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Utilization of spent drilling fluids in soil fertility enrichment composition

J. Gluzińska[a,*], P. Rusek[b], K. Borowik[b], A. Paszek[a]

[a]*New Chemical Syntheses Institute, Inorganic Chemistry Division "IChN" in Gliwice, ul. Sowińskiego 11, 44–101 Gliwice, Poland, Tel. +48322314977, email: joanna.gluzinska@ichn.gliwice.pl (J. Gluzińska), Tel. +48322313051 ext.139, email: andrzej.paszek@ichn.gliwice.pl (A. Paszek)*

[b]*New Chemical Syntheses Institute, Al. Tysiąclecia Państwa Polskiego 13A, 24–110 Puławy, Poland, Tel. +48814731473, email: Piotr.Rusek@ins.pulawy.pl (P. Rusek), Tel. +48814731458, email: Krzysztof.Borowik@ins.pulawy.pl (K. Borowik)*

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ABSTRACT

Wastes from a few plants were used as the components for manufacturing an agent to enrich soil fertility. These included spent drilling fluids, sewage sludge, biomass, and ash. The physico-chemical properties of the wastes were evaluated to calculate their propensity for fertility as well as to fulfil EU legal requirements for environmental protection. The developed technology involves a few steps. Unit operations used in the proposed technology were adjusted to actual conditions in order to obtain economic and ecological advantages. The filtration process allows to obtain sludge stream water containing less than 35% w/w. The clear filtrate may be used to prepare sealing–fluid used in drilling (for water circulation). The resulting product of the projected composition meets the requirements of measures for improving soil properties. Wastes are recovered as valuable streams and can be used in soil remediation techniques. The results of the leaching tests indicate that the tested waste streams are not dangerous to the environment in terms of susceptibility to leaching ingredients like heavy metals and inorganic ions, the levels of which are regulated by law. Therefore, they can be discharged into the soil–water environment.

Keywords: Spent drilling fluids; Waste utilization; Environment protection; Soil conditioner

1. Introduction

Shale gas is the most popular unconventional source of natural gas. Currently, only three countries conduct significant commercial extraction of this raw material; China (approx. $5·10^6$ m^3 per day), Canada ($1.2·10^8$ m^3 per day), and the USA ($9.60·10^8$ m^3/d). Shale gas makes up one third of all the natural gas consumed in the US [1]. Considering the significant influence of shale gas exploitation technology on the environment and the scale of investment, there is a need for a comprehensive approach to this problem, taking into account all environmental aspects [2].

The process shale gas removal is divided into several stages; preparatory work, drilling, hydraulic fracturing, commissioning, gas extraction, and reclamation as well as revitalization of the site. The extent of the impact of this process on the environment depends on the technologies used and is variable at different stages of work. Work performed in individual stages interacts with components of the environment in a specific way. The diversity of profiles of geological specification and the physical and chemical properties of drilling fluid components may adversely affect the environment and human health.

To minimize the environmental impact of potentially harmful substances, more environment–friendly components of drilling fluids should be used. It means that spent components should be easy to manage, ensuring a high level of drilling technology. Rational waste utilization demands that modern purification systems be used on–site so that drilling fluids, after purification and enrichment, may be returned to fluid circulation. When taken out of the

*Corresponding author.

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process, they become waste product which must be treated in accordance with environmental protection regulations. There is an urgent need for the utilization of spent drilling fluids. Taking into account legislative guidelines in accordance with the provisions of relevant legal documents, waste ingredients should be first of all recovered and, if possible, disposed of in a specific manner to minimize their negative environmental impact. One solution is [3] the method of dehydrating saline drilling fluids, which reduces the volume of waste and recovers water used in the drilling process. Due to improved storage of flocculation waste, the protection of groundwater is favoured.

A relatively cheap method of waste utilization is its injection to exploited deposit or into an insulated sorption layer. However, disposal of drilling fluids through storage shall be treated as an extreme method of utilization. There are methods of recovery or utilization of drilling fluids outside the installations developed and implemented. The ideas are based i.e., on solidification, recycling in road constructions, storage in underground landfills and utilization in soil conditioner preparation. The last one mentioned has become the subject of interest of the authors.

In the available professional literature, research results and patents, some methods of modifying wastes using to improve the quality of soil can be found. For example, the authors [4] suggest mixing the waste drilling fluid with active magnesium oxide and / or magnesium salts, or [5] with a highly reactive quicklime (CaO content > 90%). One drawback of these solutions seems to be the degree of hydration in the mixtures, causing operational problems and affecting the economic efficiency of the proposed methods. Some scientists [6] propose a formulation of mixtures having a positive impact on soil quality , in addition to the use of mineral components. These include carbonates, nitrates, silicates, waste streams of an organic nature, biomass, mature compost, bark and waste slurry. Specific allowances are intended to ensure adequate characterization of microbial and enzymatic treatments after land reclamation.

In the article, [7] the authors investigated the use of drilling waste (a fraction of cuttings separated from spent scrubber polymer) in a mix of fermented sludge originated from municipal sewage and sand. The goal was to prepare a mixture suitable for application on the surface layer of a landfill drilling for the purpose of rebuilding the soil structure. One of the most promising applications of drilling wastes is a mixture comprised of mud, cuttings and sewage sludge to improve soil properties. Additionally, to form a blended composition, wastes from other groups such as hop cones, ashes from incinerated biomass or lime are suggested.

The impact of drilling techniques on the environment in terms of the risk of pollution by radioactive substances is also observed. Contamination of groud water by radionuclides and pollution prevention techniques for drinking water are known [8]. It is necessary to control the concentration of elements such as uranium, polonium –210 and lead –210 in three types of water, i.e. a surface water reservoir of drinking water and tap water. Maintenance performed in a mining area following the migration of radionuclides to all kinds of water sources should be under control. It is recommended to analyze the quality of successive layers of the lithosphere for the presence of radioactive elements, especially before exploitation.

A considerable problem within shale gas extraction technology is the emission of gas–pollutants, i.e. CO_2, SO_2, H_2S, NO_2, NH_3. Their presence is evident in the spent drilling fluids feedback. Emission of carbon dioxide from the combustion of shale gas by-products depends on the depth of the well and the yield of deposits – the lower efficiency the higher the emission level. The authors of references [9–10] indicate that the amount of released CO_2 can vary between 3.2–9.0% by volume in relation to the production of shale gas. Carbon dioxide emission also appears in connection with the operation of equipment and vehicles necessary for the prospecting, extraction and processing of shale gas.

2. Experimental

Wastes from many branches were used as the components to manufacture an agent to enrich soil fertility. Spent drilling fluids, sewage sludge, bio-wastes and biomass ashes were used. The chemical and physical properties of the wastes were evaluated to calculate their propensity for fertility as well as to fulfil EU legal requirements for environmental protection. The study involved carrying out a comprehensive analysis of mining ore and components of spent drilling fluids, including a chemical analysis, physical and chemical testing and analysis of particle size composition. Waste drilling fluids of bentonite colloidal grains and cuttings were used, taken from drilling sites in Central and Eastern Poland. The work was carried out using the cuttings containing mostly rock and shale of the native material. Table 1 shows the selected properties of spent drilling fluids and cuttings, and the results of leaching tests as well (made for some limited elements). The leaching evaluation data are crucial from an environmental point of view, they characterise the movement of waste in terms of contamination spread risk.

Bio-wastes in the form of powder, 6–7% by mass moisture, derived from the reprocessing of cone hops. They consisted of proteins, lipids, and components with the potential for fertilizers (mainly potassium and zinc). Table 2 shows the characteristics of bio-wastes, also environmentally significant. Ash from biomass was used due to its known properties which improve soil quality (water absorption capacity, pozzolanic properties/binding capacity of calcium hydroxide due to the content of SiO_2 and Al_2O_3 / chemical composition, size distribution, the ability of a chemical immobilization and bio–availability).

Sewage sludge used in the study came from a biological sewage treatment plant of a chemical company in Eastern Poland. Sewage sludge was analyzed for an assessment of the chemical composition, physical parameters, water content and biological purity. Sewage sludge was stabilized with quicklime, the main component of which (up to 95% m/m) is calcium oxide (CaO). Furthermore, the quicklime contains carbon(IV) oxide (CO_2) up to 3.5%, silica (SiO_2) 0.5–1.0% and magnesium(II) oxide (MgO) 0.6%. In the proposed solution, a calcium component allows for the sterilization of sewage sludge, water absorption in the hydration process and the blended components enrichment (nutrient elements).

Table 1
Spent drilling fluids and cuttings properties

Parameter	Unit	Content	Concentration in leachate mg dm^{-3}	Limits [11] (Polish law) mg dm^{-3}
Drilling fluids				
Water	% w/w	60–70	–	–
Organic compounds	% w/w	6–10	–	–
Density	kg m^{-3}	1050–1250	–	–
Mean particle size	µm	7.0	–	–
– median	µm	5.5	–	–
SO_4^{2-}	% w/w	0.68	164	500
Cl^-	% w/w	4.88	925	1000
pH	–	7.8	7.6	6.5–9.0
Mineral oil	mg kg^{-1} dry mass	3.0	–	–
Aromatic hydrocarbons	mg kg^{-1} dry mass	1.5	–	–
PAH's	mg kg^{-1} dry mass	0.007	–	–
Calcium	% mass	9.5	–	–
Barium	% mass	1.0	1.45	2.0
Zinc	mg kg^{-1}	75.0	0.13	2.0
Copper	mg kg^{-1}	30.5	0.13	0.5
Cadmium	mg kg^{-1}	0.3	< 0.01	0.4
Lead	mg kg^{-1}	8.5	< 0.05	0.5
Arsenic	mg kg^{-1}	7.0	0.02	0.1
Chromium	mg kg^{-1}	35.0	0.09	0.1
Nickel	mg kg^{-1}	22.5	0.24	0.5
Mercury	mg kg^{-1}	8.0	0.006	0.06
Cuttings				
Water	% w/w	31.5	–	–
Mineral oil	mg kg^{-1}dry mass	0.2	–	–
Aromatic hydrocarbons	mg kg^{-1}dry mass	0.1	–	–
PAH's	mg kg^{-1}dry mass	< 10^{-7}	–	–
SO_4^{2-}	% w/w	1.25	338	500
Cl^-	% w/w	1.32	718	1000
Calcium	% w/w	4.5	–	–
Barium	% w/w	0.8	0.14	2.0
Zinc	mg kg^{-1}	85.0	0.05	2.0
Copper	mg kg^{-1}	32.5	0.07	0.5
Cadmium	mg kg^{-1}	0.1	< 0.01	0.4
Lead	mg kg^{-1}	12.0	< 0.05	0.5
Arsenic	mg kg^{-1}	8.5	0.02	0.1
Chromium	mg kg^{-1}	68.5	0.03	0.1
Nickel	mg kg^{-1}	35.5	0.22	0.5
Mercury	mg kg^{-1}	2.0	0.006	0.06
pH	mg kg^{-1}	8.2	8.6	6.5–9.0

Table 2
Components of hop waste (bio-mass waste)

Component	Unit	Content	Concentration in leachate mg dm^{-3}	Limits [11] (Polish law) mg dm^{-3}
Dry mass		93.2		
Ash		10.2		
Proteins		25.4		
Lipids		4.4		
Fiber		23.6		
NDF (neutral detergent fiber)		36.1		
ADF (acid detergent fiber)	% w/w	27.6		
Total phosphorus		6.4		
Magnesium		3.1		
Calcium		3.8		
Potassium		29.4		
Sodium	g kg^{-1}	0.6		
Zinc		85.6	0.08	2.0
Copper	mg kg^{-1}	87.2	0.12	0.5

2.1. Analytical methods

Chemical and physical identification of wastes as well as final products were carried out in accordance with the referenced methods. Determination of the content of cations (Al, Ba, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Ni, Pb, Sn and Zn) was carried out using the technique of inductively coupled plasma atomic emission spectroscopy (ICP–OES). Determination of mercury (Hg) content in air–dried solid samples was carried out using the cold vapour atomic absorption spectroscopy (CV–AAS). Determination of sulphate content was carried out using the gravimetric method. Phosphates content was determined using the spectrophotometric method in accordance with the PN–EN ISO 13652:2002 standard. Nitrogen content was determined using the spectrophotometric method in accordance with the PN-EN ISO 13654-1:2002 standard. Chemical oxygen demand $(COD)_{Cr}$ was determined using dichromate methods based on the PN–EN ISO157505:2005 standard. PAH content was determined using gas chromatography with gas a chromatograph coupled with a Parkin Elmer Clarus 500 mass spectrometer (GC/MS). Moisture content was analysed in accordance with the PN-EN 15169:2007 standard, and rheological properties of waste were determined using the structural rotational viscometer RHEOTEST 2. The leaching test was carried out by 24 h shaking using a laboratory shaker at 10 rpm speed and in accordance with the PN-EN 12457-4 standard. Results of testing indicates parameters of water extracts which are required if introduces into waters or soil.

Particle size analysis was performed using a laser technique with a Coulter LS13320 analyser that works based on ISO 13320 standard requirements.

3. Results and discussion

Preparation of the soil conditioner consists of a few steps, including importing and storing raw materials and additives (ash, lime, bio-wastes, sewage sludge after filtration, coagulants, sulphuric acid) and treating the drilling fluid to facilitate sedimentation of colloidal suspension. Sedimentation is achieved after mixing the spent drilling fluid with sulphuric acid – to adjust the pH – and with ferrous sulphate and coagulant Praestol 2510 to solidify the colloidal particles and intensify the sedimentation process. In the next step, dehydration is carried out using a filter press, whereby the filter cake water content decreases down to 35% w/w or less. The clear filtrate is transferred to a blender for the preparation of the sealing liquid that is re-used in the drilling process. Then, as the prepared waste stream feeds the mixer, it is combined together with the other components of the mixture (sludge from biological sewage treatment plants, cuttings, lime, ash and biowastes). Sewage sludge, prior to being introduced into the mixer is pre-treated in order to be dehydrated and sterilized. The main component of the intermediate product is calcium carbonate. Results of tests carried out with the instrumental techniques (XRF, XRD, and FTIR) confirm the presence of calcium carbonate in amounts up to 85% dry weight. The content of organic substances (marked as a loss on ignition at 550°C) was near 14%. The sediments contained inorganic compounds, derived from the additives used in the process of wastewater treatment and water purification. Ions, such as Ca^{2+}, Na^{+}, Cl^{-}, SO_4^{2-} and PO_4^{3} have been identified. The nitrogen compounds (NO_3^{-}, NH_4^{+}) present in the sediment are probably the products of microbiological processes occurring in the wastewater treatment plant (WWTP).

The soil conditioner is obtained by introducing all components into a mixer in suitable quantities, proportion and order while mixing thoroughly. Mixing time depends on the quality and quantity of added substrates. A schematic flow diagram of the process is shown in Fig. 1.

The control of the process concerns the amount of raw materials used to obtain a free-flowing form of the prod-

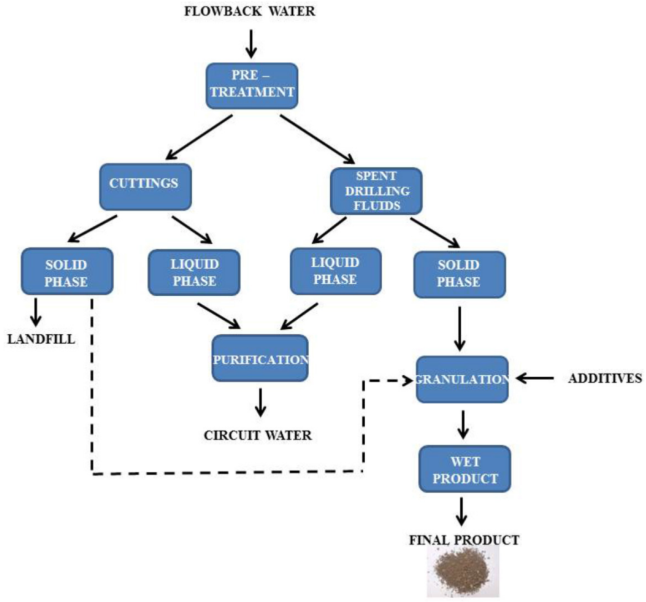

Fig. 1. Drilling wastes utilization method – schematic flow diagram.

uct. Furthermore, the controlled parameters are pH value and humidity of the cuttings, sediments and final product. Inter-operational control was carried out as well, during the whole process of soil conditioner manufacturing. Laboratory analysis consisted of a chemical analysis of raw materials, waste and the final product. Critical parameters were evaluated, especially with regard to environmental requirements (content of heavy metals), as well as pH, water content and physical parameters, like caking ability and plasticity (data not presented).

Due to the proposed environmental application, the bio-purity of prepared mixtures was evaluated. The presence of *Salmonella* and *Enterobacteriaceae*, as well as parasites: *Ascaris spp*., *Trichuris spp*., *Toxocara spp*. was not found.

Unit operations used in the proposed technology were adjusted to actual conditions in order to obtain economic and ecological advantages. The filtration process allows to obtain a sludge stream containing approx. 30–35% water. The clear filtrate may be used to prepare sealing-fluid used in drilling technology (water circulation). The final products – soil conditioners – meet the requirements for agents improving soil properties. The composition of the mixture shows the nutrient content as follows: <u>*at least*</u> 1.0% mass. N, 1.5% mass. P_2O_5, 6.5% mass·K_2O and 11% mass CaO. Moreover, the prepared soil conditioner meets the requirements of Polish fertilizer legislation for heavy metals: Hg, Cd, Pb (1.6, 22.5, 48 mg kg^{-1} dry mass, respectively).

4. Conclusions

It was found that due to their characteristic features, raw materials used for the production of soil conditioner can be utilized in agriculture. They contain macronutrients such as phosphorus, nitrogen, calcium, magnesium, sulphur and potassium at a sufficiently high level, as well as trace elements, like copper, iron, zinc, boron and manganese. The final product, in terms of environmental legislation concerning pollutants including cadmium, mercury, arsenic and lead, has fallen within the acceptable limits for soil and water application. It does not indicate the presence of dangerous pathogens.

The leaching test results indicate that the tested waste streams are not dangerous to the environment in terms of susceptibility to leaching ingredients such as chlorides, sulphates, sodium, potassium, aluminum, barium, cadmium, chromium, copper, nickel, and lead, the content of which is limited by law. The soil conditioner technology is based on sewage sludge, drilling fluids and cuttings, bio-wastes and ash waste streams. The resulting product of the projected mixtures meet the requirements for improving soil composition. The mixture's potential fertility was tested in pot-tests (Fig. 2) and field-tests (Fig. 3).

Preparation, production and evaluation of the quality of the final product show that the described technology has the potential to launch an agent on the market that exhibits the properties of soil conditioner. Moreover, mining wastes are recovered as valuable streams and can be used in soil remediation techniques. The result of the leaching tests indicate that the waste streams and the final product are not harmful to the environment in terms of susceptibility to leaching pollutants such as chlorides, sulphates, sodium, potassium, heavy metals etc., which are regulated by legislation. Therefore, they can be applied to the soil–water environment.

Fig. 2. Pot trials of soil conditioner (test plant: maize).

Fig. 3. Field trials of soil conditioner (test plant: grass).

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