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Environmental pollution by chemical substances used in the shale gas extraction—a review

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ABSTRACT

When the shale gas is extracted, various fluids for hydraulic fracturing are used. They contain several hundred different chemical compounds. Many of them may have a negative effect on the environment and human health. Even though the chemical additives make up only 2% of the fluid volume, the large fluid amount used and the fact that most of these substances are highly toxic make them a potentially high threat to the environment. To reduce their negative environmental effect, it is necessary to identify all the compounds with the product safety data sheets and to define their toxicity levels. Their use should also be reduced as much as possible or they should be replaced with similar substances that are less toxic. The following study concerns the most important chemical additives used in the fracturing fluids during the shale gas extraction. It focuses on their properties and toxicity, and defines the problems related to the determination of microelements and macroelements present in samples with such complex matrices. Additionally, the risks related to their application and migration to soils, surface water, ground water and organisms are described.

Keywords: Fracturing fluid; Shale gas; Chemical substances; Environmental threats

1. Introduction

The world is struggling with the energy crisis. That is why new energy sources have been intensively sought for. One option is shale gas, which has been discussed all over the world, including Europe. The US Energy Information Administration [1] estimates unproven technically recoverable shale gas volumes in Europe to total 13.3×10^{12} m^3 of which the largest part is in Poland and France (4.19×10^{12} and 3.87×10^{12} m^3, respectively). Next largest reserves are thought to be in Ukraine (3.62×10^{12} m^3), Romania (1.44×10^{12} m^3), Denmark (0.91×10^{12} m^3) and Netherlands and UK are both estimated to have 0.73×10^{12} m^3. At the beginning of 2014, the European Commission adopted a non-binding recommendation for "Minimum principles for the exploration and production of hydrocarbons (such as shale gas) using high volume hydraulic fracturing" [2]. The member states have been invited to implement these recommendations within six months of publication and the commission will review the

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effectiveness of the recommendation in July 2015. This statement focuses on three particular aspects that need to be addressed from a European perspective. First of them is the aspect relevant to the EU's high population density relative to many of the areas studied to date, in particular, the USA [3], Canada [4] and Australia [5]. The average population density of European countries ranges from just below 100 to above 600 people/km^2 compared to just over 3 in Canada and Australia and 32 people/km^2 in the USA, respectively. Thus, it is inevitable that fracking operations will interact more closely with other activities. Moreover, EU has the world's most comprehensive and legally binding greenhouse gas reduction and climate change mitigation policies, the net effects of fracking on meeting Europe's climate change targets are important considerations. Finally, the EU public has already shown considerable sensitivity to the issue of fracking, so the effect on public and communities is also a critical issue.

As far as financial advantages are concerned, the environmental threats related to the shale gas must be taken into consideration as it requires the new gas extraction method. The applied technology requires large amounts of water and chemical compounds necessary for fracturing fluids. It is estimated that one borehole consumes about 20,000 m^3 of water, 850 tons of proppants and about 210 tons of chemicals solutions. For the extraction of 1,000 m^3 of shale gas about 100 kg of sand and 2 tons of water is needed [2]. Thus, much of the discussion is devoted not only to the economic, political and technological matters but also to the environmental issues. The shale gas has been used in the USA for 40 years and 50,000 boreholes have been made [6]. However, Europe by no means starts from scratch on fracking. Hydraulic fracturing and horizontal drilling have been practiced in Europe since the 1950s and 1980s, respectively. In the early 1990s, horizontal drilling and multifrac stimulations were successfully executed in northern Germany. Overall, in Europe more than 1,000 horizontal wells have been created and several thousand hydraulic fracturing has been executed in recent decades. So far, there have been no serious incidents described in literature connected with the extraction of shale gas. Nevertheless, one must remember about the long-term impacts and the rapid increase in the extraction of this method in recent years.

In Poland, approx. 90% of the energy comes from hard and brown coal combustion, which is against the environmental policy of the EU [7]. In 2011, the EU guidelines on the threats related to the shale gas extraction were published [8]. The document states that it is necessary to provide all the interested parties with the information on the chemical compositions of the additives applied in the fracturing fluids. It is also essential to determine their toxicity and to monitor the pollution caused by their use. Moreover, the environmental threat resulting from the application of the hydraulic fracturing must be assessed. Thus, the challenge is seen as not so much as to produce new rules, but to control existing ones adequately. In Europe as well as in Poland, new rules about shale gas extraction are currently being developed. They should soon enter into force.

The hydraulic fracturing is used to increase the borehole efficiency. The fracturing fluid is pumped under high pressure into the borehole to form and maintain or enlarge the fractures in the rock. The procedure is used to obtain the shale gas, petroleum or uranium. The method was applied in the gas extraction for the first time in the USA in 1947 [9]. After the operation is completed, the fluid is removed from the borehole to enable the gas extraction [10]. The fluid is removed through the pressure reduction in the borehole after the hydraulic fractures are made. During the so-called flowback phase, part of the fluid returns to the surface. It is collected and either treated to be reused or removed as the industrial waste. Unfortunately, solely 40% of the fracturing fluid goes back to the surface. The remaining part stays underground [11].

The hydraulic fracturing method stirs up many controversies. In addition to land for the well pads and ancillary facilities to develop the resource, shale gas development also requires large amounts of water, chemicals and proppants for the hydraulic fracturing. Hydraulic fracturing in oil and gas operations led to a massive increase in the amount of sand being mined (the United States used some 28.7 million tons in 2011). Sources of sand require high quartz content (98%), round grains with a similar size range (100–500 μm) in large quantities in Europe require, therefore, extraction from quarries or nearshore or coastal sources. One should also remember that the mining and extraction lobby still controls the research into the potential threats related to the method, whereas the full composition of the applied fluids is not revealed. The only statutory ban on the application of hydraulic fracturing for gas and petroleum extraction was introduced in France in 2011 [12].

The fracturing fluid can be prepared in two ways. In the continuous mixing, the components are selected and mixed during the fracturing process. In the batch mixing, the components are selected before and the ready-made mixture is used for the procedure. The fluid should be properly protected and stored in tight tanks to prevent any leakages or secondary contamination at each preparation stage. After fracturing is finished, the fluid returning to the ground surface is directed into the treatment system, where it is subjected to the treatment processes to high extent (up to 98%) and placed in the tanks. The treated fluid can be used again. Sewage sludge should be collected by specialized companies and transported to the places where they can be neutralized in accordance with the regulations in force [13]. The hydraulic fracturing flowchart is shown in Fig. 1.

The fracturing fluid leakages into the surface are prevented with special double-walled tanks, trays or protective foil placed on the ground under the tanks. Additionally, each fracturing procedure is preceded with the tests of the borehole cementation condition (acoustic and pressure tests), which are used to detect any possible leakages in the borehole piping [14]. All the chemical substances used in the shale gas extraction should be properly listed and recorded. The access to them should be restricted to the authorized and qualified workers and rescue services. The chemical substances used in the EU are under control and supervision of the registration, evaluation and authorisation of chemicals (REACH) system. The regulation concerns the safety of using certain chemicals through their obligatory registration and assessment [15].

2. Compositions and applications of the fracturing fluids

A typical fracturing fluid contains approx. 95% of water and 3–4% of sand. The remaining part is made up of chemical additives. The water used in the process can be taken both from the surface and underground sources. It is necessary only at the beginning of extraction processes. The required amount depends on the borehole depth [16], and usually it is 20,000 m^3 for one borehole. The sand function is to prevent the closing of the fractures after pressure reduction. It is used so that the time in which water is pumped would be as short as possible. The substances added to the fracturing fluid contain compounds similar to those that have been used in the traditional wells and vertical boreholes for years. However, the amount of the substances used in the directional drilling is significantly higher than in the vertical drilling. The compositions of the chemical additives applied in the fracturing fluids may differ, which depends on the used technology and the quality of a rock [17].

Even though the chemical additives make up only 2% of the fracturing fluid composition, their properties and the risk of the environmental pollution raise much concern. Table 1 presents the most important types of substances found in the fracturing fluids. It also provides some examples and applications.

The compositions of the fracturing fluids depend on both their applications and the manufacturer.

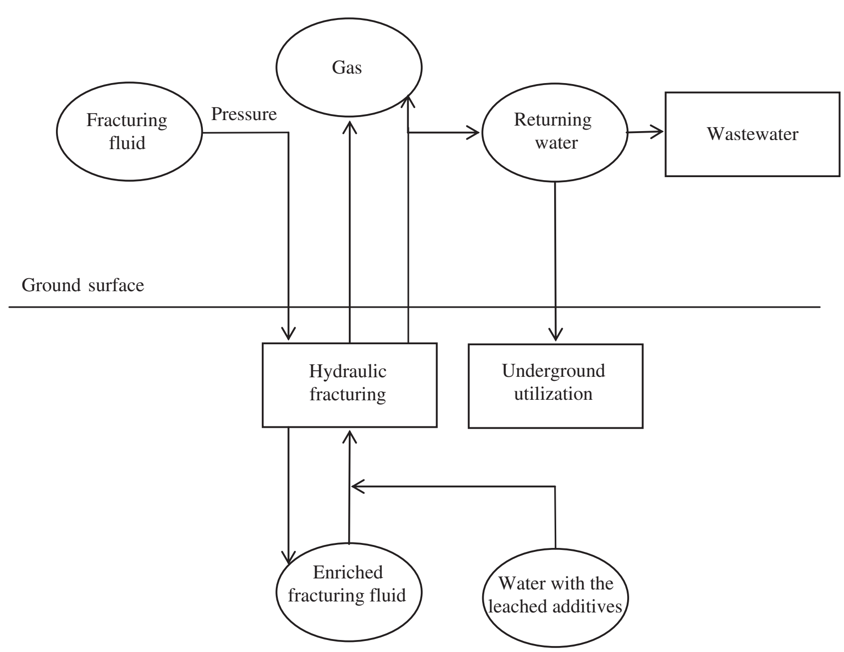

Fig. 1. The shale gas extraction flowchart [22].

Table 1
Types of chemical additives and their functions in the fluids [3]

Additive type	Function	Examples
Biocides	Preventing the growth of bacteria and other living organisms	Terpene hydrocarbons; glutaraldehyde; 1,2-benzoizothiazol-3; 2-methylo-4-izothiazolin-3-one; 5-chloro-2-methylo-2H-izothiazol-3-one
Crosslinkers	Helping gel formation, increasing viscosity	Complexes of transition metals; boron, titanium and zirconium salts; triethanolamine
Buffers	pH control	Inorganic acids and bases (e.g. HCl, HF, NaOH, KOH) and their salts (e.g. Na_2CO_3, $NaHCO_3$, $(NH_4)_2SO_4$, K_2CO_3)
Sediment inhibitors	Preventing the precipitation of the mineral sediments	Dodecylbenzenesulfonate acid; citric acid; acetic acid; thioglycolic acid
Corrosion inhibitors	Piping and equipment protection	Phosphonic acid salts; formamide; methanol; isopropyl alcohol; acetic acid; acetaldehyde
Surface tension reducers	Reducing the surface tension	Amines; glycol ethers; phenol derivatives; dodecyl sulphate laureate; ethanol; naphthalene; 2-Butoxyethanol
Friction reducers	Causing the laminar flow instead of the turbulent flow	Polyacrylamides; petroleum derivatives; benzene; toluene; ethers
Viscosity reducers	Agents facilitating the fluid recovery	Sulphates; peroxides (e.g. ammonium persulphate, calcium peroxide); $KBrO_3$
Gelling agents	Helping gel formation, increasing viscosity	Guar gum; hydroxyethyl cellulose; xanthan gum; methanol; terpenes; ethylene glycol

Table 2 presents typical data on the contents of the selected toxic substances and their concentrations in the fluids of various manufacturers. Physical, chemical and biological characteristics of compounds used in hydraulic fracturing have been described in details in recently published work [18]. Physical and chemical characteristics of these additives were determined using publicly available chemical information database. Fifty-five of the compounds are organic and 27 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 evaluated chemicals are non-toxic or of low toxicity and only three are classified as Category 2 oral toxins according to the standards in the Globally Harmonized System of Classification and Labelling of Chemicals. However, toxicity information was not located for tens of them, which can suggest deficiencies in the current state of knowledge, highlighting the need for further assessment to understand potential issues associated with the use of chemical additives in such applications.

As it is clearly seen in Table 2, the fluid manufactures use different commercial names for the same substances. Such a situation results in confusion when researchers try to determine the real chemical composition or the chemicals CAS number. There are appeals made to the shale gas extraction operators to reveal the full composition of the fracturing fluids and their volumes. The subject has become an important issue in the public debate as some of the additives used now or in the past have been dangerous or toxic. The presentation of the chemical compositions has been required by the law in some American states. Both in the USA and Canada, the fracturing fluid compositions and other data are provided individually for particular boreholes at the FracFocus website. Unfortunately, the information is often criticized for being incomplete and selective. What is more, the manufacturers often refer to the trade secret and in that way avoid presenting the full data. In Europe, the information on the composition of fracturing fluids used in particular countries is seriously limited. For example, there is available data on the Cuadrilla field in Great Britain. The International Association of Oil and Gas Producers has been operating the European Internet platform since 2013. Thus, the composition of the fracturing fluids used for the shale gas drilling is given. 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 could be made.

In Poland, there are no separate regulations on the use of chemical substances in the mining and

Table 2
Types and concentrations of the selected hazardous substances in the selected fracturing fluids [19]

Commercial name	Hazardous substance	Mass content (%)	Concentration in the fracturing fluid (mg/L)
Manufacturer—BJS			
HCl	Hydrochloric acid	8	83.68
Cl-14	Propyl alcohol	5	0.23
Ferrotrol	Citric acid	70	18.50
XLW-32	Methanol	90	176.79
GW-3LDF	Petroleum distillates	60	356.24
BF-7L	Potassium carbonate	100	63.53
GBW-15L	Sodium chloride	14	17.09
FRW-14	Light petroleum distillates	40	374.20
Alpha 125	Glutaraldehyde	30	70.43
Manufacturer—Fractech			
HCl	Hydrochloric acid	8	89.26
40 HTL	Methanol	10	1.06
NE 100	Methanol	5	0.26
B9	KOH	20	22.86
BXL-2	KOH	10	12.98
ICI-150	Glutaraldehyde	50	124.66
FRW-50	Petroleum	20	171.21
Manufacturer—Universal			
HCl	Hydrochloric acid	8	89.26
Unilink 8.5	Ethylene glycol	40	123.19
Bioclear 200	2,2-dibromo-3-nitrylopropionamide	20	55.16
CGR 20	Polyethylene glycol	60	165.48
Manufacturer—Halliburton			
HAI-OS	Methanol	60	5.64
FE-1A	Acetic acid	60	6.53
HCl	Hydrochloric acid	8	89.26
K-34	Sodium carbonate	100	141.13
BC 140	Monoethylamine	30	58.15
FR-46	Diammonium sulphate	30	330.95
Aldacide G	Glutaraldehyde	30	70.43
Manufacturer—Superior			
Al-2	Glycol ethers	30	1.54
IC-100L	Citric acid	100	8.14
OB-Fe	Polypropylene glycol	40	2.39
Super Pen 2000	Iron sulphate	30	1.79
Super OW-3	Isopropyl alcohol	40	0.95
Super 100NE	Isopropyl alcohol	30	0.82
HCl	Hydrochloric acid	8	89.26
Bioclear 200	2,2-dibromo-3-nitrylopropionamide	20	55.16
SAS-2	Light petroleum distillates	30	270.06

extraction industry. The data of the Polish Ministry of Environment (October 2013) indicated that 49 exploration boreholes had been made in the areas with the concessions for the search and recognition of the unconventional hydrocarbon deposits. The hydraulic fracturing procedure was performed in 25 boreholes (two horizontal and eight vertical boreholes). The Polish Exploration and Production Industry Organization wants to satisfy the public need for knowledge. That is why it encourages its members to reveal the composition of the fracturing fluids used in the Polish exploration boreholes [20].

3. Environmental threats

It is estimated that approx. 300,000 chemicals were present in the environment at the end of the nineteenth century [21]. At present, the regularly updated CAS database reveals the information about over 65,000,000 recognized chemical substances. People are not in contact with all of these compounds. Nonetheless, the number of the known 750 substances used in the fracturing fluids is impressive. Moreover, most of them do not naturally occur in the environment [22].

In the 1950s, the analytical technologies were much less advanced than nowadays. At that time, it was possible to determine substances at the mg/L level. The trace analysis was defined in the same way. Presently, the limits are significantly lower. It is no longer a problem for many laboratories to detect the analytes at the ng/L level, even in the complex matrix samples. The access to modern analytical techniques, such as high-performance liquid chromatography, inductively coupled plasma-mass spectrometry or gas chromatography–mass spectrometry, is more and more unrestricted. The limitations tend to result from the lack of the regulations obliging different institutions to perform such analyses rather than from the inappropriate analytical methods. The research into the shale gas extraction and fracturing fluids is a perfect example of such a situation [23]. The main problem with this kind of analysis applies to the complex sample matrix, a wide range of concentrations (from μg/L up to g/L), and the instability of the selected analytes (especially organic compounds and their by-products).

The most serious environmental threats related to the fracturing fluids are: surface and underground water pollution; soil and air pollution; high water consumption. Its consumption can be as high as 20,000 m^3 in one hydraulic fracturing procedure. Water usually comes from local resources (rivers, lakes and surface water). Consequently, there appears the threat of drought. There are also limitations in the water availability for households and a potential risk of changes in the ecosystems. As a result, the agricultural production becomes more expensive and the food prices rise. What is more, some of the farmers abandon crop cultivation or animal breeding in the places neighbouring the shale gas extraction areas. They do it to drill deep wells in their farms to sell water to the gas extraction companies.

Aquatic ecosystems may be at particular risk to the high brine content of produced waters. It is also possible that constituents of hydraulic fracturing fluids could degrade environmental quality directly or indirectly by modifying aquatic habitats [24]. It has also been suggested that ground water contamination may impact the health of farm animals and pets, and that they may be sentinels for the effects in humans.

The water pollution may be caused by the fluid leakage on the surface or in the borehole. The fluids returning to the surface after the hydraulic fracturing can be even more dangerous. They contain their own chemical compounds and many substances leached out from the deposit itself [25]. It is forbidden to transport the polluted water or leakages (due to the inappropriate wastewater treatment on the surface) into rivers or plants that are not prepared to treat such waste [15].

Some of the chemical compounds in the fracturing fluids belong to, the so-called, persistent organic pollutants. They do not usually occur in the ecosystem. If they do, their concentrations are extremely low. Moreover, their toxicity mechanisms are not fully understood. Consequently, there is a possibility of chronic exposure to these substances and their bioconcentration and/or biomagnification. The present knowledge on the toxicity of such compounds cannot help to fully recognize the environmental effects in the multiple species systems exposed to changeable and low concentrations under complex environmental conditions. The no observed effect concentration and lowest observed effect concentration values for the population or ecosystem are virtually unknown. The exposure to other fracturing fluid additives (e.g. biocides and their particular components) is also potentially dangerous. The possible toxic effects can be: the risk encountered during the inhalation and contact with the skin, allergic reactions to the skin or fertility impairment [26]. Some examples from Germany are described by Gordalla et al. [27]. There were 30 hydrocarbons in the fracturing fluid returning from the Solingen (Germany) deposit in summer 2011. Some of the hydrocarbon concentrations exceeded the permissible values for surface water by several hundred times. Such values were observed for BTEX (max. concentration 70 μg/L), PAHs (max. concentration 10.440 μg/L), many anions, cations and heavy metals. In the fracturing fluid returning from the Buchhorst T12 deposit, the following maximum concentrations were determined: chlorides (33 g/L), sodium (16.8 g/L), potassium (7.5 g/L) and acetates (0.48 g/L). The values observed for the Cappeln Z3a (Germany) field were even higher (chlorides—115 g/L; sodium—44 g/L; magnesium—2.2 g/L; zinc—0.29 g/L; acetates—0.26 g/L). The observed concentrations were extremely high. Such wastewater should be diluted at 1:10,000 to lower the contents of the hazardous substances to the permissible levels for the wastewater introduced into the environment.

Despite chemicals used in fluids, there are other environmental problems concerned with shale gas exploration. A single hydraulically fractured well may need almost 2,000 one-way truck trips to deliver supplies, mostly water, and mostly during well completion. The sources of noise during shale gas extraction include drilling and hydraulic fracturing equipment, natural gas compressors, traffic and construction. Furthermore, since drilling and completing a well is a 24 h operation, lights are also an issue. Drilling a shale gas well typically takes four to five weeks, 24 h a day compared to about one to two weeks for conventional gas development.

The substances dangerous for water may also be present in the soil. There are many technological processes to treat wastewater and soil polluted during the shale gas extraction, such as sedimentation, filtration, absorption, ion exchange, chemical oxidation and biochemical methods [28]. Some of the most popular are: thermal processes (e.g. multistage flash distillation; multiple effect distillation; vapour compression), membrane processes (e.g. electrodialysis; reverse osmosis; ultra/nano/micro filtration). Reclaiming a well site takes about five years and includes carrying out needed remediation, phytoremediation and phytostabilization. Full restoration of sites may not be possible in many cases, notably in areas of high agricultural or natural value.

Interestingly, the shale gas extraction causes more air pollution than the subsequent gas combustion. The emitted pollutants include PAHs, volatile organic compounds, hydrogen sulphide, and sulphur and nitrogen oxides. In the shale gas extraction process, approx. 200 million m^3 of the gas is burnt per year in the so-called flaring in Canada. In the USA, the value is approx. 30×10^6 m^3/d. Also, the methane emission into the atmosphere cannot be avoided in the gas extraction. It is much more dangerous for the climate than the CO_2 emission. Today, flaring and venting gas in certain US States remain a problem because gathering and utilization of gas emitted during well drilling and before production facilities are established. They may require additional investments and operating costs, prompting certain firms to try and avoid such expenditure. Flaring and venting during the production phase therefore require strict regulation and control. For this reason, the flaring process will be completely banned in the USA and Canada in 2015 and 2016, respectively [29].

When no longer economical, the well is plugged within the casing with cement to isolate different producing zones, prevent emissions and protect groundwater. Nevertheless, as a result of the gradual deterioration of materials or inadequate initial well construction, many abandoned wells leak either through the wellbore or around it. Therefore, permanent changes in the ecosystems are produced in much larger zones than the mining areas themselves. The socio-economic consequences of such processes are still hard to predict.

4. Conclusions

The shale gas extraction procedures and using fracturing fluids containing many toxic substances can have an adverse effect on the humans, wildlife, water and soil environment and air quality. The proper borehole drilling and the monitoring of the shale rock fracturing and aquifers are important factors that determine the safety of the water–soil environment. On the other hand, the composition of the fracturing fluids should be improved with non-toxic substances compounds [18]. In this way, the negative impact of the fracturing fluids could be reduced. There are serious environmental threats related to the application of the fracturing fluids. They result from both the composition and the application range. Unfortunately, most of the fluid manufacturers do not provide full information on the chemical composition. What is even more important, they also do not reveal toxicological properties of these fluids. If such data were available, it would be possible to focus on the monitoring of the most important compounds. The researchers could also define their toxicological properties, determine the maximum acceptable concentrations and assess the long-term impact on humans and the environment. Importantly, some part of the fluid returns to the surface. The substances it contains can react in various ways. Paradoxically, local "environmental bombs" are planted due to the shale gas mining. The gas extraction from the natural environment requires large amounts of hazardous compounds to be introduced into the environment itself. On the one hand, shale gas is an alternative source of energy, but its extraction using hydraulic fracturing technology creates a serious threat for the environment. Many used chemicals are toxic for living organisms. Thus, it is very important to know the composition of these fluids. However, it is very difficult to assess the risk and potential threats, particularly the long-term ones, without the full cooperation with the fracturing fluid manufacturers and users. Such close collaboration is necessary not only for the environment but also for the present and future generations. Moreover, this will make it possible to develop new or already known technological processes for their effective treatment.

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