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## Spent drilling muds management and natural environment protection

### Introduction

Drilling mud is a multi-component, dispersion-colloidal system of specific physical and chemical properties. It fulfills several important tasks in borehole drilling. The diversity of these tasks depends, among other things, on the kind of drilled rock, the formation thickness, the existence of formation water and its salinity, the existence of producing formations, the formation pressure, and the temperature depending on borehole depth. Good borehole penetration rates depend to a great extent on the drilling mud quality circulating in the well, and on the proper control of its properties (Uliasz et al. 2006).

At the time of borehole drilling, depending on the borehole's depth and the formations drilled, generally two or three kinds of water-based drilling muds are used – bentonite drilling mud, polymer drilling mud without clays that diminish shale formation hydration, and a drill-in fluid that prevents permeability damage as well as possesses inhibitory properties. The main ingredient of bentonite drilling mud is the bentonite, which acts as a structural building component (Lewicka et al. 2008). However, in clay-free mud the structure and viscosity is built by biopolymer-XCD, high viscosity, plant-derived organic polymers or their mixtures (Steliga and Uliasz 2012). Attaining adequate drilling fluid properties and controlling them during vertical or horizontal drilling demands the use of chemicals and drilling materials (organic natural polymers chemically modified, organic synthetic polymers, chemical compounds derived from plants, minerals, or synthetic materials such as

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lignosulphonates, phosphates, surfactants, defoamers, lubricants, inorganic chemicals such as salts, bases, biocides, corrosion inhibitors, weighting materials), which are also a main source of pollution due to different biodegradability and toxicity issues (Steliga et al. 2012).

After the completion of a drilling borehole section, spent drilling mud as a used up fluid together with drilled cuttings becomes a drilling waste that is highly detrimental to the environment. The amount of drilling waste produced by a given drilling process varies because it depends on the well depth, the kind of drilled formation, and on the mud and water management regime. Field data show that drilling a length of 1 meter of borehole produces 0.6 cubic meters of waste, and 60–80% of this waste constitutes spent drilling muds. The rest is a solid waste such as cuttings spoiled by mud and hydrated mud cakes removed from borehole walls during pipe trips (Raczkowski and Steczko 1997, 2001).

Drilling waste testing has shown that spent drilling mud has elevated values of pH, solid materials, dissolved solids (TDS), surfactants, chloride ions, sulphate ions, dissolved organic carbon (DOC), oil hydrocarbons, heavy metals such as arsenic, barium, cadmium, chromium, copper, mercury, nickel, lead, antimony, selenium, zinc, tin, and cobalt, and some radioactive materials from drilled shale formations. However, cuttings produced by drilling bits used on drilled formations such as clays, sands, sandstones, shales, limestones, marls, siltstones, claystones, dolomites and so on are contaminated by drilling mud, dissolved salts, and heavy metals and trace amounts of radioactive elements, such as uranium and thorium as well as their decay products such as radium and radon (Steliga et al. 2012; Uliasz and Kremieniewski 2012).

In order to diminish spent drilling muds harmful effects, the toxicity of additives used to mix drilling mud is verified. This enables the limitation of toxic additives and replaces them with lower toxicity or biodegradable materials. Selected low toxicity additives will be used to mix drilling fluids for both vertical and horizontal drilling.

## 1. Spent drilling muds management

Globally, environmental management policy shows a decided preference for recycling as the method of drilling waste treatment, resulting in these wastes undergoing complex management processes or reuse. The general scope of this study is to develop an efficient method of waste utilization, demonstrating balanced progress and pursuant to obligatory environmental standards (Fijał et al. 2004, 2005; Gonet et al. 2005; Nieć et al. 2008).

In light of existing laws and regulations, the priorities of drilling waste management are to minimize their amount, reduce their degree of toxicity during the drilling process by effective cleaning of the drilling mud, sparingly manage the drilling mud and water used, and also to segregate the dumping of wastes having different toxicity (Raczkowski and Steczko 2001; Steliga et al. 2012).

Drilling fluid cleaning via high efficiency shale shakers, desanders, desilters, centrifuges, degasers, hydrocyclones, and flocculation stations, permits reuse of the fluid both for drilling

the next well and as a base for the preparation of a new drilling mud. Such actions, most common with bentonite drilling muds, promote the sparing use of drilling mud and drilling fluid materials.

Management of spent drilling muds in a way that is safe for the environment requires the performance of a physico-chemical analysis. Such a requirement stems from the Waste Material Act (Act of December 14, 2012, Journal of Laws item 21 as amended) regarding a liquid waste storing ban including wastes containing over 95% g/g water. This is in addition to the ordinance of the Minister of Economy and Labour of September 7, 2005, indicating criteria and procedures for the release of waste to landfills depending on the kind of waste dangerous, neutral, or other than dangerous (Journal of Laws No. 186, item 1553).

Dehydration of liquid drilling wastes (spent fluids) is performed in a closed filtration process in mobile chamber presses, enhanced by chemical coagulation. As an optimum coagulant, from the point of view of the coagulation process of spent drilling mud, the most frequently used are aluminum based coagulants such as polyaluminum chloride. In the process of filtration, coagulated waste drilling mud is pumped into a space between press plates. Solid phase settles on a filtrating cloth. This phase contains 40 to 60% dry mass and may be used for terrain reclaiming, because the concentration of contaminants is below the value described in the Annex to the ordinance (Journal of Laws No. 165, item 1359) (Fig. 1).



Fig. 1. Photo of used drilling mud, filtration press, and filtration cake destined for ground reclamation

Rys. 1. Fotografia skoagulowanej zużytej płuczki wiertniczej, prasy filtracyjnej oraz osadu pofiltracyjnego przeznaczonego do rekultywacji wyrobisk

The filtrate containing high concentrations of chlorides and organic substances is liquidated by sending it to a local waste cleaning facility or to companies having permission to utilize this kind of waste (Macnar 2005, 2008; Steliga and Kluk 2010; Jamrozik et al. 2011; Steliga and Uliasz 2012).

Drilling muds, their filtrates, and cakes as well as water from coagulation and filtration possess a high content of contaminants. Because of this, trials were undertaken to examine the settling (binding) of drilling muds as a whole, which contained in their liquid phase dispersed polymers and mud materials used for drilling fluid mixing and for physical

parameters control during drilling, in addition to dispersed solids from clays contained in drilled formations. Based on several laboratory tests using different spent drilling muds with differing compositions, rheology, and density, and varying chemical contaminations, it has been shown that using a proper mixture of binding materials (sodium silicate + + hydraulic-pozzolan cement – Silment CQ 25) it is possible to bind a colloidal suspension of such fluids into a solid state with a limited possibility of contaminant leaching, eliminating in this way the contaminated filtrate production stage (Fig. 2) (Al-Ansary and Al-Tabbaa 2007; Steliga and Kluk 2010; Leonard and Stegemann 2010; Uliasz et al. 2010; Yilmaz et al. 2011; Uliasz and Steliga 2013; Uliasz et al. 2013).

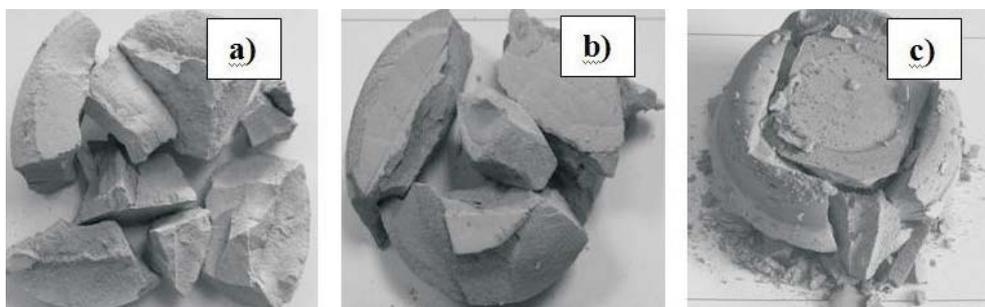


Fig. 2. Photo of solidified spent drilling mud sample using 4% sodium silicate and 25% Silment CQ 25  
a) bentonite drilling mud, b) potassium-polymer drilling mud, c) glycol-potassium-polymer drilling mud

Rys. 2. Fotografia zestawionej próbki zużytej płuczki wiertniczej  
a) bentonitowej, b) potasowo-polimerowej,

c) glikolowo-potasowej za pomocą 4% szkła wodnego sodowego i 25% Silmentu CQ 25

The byproduct obtained may be directed to such destinations as ground reclamation and the filling of underground excavations.

The purpose of the study presented in this article was to estimate the impact on the environment of different methods of spent drilling mud management, and the replacement of detrimental chemicals by less toxic chemicals with a greater degree of biodegradability in the natural environment.

## 2. Materials used and testing method

As tested materials, the following spent drilling muds were used: bentonite drilling mud (taken from a borehole after drilling down to 700 m), potassium-polymer drilling mud (1200 m), potassium drilling mud (2500 m), and glycol-potassium drilling muds (4600 m). These muds were taken from wells drilled between 2010 and 2011. Mud samples were taken after finishing drilling operations in a given section of a well.

In order to establish how harmful dehydrated or solidified drilling muds are, chemical analysis of the effluent was performed. The effluent was obtained by washing 1 kg of dry

mass of solidified fluid with 10 dm<sup>3</sup> H<sub>2</sub>O. The tests were performed classifying residues as dangerous, neutral, or other than dangerous, according to the Minister of Economy and Labour ordinance of August 7, 2005, regarding criteria and procedures of waste material storage allowance according to its type ([Journal of Laws No. 186 item 1553](#)). The tested material was subjected to chemical analysis in order to determine pH, dissolved organic carbon (DOC), total dissolved solids (TDS), chloride ions, sulphate ions, fluoride ions, dissolved total carbon, and content of heavy metals such as arsenic, barium, cadmium, chromium, copper, mercury, nickel, lead, antimony, selenium, zinc, tin, and cobalt.

Moreover, filtration cake of coagulated, spent drilling muds was analyzed to determine whether it can be used to reclaim landfills and excavations, taking into account permissible concentration values specified in the Minister of Environment ordinance of September 9, 2002 concerning soil and land quality standards ([Journal of Laws No. 165 item 1359](#)). The analysis was comprised of evaluation of hydrocarbon pollutants in the form of benzene (ΣC<sub>6</sub> – C<sub>12</sub> hydrocarbons), oils (ΣC<sub>12</sub> – C<sub>35</sub> hydrocarbons), BTEX, ΣWWA, free and complex cyanides, and heavy metals (As, Ba, Cr, Zn, Cd, Co, Cu, Mo, Ni, Pb, Hg), which can influence the toxic properties of the tested waste ([Bielowicz 2013](#)).

The possibility of self-biodegradation of the spent drilling muds and their components was tested using a modern method based on oxygen consumption in a closed measuring system, with simultaneous CO<sub>2</sub> absorption as a metabolite created in a respiration process in a sodium hydroxide solution ([Zurek et al. 2005](#); [Uliasz et al. 2010a](#)). These tests lasted 60 days. OxiTop respirometer systems with measurement heads, absorption vessels, calibrated glass bottles for gas volume, and an OC 110 controller permitted tracking, managing, storing, and displaying measured data. The controller permits the selection of several methods of BOD testing. It also shows the volume of a sample to be tested, depending on its oxygen demand.

Calculations were performed using an ACHAT OC v 2.03. program. The formula is calculated as follows:

$$BA = [M_{R(O_2)}/(RT)] \times [V_{fr}/m_{Bt}] \times [\Delta p] \quad (1)$$

- BA – soil respiration [mgO<sub>2</sub>/kg],
- M<sub>R(O<sub>2</sub>)</sub> – oxygen atomic mass [32000 mg/mol],
- V<sub>fr</sub> – gas volume coefficient [0.78 (200 g), 0.95 (150 g)],
- R – gas constant [83.141 hPa mol<sup>-1</sup>K<sup>-1</sup>],
- T – measurement temperature [293 K],
- m<sub>Bt</sub> – dry soil mass in measuring system [kg],
- Δp – pressure drop in measuring system [hPa].

Two kinds of drilling muds were prepared in a laboratory for long term tests – potassium-polymer and glycol-polymer. These tests were performed in order to explain the KCl and HCOOK impact on the biodegradation process. The tested muds was composed

using clean ingredients with low microbiological pollution; however, the addition of drilling cuttings was linked with the introduction of microorganisms which could find friendly conditions for their growth there. Additionally, a lengthy test period (60 days) permits the development of biocenosis and increased biological activity. Because of this, expecting greater oxygen demand than in previous tests, a higher measurement range was chosen (up to 400 mg O<sub>2</sub>/dm<sup>3</sup>). Drilling fluid samples had volumes of 164 ml.

Drilling muds, being a complex mixture of different additives with different biologic properties, may cause unfavorable changes in polluted environments. It should be noted that chemical or microbiological reactions may lead to the creation of metabolites with differentiated or unknown biological activity. Bioindication is a method using a live organism as an indicator. Its reaction may be the basis for estimating the biological activity of a tested system. Special attention must be paid to the Microtox<sup>®</sup> test, which was the first bioindication test performed in 1979 in the U.S.A. It connects bioindication with analytic precision. Luminescent bacteria, *Vibrio fischeri* (ISO 113480), were used as bioindicators. They use about 10% of metabolism to create light in normal conditions. In the presence of toxic substances, the luminescence drops with growth in sample toxicity. In the electron transport system within these bacteria, luciferase enzyme (alcanne oxigenase) catalyzes the oxidation of reduced substrate (reduced flavin mononucleotide, riboflavin phosphate, or flavin – adenine dinucleotide). During the process light is emitted, and this light may be measured by a photometer. In the reaction, such substrates as oxygen and long chain aldehyde are created. In the presence of substances inhibiting cellular metabolism, bacterial bioluminescence quickly decreases (Harky et al. 2000; Acheson et al. 2004; Araujo et al. 2005; Gandolfi et al. 2010; Steliga 2011; Adams et al. 2011).

The Microtox<sup>®</sup> system was used to measure drilling muds toxicity, which is the acute toxicity system using *Vibrio fischeri* luminescent bacteria. This test is produced by the SDI company (U.S.A.), distributed in Poland by the Tigret company. Lyophilized bacteria may be stored for one year at a temperature of minus 20°C, and may be used any time for testing after suspending in deionized water. Bacteria suspended in a 2% NaCl solution emit constant luminosity light for 1–1.5 hours. A screening test was performed according to standard SDI procedure with the use of a Delta Tox analyzer and lyophilized *Vibrio fischeri* bacteria. The samples were placed in test vessels. Ten-times-diluted NaCl solution was added to the samples in order to equalize the osmotic pressure needed by the bacteria (2% NaCl). The control samples were the solutions recommended by the test producer. Afterwards, the bioindicators were added, and testing was performed according to the standard SDI procedure. Each sample was tested 3 times. After a 10 minute incubation period, the test reaction PE was recorded for each sample. The results were divided into three categories:

- ◆ non toxic samples PE < 20%,
- ◆ low toxicity samples 20% ≤ PE < 50%,
- ◆ toxic samples PE ≤ 50%.

The main test was performed for samples that were toxic in the screening test. Several dilutions of the tested material were placed in test vessels. The producer recommended non

toxic fluids be used for dilution. Bioindicators were then injected and, after the incubation time, the test reaction was read for each dilution using the SDI program. Toxicity results were calculated as half maximal effective concentration  $EC_{50}$ , meaning such a concentration of tested sample (toxicant) that gives 50% of survival (PE).

For clarity,  $EC_{50}$  values were converted into toxicity units:

$$TU = \frac{100}{EC_{50}} \quad (2)$$

The toxicity scale of waste drilling fluid in the Microtox<sup>®</sup> test is as follows:

- ◆  $TU < 10$  lack of relevant toxic effect – non toxic sample,
- ◆  $10 \leq TU < 25$  relevant toxic effect – low toxicity sample,
- ◆  $25 \leq TU < 100$  relevant toxic effect – toxic sample,
- ◆  $100 \leq TU$  relevant toxic effect – high toxicity sample.

### 3. Test results

#### 3.1. Assessment of detrimental substances leaching from spent drilling muds after their coagulation and solidification

Physico-chemical evaluation of selected spent drilling muds, after their dehydration, was performed in the first step. In order to enhance the fluids' dehydration, they were coagulated using polyaluminum chloride. The test results from several filtration cakes are shown in Table 1.

Criteria outlining permission for dumping at dangerous waste storage sites were used as allowable values. The performed analysis indicates the pH value of water effluents (10:1) from the filtration cakes was 7.7–8.4. The highest value of total dissolved solids, TDS, that doesn't exceed the allowable value was observed in the effluent from the potassium-polymer drilling mud (91 254 mg/kg of dry mass.), and the lowest value was for the bentonite drilling mud (21 842 mg/kg of dry mass). The chloride content in the analyzed effluents was between 5 142 (spent drilling fluid from 700 m depth) to 23 473 mg/kg of dry mass (potassium drilling fluid from 2500 m depth). In each of the analyzed samples, the content of dissolved organic carbon exceeded the allowable value, being between 2 584 mg/kg of dry mass (bentonite drilling mud) and 10 584 mg/kg of dry mass (glycol-potassium drilling mud). In effluents from filtration cakes of coagulated spent drilling muds, heavy metal concentrations were at low levels. The measurements performed showed that the filtration cakes from the spent drilling fluids resulting from the process of coagulation and filtration don't fulfill the criteria and procedures allowing for dumping at storage sites, as they exceed the allowable values of dissolved organic carbon (DOC). The neutralization process of the tested, spent drilling muds by dehydration and coagulation via polyaluminum chloride and filtration permits the

Table 1. Results of analysis of water effluent (10:1) from filtration cake of coagulated (using aluminum chloride), spent drilling muds (dangerous waste material storage site)

Tabela 1. Zestawienie wyników badań odcieków wodnych (10:1) osadu pofiltracyjnego zużytych płuczek skoagulowanych chlorkiem poliglinu przy składowaniu na składowisku odpadów niebezpiecznych

Denotations	Units	The type of coagulated drilling mud				Allowable leaching value	
		bentonite (700 m)	potassium-polymer (1200 m)	clay free potassium drilling mud (2500 m)	glycolpotassium (4640 m)		
pH	–	7.7	8.2	7.6	8.4		
Total dissolved solids (TDS)	mg/dm <sup>3</sup>	21 842	91 254	72 900	49 570	100 000	
Chlorides	mg/dm <sup>3</sup>	5 142	19 587	23 478	10 200	25 000	
Sulphates	mg/dm <sup>3</sup>	350	2 681	874	1 266	50 000	
Fluorides	mg/dm <sup>3</sup>	9.1	11.2	8.5	10.5	500	
Dissolved organic carbon (DOC)	mg/dm <sup>3</sup>	2 584	5 589	6 850	10 584	1 000	
Heavy metals	Arsenic	<0.001	0.097	<0.001	<0.001	25	25
	Barium	2.62	33.2	5.47	4.03	300	300
	Cadmium	<0.003	<0.003	<0.002	1.5	5	5
	Chromium	<0.005	0.45	0.58	0.89	70	70
	Copper	0.16	1.73	2.51	2.16	100	100
	Mercury	0.5	0.034	<0.005	0.012	2	2
	Nickel	1.15	2.63	0.96	0.68	40	40
	Lead	<0.010	<0.010	<0.010	0.010	50	50
	Antimony	<0.050	<0.050	<0.050	<0.050	5	5
	Selenium	<0.001	0.175	<0.050	<0.050	7	7
	Zinc	0.70	5.21	6.47	14.25	200	200
Molybdenum	0.18	1.89	0.124	2.29	30	30	

fluids' transformation into solid material similar to ground, with dry mass content in the range of 40–60%.

Comparing the results from Table 2, it can be stated that in the case of filtration cake from spent glycol-potassium drilling fluid from a depth of 4640 m, allowable barium concentrations were exceeded. These values were specified in the Environment Minister's ordinance of September 9, 2002 regarding soil and ground quality standards ([Journal of Laws No. 165 item 1359](#)), for C industrial areas. Taking into account the drilling fluids' content, and especially their physical properties, the measured barium levels may originate from barium sulphate (barite), which is not considered to be dangerous according to the law related

Table 2. Results of analysis of filtration cake from coagulated drilling muds using polyaluminum chloride, which is destined for excavation reclaiming

Tabela 2. Wyniki badań osadu pofiltracyjnego zużytych płuczek skoagulowanych chlorkiem poliglinu, przeznaczonego do rekultywacji terenu wyrobiska

Parameter	The type of coagulated borehole drilling mud				C Group			
	bentonite (700 m)	potassium – polymer (1200 m)	clay – free potassium drilling fluid (2500 m)	glycol – potassium (4640 m)	Depth [m ppt]			
					0–2	2 –15		
					Soil permeability for water [m/s]			
						to	below	
Concentration [mg/kg dry mass]				Allowable concentration [mg/kg dry mass]				
Benzine ( $\Sigma C_6-C_{12}$ )	17.3	42.4	22.07	55.3	500	50	750	
Oils minerals ( $\Sigma C_{12}-C_{35}$ )	159.6	292.1	1197.4	328.9	3 000	1 000	3 000	
BTEX	1.26	3.72	2.1	4.56	200	10	250	
$\Sigma WWA$	0.25	0.61	0.36	0.87	250	20	200	
Free cyanides	<0.125	<0.125	<0.125	<0.125	40	5	100	
Complex cyanides	<0.125	<0.125	<0.125	<0.125	40	5	500	
$\Sigma$ Aliphatic chlorinated hydrocarbon	<0.05	<0.26	<0.39	<0.45	60	2	40	
$\Sigma PCB$	<0.15	<0.21	<0.32	<0.36	2	0.5	5	
Phenol	0.07	0.18	0.27	0.35	50	3	100	
Heavy metals	Arsenic (As)	30.4	0.247	0.478	5.84	60	25	100
	Bar (Ba)	985	287.4	501.7	2 894	1 000	300	3 000
	Cadmium (Cd)	4.27	<0.0005	0.85	0.74	15	6	20
	Chromium (Cr)	25.3	59.1	42.8	43.1	500	150	800
	Copper (Cu)	86.6	48.2	31.1	49.2	600	200	1 000
	Mercury(Hg)	1.89	0.76	<0.050	2.45	30	4	50
	Nickel (Ni)	20.1	35.2	22.8	16.4	300	70	500
	Lead (Pb)	201.9	40.5	54.9	<5.0	600	200	1 000
	Zinc (Zn)	253.1	183.2	589.3	310.7	1 000	300	3 000
	Tin (Sn)	<5.0	<5.0	6.78	<5.0	350	40	300
	Molybdenum (Mo)	20.6	3.58	4.51	10.3	250	30	200
Cobalt (Co)	0.20	7.56	6.32	<0.20	200	50	300	

to wastes of April 27, 2001 ([Journal of Laws 82 item 628 as amended](#)), Annex No. 3. The remaining heavy metal content in the coagulated filtration cakes from spent drilling muds didn't exceed allowable values with the exception of zinc in the cake from spent, clay-free drilling fluid from 2500 m depth. Moreover, in this cake, increased mineral oils ( $\Sigma C_{12}-C_{35}$ ) content of 1197 mg/kg of dry mass was found. These oils may have originated from lubricants added to the drilling mud.

Analyzing the above results, it can be concluded that spent drilling muds filtration cakes may be used as a waste material for excavation reclaiming for example at the excavation in Tarnogrod created during the production of ceramic clay in the 1960s ([Macnar 2005](#)).

In the case of the storage of filtration cakes, various spent drilling fluids in the cakes will be mixed together, and the resulting barium, zinc, and hydrocarbon concentrations will not surpass allowable standards for soil and ground quality.

The solidification process of spent drilling muds may constitute one of the ways of managing liquid wastes obtained in substantial quantities during the drilling operations. The composition of the solidification agent for spent drilling muds ought to be acknowledged as an efficient binder for solidifying different spent drilling muds as a whole, containing both solid and liquid phase ([Uliasz and Steliga 2013](#)). The proper choice of relevant binding materials in a composition with sodium silicate, and the method of their feeding based on the developed technology, results in obtaining a byproduct that is characterized by low toxicity to the environment, as documented by the results of measurement of dangerous substance leachability (Table 3).

Spent drilling muds solidification, as a physico-chemical process converting the wastes, showed reduced leaching of heavy metals from the end product because their content in water effluents is low. Water effluents are characterized by high pH values in the range of 10.2 to 11.9. Elevated dissolved organic carbon values were also recorded. These values exceeded allowable levels. While using a composition of binding materials (4% sodium silicate solution and 25% Silment CQ 25), water effluent from solidified bentonite drilling mud was characterized by the following leaching values: TDS at 20 874 mg/kg of dry mass, dissolved organic carbon (DOC) at 845 mg/kg of dry mass, chlorides at 2365 mg/kg of dry mass, and sulphates at 3041 mg/kg of dry mass. In the case of solidified glycol-potassium drilling mud with the use of a binding composition of 4% sodium silicate solution and 25% Silment CQ 25, the leaching values are as follows: TDS at 57 142 mg/kg of dry mass, dissolved organic carbon (DOC) at 6 321 mg/kg of dry mass, chlorides at 14 245 mg/kg of dry mass, and sulphates at 6 741 mg/kg of dry mass (Table 3).

A comparison of the recuperation and neutralization of used bentonite and glycol-polymer drilling mud revealed that the efficiency of the contaminant binding is highest in bentonite drilling mud. This was shown by TDS and DOC concentrations in effluents from solidified fluids using a binding mixture of 4% sodium silicate solution and 25% Silment CQ 25. In this case, the concentrations don't exceed allowable values set in the admission criteria for dangerous waste storage (Table 2 and 3). Compressive strength measurements showed the solidified bentonite drilling mud samples' compressive strength at 0.75 MPa,

Table 3. Results of analysis of water effluent (10:1) from solidified spent drilling muds

Tabela 3. Zestawienie wyników badań odcieków wodnych (1:10) zestalonych zużytych płuczek

Designations	Units	Solidified drilling mud type				Allowable leaching values	
		bentonite (700 m)		glycol – potassium (4640 m)			
		4% sodium silicate 25% Portland cement.	4% sodium silicate 30% Silment CQ 25	4% sodium silicate 25% Portland cement	4% sodium silicate 25% Silment CQ 25		
pH	–	11.5	10.2	11.9	11.5		
Total dissolved solids (TDS)	mg/dm <sup>3</sup>	28 800	20 874	62 145	57 142	100 000	
Chlorides	mg/dm <sup>3</sup>	2 847	2 365	16 112	14 245	25 000	
Sulphates	mg/dm <sup>3</sup>	6 060	3 041	7 214	6 741	50 000	
Fluorides	mg/dm <sup>3</sup>	1.35	0.44	8.7	8.9	500	
Dissolved organic carbon. (DOC)	mg/dm <sup>3</sup>	1. 430	845	8 475	6 321	1 000	
Heavy metals	Arsenic	0.08	0.07	<0.001	<0.001	25	25
	Barium	0.75	0.69	1.34	1.74	300	300
	Cadmium	<0.0005	<0.0005	<0.0005	<0.0005	5	5
	Chromium	1.02	0.75	0.78	0.32	70	70
	Copper	1.05	0.95	2.71	2.48	100	100
	Mercury	<0.0005	<0.0005	<0.0005	<0.0005	2	2
	Nickel	0.091	0.004	0.92	0.42	40	40
	Lead	<0.010	<0. 010	<0.010	<0.010	50	50
	Antimony	<0.050	<0.050	<0.050	<0.050	5	5
	Selenium	0.048	0.035	<0.001	<0.001	7	7
	Zinc	1.25	0.69	0.45	0.37	200	200
Molybdenum	0.54	0.44	2.84	2.97	30	30	

and that the created byproduct may be proposed as a material for filling local road substructures.

### 3.2. Discussion on drilling muds biodegradation examination

In the case of potassium-polymer drilling mud with the addition of HCOOK, two distinct periods of biodegradation are observed (Fig. 3a). The first one, lasting about 30 days from the beginning of condition stabilization, is characterized by the steep part of the oxygen consumption curve. This is evidence of dynamic development of microorganisms and fast

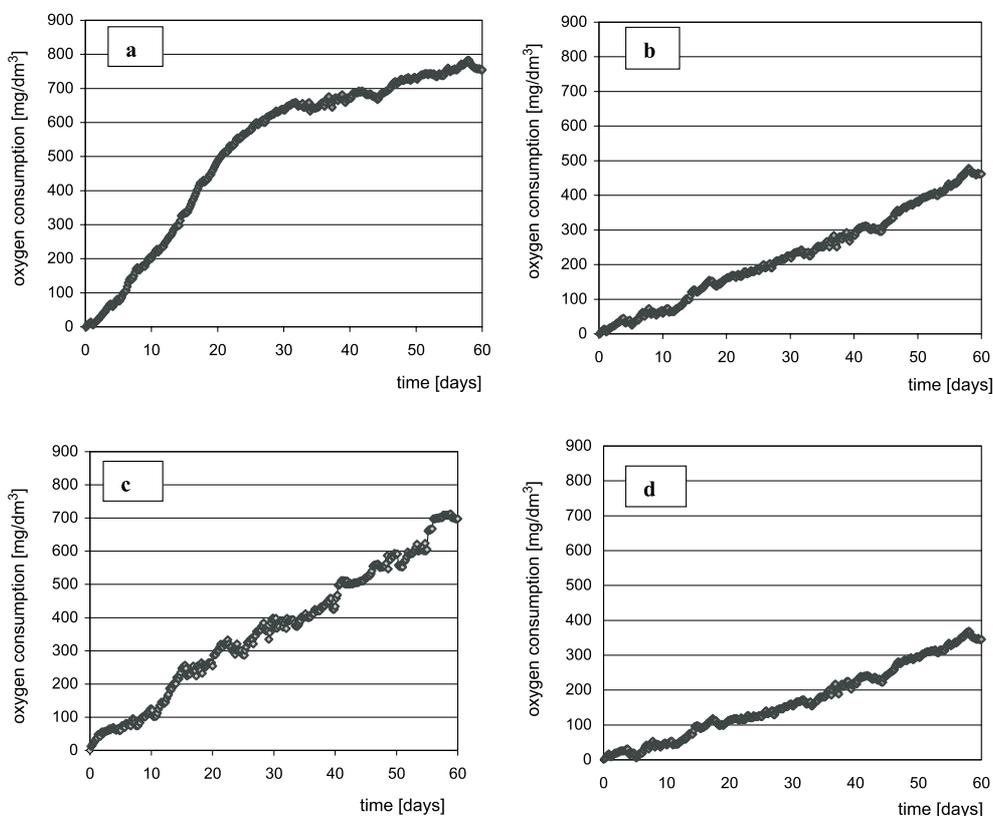


Fig. 3. Biodegradation of laboratory drilling mud prepared in laboratory

- a) potassium-polymer drilling mud with HCOOK addition, b) potassium-polymer drilling mud with KCl addition, c) potassium-glycol drilling mud with HCOOK addition, d) potassium-glycol drilling mud with KCl addition

Rys. 3. Oznaczenie biodegradacji płuczki sporządzonej laboratoryjnie

- a) płuczka potasowo-polimerowa z dodatkiem HCOOK, b) płuczka potasowo-polimerowa z dodatkiem KCl, c) płuczka potasowo-glikolowa z dodatkiem HCOOK, d) płuczka potasowo-glikolowa z dodatkiem KCl

augmentation of their biologic activity. The second period, lasting until the end of the test, has a distinctly lower oxygen consumption curve slope. This is due to some reduction in microorganism development and reduction in microbiological activity, expressed by diminished oxygen demand by living processes. It may also indicate the rise of noxious properties by the creation of transitional metabolites, or depletion of one of the nutrients necessary for the life of microorganisms. However, the potassium-glycol drilling mud biodegradation rate (Fig. 3c) takes place with a gradual increase in oxygen consumption, but about 12.5% lower than in the potassium-polymer drilling fluid with the HCOOK addition.

In the case of potassium-polymer and potassium-glycol drilling mud with the addition of KCl (Fig. 3b and 3d), biologic processes measured by oxygen consumption are at similar rates, much lower than in fluids with the addition of HCOOK (oxygen consumption two

times lower, at a level of 480–390 mg/dm<sup>3</sup>). The slope angles of biodegradation curves are constant during the entire test, which evidences the lack of additional factors inhibiting biodegradation.

Comparing the biodegradation process from the point of view of ionic polymer inhibitors (KCl, HCOOK with Stabpol – PHPA, and glycol) it may be inferred that both potassium-polymer and glycol-potassium drilling mud have higher biological activity with the use of HCOOK than with the use of KCl. Moreover, the drilling muds with potassium formate may be used for drilling vertical wells under the most demanding reservoir conditions. These fluids have stable rheology at high temperatures and in the formation fluid environment. They reduce formation damage and shale hydration, and fulfill environmental protection requirements. These fluids are more effective than water based fluids based on inorganic compounds (Uliasz et al. 2006).

In order to assess the test results obtained for laboratory-made drilling muds, borehole samples of drilling muds were tested (bentonite and glycol-potassium) (Fig. 4a and 4b). A sample of bentonite drilling mud was taken from a 700 m deep well. This fluid degraded at a relatively high rate (Fig. 4a). The fastest growth in CO<sub>2</sub> liberation (the fastest growth in the microorganism count) was observed between day 10 and 15 of the test. After thirty days the slope of carbon dioxide liberation diminished, suggesting slow stabilization, meaning a slowdown in the growth of microorganisms and proliferation. This may serve as evidence either of nutrient depletion or of accumulation of harmful metabolites. The maximum oxygen consumption after 60 days of testing was 1595 mg/dm<sup>3</sup>. This was the highest value obtained in drilling fluid biodegradation testing.

A glycol-polymer drilling mud sample was taken from a 4640 m deep well. In the case of this mud, the biodegradation process was much slower – after 30 days of testing the oxygen

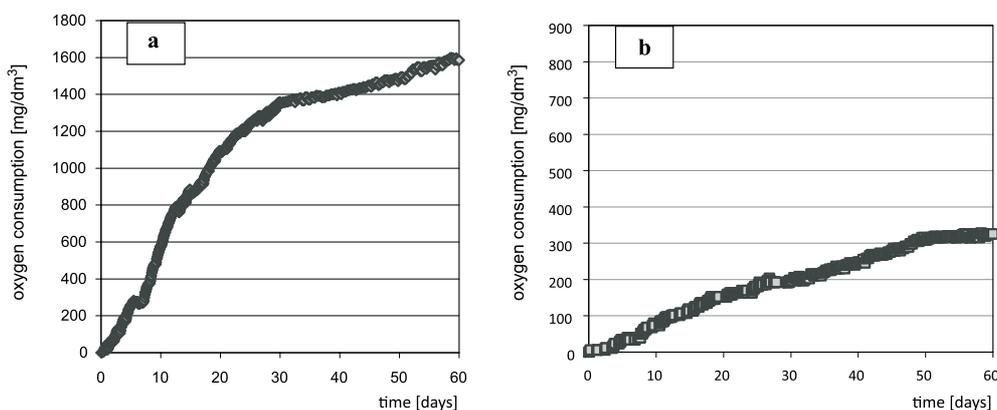


Fig. 4. Borehole drilling mud sample biodegradation  
 a) bentonite drilling mud (700m), b) glycol-polymer drilling mud (4640 m).  
 The sample was taken after drilling was finished

Rys. 4. Oznaczenie biodegradacji próbki płuczki otworowej po wykonaniu wiercenia  
 a) płuczka bentonitowa (700 m), b) płuczka glikolowo-polimerowa (4640 m)

consumption level was  $197 \text{ mg/dm}^3$  (Fig. 4b). This value is close to the values obtained for laboratory-made fluid samples where, after 30 days, oxygen consumption reached  $214 \text{ mg/dm}^3$ . During the following days of testing there was slightly slower  $\text{CO}_2$  liberation, and after 30 days the oxygen consumption reached  $325 \text{ mg/dm}^3$ . In the case of glycol-polymer biodegradation, no clear reduction in microorganism development (oxygen consumption) was observed; only the very end of the curve suggests the beginning of stabilization.

The main factors stimulating microorganism growth, thereby influencing the rate of  $\text{CO}_2$  liberation during the biodegradation test, are the availability of nutrients and the presence of trace micro-elements of toxic substances inhibiting organism growth, proper temperature provision, availability of oxygen, and the level of metabolites created by microorganisms (the higher the level, the slower the microorganism growth rate). Comparing the results of chemical analysis, it should be noted that in the case of bentonite drilling mud, much lower contamination was measured (especially the chlorides at about 5 fold lower, oil derivatives about 2 times lower, and DOC 5 fold lower than in the case of glycol-potassium drilling mud. This may be the cause of substantially faster biodegradation of bentonite drilling mud, because of better conditions for microorganism growth.

### 3.3. Chemical additives and spent drilling mud toxicity assessment

Fig. 5 and 6 show the results of measurements of the toxicity of chemical additives chosen for the preparation of drilling muds. Screening tests of potassium salts and chemicals (protective colloids, polymer hydration inhibitors for clays, viscosity reducing agents) at concentrations similar to those in the tested drilling muds showed that they have different toxicity. Ionic inhibitors ( $\text{KCl}$ ,  $\text{K}_2\text{SO}_4$ ,  $\text{HCOOK}$ ) may be counted among the low toxicity variety ( $20\% \leq \text{PE} < 50\%$ ) (Fig. 5a). Protective colloids (carboxymethylcellulose – KMC,

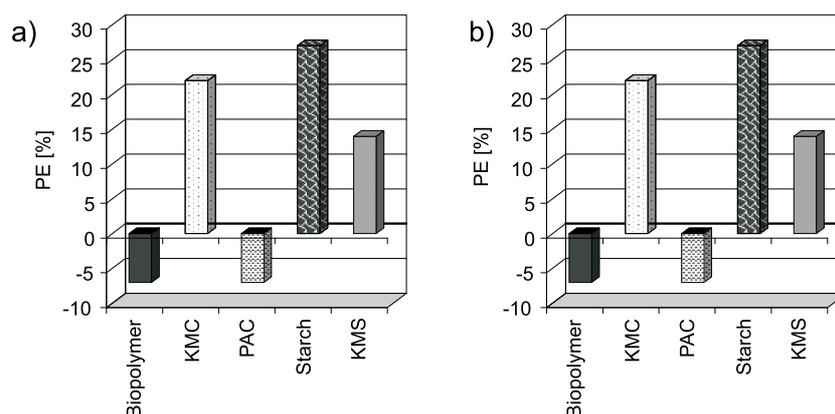


Fig. 5. Toxicity of chemical agents used in drilling mud formulations  
a) potassium salts, b) protective colloids

Rys. 5. Toksyczność środków chemicznych stosowanych do sporządzenia płuczek wiertniczych  
a) soli potasowych, b) koloidów ochronnych

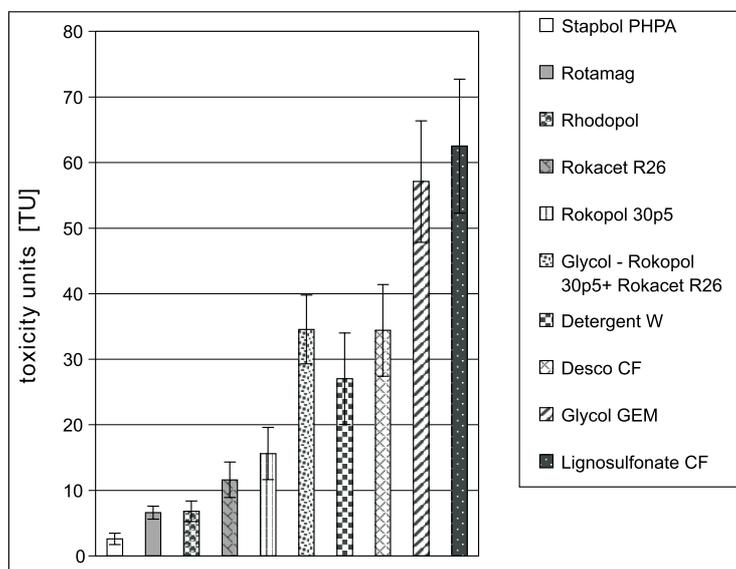


Fig. 6. Toxicity degree comparison of selected chemical agents used in drilling mud formulations

Rys. 6. Porównanie stopnia toksyczności wybranych środków chemicznych stosowanych do sporządzania płuczek wiertniczych

polyanion cellulose – PAC, starch, carboxymethylstarch – KMS, and biopolymers) have slightly lower toxicity (Fig. 5b). In contrast, polymeric inhibitors (PHPA – Stabpol) and glycols (such as Rokopol 30p5 + Rokacet R26 and GEM), as well as the remaining chemical agents (viscosity reducers, lignosulphonates, and detergents), may be treated as toxic agents (PE > 50%). Dilution tests indicate that their degree of toxicity (TU) is variable, ranging from 2.6 to 62.8 (Fig. 6).

Figure 7 compares the toxicity for solutions of KCl and Stabpol used in inhibited drilling muds and their replacements such as potassium sulphates or formates and glycols: Rokopol 30p5 + Rokacet R26 or GEM. Diluted solutions of these substances have been tested for toxicity, and the calculated TU values indicated that potassium salts with Stabpol are non toxic (TU = 2.3–5.0). Solutions of Rokopol 30p5 + Rokacet R26 have substantially higher toxicity (TU = 37.1–58.1). The highest toxicity was observed for potassium salts with GEM in the range of TU = 55.8–66.2 (Fig. 7). Special attention must be paid to organic salts (Uliasz et al. 2006) which don't supply  $\text{Cl}^-$  ions and, as was shown by biologic activity testing, are biodegradable, while TU values of polymer inhibitors with HCOOK were slightly higher in comparison with solutions containing inorganic potassium salts (Fig. 3 and 7).

Each drilling fluid containing drilled solids, after drilling completion, constitutes a drilling waste which is characterized by its potential to do harm to the environment. This depends on the drilling fluid composition and drilled formation type.

In order to estimate toxicity (TU = 100/EC<sub>50</sub>), dilution tests were performed for selected, spent drilling muds (Table 4). These tests indicated that bentonite spent drilling muds may be

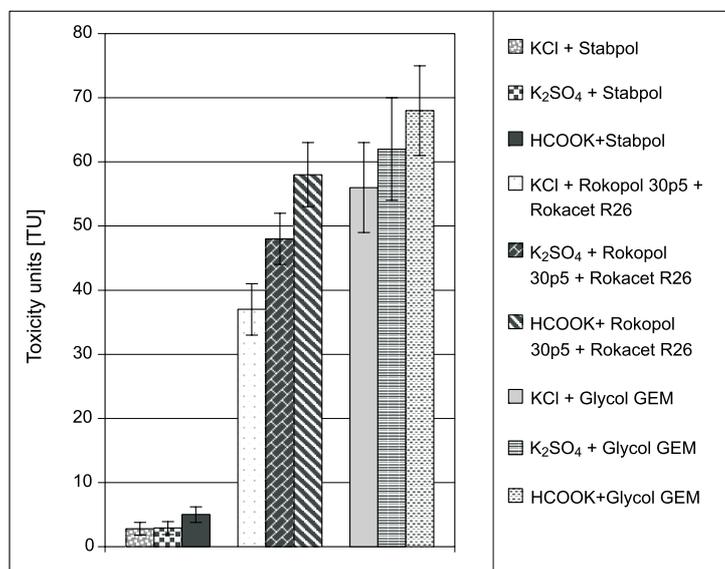


Fig. 7. Toxicity degree comparison for chemical agent solutions used in drilling mud formulations

Rys. 7. Porównanie stopnia toksyczności roztworów środków chemicznych stosowanych do sporządzania płuczek wiertniczych

treated as non toxic and low toxicity fluids. Toxicity values (TU) ranged from 3.6 to 8.6 and were in the range indicating a lack of essential toxic effect ( $TU < 10$ ).

Potassium-polymer spent drilling muds containing a polymer inhibitor of type PHPA have relevant toxic effects ( $10 \leq TU < 25$ ), because TU values are in the range of 11.9–19.6. Glycol-polymer spent drilling muds containing GEM, taken from different depths, were toxic. Their toxic effect was  $25 \leq TU < 100$ , increasing with depth, with a TU value 58.5 and 68.1 (Table 4). It seems the glycol type will decide the glycol-potassium drilling mud toxicity level.

Table 4. Toxicity tests of industrial spent drilling muds

Tabela 4. Badania toksyczności zużytych otworowych płuczek wiertniczych

Spent industrial drilling muds	TU
Bentonite drilling mud from depth of 390 m	$3.6 \pm 0.5$
Bentonite drilling mud from depth of 700 m	$8.6 \pm 1.1$
Potassium-polymer drilling mud from depth of 1000 m	$11.9 \pm 1.8$
Potassium-polymer drilling mud from depth of 2500 m	$19.6 \pm 2.5$
Glycol-potassium drilling mud from depth of 4300 m	$58.8 \pm 4.9$
Glycol-potassium drilling mud from depth of 4600 m	$68.1 \pm 7.6$

## Summary

Drilling operations generate a huge amount of drilling waste – a drilling mud with drilled solids. These wastes are characterized by varying levels of harmfulness depending on the type of drilling mud additive. An analysis of test results and applied waste management technology leads to the following conclusions:

- ◆ The optimum means of managing drilling waste rests in the technology of drilling mud coagulation by aluminum based coagulants such as aluminum polychloride, the dehydration of coagulant, and dehydrated coagulant solidification.
- ◆ Filtration cakes resulting from coagulant filtration are not safe enough to dump them at waste storage sites because they surpass the permissible levels of dissolved organic carbon (DOC) by 6–7 times, and contain relatively high  $\text{Cl}^-$  ion concentrations, mainly in inhibited fluids.
- ◆ Another optimum method of waste management is solid phase immobilization through solidification with the use of binding substances which are designated based on laboratory analysis (sodium silicate + Silment CQ 25). Comparison of spent drilling mud recuperation and neutralization performed for bentonite drilling mud and glycol-polymer drilling mud indicated that contaminant binding is most efficient in bentonite drilling fluid, as is evidenced by the TDS and DOC values obtained from effluents from solidified muds.
- ◆ Long term (60 days) biodegradation testing performed on sets of borehole drilling fluids indicated that they do biodegrade; however, this biodegradation is afflicted by biocide additive, which slows down the living processes of microorganisms. Additionally, the type of potassium salt contained in the drilling mud influences the biodegradation process. Comparing the biodegradation process from the point of view of ion-polymer inhibitor type (KCl and HCOOK, as well as PHPA and glycol), it can be concluded that both in the case of potassium-polymer and glycol-polymer drilling mud, the biodegradation rate in potassium formate is faster than in potassium chloride.
- ◆ Based on this new method, developed for toxicity analysis using *Vibrio fischeri* organisms, the toxicity units (TU) were determined for some of the drilling mud additives and for spent drilling muds from boreholes. Toxicity testing of borehole drilling muds indicated that bentonite and potassium-polymer drilling muds are characterized by low toxicity, while glycol-potassium drilling fluids indicated high toxicity.

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#### ZAGOSPODAROWANIA ZUŻYTYCH PŁUCZEK WIERTNICZYCH W ASPEKTCIE OCHRONY ŚRODOWISKA

#### Słowa kluczowe

zużyte płuczki wiertnicze, zagospodarowanie, wymywalność szkodliwych zanieczyszczeń, biodegradacja, testy toksyczności

#### Streszczenie

Celem pracy jest przedstawienie optymalnych metod zagospodarowania zużytych płuczek wiertniczych zgodnie z podstawami funkcjonowania współczesnej gospodarki odpadami oraz biorąc pod uwagę ich potencjalną szkodliwość dla środowiska. Badania wykonano na przykładzie płuczek: bentonitowej oraz beziłowej (potasowej, potasowo-polimerowej i glikolowo-potasowej) prowadząc proces usuwania fazy płynnej przy wykorzystaniu procesu koagulacji połączonej z filtracją, bądź proponując nową technologię zestalania opracowaną przy użyciu środków wiążących wytypowanych

na podstawie badań laboratoryjnych (szkło sodowe + Silment CQ 25). Przeprowadzone wyniki analiz wymywalności substancji szkodliwych z osadów po koagulacji i filtracji oraz po zestaleniu zużytych płuczek wiertniczych dowodzą, że nie spełniają one kryteriów dopuszczenia odpadów do składowania na składowisku ze względu na przekroczenie dopuszczalnej zawartości rozpuszczonego węgla organicznego (DOC i TDS) z wyjątkiem zestalanej zużytej płuczki bentonitowej.

W pracy przedstawiono badania w zestawie OxiTop pod kątem biodegradacji zużytych płuczek wiertniczych oraz wpływu na jej przebieg, doboru soli potasowych oraz inhibitorów jonowo-polimerowych, na podstawie których można stwierdzić, że przy zastosowaniu mrówczanu potasu występuje szybsze tempo biologicznego rozkładu niż w przypadku chlorku potasu.

Głównym i podstawowym kryterium doboru środków chemicznych przy opracowaniu płuczek wiertniczych jest ich wpływ na parametry technologiczne sporządzanych płuczek i zapewnienie stabilności otworu wiertniczego. Często natomiast pomija się wpływ stosowanych środków chemicznych na środowisko, a powinny one być dostosowane do ogólnych wymogów z zakresu ochrony środowiska, tak aby w jak najmniejszym stopniu stanowiły dla niego zagrożenie. Możliwe jest to na drodze zastąpienia środków toksycznych środkami o zmniejszonej toksyczności, a zarazem zapewniającymi podstawowe parametry sporządzanych płuczek wiertniczych.

Do oceny stopnia toksyczności (TU) zużytych płuczek wiertniczych oraz środków chemicznych wykorzystanych do sporządzania płuczek wiertniczych, zaproponowano nową metodę DeltaTOX z zastosowaniem mikroorganizmów *Vibro fischeri*. Przeprowadzone badania potwierdziły, że spośród stosowanych inhibitorów polimerowych glikol GEM wykazywał wyższą toksyczność niż pozostałe testowane środki spełniające równorzędne funkcje w płuczce wiertniczej (Rokpol 30p5 + Rokacet R26 oraz Stabpol). Testy toksyczności zużytych płuczek otworowych dowiodły, że płuczki bentonitowe i potasowo-polimerowe charakteryzują się niską toksycznością (TU = 3,6–19,6), zaś płuczka glikolowo-potasowa zawierająca glikol GEM cechuje się wysoką toksycznością (TU = 58,8–68,1).

Przedstawiona wielokryterialna ocena szkodliwości zużytych płuczek i czynników mających wpływ na jej obniżenie, powinna się przyczynić z punktu ekologicznego do prawidłowego doboru środków chemicznych stosowanych do sporządzania płuczek wiertniczych oraz bezpiecznych dla środowiska metod zagospodarowania płuczek wiertniczych zużytych.

#### SPENT DRILLING MUDS MANAGEMENT AND NATURAL ENVIRONMENT PROTECTION

##### Key words

spent drilling muds, waste management, detrimental contaminant leaching, biodegradation, toxicity test

##### Abstract

The purpose of this work is to present the optimum method for spent drilling mud management according to waste management principles, taking into account the potential harmful effects of such wastes on the environment. Research was conducted on samples of bentonite drilling mud (potassium), potassium polymer, and glycol-potassium. A coagulation and filtration process was employed to remove the liquid phase. As an alternative method, a new technology of solidification was proposed making use of binding agents, which were chosen based on laboratory tests (sodium silicate + Silmet

CQ 25). Harmful substances leached from coagulation and filtration deposits were analyzed, and the results offer evidence that these deposits don't fulfill the criteria allowing for their dumping at storage sites as they surpass the permissible concentrations of dissolved carbon DOC and TDS, with the exception of spent bentonite drilling mud.

This work presents tests that were performed using OxiTop instrumentation for the biodegradation of spent drilling muds, as well as examination of the influence of potassium salt and polymer-ionic inhibitors on the biodegradation rate. These tests indicated that potassium formate gives a higher biodegradation rate than potassium chloride.

The essential criterion for the selection of chemical agents for a drilling mud formula is their impact on the drilling fluid technical parameters and borehole wall stability. Unfortunately, drilling muds impact on the natural environment is often neglected, though they should be adapted to general environmental requirements in order to minimize any detrimental effects. This can be accomplished by replacing more dangerous drilling mud additives with others possessing lower toxicity while still fulfilling the proper drilling mud parameters.

In order to evaluate the degree of toxicity (TU) of spent drilling muds and drilling mud additives, this study proposes a new DeltaTOX method utilizing *Vibrio fischeri* microorganisms. The tests performed have proven that among the various polymer inhibitors examined, GEM glycol had higher toxicity than the remaining additives performing the same function in the drilling mud (Rokpol 30p5 + Rokacet R26 and Stabpol). The toxicity tests performed on borehole spent drilling muds have proven that bentonite and potassium-polymer drilling muds are characterized by low toxicity (TU = 3.6–19.6), while glycol-polymer drilling mud containing GEM glycol is highly toxic (TU = 58.8–68.1).

A multi-criterion evaluation of the harmfulness of spent drilling muds and evaluation of additives that diminish fluid harmfulness may permit the selection of such additives which, from an ecologic point of view, will serve to create safer drilling muds and insure better spent drilling mud management.

