b, Stringfellow et al., 2014, US-EPA 2015b). See table 1 for a summary.

Biocide

Biocides are applied against bacteria present in the base fluid and the introduction of anaerobic sulfate-reducing bacteria into the reservoir. Biocides frequently used for HF include quaternary ammonium compounds (QACs), glutaraldehyde, tetrakis(hydroxymethyl)phosphonium sulfate (THPS), tributyl tetradecylphosphonium chloride and brominated compounds (Stringfellow et al., 2014). Glutaraldehyde is the most commonly used electrophilic biocide in HF operations (Kahrilas et al., 2015). Biocides are typically used in concentrations ranging from 10 to 800 mg/l.

Clay control agents:

Clay stabilizers are used to prevent the swelling of clays found in gas shale layers, particularly smectite. 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 (Zhou et al., 1995, Stringfellow et al., 2014). Clay stabilizers typically comprise 0.05–0.2% of the total fracturing fluid by volume and concentrations range from 500 to 2000 mg/l (Stringfellow et al., 2014). Clay stabilizers include choline chloride, tetramethyl ammonium chloride, potassium chloride, and sodium chloride. Potassium chloride and



sodium chloride are widely used in industry. Tetramethyl ammonium chloride is one of the most toxic chemicals identified in HF (Stringfellow et al., 2014). Current trends are towards the use of choline chloride, as choline chloride is more effective at reducing clay swelling at lower concentrations (Stringfellow et al., 2014).

Table 1: Examples of common additives and their functions (adapted from US-EPA 2015b and fracfocus.org).

| Additive | Function |
|---------------------|--|
| Acid | Helps dissolve cement, minerals and clays to reduce clogging of the pore space |
| Biocide | Controls or eliminates bacteria, which can be present in the base fluid and may have detrimental effects on the fracturing process |
| Breaker | Allows a delayed break down of gels (reducing viscosity) when required |
| Clay Control | Prevents the swelling and migration of formation clays in reaction to water-based fluids |
| Corrosion inhibitor | Protects the iron and steel components in the wellbore and treating equipment from corrosive fluids |
| Crosslinker | Maintains viscosity as temperature increases by connecting polymer molecules |
| Friction reducer | Reduces the friction pressures experienced when pumping fluids through tools and tubulars in the wellbore |
| Gelling agent | Thickens the water in order to suspend the proppant, to carry more proppant into the fractures and to reduce fluid loss to the reservoir |
| Iron control | Controls the precipitation of iron from solution |
| pH control | Maintains the effectiveness of other additives (e.g. crosslinkers) by either changing or stabilizing pH |
| Scale inhibitor | Controls or prevents scale deposition in the production conduit or completion system |

Corrosion inhibitor

These chemicals are added to form a protective layer on metal well components, preventing corrosion by acids, salts and corrosive gasses (Stringfellow et al., 2014). Corrosion inhibitor mixtures often include acetaldehyde, acetone, formic acid, propargyl alcohol, isopropanol and methanol. Typical doses of corrosion inhibitors range in concentrations from 10 to 7000 mg/l (Stringfellow et al., 2014).

Friction Reducers

These materials are added to reduce the friction generated as the fluid is pumped down the well tubulars. A commonly used friction reducer is polyacrylamide, reported application rates in fracturing fluids are 30 – 1200 mg/L (King 2012, Stringfellow et al., 2014). According to King (King 2012), nearly all slickwater fracturing projects use polyacrylamide as a friction reducer and this is typically delivered in 50% active dispersion of the solid in mineral oil (Montgomery 2013b).



Gelling agents

Polymers are added to the fracturing fluid to increase the viscosity, improve the proppant transport and reduce the friction pressure. Guar and its derivatives are the most common gelling agents used for HF (Montgomery 2013b).

Iron control agent:

Iron precipitates will block flowpaths within the formation, reducing reservoir rock permeability, well productivity and fluid recovery. This will be avoided by using iron controlling agents such as thioglycolic acid, citric acid, acetic acid and sodium erythorbate. They are typically used in concentration of 50 – 200 mg/l. (Stringfellow et al., 2014)

pH control:

Buffers are added to adjust the pH of the base fluid and to improve effectiveness of other chemical additives. As some buffers dissolve slowly they can be used to delay crosslinking for a set period of time to reduce friction in the tubing (Montgomery 2013b). Typical pH adjusters include acetic acid, potassium hydroxide, sodium hydroxide, sodium carbonate and potassium carbonate. Typical concentrations for pH adjusters range from 100 to 300 mg/l (Stringfellow et al., 2014).

Crosslinkers

These chemicals are used to increase the molecular weight of the polymer (e.g. guar) by crosslinking the polymer backbone. If guar is used as gelling agent, borate salts and several metal compounds including titanium and zirconium are used as crosslinkers (Montgomery 2013a). Concentrations of crosslinkers in fracturing fluid are relatively low and range from 0.5 to 250 mg/l (King 2012, Stringfellow et al., 2014).

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 (Stringfellow et al., 2014). The breaker reacts with and disrupts polymers, resulting in reduced molecular weight and fluid viscosity, allowing fracturing fluid to be recovered from wells (Zimmermann et al., 2011). At temperatures below 66°C, enzyme breakers can be used to break guar gels (Stringfellow et al., 2014) 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 (Montgomery 2013b). The commonly used enzyme breakers are hemicellulases. Inorganic oxidants, including ammonium, potassium, and sodium salts of peroxydisulfate, calcium and magnesium peroxide, and magnesium oxide are used as breakers. Breakers are typically used in concentrations ranging from 1 to 400 mg/l (Stringfellow et al., 2014).

Scale inhibitors

Scaling reduces well production by blocking formation pores, reducing permeability and by blocking flow in piping and tubing. Scale inhibitors include phosphonic acid salts, sodium polycarboxylate and copolymers of acrylamide and sodium acrylate



(Stringfellow et al., 2014). Also ethylene glycol and methanol will be used to prevent scaling (US-EPA 2015). Scale inhibitors are typically used in concentrations ranging from 75 to 400 mg/l in FF.

2.3 Chemicals used for hydraulic fracturing in the USA

The booming application of HF in unconventional shale reservoirs has started in the US. As response to increasing public concerns about the environmental issues and health effects of HF, the Committee on Energy and Commerce launched an investigation to examine the practice of HF in the US. The 14 leading oil and gas service companies were asked to disclose the types and volumes of the HF products they used in their fluids between 2005 and 2009 and the chemical contents of those products. These results have been summarized by Waxman and others in 2011 (Waxman et al., 2011).

Table 2: Chemical components appearing most often in hydraulic fracturing products used between 2005 and 2009 (data from Waxman et al., 2011).

| Chemical Compound | Number of Products |
|---|--------------------|
| Methanol (Methyl alcohol) | 342 |
| Isopropanol (Isopropyl alcohol, Propan-2-ol) | 274 |
| Crystalline silica- quartz (SiO ₂) | 207 |
| Ethylene glycol monobutyl ether (2-butoxyethanol) | 126 |
| Ethylene glycol (1,2-ethanediol) | 119 |
| Hydrotreated light petroleum distillates | 89 |
| Sodium hydroxide (Caustic soda) | 80 |

In this report it was stated that between 2005 and 2009, the 14 oil and gas service companies used more than 2,500 hydraulic fracturing products containing 750 chemicals and other components. Overall, these companies used about 3 million m³ of hydraulic fracturing products – not including water added at the well site – between 2005 and 2009. The most widely used chemical was methanol. It was a component in 342 products. Some of the other most widely used chemicals include isopropyl alcohol, which was used in 274 products, and ethylene glycol, which was used in 119 products (Waxman et al., 2011). Table 2 has a list of the most commonly used compounds in reported hydraulic fracturing fluids between 2005 and 2009.

Within this high number of chemicals, also 29 chemicals were present that are known or possible human carcinogens, pose a risk to human health or are listed as hazardous air pollutants. These 29 chemicals were used in 652 different products. Many chemical components were listed as “proprietary” or “trade secret” and were not disclosed. The hydraulic fracturing companies used about 0.35 million m³ of 279 products containing at least one proprietary component (Waxman et al., 2011).



In 2011, FracFocus, a web-based database, was launched to provide public access to reported chemicals used for HF and serves as the national HF chemical registry. FracFocus is managed by the Ground Water Protection Council and Interstate Oil and Gas Compact Commission and is in use in currently 23 states as a means of chemical disclosure. FracFocus database contains 106132 registered well sites and disclosures of the applied chemicals used for HF. This database was searched and evaluated by several authors at different times.

Stringfellow and coauthors wrote an excellent review on the physical, chemical and biological characteristics of compounds used in HF and selected the individual chemicals based on their appearance in the FracFocus database (operations from Jan 2011 – August 2012), an US-EPA report on HF fluids, HF textbook and different industry reports (Stringfellow et al., 2014). Based on these data, he developed a list with 81 commonly used fracturing chemicals. Kahrilas and coauthors performed a FracFocus search with focus on the applied biocides and presented the most frequently used biocides in HF. In most disclosed HF applications, glutaraldehyde and dibromonitrilopropionamide are used as biocides (Kahrilas et al 2015). Patel performed a FracFocus search comprising 55000 HF treatments from 2011 to first half of 2013 and focused the evaluation on the applied fluid systems and proppants (Patel et al., 2014). Carter performed FracFocus search for over 1000 registered wells in western Pennsylvania and West Virginia (Marcellus Shale) with HF application from August to December 2012. Here, focus was on the most applied organic compounds for different functions (Carter et al., 2013). Arthur performed FracFocus search for all disclosures from January 2011 to November 2013 (more than 55000 wells) and presented the geographic distribution of all disclosures in 10 US-states with focus on water use as well as the most applied chemicals in different shale gas plays (Eagle Ford, Bakken, Utica) (Arthur et al., 2014). The most comprehensive evaluation of FracFocus data was presented by US-EPA (US-EPA 2015a). This report evaluated more than 39000 disclosures being provided until March 2013. Beside an overall summary of water use and application of chemicals in HF, state reports have been generated and five counties were selected to illustrate diversity in additive ingredients at small scales. The following presentation on the diversity of chemicals used in HF in the US is based on the results of this US-EPA study (US-EPA 2015a).

From January 2011 to February 2013, HF activities were reported for well locations in 406 counties in 20 states by 428 well operators. More than 93% of disclosures reported use of water as base fluid. Among proppants, quartz was the most common material reported. HF fluids were generally found to contain 88% by mass water, 10% by mass quartz and <1% by mass additive ingredients. The database contains 692 unique chemical ingredients for additives, base fluids and proppants. Per gas disclosure, the median number of additive ingredients was 12. One or more ingredients were claimed confidential in more than 70% of the evaluated disclosures and operators designated 11% of all ingredient records as confidential business information. The most commonly reported additive ingredients for gas disclosures were hydrochloric acid, methanol and hydrotreated light petroleum distillates (Table 3). But a valid CAS-number for



identification of the compounds was only assigned to about 65% of the over 1.2 million ingredient records in the database (US-EPA 2015a).

Table 3: Twenty most frequently reported additive ingredients in hydraulic fracturing of gas wells (frequency of occurrence) (data from US-EPA 2015a).

| Chemical Compound | CAS-No. | Number of Disclosures (%) |
|--|----------------|----------------------------------|
| Hydrochloric acid | 7647-01-0 | 12,351 (73%) |
| Methanol | 67-56-1 | 12,269 (72%) |
| Distillates, petroleum, hydrotreated light | 64742-47-8 | 11,897 (70%) |
| Isopropanol | 67-63-0 | 8,008 (47%) |
| Water | 7732-18-5 | 7,998 (47%) |
| Ethanol | 64-17-5 | 6,325 (37%) |
| Propargyl alcohol | 107-19-7 | 5,811 (34%) |
| Glutaraldehyde | 111-30-8 | 5,635 (33%) |
| Ethylene glycol | 107-21-1 | 5,493 (32%) |
| Citric acid | 77-92-9 | 4,832 (28%) |
| Sodium hydroxide | 1310-73-2 | 4,656 (27%) |
| Peroxydisulfuric acid, diammonium salt | 7727-54-0 | 4,618 (27%) |
| Quartz | 14808-60-7 | 3,758 (22%) |
| 2,2-Dibromo-3-nitrilpropionamide | 10222-01-2 | 3,668 (22%) |
| Sodium chloride | 7647-14-5 | 3,608 (21%) |
| Guar gum | 9000-30-0 | 3,586 (21%) |
| Acetic acid | 64-19-7 | 3,563 (21%) |
| 2-Butoxyethanol | 111-76-2 | 3,325 (20%) |
| Naphtalene* | 91-20-3 | 3,294 (19%) |
| Solvent naphta, petroleum, heavy arom. | 64742-94-5 | 3,287 (19%) |

2.4 Chemicals used for hydraulic fracturing in Canada

The situation in Canada seems to be more diverse concerning composition of fracturing fluids but quantitatively on a lower level than in the US. In Canada, horizontal drilling and HF are focused on large plays such as the Horn River, Liard Basin, Cordova Embayment and Montney basins in northeast British Columbia and the Montney and Duvernay basins in Alberta. HF is also applied in Saskatchewan and Manitoba with shale oil in the Bakken Formation along the US border (Quinn et al., 2015). The first shale gas production in Canada came from the Montney Play Trend (tight gas and shale gas) in 2005 and the Horn River (exclusively shale gas) in 2007, both located in northeastern British Columbia, where drilling activities have rapidly expanded. Industry interest for other Canadian shale and tight sand plays started around the same period in



British Columbia, Alberta, New Brunswick and Quebec. As of the end of 2012, over 1100 wells have been either drilled for shale gas exploration and production mostly in British Columbia and Alberta (Rivard et al., 2014). While comprehensive data is not available for each province, the British Columbia Oil and Gas Commission mentioned that more than 7,300 wells have been fractured in British Columbia since 2005, and that between 500 and 1,000 new wells are being permitted in the province each year, the majority of which will use hydraulic fracturing (CESD 2012).

In British Columbia, slickwater is used in the Horn River Basin, while Montney liquid-rich gas shales and siltstones are mainly fracked with foams (mix of gas and water). In Alberta, slickwater, cross-linked fluids and a combination of the two have been used in the Duvernay Formation. In New Brunswick, predominantly gelled propane was successfully used in the first vertical shale gas well (Rivard et al., 2014).

The province of British Columbia has implemented the Canadian FracFocus database in 2012 and since January 2012 disclosure of used additives is required for HF activities in British Columbia. Since its inception, the Canadian website has signed agreements with the National Energy Board (2013), Alberta (2012), Saskatchewan, Northwest Territories (2015) and Yukon to join the registry, although not all have mandatory reporting requirements. To date, more than 8000 entries are available for wells in Alberta, about 1900 entries for sites in British Columbia, 18 entries for New Brunswick, and 2 entries for Northwest Territories (fracfocus.ca).

Environment Canada and Health Canada have compiled a list of over 800 substances known or suspected to be used in hydraulic fracturing in Canada, 33 of which have been assessed as toxic (CESD 2012). Van Stempvoort and Roy have identified those manufactured chemicals and fluids used in natural gas production in Canada as well as the formation fluids (gases, saline waters, brines, and condensates) that are extracted. They also summarized what little information exists about the fate of various natural and manufactured chemicals in groundwater relevant to shale gas development operations (Van Stempvoort and Roy, 2011). However, this report is not available and evaluations of the Canadian fracfocus database with respect to the applied chemical additives are also not available.

2.5 Chemicals used for hydraulic fracturing in Europe

Shale gas is widely considered to be the unconventional fossil fuel with the greatest potential for development in Europe. To date, EU countries have adapted different policies towards shale gas and its exploitation. HF was applied in Poland, United Kingdom and Germany. To date, France, Scotland and Bulgaria have banned HF. Netherlands, Romania, Denmark, Ireland, and the Czech Republic have moratoria on HF.

In Poland, intensive environmental monitoring was performed and data have been published for 7 test sites around exploratory wells Lubocino-2H; Stare Miasto-1K; Wysin-1 (HF was cancelled); Syczyn OU-2K; Zwierzyniec-1; Gapowo B-1A; and Lebien LE-2H (PGI 2015). For these sites, fracturing fluids and resulting flowback waters were analysed for standard inorganic and organic compounds. Chemical additives used in the different HF activities are not named in this report. However,



chemicals used in HF of 13 different wells in Poland have been published on the NGS facts webpage (www.ngsfacts.org), for summary see Table 4.

Table 4: Most frequently used chemicals in HF operations in Poland (n=13) (data from ngsfacts.org).

| Chemical compound | Number of disclosures |
|---|-----------------------|
| Ethyleneglycol | 13 |
| Hydrochlorid acid | 13 |
| Methanol | 12 |
| Silicate material (quartz) | 11 |
| Prop-2-yn-1-ol | 8 |
| Aliphatic alcohols (ethoxylated) | 8 |
| 5-chlor-2-methyl-2H-isothiazol-3-one and 2-methyl-2H-isothiazol-3-one | 6 |
| Propan-2-ol | 6 |
| Boric acid | 5 |
| Formic acid | 5 |
| Guar gum | 5 |
| Heavy aromatic naphtha | 5 |

Beside this, BNK petroleum reported the additives used during HF of the Saponis Lebork S-1 Ordovician stimulation to be butyl diclycol (foaming agent, 0.02 %), cholinium chloride (clay control, 0.07%) and polyethylene glycol monohexyl ether (emulsifier, 0.007%) (bnk petroleum, 2015). OPPPW presents very general information on their webpage on the chemical additives used during HF in Poland. The most frequently used natural polymer is guar and its derivates (50% of chemical additives), other used additives are crosslinkers (boron, titanium and zirconium compounds), buffers (hydrofluoric acid, ammonium bisulfate), biocides, stabilizers (sodium chloride, ethylene glycol, calcium chloride, isopropanol, methanol), surfactants (amines, glycol ethers, (nonyl-)phenol ethoxylates), viscosity breakers (lithium hypochlorite, ammonium persulfate, calcium peroxide), clay control (acids, phosphonates, polyglycol) and gelling agents (cellulose, guar) (OPPPW 2015).

In United Kingdom only one shale gas well has been hydraulically fractured until now, this is the Preese Hall 1 well in the Bowland shale. According to information from company Cuadrilla, fracturing fluid consisted of fresh water (about 8400 m³), sand (463 m³), polyacrylamide emulsion in hydrocarbon oil (3.7 m³) as friction reducer and sodium salt as chemical tracer. No addition of biocide was necessary as the water was treated by the supplier before (Cuadrilla 2015).

In Germany, HF is in operation for the exploitation of tight gas reservoirs in the deep sandstone of Lower Saxony since the 1980s (Gordalla et al., 2013). The chemical additives used by ExxonMobil in different HF operations in Germany have been published online (ExxonMobil 2015a). About 150 substances with different chemical



identities could be identified, 119 of them were specified by CAS numbers (Gordalla et al., 2013). The only HF in shale was performed in well Damme3 in 2008, the composition of the fracturing fluid is presented in table 5. Here, it is surprising to see that there is no chemical disclosure for 4 out of 10 additives and these 4 not-disclosed additives represent 40% by mass of all chemical additives (Gordalla et al 2013). With respect to possible future HF operations, the application of chemicals may be limited to biocide (ethylenedioxy-dimethanol), clay stabilizer (choline chloride), surfactant (polyethylene glycol monohexyl ether), friction reducer (2-butoxy-ethoxy-ethanol), or thickener (carbohydrate polymer derivative) (Gordalla et al., 2013). ExxonMobil provided a public statement that future fracturing fluids will only consist of water, proppant and only 2 chemical additives (clay stabilizer choline chloride and friction reducer butoxyethoxyethanol) (ExxonMobil 2015b)

Table 5: Constituents of Damme3 fracturing fluid (data from Gordalla et al., 2013).

| Function | Chemical Compound | CAS-No | Employed mass (kg) |
|----------------------------------|--|------------|--------------------|
| Base fluid | water | 7732-18-5 | 12095000 |
| proppant | proppant | 66402-68-4 | 588000 |
| biocide | “Kathon”® 5-chlor-2-methyl-2H-isothiazol-3-one; 2-methyl-2H-isothiazol-3-one (3:1) | 55965-84-9 | 46 |
| Stabilizing component of biocide | Magnesium chloride | 7786-30-3 | 23 |
| Stabilizing component of biocide | Magnesium nitrate | 10377-60-3 | 46 |
| Component of biocide | n.a. | n.a. | 345 |
| Clay stabiliser | Tetramethylammonium chloride | 75-57-0 | 6367 |
| Component of clay stabiliser | n.a. | n.a. | 4245 |
| Friction reducer | Polyethylene glycol-octylphenyl ether | 9036-19-5 | 440 |
| Friction reducer | Hydrotreated light petroleum distillates | 64742-47-8 | 2640 |
| Component of friction reducer | n.a. | n.a. | 1760 |
| Component of crosslinker | Inorganic salts, n.a. | n.a. | 103 |



3 COMPOSITION OF FLOWBACK AND PRODUCED WATERS

3.1 General aspects

After hydraulic fracturing is completed, the pressure will be reduced and the water will flow back from the well. Composition of flowback is related to the composition of the initial fracturing fluid, the composition of the natural formation water of the shale and the possible interactions between fracturing fluid and shale system over time at the in-situ conditions. Initially this water, called flowback, is mostly fracturing fluid, but with time, it becomes more similar to the natural formation water, e.g. increase in salinity, and decrease in DOC (Cluff et al., 2014). This later stage water is also called produced water. Concerning composition of flowback water, inorganic constituents (metals, salts), organic compounds (hydrocarbons, organic acids) and naturally occurring radioactive material (NORM) have to be considered. Therefore, to understand controls on the flowback water composition, composition of the initial fracking fluids, natural formation waters and possible processes relevant in the reservoir need to be clarified. Besides quality of flowback water composition, also the amount of flowback is interesting. Here, several statements on the recovery of injected fracturing fluid exist. Jia declared that industry data revealed that about one third of the injected water is typically recovered (Jia et al., 2013). Stringfellow stated that 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 (US-DOE 2009, King 2012, Stringfellow et al., 2014).

To date, most publications on composition of flowback and produced water deal with samples from the Marcellus shale gas exploitation, only few publications exist from other shale gas sites in the US, Canada or Europe.

3.2 Flowback and produced water composition in the USA

Hayes provided a large dataset with compositional analysis of samples from 19 shale gas wells of the Marcellus play (Hayes, 2009). Here, samples of the influent water streams (supply water and water sample including chemical additives but no proppant) and flowback water samples from day 1 to day 90 after the HF operation were investigated. All samples were analysed for basic parameters like pH, Total Dissolved Solids (TDS), Dissolved Organic Carbon (DOC), 70 volatile organic compounds, 112 semivolatiles organic compounds, 23 pesticides, 7 polychlorinated biphenyls (PCBs), and metals. Based on these results Hayes summarized that halogenated hydrocarbon compounds and polynuclear aromatic hydrocarbons are not part of the typical components in flowback waters. Organic compounds that were detected are BTEX (benzene, toluene, ethylbenzene, xylenes), methylated benzenes, naphthalene, naphthenic acids, volatile acids and simple alkanes. These compounds are also present in produced waters from conventional reservoirs and derive from the reservoir formation. The dominant cations in the flowback water samples were sodium and calcium, dominant anion was chloride. Also occurrence of metals in flowback waters is



within the ranges for normal produced waters from conventional reservoirs (Hayes, 2009).

Several other studies have been conducted to characterize the constituents that are found in flowback water from numerous locations across the Marcellus shale region. Four different studies with a total of 35000 entries have been summarized by Abualfaraj (Abualfaraj et al., 2014). Here, the concentrations of individual constituents in flowback water samples have been compared with the maximum contamination level (MCL) guidelines for drinking water, if available. The following constituents were found to have mean concentrations over 10 times greater than the MCL: 1,2-dichloroethane, antimony, barium, benzene, benzo(a)pyrene, chloride, dibromochloromethane, gross alpha, iron, manganese, pentachlorophenol, radium, thallium, and vinyl chloride (Abualfaraj et al., 2014). They also stated that “concentrations of anthropogenic chemicals are tightly correlated with each other, but not with chloride concentrations, and not with naturally occurring inorganics and radionuclides” and that “with the exception of chloride, none of these constituents is listed as a known chemical additive to fracturing fluids” (Abualfaraj et al., 2014).

Focus of the study from Cluff and coworkers (Cluff et al., 2014) was on the changes in flowback water composition and microbiology over time. Their results very nicely show the mixture of injected fracturing fluids with the natural formation fluids in the Marcellus Shale. The injected fracturing fluid has lower chloride content but higher DOC content than the natural formation fluid and the mixture of both fluids after HF operation is obvious from increasing chloride but decreasing DOC concentrations in the flowback (Cluff et al., 2014). Organic carbon in the injected fluids may be sorbed, exchanged, or diluted within formation fluids, reacted within the rock-fluid matrix or through microbially mediated mineralization of organic constituents. For additional characterization of the DOC, LC-QTOF and GC-MS techniques were applied and different benzene compounds, naphthalene, toluene, undecane, dodecane, acetic acid and ethoxylated surfactants were detected. With exception of ethoxylated surfactant, all other compounds were not present in the injected fluids but in the flowback water samples (Cluff et al., 2014). Orem and coauthors reported that the most consistently detected organic compound in flowback include PAHs, heterocyclic compounds, alkyl phenols, aromatic amines, alkyl aromatic (alkyl benzenes, alkyl biphenyls), long-chain fatty acids, and aliphatic hydrocarbons (Orem et al., 2014). Concentrations of individual organic compounds increased during the flowback, which suggest an origin from formation water and host rock (Ziemkiewicz & He, 2015). The detection of organics in the HF fluids while not in the initial makeup water indicates that additives are also a possible source of organic compounds in the flowback (Ziemkiewicz & He, 2015). Produced water samples, taken 38 months after HF operation, showed DOC concentrations between 7 and 49 mgC/l (Akob et al., 2015), similar to the concentrations reported by Cluff and coauthors (Cluff et al., 2014) and Orem and coauthors (Orem et al., 2014). A substantial portion of the DOC consisted of low molecular weight organic acids like acetate, formate and pyruvate. Acetate was also present in produced water from Marcellus investigated by Orem and coauthors (Orem et al., 2014).



Maguire-Boyle and Barron compared composition of produced waters from Marcellus, Eagle Ford and Barnett shales. Non-purgeable organic carbon (NPOC) contents of the Barnett samples (43550 mg/l) are much higher than of the Eagle Ford (6095 mg/l) and Marcellus samples (2348 mg/l) (Maguire-Boyle & Barron, 2014). These values are much higher than the reported DOC values for other produced water or late flowback water samples from Marcellus.

Lester and coauthors investigated flowback water samples from an oil/gas well in the Denver-Julesburg Basin in Colorado, where they observed extremely high concentration of acetic acid. The water samples were also analysed for 70 different VOC, 112 SVOC and trace organic contaminants by LC-TOF-MS. Of the analyzed VOC compounds only xylenes, acetone and 2-butanone were detected, and less than 10% of the tested SVOC compounds (1,4-dioxane, 2-methylphenol, 3-methylphenol, 4-methylphenol, 2-methylnaphthalene, dimethyl phthalate, phenanthrene, pyrene, butyl benzyl phthalate, bis(2-ethylhexyl)phthalate, phenol, 2,4-dimethylphenol) (Lester et al., 2015). LC-TOF-MS analysis revealed the presence of cocamidopropyl dimethylamine, a commercial surfactant widely used in cosmetics and detergents, and linear alkyl ethoxylates, typically used as chemical additive to enhance surfactant properties and movement of sand and oil substances during HF operation (Lester et al., 2015). Linear alkyl ethoxylates were also detected in flowback water samples sampled in Colorado and Texas by Thurman and coauthors (Thurman et al., 2014). These authors used LC-QTOF/MS also to detect polyethylene glycols.

Continued analyses of both, the HF fluid and the flowback or produced water have shown that not all organic compounds that were injected into the well return to the surface but that others, native to the shale environment will be present in the flowback or produced waters only. If not all injected compounds will return in the flowback than adsorption/desorption and/or chemical transformation processes are taking place within the formation. Determination whether organic compounds detected in produced waters are synthetic or naturally-derived from the reservoir is complicated by the number of compounds that exist both naturally in the formation and are injected with the HF fluid (Carter et al., 2013, Ferrer & Thurman, 2015).

The inorganic chemistry of the Marcellus flowback is dominated by Na, Cl and the divalent cations Mg, Ca, Sr and Ba (Barbot et al 2013; Ziemkiewicz & He, 2015). Also in produced water samples, taken 38 months after HF operation, Marcellus water samples were dominated by these ions (Haluszczak et al., 2013, Akob et al., 2015). The origin of the dissolved solids in the produced water is an unresolved issue, with suggestions including dissolution of water-soluble salts in the shale formation, extraction of pore-bound water, diffusion osmosis, and accessing of formation water in shale fractures or adjacent formations (Stewart et al., 2015).

Metal concentrations in flowback exceeded the drinking water MCL for Pb, Se, Al, Mn and Fe. This suggests that these metals originate from formation brine or were otherwise mobilized during HF (Ziemkiewicz & He, 2015). Mobilization of trace elements



through changes in local geochemical conditions of the fractured shales was also described by Chermak and Schreiber (Chermak & Schreiber, 2014) and Tuttle and Breit (Tuttle & Breit, 2009) and was reported from laboratory experiments where shale samples were exposed to artificial fracturing fluids (Wilke et al., 2015).

Ra-226 and Ra-228 are the most abundant NORM in flowback and are derived from the radioactive decay of U-238 and Th-232, which commonly occur in sandstones and shales in hydrocarbon reservoirs. Radioactivity of NORM tends to increase during flowback and seems to be a function of the amount of flowback that has come in contact with the reservoir formation over time (Ziemkiewicz & He, 2015).

3.3 Experiences from Canada

Similar to reports on fracturing fluid composition, also data on composition of flowback and produced water samples from Canadian shale gas plays are very rare. Paktinat and coauthors (Paktinat et al., 2011) reported concentrations of few anions and cations in produced and flowback waters from Horn River and Montney plays, respectively. At both plays, water is dominated by chloride and sodium. Bicarbonate is high in Horn River (2195 mg/l) but lower in Montney (54 mg/l). Sulfate and carbonate concentrations are low. Beside sodium, also calcium and magnesium were detected, barium is only present in Horn River samples. Elliott and coauthors investigated the microbial communities in fresh waters, fracturing fluids and flowback water from Montney formation in Western Canada. Beside microbiological studies, few chemical and physical properties of the samples were determined, concentrations of nitrate, sulfate, lactate, acetate, propionate and butyrate are low (< 1mM) (Elliott et al., 2014).

3.4 Experiences from Europe

In Poland composition of flowback water from different sites of HF operation in Poland was published by PGI (PGI, 2015). Sites in Pomeranian Basin (Lubocino, Stare Miasto) are characterized by significant concentrations of calcium, potassium and sodium, flowback from Gapowo also shows elevated concentrations of barium, cesium, selenium, strontium, arsenic and sulphur (PGI, 2015). Concentrations of natural isotopes in flowback fluids were slightly higher than in fracturing fluids, but generally still within natural concentration ranges in the environment. Fracturing fluids and flowback water from sites in the Pomeranien and Lublin basin were compared for their concentrations of bulk organic parameters as well as selected individual organic compounds. In the Lublin basin, bulk parameters like total hydrocarbons, sum of aliphatic hydrocarbons, total mineral oil, DOC, chemical oxygen demand and (anionic) surfactants have higher maximum concentrations in fracturing fluids than in flowback waters. But concentrations of PAHs tend to be higher in flowback water than in fracturing fluids (PGI, 2015).

At the Preese Hall 1 site in the UK, flowback water samples were investigated by the UK Environmental Agency (UK-EA 2011). Few results were reported by residents of the Preese Hall area. Flowback from Preese Hall was characterized as Na-Cl water type



(Na 34.8 g/l; Cl 92.8 g/l) containing also bromide (1 g/l), magnesium (2.1 g/l) and potassium (0.1 g/l) (UK-EA, 2011). Flowback also contained significant levels of Ra-226, above legal limits. Concentrations of lead were about 90 – 100 µg/l, cadmium up to 6 µg/l, magnesium up to 397 mg/l, chromium 222 µg/l and aluminium reached up to 596 µg/l.

In Germany, composition of the flowback water from the only shale gas HF operation, Damme3, was provided by Olsson and coauthors. Flowback water in Damme3 is characterized by high chloride concentrations between 40,360 and 88,440 mg/l, high sodium (17,690 – 36,390 mg/l) and high calcium (6700 – 16,550 mg/l). In comparison to flowback from tight gas HF operations, Damme3 flowback contains higher concentrations of strontium, barium and magnesium with maximum concentrations of 1720, 593, and 2130 mg/l, respectively. No information is available about DOC content or presence of specific organic compounds (Olsson et al., 2013).



4 OUTLOOK

Based on the available literature on chemical composition of fluid in HF operations, the most prominent knowledge gap is the missing full disclosure of all chemicals and their used amounts. Tracing the fate of individual chemicals and chemical mixtures used in HF operations is necessary from injection to production and water treatment. The full disclosure of the applied chemicals also is prerequisite for a knowledge-based decision about necessary water treatment and possible ways of disposal for the huge amounts of flowback and produced waters. On the other hand, if spills or leakages or other accidents happen where fracturing fluids or flowback and produced waters are released to the environment (e.g. soil, surface and groundwater) also information on the chemical composition is necessary for proper treatment and remediation. With full disclosure of chemicals it will be possible to elucidate suitable chemical tracers of the applied fracturing fluids for contamination issues. Full disclosure of the chemicals should not be limited to CAS numbers but should also provide the IUPAC name, which is essential for further research (Elsner et al., 2015).

As the in-situ conditions in the reservoir formations are significantly different to standard conditions used for routine assessment of chemical's toxicity and environmental and health effects also these tests have to be adapted to expected in-situ conditions including salinity, temperature, pH, pressure, redox state. This testing should also comprise possible degradation and reaction products of the applied chemicals. However, without full disclosure of the applied chemicals, even the existing data gaps concerning toxicity, biodegradability, physical constants of applied chemicals under standard conditions cannot be closed.

Until now, the influence of the shale formation on the flowback water composition is quite often mentioned but not evaluated. Here, also experimental studies seem to be necessary to assess the respective shale's potential to release organic and inorganic constituents into the flowback water. Based on the extraction results of two European shale samples with an artificial fracturing fluid it became obvious that the flowback shows shale-specific characteristics in both, inorganic and organic composition (Wilke et al., 2015). In addition to this, it was shown that the thermal maturity of the individual shale sample has a strong influence on the extracted organic compounds (Zhu et al., 2015).



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