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Distribution Of Heavy Metals In The Various Phases Of Spent Oil-Based Mud

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***Abstract:** Heavy metals are one of the parameters that are considered during disposal of contaminated drilling mud. The oil and gas industry generates huge volumes of solid and liquid waste per well that require treatment prior to disposal. These could be drilling mud, drilled cuttings, produced water etc. Heavy metals are toxic to both human and animal life forms and have therefore attracted widespread attention in relation to waste disposal. These metals are carcinogenic and teratogenic. Two drilling mud samples, INV and ENV, from an offshore oilfield in Ghana were analysed for the concentration of heavy metals in the solid and liquid phases. The solids were dried, digested and spectrophotometrically analysed for six (6) heavy metals (Cadmium, Chromium, Lead, Copper, Zinc and Manganese). The results showed ENV recorded the highest concentrations of heavy metals in the liquid phase; Lead (39.78 mg/L), Manganese (19.37 mg/L), Zinc (4.82 mg/L), and Copper (4.54 mg/L) in that order which far exceeded regulatory limits by United States Environmental Protection Agency (USEPA). Heavy metals in the liquid phase of INV were in the range of about 3.45 mg/L (Manganese) and 4.70 mg/L (Lead) for samples that showed appreciable concentrations of heavy metals. Solid phase concentration was highest in both ENV and INV mud. Cadmium and Chromium concentrations were less than 0.002 mg/L in both solid and liquid phases of INV and ENV. There is a possibility that these spent muds will lead to increased levels of some of these heavy metals in aquatic environments. Therefore, disposal of these muds into offshore environments should be highly discouraged. Treatment to reduce contaminants to acceptable levels is required before disposal.*

***Keywords:** Heavy Metals, Drilling Mud, Drilling Wastes, Disposal*

I. INTRODUCTION

Oil and gas drilling operations generate two main types of wastes; drilling cuttings and drilling muds (Siddique *et al*., 2017). Konkel (2016) stated that, produced water is another component of drilling waste. Drilling fluids are employed in drilling varied types of oil and gas wells. They are employed to control downhole formation pressures, cool and lubricate bits and remove rock fragments called cuttings from the well being drilled, etc. (Goodarznia and Esmaelizadeh, 2006). Oil based drilling fluids (OBFs) have become a great source of concern in relation to regulations of zero discharge (Siddique *et al*., 2017).

The properties of mud change when foreign materials from mud treatment additives and the formation being drilled get into the mud system. Many of the additives used in the formulation of OBM are toxic and require treatment before disposal of any form is possible. Mud is said to be toxic when hydrocarbons, heavy metals, inorganic salts, surfactants, Hydrogen Sulphide (H_2S), Carbon dioxide and Benzene, Toluene, Ethyl Benzene and Xylene (BTEX) are present. The presence of these toxic materials prevents them from being disposed into the environment (Darley and Gray, 1988).

SOURCES OF HEAVY METAL CONTAMINANTS

Heavy metals have varied means of entering the mud systems which include formation drilled, additives to drilling fluids, thread compound on pipe threads and crude oil. Some metals can enter the mud systems through additives that are added to alter some parameters. The metals that are commonly found include Barium from barite which is included as weighting agent and Chromium from chrome-lignosulfonate deflocculants. These are added during formulation to achieve desired properties such as appropriate mud rheology, density, mud activity, fluid loss control property etc (Bakhshian *et al*., 2009).

The heavy metals can also get into the system from the formation being drilled. When drilling through a formation containing crude oil or if a kick occurs and oil flows into the well, heavy metals can get into the mud system. Crude oil therefore will typically contain varied concentrations of heavy metals (Al-Haleem *et al*., 2013).

According to McDonald (1993), a source of heavy metals in drilling fluid is the thread section (pipe dope) used in the threads of drilling downhole drill strings. The metals have the potential to leach out into the drilling mud especially if the pipe dope is used in excess.

Several barrels of mud and cuttings per foot are generated from a single well being drilled (Gbadebo *et al*., 2010a). In fact, for a 1 m length of hole drilled 0.6 cubic meters of waste can be generated. Of this amount, between 60 – 80 % is made of spent drilling mud (Steliga and Uliasz, 2014). According to Gbadebo *et al*. (2010b), the differences in drilling compositions and geology of the formation lead to complex mixtures of drilling mud waste which cannot be easily grouped into any waste profile.

Spent drilling fluids contain drilled cuttings which ultimately record some amounts of heavy metals such as zinc, Lead, Copper, Cadmium, Mercury, Barium and Chromium which pose serious environmental problems due to their toxicity and high mobility in natural water ecosystems (Reis, 1996; Iyagba and Opete, 2009).

According to Obianuju (2014) heavy metals are among the parameters such as pH, salt, hydrocarbons, and cuttings that should be considered during disposal of mud. Heavy metals are metallic elements having density greater than 5 g/cm^3 (Manea and Popescu, 2008; Obianuju, 2014). Due to their potential toxicity, it is important to analytically estimate their presence in drilling wastes when these materials are to be disposed of to the environment (Obianuju, 2014).

Khan *et al*. (2004) stated that excessive disposal of heavy metals into the environment arising from industrialization and urbanization leads to varied problems worldwide. Contrary to organic pollutants which are biologically degradable, heavy metals cannot degrade into harmless end products.

EFFECTS OF HEAVY METALS ON LIVING ORGANISMS

According to Essoka *et al*. (2006) naturally, the concentrations of heavy metals in living tissues are normally at low levels and for proper functioning, human systems are required to be maintained at tolerable optimum levels. However, carcinogenic, teratogenic heavy metals pose severe health problems and may be accumulated in the human bodies through food chain (Zhao *et al*., 2016). Some metals are essential for proper functioning, while others like Lead, Cadmium and Arsenic are not essential and may be toxic. The effects of some selected heavy metals on living organisms are outlined in Table 1.

Heavy Metal	Health Effects
Cadmium	Carcinogenic Fever Muscle pain Lung diseases
Chromium	Lung cancer Kidney, liver disease Gastric damage
Zinc	Nausea Vomiting Diarrhea
Lead	Brain damage Teratogenic

Table 1: Effects of Heavy Metals on Living Organisms

II. MATERIALS AND METHODS

Two samples of oil-based muds were analysed: INV and ENV. The samples were used to drill a single offshore well but on different depth intervals. With INV, the weighting agent is calcium carbonate ($CaCO_3$). This mud type is employed in lengths close to the pay zone of the wellbore. ENV, the second mud sample is made of barite as the weighting agent. It was used in the upper section of the well. Tables 2 and 3 show the constituents of each mud sample.

The samples were centrifuged in a Centurion centrifuge to separate the liquid phase of the mud from the solid. After the set time, the liquid is poured out filtered. The weights are recorded. The solid mud samples are heated in an oven at a temperature of 120 ˚C overnight till a constant weight was obtained. The samples are then cooled to room temperature in a desiccator.

The centrifuged samples showing Liquid and semi-solid samples of ENV and INV muds are shown in Figure 1. The semi-solids phases showing ENV and INV mud: before drying (Left) and after drying (Right) is shown in Figure 2. The samples are then reweighed, and their weights recorded.

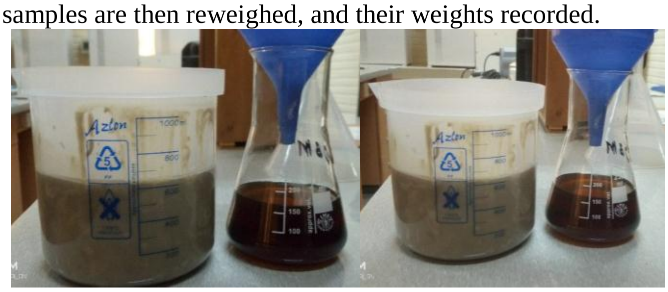

Figure 1: Centrifuged Samples showing Liquid and Semi-Solid Phases of ENV (Left) and INV (Right)

The dried mud samples are then digested according to ASTM 3974 – 81 standards. A 10 g sample each of dried mud INV and ENV is weighed into a 100 ml beaker. The weight is read and recorded. 20 ml of concentrated HNO_3 was slowly

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added to the sample. 60 ml of concentrated HCl was also added. The beakers were then covered and heated for 15 mins on a hot plate. To prevent splattering, the solution was not allowed to boil or bump. The beaker was removed from the hot plate and the content cooled in a desiccator. The solution is then filtered and topped up to 100 ml with distilled water.

Figure 2: Mud Samples showing ENV and INV Mud: before Drying (Left) and after Drying (Right)

The liquid and digested solid samples of both mud samples INV and ENV are analysed using the Atomic Adsorption Spectrophotometer (AAS).

ENV	Function
Saraline 185 V (70 %)	Base oil
Calcium Chloride Brine (30%)	Water/salinity source
Lime	Alkalinity source and emulsifier activator
Ez Mul NT	Primary emulsifier
Baracarb	Bridging agent
Vis Plus	Secondary viscosifier
Duratone	Filtration control additive
Geltone II	Primary Viscosifier
Invertmul	Primary emulsifier
Drill Treat	Oil-wetting agent
Barite	Weight additive

Table 2: Properties of ENV Oil – Based Mud

INV	Function
Saraline 185 V (70 %)	Base oil
Calcium Chloride Brine (30 %)	Water/salinity source
Lime	Alkalinity source and emulsifier activator
Ez Mul NT	Primary emulsifier
Baracarb	Bridging agent
Vis Plus	Secondary viscosifier
Duratone	Filtration control additive

Table 3: Properties of INV Oil – Based Mud

III. RESULTS AND DISCUSSIONS

The results of heavy metals analysis for ENV and INV are graphically displayed in Figures 3, 4, 5 and 6. From the distribution profiles of heavy metals concentrations in the drilling muds shown, it can be observed that the liquid phase of both ENV and INV contain appreciable concentrations of Lead, Copper, Zinc and Manganese. Some of these metals may be vital to humans, animals, and plants if within allowable concentrations. In this case however, most of them are detrimental to life forms especially in high concentrations and in cases of continual exposure.

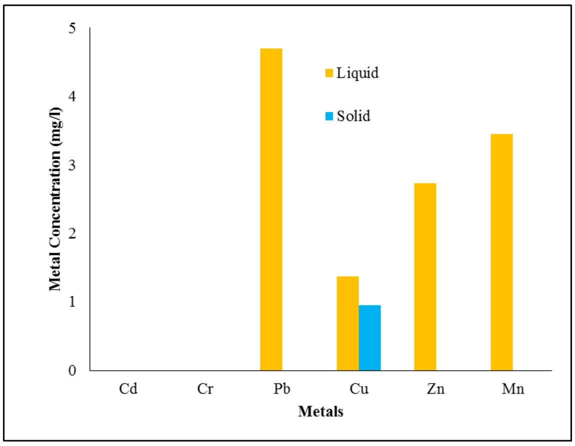

Figure 3: Comparison of Heavy Metal Distribution in Liquid and Solid Phase of ENV Spent Mud Sample

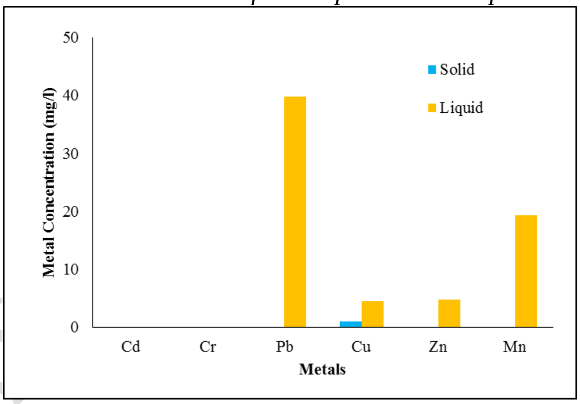

Figure 4: Comparison of Heavy Metal Distribution in Liquid and Solid Phases of INV Spent Mud

Apart from Copper, all other heavy metals analysed recorded concentrations less than 0.002 mg/L in the solid phases of both ENV and INV mud samples. Copper in the solid phase recorded concentrations of 0.9557 and 1.0357 mg/L in ENV and INV muds, respectively. This showed that the concentration of Copper was less than the limits by United States Environmental Protection Agency (USEPA) which is 1.3 mg/L.

In both ENV and INV the distribution of heavy metals followed the same trend. The order of heavy metal concentration is Lead > Manganese > Zinc > Copper for the liquid phases which corresponds to 4.7032, 3.4472, 2.7319, and 1.3692 mg/L respectively for ENV mud and 39.781, 19.368, 4.8289 and 4.5436 mg/L for INV as shown in Figure 6.

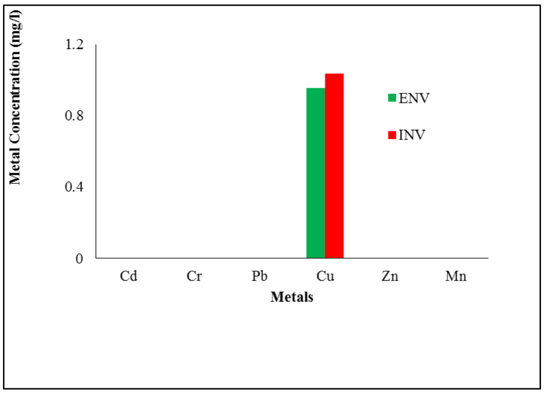

Figure 5: Comparison of Heavy Metal Distribution in Solid Phase of ENV and INV Spent Mud

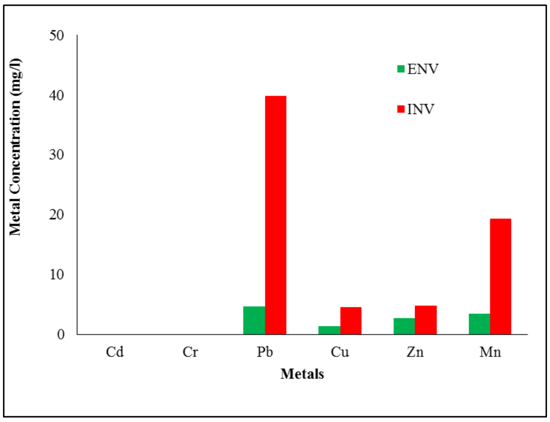

Figure 6: Comparison of Heavy Metal Distribution in Liquid Phase of ENV and INV Spent Mud

Of the six (6) heavy metals analysed in the liquid phase of the two mud samples, three (3) of them exceeded regulatory limits. These metals are Lead, Copper and Manganese. In ENV, the concentration of Lead was recorded as 4.7032 mg/L and the limit set by USEPA requires that the concentration should not exceed 0.01 mg/L.

The maximum value of 39.7810 mg/L obtained for Lead in this study far exceeds USEPA acceptable limit of 0.01 mg/L. This metal was more abundant in the liquid phase of INV than ENV. However, the concentration of 4.7032 mg/L in the liquid phase of ENV still exceeds regulatory limits. This metal ranks first in concentration in the two oil-based muds analysed. There is a possibility of increased Lead concentration in any environment that these muds are disposed. If these metals get into the environment by accident spills or through intentional disposal it can result in serious contamination. According to Veil *et al.*, (1999), unlike WBMs, OBMs have the potential of producing long term and more severe environmental impacts on flora and fauna.

Generally, the Lead content of the contaminated oil-based muds from the offshore field are far higher than the recommended allowable concentration of 0.01 mg/L by USEPA. What this means is that, if these waste muds were disposed of in an aquatic environment, it could lead to increased Lead levels. Lead is relatively higher in concentration in the INV mud than in ENV oil-based mud. Lead can cause brain damage and foetal development.

Cadmium and Chromium were almost non-existent (<0.002 mg/L) in both ENV and INV oil-based muds as displayed in Figures 3 and 4. In the solid phase the metal with the highest abundance was Copper (0.9557 mg/L for ENV and 1.0357 mg/L for INV) as shown in Figure 5. Of the six heavy metals analysed in the solid phase of the two contaminated mud samples, Cadmium, Chromium and Zinc showed concentrations less than the allowable limits for drinking water set by USEPA.

The concentrations of Zn in the solid phase of both mud samples were all less than 0.002 mg/L. However, in the solid phase the concentration of Zn was higher in INV (4.8289 mg/L) than ENV (2.7319 mg/L) mud. Both were however lower than the allowable limit of 5.0 mg/L. Gbadebo *et al*. (2010a) stated that, even though Zn has been found to be present in humans in low concentrations, its prolonged presence in the human body in large concentrations could lead to health effects such as fatigue, dizziness etc.

Manganese is about six (6) times higher in INV (19.3680 mg/L) than in ENV (3.4472 mg/L) mud in the liquid phase and less than 0.002 mg/L in the solid phase. The allowable limit by USEPA is 0.05 mg/L concentration.

IV. CONCLUSIONS

This study revealed the high concentration of some heavy metals in the two (2) OBM samples in a Ghanaian oilfield. The concentrations of Cadmium, Chromium were below regulatory limits. The heavy metal analyses conducted in this study revealed high concentrations of Lead, Copper, Zinc and Manganese above regulatory limits. This could result in their bioaccumulation in aquatic and land organisms in the event of a spill. It is therefore recommended, for the purpose of this study, that waste drilling mud should be properly analysed for these metals and treated accordingly to reduce their concentrations to levels accepted by regulatory bodies. After this the wastes can be disposed of properly by following standards laid down for such purposes. Offshore disposal of these muds should be totally discouraged and prohibited.

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