

Evaluation of low temperature thermal desorption (LTTD) method of treating cuttings

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Abstract

Drill cuttings which are soil produced with contaminants during drilling activities were treated using the Low Temperature Thermal desorption (LTTD) Unit. The LTTD unit is an innovative treatment (technology that treats soils contaminated with hazardous wastes by heating the soil at relatively low temperatures (200-1000 deg F) so that contaminants with low boiling points will vaporize (turn into gas) and, consequently, separate from the soil. There are three steps employed in thermal desorption treatment: Heating the soil to vaporize the contaminants, treating the vaporized contaminants and testing the treated soil. The residue/cuttings to be discharged to the environment were evaluated in this project to ascertain the effectiveness of the LTTD system. The residue cuttings which appear like ash after the treatment were treated to determine whether any contaminant still found in the material before discharging safely into the environment. The results showed that most of the contaminants were treated to below the DPR accepted level of discharge into the environment which are very stringent levels. However there were traces of contaminants like Iron and Manganese which were still found in the soil after the treatment. This project evaluates the Drillings cuttings treatment and the results obtained after the treatment.

Keywords: Evaluation, temperature, thermal, desorption method, cuttings.

1. Introduction

Exploration, development and production are three important aspects of oil industry activities that have a lot of impact on the environment. Each of these processes is associated with the use of material that eventually ends up in the environment. Its continuous existence in the environment may constitute a hazard. Such materials are classified as wastes. Drilling as an aspect of exploration is associated with sub-sectoral activities and each activity has its associated waste (Atuanya, 1987; Bansal and Sugiarto, 1999). These wastes could be solids such as drill cuttings or mud, liquids such as deck drains, rig effluent, work over fluids and sometimes gaseous emissions in case of blowouts. Drilling fluids are required for oil exploration and development to remove cuttings from beneath the bit, control well pressure, cool and lubricate the drill string and seal the well bore. Although drilling fluids are re-circulated during drilling and sometimes can be held in re-used in drilling multiple production wells, they must be eventually disposed of because of their contamination with suspended material and the loss of some plant properties (Lee and Bal, 1991; Meg and Michigan 2007). Cuttings from the drilled formation are removed from drilling and must also be disposed of in an environmentally friendly manner. In order to characterize these wastes and hence determine their potential for environmental pollution the effluents and waste generated during the drilling of any well is monitored by regular sampling and analysis.

An oil practice in Nigeria and all over the world has had its peculiar problem of its management. Over the years, the difficulties imposed by its operations in the area have endangered lives and properties so much in the Niger Delta (DPR, 2002; Snyder, 1999). Oil-based cuttings are toxic and detrimental to human, animal and plant. The hydrocarbon content when emitted to the atmosphere causes more harm than good, oil spill and dumping of cuttings coats the soil with dark-like soot, thereby preventing the release of heat from the ground hence the air pores are covered and this evidently devoids the plants of necessary nutrients (CO₂), hence photosynthesis cannot take place. The oil that goes to the ground is said to be responsible for groundwater pollution, the fish in the sea, rivers, ponds, etc are not saved, neither do birds nor man breathe good air for good living. It therefore becomes very essential that our environment must be protected for human habitation (Morillon et al., 2002). The problems associated with oil drilling wastes also include pollution of the environment, destruction of natural vegetation, poisoning of drinking water, destruction of wildlife. Biodiversity, contamination of groundwater, loss of soil fertility, degradation of farmland, damage to aquatic ecosystems etc and the resultant effect is the serious health problem. Indeed, drilling wastes and oil spills have been identified as major handicaps to the oil producing companies and the environmental impact has since been over-flooded in recent times. Because of the environmental effect of its operations, the industry has intensified its effort in proffering solutions to this ugly situation. Researchers have been empowered to identify the best ways technologically to reduce to the barest minimum effects of oil spills and disposal of oil waste cuttings. In this noble adventure, cutting slurification and subsurface re-injection [CRI] were introduced as trial projects using Bonny-8 as the injector well with cuttings and waste mud/fluids produced from Bonny - 24- (Ex Bonny TLLV- 2). The trial project was successful with a total of 12,000 bbls of waste including 2500bbls drilled cuttings and all other waste mud, oily sludge, waste chemicals, brines, etc. It was therefore obvious that the technology however was geared into reducing the impact of the disposal effect (Smith, 2003; Udo and Fayemi, 1975).

Basically, the first application of the drilled cuttings re-injection technique in Nigeria was carried out by SPDC-The Shell Petroleum Development Company, Nigeria in the fourth quarter of 1995, using Petro-Scan Ltd, an indigenous contractor. The design of the system was on-line, which means that the drilled cuttings were received in the CR1 units, crushed or slurified and thereafter re-injected into the nearby Bonny- 8 injector well, the CR1 has a handling capacity of 20ton/hr. At about 1998, a new technology was still introduced in pursuance of achieving optimum efficiency in operating a more friendly environmental system, called TDU. "Thermal Desorption Unit" was introduced to enforce a more effective environmentally compliance technology of reducing to the barest minimum, the impact of waste disposal on the environment. This process, under the operational eyes of ORES "Oil Recovery Energy services" as located at Bonny terminal, was subjecting the cuttings/sludge to thermal treatment basically reducing the oil and grease content for land filling, block moulding, etc. of the residues. Thermal technologies use high temperatures to reclaim or destroy hydrocarbon-contaminated material. Thermal treatment is the most efficient treatment for destroying organics, and it also reduces the volume and mobility of inorganics such as metals and salts (Bansal and Sugiarto 1999). Additional treatment may be necessary for metals and salts, depending on the final fate of

the wastes. Waste streams high in hydrocarbons (typically 10 to 40%), like oil-based mud, are good candidates for thermal treatment technology. Thermal treatment can be an interim process to reduce toxicity and volume and prepare a waste stream for further treatment or disposal (e.g., landfill, land farming, land spreading), or it can be a final treatment process resulting in inert solids, water, and recovered base fluids. Thermal treatment technology is generally set up in a fixed land-based installation, but some efforts are under way to develop mobile thermal treatment units and units that might fit on an offshore platform. Its application is not geographically limited, but large size and weight coupled with limited processing capacity have limited its use offshore.

With the current stringent measures introduced by the Federal government through its regulatory body for oil operations and its associated environmental matters — Department of Petroleum Resources (DPR) - in line with the Environmental World Standards (EV-WS), it is therefore, very pertinent that the current petroleum waste management technologies need to be reviewed to accommodate the new specifications for effective environmental protection. To this end, several attempts have been made by the oil operators world-wide to proffer solutions to the fundamental problem of how to dispose of hazardous waste from drilling operations such as drill cuttings with no impact on the environment. Over the years this has been achieved through prior treatment of the drill cuttings using solidification and stabilization processes (Akinlade et al, 1996), thermal technologies (Zupan and Kapila, 2000; RLC Technologies, 2004) and only recently by bioremediation (KMC Oiltools, 2005). There are two main categories of thermal treatment namely; incineration and thermal desorption using Low Thermal Desorption Units (LTDUs). Thermal desorption refers to the indirect heating of cuttings to vaporize volatile and semi-volatile compounds under an oxygen deficient condition without incinerating the soil. However, since the introduction of LTDUs in the country by some oil producing companies, the environment is reported to have continued to witness repeated cases of land pollution due the land application of the thermally desorbed drill cuttings. The evaluation of the effectiveness of these LTDUs therefore, becomes a consequent tandem. Figure 1 illustrates the artificial oil spill site as well as the impact on the environment was seen. The flow diagram of distillative cracking chamber of the given process was illustrated in Figure 2.

The aim of this research work is to assess the effectiveness of the LTDU in terms of its potentials to reduce the contaminants level in drill cuttings to the discharge limits spelt out by the Department of Petroleum Resources (DPR). To achieve this aim, the following specific objectives were pursued: Conduct an initial chemical characterization of the untreated drill cuttings. Carry out the performance evaluation of the LTDU, in terms of amounts of contaminants remaining after treatment in the LTDU, by conducting laboratory analyses of the resulting thermally desorbed drill cuttings. Compare the contaminants levels in the thermally desorbed drill cuttings with the discharge limits of the Department of Petroleum Resources (DPR). Make appropriate recommendations to government, industries and stakeholders engaged in the disposal and treatment of drill cuttings. Usually, as the need arises, environmental standards are raised by government regulatory agencies and it is expected that the oil producing companies strive to meet these standards in order to remain in operation. However, whether or not these standards are met by these oil companies remains a subject for debate especially in developing countries like Nigeria. This is because, more often these regulatory agencies lack the necessary personnel and equipment to monitor the activities of these oil producing companies and rely on whatever report is made available to it by these companies. This is the reason this study is being carried out to ascertain the truth in what the oil producing companies will have us believe about the efficiency of LTDUs currently in use in the counting taking into account the dwindling emphasis now being placed on the use of thermal technologies in the treatment of exploration and production (E&P) wastes because of apparent adverse effects the technology poses to the environment, personnel and equipment.

Therefore, this study would provide (among other things) information on whether or not the use of LTDU in the treatment of drill cuttings is able to reduce the contaminants levels in the drill cuttings to the specified discharge limits. Apart from finance, technically speaking, some limitations were also encountered in the field. Worthy of mention is the difficulty encountered in the use of the equipment. In fact, the production of fugitive dust by the LTDU almost marred this study. The personal protection equipment provided was of low quality and could not properly keep off the dusts. The main focus of this project was to study the effectiveness of the Low Thermal Desorption Unit (LTDU) in terms of the level of contaminants remaining in the LTDU-treated drill cuttings, by conducting laboratory analyses of the resulting thermally desorbed drill cuttings.

2. Materials and Method

Sampling Containers/Preservations: Sampling, preservation in transportation were carried out in accordance with recommended method as contained in APHA, (2002). Samples were collected using glass bottles and containers. Reagents: All reagents used in this analysis were of analytical grade. This include: Methyl orange indicator, Phenols, trichloromethane, Equipment: Digital HANNA micro computer pH meter (model HI95

HANNA Conductivity/TDS meter (HI 9835), Atomic Absorption spectrophotometer

(GBC SenSAA) & HACH DR 4000U Spectrophotometer (model 48000-82), HACH

DRB200 COD reactor and DR/2500 spectrophotometer, Thermometer, Probe, Millipore filter paper, Vacuum pump, Pipette, Titration unit, 50ml volumetric flask, 500ml separator's funnel.

pH, CONDUCTIVITY, TDS AND TEMPERATURE

pH and conductivity were measured using a digital HANNA micro computer pH meter (model HI 9025) and HANNA Conductivity/TDS meter (1-11 9835) respectively. Temperature was measured using a thermometer. The pH and Conductivity/TDS meters were standardized with buffer solutions and conductivity standard solution respectively. The tip of the probe in each case was rinsed with deionizer water and cleaned with tissue paper. The probe was then immersed in the sample and the corresponding reading was taken in each case.

TOTAL SUSPENDED SOLIDS (TSS):

The samples were well mixed and filtered through a filtration unit fitted with a pre-weighed 0.45mm Millipore filter paper using a vacuum pump. The used filter paper was dried at 105°C to constant weight. TSS was then calculated using the appropriate formula.

$$TSS, \text{ mg/l} = \frac{\text{wt of filter paper} + \text{residue} - \text{wt of filter paper}}{\text{Volume of sample} \times 10^6}$$

HYDROGEN CARBONATES:

The sample pH was adjusted to 4.0 at room temperature. Then 50ml of sample was pipetted into a volumetric flask and 0.2ml of methyl orange indicator was added and swirled. It is then titrated with 0.1N sulphuric acid to a color change from pink to brick red. A constant end point was recognized for the sample.

(Result in mg/l HC03) was calculated thus:

$$\frac{\text{Vol. of acid used} \times 61 \times \text{Normality of acid} \times 1000}{\text{Vol. of sample}}$$

TOTAL HYDROCARBON CONTENT (THC):

Total Hydrocarbon Content was determined using a spectrophotometer. The sample was extracted with 35ml of trichloromethane. The extract after centrifuging, was read in the spectrophotometer at 540nm using trichloromethane as the blank. Readings obtained from the spectrophotometer were traced out on the calibration graph and used to calculate the concentration of THC in mg/l putting into consideration the total volume of the sample and the volume of the extracting solvent.

CHEMICAL OXYGEN DEMAND (COD):

COD was carried out spectrometrically with HACH DRB200 COD reactor and DR/2500 spectrophotometer. Firstly, the COD reactor was turned on and pre-heated to 150°C while homogenizing 100ml of stock sample in a 250ml beaker with a magnetic stirrer. An aliquot of 0.5ml of the mixed sample was pipetted into the Mn III COD vial and 0.5ml of distilled water into another vial then both vials capped and inverted several times to mix, The vials were placed in the COD reactor to digest for one hour after which the vials were removed and kept to cool for 15 - 20 minutes then inverted several times to mix before placing in the cell holder. A colour change from orange to purple was observed. The stored program number for COD was selected to obtain the COD values in mg/l.

PHENOLS:

300ml of sample were added to 500ml separatory funnel. Phenol 1 and 2 reagents were then added each followed by thorough shaking. Then 30ml of chloroform was added, shaken over 30 seconds and allowed to settle. The same process was repeated for the blank (de-ionized water). The preparations were drained and the blank was used to zero the equipment.

CYANIDE

Stock solution was used to prepare a standard curve and the developed Absorbance measured at 578nm. A portion of the absorption solution was prepared into 50ml volumetric flask, diluted to 40ml and aliquots of the stock solutions added for color development. Concentration using regression feature available on most scientific calculator, slope and intercept at standard curve was computed.

AMMONIA

Three drops each of mineral stabilizer and polyvinyl alcohol were added to 25ml of sample. Each addition was followed with mixing. Then 1ml of Nessler reagent was added and thoroughly mixed. The color development was measured and the same procedure was repeated for the blank. Result in mg/l NH₃-N was read.

HEAVY METALS (AAS)

Metal analysis was carried Out using Atomic absorption spectrophotometer (GBC SenSAA) and HAD-I DR 4000U spectrophotometer (model 48000-82). This involved direct aspiration of the sample into an air/acetylene or nitrous oxide/acetylene flame generated by a hollow cathode lamp at a specific wavelength peculiar only to the metal programmed for analysis. For every metal investigated, (Arsenic ASTM D2972, Chromium ASTM as adopted by HACH method 8023, Copper ASTM as adopted by HACH method 8026, Lead ASTM D3559, Nickel ASTM D 1886, Vanadium ASTM D3373, Mercury ASTM D3223 and Zinc ASTM as adopted by HACH method 8009) standards and blanks were prepared and used for calibration before samples were aspirated and concentrations at specific absorbance displayed on the data system monitor.

SAFETY PRECAUTIONS:

For safety during sample collection and laboratory analyses, reactions which dissolved, the release of toxic fumes were carried out in the fume cupboard while appropriate PPEs such as, hand gloves, eye goggles, safety shoes, coverall and nose masks were used when necessary.

The generator of the soil shale certify, based upon site history or previous sampling/characterization, that halogenated organic compounds (including PCB's) are not contained in the soil to be treated. As an added precaution, to prevent inadvertent treatment of chlorinated contaminants, soil shall be pre-tested for total organic halogen (TOX), using EPA SW846 Method 9020. TOX analysis is not required if site soils have been analyzed for chlorinated volatile organics, pesticides and PCB's. (The LTTD Task Group is drafting a separate document which specifies requirements for treating soils contaminated with chlorinated constituents.) If there is any doubt as to the nature of constituents, sampling is required. Soil contaminated with elevated levels of heavy metals shall not be treated unless the air permit specifically allows treatment of the material. The following soil conditions require pre-treatment or a test run to ensure the technology will be effective: soil moisture >35% , material > 2" diameter, and soil has high plasticity. The value will be regarded as "high" if the plasticity or humus content is significant enough to impact the efficiency of the treatment unit.4, soil has high humus content 25, for petroleum contaminated media only - either soil TPHC >20,000 ppm or greater than 25% LEL in gas in desorption chamber 3 Limitation is included to address explosively and is not applicable for inert environments. 6). for coal tar contaminated media only - coal tar product > 2% A Sample Parameters, Soil treatment verification sampling for petroleum or coal tar/MGP contaminated soils shall include the parameters outlined in Table 1 and Table 2. BTEX may be eliminated from verification sampling of coal tar contaminated soils because PAH-I compounds are surrogate for BTEX. In addition, any other site specific contaminants of concern for the treated soil shall be included in the parameter list. Verification sampling is not required for any contaminants which will be unaffected by thermal treatment, including metals.

B. Sample Frequency. Post-treatment soil sampling will require one (1) composite sample for each one hundred (100) cubic yards or one hundred and forty (140) tons of treated soil, using method ASTM C702-87. Each composite shall be comprised of five (5) discrete samples. As an alternative to composite samples, five (5) discrete samples for each one hundred (100) cubic yards or one hundred and forty (140) tons of treated soil may be collected. On a case by case basis, based upon documented efficiency of the treatment system, the post-treatment sample frequency may be reduced. This situation may be particularly applicable to high throughput units. Special consideration is required for volatile organics sampling. Samples for volatiles shall be collected using specialized sampling techniques to minimize loss of volatile contaminants.

C. Analytical Methods. EPA/ASTM methodologies presented in Table 3 shall be used. For verification sampling, gas chromatography methods with a mass spectrometer detector system are required for analysis of volatile/semi-volatile contaminants. Mass spectrometer methods are not required if Contaminant identity is known; The contaminant chromatographic peak is adequately resolved from any other

peak; and at least 10% of the sample analyses (minimum of one sample) are confirmed using the appropriate gas chromatograph/mass spectrometer detection system.

D. Sample QA/QC. All QA/QC required by the analytical method shall be completed. Lab QA/QC summary documentation (including non-conformance summary report and chain of custody) shall be submitted with analytical results. Full QA/QC deliverables as specified by the analytical method shall be maintained and shall be available upon request for at least three years. Ultimate responsibility for QA/QC documentation belongs with the responsible party of a site or the vendor conducting a demonstration. However, the responsible party may contract with another entity, such as an analytical laboratory, to house the actual QA/QC data.

E. Monitoring Parameters. The following parameters shall be monitored and recorded during operation of the unit; exit soil temperature, baghouse pressure drop soil processing rate, afterburner temperature (if applicable), exit air temperature from the desorption chamber

F. Automatic Shutdown Provisions. The following shall trigger automatic shutdown of contaminated soil feed:

Model unit: The thermal desorption unit used by the selected remediation contractor was the ADM RS-15, a trailer-mounted unit with a throughput capacity of up to 20 tons per hour and physical dimensions of 50 feet by 13 feet by 10 feet. A front-end loader is used to load contaminated soil into the first stage of the unit, a 12.5-ton cold-feed bin used to size and crush large pieces. The ADM could treat soil only with total petroleum hydrocarbon (TPH) concentration of 5,000ppm or less. Soil is transported by a conveyor into a counter-flow rotary dryer, where the temperature of the soil is raised to 950 degrees F in seven minutes. As the soil is heated in the desorber, the volatile compounds are driven into the oxidizer and the treated soil is discharged, cooled, re-moisturized, and stockpiled. The heated exhaust gases from the desorber are discharged to a baffled high-temperature baghouse at a rate of 7,400 scfm for removal of soil fines and dust particles. The baghouse is an automatic continuous collector using a venturi-type orifice for compressed air cleaning of collected particles from the fabric filter. Dust collected from the baghouse is combined with the hot soil leaving the desorber. The particle-free exhaust gases are then forced through the oxidizer at 7,400 scfm where combustion of the desorbed organic compounds is completed. The oxidizer is operated at a temperature of up to 1,750 degrees F, with a retention time of 0.95 second. The treated air is then emitted to the atmosphere as illustrated in the flow diagram as shown in Figure 3 and 4.

3. Results and Discussions

In the current edition of "Environmental Guidelines And Standards for Petroleum Industries In Nigeria", (*EGASPIN*) published by the Department of Petroleum Resources, it stipulates the guidelines and standards of the state of any treated drill cuttings before any approved discharge to the offshore, swamp or land as presented in Table 2.

DPR Compliance Using DCT: for environmental disposal of treated materials using Low Temperature Thermal Desorption- LTTD, the followings are the laboratory obtained results for parameters such, as hydrocarbons, chlorides, Copper, Iron, etc. The technology has been consistent in achieving the goal of reducing the parameters within DPR and ENV-Ws, approved standards for environmental disposals and reuse as presented in Table 3.

DPR guidelines specifies that treated cuttings for chloride content could be discharged to the environment (Offshore and swamp) at maximum level of 2,000ppm. However, from Figure 1 above, the 2,000ppm level was recorded at the 10th treatment from the initial concentration of 86,200ppm and has been consistently reduced to 1,000ppm at the 19th treatment. Apparently, the technology has the potentials of treating to below 600ppm Egaspin of 2002 edition stipulates the allowable disposal limits of treated synthetic drill cuttings to 10-20 ppm. However the new technology was able to treat an initial Oil & Grease concentration of 83,800ppm to less than 0.001ppm apparently all the treatments from the 3rd treatment to the 18th indicate consistency in the treatments. For chromium content, about two treatments were carried out reducing an initial concentration of 34ppm to 0.4740ppm, though, DPR specification is 0.03 - 0.5ppm. Invariably, the chromium content can still be reduced further to conform to the minimum approved specification, as presented in Table 3 and 4.

Summary The initial concentration of zinc in the drill cuttings was reduced from 4.1032 to 0.8679, while the DPR approved specification is 1.0ppm. Moreso, the initial concentration of Cadmium in the drill cuttings was reduced from 6ppm to <0.001, while the DPR approved specification is 1.0ppm. The samples used in these experiments were the samples collected from T26, MINI-NTA and Searex 12 - Soku 51, the synthetic drill cuttings sampled recorded some insignificant presence of some heavy metals such as Mercury and Lead. Also, samples were collected from: RIGDuetagT76, AssaNorth4, RIG HPEB I 19, Location Zarama 7 and Specialty Drilling Fluids - Treated Sample, and are at the point of this report awaiting for chemical analysis in Petroleum chemistry laboratory of SPDC as presented in Figure 5 and 6. From Figure 5 it is seen that the chlorine concentration decreases with increase in number of treatment. The variation on the chlorine concentration can be attributed to the variation on the number of treatment. Similarly, from Figure 6, it is seen that decrease in chromium and zinc concentration was observed with increase in number of treatment.

Thermal desorption is not incineration. The volatilized contaminants are then either collected or thermally destroyed. A thermal desorption system therefore has two major components; the desorber itself and off gas treatment system.

4. Conclusion

Technology is defined as the practice of any or all of the applied sciences that have practical value and / or industrial use and it is often said that the technological emancipation of any individual of national could only be actualized when value is placed on ingenuities. Exploration and development are known activities that generate wastes such as atmospheric emissions, drill cuttings, drilling fluids, deck drainage, well treatment fluids, sanitary and domestic wastes as well as accidental oil spills. Drilling fluids are suspensions of solids and dissolved materials in base of water or oil that are used to maintain hydrostatic pressure control in the well, it is used in lubricating the drill bit, remove drill cutting from the well and stabilize the well during drill or work over operations. Water based mud consist of natural clays, and additives (organic and inorganic) to achieve proper density, viscosity and lubrication characteristics. Additives of particular concern from pollution viewpoint are ferrocchrome lignosulphate (chromium pollution) and lead compounds called lead pollution. Moreso, oil base mud contains oxidized asphalts, organic acids, alkali, stabilizing agents and low toxic or synthetic oil. Clay solids and weighting agents are most times added, some of the oil emulsion equally used are mostly oil-in-water or water — in oil varieties. Some of the synthetic drilling mud systems used is Acetyl, Internal Olefins (IO), esters, Linear Alpha Olefins (LAO), Poly Alpha Olefins (PAO), n-paraffin, etc. However, drilling fluids are specifically formulated to meet the physical and chemical requirement of a particular well, though, the mud compositions are affected by geographic location, well depth, and rock type, this is why various products are used at different times to control particular properties of mud systems.

The cuttings are coated with drilling fluid, while the drilling fluid from the well discharges to a rig shale shaker where the cuttings are separated from the drilling fluid, however, this form of separation does not completely remove drilling fluid from the cuttings and with the stringent regulations by the Department of Petroleum Resources in their EGASPIN 2002 edition, section 35,1 that states that “wastes from drilling and work over activities from offshore, near shore, and inland areas, spent water — based mud fluids, well treatment wastes, oil and water based drill cuttings, brine deck drainages, or residues, shall be treated to the satisfactory of the Director of Department of Petroleum Resources”. And in total compliance to the Zero Discharge of Cuttings, this research was carried out with the aim of complying in totality to the specified guidelines. The technology Low Temperature Thermal Desorption was used to treat drill cuttings produced during drilling and the evaluation showed that most of the contaminants were treated below the DPR and Internationally acceptable standards. This can be used effectively for zero discharge. Most of the treated materials can be reused safely in the environment. LTTD unit is equally an on-site technology also aimed at cost reduction of operations, while ensuring environmentally pollution free operations.

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Nomenclature

Btu: “British Thermal Unit”

Psi Pounds per square unit

Psig Pounds per square inch (gauge): 0 psig = 14.696 psia (psi absolute)
= 1.0 atmosphere.

Bbls: Barrels

CRL: Cuttings Re-injection Injection

TSS: Total Suspended Solids (TSS)

COD: Chemical Oxygen Demand

THC: Total Hydrocarbon Content

Appendix

For the purposes of this document, the objective of pre-treatment sampling is to identify the range of soil types and contaminant concentrations expected on the site. This information is necessary in order to select the appropriate soil for the thermal treatment test runs and to insure that the most heavily contaminated samples are selected for the test run. It is assumed that the site has been adequately characterized during a remedial investigation. Therefore, sample frequency requirements are not addressed in this document. Pre-treatment soil sampling for petroleum contaminated or coal tar/MGP wastes and contaminated soils shall include the parameters for the contaminant source outlined in Tables 1 and 2, respectively. Pretreatment soil sampling parameters shall also include any additional contaminants of concern associated with the soil, and feed soil limitations. Recommended methods for the various sampling parameters are presented in the paper. Sample data collected during an investigation of the site may be substituted for the following requirements, as appropriate.

Soil Sampling Parameters for LTTD Treatment of Petroleum Contaminated Soils

PETROLEUM CONTAMINANT ANALYTICAL PARAMETERS

Gasoline, Mineral Spirits VO + 10 1, Lead 2

Kerosene, Jet Fuel VO + 10,

Naphthalenes 3

Fuel Oil No. 2, Diesel Fuel TPHC, PAH 4

Fuel Oil Nos. 4 & 6., Hydraulic Oils, Cutting Oil, Crude Oil,

Lubricating Oil, TPHC, PAH 4

Table Footnotes

- Environmental Protection Agency (EPA) target compound list volatile organic (VO) or priority pollutant VO scans including xylene with a gas chromatograph/mass spectrometer (GC/MS) library search for the ten highest peaks.
- Lead analysis required for leaded gasoline sources. Soil may have elevated metals prior to petroleum spills occurring. However, metals other than lead are not typically parameters of concern for petroleum spills. Operating temperatures are usually low enough to prevent significant volatilization of metals.

3. Naphthalene's, including naphthalene, methyl naphthalene, di-methyl naphthalene; may be analyzed in base/neutral + 15 (B/N+15) fraction or infractions; if analyzed in VO fraction, instrument shall be calibrated for these analytcs. Quantat of all isomers found shall be performed against at least one methyl naphthalene standard and at least one di-methyl naphthalene standard.

4. Polynuclear Aromatic Hydrocarbons (PA11) as per EPA Priority Pollutant List
 TABLE A2 Soil Sampling Parameters for LTTD Treatment of Coal Tar/Gas Plant Wastes and Contaminated Soils.

CONTAMINANT	ANALYTICAL PARAMETERS
Coal Tar and Coal Tar Contaminated soil	BTEX1, PA11, TPHC2, Metals3, BNA4 Sulfur
Purifier Box Waste and Metals3, Total Cyanide, Total and Reduced Box Waste Contaminated Soils Sulfur	
Combined Coal Tar and Box Wastes	BTEX1, PA11, TPHC2,, Metals3, BNA4, or Contaminated Soils Total Cyanide, Total and Reduced Sulfur

Table Footnotes

1. BTEX compounds consist of benzenes, toluenes, ethyl benzenes and xylenes.
2. TPHC - Total petroleum hydrocarbons.
3. Metal – At MGP sites, certain metals (e.g. arsenic, cadmium, chromium, copper, lead and nickel) could be present at elevated levels, typically up to several hundred parts per million. However, operating temperatures are usually low enough to prevent significant volatilization of metals.
4. BNA compounds are base/neutral/acid extractable. This includes PAH compounds.

Analytical Methods

EPA/ASTM methodologies shall be utilized for all parameters. The specific methodologies are presented in Table A3.

TABLE A3 Methods of Analysis for LTTD Sites

Parameter	Method of Analysis
BTEX, VO+10	SW846 8240 (Packed Column) or 8260 (Capillary Column)
PAH	SW846 8270
TPHC	SW 846 8015B
Metals	SW846 6010
BNA	SW846 8270
Total Cyanide	SW846 9010 (manual) or 9012 (automated)
Sulfur	ASTM 3176, 3177 methods 427C, 428A

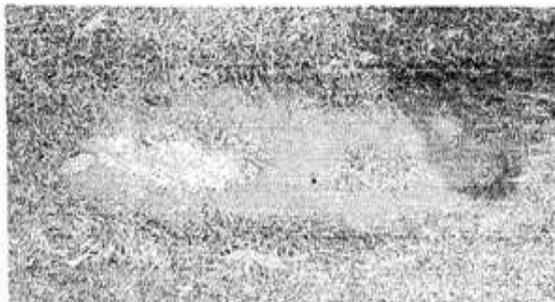


Figure 1 Artificial Oil Spill Site

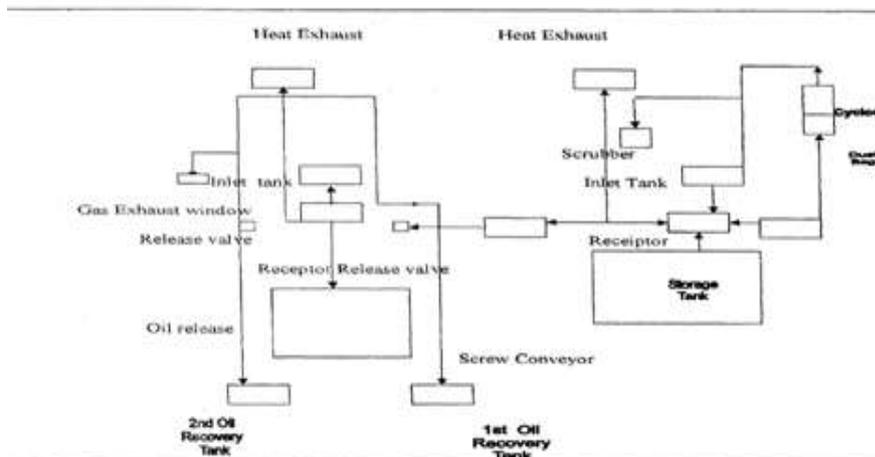


Figure 2: Flow diagram of Distillative/Cracking Chamber

Table 1: Systematic Illustration of Condition Shot down process

1. Primary burner failure	Instantaneous shutdown
2. Outlet soil temperature below set point which is based on type and amount of contamination, soil type, and test run.	10 minute delay
3. Afterburner temperature (if applicable) below set point used in test run.	30 second to 2 minute delay
4. Blower failure or positive pressure at the desorber.	Instantaneous shutdown
5. Bag house pressure drop (if applicable) outside the operating envelope determined during test run.	Instantaneous shutdown

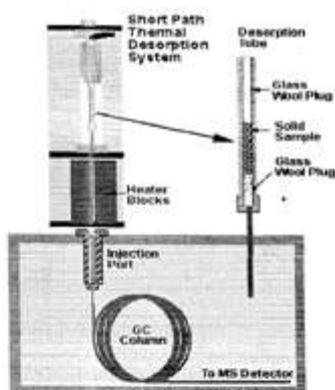


Figure 3: Short Path Thermal Desorption System

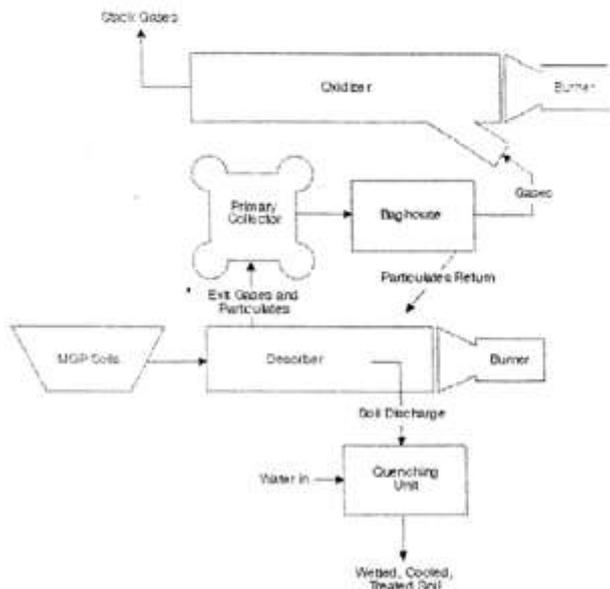


Figure 4 Schematic of thermal desorption process

Table 2: Egaspin Guidelines for Disposable of Treated Wastes

S/N	Pollutant or Effluent Characteristics	Values (Once / dav During Discharge	
		inland (flesh water	Near Shore (Blackish/Saline waters)
1.	pH	6.5 - 8.5	6.5-8.5
2.	Temperature °C	25	30
3.	Total Hydrocarbon Content, mg/1	10	20
4.	Salinity As Chloride, mg/1	600	2,000
5.	Chemical Oxygen Demand (COD), mg/I	10	125
6.	Turbidity, NTU	10	15
7.	Total Dissolved Solids (TDS), mg/1	2,000	5,000
8.	Total Suspended Solids (TSS), mg/1	30	50
9.	Odour	Unobjectionable	unobjectionable
10.	Pb ⁺² , mg/1	0.05	No Limit
11.	Total Iron (Fe), mg/1	1.0	No Limit
12.	Cu ⁺ , mg/1	1.5	-do-
13.	Zn ² , mg/1	1.0	-do-
14.	Cr ^{+b} , mg/1	0.03	0.5

Source: -Egaspin, 2002 Edition, pg. 14

Table 3 - DPR - LTTD Treatment Chart

S/N	Parameters	Initial Concentration	Latest Obtained	Lab. Results	DPR Spec.
1.	Hydrocarbon (mg/l)	83,800	< 0.001		5-10
2.	Chloride (mg/l)	86,200	1,000		600 - 2,000
3.	Copper (mg/l)		< 0.001		1.0
4.	Zinc (mg/l)	4.02	< 0.001		1.0-5.0
5.	Iron (mg/l)	3.16	0.56		1.0 -Nil
6.	Cadmium (mg/l)	6	0.001		1.0
7.	Chromium (mg/l)	34	0,4740		0.3-0.7
8.	Lead (mg/l)	<0.001	0.001		0.05
9.	Mercury (mg/l)	0.001	0.001		1.0

Table 4 Laboratory Obtained results of treated drill cuttings

S/No		Concentration (mg/l)				
		Chloride	Oil& Grease	Chromium	Zinc	Cadmium
I.	Initial Cone.	86,200	83,800	34	4,1032	6
2.	LTTD Treatment	35,500	2,000	0.7113	0.8679	<0.001
3.	-do-	13,000	<0.001	0.4740	0.3142	
4.	-do-	9,600	<0.001			
5.	- do-	4,700	<0.001			
6.	t-do -	4,300	<0.001			
7.	-do-	4,200	<0.001			
8.	-do-	3,800	<0.001			
9.	-do-	3,500	<0.001			
10.	-do-	2,200	<0.001			
11.	-do-	2,000	<0.001			
12.	-do-	1,700	0.001			
13.	-do-	1,500	0.001			
14.	-do-	1,300	0.001			

15.	-do-	1,300	<0.001
15.	-do-	1,300	0.001
16.	-do-	1,400	<0.001
17.	-do-	1,200	<0.001
18.	- do-	1,000	<0.001

(The presence of Mercury and Lead in the treated wastes were very insignificant)

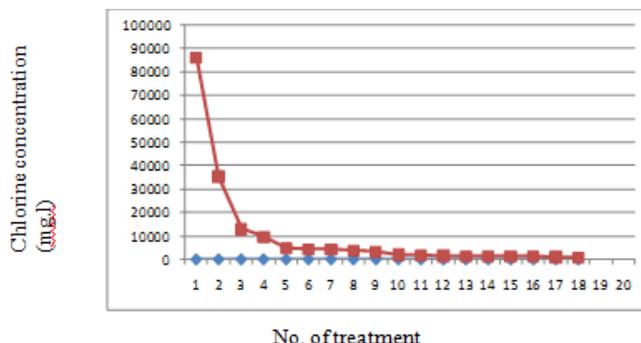


Figure 5: Chlorine concentration versus number of treatment

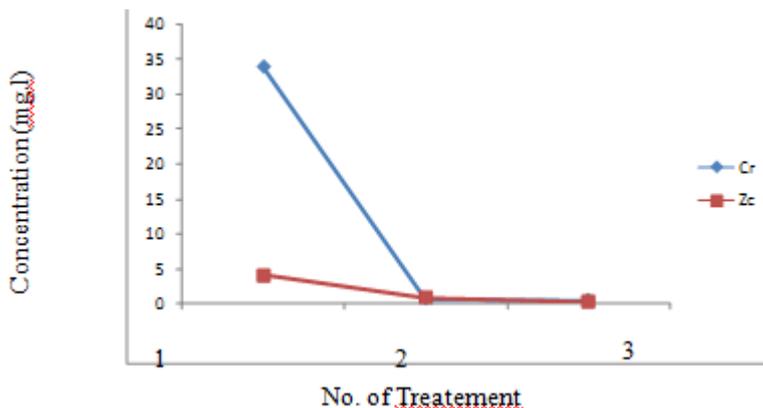


Figure 6: Concentration of chromium and zinc versus No. of treatment

Table 6: Comparison of Advantages and disadvantages of LTTD method of treating cuttings

Advantages

Readily available equipment for onsite or offsite treatment,
 Very rapid treatment time; most commercial systems capable of over 25 tons per hour throughput.
 Cost competitive for large volumes (greater than 1 000 yd³) of soils: \$30-70/ton of: contaminated soil exclusive of excavation and transportation costs.
 Can be used to mitigate hot spot source areas with very high concentrations of: petroleum hydrocarbons.
 Easily combinable with other technologies, such as air sparging or groundwater extraction
 Treated soil can be redeposited onsite or used for landfill cover (if permitted by a regulatory agency).
 Can consistently reduce TPH to below 10 ppm and BTEX below 100 ppb (and sometimes lower).

Disadvantages

:Requires excavation of soils; generally limited to 25 feet below land surface.
 Onsite treatment will require significant land area to locate LTTD unit and store process soils.
 Offsite treatment will require costly transportation of soils and possibly: manifesting.
 Soils excavated from below the: groundwater table require dewatering prior to treatment because of high moisture content.