



## Biodegradation Potential of Oil-based Drill Cuttings Encapsulated with Cement in the Soil Environment

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**ABSTRACT:** Biodegradation potential of slabs made from oil-based drill cuttings encapsulated with cement in a soil environment has been experimentally investigated. Results of soil analyses show that physico-chemical and biological characteristics of the soil environment as; pH (5.6 – 3.9), temperature (27.7 – 39.5 °C), redox potential (-114mV – (-80mV), total organic carbon (12.7% - 7.3%), sulphate (0.7 – 0.2mg/l), nitrate (6.7 – 2.2mg/l), moisture content (82-89%) and total microbial count ( $10^5$  –  $10^{13}$  cfu/g). Experimental results shows a mass loss of oil base drill cuttings encapsulated with cement slab during the period of the study, indicating approximate linear relationship between mass loss and time. When the log of mass-loss is plotted against time, an approximate linear relationship is obtained confirming a first-order chemical reaction for the biodegradation process. Results of the analyses of the soil sample indicate an environment that has the potential to degrade cement encapsulated oil based drill cuttings. @JASEM

Environmental management of drilling cuttings have been a source of worries to various crude oil producing companies in Nigeria probably because of its large volume generated and environmental consequences. For example, during the drilling campaign in Azuzuama Field, an estimated amount of 900,000 tonnes of cuttings material was generated (EIA Report, 2001). Environmental impacts of improper management of drill cuttings have reported. For example, its effects on sea-bottom (benthic) ecosystems (Atlas, 1988) increased turbidity of surface water bodies (Atlas, 1981) and its unsightly nature (Rim-Rukeh, 2009). Generally, drill cuttings have been classified as environmental toxic (Atlas 1981; Atlas 1988; Davies *et al.*, 1989; Kingston, 1992; Olsgard and Gray 1995).

Various methods are available or have been proposed for handling and subsequent treatment or disposal of drill cuttings (Kjeilen *et al.*, 1996; Brown and Root, 1997; DPR 2002). One of the most common methods of drill cuttings management in Nigeria is encapsulation. This method involves chemical stabilization/immobilisation of the drill cuttings (contaminants) within a solid matrix that has favourable leaching characteristics. Common fixation formulations include those based on cement. It has the advantages of having ready available materials and improves waste handling. Fixed drill cuttings are commonly used for block moulding which are eventually used in the fencing of oil facilities and other construction activities in Nigeria. Lately significant attention has been turned toward encouraging the natives within the Niger Delta area of Nigeria to use such material (blocks made with cement encapsulated oil based drill cuttings) in the building of residential houses. In the United States of America, a report on the degradation of pile made with cuttings fixed with cement at Heather alpha showed that in the top 2 cm of the pile, oil content decreased on average by 22 % after 2 years (IOE, 1985). Unfortunately, the level of understanding concerning the rate of these natural occurring

reactions is quite limited, especially in the Niger Delta area of Nigeria. This work examines biodegradation of oily drill cuttings fixed with cement that are commonly used for the moulding of building blocks and other construction activities in the Niger Delta area, Nigeria.

### MATERIALS AND METHODS

Soil sample used for the study was collected from the site of an oil producing well (Odugri Well 5 in Odugri Field) located in Oguta Local Government Area, Imo State. The geographical coordinates of the well is N 05° 38' 39.9" E006° 39' 37.7". The choice of the site was based on the following: history of collapsed fence built with blocks made from cement-encapsulated oil base drill cuttings. Ecologically the area lies within the lowland swamp forest of the Niger Delta region of Nigeria. The area is characterized by streams, floodplain and waterlogged borrow pits. The vegetation type is typical of freshwater types, diverse and rich in floristic composition.

At the oil well location, about 50kg of soil sample was collected at a depth of about 500cm using a soil auger. The choice of 500cm is based on the average depth at which the foundation of the oil well location fence was dug. At the location, soil sample was collected from three points and composited to form a representative sample. Soil samples for microbial analysis were collected in sterilized McCartney glass bottles and stored in an ice-chest, while those for physico-chemical analysis were collected in polyethylene bags. The study was conducted in the month of July, 2011. Soil sample was transported immediately to the Federal University of Petroleum Resources, Effurun, Delta State Environmental Science department laboratory for analysis.

At the laboratory, soil sample was analysed for the following parameters; pH, temperature, redox potential, total organic carbon (TOC), nitrate,

sulphate, total microbial count (TMC), and moisture content. These parameters are good environmental impact indicators for biodegradation of wastes and environmental assessment (Videla, 1996; Godley 2003; Stein, 1995). pH, and temperature was measured *in-situ* using a multi-parameter water quality (model 600 UPG). Note that the multi-parameter water quality monitor was properly checked and calibrated before and after use. Redox potential was measured *in-situ* using Orion multimeter (model 1260) and combined platinum / silver (silver chloride electrodes). Total organic carbon of samples was determined using an automated TOC analyzer (ESML 690). Nitrate and sulphate concentration of samples was determined using the Ultraviolet Spectrophotometric Screening technique (Unicam uv/visible spectrophotometer-MS/27), and turbidimetric method respectively. The amount of moisture was determined by mass difference (mass – loss technique) and expressed as a percentage. Total microbial count of samples was determined using the rapid agar dipstick method. The choice of the rapid agar dipstick method is based on its ease of application and reliability; it can be used on site and is widely reported in literature (Bloomfield *et al.*, 1998; Wang *et al.*, 2006; Willinger *et al.*, 2005; Nato *et al.*, 2003; Olsen *et al.*, 2004). Into each sample, an agar nutrient dipstick was dipped into it for 20 minutes. The stick was then retrieved from the system and incubated in a warm oven for 24 hours. The population of microorganisms was determined by comparing it with a calibrated chart provided by the manufactures (Boots Micro – check company, Nottingham, UK). All methods of analyses applied in this study are consistent to that of the Department of Petroleum Resources (DPR, 2002), American Public Health Association (APHA, 1992).

At the laboratory, the 50kg of the soil sample was equally divided into 5 plastic containers. Cement encapsulated oil-based drill cuttings were prepared by mixing 1.0 kg Eagle cement; 500g of the oil-based drilling cuttings and 2L of water. Mixing was mechanically carried out to ensure homogeneity in composition. The mixture was cast into a rectangular mould of dimension 1cm x 3cm x 5cm and allowed to stand for 24 hr. The demoulded concrete is now ready for the experiment. The average mass of the prepared slabs ranges from 29.50g to 30.80g, and 5 (five) pieces of the cement encapsulated drill cutting slabs were prepared for the study. The method used in preparing the slabs is consistent with known methods (Sand *et al.*, 1987). The prepared slabs were weighed before and after each test using a weighing balance (Mettler Balance Model AE 166) with the mass of each slab determined to the nearest 0.001g.

Into each of the plastic containers containing the soil sample, one slab each of the cement encapsulated drill cuttings was buried to a depth of about 5cm. The experimental set-up was left for a total of 20 weeks expose to the natural atmospheric environment. At the end of each experimental period, which is at intervals of 4 weeks (i.e. 4, 8, 12, 16, and 20 weeks) the slab was retrieved from soil environment, washed, dried, and weighed.

## RESULTS AND DISCUSSION

Results of the physico-chemical and biological analyses of soil sample are presented in Table 1.0. pH values of the soil sample observed throughout the study period indicate a decrease i.e. from 5.1 (at the start of the study) to 3.9 (at the end of the study). The changes in pH could be ascribed to the production of acidic metabolites. Aerobic and anaerobic biodegradation of aliphatic and aromatic hydrocarbons leads to production of organic acids (Madigan *et al.*, 1997; Gottschalk, 1986; Cerniglia, 1992; Cerniglia and Heitkamp, 1989). Verstraete *et al.* (1976) reported a near doubling of rates of biodegradation of gasoline in an acidic (pH 4.5) soil. Rates dropped significantly, however, when the pH was further made to be more acidic.

**Table 1.0:** Physico-chemical and biological Characteristics of Soil Sample

Parameters/Units	Exposure period (weeks)				
	4	8	12	16	20
pH	5.1	4.9	4.5	4.1	3.9
Temp. (°C)	27.7	31.5	33.2	37.7	39.5
Redox Potential (mV)	-80	-97	-99	-102	-114
TOC (% dry wt)	12.3	10.1	9.4	8.7	7.3
NO <sub>3</sub> (mg/g)	6.7	5.6	4.1	3.6	2.2
SO <sub>4</sub> <sup>2-</sup> (mg/g)	0.7	0.5	0.3	0.3	0.2
Moisture content (%)	85	89	82	89	83
TMC (cfu/mg)	10 <sup>5</sup>	10 <sup>7</sup>	10 <sup>8</sup>	10 <sup>11</sup>	10 <sup>13</sup>

Temperature is an important parameter in the investigation of microbial degradation, because it can modify the state of substance to be degraded. Rates of degradation are generally observed to decrease with decreasing temperature; this is believed to be a result primarily of decreased rates of enzymatic activity, (Atlas and Bartha, 1972; Gibbs *et al.* 1975). Higher temperatures increase the rates of hydrocarbon metabolism to a maximum, typically in the range of 30 to 40°C, above which the membrane toxicity of hydrocarbons is increased (Bossert and Bartha, 1984). For example, the growth rate of *E. Coli* bacteria was found to be slow at temperature below 20°C and faster at temperature ranging from 25°C to 40°C (Booth, 1971). Temperature of the soil sample was within the range of 27.7°C –39.5°C and is within limits for growth of microbial activity. This observed

temperature range is suitable for microbial growth and degradation of hydrocarbons.

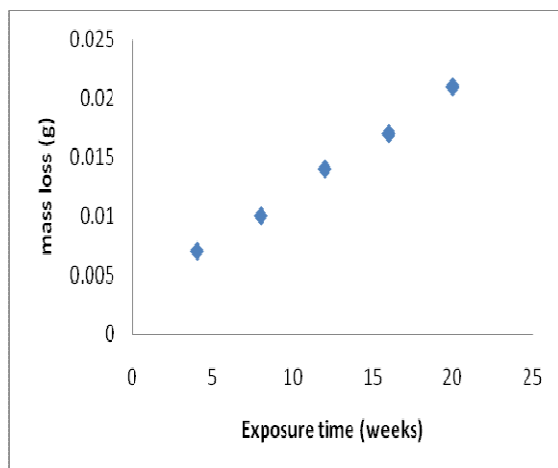


Fig. 1: Variation of mass loss of slabs with time.

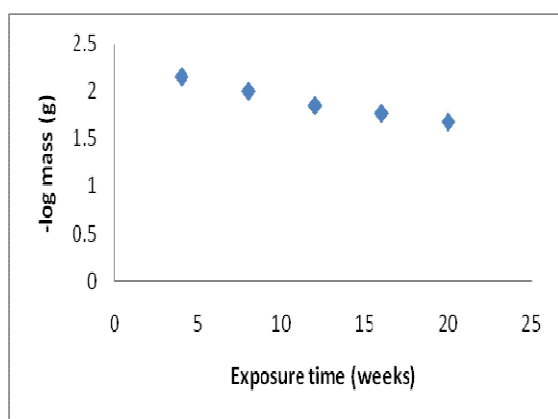


Fig. 2: Plot of log of mass log versus exposure time

Redox potential (Eh) describes the oxidizing or reducing state of an environment and is related to the amount of oxygen in the environment. It can be used to determine the class of bacteria that is likely to grow in an environment. Eh has been used to determine the suitability of a culture medium for anaerobic or aerobic bacterial growth. It has also been used to assess corrosion hazard due to Sulphate Reducing Bacteria (SRB) in soils and to predict the corrosion behaviour of aluminium nickel and zinc in cultures of different bacteria (Pritchard, 2002). SRB are only able to grow in highly reduced conditions (redox potential less than  $-100\text{mV}$ ) (Pritchard, 2002). Experimental results showed soil samples have very low redox potential values ( $-114\text{mV}$  to  $-80\text{mV}$ ). A low potential indicates that the oxygen content of the soil is low, and consequently the conditions are ideal for the proliferation of anaerobes.

The supply of organic matter is an important factor for the survival of microorganisms as they require

organic carbon as an electron donor. Organic carbon is utilized by bacteria for the production of new cellular material (assimilation) and as an energy source (dissimilation). TOC values of the soil sample observed throughout the study period indicate a decrease i.e. from 12.3 % dry wt (at the start of the study) to 7.3 % dry wt (at the end of the study). The levels of  $\text{NO}_3^-$ , and  $\text{SO}_4^{2-}$ , in the soil sample observed throughout the study period indicate a decrease i.e. from 6.7 mg/g (at the start of the study) to 2.2 mg/g (at the end of the study) and from 0.7mg/g (at the start of the study) to 0.2 mg/g (at the end of the study) respectively. It is well established that the adjustment of carbon/nitrogen /phosphorus ratios by the addition of nitrogen and phosphorus in the form of inorganic fertilizers, stimulates the biodegradation of crude oil and individual hydrocarbons in terrestrial environment (Rim-Rukeh *et al.*, 2005). The supply of organic matter is an important factor for the growth of microorganisms because it is usually required organic carbon as an electron donor. Organic carbon is utilized by bacteria for the production of new cellular material (assimilation) and as an energy source (dissimilation). Organic materials of any type are suitable foodstuffs for bacteria growth. Adequate supply of nitrate and sulphate are essential for increased activity of microorganisms since nitrogen, sulphur, and carbon are essential elements for cellular metabolism in microbial life.

The moisture content in the soil samples range from 82% to 89%. Dibble and Bartha (1979), in a study of oil sludge degradation in soil, reported optimal rates of biodegradation at 30 to 90% water saturation. The failure to observe inhibition of degradation at the lower values was ascribed to a hydrocarbon-mediated reduction in the water holding capacity of the soil. A key feature that initiates and promotes microbial degradation is water or an aqueous phase. Thus water is the main requirement for microbial life and also for degradation to occur (EPA, 1992).

The high population of total micro count (TMC) in the soil sample ( $10^5 - 10^{13}\text{cfu/g}$ ) is an indication of availability of good food supply. In addition, crude oil meshed in the cement encapsulated blocks is a suitable substrate for microbial bacteria growth (Rim-rukeh *et al.*, 2005). Microbial population of  $10^5\text{cfu/g}$  in soil sample is an indication of microbial degradation problem (Costello, 1969). The soil samples correspond to an environment that is highly susceptible for microbial degradation. Figure 1 illustrates the mass loss of oil base drill cuttings encapsulated with cement slab during the period of the experiment, indicating approximate linear

relationship between  $\Delta M$  and  $t$  as obtained by Uhlig (1948) in the form

$$\Delta M = kt \quad (1)$$

where  $k$  is a proportionality constant that depends on the conditions in a specific environment. Figure 1 shows increase in mass loss of the slabs with time. When the log of mass-loss is plotted against time, an approximate linear relationship is obtained (see Fig. 2), confirming a first-order chemical reaction for the biodegradation process. This method of using a linear relationship between log of mass-loss and time in determining the order of a reaction is reported in the literature (Jones, 1988; Omo-Odudu and Oforka, 1999; Rim-Rukeh, 2005).

Results of the analyses of the soil sample indicate an environment that has the potential to degrade encapsulated oil based drill cuttings. Although isolates of microorganisms was not carried out, the ability of a wide variety of bacterial and fungal genera to degrade and/or utilize hydrocarbon substrates have been reported Okpokwasili and Nnubia (1999); Nweke and Okpokwasili (2003). Bossert and Bartha (1984) had isolated 22 genera of bacteria and 31 genera of fungi from a similar soil environment. Based on the number of published reports, the most important hydrocarbon-degrading bacteria in both marine and soil environments are *Achromobacter*, *Acinetobacter*, *Alcaligenes*, *Arthrobacter*, *Bacillus*, *Flavobacterium*, *Nocardia*, and *Pseudomonas* spp. and the *coryneforms*. In addition, the ability of heterotrophic microorganisms to induce degradation of cement by excreting carboxylic acids during the decomposition of organic matter have been reported (Lea, 1970). Maruthamuthu *et al.*, (1997) demonstrated that heterotrophic bacteria adversely affect the compression strength of concrete. Perfettini *et al.* (1991) evaluated degradation of cement binder as induced by metabolic products of two fungal strains, *Aspergillus niger* and *Mycelia* sterile, isolated from soil sample. Portland cement (15 percent (w/w) portlandite (Ca (OH)<sub>2</sub>) was exposed in direct contact to the two solved cement, increasing porosity by 11.4 percent and reducing the bending strength (strength applied to three points on the surface that causes breakage) by 78 percent. Increased porosity indicates cement dissolution and permits penetration of biological and chemical species. *Mycelia* sterile (gluconic and malic acids) caused a significant 4.2 percent leaching of original calcium content, an 11-percent increase by fungi solubilise calcium, silica, aluminium, and iron minerals. Solubilisation is

related more to the nature of the acid than to concentration.

**Conclusion:** Physicochemical and biological characteristics of soil samples collected in the Odugri well 5 locations have been presented. It is shown that the levels of measured parameters in soil samples are consistent with the conditions in an environment that favours microbial activity. Conclusively, the rapid degradation of the slabs made with oil based drill cuttings encapsulated with cement can be attributed to the semi continuous bacterial/fungi culture, in which slab samples were exposed to a sequence of several biodegradation cycles. The results of this work showed that organism naturally present in soil has potential application in the degradation of oil-based drilling cuttings encapsulated with cement.

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