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The characteristics of drilling fluids from natural gas extraction processes and composition of the drilling slurry obtained

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Abstract. The paper shows that the sources which act on environmental factors through specific agents are considered possible pollutants. Depending on their physical and chemical properties, their aggressiveness toward the air-water-soil system can be determined. The paper characterizes the main waste obtained from natural gas extraction, specifically the drilling slurry, as well as the drilling fluid used as a raw material. Furthermore, the paper presents some proposals for reducing the risk of environmental pollution, discussing conventional versus unconventional drilling.

Key Words: waste, natural gas extraction, conventional drilling, unconventional drilling, drilling waste.

Introduction. The aim of the paper is to determine the aggressiveness of this type of waste, common in natural gas extraction, starting with the used materials in the drilling process and up to the proposals for reducing the environmental pollution risk. In the technological process of drilling, specifically in the composition of the drilling fluid, the used substances do not fall under the Health Ministry Ordinance no. 43/07.02.1980 regarding the approval of the toxic substances list. All substances used in the drilling process comply with the Romanian Government Emergency Ordinance no. 200/09.11.2000, regarding the classification, labeling and packaging of dangerous chemical substances and products, Law no. 451/18.07.2001 for the approval of the Government Ordinance no. 200/2000 regarding the classification, labeling and packaging of dangerous chemical substances and products, and the Romanian Government Decision no. 490/16.05.2002 for the approval of the methodological norms of applying the Government Ordinance no. 200/2000. The used chemical substances are not found on the “List of dangerous substances” included in Appendix 2 of the Romanian Government Decision no. 490/16.05.2002.

Chemical products used. In the technological process of well drilling, the following chemicals are used for the preparation, maintenance and conditioning of the drilling fluid (Specifications for Drilling Fluid Materials 2004): bentonite; caustic soda; soda ash; tripolyphosphate; aqua control; lube; proterm; proterm packaging; CMC HV; poly glycol; $CaCO_3$ (medium); $CaCO_3$ (fine); XC polymer.

In the beginning of modern rotary drilling – the last decades of the past century – the water was being pumped through pipes for the constant washing of the probe and for evacuating the detritus towards the surface (Manual on sewerage and sewage tratament, part. B Operation and maintenance 2002). By using fine rock particles, especially those dispersible in water, a mud was formed along the ringed space. It has been observed that this mud had certain advantages over today’s situation: a better evacuation capacity, including the maintaining of suspended detritus in the event of circulation disruption and, especially, the ability to stabilize the well walls near unconsolidated rocks.

Step by step, the demands imposed on the fluid increased. It began to be prepared on the surface, from colloidal clays, studied in the laboratory, tested at the probe, treated and cleaned more thoroughly. In order to obtain better properties, the composition of drilling fluids has been diversified continuously. Nowadays, many of them are not prepared from water and clay anymore. The term “drilling muds” becomes, in these cases, void (Harvey & White 2013).

In principle, the nature, composition, properties and debit of the fluid used in the drilling of the well are established in order to obtain optimal parameters for each drill in particular. However, the drilling fluid must meet numerous other requirements, of which some are essential for drilling wells without accidents and complications, in a minimum interval, and for putting the wells into operation without difficulties with maximum productivity:

- the chosen fluid must not affect, physically or chemically, the transverse rocks (Crampin 1977), must not swell or disperse the un-hydrated clays and marls, must not dissolve soluble rocks, must note rode weakly consolidated rocks; must not, as much as possible, disperse or dehydrate the detritus;
- the fluid must keep its properties, within acceptable limits, when contaminated with: soluble minerals (salt, gypsum, anhydrite), mineralized groundwater, gases (hydrocarbons, carbon dioxide, hydrogen sulfide), loamy detritus;
- the fluid must maintain its technological properties, when subjected to the high temperatures and pressure found within the wells, and to their variations within the circuit;
- the fluid must allow the geophysical investigation of the rocks and fluids contained within their pores, and the sampling of rock in conditions as close as possible as those on site;
- the fluid must prevent corrosion and erosion of the well equipment, both through its nature as well as through the neutralization of aggressive agents introduced to the fluid from the penetrated layers;
- the fluid must maintain the un-evacuated particles of rock in suspension during circulation disruptions;
- the fluid must conserve the permeability of open productive layers;
- the fluid must not be toxic or flammable and must not pollute the environment and groundwater;
- the fluid must be easily prepared, handled, maintained and cleaned of gases or detritus;
- the fluid must allow high advancement speed of the drill;
- the fluid must be cheap, not to need deficient and difficult to procure additives, and its pumping must be performed with minimal costs.

Drilling fluids are made by combining different quantities of materials and substances – additives. Among the compounds of drilling fluids, the following substances present a high degree of toxicity: hydrocarbons (diesel, lubricants, crude oil), additives containing heavy metals (chrome, mercury, cadmium), some salts (KCl, $ZnCl_2$, $ZnBr_2$), caustic soda, halogenated phenols and some radioactive substances.

The chrome is found in additives used on a wide scale: ferrochromelignosulphonate, chromelignosulphonate, chromlignite, chromate and sodium or potassium dichromate. It is worth noting that heavy metals also have a high capacity of soil migration. In 1970, a method for the toxicity assessment of drilling fluids, residual waters and detritus has been developed, either in whole or in parts: liquid phase, solid phase, suspended solids.

The procedure is performed by testing a range of microorganisms susceptible to pollution. In the United States, the use of a variety of “Mysidopsisbahia” shrimp is recommended (De Queiroz et al 1989). They are held for a specific duration, usually 96 hours, in a blend of fresh or sea water, containing various concentrations of the tested fluid or substance. The concentration at which the mortality of the population reaches 50% is called “lethal concentration”, noted as LC50 and is expressed in ppm (part per million). The toxicity is inversely proportional to the parameter of LC50, high values of the latter mean low toxicity, while low values indicate high toxicity levels. For drilling fluids, the standard test is performed through the dilution of the mud 1:9, meaning one part mud and nine parts fresh or sea water. This method is not applied in Romania. The E.P.A. (Environmental Protection Agency) has imposed that the limit value of LC50 at

96 hours for drilling fluids and additives (noting that toxicity is inversely proportional to the LC50 value) is of 30000 ppm (http://worldwidescience.org).

In Romania, the first steps for determining the toxicity of drilling fluids and additives on fresh water fish have been initialized, and the results highlight the non-toxic nature of these materials. Thus, common fluids, prepared with fresh or sea water have a LC50 value of over 1000000 ppm. The fluids treated with lignosulphonates and lime have the LC50 value included in a very wide range: 50000–1000000 ppm. The fluids containing polymers and KCl have an LC50 value between 20000–80000 ppm. In general, the fluids with an LC50 value under 30000 are forbidden.

In order to avoid or mitigate the ecological impact of drilling, several possibilities exist (Giurgiu 1984):

- the use of a closed and safe system – protected against accidents for the surface circuit of the drilling fluid, for the residual water and for detritus;
- the separation of the solid particles infiltrated in the traversed rocks, in order to avoid the fluid's excessive dilution and to reduce the total volume of mud used on a well;
- the reuse of the slurry remaining at one well in other neighboring wells, through a central preparation, storage and reconditioning station;
- the recycling of the fluid and residual waters. For example: basic muds, rich in humates can be spread on acid soils, contributing to their improvement;
- the clarification of residual water through the addition of some coagulants and flocculants, followed by the separation of solid particles by way of high speed centrifuges;
- the replacement of compounds and additives, including lubricants and corrosion inhibitors which have a higher toxicity with other, less toxic compounds: caustic soda with organic bases, ferrochromlignosulfonates with ammonium lignosulfonate, oil products from inverse emulsion fluids with mineral oil, with a poor content of aromatic compounds;
- the injection of residual waters underground, below ground waters;
- the use as additives for mud of biodegradable polymers.

In order to decrease the degree of pollution and toxicity of fluids used in Romania, it is necessary to establish some regulations regarding their composition, keeping in mind the imposed worldwide restrictions for their preparation and maintenance, as well as laboratory experiments (Iordache 1999):

- pH = 7, maximum 8.5;
- total content of oil products = 0 – maximum 2 ppm;
- total content of suspended materials = maximum 30%;
- total content of active colloidal solids (M.B.T.) = maximum 50 kg/m^3;
- content of chloride (Cl^-) = maximum 5000 ppm;
- content of sodium chloride (NaCl) = maximum 50 kg/m^3
- content of calcium (Ca^{2+}) = maximum 200 ppm;
- to avoid in the preparation and maintenance of non-polluting drilling fluids the use of ferrochromlignosulfates, chromates, dichromates, corrosion inhibitors, formaldehyde and any other oil-based additives.

The drilling fluid used in well drilling has as a base a water and clay system which, depending on the type and characteristics of the traversed rocks, can be conditioned with a series of materials in order to give it the properties required by the process. Along with the drilling of each interval, casing and cementing takes place. After the casing of each column, the cementing of the annular space between the column and the borehole takes place. The cement is transported in specialized auto containers from which, by means of cementing aggregates, it is placed behind the column through a pipe system. Cementing is a closed process, so that the cement is not in contact with the environment. The cementing operations will use approximately 98.5 tons of class G cement and 50 tons of class S1 cement.

Material and Method. The paper presents information regarding the composition of drilling slurry (from the extraction area Buzau, well 1 Florica, belonging to S.N.G.N. Romgaz S.A.), a waste resulted from the extraction process of natural gas. This slurry is named by experts in the field as detritus contaminated with drilling fluids. The processing steps of this type of waste is shown in Figure 1 (ASME Shale Shaker Committee 2005).

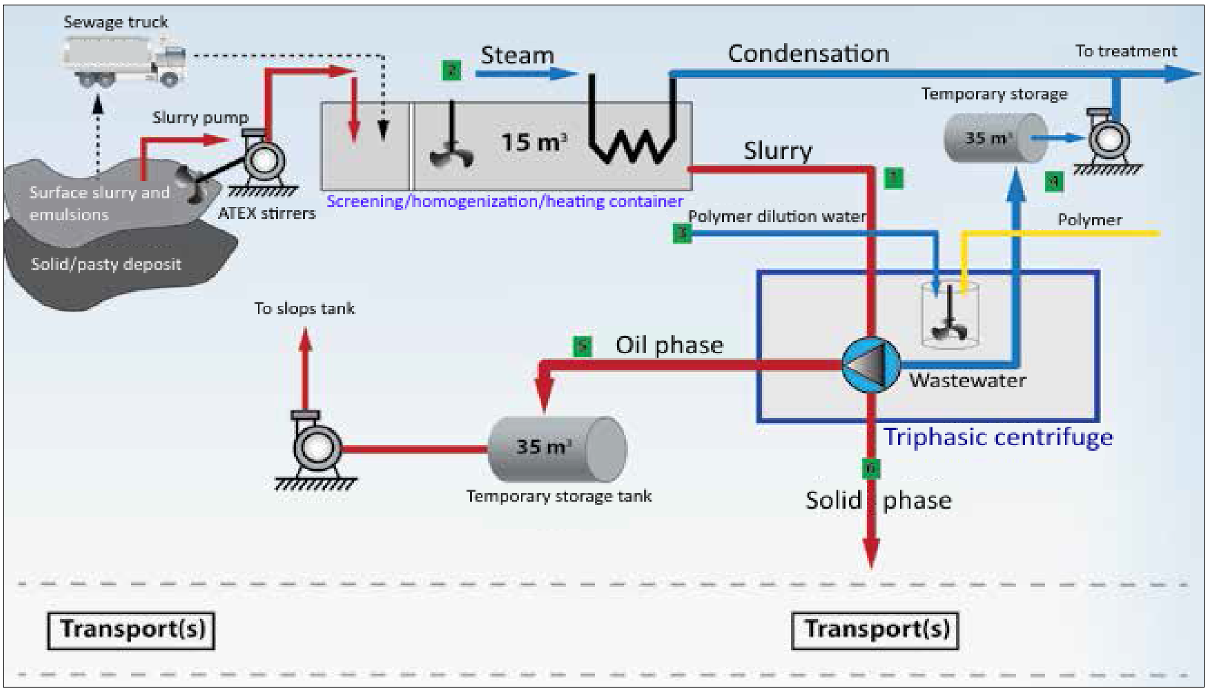

Figure 1. Drilling slurry processing.

Each drilling has its own characteristics depending on pedogenetical factors – climate, terrain, substrate, lithology, groundwater and stagnant water frequency – and depending on the land employment – arable, forestry, etc.

In order to assess the level of pollution, samples from the drilling areas must be taken and analyzed. The results of these determinations can give clues to the severity of soil degradation, but also of possible soil remediation measures.

Results and Discussion. As can be seen in the forthcoming analysis reports, regarding the chemical composition of drilling slurries, there are major differences, within wide ranges, depending on the characteristics of the exploitation area and on the compliance with the extraction technology.

The Table 1 presents the result of an analysis performed on a drilling slurry sample from the extraction area Buzau, well 1 Florica, belonging to S.N.G.N. Romgaz S.A. The samples were taken on March 2013, for a drilling slurry containing chlorides. Also, for laboratory analyses, three samples were taken: T1 – leaching test L/S = 2 L/kg, T2 – leaching test L/S = 10 L/kg and T3 – C(0) the first elute of the percolation test at L/S = 0.1 L/kg.

Table 1

The result of an analysis performed on a drilling slurry sample, area Buzau, well 1 Florica

No	*Analyzed parameter*	*Unit*	*Value*	*STAS analysis method*
1	Humidity	%	26.22	SR EN 12880/2000
2	Dry matter	%	73.78	SR EN 12880/2000
3	Inorganic matter	%	95.5	SR EN 12879/2005
4	Organic matter (calcination loss)	%	4.5	SR EN 12879/2005
5	Total organic carbon (TOC)	mg/kg dry matter	2.64 26400	SR EN 13370/2005 SR EN 1484/2001
6	Cadmium	mg/kg dry matter	< 0.02	SR ENV 12506/2005 SR ISO 8288/2001

7	Copper	mg/kg dry matter	0.38	SR ENV 12506/2005 SR ISO 8288/2001
8	Chrome	mg/kg dry matter	< 0.05	SR ENV 12506/2005 SR ISO 8288/2001
9	Nickel	mg/kg dry matter	< 0.1	SR ENV 12506/2005 SR ISO 8288/2001
10	Lead	mg/kg dry matter	0.64	SR ENV 13370/2005 SR ISO 8288/2001
11	Zinc	mg/kg dry matter	2.82	SR ENV 13370/2005 SR ISO 8288/2001

No	*Analyzed parameter*	*Values*			*STAS analysis method*
		T1 L/S = 2 L/kg	*T2 L/S = 10 L/kg*	*T3 C(0)*	
1	Hydrogen ions pH concentration	8.20	8.26	8,.18	SR ENV 12506/2002
2	Chlorides	8926	12126	7364	SR ENV 12506/2005
3	Sulphates	1892	3654	1224	SR ENV 12506/2005
4	Dissolved organic carbon (DOC)	240.2	415.6	112.6	SR ENV 13370/2005
5	TDS (total dissolved solids)	1488	21862	-	SR ENV 13370/2005
6	Copper	< 0.5	< 0.5	< 0.05	SR ENV 12506/2005
7	Nickel	< 0.1	< 0.1	< 0.01	SR ENV 12506/2005
8	Zinc	0.6	1.24	0.52	SR ENV 12506/2005
9	Cadmium	< 0.02	< 0.02	< 0.002	SR ENV 12506/2005
10	Total Chrome	< 0.5	< 0.5	< 0.005	SR ENV 12506/2005
11	Molybdenum	< 0.1	< 0.1	< 0.01	SR ENV 12506/2005
12	Lead	< 0.2	< 0.2	< 0.02	SR ENV 12506/2005

Limits imposed by Ord. 95/2005 for waste classes

No	*Analysis parameter*	*Maximum limits for inert wastes*	*Maximum limits for non-dangerous wastes*	*Maximum limits for dangerous wastes*	*STAS analysis method*
1	pH	-	Minimum 6	-	SR EN 12506/2005
2	Calcination losses (LOI)	-	-	10%	SR EN 14346/2005
3	Total organic carbon (TOC)	30.000 mg/kg s.u.	5%	6%	SR EN 16192/2012 SR EN 1454/2001

No	*Analyzed parameter*	*Maximum limits for inert wastes*			*STAS analysis method*
		L/S = 2 L/kg (mg/kg.s.u.)	*L/S = 10 L/kg (mg/kg.s.u.)*	*C(0) (mg/L)*	
1	Hydrogen ions pH concentration	-	-	-	SR ENV 12506/2005
2	Chlorides	550	800	480	SR ENV 12506/2005
3	Sulphates	660	1000	1500	SR ENV 12506/2005
4	Dissolved organic carbon (DOC)	240	500	160	SR ENV 13370/2005
5	TDS (total dissolved solids)	2500	4000	-	SR ENV 13370/2005
6	Copper	0.9	2.0	0.6	SR ENV 12506/2005
7	Nickel	0.2	0.4	0.12	SR ENV 12506/2005

8	Zinc	2.0	4.0	1.2	SR ENV 12506/2005
9	Cadmium	0.03	0.04	0.02	SR ENV 12506/2005
10	Chrome total	0.2	0.5	0.1	SR ENV 12506/2005
11	Molybdenum	0.3	0.5	0.2	SR ENV 12506/2005
12	Lead	0.2	0.5	0.16	SR ENV 12506/2005

No	*Analyzed parameter*	*Maximum for non-dangerous wastes*			*Maximum limits for dangerous wastes*			*STAS analysis method*
		L/S = 2 L/kg (mg/kg.s.u.)	*L/S = 10 L/kg (mg/kg.s.u.)*	*C(0) (mg/L)*	*L/S = 2 L/kg (mg/kg.s.u.)*	*L/S = 10 L/kg (mg/kg.s.u.)*	*C(0) (mg/L)*	
1	Hydrogen ions pH concentration	-	-	-	-	-	-	SR ENV 12506/2005
2	Chlorides	10.000	15.000	8.500	17.000	25.000	15.000	SR ENV 12506/2005
3	Sulphates	10.000	20.000	7.000	25.000	50.000	17.000	SR ENV 12506/2005
4	Dissolved organic carbon (DOC)	380	800	250	480	1000	320	SR ENV 13370/2005
5	TDS (total dissolved solids)	40.000	60.000	-	70.000	100.000	-	SR ENV 13370/2005
6	Copper	25	50	30	50	100	60	SR ENV 12506/2005
7	Nickel	5	10	3	20	40	12	SR ENV 12506/2005
8	Zinc	25	50	15	90	200	60	SR ENV 12506/2005
9	Cadmium	0.6	1	0.3	3	5	1.7	SR ENV 12506/2005
10	Chrome total	4	10	2.5	25	70	15	SR ENV 12506/2005
11	Molybdenum	5	10	3.5	25	30	10	SR ENV 12506/2005

As seen in the analysis report for the three slurry samples (T1 – leaching test L/S = 2 L/kg, T2 – leaching test L/S = 10 L/kg and T3 – C(0) the first elute of the percolation test at L/S = 0.1 L/kg) the hydrogen ions pH concentration is high, requiring the treatment with diluted citric acid solution until the pH value is between 5.5–7.5. After neutralization, this is treated with PLUSPAC flocculent, consuming between 15-35 L/m^3, homogenized in the loading tub and the resulting mixture is pumped in the processing-separation unit, where the liquid-solid separation takes place. The resulting liquid (water) is collected through a pipeline route in a tub of typically 30 m^3. Some amount of water (approx. 10-20%) is reused in the technological process, the rest being transported to the drilling fluid user to be reused in the production process.

The resulting solid phase is analyzed by an accredited laboratory and then transported for disposal by landfilling to the nearest landfill accepting this kind of waste, on the basis of a contract signed with the landfill operator, according to OM 95/2005 regarding the establishment of the acceptance criteria and preliminary waste acceptance procedures, and the national list of accepted wastes for each waste class.

Conclusions. In Romania, at present, because of the underperforming purification technology, drilling slurries are processed and finally disposed in specific landfills (Petrescu 2003). It should be mentioned that, worldwide, working platforms (pads) are being created for which other facilities are provided, such as access roads, water sources, energy sources, drilling fluids preparation and conditioning stations, stations for the processing of detritus and solids from the drilling fluid, wastewater treatment and filtration stations etc. The drilling sites are enclosed as an industrial hall with antipollution and antiphonic protection. Regardless of the type of probe – vertical, directional or horizontal – the drilling fluid needs to fulfill the same functions: release the detritus foot, detritus disposal, ensuring the stability of the drilled hole wall, providing layer backpressure and the cooling of the dislocation device.

For directional and horizontal probes, however, specific requirements are imposed, related to: severe deviation intensities (fluids with improved lubricant abilities are recommended), detritus evacuation (in order to prevent the deposition of solid particles on the inner wall of the borehole), the risk of catching on the productive layers (it is intensified with the increase in probe inclination), barite depositing during interrupted circulation (the risk of circulation loss or eruptive manifestations is increased), different pressure distribution (the density of the slurry must take into account the stability of the walls and to avoid the cracking of the rocks etc.).

A solution with insignificant ecological effects is the use of synthetic fluids, among which inverse pseudoemulsions can be found (instead of oil products, a synthetic, biodegradable fluid is used as a dispersion phase) (European Centre of Excellence in Gas from Shale Gas 2013). This type of fluid is suitable only for horizontal drills. Another relatively new category of fluids used in horizontal and directional drilling (Figure 2) is that of fluids containing biopolymers, usually without solid particles (Byrd & Zamora 1988).

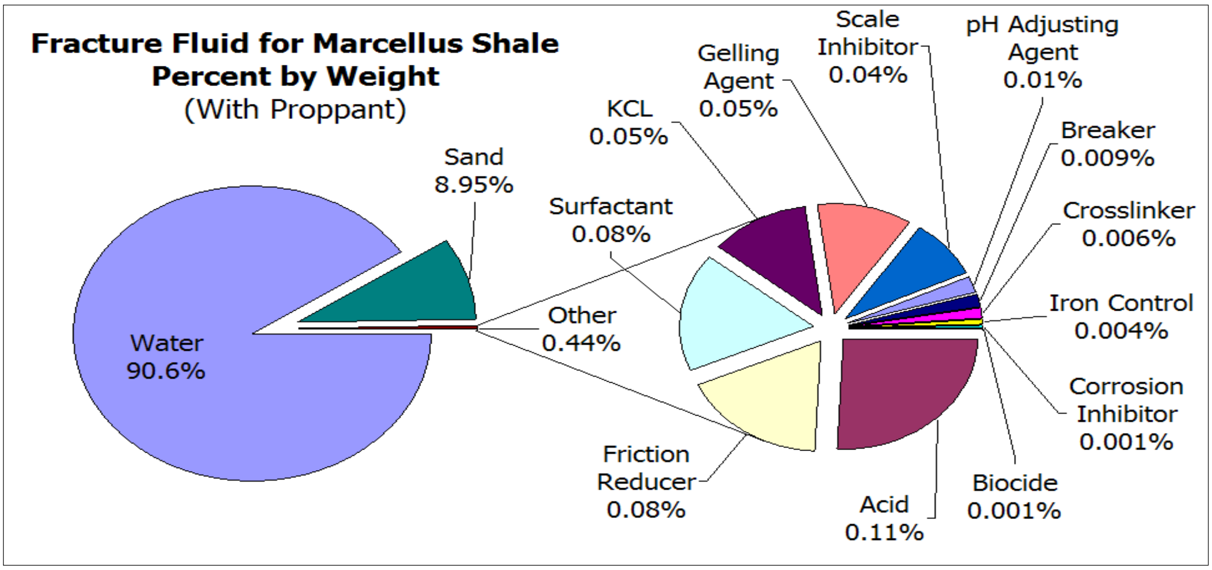

Figure 2. Synthetic fluids used in vertical drilling.

Among the widespread polymers are: Xanthan gum at concentrations of 3-7 kg/m^3 and sodium hydroxyethyl cellulose (HEC). The system based on amphoteric biopolymers and polymers, through their components, inhibit the hydration and dispersion of clays (through the use of potassium chloride, potassium acetate, potassium sulfate etc.).

For the simplification of the completion methods of boreholes, all products used in a biopolymer system are degradable by either acid solutions or oxidants (sodium hypochlorite, lithium hypochlorite etc.).

Thus, the correct choice of drilling fluid represents one of the most important processes in the establishment of a drill, integrating drilling and completion in an interdependent cycle: Environmental policy – Planning – Implementation and running – Checking and corrective action – Analysis at the leading level, with the purpose of continuous improvement towards a clean production.

The classical natural gas extraction method through vertical drilling is accomplished with generating drilling slurries containing dangerous substances, while the horizontal, unconventional drilling allows the use of biodegradable synthetic drilling fluids, but generating with about 40% more waste (National Energy Board 2008) (Figure 3). For example, a single horizontal drill with a length of 1200 m, at a depth of 2100 m, can produce approximately 170 m^3 of slurry and wastes, while the conventional method, for the same depth, produces about 69 m^3 of slurry and waste.

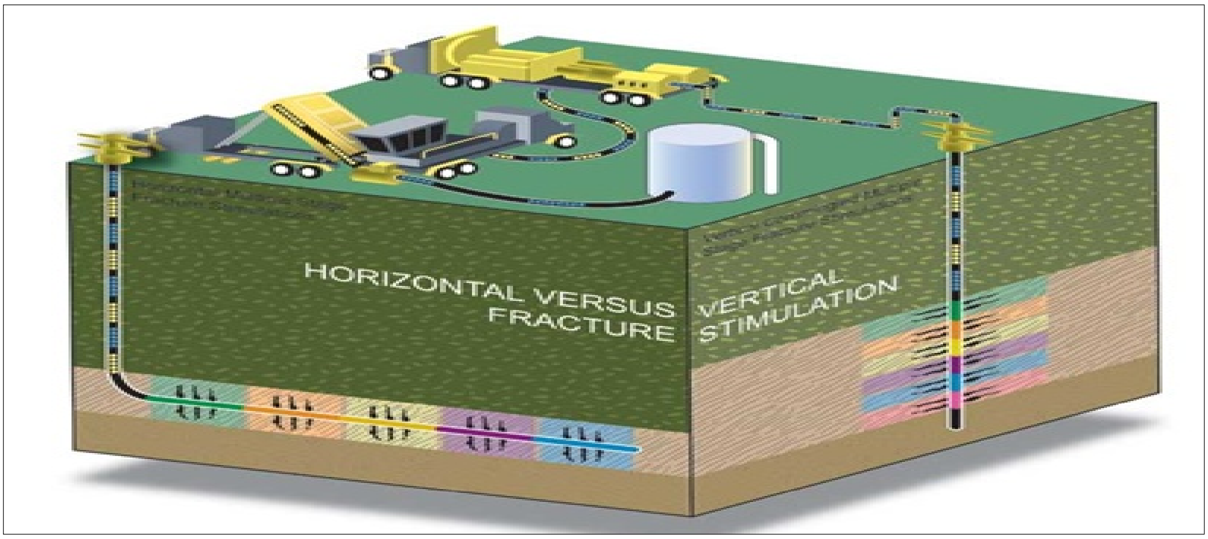

Figure 3. Vertical versus horizontal drilling.

References

Byrd B., Zamora M., 1988 Fluids are key in drilling highly deviated wells. Pet Eng Int 60(2):24-26.

Crampin S. A., 1977 A review of the effects of anisotropic layering on the propagation of seismic waves. Geophysical Journal International 49(1):9-27.

Ferraz De Queiroz J., Leger P., Solgeloos P., 1989 Description of a test system for year-round reproduction studies with *Misydopsis bahia* (M.) (Crustacea, Mysidacea).

Giurgiu G., 1984 Cartea sondorului de extracție [Driller's book extract]. Edit. Tehnică Bucharest [in Romanian].

Harvey Galson E., White M., 2013 Monitoring in geological disposal of waste objectives, strategies, technologies and public involvement. International Conference and Workshop, Luxembourg 19-21 March, 60 pp.

Iordache G., 1999 Ecologie și protecția mediului în foraj [Ecology and environmental protection in drilling]. Edit. Universităţii Petrol-Gaze din Ploieşti [in Romanian].

Petrescu I., 2003 Management, protection and research. Cluj University Press.

*** API 13A: Specifications for Drilling Fluid Materials, 2004, 16th Edition [ISO 13500:1998 (Modified)], American Petroleum Institute).

*** Manual on sewerage and sewage tratament, part B: Operation and maintenance, 2002, Central Public Health and environmental engineering organization, Ministry of Urban Development, New Delhi.

*** http://worldwidescience.org/topicpages/a/addressing+contaminated+volume.html).

*** ASME Shale Shaker Committee, 2005 The Drilling Fluids Processing Handbook. ISBN 0-7506-7775-9.

*** European Centre of Excellence in Gas from Shale Gas, 2013 Natural Gas Resource from unconventional fields-potential and recovery.

*** National Energy Board, 2008 JuneWarren Publishing - Drilling and Completing Shale Gas Wells.

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