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ENVIRONMENTAL POLLUTION BY CHEMICAL SUBSTANCES USED IN THE SHALE GAS EXTRACTION: A REVIEW

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ABSTRACT

Various fluids for hydraulic fracturing are used to obtain shale gas. Several hundred distinct chemical compounds may be found in them. Many of them may be harmful to the environment and human health. Despite the fact that chemical additives make up just 2% of the fluid volume, the huge quantity of fluid utilized and the fact that the majority of these chemicals are extremely toxic make them a potentially significant environmental hazard. To minimize their negative environmental impact, product safety data sheets must be used to identify all chemicals and specify their toxicity levels. Their usage should likewise be minimized to the greatest extent feasible, or they should be replaced with less hazardous alternatives. The following research looks at the most common chemical additions used in shale gas extraction fracturing fluids. It focuses on their characteristics and toxicity, as well as the difficulties in determining the presence of microelements and microelements in samples with such complex matrices. There are other hazards associated with their application and movement to soils, surface water, ground water, and creatures.

KEYWORDS: *Fracturing fluid; Shale gas; Chemical substances; Environmental threats*

1. INTRODUCTION

The globe is in the midst of an energy crisis. As a result, new energy sources are being actively explored. Shale gas is one possibility that has been considered all around the globe, including in Europe. According to the US Energy Information Administration, Europe's unconfirmed theoretically recoverable shale gas quantities total 13.3 1012 m3, with Poland and France accounting for the majority (4.19 1012 and 3.87 1012 m3, respectively). Ukraine (3.62 1012 m3), Romania (1.44 1012 m3), Denmark (0.91 1012 m3), and the Netherlands and the United Kingdom (both 0.73 1012 m3) are believed to hold the next biggest deposits. The European Commission issued a nonbinding proposal in January 2014 entitled "Minimum guidelines for the exploration and production of hydrocarbons (such as shale gas) utilizing high volume hydraulic fracturing." The member states have been asked to put these proposals into action within six months after their publication, and the commission will assess their efficacy in July 2015[1]. This declaration focuses on three specific issues that need attention from a European standpoint.

The first is the issue of the EU's high population density in comparison to many of the places examined so far, including the United States, Canada, and Australia. European nations' average population density varies from just under 100 to over 600 persons per square kilometer, compared to little over 3 in Canada and Australia and 32 in the United States, respectively. As a result, fracking operations will inevitably interact more intimately with other activities. Furthermore, since the EU has the world's most extensive and legally enforceable greenhouse gas reduction and climate change mitigation measures, the net impacts of fracking on achieving Europe's climate change goals are significant. Finally, since the European public has previously demonstrated a high level of sensitivity to the subject of fracking, the impact on the public and communities is also a major concern[2].

In terms of financial benefits, the environmental risks associated with shale gas must be considered, since it necessitates the new gas extraction technique. For fracturing fluids, the applied technique requires huge quantities of water and chemical substances. One borehole is expected to use 20,000 m3 of water, 850 tons of proppants, and 210 tons of chemical solutions. A total of 100 kilograms of sand and 2 tons of water are required to extract 1,000 m3 of shale gas. As a result, a large portion of the debate is dedicated not just to economic, political, and technical problems, but also to environmental concerns. Shale gas has been utilized in the United States for 40 years, with 50,000 boreholes drilled. However, Europe is far from starting from scratch when it comes to fracking. Since the 1950s and the 1980s, hydraulic fracturing and horizontal drilling have been used throughout Europe. Horizontal drilling and multitrack stimulations were successfully carried out in northern Germany in the early 1990s[3]. Throughout recent decades, more over 1,000 horizontal wells have been drilled in Europe, including thousands of hydraulic fracturing operations. So far, no severe events related to shale gas extraction have been reported in the literature. However, one must consider the long-term consequences of this technique of extraction, as well as the fast rise in its use in recent years.

Approximately 90% of Poland's energy originates from the burning of hard and brown coal, which is in violation of EU environmental regulations. The EU recommendations on the risks posed by shale gas production were released in 2011. According to the agreement, all interested parties must be provided with information on the chemical compositions of the additives used in fracturing fluids. It's also crucial to figure out how hazardous they are and keep track of the pollution they create[4]. Furthermore, the environmental risk posed by the use of hydraulic fracturing must be evaluated. As a result, the issue is viewed as one of properly controlling current regulations rather than creating new ones. New regulations for shale gas production are presently being established in Europe and Poland.

They should go into effect shortly. Hydraulic fracturing is a technique for improving borehole efficiency. Fracturing fluid is injected into the borehole at high pressure to create, maintain, or expand cracks in the rock. To extract shale gas, petroleum, or uranium, this method is utilized[5]. In 1947, the technique was used for the first time in gas extraction in the United States. The fluid is evacuated from the borehole once the procedure is finished to allow for gas extraction. After the hydraulic cracks are created, the fluid is evacuated by lowering the pressure in the borehole. During the flow back phase, a portion of the fluid is returned to the system. to the surface. It is collected and either recycled or disposed of as industrial trash. Regrettably, only 40% of the fracture fluid is returned to the surface. The remaining portion is buried[6].

The use of hydraulic fracturing is fraught with controversy. Shale gas production requires huge quantities of water, chemicals, and proppants for hydraulic fracturing, in addition to land for well pads and associated infrastructure to exploit the resource. The use of hydraulic fracturing in oil and gas operations resulted in a huge rise in sand mining (the United States used some 28.7 million tons in 2011). Sand requires a high quartz content (98%) and round grains with a comparable size range (100–500 m) in significant numbers, which can only be obtained from quarries or nearshore or coastal sources in Europe[7]. It's also worth noting that the mining and extraction lobby continues to exert control on study into the method's potential dangers, despite the fact that the entire composition of the applied fluids remains unknown. In 2011, France became the first country to enact a law prohibiting the use of hydraulic fracturing for gas and petroleum production.

There are two methods to make the fracturing fluid. During the fracturing process, the components are chosen and combined in continuous mixing. The components are chosen ahead of time in batch mixing, and the ready-made combination is utilized for the process[8]. At each step of preparation, the fluid should be carefully secured and kept in tight tanks to avoid leaks or secondary contamination. After fracturing, the fluid that returns to the ground surface is routed into the treatment system, where it is treated to a high degree of treatment (up to 98 percent) before being put in the tanks[9]. The fluid that has been treated may be reused. Specialized businesses should collect sewage sludge and transfer it to locations where it may be neutralized in line with current laws. Figure 1 depicts the hydraulic fracturing flowchart.

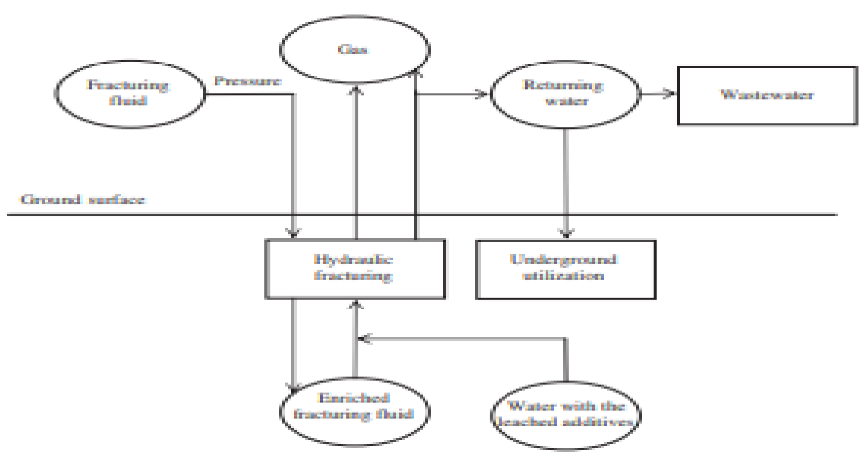

Figure 1: Flowchart Representing the Shale Gas Extraction

Special double-walled tanks, trays, or protective foil put on the ground underneath the tanks prevent fracturing fluid leakages into the surface. Furthermore, each fracturing operation is preceded by borehole cementation condition tests (acoustic and pressure tests), which are utilized to identify any potential borehole pipe leaks. All chemical compounds utilized in the production of shale gas should be documented and recorded correctly. Only authorized and competent personnel, as well as emergency services, should have access to them. The registration, assessment, and authorisation of chemicals (REACH) system regulates and supervises the chemical compounds used in the EU. The law addresses the safety of utilizing specific compounds by requiring their registration and evaluation.

TABLE 1: TYPES OF CHEMICALS ADDITIVES AND THEIR FUNCTIONS IN THE FLUIDS

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

A typical fracturing fluid includes about 95 percent water and 3–4% sand. Chemical additives make up the remaining portion. The water utilized in the process may come from both above and below ground sources. It is only required at the start of the extraction process. The necessary quantity varies depending on the drilling depth, however it is typically 20,000 m3 per borehole. The purpose of the sand is to keep the cracks from sealing up once the pressure is reduced. It's utilized to keep the time it takes to pump water as short as feasible. The chemicals added to the fracturing fluid are identical to those that have been used for years in conventional wells and vertical boreholes. The quantity of chemicals utilized in directional drilling, on the other hand, is considerably greater than in vertical drilling. Chemical additives used in fracturing fluids may have different compositions depending on the technique employed and the condition of the rock. Despite the fact that chemical additives make up just 2% of the fracturing fluid mix, their characteristics and potential for contamination cause a lot of worry. The most common kinds of chemicals detected in fracturing fluids are listed in Table 1. It also includes various applications and examples[10]. Fracturing fluid compositions are determined by the application as well as the manufacturer.

Table 2 shows typical information on the contents of chosen hazardous chemicals and their concentrations in different manufacturers' fluids. In a newly published study, the physical, chemical, and biological properties of chemicals employed in hydraulic fracturing were detailed in depth. These additives' physical and chemical properties were evaluated using a publicly accessible chemical information database. Organic compounds account for 55 of the chemicals, with 27 of them being regarded easily or intrinsically biodegradable. Seventeen compounds have a high theoretical chemical oxygen demand and are utilized at levels that pose treatment difficulties. According to the Globally Harmonized System of Classification and Labeling of Compounds, the majority of the assessed chemicals are non-toxic or have minimal toxicity, with just three being categorized as Category 2 oral toxins. However, toxicity data for tens of them could not be found, indicating flaws in the present state of knowledge and emphasizing the need for additional investigation to fully comprehend possible problems connected with the use of chemical additives in such applications.

The fluid manufacturers, as shown in Table 2, employ various marketing names for the same chemicals. When researchers attempt to figure out the actual chemical composition or the CAS number of a substance, they become confused. There have been calls for shale gas extraction companies to disclose the entire composition and amount of their fracturing fluids. Because some of the chemicals used today or in the past have proven harmful or poisonous, the topic has become a hot topic in the public discussion. In certain American states, the display of chemical compositions is mandated by law. The FracFocus website in the United States and Canada provides individual fracturing fluid compositions and other data for specific boreholes. Unfortunately, the data is often criticized for being incomplete and biased. Furthermore, manufacturers often resort to the trade secret in order to avoid disclosing all relevant information. Information on the composition of fracturing fluids used in certain nations is very restricted throughout Europe.

For example, data about the Cuatrillo field in the United Kingdom is accessible. Since 2013, the European Internet platform has been run by the International Association of Oil and Gas Producers. The composition of the fracturing fluids used in shale gas drilling may therefore be determined. All of the chemicals utilized in unconventional production are extensively used in industry, and data gaps in terms of toxicity, biodegradability, physical constants, and usage concentrations should be filled in order to provide accurate and informed environmental and health evaluations.

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

TABLE 2: TYPES AND CONCENTRATIONS OF THE SELECTED HAZARDOUS SUBSTANCES IN THE SELECTED FRACTURING FLUIDS

Commercial name	Hazardous substance	Mass content (%)	Concentration in the fracturing fluid (mg/L)
Manufacturer—BJS			
HCl	Hydrochloric acid	8	83.68
CI-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			
AI-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

(There are two horizontal boreholes and eight vertical boreholes.) The Polish Exploration and Production Industry Organization aspires to meet the public's need for information. As a result, it urges its members to disclose the fracturing fluid composition used in Polish exploratory boreholes.

2. CONCLUSION

Shale gas extraction techniques and the usage of fracturing fluids containing many toxic chemicals may damage humans, animals, the water and soil environment, and air quality. Borehole drilling and monitoring of shale rock fracture and aquifers define the safe functioning of the water–soil ecosystem. Fracturing fluid composition, on the other hand, should be improved with non-toxic chemical components. In this way, the negative effects of fracturing fluids may be reduced. The use of fracturing fluids is linked with substantial environmental concerns. They are a result of both the composition and the application range. Regrettably, the majority of fluid manufacturers do not offer complete chemical composition information. Furthermore, they make no mention of the fluids' toxicological properties. If such data were available, it would be possible to focus on monitoring the most important substances. Toxicological features, maximum allowed dosages, and long-term impacts on humans and the environment may all be defined by researchers. The fluid returns to the surface in large amounts.

Chemicals that may react in a number of ways are included. Ironically, shale gas production has resulted in the placement of local "environmental bombs." The extraction of natural gas from the environment requires the release of large amounts of hazardous substances into the ecosystem. On the one hand, shale gas is a renewable energy source, yet hydraulic fracturing technique used to obtain it presents a major environmental danger. Living beings are poisoned by several widely used substances. As a consequence, it's crucial to know what these fluids are made of. However, evaluating risk and potential issues, particularly long-term hazards, is challenging without full cooperation from fracturing fluid producers and consumers. Such tight collaboration is needed not just for the environment, but also for present and future generations. This will also allow for the development of new or current technological techniques for their effective treatment.

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