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Original Research

Analysis of Chemical and Toxicological Properties of Fluids for Shale Hydraulic Fracturing and Flowback Water

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Abstract

An analysis of environmental threats showed that the complete influence of shale gas production on the environment is bigger than in the case of gas production from a traditional oilfield. Hydraulic fracturing of shale, done on a much larger scale, results in huge amounts of liquid waste that must be managed in a rational way. An optimum solution to this problem is reusing flowback water to develop fluids for later fracturing. This article discusses the composition of the fluids used in hydraulic fracturing of non-conventional deposits as well as the flowback water. In the case of the examined liquids, toxicological tests have been carried out using microbiotests of ToxKit types Microtox, MARA, Daphtoxkit F magna, and Thamnotoxkit F. The research was done on a sample of fluids for hydraulic fracturing, and on flowback water obtained in hydraulic fracturing of shale formations in Poland. The tests are essential for correctly managing flowback waters after fracturing.

Keywords: shale gas, fracturing fluid, flowback water, ecotoxicological tests

Introduction

Hydraulic fracturing of non-conventional (tight and shale) deposits is a controlled process of technological fluid injection into a deposit. The fluid consists mainly of water and chemical components (Fig. 1) and the injection is done with high effectiveness (6-20 m^3/min) with high pressure – up to 100 MPa, which cracks rocks in a deposit and creates chains of cracks, or clefts.

Further injecting the fluid results in propagation of cracks to a size determined in a technological project. After opening the crack, a proppant material (sand of proper granulation and mechanical strength) is added to the technological fluid and gets into the cracks and stops their closure. Simultaneously, it creates access for gas flowing to an excavation slot [1-4].

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Compositions of technological fluids used in hydraulic fracturing depend on the geological formation of a deposit and on the type of well (vertical or horizontal).

During development of a fracturing fluid and selection of additives, the following factors should be taken into account:

- Effectiveness and pressure during injection of the fluid
- Percentage content of clay in a deposit rock
- Potential possibility of creation of both silicate and organic particles
- Solubility of a rock in an acid
- Microbiological activeness
- Potential possibility of non-organic sediments forming
- Difficulties with injected fluid collection (receiving) [1, 5-8].

One type of fracturing fluid frequently used in shale is slickwater. It contains high amounts of water and a slight additive of chemicals (including a polymer 0.6-1.2 kg/m^3).

Hydraulic fracturing done with this type of fluid results in:

- Increased fluid filtration, which leads to enlargement of gas flow channels
- Getting a high contact surface (due to using huge amounts of water), whereas permeability of a rock matrix remains small
- The geometry of generated cracks becomes more complex (because of low viscosity and high injection speed)
- Cracks decrease in height and part of the flowback water can be re-used to develop another fracturing fluid [6, 9]

Fracturing fluids prepared on the basis of surfactants (the so-called viscoelastic surfactant (VES) fluids) belong to another group. Required viscosity parameters are obtained by surfactant particles forming larger assemblies, in which hydrocarbon chains are associated and form micellar structures having a shape of a bar surrounded by water molecules. The lattice formed in the entire volume of fluid by the micelles of surfactants increases the viscosity. Such fluids cause less damage to conductivity of the fracture compared to fluids prepared on the basis of polymers [5-7, 10].

High amounts of fluid wastes (flowback waters) are a result of hydraulic fracturing. After cracking a well, the fluid is removed from the drillbore as well as from the cracks and gaps in the surrounding rock. As has been proved in American research, the amount of the fluid obtained in shale gas fracturing is lower than in the case of a tight oilfield: 40-60% for a vertical well and 10-30% for a horizontal well [11, 12].

The majority of flowback water outflow takes place during the first hours to a dozen or so days.

During contact with the deposit, the fracturing fluid creates various reactions with the rocks, and mixes with deposit water in rock pores. As a result, the chemical composition of the flowback water differs from the fracturing fluid composition. Besides, the longer the fracturing fluid is in the deposit, the more the change becomes visible.

In the beginning the flowback water composition is close to the fracturing fluid composition. When the total volume of the obtained flowback water increases in time, the content of dissolved solid parts (TDS) increases up to 160 g/dm^3 together with chloride content [13].

Until now, the harmful influence of deposit waters and sewage to the natural environment has been determined only in physical-chemical analyses.

Because of the poorly known influence of chemicals on most groups of organisms, the analytical data do not give much information about the threatening effects of deposit waters on the environment.

Additionally, significant diversity of concentrations as well as types of associated pollutants in deposit waters and possible interactions between toxic substances and biotic/abiotic elements of the environment make things more complicated [14].

Therefore, in order to evaluate both the quality of the fluids used in the operations of hydraulic fracturing of non-conventional deposits and their waste in the form of flowback water, toxicological tests using living organisms as bioindicators have been done. ToxKit-type microbiotests were used to ensure ease of use and adequate sensitivity and repeatability of tests [15-17].

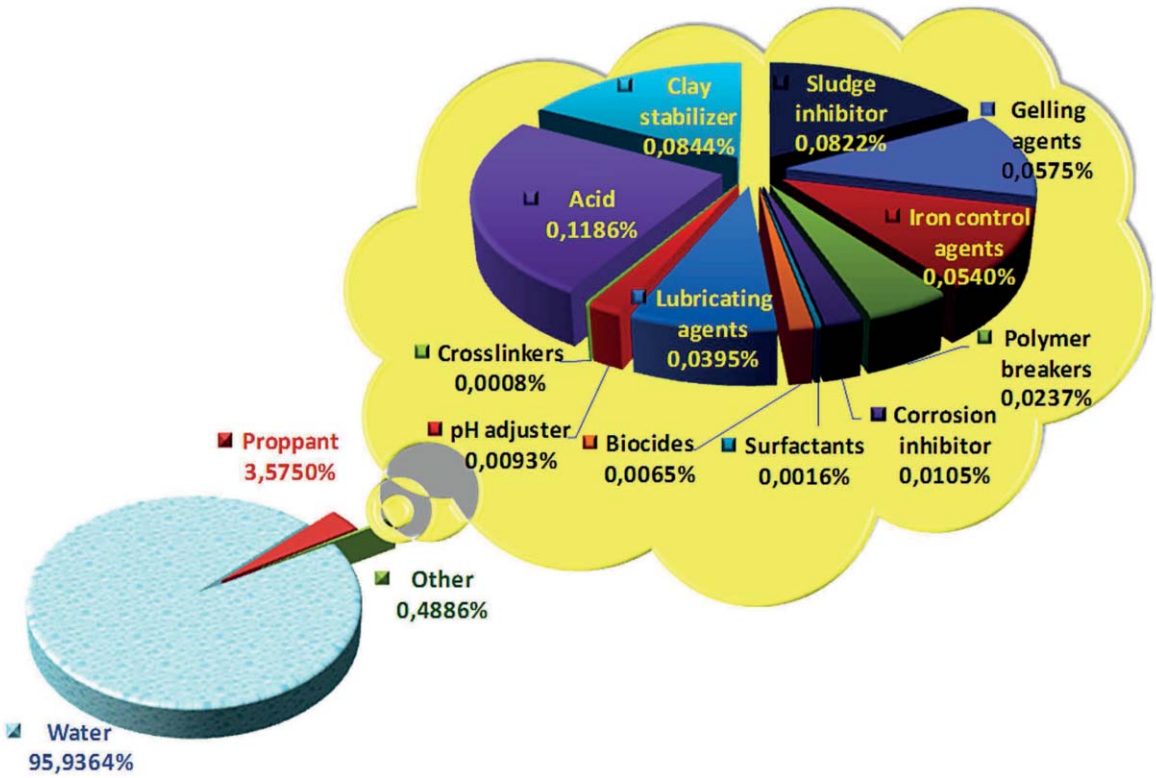

Fig. 1. Exemplary hydraulic fracturing fluid composition.

The research takes advantage of test organisms (representing various levels in a trophic chain) kept asleep or immobilized (as cryptobiotic forms), which can be used after a simple release procedure. This way, microorganisms are available on request, without the need for specialized equipment, infrastructure, and knowledge – all necessary for culturing test organisms. A living organism is a specific reagent, inside which biochemical processes occur, and the results of which are the observed symptoms: morphological changes of the body, and eventually death [18-21].

The performed toxicological tests allow simultaneous determination of harmful effects of all the substances contained in the water sample on select living organisms, taking into account interactions between all the elements of the tested system [22]. The research results are presented in toxicity units (TU):

$$TU = [1/LC_{50}] \times 100$$

...where LC_{50} means 50% of test reaction – survival.

Liquid toxicity assessment has been based on a toxicity scale of environmental samples [23, 24]:

TU < 1 – non toxic
1 ≤ TU < 10 – toxic
10 ≤ TU < 100 – acute toxic
100 ≤ TU – very toxic

Physical-chemical analyses aided with toxicological tests of a new generation enable complete estimation of a potential influence of fracturing and flowback fluids on the environment after hydraulic fracturing. Moreover, they will serve as a basis to determine proper water management.

Research Methodology and Material

In order to characterize liquids used in the operations of hydraulic fracturing of non-conventional deposits, water-based fluids have been selected for tests:

- Laboratory-prepared cross-linked fracturing fluid with a composition of polymer *WGA-15*, crosslinking substance *BXL.10.OC*, clay stabilizer *KCl*, agent reducing flow resistance *Revert Flow*, viscosity breaker *AP1*
- Slickwater-type fracturing fluid collected in the course of well A hydraulic fracturing operation
- Liquids collected as "flowback water" after hydraulic fracturing of shale formations in Poland, carried out on A and B wells

Chemical Analyses

Phenols and nutrients (nitrogen and phosphorus), observed as ions NH_4^+-N (Hach-Lange cuvette test LCK304), NO_3-N (LCK339), and PO_4-P (LCK349), and actions Ca^{2+} (MERC Spectroquant Test 14815), Mg^{2+} (LCK326), and Fe_{total} (LCK321) were determined by a Perkin Elmer Lambda 35 spectrophotometer. Chemical (COD) and biological (BOD_5) oxygen demand as well as anionic and non-ionic surfactants were analyzed by an ISIS 900 spectrometer with Hach Lange cuvette tests (LCK514, LCK555, LCK332, LCJ333) [25]. Total Petroleum Hydrocarbon (TPH) was analyzed by gas chromatography (GC) [11]. Chloride analyses were done with an argentometric method. In order to determine heavy metals (Zn, Sn, Al., Co, As, Ba, Si, Cr, Pb, Cu, Mn, Cd, Ni), ion chromatography (IC) with post-column reaction and ultraviolet-visible detection was applied [26].

Ecotoxicological Analyses

In ecotoxicological research on fracturing and flowback fluids we used toxicological tests (Microtox, MARA) and microbiotests (Daphtoxkit F magna and Thamnotoxkit F) [27-32].

Microtox/DeltaTox – an acute toxicity test is based on a measurement of fluorescence of *Vibrio fischeri* bacteria, which normally use about 10% of metabolism for production of light. In the electrons transport system of these bacteria, a luciferase enzyme (alkane oxygenase) catalyzes oxidation of a reduced substrate (reduced flavin mononucleotide, lactoflavin phosphate, or flavin adenine dinucleotide), and during this process luminescence takes place, which can be measured by a photometer. The resulting substrates participating in this reaction includes oxygen and long-chain aldehyde. In the presence of substances impairing cell metabolism, bacteria react very quickly, decreasing luminescence.

A screening test is done according to a standard procedure (SDI) with the use of Delta Tox analyzer and lyophilized bacteria of *Vibrio fischeri*. Non-diluted samples are placed in test plates. Next, a diluted water solution of NaCl is added to the samples in order to adapt osmotic pressure to luminescence bacteria pressure (2% NaCl).

Three repetitions were done for each sample. After 15 minutes of incubation, a test reaction (PE) was read in each sample. The main test was led for samples that were toxic in a preliminary test. In test plates, numerous dilutions of the research material were made, with the use of a non-toxic solution recommended by a test producer. Bioindicators were introduced, and after a given time of incubation a test reaction for each dilution was read, with the application of SDI software. Toxicity results were estimated as EC_{50}, which means a tested sample concentration causing 50% of test reaction-survival (PE) [20, 33, 34].

Microbial assay for risk assessment (MARA) is an innovative environmental risk assessment test in which the system for assessing chronic toxicity of samples uses 10 prokaryotic organisms – bacteria of different taxonomy and one eukaryotic organism – yeast – as bioindicators. Strains used in the MARA test include: *Microbacterium spaciec*, *Brevundimonas diminuta*, *Citrobacter freudii*, *Comamonas testosteroni*, *Enterococcus casseliflavus*, *Delftia acidovorans*, *Kurthia gibsoni*, *Staphylococcus warneri*, *Pseudomonas aurantiaca*, *Serriatia rudidaea*, and *Pichia anomala* [35].

Lyophilized bioindicators are placed by the manufacturer in the cells of the polystyrene 96-well microplate, which is then hermetically packaged under aseptic conditions. In the MARA test, toxicity of the sample is evaluated

based on the degree of inhibition of growth of the test organisms after 18 hours of incubation. An observed visual effect is water-insoluble red dye pellets produced by healthy bacteria (reduction of a tetrazolinum red). After the test, the plate is scanned, and its image is analyzed by special image analysis software.

For the purposes of conducting research using multiparameter MARA tests, a new method of calculation and presentation of results has been developed. MTC value (microbial toxic concentration) has been introduced, which is calculated from the formula provided below [36, 37]:

$$MTC = c_{\min.} d\ (P_{tot}/P_0) - 0.5$$

...where $c_{min.}$ is the lowest concentration in the concentration gradient of the tested substance, d is the dilution factor, P_0 is the size (diameter) of the granule in a control well, and P_{tot} is the total of the sizes of granules in all wells exposed to contact with the test sample.

The obtained data are evaluated as:

- Minimum MTC value: the concentration that is toxic to the most sensitive organism.
- Maximum MTC value: the concentration that is toxic to the least sensitive organism.
- Average MTC value: the average value of concentrations toxic to all organisms
- Information on the toxic effects of a substance (fingerprint): a unique array of values of toxic concentrations of a given substance (sample) for each of the test organisms that can be compared with the unique information (fingerprint) determined for other substances.

MTC values calculated for specific strains of microorganisms used in the test corresponding to the EC_{50} parameter (concentration inducing a 50% effect – in this case the inhibition of growth).

Daphtoxkit F magna – acute toxicity screening test using *Daphnia magna* crustacean is a recommended tool used to determine water quality and applied to control effectiveness of treatment of polluted industrial waters and bottom sediments [38, 39].

Daphnia magna crustaceans are provided by a manufacturer in a form of spore eggs protected by chitinous capsules called ephippias. In order to release the eggs from the shells and make the organisms hatch, they should be placed in an appropriate environment (media, temperature 20-22ºC, light intensity of 6,000 lux), and then incubated for 3-4 days. The test is performed in wells containing 20 organisms. Plates are used to assess mortality and immobilization of crustaceans in solutions containing toxic substances. Daphtoxkit F magna test allows us to determine 24- and 48-hour acute toxicity in direct contact of test organisms with a tested sample [40-44].

Calculations of toxic effect (EC_{50}) can be done with a graphic method with the use of the enclosed sheet [40-44].

Thamnotoxkit F is an acute toxicity test performed using *Thamnocephalus platyurus* crustaceans, which are provided by a manufacturer in a form of cysts. The condition for hatching of test organisms is their 20-22 hour incubation at 25ºC in a light intensity of up to 3000-4000 lux. The test is performed in wells containing 30 organisms. After 24 hours of contact with a tested sample, the number of killed organisms is determined.

Ten organisms are carried to each tested hole. Each five dilutions (or five samples in a preliminary test) are tested during three repetitions and control. When the organisms are placed in the test wells, 24-hour incubation takes place, and then the results are read – including a number of dead organisms in every well [20, 45-47].

Toxic concentration for 50% of organisms (EC_{50}) is calculated by the graphical method using the attached sheet.

Results and Discussion

Fracturing fluid with appropriately selected properties is the main element that guarantees the success of hydraulic fracturing and unlocking of the deposit, enabling its further exploitation. Due to highly diversified conditions in fractured deposits, many different types of fracturing fluids have been developed [3, 6]. Among them laboratory-prepared crosslinked fracturing fluid and slickwater-type fluid, used during the actual operation of hydraulic fracturing of non-conventional hydrocarbon deposits have been analyzed in terms of their physiochemical properties, and the test results have been summarized in Table 1.

Physical-chemical analysis of the tested fluids showed their diversity (primarily in terms of pH), their mineralization, and the content of organic substances.

Tested slickwater-type fracturing fluid is characterized by pH=6.3, while the pH of crosslinked fracturing fluid is alkaline (pH 8.7). Significant differences were also noticed in the dry mass of the tested fluid residues, since this value in crosslinked fracturing liquid amounted to 10,700 mg/dm^3, while in the slickwater it was significantly smaller (1,347 mg/dm^3). Both tested fracturing fluids are characterized by considerable content of organic substances, as demonstrated by the loss of mass after roasting dry residue of examined fluids at 600ºC. Such large mass losses (1,879 mg/dm^3 in the case of the crosslinked and 942 mg/dm^3 for the slickwater) suggest the presence of compounds that decompose at temperatures of up to 600ºC – e.g., organic compounds (mainly polymer) or certain inorganic salts (e.g. carbonates and bicarbonates, ammonium salts). The high content of organic matter in the examined fluids is also demonstrated by indicators such as: COD, BOD_5, or TOC (COD=19,770 mgO_2/dm^3, BOD_5=1,784 mgO_2/dm^3, TOC=293 mgO_2/dm^3 in the case of crosslinked fluid and COD=1,824 mgO_2/dm^3, BOD_5=248 mgO_2/dm^3, TOC=77 mgO_2/dm^3 in the case of slickwater). Anions assayed in the examined fluids include chlorides and bicarbonates, with little presence of nitrates and sulphates. Main cations included in the examined fracturing fluids are sodium, potassium and, in smaller amounts, calcium and magnesium. Other cations, including heavy metals, are present in trace amounts. In addition, the presence of a small amount of silicon and aluminum was found in the composition of the fracturing fluid.

Table 1. Results of physiochemical analysis of fluids used in hydraulic fracturing.

Parameters	Units	Fracturing fluid	
		Crosslinked fracturing fluid	Slickwater fracturing fluid
pH	-	8.7±0.2	6.3±0.2
Density (20ºC)	g/cm^3	1.005±0.001	1.000±0.001
TDS	mg/dm^3	10,721±764	1,347±121
Residue on ignition		8,842±795	405±36
TSS		68±6	69±6
COD	mgO$_2$/dm^3	19,770±589	1,824±164
BOD		1,784±122	248±22
TOC	mg/dm^3	293±26	77±7
TPH		3.9±0.3	8.2±0.8
Anionic surfactants		11.6±1.0	12.8±1.0
Nonionic surfactants		0.5±0.05	1.1±0.05
Cl^-		914±52	145±15
SO_4^{2-}		38±5	21±5
CO_3^{2-}		24±2	1.2±0.2
HCO_3^-		195±17	243±17
NO_3^-		1.4±0.12	0.21±0.02
NH_4^+		5.6±0.5	0.56±0.06
PO_4^{3-}		3.2±0.3	0.58±0.06
Na^+		824±74	34±5
K^+		792±51	57±5
Ca^{2+}		51.3±4.1	24±2.0
Mg^{2+}		10.2±0.9	8.2±0.9
Fe		0.21±0.02	1.58±0.14
Mn^{2+}		0.028±0.003	0.251±0.022
Cu		0.010±0.001	0.100±0.011
Pb		0.018±0.002	0.142±0.012
Zn		0.019±0.002	0.070±0.006
Ni		<0.01	0.010±0.001
Cr		<0.01	<0.01
Co		0.015±0.002	<0.01
Cd		<0.01	<0.01
Sr		0.012±0.002	0.011±0.002
Ba		<0.01	0.012±0.002
Si		1.40±0.12	1.53±0.12
Al		0.2±0.02	1.5±0.14

Due to the content of the crosslinking agent BXL.10.OC, the structure of laboratory-prepared crosslinked fracturing fluid changed into a gel. This has prevented the direct performance of toxicological tests and obtaining reliable results – a significant limitation of mobility of living test organisms and difficulties in mixing and diluting tested samples. Therefore, it has been decided to perform toxicological tests after breaking the structure of a polymer. For this purpose, the sample of fracturing fluid was conditioned at 85ºC (at the level of temperature found in shale formations) for 12 hours, which allowed (by activating the oxidizer – AP-1 structure breaker) for a partial tear of crosslinks and liquefying the gel to an extent that enables the performance of toxicological tests using the Microtox, MARA, Daphtoxkit F magna, and Thamnotoxkit F tests.

Microtox toxicity tests of samples of fracturing fluids, both crosslinked and slickwater, allowed us to state that they have no toxic properties for *Vibrio fischeri* bacteria. It was impossible to determine EC_{50} concentrations resulting in 50% inhibition of luminescence of test bacteria. During testing it was stated that at the concentrations of samples amounting to 11.25% and 5.50%, luminescence increased above the value specified for the control samples (Fig. 2). This is caused by the creation of better conditions for the growth of bacteria than in the standard test conditions – probably by a reduction of concentrations of toxic agents below threshold values and the advantageous impact of the polymer on bacterial growth.

The results of environmental risk assessment studies for the examined fracturing fluids performed using MARA tests indicate that the mean value of microbial toxic concentration $MTC_{avg.}$ (equivalent of EC_{50}) for the crosslinked fracturing fluid amounted to 88 wt%, and the lowest toxic concentration amounting to $MTC_{min.}$=68 wt% was determined for strain No. 6. In the case of slickwater, the average value of toxic concentration was higher than maximum concentration ($MTC_{avg.}$>100 wt%). The lowest toxic concentration amounting to $MTC_{min.}$=85 wt% was determined for strain No. 2. In the case of other strains, the toxic concentration amounted to more than 90 wt%. After converting

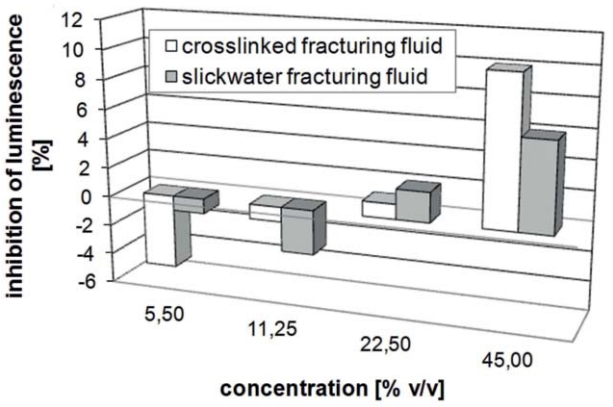

Fig. 2. Microtox test results performed for the crosslinked and slickwater fracturing fluids used to perform operations on A and B wells.

mean toxicity values into toxicity units (TU=1.14 for crosslinked and TU=0.94 for slickwater), these fluids were classified as low toxic and as non-toxic, consecutively (Fig. 3).

The performed acute toxicity tests using *Daphnia magna* and *Thamnocephalus platyurus* crustaceans allowed us to state that the tested fluids have no toxic impact on the test organisms.

In the case of crosslinked fluid, only in the 48-hour Daphtoxkit F magna test was maximum mortality of organisms at the level of 5% stated. Other test organisms remained alive. In the case of tests performed on slickwater-type fluids, in the 48-hour Daphtoxkit F magna test 100% survival of the tested organisms was observed. This means that the fluid has no toxic properties adversely affecting the development of the test organisms (inability to determine EC_{50}).

The performed tests of toxicity of fracturing fluids, used in the operations of hydraulic fracturing of the deposits of gas trapped in shale structure, showed that they are safe for the environment, which is proved by the inability to determine EC_{50} in most of the performed tests. It was possible to determine their level of toxicity only on the basis of MARA tests, and on the basis of their results these crosslinked fracturing fluids (TU=1.16) were classified to the group of substances with toxicity falling within the range of 1<TU<10. Slickwater (TU=0.97) was classified as a non-toxic substance.

Results of the Tests of Flowback Water from Hydraulic Fracturing Operations

After the operations of hydraulic fracturing on A and B wells, samples of flowback water from separators of individual wells were collected. The water containing the remains of fracturing fluid, substances washed out from wells (remains of hydrochloric acid used in a preliminary treatment (acidizing) before hydraulic fracturing, plus dissolved minerals coming from a store rock), and deposit waters (if they flow in to the apertures), were subjected to physical-chemical analyses in order to determine the basic properties (Table 2).

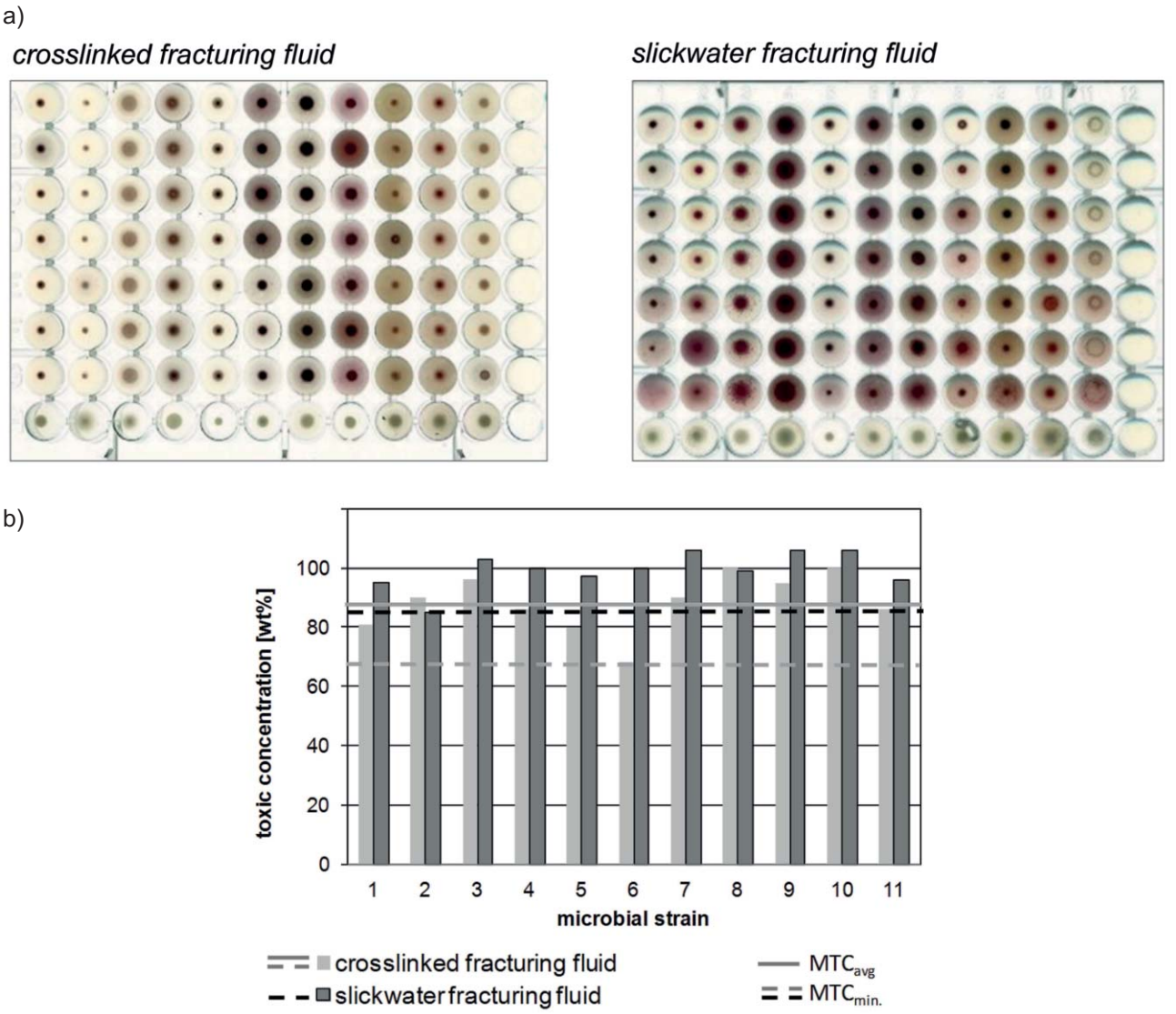

Fig. 3. Comparison of MARA test results performed for the crosslinked and slickwater fracturing fluids used to perform operations on A and B wells: a) Image of MARA test plates, b) MARA test results.

Table 2. Results of physical-chemical analysis of flowback water after hydraulic fracturing.

Parameters	Units	Flowback water			
		Well A		Well B	
		Separator I	Separator II	Separator I	Separator II
pH	-	6.6±0.2	6.2±0.2	6.2±0.2	6.2±0.2
Density (20ºC)	g/cm^3	1.067±0.002	1.057±0.002	1.057±0.002	1.078±0.002
TDS	mg/dm^3	106,396±9,576	92,288±8,350	74,176±6,675	129,788±10,516
Residue on ignition		84,560±7,610	79,408±7,146	61,460±5,538	105,164±9,465
TSS		166±15	652±58	262±24	170±15
COD	mgO_2/dm^3	5,459±490	4,911±490	9,617±865	12,608±1,135
BOD		542±49	359±35	1,026±92	1,234±110
TOC	mg/dm^3	445±40	258±22	1,568±141	879±80
TPH		67.6±6.2	18.3±1.7	614±60	127±12
BTEX		2.42±0.22	0.59±0.06	6.41±0.62	5.22±052
PAH		0.04±0.005	0.02±0.005	0.11±0.005	0.08±0.005
Anionic surfactants		7.24±0.68	8.06±0.68	8.6±0.70	9.7±0.70
Nonionic surfactants		0.7±0.05	0.5±0.05	10.9±1.1	6.0±0.6
Cl^-		53,175±4,786	47,857±4,310	40,767±3,670	54,950±4,945
SO_4^{2-}		16.7±1.5	7.4±0.7	171±15	228±20
CO_3^{2-}		-	-	-	-
HCO_3^-		152±15	183±15	213±15	137±15
NO_3^-		0.35±0.04	0.11±0.02	0.46±0.05	0.54±0.05
NH_4^+		0.48±0.05	0.36±0.05	53.6±4.8	82± 7.6
PO_4^{3-}		0.48±0.05	0.46±0.05	0.55±0.05	0.62±0.05
Na^+		30,321±2,728	26,621±2 395	13,970±1 257	16,190±1,457
K^+		145±10	112±10	1,150±103	1,380±121
Ca^{2+}		2,474±222	1,875±168	8,176±735	13,266±1,195
Mg^{2+}		609±58	467±46	1,337±120	1,945±175
Fe		15.1±1.2	10.6±1.0	8.4±0.8	14.8±1.2
Mn^{2+}		0.95±0.10	0.78±0.08	0.6±0.07	0.8±0.07
Cu		0.29±0.03	0.22±0.03	0.33±0.03	0.42±0.03
Pb		0.41±0.05	0.32±0.05	0.15±0.05	0.23±0.05
Zn		0.025±0.005	0.023±0.005	0.028±0.005	0.031±0.005
Ni		0.017±0.005	0.014±0.005	0.022±0.005	0.023±0.005
Cr		0.025±0.005	0.020±0.005	0.025±0.005	0.027±0.005
Co		0.014±0.005	0.016±0.005	0.015±0.005	0.016±0.005
Cd		0.013±0.005	0.011±0.005	0.009±0.005	0.011±0.005
Sr		1,196±107	916±85	26±2.3	8.8±0.8
Ba		2.54±0.25	1.95±0.20	1.88±0.20	1.98±020
Si		18.1±1.6	21.5±2.0	22.5±2.0	25.2±2.0
Al		0.45±0.05	0.32±0.05	0.7±0.05	0.8±0.05

Tested liquids collected from separators I and II after hydraulic fracturing of well A showed pH close to neutral (slightly acidic). The results of assaying of dry mass residues (106,396 mg/dm^3 in separator I, and 92,288 mg/dm^3 in separator II) and residues after roasting allow us to state that flowback water samples are highly mineralized and contain substantial quantities of substances that decompose at temperatures up to 600ºC (20% and 13%, respectively). Assayed high oxygen demand indicators COD, at the level of 5,459 mg/dm^3 (sample No. 1) and 4,911 mg/dm^3 (sample No. 2) indicates the presence of substances with reducing properties eluted from the deposit during fracturing. The presence of significant quantities of chlorides at the level of 50,000 mg/dm^3, and low content of bicarbonates and sulfates were revealed. Among the cations, the highest values were determined for sodium (30,321 mg/dm^3 in sample No. 1 and 26,621 mg/dm^3 in sample No. 2), calcium (2,474 and 1,875 mg/dm^3, respectively), strontium (1,196 and 916 mg/dm^3), and magnesium (609 and 467 mg/dm^3). Potassium, silicon, total iron, and barium were present in low content. The content of other cations, including heavy metals, did not exceed 1 mg/dm^3. The tested liquid from separator I was characterized by an increased content of petroleum pollutants TPH (67.6 mg/dm^3).

Flowback water after hydraulic fracturing of well B was collected from the separator at the initial phase of fluids return and after 10 days from the commencement of well lifting. Physico-chemical analysis of the tested liquids showed that their reaction was close to neutral. The masses of substances dissolved in liquids from separators increased with the time of taken samples, from 74,176 to 129,788 g/dm^3. The content level of pollutants in the tested liquids increased 170-262 mg/dm^3. Furthermore, the data presented in Table 1 show that the dry mass is composed in 17.1 to 19.0% from substances that decompose at temperatures up to 600ºC. High oxygen demand indicators at the level of 9,617 to 12,608 mg O_2/dm^3 were also assayed in the tested liquids, which indicates the presence of substances with reducing properties eluted from the deposit during fracturing. In subsequent samples of liquids from separators, an increase in the chloride content was also stated, the values of which ranged from 40,767 to 54,950 mg/dm^3. The content of sulfated and bicarbonates in the tested liquids was assayed at a significantly lower level.

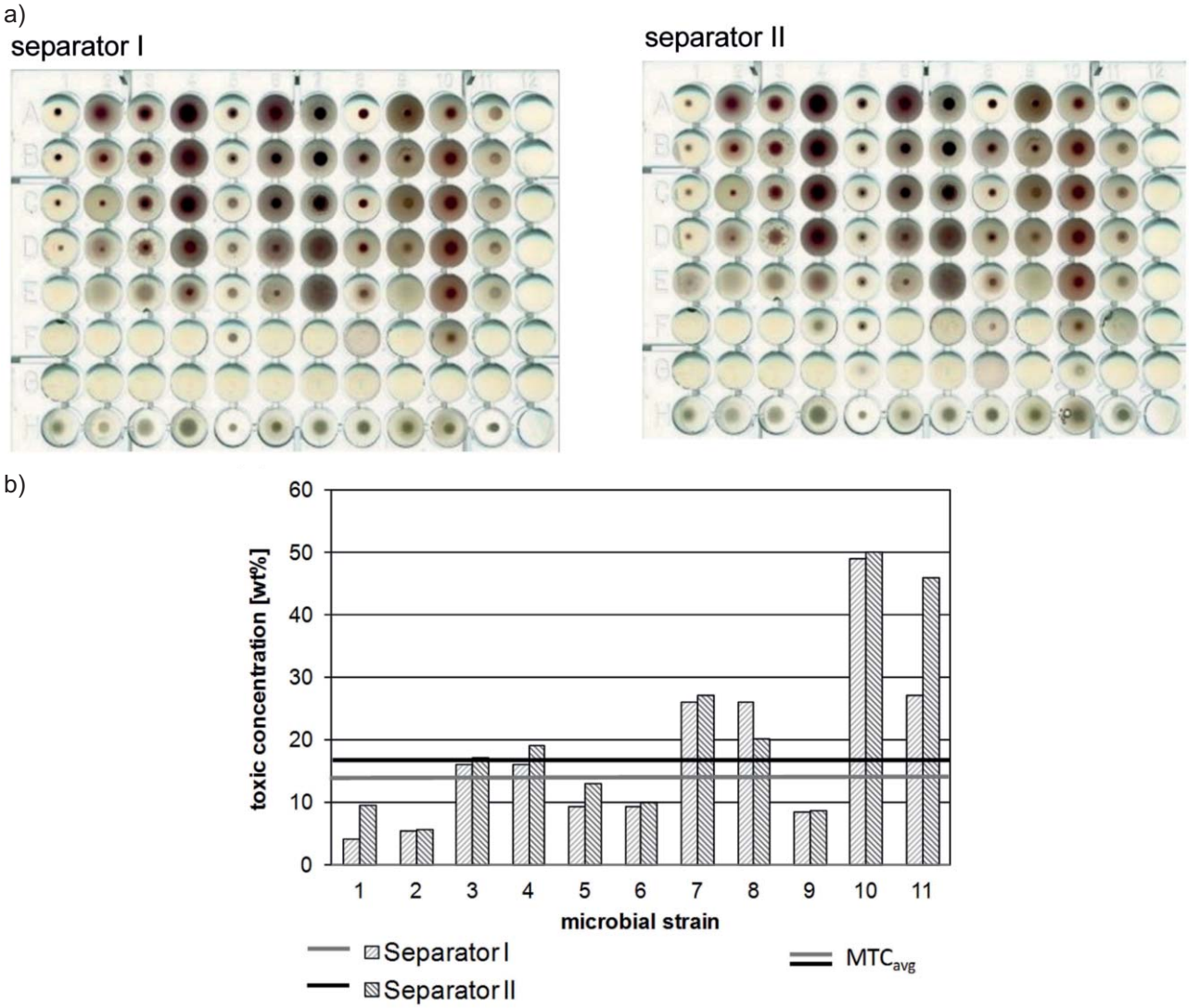

Fig. 4. Comparison of toxic concentrations of tested samples of flowback water collected from well A after fracturing, as determined by MARA test: a) Image test plates MARA, b) MARA test results.

During the analysis of cations, an increase in their content with increasing mineralization of water samples was noted. Among the cations, the highest values were assayed for sodium (13,970-16,190 mg/dm^3), potassium (1,150-1,380 mg/dm^3), calcium (8,176-13,266 mg/dm^3), and magnesium (1,337-1,945 mg/dm^3). The tested liquids contained a significant amount of total iron (8.4-14.8 mg/dm^3) and silicon (22.5-25.2 mg/dm^3). The content of other cations, including heavy metals, did not exceed 1 mg/dm^3 (Table 1).

The results of chemical analysis showed that flowback water from hydraulic fracturing contains mainly the components present in formation waters and polymer residues. This may indicate elution of substances from the well-adjacent zone by injected fracturing fluid or inflow of formation water into the well through the created fractures.

The tested liquids collected from flowback after fracturing of non-conventional hydrocarbon deposits were subjected to toxicological tests. Figs. 4 and 5 present the MARA environmental risk assessment test results, while Fig. 6 presents toxicity test results (in toxicity units) assayed using MARA, Microtox, Daphtoxkit F magna, and Thamnotoxkit F.

MARA environmental risk assessment results showed that the mean values of microbial toxic concentration $MTC_{avg.}$ in samples of flowback water after hydraulic fracturing of well A are similar (14.2 wt% and 16.1 wt%). The lowest value was observed in the case of liquid from separator I from fracturing of well A, in which the lowest toxic concentration, amounting to $MTC_{min.}$=4.0 wt%, was determined for strain No. 1. Only a slightly higher toxic concentration was observed in the case of strains No. 2 (MTC=5.4 wt%), No. 9 (MTC=8.4 wt%), No. 5 (MTC=9.2 wt%), and No. 6 (MTC=9.3 wt%) (Fig. 4).

In the case of liquid from separator II after well A fracturing, the mean value of toxic microbial concentration amounted to $MTC_{avg.}$=16.1 wt%, and the lowest toxic concentration amounted to $MTC_{min.}$=5.6 wt% as assayed for strain No. 2. Apart from strain No. 2, strains No. 9 ($MTC_{min.}$=8.5 wt%), No. 1 ($MTC_{min.}$=9.5 wt%), and No. 6 ($MTC_{min.}$=9.8 wt%) proved to be the most sensitive organisms.

The results of the performed tests indicate that flowback water samples collected from both I and II separators after

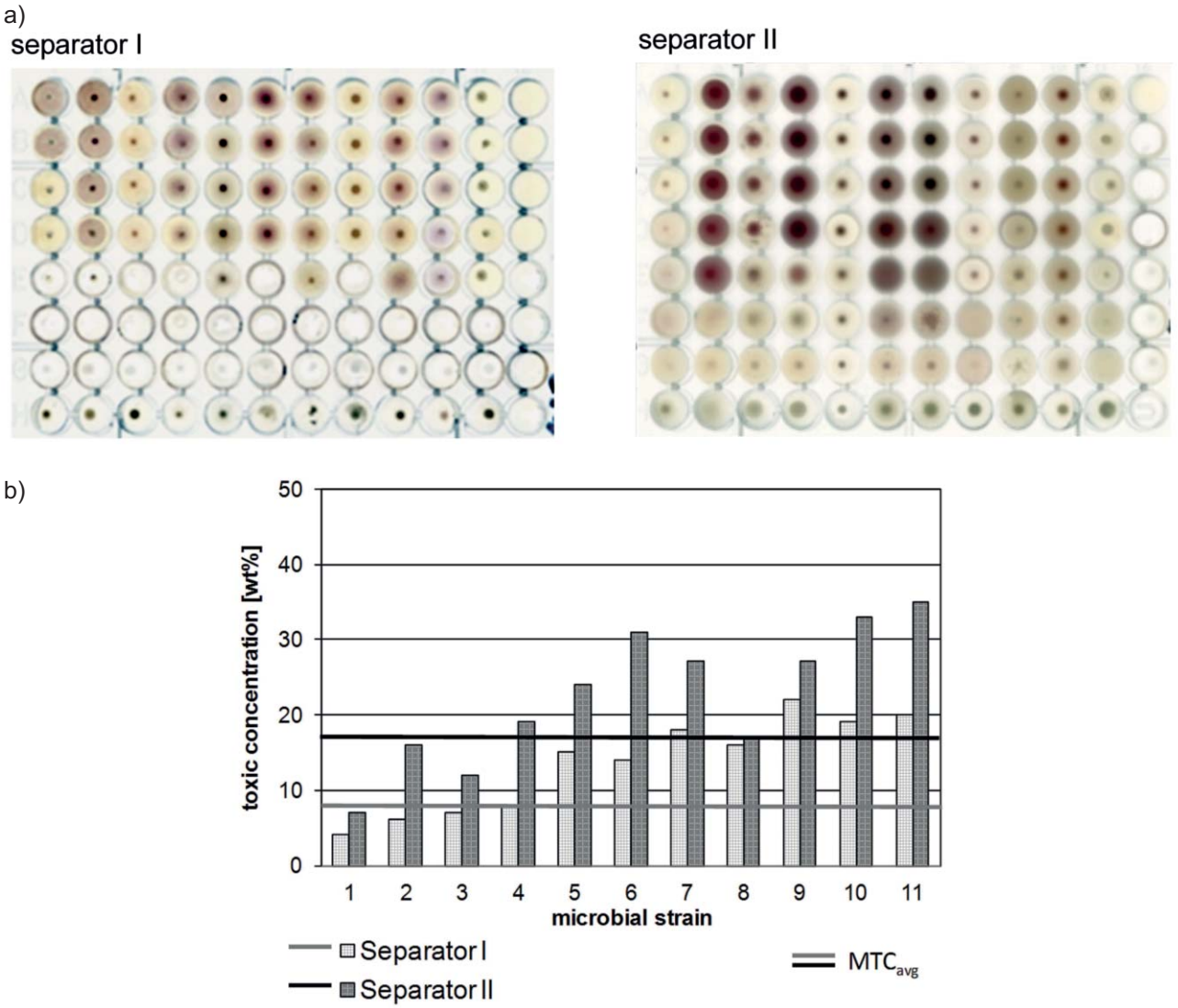

Fig. 5. Comparison of toxic concentrations of tested samples of flowback water collected from well B after fracturing, as determined by MARA test: a) Image test plates MARA, b) MARA test results.

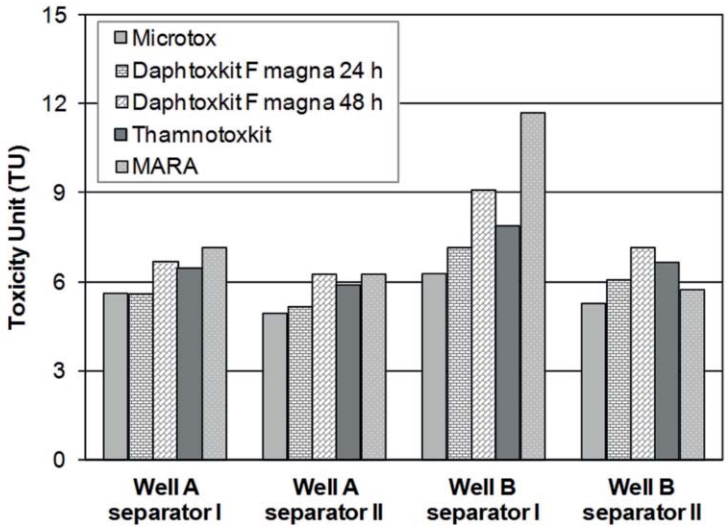

Fig. 6. Comparison of toxicity tests results (in toxicity units) performed for samples of flowback water from fracturing of wells A and B.

fracturing of well A are toxic only for some bacteria strains. After converting the mean toxic value into toxicity units (TU), the following values were obtained: TU=7.14 for water from separator I and TU=6.25 for water from separator II.

MARA environmental risk assessment tests performed for flowback water from hydraulic fracturing of well B showed significant differences in toxic properties of subsequently tested samples (Fig. 5). Mean values of microbial toxic concentration ($MTC_{avg.}$) for flowback water from separators I and II were assayed at the level of 8.5 wt% and 17.5 wt%, which, after converting into TU, amounts to 11.8 and 5.7, respectively. The tested liquids were characterized by the lowest toxic concentrations ($MTC_{min.}$) in the case of strain No. 1, within the range 4-12 wt%. In turn, the highest resistance in the tested liquids was shown by strains:

- Nos. 7, 9, 10, and 11 (toxic concentrations within the range of 18-22 wt%) for liquids from separator I
- Nos. 6, 7, 9, 10, and 11 (toxic concentrations within the range of 27-35 wt%) for liquids from separator II

The results of Microtox test used for rapid assessment of acute toxicity allowed us to state that the samples of flowback water from hydraulic fracturing of wells A and B collected from both separators show small differences in chemical composition. EC_{50} values (concentration causing 50% inhibition of luminescence of *Vibrio fischeri* bacteria) for liquids from fracturing of both wells A and B fall within the range of from 15.9-20.2%, which corresponds to TU value of: 5.0-6.3 (Fig. 6). Increases in the toxicity of the tested samples correlated primarily with the contents of TPH, TOC, and COD indicators and dry residues.

The toxicity test based on *Daphnia magna* crustaceans showed, in the case of flowback water from fracturing of both wells A and B, the presence of toxic components adversely affecting living organisms. Calculated EC_{50} values for particular liquids in the 24-hour test are close to EC_{50} values determined by the Microtox test, since they fall within the range of 14-19.5%, which corresponds to TU values of 5.1-7.1. Higher differences were determined in the 48-hour test, in which the toxicity of tested liquids increased adequately to TU values of: 6.3-9.1. The difference in the toxicity of the tested samples can be observed in the chart showing TU values calculated for concentrations inducing a 50% effect (EC_{50}) (Fig. 6).

Another test based on *Thamnocephalus platyurus* crustaceans performed for the samples of flowback water from hydraulic fracturing of deposits was the Thamnotoxkit F test. The results of this test showed the harmful effects of the components of each tested liquid on test organisms. After converting toxic concentrations EC_{50} of tested liquids into toxicity units, it was stated that they fall within the range of 5.9-7.9 (Fig. 6).

Comparing the results of toxicological tests, it can be concluded that the harmfulness of flowback fluids after hydraulic fracturing of well A, collected from both separators, are similar, with slightly higher TU values in the case of liquid from separator I. Slightly higher values in toxicity units obtained in particular tests were observed in the case of flowback water collected from separators of well B. Furthermore, liquid from separator I of this well was characterized by the highest toxicity units among all the tested liquids (Fig. 6). In analyzing the obtained results of toxicological tests and physical-chemical analyses, it can be seen that the liquid collected from separator I is, in addition to the content of petroleum hydrocarbons, characterized by elevated values of surfactants compared to other liquids. The dispersion of hydrocarbons increases with the increasing content of surfactants in the tested liquids, hindering the separation of organic and inorganic phases, which results in the growth of their toxicity (Table 2, Fig. 6).

The performed toxicological tests of flowback water from hydraulic fracturing of non-conventional deposits showed that the increased content of pollutants results in the increase of toxic properties of extracted liquids.

However, the majority of liquid samples analyzed in order to determine the toxicity were classified to the group of substances with 1<TU<10 toxicity. Only flowback water collected from separator I after hydraulic fracturing of well B was classified, based on the MARA test results, to the group of toxic substances falling within the 10<TU<100 range.

Conclusions

Recognition of physical-chemical properties of fluids (used in hydraulic fracturing of non-conventional hydrocarbon deposits) as well as their wastes, aided with toxicological research (with the use of new-generation toxicological tests), enable estimation of dangers to the natural environment.

1. Physical-chemical analyses of crosslinked and slickwater fracturing fluids showed their diversity, which means that their reaction, mineralization, and organic substances contents are different. As the toxicological analyses proved, these fluids are non-toxic to living organisms.
2. Analyses of flowback liquids after fracturing of wells A and B showed that the content of diluted substances increases with the volume of the excavated liquids and it contains mainly components presented in deposit. On the one hand, it can indicate washing out the substances from the deposit by the pumped fracturing fluid. On the other, it can mean an inflow of deposit waters to the well through the cracks. According to the toxicological research, the tested flowback waters after hydraulic fracturing can be classified as substances of low toxicity, because their toxicity level (TU) ranges from 5.9 to 11.8.
3. Rational management of flowback waters after hydraulic fracturing of shale formations, particularly by their re-use, after preliminary treatment, to develop another parts of fracturing fluids, can result in significant reduction of harmful influences of the oil industry on the natural environment.

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