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TOXICOLOGICAL EVALUATION OF THERMAL TREATMENT OF DRILLING WASTE FROM SHALE GAS EXPLORATION IN POLAND[☆]

OCENA TOKSYKOLOGICZNA TERMICZNEGO OCZYSZCZANIA ODPADÓW WIERTNICZYCH Z POSZUKIWAŃ GAZU ŁUPKOWEGO W POLSCE

Abstract: The oil containing drilling waste is a worldwide environmental problem associated with oil and gas exploration. In Poland, the problem of the drilling waste has become important since starting of shale gas exploration. The results of thermal treatment of drilling waste from shale gas exploration are presented. It has been shown that organic content vaporized completely at temperature up to 500 °C. The main problem is high content of chloride, sulfate, sodium, potassium, magnesium in the waste and its water leachate. Toxicity tests confirmed that high salinity of the samples pose important risk for environment. Due to the high content of barium, the drilling waste may be utilized in production of cement with high chemical and heat resistance and opaque to X-ray. Thermal treatment process is a viable option for remediation of the drilling waste; however, the product of the process needs further treatment in order to remove its high salinity.

Keywords: thermal treatment, oil containing drilling waste, toxicity, shale gas

Introduction

The drilling for exploration or/and extraction of hydrocarbons from rocks requires the use of drilling fluids [1]. Drilling fluids are continuously pumped down the well through the drilling pipe and return through the well annulus carrying the rock phase that is extracted from the well. The main purpose of the fluids is to supply the drill cuttings transport phase, but they also cool and lubricate the drill bit, stabilize the well bore and control subsurface (down-hole) pressures. Pressure is achieved by controlling fluid density,

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balancing it with the pressure that is experienced down-hole and by including very heavy minerals such as barites to counteract the pressure in the hole. As the drill bit grinds rocks into drill cuttings, these cuttings become entrapped within the fluid flow and are carried to the surface where the drilling cuttings are separated from the fluids. The solid waste is separate on vibrating shaker. Fine solids are separated additionally in mechanical processes such as hydrocycloning, decanting in centrifuge and gravitational settling [1]. Usually, drilling waste contains residues of drilling fluids which adheres to solids such as corrosion and scale inhibitors, biocides, lubricants, viscosifiers and chemical additives for shale stability (preventing hydration) [1, 2]. In Poland, the oil-based drilling fluids are commonly used for horizontal drilling, mainly due to high content of clay minerals in shale formations [3]. Addition of oil to drilling fluid stabilizes also rheological properties, better than water-based fluids [2]. Oil-based drilling waste slowly undergoes bioremediation processes and thus it is not suitable for landfilling [1]. There is the environmental risk associate with emission of toxic pollutants due to leaching and weathering processes during storage. Additionally, local residents are often against storage of such hazardous waste in their neighborhood. The most applied option for treatment of oil contaminated waste is thermal desorption of organic compounds [4, 5]. The thermal process can be conducted in cement kiln and, additionally, leachable inorganic residues can be immobilized by in situ formed mineral phases (for example hydroxyapatite) [6]. Such material can be used for road construction [1].

The aim of this study is to evaluate thermal treatment of oil containing drilling waste from shale gas exploration in Poland based on its possible environmental impact.

Experimental

Materials

The sample of drilling waste was collected from borehole in Kosciierzyna County, Pomeranian Voivodeship, North of Poland in 29 July 2015. This waste was taken from horizontal drilling at around 3800 m borehole true vertical depth (4400 m borehole measured depth) - Silurian-Ordovician shale formation containing hydrocarbons. The drilling waste was collecting after dewatering process. The remained water was further recycled and reuse in drilling. The chemical composition of inorganic part of the sample is given in Table 1. The drilling waste contains drilling cutting and residuals of drilling fluids (muds). Mineralogical composition determined by X-ray diffraction (XRD): 25 % quartz, 18 % barite, 5 % calcite, 3 % dolomite, 3 % feldspar, 32 % clay minerals (kaolinite, serpentine, illite). Loss on ignition was 14 %.

Chemical analyses

The chemical analyses were performed at Central Chemical Laboratory in Polish Geological Institute-Polish Research Institute. The Laboratory is accredited according to ISO 17025. The analytical procedures were based on standard methods listed by Polish Environmental Law (Polish Environmental Law is harmonized with European Union Law). The results are presented in Table 1.

Table 1

Inorganic analysis of untreated drilling waste sample

Parameter	Unit	Untreated sample	Description of analytical method; laboratory procedure; version number
SiO ₂	[%]	7.54	X-ray fluorescence, fused sample; PB-33; ver. 6
TiO ₂	[%]	1.11	
Al ₂ O ₃	[%]	0.18	
Fe ₂ O ₃	[%]	2.93	
MnO	[%]	0.058	
MgO	[%]	1.51	
CaO	[%]	4.36	
K ₂ O	[%]	0.87	
P ₂ O ₅	[%]	0.168	
SO ₃	[%]	6.39	
Cl	[%]	0.062	
F	[%]	< 0.01	
Loss on ignition	[%]	14.7	Furnace, 1000 °C
As	[mg/kg]	5	X-ray fluorescence, sample was ground and pressed into pellet; PB-33; ver. 7
Ba	[mg/kg]	63073	
Br	[mg/kg]	< 1	
Ce	[mg/kg]	64	
Co	[mg/kg]	9	
Cr	[mg/kg]	75	
Cu	[mg/kg]	73	
Ga	[mg/kg]	5	
Hf	[mg/kg]	< 3	
La	[mg/kg]	17	
Mo	[mg/kg]	11	
Nb	[mg/kg]	16	
Ni	[mg/kg]	89	
Pb	[mg/kg]	< 3	
Rb	[mg/kg]	71	
Sr	[mg/kg]	1210	
Bi	[mg/kg]	6	
Th	[mg/kg]	< 3	
U	[mg/kg]	5	
V	[mg/kg]	357	
Y	[mg/kg]	14	
Zn	[mg/kg]	155	
Zr	[mg/kg]	213	
Cd	[mg/kg]	17	
Sn	[mg/kg]	2	
Hg	[mg/kg]	1.84	Atomic Absorption Spectrometry with amalgamation on gold, PB-06, ver. 6

Leaching procedure

The European Union regulation on solid waste landfilling set forth parameters for waste storage at dumpsite [7]. The compliance tests for the treated waste were performed according to EN 12457-4:2006 [8], which include leaching with distilled water at liquid-to-solid ratios (L/S) 10 dm³/kg for 24 hour of shaking.

Thermogravimetric analysis

The experiments on oil containing drilling waste from shale gas pyrolysis and air gasification were conducted by use of thermogravimetric analyzer SDT Q600, TA Instruments. Sample (particle size below 0.1 mm and mass of 36.15 mg) were placed in a crucible made of corundum ceramics. The drilling waste sample was heated in the nitrogen atmosphere with the heating rate 10 °C/min to the set air gasification temperature (1000 °C). After that, nitrogen was replaced with air (flow rate of 0.1 dm³/min), and the sample was kept in the set temperature until a constant weight was obtained.

Thermal treatment of drilling waste

The thermal treatment experiments were performed in Jerzy Haber Institute of Catalysis and Surface Chemistry using muffle furnace (Czylok FCF 12 SHM). The furnace is equipped with the PID digital temperature programmer (Czylok SM-2002), which was used for precise control of temperature inside the chamber. The samples of drilling waste were treated in air at 250, 500, 800 and 1000 °C for 2 h. Due to safety reason (fire hazard), the sample treated at 800 °C was brought to the temperature in 2 h, whereas the sample treated at 1000 °C was brought to the temperature in 2,5 h.

Toxicity analysis

Toxicity analysis was performed at Department of Environmental Health Sciences, Medical University of Warsaw.

Sample preparation: 200 grams of the tested sample was poured with 200 cm³ of deionized water (MilliQ) and shaken at 25 °C. After 1 and 24 h the pH of the water was measured and the sample was adjusted to the pH range 6-8 with few drops of concentrated HCl (analytical grade). Aqueous phase was tested by the Spirotox, Microtox and umu-test whereas the solid phase - by the direct contact assays Microtox-SPT, Ostracodtoxkit F and Phytotoxkit. Prior to the Phytotoxkit test, the solid samples were mixed with sand 1:10. In case of Ostracodtoxkit F, undiluted and diluted samples with sands 1:10 and 1:100 were tested. The sand was used as a negative control.

Spirotox test: Acute toxicity assay with the ciliated protozoan *Spirostomum ambiguum* was performed according to procedure developed by Nalecz-Jawecki [9]. Shortly, the test was carried out in a 24-well polystyrene multiwell plate. Each test comprised one control and five toxicant concentrations with three duplicates per concentration. Each well contained 1 ml of the sample and 10 protozoans. The plates were incubated in darkness at 25 °C. After 24 and 48 h two kinds of test responses were observed: (1) different deformations, morphological changes, such as shortening and bending of the cell; (2) lethal response (L). As a diluent and a control Tyrod solution was used.

Microtox: Acute toxicity assay with the luminescent bacteria *Vibrio fischeri* was performed according to the ISO 11348-3:2007 [10]. Samples were incubated at 15 °C for 15 and 30 min and the light output of the samples was recorded with a Microtox M500 analyzer. Standard procedure was used for testing water extracts, whereas a solid phase test (SPT) was used for testing solid samples. The SPT is a direct contact assay and the bacteria were incubated in the suspension of the solid sample in the SPT diluent (3.5 % NaCl) for 30 min. As a diluent and a control 2 and 3.5 % NaCl was used in the standard and SPT procedure, respectively.

Ostracodtoxkit F: Direct contact toxicity assay with the ostracods *Heterocypris incongruens* was performed according to the ISO 14371:2012 [11]. The assay, purchased from MicroBioTests, was performed in the 6-well polystyrene multiwell plate. Each control and a sample was in 6 replicates. Ten neonates of the ostracod hatched from cysts were added to each well of the microplate containing 1 cm³ of the solid sample and 4 cm³ of the algal suspension (food). After 6 days of contact with the sample the percentage mortality and the growth of the ostracods were determined and compared to the control. As the control non-toxic sand was used.

Phytotoxkit: Seed germination and early growth assay with higher plants was carried out according to the ISO/DIS 18763 [12]. Flat and shallow transparent test plates were used in the Phytotoxkit from MicroBioTests. Seeds of the selected plants were laid on a black filter paper placed on top of the hydrated solid sample. After closing the test plates with their transparent cover, the test plates were placed vertically in a holder and incubated at 25 °C for at least 3 days. At the end of the incubation a photo was taken with a digital camera and the length of the roots was measured with the use of the image analysis program (ImageTool, UTHSCSA). The assay was performed with the seeds of 5 plant species: one monocotyl (*Sorghum saccharatum*), and 4 dicotyls (*Lepidium sativum*, *Sinapis alba*, *Beta vulgaris* and *Medicago sativa*).

Umu-test: Umu-test detects the induction of the SOS system in the strain *Salmonella typhimurium* TA1535/pSK1002. The test is based on the capability of genotoxic agents to induce the umuC-gene in the *S. typhimurium* strain in response to genotoxic lesions in the DNA. Due to its capability to respond to different types of genotoxic lesions, only one single strain is necessary to detect different kinds of genotoxic substances. The umu-test was carried out in the 96-well microplate with and without the metabolic activation by S9 fraction according to the ISO 13829 [13]. S9 fraction was prepared from liver of male Sprague-Dawley rats pretreated with Aroclor 1254 (500 mg/kg) 5 days prior to isolation. The 1.5 fold and greater increase of the β -galactosidase activity resulting in induction ratio, *IR* value of 1.5 and greater indicated the genotoxicity of the sample. Additionally, toxicity assessment was performed by measurement of bacterial growth inhibition expressed as the growth factor.

Results and discussion

Thermogravimetric analysis of drilling waste

Thermogravimetric analysis revealed two inflection points (Fig. 1). The first one occurred in temperature interval from 50 to 200 °C with maximum at around 130 °C. The observed weight loss was 12.17 %. This weight loss may be a result of vaporization of light aliphatic hydrocarbon and single to three rings aromatic compounds and their aliphatic substituted derivatives. Boiling point and flash point of those compounds are within or close to the temperature interval [14]. Those compounds are very volatile, and thus they can be easily removed from drilling waste by heating. The formed vapor can be easily flared up or used for heating purposes. The sample was air dried in order to avoid the loss of volatile hydrocarbons before measurement. Therefore, the weight loss may be partially accounted for removal of sample moisture. In the temperature interval from 300 to 550 °C, the hydrocarbons with higher molecular weight and number of carbon atoms were removed from the waste. Part of those compounds may come from the shale. Silurian-Ordovician shale formation contains up to 4 % of total organic carbon; the median value is around 2 %

[15]. The observed weight loss was 7.22 %. Due to heating of the sample up to 550 °C, the observed total loss weight was 20 %. Further loss of weight, up to 1000 °C, was likely caused by loss of crystalline water and dehydroxylation of clay minerals (illite, kaolinite and serpentine) as well as partial decomposition of barite and carbonates.

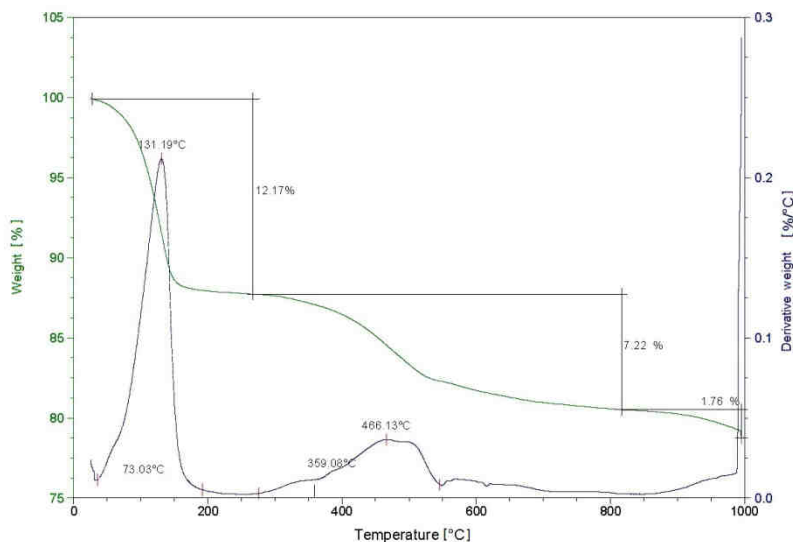


Fig. 1. Thermogravimetric curve of the investigated sample of drilling waste

Thermal treatment of drilling waste

Based on thermogravimetric analysis, the temperature for drilling waste treatment was set at 250 and 500 °C. However, taking into account that the waste can be treated in an incineration plant or cement kiln, two points at 800 and 1000 °C were added. According to Council Directive 89/429/EEC, the temperature of the gases from incineration of municipal waste should be at least 850 °C in order to avoid formation of polychlorinated dibenzodioxins (PCDDs) and of polychlorinated dibenzofurans (PCDFs) [16]. However, in modern plants, the wastes are usually incinerated in multistep process at different condition and temperatures in order to reduce pollution and improve waste-to-energy conversion efficiency [17].

The results of organic analysis of the untreated drilling waste have shown high contents of organic compounds (Table 2). Total petroleum hydrocarbons (TPH) concentration was very high - 31 g/kg and total organic carbon (TOC) was 4 %. However concentration of volatile (BTEX) and 16 priority polycyclic aromatic compounds (PAH) was low. Only concentration of phenanthrene, pyrene and benzo[e]pyrene was above 0.1 mg/kg. The oil based drilling fluids are prepared from synthetic mineral oils containing olefins and paraffinic (mostly cyclic) hydrocarbons with low content of aromatic compounds in order to meet environmental safety criteria imposed by many environmental protection authorities [18]. Therefore, the traces of aromatic compounds may come from shale formation or they may be impurities of synthetic oil used in borehole drilling.

The water leaching test has shown that hydrocarbons were strongly bound to the solid content of the waste. In water solution only traces of 16 priority PAH were found. The leaching of each compound was below 1 µg/kg, except phenanthrene - 2.45 µg/kg. The concentration of TPH in the solution after leaching was below the limit of quantification. The mineral composition of the waste was characterized by X-ray diffraction. The waste contained (by weight): 25 % of quartz, 18 % of barite, 5 % of calcite, 3 % of dolomite, 3 % of feldspar and 32 % of clay minerals (illite, kaolinite, serpentine). The clay minerals are very good adsorbent of organic compounds [19]. In order to prevent clay hydration and swelling, the quaternary amines are frequently added to drilling muds [20]. Amine modified organoclays strongly immobilize oil hydrocarbons [21, 22]. It seems that such material is appropriate for landfilling. However, there is the risk that during biodegradation and weathering of the waste may release olefins and paraffinic compounds to environment. The compounds can be also transformed to very toxic naphthenic acids in the environment [23, 24].

Table 2

Organic analysis of untreated and treated drilling waste sample

Parameter	Unit	Untreated sample	250 °C	500 °C	800 °C	1000 °C	Description of analytical method; laboratory procedure; version number
Total C	[%]	7.54	3.68	1.16	1.76	1.31	Elemental analyzer
Total H	[%]	1.11	0.50	0.21	0.09	0.07	
Total N	[%]	0.18	0.18	0.05	0.05	< 0.05	
Total S	[%]	2.93	2.56	2.42	1.94	1.32	
Total Organic Carbon TOC	[%]	4.16	2.88	0.62	-	-	Combustion with coulometric titration, PB-23, ver. 6
Total Petroleum Hydrocarbons	[mg/kg]	31000	1220	386	< 10	< 10	Tetrachloroethylene extraction, Fourier Transform Infrared Spectrometry, PB-23, ver. 6
Acenaphthylene	[µg/kg]	35	57	9	< 1	< 1	Gas chromatography-mass spectrometry, PB-22, ver. 7
Acenaphthene	[µg/kg]	53	14	7	< 1	< 1	
Fluorene	[µg/kg]	13	35	17	< 1	< 1	
Phenanthrene	[µg/kg]	224	55	42	< 1	< 1	
Anthracene	[µg/kg]	14	8	6	< 1	< 1	
Fluoranthene	[µg/kg]	44	8	11	< 1	< 1	
Pyrene	[µg/kg]	121	7	16	< 1	< 1	
Benzo[a]anthracene	[µg/kg]	21	< 2	4	< 2	< 2	
Chrysene	[µg/kg]	56	< 2	5	< 2	< 2	
Benzo[b]fluoranthene	[µg/kg]	33	< 3	< 3	< 3	< 3	
Benzo[k]fluoranthene	[µg/kg]	5	< 3	< 3	< 3	< 3	
Benzo[e]pyrene	[µg/kg]	122	< 3	< 3	< 3	< 3	
Benzo[a]pyrene	[µg/kg]	27	< 3	< 3	< 3	< 3	
Perylene	[µg/kg]	9	< 3	< 3	< 3	< 3	
Indeno[1,2,3-cd]pyrene	[µg/kg]	12	< 5	< 5	< 5	< 5	
Dibenzo[ah]anthracene	[µg/kg]	14	< 5	< 5	< 5	< 5	
Benzo[ghi]perylene	[µg/kg]	80	< 5	< 5	< 5	< 5	
Benzene	[µg/kg]	2.3	-	-	-	-	Head space-gas chromatography-mass spectrometry, PB-23, ver. 7
Toulene	[µg/kg]	21	-	-	-	-	
Ethylbenzene	[µg/kg]	8.3	-	-	-	-	
1,4-dimethylbenzene	[µg/kg]	17	-	-	-	-	
1,3-dimethylbenzene	[µg/kg]	28	-	-	-	-	
1,2-dimethylbenzene	[µg/kg]	26	-	-	-	-	

The leachable total organic carbon was 1350 mg/kg. The soluble part of organic compounds in drilling waste may contain various surfactant, quaternary amines, scale and corrosion inhibitors (EDTA, citrate) etc. [2]. Those compounds are usually selected for preparation of drilling fluids because of their high biodegradability and low or no toxic effect to environment. In many countries, environmental law and good practices impose usage of environmental friendly drilling fluids.

The X-ray fluorescence analysis has shown that investigated drilling waste consisted high concentration of sodium, barium, potassium, magnesium mainly in sulfate or/and chloride salts (Table 1). There are also elevated concentrations of zinc, manganese, strontium and vanadium probably coming from shale formation or/and drilling fluid and abrasion of rig and borehole construction parts during drilling. However, only sodium, potassium and calcium leached significantly from untreated drilling waste (Table 3). Those cations are well known macroelements, crucial for life; however, their high concentration has an adverse effect on environment due to increasing the osmotic pressure that may disrupt cells in organisms. The presence of high concentration of chloride causes salinity stress to organism. The presence of chloride in aquatic environment is responsible for decreasing of available nutrient, decreasing of dissolved oxygen content and increasing of toxic heavy metals mobilization from sediments. Sulfate causes salinity stress to organism too, and may be responsible for mobilization of heavy metals in environment and increases leaching of essential nutrients.

Table 3

Inorganic analysis of leachate from drilling waste before and after the treatment

Parameter	Unit	Untreated sample	250 °C	500 °C	800 °C	1000 °C	Analytical method, laboratory procedure, version number, issue date
Conductivity	[mS/cm]	1.5	3.5	3.4	2.6	3.4	Electrical conductivity meter, PB-02, ver. 8
pH		8.56	7.13	10.52	4.7	3.5	Potentiometer, PB-01, ver. 8
Fluoride	[mg/kg]	< 1	< 3	< 3	< 3	< 3	Ion chromatography with electrical conductivity detector, PB-04, ver. 14
Chloride	[mg/kg]	4100	5900	6100	4200	3500	
Nitrite	[mg/kg]	3.5	< 30	< 30	< 30	< 30	
Nitrate	[mg/kg]	2.4	< 30	< 30	< 30	< 30	
Sulfate	[mg/kg]	215	5800	7600	6400	14500	Inductively coupled plasma optical emission spectrometry, PB-28, ver. 6
Na	[mg/kg]	1064	1160	716	816	588	
K	[mg/kg]	306	353	505	732	818	
Sr	[mg/kg]	9.1	120	181	4.6	13.1	
Mg	[mg/kg]	4	177	22	298	363	
Ba	[mg/kg]	3.68	< 1	18	6.4	8.3	
Ca	[mg/kg]	1294	3523	5225	2600	3180	
Hg	[mg/kg]	< 3	< 3	< 3	< 3	< 3	

The thermal treatment did not affect significantly leaching of the elements from the drilling waste. However, the organic part of drilling waste vaporized completely at 800 °C. The experiments were conducted in air atmosphere, in a lab furnace, therefore part of the organics was burn down during the process. It is worth to mention that total organic carbon concentration is not a good parameter for assessment of the process effectiveness. The formation of soot may affect the measurements. The soot, contrary to carbonate, cannot be remove from the sample with hydrochloric acids prior to analysis of TOC. Therefore, further studies will be continued in specially design reactor with hot air flow or microwave

heating. This allows to design a reactor, in which the drilling waste can be burnt down completely without soot formation and emission of toxic substances, for example, polycyclic aromatic hydrocarbon or dioxin.

The XRD analysis of samples heated above 500 °C has shown formation of barium sulfides, and various barium minerals (barium aluminosilicate-cymrite) as well product of thermal transformation of clay minerals - Fe, Ti oxides and quartz, hydroxyapophyllite, sanidine. It is likely that the most toxic elements such barium and strontium as well as other elements were incorporated in the structure of formed minerals; thus leaching of such element was restrained. However, those elements may be released during weathering of the treated waste in the landfill.

Toxicity analysis

The samples of drilling waste, untreated and treated at 250 and 500 °C, were subjected to various toxicity assays. The untreated and treated samples were not toxic to Spirotox test assay. In Microtox test, the dilution of the samples that caused 20 % inhibition of the light output of the luminescence bacteria, *Vibrio fischeri*, was calculated (EC_{20}). The most toxic was untreated drilling waste whereas treated one at 250 and 500 °C was 2 and 4-fold less toxic, respectively (Table 4).

Table 4
Toxicity of the samples in the Microtox assay

Sample	Tests with extracts		Solid phase test (SPT)
	EC_{20} [%] ¹ , 15 min exposure	EC_{20} [%] ¹ , 30 min exposure	EC_{20} [mg/dm ³] ² , 30 min exposure
Untreated	22.9 (20.3-25.8)	21.8 (17.9-26.4)	960 (701-1313)
250 °C	48.0 (45.0-50.3)	39.7 (29.6-44.4)	441 (172-1130)
500 °C	89.3 (79.8-99.1)	85.5 (72.6-99.3)	1425 (1132-1794)

¹ EC_{20} (95% confidence limit) expressed as a percent of undiluted aqueous extract

² EC_{20} (95% confidence limit) expressed as a concentration of a solid sample in water [mg/dm³]

Extending the exposition time from 15 to 30 minutes resulted in slightly increasing toxicity to Microtox test assay. *Vibrio fischeri* is saline bacteria therefore, high salinity of the tested samples did not affect obtained results.

Table 5
Toxicity of the samples in the Ostracodtoxkit F assay

Endpoint	Mortality [%] ¹			Growth inhibition [%] ²		
Sample	undiluted	1:10	1:100	undiluted	1:10	1:100
Untreated	100	100	100	-	-	-
250 °C	100	0	0	-	4	-7 ³
500 °C	100	10	7	-	21 ³	-2

¹ percent of the dead ostracods in the 6 d assay

² inhibition of the growth of the ostracods after 6 d in comparison to the control (sand)

³ significantly different from the control, $p < 0.05$ (Student t -test)

Another test used for toxicity assessment was Ostracodtoxkit F. The benthic crustaceans in test assay fed on algae and detritus. (Table 5). The organism is sensitive to soluble and insoluble constituents of the investigated samples. The mortality of the organism was 100 % for all undiluted samples. Drilling waste diluted with sand in ratio

1:10 was non-toxic and further dilution to 1:100 caused even 7 % increasing of crustacean growth.

High salinity of undiluted samples was probably responsible for their toxicity to the test organisms because they live in fresh water sediments and they are not immune to such harsh conditions. Additionally, pyrolytic/combustion by-products formed during thermal the treatment may be also responsible for toxicity. This should be taken into account in further development of the thermal process.

Additionally, phytotoxicity test were performed using Phytotoxkit assay. Five higher plants were seeded in the samples diluted with the non-toxic sand (1:10). Although the investigated sample did not affect germination of the plant, early root growth of the plants was inhibited in case of three species (Table 6).

Table 6

Toxicity of the samples in the Phytotoxkit

Sample	<i>Sorgum saccharatum</i>	<i>Lepidium sativum</i>	<i>Sinapis alba</i>	<i>Beta vulgaris</i>	<i>Medicago sativa</i>
Untreated	10 ¹	8	46 ²	24	3
250 °C	-2	-25	4	7	-13
500 °C	-4	-11	18	33 ²	25 ²

¹ inhibition of the root growth in comparison to the control expressed as percent

² significantly different from the control, $p < 0.05$ (Student *t*-test)

S. alba was affected by untreated waste, whereas *B. vulgaris* and *M. sativa* by the sample treated at 500 °C. The high salinity of sample did not affect germination and root development of the plants. It is likely that organic part of the sample that changing during thermal treatment may affect selectively development of certain plants.

Table 7

Bacterial growth in the umu-test

Sample	-S9 ¹			
	Sample concentration			
	67 %	34 %	17 %	8 %
Control	0.95 ±0.19 ²	0.87 ±0.10	1.24 ±0.18	1.24 ±0.17
Untreated	0.64 ±0.18	0.71 ±0.12	0.96 ±0.09	1.06 ±0.05
250 °C	0.54 ±0.12	0.66 ±0.10	0.94 ±0.23	1.10 ±0.03
500 °C	0.50 ±0.27	0.52 ±0.07	0.76 ±0.04	0.94 ±0.18
	+S9 ¹			
	67 %	34 %	17 %	8 %
Control	1.23 ±0.20	1.03 ±0.11	1.11 ±0.12	1.26 ±0.18
Untreated	1.13 ±0.09	1.05 ±0.05	1.03 ±0.05	1.27 ±0.15
250 °C	1.16 ±0.05	1.08 ±0.10	1.08 ±0.03	1.13 ±0.09
500 °C	0.85 ±0.08	1.20 ±0.29	0.99 ±0.06	1.23 ±0.04

¹ +S9 / -S9 - with / without metabolic activation

² growth factor, *G*. Average ± standard deviation from 3 replicates

Genotoxicity of untreated and treated drilling waste was also evaluated using *S. typhimurium* bacteria. The test measured bacterial growth inhibition expressed as the growth factor and detection of induction of the umuC-gene in the *S. typhimurium* strain in response to genotoxic lesions in the DNA. According to the ISO 13829 [13] standard

method, if growth inhibition is higher than 50 % the induction ratio cannot be calculated. This was observed in the highest concentration of the sample treated at 500 °C. The aqueous extracts of the samples were tested. The growth inhibition of the bacteria decreases with increasing of dilution of the extract (Table 7).

Metabolic activation caused that growth inhibition of the bacteria was independent from concentration of the samples. It has been shown that the samples were not toxic in umu-test (Table 8).

Table 8

Induction ratio *IR* in the umu-test

	-S9 ¹			
	Sample concentration			
Sample	67 %	34 %	17 %	8 %
Control	0.74 ±0.17 ²	0.99 ±0.06	0.97 ±0.25	0.97 ±0.14
Untreated	0.66 ±0.11	0.97 ±0.22	0.95 ±0.18	1.02 ±0.03
250 °C	1.18 ±0.09	0.90 ±0.17	0.95 ±0.23	0.97 ±0.16
500 °C	- ³	0.95 ±0.17	0.83 ±0.15	0.81 ±0.27
	+S9 ¹			
Sample	67 %	34 %	17 %	8 %
Control	1.17 ±0.04	1.16 ±0.10	1.00 ±0.03	1.03 ±0.11
Untreated	1.02 ±0.07	0.94 ±0.03	0.87 ±0.14	0.91 ±0.01
250 °C	0.92 ±0.04	0.89 ±0.07	0.89 ±0.11	1.02 ±0.21
500 °C	0.95 ±0.07	0.86 ±0.06	0.88 ±0.06	0.95 ±0.03

¹ +S9 / -S9 - with / without metabolic activation

² induction factor *IR*. Average ± standard deviation from 3 replicates

³ toxic sample

All the samples were not genotoxic to the bacteria, as the *IR* was lower than 1.5. Moreover, no promutagens occurred in the tested samples. During the umu-test with metabolic activation (+s9), these compounds might be metabolized to mutagens by enzymes present in s9 fraction.

Conclusions

Thermal process conducted at low temperature may be a viable option for treatment of oil containing drilling waste. The oil can be vaporized at relatively low temperature between 250 to 500 °C and may be recovered for drilling or burn down in order to use as a fuel for the treatment process. However, the main problem is inorganic product of the thermal process. High concentration of chloride, sulfate, calcium and magnesium in water leachate strongly limits further application of the waste in, for example, road construction. Mixing with fly-ash, gypsum may restrain the leaching of those elements [1, 25]. Earlier studies have shown that drilling waste do not pose any risk related to radioactivity [26-28]. Due to high content of barium sulfate, the waste may be used for preparation cement with high chemical and heat resistance and opaque to X-ray radiation. Barium and strontium aluminosilicate is common constituent of such cement [29]. Formation of soot, fly ash and emission of toxic compounds during incomplete combustion of the waste is the main problem to overcome in further development of thermal treatment processes. The design of industrial installation and optimization of process parameters will be subject of further works.

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