Full Length Research Paper

Stabilization/solidification of synthetic Nigerian drill cuttings

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In the Nigerian oil and gas industry, large guantities of oily and synthetic drill cuttings are produced annually. These drill cuttings are heterogeneous wastes which comprises of hydrocarbons, heavy metals and chlorides. Currently, the treatment option for these drill cuttings is thermal treatment, which does not remove these toxic contaminants. In this study, the use of stabilization/solidification as a means of treating synthetic drill cuttings for potential reuse in construction products is investigated. Portland cement was used as a binder. The ratio of water-to-dry binder was 0.4:1. Three different mix ratios of the drill cuttings and binder (2:1, 3:1, 4:1) were investigated. A set of physical tests (Unconfined compressive strength test and Durability test) as well as Toxicity Characteristic Leaching Procedure tests were conducted on the different mixes. For the drill cuttings, the moisture content, sodium adsorption ratio and exchangeable sodium percentage values of 4.04, 6.37 and 7.44% were below the DPR limits of 50, 12 and 15%, respectively. Heavy metals such as arsenic, mercury and silver were below 0.01, 0.001 and 0.001 mg/l compared to the DPR limits of 5, 12 and 5 mg/l, respectively. However, cadmium, chromium and zinc contents of 1.63, 54.80 and 121.17 mg/l were higher than the DPR limits. The unconfined compressive strength test results for the drill cuttings-binder ratios of 2:1, 3:1 and 4:1 were 1040, 606 and 490 psi, respectively much higher than the DPR limit of 20 psi. The Toxicity Characteristic Leaching tests and the Wet/Dry Durability tests produced satisfactory results as well.

Key words: Drill cuttings, stabilization, solidification, portland cement.

INTRODUCTION

Drill cuttings consist of various rocks, particulate and liquids released from geologic formations in the drill hole. These drill coatings are coated with drilling fluid from well discharges and also contain some additives which remain on the drill cuttings. Hydrocarbons, purge able organics, acid extractable and heavy metals are usually contained in drill cuttings. The drill cuttings produced by an oil based drilling fluid are rather heavily contaminated by the oil base and additives used for preparing the drilling fluid. Therefore, the drill cuttings cannot be discharged directly into a disposal site, not only because of their adverse effect on the environment, but because of the great value of the oil contained in them. It has become common practice to treat the drill cuttings in order to produce a solid material that can be disposed safely into the environment. Cuttings generated from water - based muds are generally not considered as toxic, so much so that, in offshore drilling operations, they are discharged overboard. Research has shown that this practice has serious adverse environmental impacts, one of which is the smothering of seabed life (Olsgard and Gray, 1995). In any case, it would make sense to find ways and means of converting the cuttings (a waste) into a useful product and solve an environmental problem at the same time. Solidification/stabillization is basically an attempt towards achieving this goal.

Solidification as defined by Conner and Hoeffner (1998) is a waste conversion process that produces an entity with structural integrity that is more compatible for storage, landfill or reuse. They also defined Stabilization as a chemical process used to reduce to the barest

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minimum the hazardous potential of waste by converting the contaminants into a form which is less soluble, mobile or toxic. Solidification/Stabilization has many advantages since it requires minimal energy input and results in minimal emissions to air (Smith et al., 1999). The limitations and drawbacks of this technique to treat drill cuttings have been highlighted (Page et al., 2003; Smith et al., 1999). The problems mainly arose from the interference of high concentrations of organic compounds, chlorides and bentonite with the hardening and the curing process of cement. Furthermore, the presence of high percentages of chloride prohibited the use of drill cuttings in reinforced concrete applications.

Portland cement, Pozzolans, Bentonite, Lime, Plaster of Paris, Thermoplastic Resins and ion exchange resins (Zeolites) are some of the commonly used solidification agents. Of these, the most important agents for waste fixation are Portland cement, Pozzolans, Bentonite and Zeolite, Page et al. (2003) reported that stabilization and solidification with cement or pulverised fuel ash is a viable solution and concluded that the disadvantage of this option is the high embodied energy from cement, transportation of the additives and increased bulk material for disposal. Tuncan et al. (2004) used kalonite, gypsum, bentonite, clinker, lime and fly ash to stabilize drill cuttings prior to landfilling and for use in road construction applications. A source in Algeria recommended the stabilization of drill cuttings with the addition of 70% of a hydraulic binder for subsequent use as a sub - base material in road construction (Boutemeur et al., 2003). A detailed discussion of the chemistry of stabilized wastes is provided by Conner et al. (1992).

Macky and John (1992) described a case where waste stabilization has been used successfully to fix metals and carbons. This involved a contaminated road pavement at Clear Lake, Ontario. Following laboratory screening trials, a mix of 10% Portland cement (dry soil basis) was added to the contaminated material and the Ontario Ministry of Environment criteria were used for the treatment product which were met. Akinlade et al. (1996) is a case study concerning drilling waste disposal in Nigeria using Portland cement and a proprietary additive – Geosta - A. Following screening trials, a 1:12 (8%) mix of Portland cement and 0.1 to 0.3% Geosta - A were applied to the cuttings which met Department of Petroleum Resources (DPR) and Federal Environmental Protection Agency (FEPA) guidelines, except for chloride. The objective of this study is to use stabilization/solidification as a means of treating the Nigerian synthetic drill cuttings for potential reuse in construction products. This will result in a recycled product of potential value to local communities. Operating companies may seek permission for the production of reusable materials from oil field waste with certain obligations met. Reusable materials e.g. for daily cover in sanitary landfill or construction material shall comply with the testing criteria for reusable material as stipulated in the guideline. The Testing criteria as prescribed in the DPR's Environmental Guidelines and

Standards, 2002 are stated in Table 1.

MATERIALS AND METHODS

A cement based technique was developed for the application and solidification of the drill cuttings. The following processes were involved:

- Chemical Characterization of the drill cuttings.
- Casting and curing of the moulds.
- Toxicity Characteristic Leaching Procedure Testing on moulds.
- Wet/Dry Durability Testing.
- Hardness (Unconfined Compressive Strength) Testing.

Chemical characterization of the drill cuttings

This involved the analyses for parameters as listed in DPR's Testing Criteria for Reusable Materials, using the methods listed (Table 1).

Casting and curing of the moulds

A binding material (Portland cement) was first mixed together with water in a water-dry binder ratio of 0.4:1 (after Jansen, 1997, Al-Ansary and Al-Tabbaa, 2005) and added to the drill cuttings. Water to cement ratio was within the range 0.4 - 0.9 : 0.4 depending on the desired quality of the resulting product. Three different mix ratios of the drill cuttings and binder (2:1, 3:1, 4:1) were investigated using a total of 8.4 kg of cement, 25.3 kg of drill cuttings and binder, the mixture was cast into cylindrical moulds of 50 x 100 mm and left to cure for 20 days in an open space under a light cover. The samples from each mix were tested for their unconfined compressive strength, Toxicity Characteristic, Leaching Procedure and Durability.

Unconfined compressive strength test (UCS)

This test was carried out according to BS 1881:116 method (British Standard [BS] 1881 Part 116, 1983). The stabilized sample was crushed and allowed to pass through a 20 mm test sieve. A UCS mould was filled with a calculated mass of the stabilized material. This was compacted using a hammer to drive home the upper plunger. The sample was ejected with an ejecting plunger and weighed to the nearest 1 g. The sample was wrapped with a cardboard paper, waxed and stored at a temperature of 20 °C for six days. Thereafter, the wax and cardboard paper were removed and the sample weighed to the nearest 1 g. The sample was then placed in a water bath for 24 h, removed and allowed to drain for 15 min. The compression testing machine plunger was set under a CBR ring capacity of 50 kN and the sample crushed at a uniform rate of 1 mm/min. Readings of the maximum force required to shear the sample were recorded.

Toxicity characteristic leaching procedure test (TCLP)

The solidified matrix was crushed to a particle size of approximately 1 mm in diameter. 5 g of the crushed/ground sample was homogenized in reagent water. The pH of the medium was determined, using a digital pH meter (HANNA Model PH-211) and the obtained value was used in the selection of the extraction fluid for the leachate extraction. The crushed sample (100 g) was then extracted for 18 h at 30 rpm at 22 °C with the chosen extraction

Table 1. Chemical characterization of the drill cuttings and dpr testing criteria.

S/N	Parameter	Method	Mean values	Variance (σ^2)	DPR limit
1	Moisture content	Gravimetric	4.04%	0.023	<50%
2	рН	APHA 4500-H⁺	9.00	0.010	6.5 - 9.0
3	Electrical conductivity (EC)	APHA 2510B	40.50 mmhos/cm	1.750	8 mmhos/cm
4	Sodium adsorption ratio (SAR)	APHA 311B	6.37	0.023	12
5	Exchangeable sodium percentage (ESP)	CAEM	7.44%	0.047	15%
	Leachate testing for:				
Α	Oil and Grease	API RP 45	85.00 mg/l	4.0	100 mg/l
В	Chlorides	APHA 2520B	7800 mg/l	25	5000 mg/l
С	Arsenic	APHA 3111B	< 0.01 ^{***} mg/l	-	5 mg/l
D	Barium	APHA 3111B	30.75 mg/l	0.817	100 mg/l
Е	Cadmium	APHA 3111B	1.63 mg/l	0.004	1 mg/l
F	Chromium	APHA 3111B	54.79 mg/l	3.490	5 mg/l
G	Lead	APHA 3111B	25.87 mg/l	1.053	5 mg/l
Н	Mercury	APHA 3111B	< 0.001 ^{***} mg/l	-	12 mg/l
Ι	Silver	APHA 3111B	< 0.001 ^{***} mg/l	-	5 mg/l
J	Zinc	APHA 3111B	121.17 mg/l	5.583	50 mg/l

Source: DPR's Environmental Guidelines and Standards for the Petroleum Industry, Revised Edition 2002.

Fernades and Coutinho (1997).

Below the detectable limit of instrument.

fluid. After the agitation period, the mixture was filtered and the filtrate is defined as the TCLP extract.

calculated to provide a measure of variation of the results (Table 1).

Wet/Dry durability test (DT)

This test evaluates the resistance of the stabilized material to the natural weathering stresses of repeated wetting and drying cycles. The test was carried out in accordance with ASTM D-4843 method (Annual Book of ASTM Standards, 1999). Cured test samples were subjected to ten test cycles. Each cycle consists of a period of five hours submerged under water and 42 hours in an oven under low drying conditions (71 °C). The change in volume, moisture content and weight loss were determined after each cycle. After the ten cycles, the total sample weight loss was determined.

RESULTS AND DISCUSSION

A set of physical and chemical tests were conducted on the different mixes. These are presented below:

Chemical characteristics of the drill cuttings

Following the chemical characterization of the drill cuttings, the main contaminants after thermal treatment were found to be chloride, zinc, lead, chromium and cadmium. The results indicate that some of the parameters far exceed the limits spelt out by the DPR thereby making the drill cuttings unsafe for use. The results are shown in Table 1. For each property, three measurements were carried out and the arithmetic mean was calculated. The variance of each set of data was

Unconfined compressive strength

A summary of the UCS at 20 days is presented in Table 2. The different mixes were presented in the order of drill cuttings - binder content. The UCS results reveal that in comparison with the DPR's limit for Unconfined compressive strength tests on solidified materials, the results obtained agreed with the pass mark of 20 lbs/in² (psi). Jansen (1997) while studying the solidification of drill cuttings from SPDC with cement (also using cuttings cement mix ratio of 4:1) obtained excellent results for compressive strength as well. In a similar investigation of two synthetic drill cuttings from the North Sea and Red sea areas with hydrocarbon contents of 4.2 and 10.95% by weight, the values of UCS were found to be similar for the same binder type and content in spite of the significant difference in hydrocarbon content (Al-Ansary and Al-Tabbaa, 2007). In addition, the results of the leachability tests showed that the drill cuttings were reduced to forms that met the criteria for acceptable nonhazardous landfills.

Toxicity characteristic leaching procedure test

The results obtained from the mix ratios used during the casting, all passed the DPR's Testing Criteria for

Sample name	Mix ratio (Drill cuttings : cement)	Result (Psi)	DPR limit (Psi)
DC 1	4:1	490	20
DC 2	3:1	606	20
DC 3	2:1	1040	20

Table 3. Toxicity characteristic leaching procedure test result.

S/N	Parameter	DC (4:1)	DC (3:1)	DC (2:1)	DPR limit
1	Moisture content	5.25	8.92	17.92	<50%
2	рН	9.5	10.2	10.5	6.5 - 9.0
3	Electrical conductivity (EC)	32.10	11.8	5.10	8 mmhos/cm
4	Sodium adsorption ratio (SAR)	1.50	2.0	2.53	12
5	Exchangeable sodium percentage (ESP)	0.943	1.661	2.412	15%
	Leachate testing for:				
А	Oil and Grease	5.25	2.75	0.89	100 mg/l
В	Chlorides	5,900	3,975	1,867	5000 mg/l
С	Arsenic	< 0.01	< 0.001	< 0.001	5 mg/l
D	Barium	23.5	19.7	15.9	100 mg/l
Е	Cadmium	0.56	0.29	< 0.002	1 mg
F	Chromium	4.5	2.00	< 0.10	5 mg/l
G	Lead	1.15	0.36	< 0.002	5 mg/l
Н	Mercury	< 0.001	< 0.001	< 0.001	12 mg/l
I.	Silver	< 0.001	< 0.001	< 0.001	5 mg/l
J	Zinc	15.30	6.00	0.30	50 mg/l

reusable materials except for the 4:1 ratio which failed the leachate test for chloride (Table 3). The reason may be attributed to the fact that the construction blocks become well binded as the weight or amount of the binding material increases. The potential for the contaminants to be transferred from the stabilized matrix to a medium therefore becomes low as the weight of the binding material is increased. Also, previous work has shown that cement - based and pozzolanic materials are particularly effective for stabilization of metals in the wastes due to the fact that at the high pH of the cement mixture, most compounds are converted into insoluble metal hydroxides (Wiles, 1987). Apart from this chemical action, tests have shown that the end product of stabilization with Portland cement is a concrete that has a very low permeability with respect to both water and oil and petroleum hydrocarbons (Clark and Perry, 1985; Poon et. al., 1985; Zhao et al., 1999). Other properties include the formation of a strong solid matrix as well as a suitable pore structure for storage of materials within the matrix (Young, 1992). This would explain why the levels of Arsenic, Barium, Cadmium, Chromium and Lead are all below the DPR limits for these metals after the treatment. even for the mix with the lowest cement content (drill cuttings - cement ratio of 4:1, Table 3).

Durability test

The best out of the drill cuttings: cement ratio was selected for wet/dry durability. This evaluates the resistance of the stabilized material to the natural weathering stresses of repeated wetting and drying cycles. The results showed that the solidified material remained intact after the 10th cycle thus passing the DPR's requirement (Table 4). This however, does not agree with Jansen (1997) who obtained a less satisfying result for durability of drill cutting samples. This may be as a result of the clay in the cuttings from deeper hole sections which he worked with.

Conclusion

The utilisation of S/S techniques to treat drill cuttings by using Portland cement a conventional binder in this study indicated the following:

i. Solidification of the synthetic drill cuttings with cement in the form of construction blocks has been identified as an attractive drill cuttings disposal option.

ii. Contaminant leaching concentrations decreased as the

Table 4. Wet/dry durability test result.

Sample ID	Initial weight (kg)	Weight after 1 st cycle (kg)	Weight after 2 nd cycle (kg)	Weight after 10 th cycle (kg)	Weight loss (kg)
DC (2:1)	6.10	6.10	6.05	5.90	0.20

dry binder content increased thus allowing the drill cuttings to be classified as non-reactive non hazardous waste.

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