Characterization of drilling waste from shale gas industry and their use in soil amendment production technology

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Abstract

Drilling operations produce two major wastes which are drilling fluids and drill cuttings. The drilling waste shall be properly managed to ensure no impact on the environment and human health. Use of drilling waste, generated from shale gas industry, for land reclamation has the potential to be a practical and economical means to improve soil fertility and to decrease landfills. The aim of the study was to obtain soil amendment using drilling waste and other waste materials as the main components. According to research, it is possible to obtain soil amendment using waste materials such as drilling fluids, cuttings, sewage sludge, biomass ash and spent hops. We also propose technology production of such soil amendment.

Keywords: drilling fluid, cuttings, sewage sludge, spent hops, biomass ash, soil amendment, recycling.

1. Introduction

Drilling fluid (drilling mud) is one of primary wastes generated from drilling. It is used to lubricate and cool drilling apparatus, transport drill cuttings to the surface and seal porous geologic formation (Yao and Naeth, 2014, Fink, 2011). Drilling fluids are made up of a base fluid (water, diesel or mineral oil, or a synthetic compound), weighting agents (e.g. barium sulphate), bentonite clay, lignosulphonates and lignites, and various additives that serve specific functions. Bentonite clay is used in drilling fluids to remove cuttings from the well and to form a filter cake on the walls of the hole, while lignosulphonates and lignites are used to keep the mud in a fluid state. Drilling fluid can be a potentially, toxic complex chemical mixture and are therefore considered environmentally damaging (Fink, 2011, Drilling Waste Management Information System, 2017). Drill cuttings are produced as the rock is broken by the drill bit advancing through rock or soil. They are made up of ground rock coated with a layer of drilling fluid.

Few studies have addressed the impact of disposal of spent drilling fluids on soil-plant-water systems. Some researchers found that high soluble salts, heavy metals and petroleum residue content of used drilling fluid were detrimental to soil quality and plant growth (McFarland et al. 1994; Wojtanowicz, 2008; Zvomuya et al. 2011). Others found positive or no impacts from drilling fluid applied at low rates in coarse textured soils in arid regions due to pH increase, potential micronutrient addition and improved soil properties (Lesky et al, 1989; Bauder et al. 2005,Yao and Naeth, 2014, 2015). Few studies have focused on the release of toxic elements from oil well drill cuttings and their effect on soil and aquatic ecosystems (Magalhães et al. 2014; Purser and Thomsen, 2012).

The management technologies and practices for drilling waste can be grouped into three major categories: waste minimization, recycle/reuse, and disposal (Drilling Waste Management Information System, 2017).

In Poland, the first borehole, aimed at the exploration of natural gas from shale was drilled in the year 2010. Natural gas from shale accumulations is released through drilling holes reaching depths of several thousand meters. Hydraulic fracturing operations generate a considerable amount of waste (Pyssa, 2016).

The aim of the study was to use drilling waste and other waste materials as components for soil amendment technology production.

2. Material and methods

2.1 Samples

Spent bentonite potassium drilling fluids and cuttings were collected from well sites after drilling in Masovian Voivodeship, Central and Eastern Poland in 2015.

2.2. Samples preparation

A collected sample of drilling fluid was dried at 50°C to obtain a solid; after it was grounded and homogenized. A drill cuttings sample was dried in a laboratory oven at 105°C, in amount of 1.2 kg. The dried sample was preliminary crushed and then grounded using a laboratory ham mill.

For XRD analysis, a collected drilling fluid, in suspension, was dried at 50°C in order to obtain a solid. Cuttings were dried in a laboratory oven at 105°C in order to obtain a solid. Dried samples were crushed in a porcelain mortar and sieved to obtain a homogenous powder with grains under 50 µm.

2.3. Analytical methods

Analytical methods, used for determination of metal contents in drilling fluid and cuttings samples by ICP-OES and mercury content by CV-AAS, are described in previous article (Gluzińska et al., 2017).

2.4. Ion chromatography (IC)

2.4.1. Equipment

Chloride and sulphate analysis in drilling waste water extracts were conducted using an ion chromatograph ICS-3000 (Dionex Company) working in an external water mode. Chromeleon 6.7 Chromatography Management Software (Dionex) was used for system control and data processing.

2.4.2. Reagents and solutions

Multi-Component Anion Mix 4, (F^-, Br^-, Cl^-, PO_4^{3-}, NO^{3-}, SO_4^{2-}, c=100μg/ml) (Acculon) as a reference standard for quantitative determination of studied anions was used. Water, 18.2 MΩ WaterPro PS Labconco, free of particles of diameter >0.2μm was used. As an eluent: 30 mM NaOH (Fluka; sodium hydroxide; puriss. p.a. ACS; ≥ 98.0 %; pellets) was used. Calibration standard solutions for those ions determinations were prepared from the standard solution by dissolution with deionized water. A calibration concentration range for determined ions was 0,1; 0,5; 2,0; 5,0 $mg \cdot dm^{-3}$.

2.4.4. Sample preparation

Samples of water extracts of drilling waste, weighing about 1-2 g, were dissolved in water in a 250 ml volumetric flask and was made up to the mark. An analytical sample was prepared from the solution by dilution with water in a ratio 1:100. Analysis was carried out in three parallel repetitions. The diluted sample was passed through a 0.45 μm membrane filter just before injection to the chromatographic column.

2.4.5. Chromatograph operating conditions

Conditions of carried out chromatographic analysis are presented in Table 1.

Table 1. Chromatographic analysis conditions.

Analytical column + guard column	AS11-HC (4 x 250 mm) + AG11-HC (4 x 50 mm)
Eluent	30 mM NaOH
Eluent flow rate	1.5 ml/min
Pressure in the column	~ 1940 psi
Injection volume	25 μl
Column operating temperature	30° C
Conductometer cell temperature	35° C
Suppression type	ASRS 300 - 4mm
Suppressor current intensity	112 mA

Detection	conductometric
Analysis time	10 min

2.5. Powder X-ray diffraction (XRD)

The XRD measurements of samples were performed on a PANanalytical Empyrean system (Bragg-Brentano geometry) equipped with a PIXcel^{3D} detector using Cu Kα radiation (λ=1.542 Å) and operating at 40 kV and 40 mA. The samples were scanned between $10<2\theta<70°$, with the step size 0.01° 2θ and time/step 30 s. The quantity analysis of crystallographic phases was automatic using Rietveld's method with Brindley corrections for micro-absorption and manual corrections of results for better fitting parameters. The line broadening was determined in the High-Score Plus software. The pseudo-Voigt function for peak size approximations was used.

3. Results and discussion

3.1. Metal contents by ICP-OES and mercury content by CV-AAS

Following the chemical characterization of the drilling fluids and drill cuttings, the main contaminants were found to be barium, nickel, manganese, copper, chromium, lead, arsenic, and mercury. The results are shown in Table 2. According to Polish regulations, the heavy metal levels in studied waste should not exceeded the limits for their contents in soils of IV class. Research conducted by Steliga and Uliasz (2014) showed that bentonite drilling fluid after coagulation contained 985 mg·kg^{-1} of Ba, 201.9 mg·kg^{-1} of Pb, 86.6 mg·kg^{-1} of Cu, 25.3 mg·kg^{-1} of Cr, 20.1 mg·kg^{-1} of Ni, and 1.8 mg·kg^{-1} of Hg.

Drilling waste can be characterized with considerable variations in terms of chemical composition as well as potential harmfulness to the environment. Each drilling fluid has an increased pH value, increased amounts of undissolved and dissolved solid substances, chloride and sulphate ions and dissolved organic carbon. It also includes small amounts of petroleum-derived hydrocarbons, heavy metals and trace amounts of radioactive substances which come from shale formations. The chemical composition of post-operation liquids depends on the composition of the fracturing fluid, and on the rock mass into which it is injected (Pyssa, 2016).

Table 2. Metal contents in drilling fluids and drill cuttings (Central and Eastern Poland, 2015).

Metal contents	Method	Unit	Drilling fluid	Cuttings	Regulation*
Ca	ICP-OES	g·kg^{-1}	107	116	
Ba	XRD		61.1	81.4	1.5
Al	ICP-OES		18.3	30.6	
Fe	ICP-OES		16.1	27.3	
K	ICP-OES		60.4	16	
Mg	ICP-OES		6.25	8.19	
Na	ICP-OES		11.4	3.68	

Mn	ICP-OES	mg·kg^{-1}	460	470	
Cr	ICP-OES		31	140	1000
Cu	ICP-OES		45.8	53	600
Ni	ICP-OES		67.8	70.1	500
Pb	ICP-OES		27.1	28.1	600
Cd	ICP-OES		0.26	0.4	15
As	ICP-OES		8.05	8.1	100
Hg	CV-AAS		8.77	0.774	30
*) limits of heavy metal contents in soils (depth 0-0.25 m below the ground level) for IV class of soil according to Polish legislations					

3.2. Ion chromatography (IC)

Figures 1-2 show chromatograms of water extracts of drilling fluid and cuttings. Among determined ions, only chloride (R_t=2.9±0.1 min) and sulphate (Rt=3.69±0.1 min) were identified. In an anionic chromatogram of water extracts of drilling waste, carbonate peaks were identified (R_t=3.18±0.1 min). In the chromatogram of water extracts of drilling fluid is an unidentified peak with a retention time of 6.6 min. Quantity analysis showed that water extracts of drilling fluid contained 24.4 mg·kg^{-1} of chloride and 0.87 mg·kg^{-1} of sulphate. Water extracts of drill cuttings contained 5.7 mg·kg^{-1} of chloride and 6.37 mg·kg^{-1} of sulphate. F^-, Br^-, PO_4^{3-}, NO^{3-} ions were not identified in studied water extract samples of drilling waste.

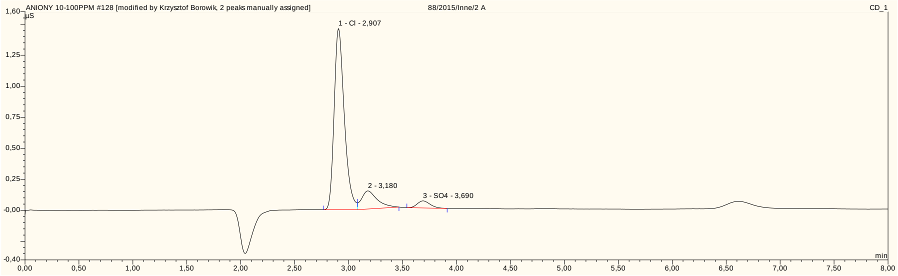

Figure 1. An anionic chromatogram of water extract of drilling fluid.

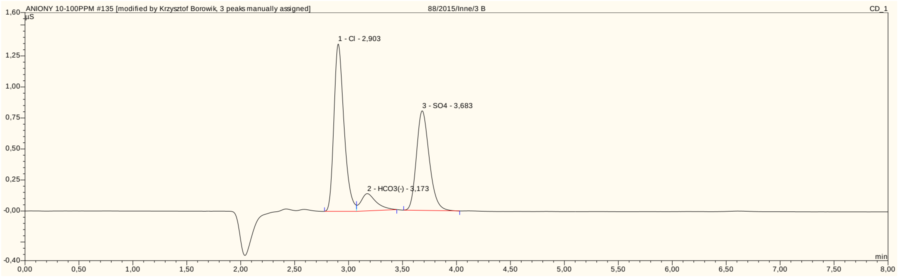

Figure 2. An anionic chromatogram of water extracts of drill cuttings.

3.3. XRD analysis

XRD analysis was used to identify crystalline compounds (mineral) based on their crystal structure. Each compound gives a unique pattern of diffraction peaks. Both dried drilling fluid solid and dried cuttings are characterized by very complex phase compositions. Rietveld's analysis showed a very good fitting of a model and an experimental diffraction pattern. A result of the study is quality and semi-quantity analysis of compounds occurring in a crystalline form which are summed up to 100%. Phases of amorphous, organic and other compounds that are present in trace amounts in the samples are not taken into consideration in the balance, which means that the real element contents in studied samples are slightly lower. X-ray powder diffraction patterns of drilling waste are shown in Figs 3-4.

Analysis of the mineralogical character of a solidified drilling fluid revealed that it contained 35.8% of calcite ($CaCO_3$), 24.6% of quartz (SiO_2), 12.7% of muscovite 2M1 ($KAl_{2.9}Si_{3.1}O_{10}(OH)_2$), 11.0% of sylvite, 10.4% of barite ($BaSO_4$), 2.8% of dolomite ($CaMg(CO_3)_2$) and 2.7 of orthoclase ($KAlSi_3O_8$).

Analysis of the mineralogical character of drill cuttings revealed that they contained 43.5% of calcite ($CaCO_3$), 29.2% of quartz (SiO_2), 10.1% of muscovite 2M1 ($KAl_{2.9}Si_{3.1}O_{10}(OH)_2$), 13.3% of barite ($BaSO_4$), 3.4% of dolomite ($CaMg(CO_3)_2$) and 0.5% of barium chloride ($BaCl_2$).

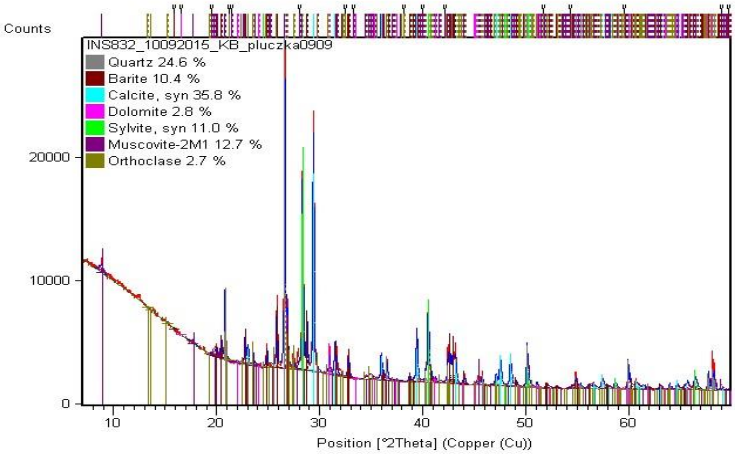

Fig. 3. XRD pattern of drilling fluid dried at 50°C.

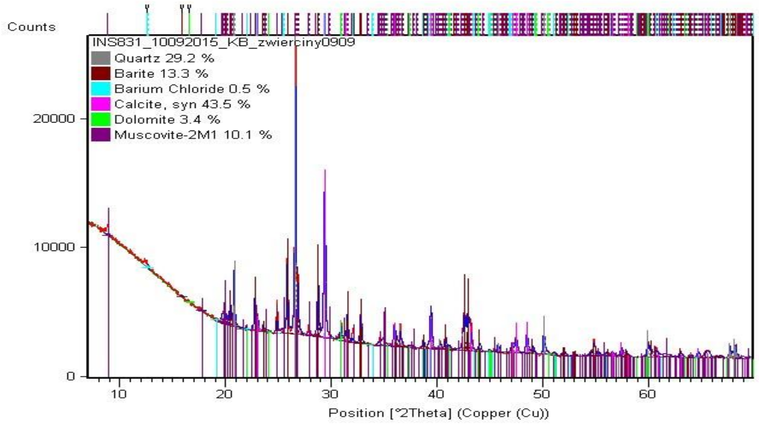

Fig. 4. XRD pattern of cuttings sample dried at 105°C.

3.4. Characterization of other soil amendment components

A characterization of spent hops was showed in previous papers (Gluzińska et al., 2016; 2017) and biomass ash characterization was showed in paper (Gluzińska et.al., 2016). Sewage sludge, used for the study, was from a biological sewage treatment plant of a chemical company located in Eastern Poland. Sewage sludge underwent a physical, chemical and biological properties assessment. It was stabilized and hygenized with quicklime (95% of CaO).

3.5 A description of a technological process of obtaining soil amendment

A technological process for obtaining soil amendment consists of: transportation and storage of raw materials and additives (quicklime, ash, spent hops, filtrates of sewage sludge from biological treatment plant, sulphuric acid, coagulant); pre-treatment of drilling fluid in a mixer for sedimentation of colloidal suspension; drilling fluid de-watering on a filter press; pre-treatment of sewage sludge such as de-watering and hygenization with quicklime; dosing of raw materials to a second mixer in order to obtain a desired product.

Mass balance is shown in Fig. 5. Spent drilling fluid containing 75% of water and pH=8, is transported to a mixer (M-1). Sulphuric acid (98%) in order to decrease pH value to 5, iron sulphate and coagulant (Praestol 2510) are added to a mixer (M-1). During mixing process, colloidal particles in a solution are solidified and could be separated from liquid (filtrate) on filtration press (F-1). After filtration, drilling fluid sludge contains about 30-35% of water. Filtrate is transported to a storage tank and can be used for drilling purposes or is transported to biological treatment plants. De-watered drilling fluid sludge from a filtration press is transported to a main mixer (M-2). Sewage sludge from a biological treatment plant is de-watered and hygenized with quicklime (95% CaO) before adding it to the mixer (M-2). The temperature of sewage sludge after pre-treatment is 90°C. Stabilized and hygenized sewage sludge, drill cuttings, drilling fluid sludge, biomass ash and spent hops are mixed in the mixer (M-2), than granulated and dried in order to obtain soil amendment. All components of soil amendment mixture should be mixed together in recommended ratios (Table 3).

Table 3. A quantity composition of soil amendment mixtures.

No. of trials	Composition, (% w/w)						pH	Loss of drying at 105°C, (%)
	Sewage sludge	CaO	Drill cuttings	Drilling fluid	Spent hops	Ash		
1.	42.5	15	42.5	-	-	-	12.69	27.01
2.	18.8	8	26.6	26.6	20	-	9.04	47.66
3.	70	30	-	-	-	-	12.7	39.86
4.*	24.4	8.2	32.4	5.4	8	21.6	9.0	
A recommended mass ratio of components	Sewage sludge after pre-treatment		Cuttings	Drilling fluid after dewatering to 32%	Spent hop	Ash		
	6		6	1	1.5	4		

*Patent application P 413584

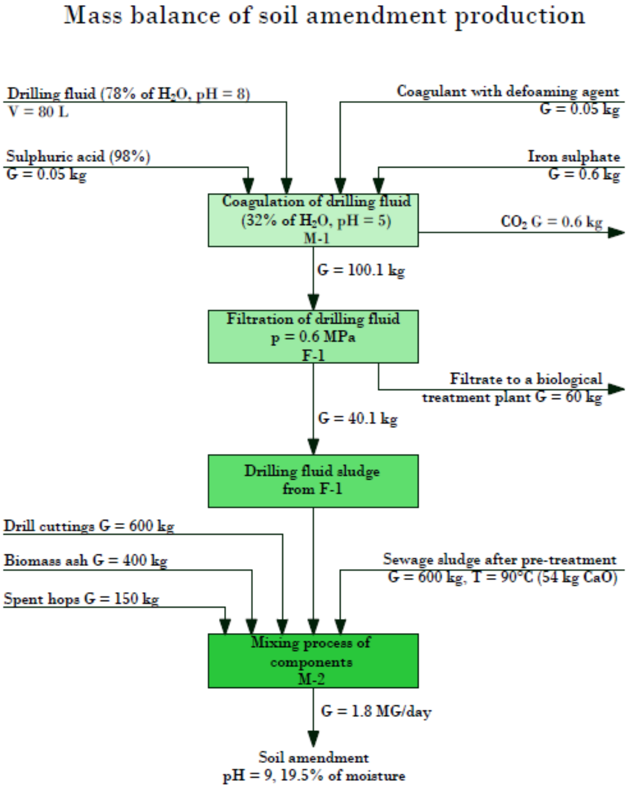

Figure 5. Mass balance of soil amendment production.

Table 4 shows a chemical composition of obtained soil amendment. Soil amendment contains at least 1% of total nitrogen, 7% of potassium oxide, 1.2% of phosphorus oxide, 12%

w/w calcium oxide. Moreover, it meets Polish fertilizer legislation requirements for chemical element contents: Pb, Cd, As, Hg (52, 25, 9, 1.8 mg·kg^{-1}, respectively).

Table 4. An example obtained soil amendment composition for land reclamation.

Parameter	Unit	Content	Regulation*
CaO	% w/w	12.0	
K_2O	% w/w	7.0	
P_2O_5	% w/w	1.2	
N	% w/w	< 1.0	
Pb	mg·kg^{-1}, DM	52.0	140
Cd	mg·kg^{-1}, DM	25.0	50
As	mg·kg^{-1}, DM	9.0	50
Hg	mg·kg^{-1}, DM	1.8	2
PAH	mg·kg^{-1}, DM	$< 10^{-5}$	
pH	-	8	

*) limits of heavy metal contents in mineral fertilizers according to Polish legislations; DM-dry mass; PAH-polycyclic aromatic hydrocarbons.

Due to the environmental application of soil amendment, the presence of *Salmonella* and *Enterobacteriaceae*, as well as parasites: *Ascaris* spp., *Trichuris* spp., *Toxocara* spp. in the obtained soil amendment mixtures was not found (Gluzińska et al. 2016, 2017). The conducted field experiments confirmed a positive influence of this studied product on maize and grass growth (Gluzińska et al. 2017).

Conclusions

Characteristics of studied drilling waste, sewage sludge, biomass ash, and spent hops showed that they can be used, as the main components of soil amendment at appropriate mass ratios and after a chemical characterization. They contain macronutrients (P, N, Ca, Mg, S, K) as well as trace elements (Cu, Fe, Zn, B, Mn) that are essential for plant growth. According to the study, the final product, in terms of environmental legislations concerning pollutants (Cd, Hg, As, Pb), has fallen within the acceptable limits for soil and water. The presence of dangerous pathogens in it was not found. The obtained soil amendment can be used for land reclamation of well sites, hard rock mining sites, abandoned coal mines, refining and smelting sites, construction sites and other contaminated sites. Revitalization of these sites can be improved when soil amendments are used. Production technology of soil amendment based on waste materials has been developed. The positive influence of obtained soil amendment on maize and grass growth has been shown in a previous research paper.

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