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Toxicity Analysis of an Oilfield Reserve Pit in India

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ABSTRACT
Drilling processes in Oil and Gas Industry generates a large volume of spent mud which are being directly dumped into pits in the vicinity of the operational site. This paper reports the qualitative analysis of various environmental factors on 8 samples (4 water phase and 4 sludge phase) collected from a reserve pitX in India. Heavy metal detection analysis was also performed on the samples, and the results put on an alarm to it proper disposal in order to prevent the toxicity which will be hazardous to the commoners residing near these sites. Moreover, Bioremediation technique has been tested on these samples to bring a slag to its toxicity, which has proved its potential as an efficient waste disposal method.
Keywords: *Oil Field Reserve Pit; Drilling Mud; Toxicity; Cutting Disposal*

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Introduction

In Oil and Gas Industry, drilling operation usually generates a large volume of drill cuttings and spent mud and hence drilling mud system has become an integral part of it [1]. Due to the potentially detrimental effect of drilling fluids on the environment, it becomes a strenuous job to safely dispose the used drilling mud [2,3]. In the entire period of drilling a well, various mud systems maybe adopted depending on the economical, technical, geological and environmental factors [4].The final disposed mud is a complex mixture of fluids based on water (Water based mud (WBM)), oil (oil based mud (OBM)) and various chemical additives. This complex mixture along with the drill cuttings settles in a reserve pit, and splits into a water phase and a sludge (or mud)phase[5].
Many parts of India is rich in agriculture and farm. It is also full of hydrocarbon resources and taking that in context various oil giants are operating in various sites of the country. The area near these sites are suffering from the issues of pollution due to industrial activities. The land near oilfields are getting barren [6]. The ineffective disposal of drilling mud causes great complication for the people living near the oil rigs. Their fields and farms are getting contaminated from the complex chemical constituents of the drilling mud[4]. Heavy metal is one of the most feared contaminants in the nearby areas, whose effects are still not known by the science community. This toxin drains man's health without even knowing[7]. By the time commoners realize, it is too late. Numerous methods for disposal and treatment of drilling waste have been discussed in literature[4, 8, 9]. Methods to be implemented are solely based on Chemical Treatment. Currently, various physical treatment plants are installed in rig sites, but these require specifically skilled rig personnel. Moreover, the physical treatment plants requires to be setup at the site and are often limited to economy and site availability in the region. Chemical methods are intuitive to use as it requires a lesser workspace, and no specific installation of equipment is required[9].
This paper discusses the toxicity of a reserve pit X in India. The qualitative environmental and heavy metal analysis were performed on these samples. The results showed the presence of toxic elements in the studied reserve pit. Probable disposal methods were discussed. Bioremediation method is employed to the collected samples for it eco-friendly degradation, which will be a boon to the commoners from the hazardous effect of the toxicity of landforms in the vicinity of the scrutinized reserve pit.

MATERIAL AND METHODS

Collection of Samples

In this study, a total of 8 samples (4 water phase and 4 sludge phase) were collected from reserve pit ofX-field. The pit was divided into four sections, as shown in Figure 1, two samples were collected from each section. Section I is nearest to the discharge point of the solids-control equipment. The water-phase samples (WP1, WP2, WP3, WP4) were collected by dipping the sampling container just below the surface of the water to mid-depth where possible. The sample collection point depend on access to the water phase at the edge of the pits. The sludge phase (or mud phase) comprises of solids including clay, sand and other drill cuttings. These samples were collected by scooping the top of their serve pit sludge with sampling containers. Sampling was done carefully to minimize air bubbles in the containers.

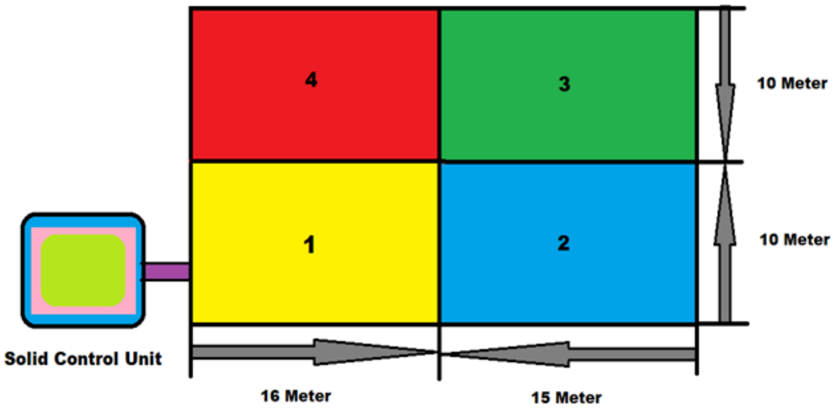

Figure 1. Schematic of Candidate Reserve Pit

Environmental Parameter Analysis

Analysis for various parameters including pH, salinity, dissolved oxygen (DO), odour, turbidity of sludge phase and water phase were carried out according to standard guidelines. These parameters were measured within 1-2 days after sampling to obtain representative results of the pit conditions.

Temperature

Temperature of each sample was measured on field after sampling from the pit using laboratory thermometer.

pH

The pH of the water phase was measured directly. For the sludge samples a sludge-water suspension of equal volumes of sludge and distilled water were mixed vigorously, allowed to settle and then the pH of the suspension was measured with the HannaH198304 pH meter.

Electrical Conductivity (EC)

Water phase conductivity was measured directly using the Hanna H198303 EC meter whereas conductivity readings of the sludge-water suspension were recorded for the sludge phases alone using the same instrument.

Dissolved Oxygen (DO)

DO (mg/l) readings were recorded for all the samples using Hach 2968800 DO meter according to standard procedures.

Salinity & Total Dissolved Solids (TDS)

The salinity and total dissolved solid of the samples were measured by standard electrical conductivity methods using the REED SD-4307 Salinity meter and Hach HQ 40D Portable TDS meter.

Turbidity

Turbidity was measured using the Hanna TU5200 Turbidimeter.

Qualitative Heavy Metal Analysis Experimental

The presence of heavy metals viz. Arsenic, Lead, Mercury, Chromium and Cadmium leading to the toxicity of the sludge phase and water phase was analysed experimentally using the procedure stated in literature [10].

Arsenic (As)

1 ml of 3M HCl was added to the samples, centrifuged and the centrifugate separated. 10 drops of concentrated HCl added to the residue, stirred and heated in water bath for one minute. Later it was centrifuged again and the centrifugate removed. Further, 8 drops of water and 4 drops of concentrated HCl was mixed with the residue, centrifuged and the residue obtained was washed with 4 drops of

concentrated HNO_3, heated for 5 minutes in water bath and 5 drops of 0.5M $AgNO_3$ added and stirred. Finally, 15 drops of 2.5M Sodium Acetate solution was added. The formation of reddish-brown precipitation confirms the presence of Arsenic.

Lead (Pb)

4 drops of 3M HCl was added to the sample, mixed thoroughly and centrifuged. It was then allowed to precipitateandanother1ml of 3MHCladded to the supernatant liquid for effective precipitation. The solution was then centrifuged and the centrifugate removed. The precipitate was washed with 10 drops of cold water and 1 drop of 3M HCl and the water wash was removed. 10 drops of water was then added and heated for 3 minutes in water bath. It was centrifuged quickly and the centrifugate removed immediately while keeping the mixture hot in the water bath. 4 drops of 1M K_2CrO_4 was added to it and the mixture centrifuged. A yellow precipitation confirms the presence of lead.

Mercury (Mg)

10 drops of 3M HNO_3 was added to the samples and heated in water bath for 3 minutes. It was then centrifuged and the centrifugate separated. To the residue 4dropsofAquaRegiaand10drops of water was added and heated in water bath for 2 minutes. Then the mixture was cooled and 2 drops of $BaCl_2$ solution added. Greyish precipitation indicates the presence of mercury.

Chromium (Cr)

10 drops of saturated NH_4Ac was added to the sample. Then to it 1ml of 3M Acetic acid and then 3M ammonia added until the solution becomes ammoniacal. The resulting solution was centrifuged and separated. 1M $Ba(Ac)_2$ was then added dropwise to the centrifugate until the precipitation was complete. The solution was again centrifuged and 10 drops of 3M HCl added to it, heated for 1 minute in water bath and centrifuged. 2 drops of centrifugate was taken on a piece of filter paper and 2 drops of H_2O_2 was taken on the same paper. A faded formation of blue colour confirms the presence of chromium.

Cadmium (Cd)

10 drops of $HNO_3$was added to the samples, heated in water bath for 3 minutes and centrifuged. The centrifuge was taken out into a petri dish and 3 drops of conc. H_2SO_4added. The solution evaporates with dense white fumes and only 2-3 drops of liquid remained. The solution was allowed to cool and 5 mL of water added to it and centrifuged. The centrifugate was removed and to the precipitate, 3 drops of conc. NH_3 was added while stirring. The solution was again centrifuged and the residue removed. To the centrifugate 1M KCN was added to decolourize the solution. Then 5 drops of thioacetamide solution added and placed in boiling water for 5minutes. Yellow precipitation indicates the presence of cadmium.

RESULTS AND DISCUSSION

Environmental Parameters

Temperature: Figure 2. shows the variation of temperature of the four water phases. It was observed that the temperature of the four water phases was in the order- WP3 < WP2 < WP4 < WP1, which is distance depended from the solid control unit.

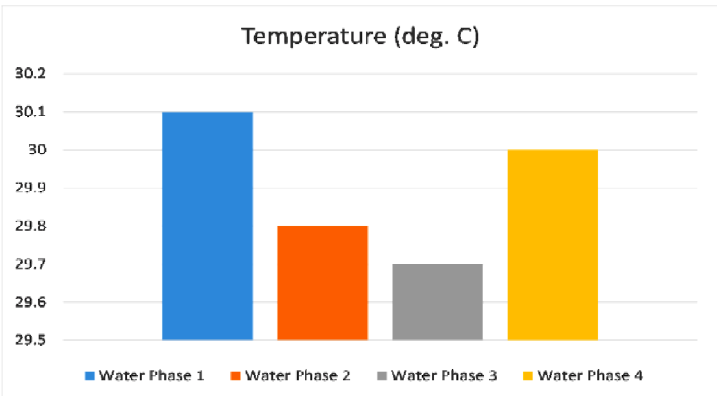

Figure 2. Temperature Dependence of the Four Water Phases

Water Phase 1, which is nearest to the solid control unit has the highest temperature. The average temperatureofthecollectedsampleswas29.7^{0}C which was because of the ambient temperature conditions of the area.

Odour: Thewaterphaseandsludgephasesamples2&3hadapungentodourwhichmight be due to the trapped H2S gas or other chemicals. Mud phase 1 is predominantly an oil-based mud or diesel spotted mud system which gave an oily odour. The odour of all the phases is detailed in Table 1 below.

Table 1: The Odour of the water phase and sludge phase samples collected from reserve pit of X-field

Samples	Odour
Water Phase	Pungent
Sludge Phase 1	Oily
Sludge Phase 2	Muddy and Pungent
Sludge Phase 3	Pungent
Sludge Phase 4	Muddy

pH: The pH analysis indicated that all the samples are basic in nature, with values lying within the range of 8.8 to 9.4 on the pH scale, which is an obvious characteristic of drilling muds. The results thus implied that all the phases of the drilling mud are free from any acidic content. Table 2 shows the change in pH w.r.t time in laboratory condition.

Table 2: Change in pH with Time in Laboratory Condition

Sludge Phases	0 days	7 days	14 days	28 days	35 days
pH of SP 1	9.1	8.9	8.5	8.3	8.0
pH of SP 2	9.0	9.0	8.8	8.7	8.5
pH of SP 3	8.8	8.7	8.6	8.3	8.1
pH of SP 4	9.1	8.7	8.5	8.4	8.2

The results of Table 2 also indicates that the pH of all the samples decreases by around 5% per week. This decrease in pH can be backed by slight decrease in temperature because with decreasing temperature, H^+ ion decreases due to increased tendency to form H bond. And thus, pH increases. The above statement is justified from the results shown in Figure 3.

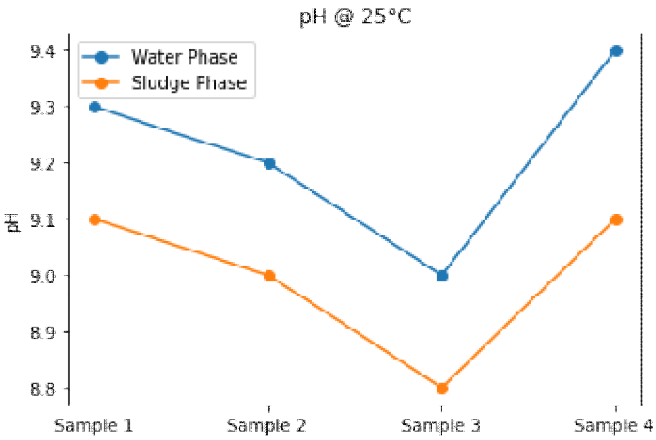

Figure 3. Change in pH of Water and Sludge Phase at a Constant Temperature of 25°C.

Electrical Conductivity (EC): The Electrical Conductivity is a measure of the ability of the phases to conduct electricity and a qualitative measurement of the number of ions or nutrients present in water and sludge phases. The low EC values of Sludge Phase (SP) samples 1 & 4 is a characteristic of its high sand content as it was sampled near the solids discharge point. Relatively high ECs of SP Samples 2 & 3 is an indication of availability of relatively more negative charged sites (clay) for the cations to be held in the sludge. This variation is depicted in figure 4.

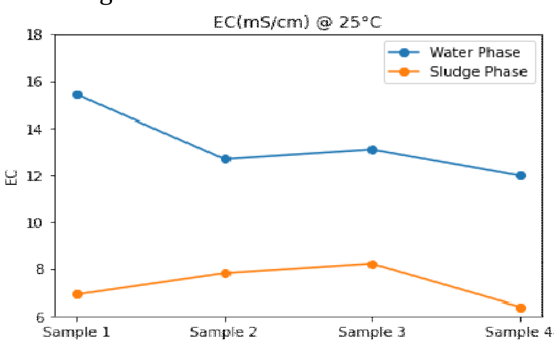

Figure 4. Electrical Conductivity Variation of Water and Sludge Phase at Constant Temperature of 25°C.

Dissolved Oxygen (DO): Dissolved Oxygen (DO) measures the amount of gaseous oxygen dissolved in an aqueous solution. An average DO value of 1.474 mg/L shows the ability of microbes to biodegrade the drilling fluid and some of itsproducts. The DO of the water phase is higher than the sludge phase as the sludge phase consists of solid particles, hence the oxygen content of it is much lower than the water phase (Figure 5).

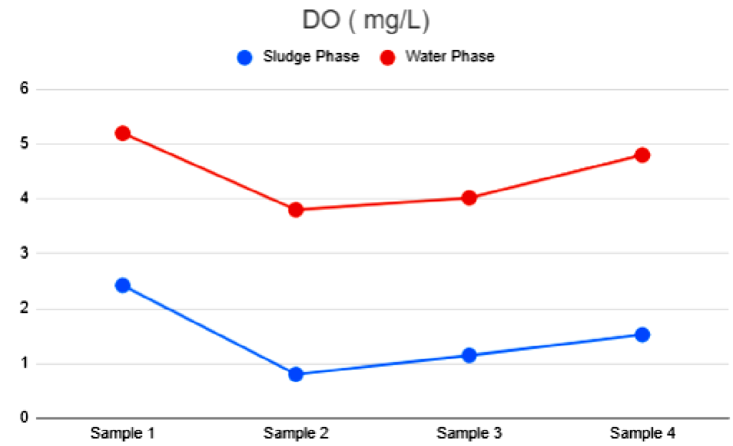

Figure 5. DO Variation of the Four Samples in Water and Sludge Phase

Salinity: The average salinity is 3006.80 mg/L which is an approximate indication of total concentration of salts dissolved in the drilling fluidsystem. Figure 6 depicts that the salinity of sample 1 and 3 are in higher range than sample 2 and 4. This implies that the salinity follows a diagonal distribution for both water and sludge phase of the samples.

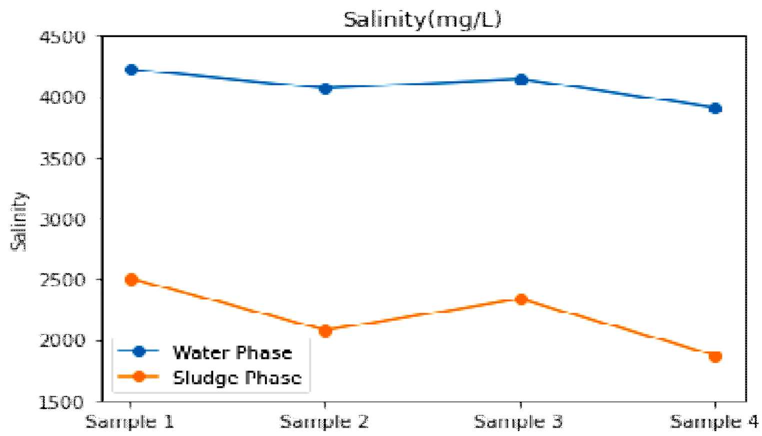

Figure 6. Salinity Effect onWater and Sludge Phase of the Four Samples

Total Dissolved Solids (TDS):TDS is the amount of organic and inorganic matter dissolved in the water phase. It is evident that TDS is high in site 1 and 4. It is because of the fact that these two sites are close by to the solid control unit. This is depicted in Figure 7 below.

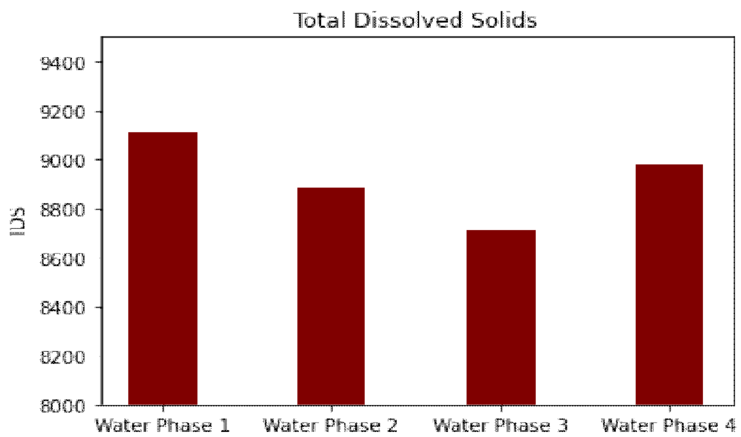

Figure 7. TDS Variation of the Four Water Phase Samples

Turbidity: Figure 8 shows the turbidity of the water and sludge phase of the four samples. The sludge phase samples exhibits higher turbidity compared to the water phase samples because of the presence of solid content in the sludge phase. The range of turbidity of these samples varies from 85.2 – 1245.3NTU.

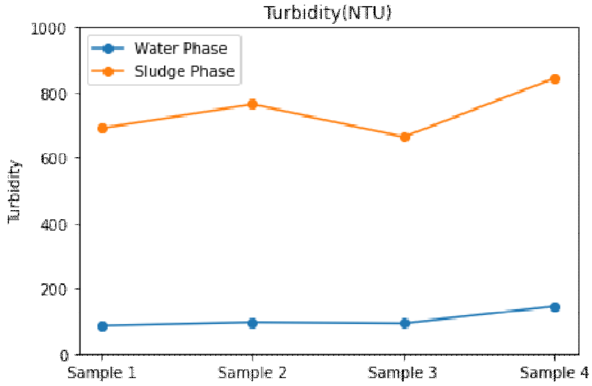

Figure 8. Turbidity Disparity of the Four Samples in Water/Sludge Phase

Results of Qualitative Heavy Metals Analysis

Effective detection of heavy metal from water phase is necessary because a high degree of damage is incurred by the nearby landforms due to seepage of the water-phase into them. Table 3 below exhibits the presence and absence of heavy metals viz As, Pb, Hg, Cr and Cd in all the four water phase samples. Presence of As, Cr and Hg in almost all the phases is a risk factor for the people residing near the disposal areas. Thus, proper and eco-friendly disposal techniques are to be incorporated to nullify the heavy metal content in water phase that seepage to the landforms of nearly areas. A few of such disposal methods are discussed in the next section.

Table 3: Heavy metal contents in all the four water phases.

Heavy Metals	Water Phase 1	Water Phase 2	Water Phase 3	Water Phase 4
Arsenic	Present	Present	Present	Present
Lead	Absent	Absent	Absent	Absent
Mercury	Present	Absent	Present	Present
Chromium	Present	Present	Present	Present
Cadmium	Present	Absent	Present	Present

Bioremediation Studies

The regions in India where humidity is always higher than the average, the technique incorporating microorganisms is very likely to be acceptable. It takes microorganisms like bacteria, fungi, etc. into account for biologically degrading organic waste into innocuous state [11-14]. The microorganisms break the long chained aliphatic and aromatic hydrocarbons and decreases the total petroleum hydrocarbon content from the target sample. Indigenous microorganisms are used to prevent antagonistic interaction with the native microorganisms[14-16].

In this paper we report the performing of a pilot experiment on our samples. We incorporated Biosurfactants composing of *P. aeruginosa,* a Pseudomonad was incorporated into the samples. The result implied that the petroleum hydrocarbon (PAH) was digested by the bacteria strains with time as indicated by UV-Visible Spectroscopy. This bioremediation of PAH by biosurfactant with time in days is plotted in the figure 9 below. The decrease in the %PAH with time implied that biosurfactants containing bacteria strain shows potential as good bioremediation agents.

However, this process is inefficient for small quantity and is time consuming. Moreover, proper environment should be provided for the bacteria to culture.

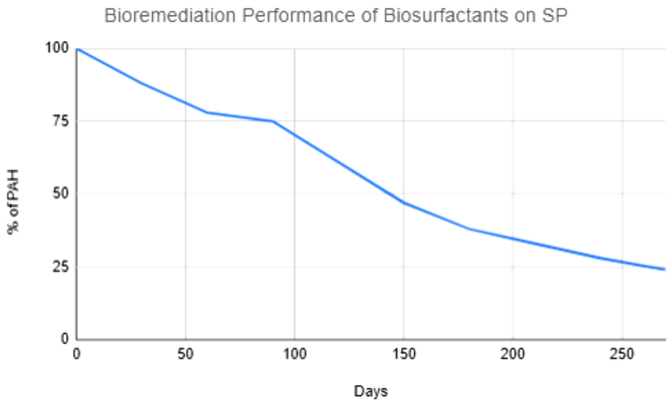

Figure 9. Bioremediation Performance of Biosurfactants on Sludge Phase

DISPOSAL METHODS

Drilling operations generate a large volume of wastes, although some of these waste materials can be recycled, which needs to be disposed off safely. Currently numerous methods are taken up by operators and some of the important methods for onshore disposal are discussed below[4,17]. Land farming, Annular Injection, Incineration, Thermal Desorption, Solidification, Deep, Pitless Drilling

Land farming

Liquid portion of the reserve pit is drained off and properly disposed so thatpotential of liquid running off to the water table is prevented. The remaining non-pumpable materials are allowed to dry prior to burial. Land spreading reduces the organic and inorganic constituents through dilution, biodegradation and adsorption [18]. Low concentration of aromatic hydrocarbons does not impose long term problem to soil formation [4].

Annular Injection

If the conditions allow and the ground water level is known to the drilling operator, then the reserve pit materials can be slurrified and injected into the casing annulus [2]. Drilling with OBM in environmentally sensitive areas are also feasible with this.

Incineration

High temperature waste treatment system can be installed on the rig site. These units generate air emission in the form of partially combusted hydrocarbon particulates. But the cost associated is high and requires large installation facility. Moreover, there is short term GHG emission and safety issue due to heat source. The incinerator must keep up with the ROP to achieve high efficiency [4].

Thermal Desorption

Low temperature thermal desorption uses thermal stripping to heat the oil and separate petroleum hydrocarbon from the drilling fluids. This process results in decrease in TPH and heavy metals by a significant amount, thus keeping them below the permissible level[19]. This also reduces the size of surface facility to treat and recycle the used fluid.

Solidification

Solidification of the wastes offers improvement over landfarming. It reduces the potential mobility of heavy metals and other hazardous materials. Reserve pit materials can be mixed with solidification agents such as commercial cement, lime kiln dust, etc. to form a hard matrix[4]. This has commercial benefits and can be used as construction materials. This method is not widely practised, but it is the responsibility of the operators to accept it widely.

Deep-Well Disposal

This process includes injection of drilling waste into permeable subsurface rocks below the aquifer. But disposal option is available to only certain geological areas [2]. There is also a possible contamination risk of oceanic zone due to casing failure.

Pitless Drilling

Industry leaders are developing solid control devices for processing waste using continuous wireline operation to eliminate need of reserve pits. This process uses both mechanical and chemical separation methods to retrieve the cuttings from drilling fluid during the process of drilling operation[4].

The processing steps involves the following protocols-

- Used drilling fluid is pumped through the hydrocyclones that separate the solids. Useable drilling fluid is returned to the system.
- Flocculation process is involved to reduce the waste from the hydrocyclone stream. Extracted water is stored in a water tank for reuse.

- The flocculated material is dried and compressed into bags and disposed safely.

Looking into the environmental benefits incorporated with the system, use of this process is highly valued.

CONCLUSION

Environmental parameter analysis and heavy metal analysis was performed on a total of 8 samples (4 water phase and 4 sludge phase)collected the reserve pit of X-field by dipping the sampling container just below the surface of the water to mid-depth where possible. Based on the result of these analysis, we can conclude that the qualitative environmental parameters tested on the samples tend to increase towards the side of the reserve pit which is near the solid control unit. This is because at that part of the pit, there is lower entropy in the fluid. The drilling mud is emptied on to the pit through part 1. So, there is always a movement taking place in that part and thus the contaminants never get accumulated at that part. This project enabled us to gain insights not only on various parameters that governs the physical and chemical behaviour of drilling mud waste in a reserve pit, but also on the different methods widely used in the industry to safely dispose off the wastes. As future prospects in this study, the quantitative analysis for heavy metal concentration will be performed for a better understanding of concentration distribution in the pit.

Moreover, bioremediation of the petroleum hydrocarbon was studied and results look effective when done in a large scale. Also, some mechanical and chemical techniques were discussed which deal with all the waste solids. Practising these methods and techniques will allow the petroleum industry for more precise and safe disposal methods, hence minimizing environmental footprint and sustaining its way through the competition it is facing.

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