FracRisk

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This deliverable presents results of the data collection effort on the chemical, physical and toxicity properties as well as permitted concentration levels in drinking water of chemicals that are frequently used in the fracking process.

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FracRisk: Furthering the Knowledge Base for Reducing the Environmental Footprint of Shale Gas Development

Database of physical and chemical properties and thresholds relevant to shale gas

July 2016

This project has received funding from the European Union's Horizon 2020 Research and Innovation programme under Grant Agreement No. 640979

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1. Introduction

This deliverable presents results of the data collection effort on the chemical, physical and toxicity properties as well as permitted concentration levels in drinking water of chemicals that are frequently used in the fracking process.

Data on the chemicals used in the fracking process is key since the main goal of WP4 is to develop a risk assessment (RA) tool based on the Risk Based Corrective Action - RBCA methodology [1].

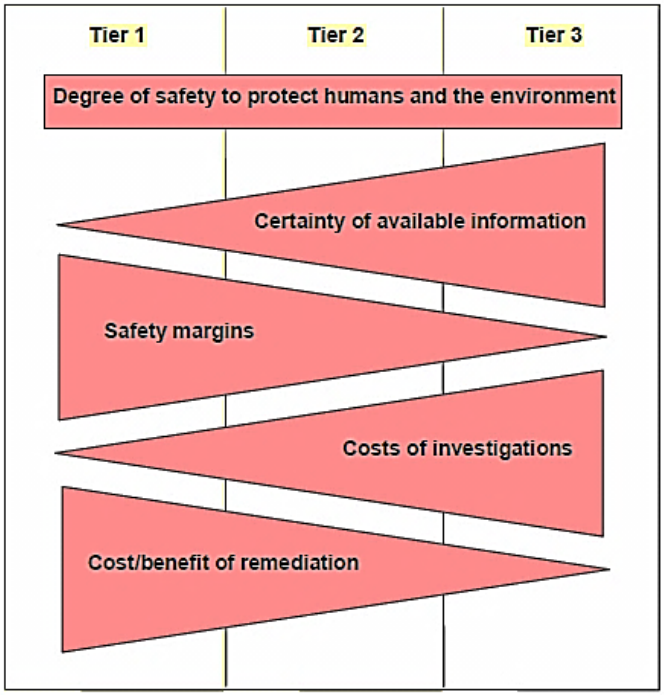
1.1 The RBCA methodology

In the frame of FracRisk, RBCA refers to a philosophy for managing contaminant release sites. Decisions related to urgency of response, target cleanup levels and remedial measures are based on current and reasonable potential risks to human health and environmental resources. The RBCA process is based on three tiers of possible activities, where the user begins at the first tier and then progresses to higher tiers, if warranted [2].

This tiered approach will ensure that simple cases can be completed relatively quickly with minimum efforts and cost. More data collection and tests are required to assess the risk of complex cases and potentially serious situations. Information can be gradually expanded to reduce the uncertainty and subsequently improve the rationale for making a decision (see Fig. 1). Tiers approach start from one to three, the uncertainty for tier 1 is higher than that of tiers 2 and 3, but the safety margins decreased from tier 1 to tier 3 which depends on the quantity of collected information and lead to increase the cost of data collected. Thus, the cost of remediation reduced from tier 1 to tier 3 if the contaminated site required for remediation [3].

Figure 1 - The three tier approach of RBCA

(after [3])



1.2 Data needed for SG-RBCA

In the next stages of WP4, a SG-RBCA software will be developed (Deliverable 4.4, to be submitted in January 2018). This tool is aimed to enable users to evaluate the risks related to fracking activity at a specific site and

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to suggest risk reduction and or control measures (such as monitoring, corrective action and/or limitations and regulation).

In order to calculate the risk in a site-specific context, information on the chemicals that are present in the environment, or may be present in case of malfunction or accident in the fracking process, is needed. The general information includes properties of the chemicals used: physio-chemical properties; toxicity information; and maximum allowable concentration levels.

In this deliverable, we present a database with most frequently used chemicals in the fracking industry – their properties and toxicity, and point out the gap in the available data and current knowledge.

Additional data that is needed to evaluate the risks is more site-specific, for example - geology and hydrology of the operation site; type of receptors; fracking information (amount of wells, depth) etc. This site-specific information will be obtained for three suggested fracking sites in Europe in deliverable D4.5 (to be submitted on June 2018).

1.3 Categories of chemicals

The main components (98–99.5%) of a typical fluid used for fracking are water and sand (proppant). The remaining components (forming 0.5–2% of the injected fluid) are chemical mixtures, used at various stages of the fracking process (Table 1). Although hundreds of chemicals are used to make thousands of different compounds, any individual fracking work in an individual well will typically involve 6 to 12 chemicals, depending on the nature of the fluid used [4, 5]. The specific agents can vary depending on the geology of the site and the drilling company. Accordingly, the potential human and environmental implications may differ greatly from site to site [6].

The chemicals used in the fracking process are commonly divided into 9-14 categories based on the purpose of use, as depicted in Fig.2 and Table 1. It is beyond the scope of FracRisk to create a database of all chemicals that can be deployed in the process of hydraulic fracturing. Instead, we focus on the most frequently used chemicals in each category (to a maximum of ten chemicals per category).

Figure 2 – Typical fluid composition for Marcellus Shale region, Pennsylvania, USA

(after [7])

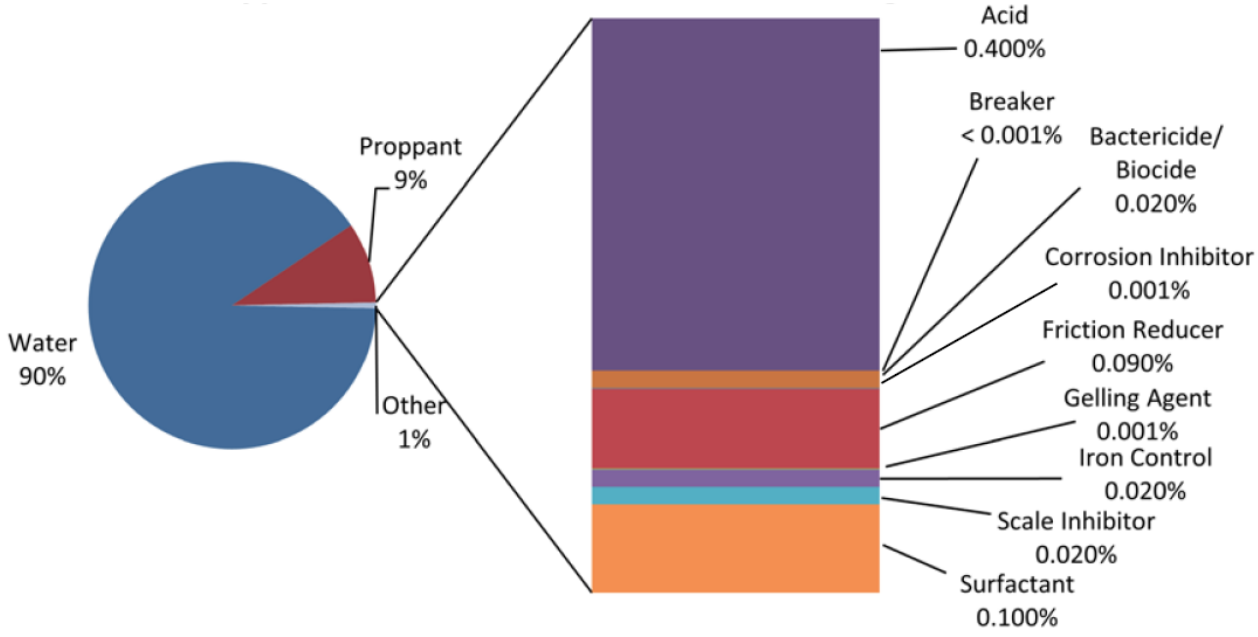

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Table 1 – Categories of chemicals used in HF and their main purposes

(after [8])

Additive	Purpose	Downhole result
Acid	Helps dissolve minerals and initiate cracks in the rock	Reacts with minerals present in the formation to create salts, water, and carbon dioxide (neutralized).
Acid/corrosion inhibitor	Protects casing from corrosion	Bonds to metal surfaces (pipe) downhole. Any remaining product not bonded is broken down by micro-organisms and consumed or returned in produced water.
Biocide	Eliminate bacteria in the water that can cause corrosive byproducts	Reacts with micro-organisms that may be present in the treatment fluid and formation. These micro-organisms breakdown the product with a small amount of the product returning in produced water.
Breaker	Allows a delayed break down of gels when required	Reacts with the "crosslinker" and "gel" once in the formation making it easier for the fluid to flow to the borehole. Reaction produces ammonia and sulfate salts which are returned in produced water.
Clay and shale stabilization/ control	Temporary or permanent clay stabilizer to lock down clays in the shale structure	Reacts with clays in the formation through a sodium-potassium ion exchange. Reaction results in sodium chloride (table salt) which is returned in produced water. Also replaces binder salts like calcium chloride helping to keep the formation in tact as the calcium chloride dissolves.
Crosslinker	Maintains viscosity as temperature increases	Combines with the "breaker" in the formation to create salts that are returned in produced water.
Friction reducer	Reduces friction effects over base water in pipe	Remains in the formation where temperature and exposure to the "breaker" allows it to be broken down and consumed by naturally occurring micro-organisms. A small amount returns with produced water.
Gel	Thickens the water in order to suspend the proppant	Combines with the "breaker" in the formation thus making it much easier for the fluid to flow to the borehole and return in produced water.
Iron control	Iron chelating agent that helps prevent precipitation of metal oxides	Reacts with mineral in the formation to create simple salts, carbon dioxide and water all of which are returned in produced water.
Non-emulsifier	Used to break or separate oil/water mixtures (emulsions)	Generally returned with produced water, but in some formations may enter the gas stream and return in the produced natural gas.
pH adjusting agent/buffer	Maintains the effectiveness of other additives such as crosslinkers	Reacts with acidic agents in the treatment fluid to maintain a neutral (non-acidic, non-alkaline) pH. Reaction results in mineral salts, water and carbon dioxide which is returned in produced water.
Propping agent	Keeps fractures open allowing for hydrocarbon production	Stays in formation, embedded in fractures (used to "prop" fractures open)
Scale inhibitor	Prevents scale in pipe and formation	Product attaches to the formation downhole. The majority of product returns with produced water while remaining reacts with micro-organisms that break down and consume the product.
Surfactant	Reduces surface tension of the treatment fluid in the formation and helps fluid recovery from the well after the frac is completed	Some surfactants are made to react with the formation, some are designed to be returned with produced water, or, in some formations they may enter the gas stream and return in the produced natural gas.

2. Format of the database

The database was designed in an Excel file with four sheets:

a) Table 1-Physical and chemical properties: the first three columns on the left present the purpose, name and CAS number of the chemicals and the following 17 columns contain the chemical and physical properties; the last column on the right indicates the sources for the information.
b) Table 2 –Toxicity information for certain chemicals (based on available information). The last column on the right indicating the source for the information.
c) Table 3 – Screening levels and guideline values for certain chemicals (based on available information).
d) Table 4 –Meta data contains a list of the abbreviations that appear as the headings on the main table and a list of references (papers, websites, scientific databases etc.) from which the information was extracted.

2.1 Table 1 - Chemical and physical properties

The chemical and physical properties recorded in the database were selected based on their environmental impact [9], for example:

- The octanol–water partition (K_{OW}) coefficient is important for organic sorption, directly linked to aqueous solubility [10].
- The soil organic carbon partition coefficient (K_{OC}) is useful for determining soil sorption and contaminant transport rates.
- Henry's law constant (K_H) is an indicator of partitioning that occurs between aqueous and gaseous phases and is used in many modeling applications.
- Enthalpy of Henry's law constant (ΔH Henry) is describing its change with temperature.
- Aqueous solubility (Sw) is directly linked to Kow and Koc, important for organic sorption and is used in determining possible health risks.

Information on the chemicals was obtained from various sources, amongst which are online chemical information databases such as SciFinder and PubChem; materials safety data sheets (MSDS); reports authored by the U.S. EPA, the European Chemicals Agency (ECHA) and peer-reviewed scientific publications. Please see the "Meta" table in the database for a complete list of references.

2.2 Table 2 - Toxicity

Toxicity information for the chemicals in the database consists of the median lethal dose (LD_{50}) and median lethal concentration (LC_{50}) and the USEPA classification for carcinogen and non-carcinogen assessments [11].

The oral toxicity median lethal dose LD_{50} parameter is the average amount of a chemical capable of killing half of the population exposed under specific conditions. Commonly expressed in mg/kg, by oral intake or skin exposure.

The inhalation toxicity median lethal concentration LC_{50} is the average concentration of a chemical or mixture in air as a gas, vapor, mist, fume or dust capable of killing half of the population exposed by inhalation under specific conditions. Often expressed in ppm or mg/m^3.

EPA's Integrated Risk Information System (IRIS) database [11] provide the following toxicity values for health effects resulting from chronic exposure to chemicals:

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- Oral reference dose (RfD) is the amount of a chemical that one can ingest every day for a lifetime that is not anticipated to cause harmful non-cancer health effects. The RfD can be compared to an estimate of exposure in mg/kg-day.
- Inhalation reference concentration (RfC) is the concentration of a chemical that one can breathe every day for a lifetime that is not anticipated to cause harmful non-cancer health effects. The RfC can be compared to an estimate of exposure concentration in mg/m^3.
- Oral slope factor (OSF) is a plausible upper-bound estimate of the probability that an individual will develop cancer if exposed to a chemical for a lifetime of 70 years (CHEST). The OSF can be multiplied by an estimate of lifetime exposure (in mg/kg-day) to estimate the lifetime cancer risk.
- Inhalation unit risk (IUR) is an estimate of the increased cancer risk from inhalation exposure to a concentration of 1 $\mu g/m^3$ for a lifetime (70 years). The IUR can be multiplied by an estimate of lifetime exposure (in $\mu g/m^3$) to estimate the lifetime cancer risk.

More information on deriving RfD, RfC values and cancer risk estimates can be found in EPA's 2002 *A Review of the Reference Dose and Reference Concentration Processes* and in *EPA's 2005 Guidelines for Carcinogen Risk Assessment*.

2.3 Table 3 - Water quality standards and screening levels

2.3.1 Water quality standards

Water quality standards are set to limit the concentrations of certain chemical substances that pose a significant risk to the environment or to human health. There are standards for drinking water (e.g., Council Directive 98/83/EC "the quality of water intended for human consumption"), surface water (e.g. Directive 2008/105/EC "Environmental quality standards applicable to surface water"), wastewater etc. The standards include a list of chemicals and their maximum concentration limit (MCL).

For most of the chemicals that are used in fracking, no MCLs have been set. In the databse, we present the few MCLs for drinking water available from the EU council directive, the Australian drinking water guideline and the Canadian drinking water quality guidelines (columns D, E, F in table 3, respectively).

2.3.2 Screening levels

Risk-based screening levels (SLs) are chemical-specific concentrations for individual contaminants in air, drinking water and soil. These values are used to determine the concentration of a chemical in an environmental media, which is protective of human health based on the acceptable cancer risk or hazard quotient (TR or THQ, respectively). The SLs are derived from equations combining exposure assumptions with chemical-specific toxicity values. The SLs are not cleanup standards [12].

The SLs in table 3 of the database were extracted from the "US EPA Regional Screening Levels (RSLs) – generic table (May 2016)". They are divided in two sections, based on the acceptable hazard quotient (THQ) of 0.1 (columns G to R) and 1.0 (columns S to AD). The target cancer risk (TR) is set to 1,000,000 in both sections. Each section includes three types of information: (a) type of media – soil, air, tapwater; (b) type of receptors – industrial and residential; (c) screening levels in soil (SSLs) that are protective of groundwater.

Further information on SLs can be found in the US EPA website [12].

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3. Updating the database

As the work on FracRisk continues, and in particular, the modelling work in WP5 and the development of a SG-RBCA software in WP4, the database is expected to be updated with more relevant physio-chemical properties and additional chemicals in categories that holds less than 10 materials, at the moment.
MCLs will be updated, if new regulations will be commissioned.

The US EPA updates the regional SLs tables (including toxicity and chemical properties) semiannually, therefor the information extracted from that source (especially Table 3 in the database) would also be updated.

The lack of data on generic SLs might be addressed in future research using the backward calculation feature of the SG-RBCA software, which will be developed next year as part of WP4.

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