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**Development of an innovative and environmentally sustainable solid
waste stream treatment process**

A thesis submitted to The Robert Gordon University for the degree of Master of Research
in the Centre for Research in Energy and Environment.

November 2010

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B.E. (Environmental), M. Enterprise (Environmental Innovation)

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Abstract

Oily sludges and oil contaminated solid wastes are generated from various sources such as from a) interceptors in petrol stations, automobile garages and rail service stations b) tank oil bottoms from crude oil storage tanks c) drill cuttings from oil and gas exploration and d) Oil based drilling muds . The petroleum sludge wastes typically are water-in-oil emulsion that are stabilised by fine solids.

The Hazardous Waste Directive classifies oily sludges and oil contaminated solids as hazardous waste due to its carcinogenic nature. The directive specifies that an oil concentration of more than 0.1% in solids have a risk of causing cancer to humans making it hazardous. Traditionally such wastes have been landfilled. Hazardous waste such as the above has higher landfill costs charged by the landfill operators and also higher landfill tax compared to non-hazardous waste. Such wastes generated throughout Scotland needs to be transported to England and Wales for suitable disposal or treatment and recovery. With the implementation of new legislations such as EU landfill directive the existing option of transportation and disposal turns out to be costly to the tune of £300 per tonne. Hence it is important to find an alternative option for treating such wastes locally in order to avoid transportation of these wastes and also position industries to offer an environmentally sustainable solid waste treatment system.

This thesis reports a study of various technologies examined in the development of an oily sludge treatment process and summarises results from lab trials, site trials and site visits to technology suppliers. In addition to developing a treatment chain this report concludes by recommending that treatment of oily sludge from hazardous waste to inert waste standards can only be achieved utilising thermal treatment methods. This can either be plasma, microwave or infrared technology based thermal treatment and needs to be decided on a case to case basis. An indicative cost benefit analysis presented provides an indication of capital and operational expenditure for the above technology.

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1. Introduction

Oily sludges and oil contaminated solid wastes are generated from various sources such as from a) interceptors in petrol stations, automobile garages and rail service stations b) tank oil bottoms from crude oil storage tanks c) drill cuttings from oil and gas exploration and d) Oil based drilling mud . The petroleum sludge wastes typically are water-in-oil emulsion that are stabilised by fine solids. It is a complex mixture of petroleum hydrocarbons (such alkanes, aromatics, resins and asphaltenes), waste oil (40-60%), waste water (30-90%), and mineral particles (5-40%) (*I. Lazar et al., 1999*). Such varied composition makes them recalcitrant and very difficult to utilise.

The marked stability of the multiphase system is due to the adsorption of oil into solid particles producing a highly protective layer (as they tend to settle to the bottom of the tanks), and also the presence of surface active compounds which are responsible for the formation of emulsions. Additionally the presence of organic polar fractions brings about charge repulsion, impairing the formation of homogeneous phase. From the chemical point of view, recalcitrance can be ascribed due to the presence of aromatic hydrocarbons and heavier molecular fractions such as asphaltenes. (*A.U.Soriana et.al., IPEC, 2002*) It is estimated that each refinery produces 30,000 tonnes of these sludge each year.

The Hazardous Waste Directive (*Hazardous Waste Regulations 2003, OPSI*) classifies oily sludges and oil contaminated solids as hazardous waste due to its carcinogenic nature. The directive specifies that an oil concentration of more than 0.1% in solids have a risk of causing cancer to humans making it hazardous. Traditionally such wastes have been landfilled. Hazardous waste such as the above has higher landfill costs charged by the landfill operators and also higher landfill tax compared to non-hazardous waste. Such wastes generated throughout Scotland needs to be transported to England and Wales for suitable disposal or treatment and recovery. With the implementation of new legislations such as EU landfill directive (*The pollution handbook, 2005*) the existing option of transportation and disposal turns out to be costly to the tune of £300 per tonne. Hence it is

important to find an alternative option for treating such wastes locally in order to avoid transportation of these wastes and also position industries to offer an environmentally sustainable solid waste treatment system.

Currently such waste arisings in Scotland are managed by physico-chemical treatment to reduce the quantity of waste and further transporting them to hazardous landfill sites in England. This leads to transportation costs to the tune of £ 30 per tonne of waste and additional £300 per tonne towards treatment and disposal costs. The aim of developing a treatment plant is to primarily reduce the quantity of hazardous waste and further to treat and convert it to nonhazardous waste.

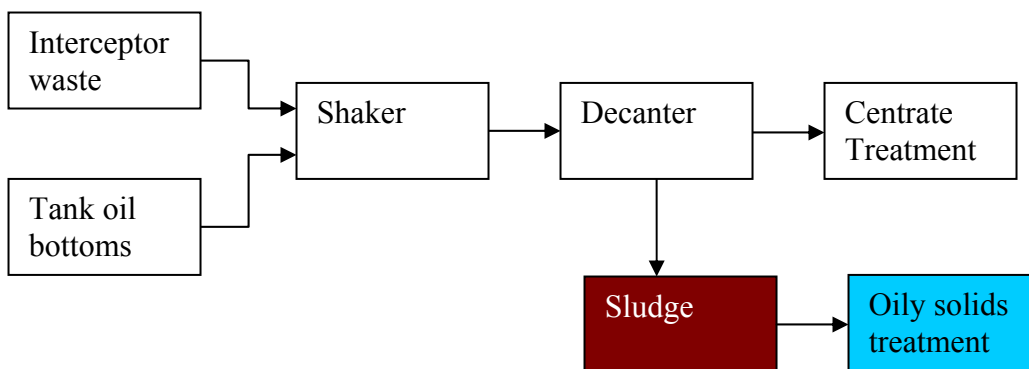


Figure 1-1: Treatment first stage

In solid waste management practices reduction of waste volume is the first strategy in order to reduce the amount of waste handled. In this case the shaker and decanters are aimed at reducing the volume by reducing the water content of solid waste. Within this thesis, initially previous work and literature is reviewed in order to provide the necessary background information regarding the problem of oily solids as hazardous waste and the science supporting the treatment process. The experimental methods, analytical techniques and treatment trials are then documented, followed by a detailed description and analysis of the results from the experiments. This is followed by cost benefit analysis for the options in sludge treatment and wastewater treatment. Finally, conclusions are

drawn in relation to the project aims and objectives and recommendations are made for further work.

2. Literature Review

2.1. Legislative Overview

2.1.1. Hazardous waste directive (HWD-2005)

The aim of the HWD (<http://www.opsi.gov.uk/si/si2005/20050894.htm>) is to provide a precise and uniform European-wide definition of hazardous waste and to ensure the correct management and regulation of such waste. The starting point of the HWD is to identify which wastes are deemed to be hazardous. Article 1(4) of the HWD defines hazardous waste as wastes featuring on a list drawn up by the European Commission, because they possess one or more of the hazardous properties set out in the HWD. There are 14 hazardous properties set out as

- H1-Explosive
- H2-Oxidising
- H3A- Highly flammable
- H3B-Flammable
- H4-Irritant
- H5-Harmful
- H6-Toxic
- H7-Carcinogenic
- H8-Corrosive
- H9-Infectious
- H10-Toxic for reproduction
- H11-Mutagenic
- H12-Waste producing toxic gases
- H13-Waste liable to produce other hazardous waste after disposal
- H14-Ecotoxic wastes

The petroleum based oil contaminated soils fall under the carcinogenic category H7. This indicates that at an oil concentration greater than 0.1% in the wastes from interceptors, tank bottoms and drill cuttings are classified as hazardous waste and hence needs to be maintained, transported and disposed according to the regulations set in place for hazardous waste management.

2.1.2. The Landfill Directive (1999)

The European Landfill Directive (http://ec.europa.eu/environment/waste/landfill_index.htm) was introduced in 1999. The main objectives of the directive are the prevention of many of the environmental impact that arise as a result of the landfilling of waste. These may be broadly described as the pollution of surface and ground waters, pollution of soils, and methane emissions to the air.

In order to achieve those objectives, the directive requires landfill sites to be classed into one of three categories: hazardous, non-hazardous, or inert depending upon the type of waste that they receive. It also requires operators to demonstrate that they and their staff are sufficiently technically competent to manage the site, and have adequate finances to cover the maintenance and aftercare provisions.

Two of the more significant consequences of the directive however, are that pre-treatment of wastes prior to landfilling have become a requirement, and that a demand for a progressive diversion of the amount of waste being sent from landfill to other treatment methods has occurred. The pre-treatment of the waste may be carried out by either chemical, thermal or biological means, and is aimed at reducing the volume of the waste being sent to landfill, reducing its hazardous nature, helping to facilitate its handling, and enhancing its recovery.

Landfill site management has been affected as landfill operators have been forced to scrutinise and treat the incoming waste to make sure that they are falling in line with regulation, which in turn has had major impacts on operating costs. The resulting change

to the infrastructure of the waste management industry, including the vast increases in handling capacities needed to cope with the gradual phasing out of landfill sites, coupled with the environmental demand of future disposal techniques has prompted the need for alternative methods that maximise the level of reuse and recycling of the waste stream.

The landfill tax for disposal of hazardous waste such as oily sludge is £33 per ton and will increase £3 every year.

2.1.3. The Waste Incineration Directive (2000)

The Waste Incineration Directive

(http://europa.eu/legislation_summaries/environment/waste_management/128072_en.htm) is a piece of legislation that was introduced into Europe in the year 2000. It did not come into force within the U.K until 2002, and was introduced in an attempt to reduce some of the environmental impact that arise as a result of the incineration of waste.

The Waste Incineration Directive sets limits on the emission levels of various harmful substances released into the environment as a result of the incineration of waste, and introduces targets for future emission levels

There are a number of other guidelines within the directive, and there are a number of techniques available to keep emissions within the required levels. However, the guidelines are often restrictive, and the emission controls costly to implement. The constant upgrading of the equipment required to keep pace with increasingly strict controls, often results in the waste incineration option becoming expensive and not always economically viable.

This increase in restrictions and cost associated with the operation of waste incinerators have contributed towards the development of alternative methods of waste disposal.

2.1.4. Summary

The centrifuge changes the physical properties of the sludge (i.e. changes it from a liquid to a solid) and removes some oil. For classification purposes, the cake from the centrifuge should therefore be describes as:

19 03 04* wastes marked as hazardous, partly stabilised

19 03 05 stabilised wastes other than those mentioned in 19 03 04 (e.g. non hazardous).

*- refers to absolute hazardous classification

Description and subsequent disposal of centrifuge cake as stabilised (non hazardous) waste would require chemical analysis and a demonstration that the sludge contains no compounds that exhibit hazardous properties H1 through H14, as defined in the Environment Agency's interpretation of the definition and classification of hazardous waste, Technical Guidance document WM2.

Current understanding is that for sludges originating from refineries, this would include reducing oil levels to below 0.1%, reducing total PCB levels to less than 0.005% and ensuring there is no measured aquatic toxicity on a leachate from the sludge (www.sepa.org.uk/waste/waste_regulation/landfill.aspx). For disposal to landfill as a hazardous partially stabilised waste would require chemical analysis and assessment against the Waste Acceptance Criteria (WAC) for both hazardous waste (HW) and stable non reactive hazardous waste (SNRHW). Experience has demonstrated that the key requirements here are to reduce the total organic carbon content of the waste to below 6% for HW and 5% for SNRHW. The other key requirement is to reduce the leachable dissolved organic carbon content to below 1000 mg/kg for HW and 800mg/kg for SNRHW.

2.1.5. Impact on Disposal

2.1.5.1. Totally Stabilised Sludge

Totally stabilised sludge is considered non-hazardous and could be disposed of in a number of ways including disposal to a non-hazardous landfill. This could only be achieved by demonstrating through chemical analysis that the sludge contains no materials that can exhibit hazardous properties H1 through H14..

For refinery sludges, this is believed to be ensuring that:

- oil levels were reduced to less than 0.1%
- total PCB levels were reduced to less than 0.005% and
- there is no measured aquatic toxicity on a leached sample.

2.1.5.2. Partially Stabilised Sludge

Partially stabilised would be considered as hazardous waste. For disposal to landfill, the waste must achieve a required quality, termed the Waste Acceptance Criteria (WAC). This gives absolute values for sludge quality (see Table below) as well as values for how much material can be leached out of the sludge after a standard leaching test.

Two levels of quality are presented; for Hazardous Waste (HW) and for Stable Non Reactive Hazardous Waste (SNRHW). Under some circumstances, SNRHW can be disposed of in a SNRHW cell in a non hazardous landfill with a potential cost saving.

Parameter	Values, SNRHW	Values, HW
Total Organic Carbon (TOC)	5%	6%
Loss on Ignition	-	10

pH	Minimum 6	Minimum 6
Acid Neutralisation Capacity (ANC)	Must be evaluated between the pH of the waste in question, at pH6 and the pH of the site leachate	

Table 2-1: Absolute WAC values of Sludge Quality

The key parameter is believed to be the TOC content of the waste.

Compliance with Waste Acceptance Criteria for Hazardous Waste		
Compound	mg/kg dry weight @ L/S = 10 litres/1 kilogramme, WAC SNRHW	mg/kg dry weight @ L/S = 10 litres/1 kilogramme, WAC HW
Arsenic (As)	2	25
Barium (Ba)	100	300
Cadmium (Cd)	1	5
Total Chromium (Cr total)	10	70
Copper (Cu)	50	100
Mercury (Hg)	0.2	2
Molybdenum (Mo)	10	30
Nickel (Ni)	10	40
Lead (Pb)	10	50
Antimony (Sb)	0.7	5
Selenium (Se)	0.5	7
Zinc (Zn)	50	200
Chloride (Cl)	15,000	25,000
Fluoride (F)	150	500
Sulphate (SO ₄)	20,000	50,000
Dissolved Organic Carbon (DOC)	800	1,000

Compliance with Waste Acceptance Criteria for Hazardous Waste		
Compound	mg/kg dry weight @ L/S = 10 litres/1 kilogramme, WAC SNRHW	mg/kg dry weight @ L/S = 10 litres/1 kilogramme, WAC HW
Total Dissolved Solids (TDS)	60,000	100,000

Table 2-2: Leaching WAC values of Sludge Quality

The key parameter is believed to be the leachable DOC content of the waste.

2.2. Technology review

The waste analysis indicates that the concentration of hydrocarbon/oil from the above sources renders the waste hazardous and hence the aim of the treatment plant should be to reduce the hydrocarbons to less than 0.1%. There are several treatment technologies either currently in use or being developed. These treatment technologies based on the principle of operation can be divided into physical, chemical, biological and thermal based technologies. Each of these methods is discussed in detail herewith. For aid of comparison the technologies discussed are presented in summary tables 2.3 to 2.6, where the advantages and disadvantages are compared and conclusions provided on technology review.

2.2.1. Physical treatment technologies

2.2.1.1. Centrifuging

Centrifuges depending on the type of filtration can be classified as either decanting or filtering type systems. The purpose of decanting centrifuges is to separate heavier

solids (higher specific gravity) from the lighter liquid (lower specific gravity). The filtering centrifuges use a medium such as filter cloth or a screen to separate the solids from liquid.

In solid waste management, this technology is used for volume reduction of waste samples by reducing the water content. The reduction in water content improves the efficiency and reduces the waste handling costs for downstream treatment processes.

The important parameters while selecting centrifuge for oily sludge application includes operating temperature, particle size of solids and facilities for feed homogenisation.

2.2.1.2. *Electrokinetic separation*

The principle of electrokinetic remediation relies upon application of a low-intensity direct current through the sludge between opposite charged electrodes. This mobilises charged species, causing ions and water to move toward the electrodes. Metal ions, ammonium ions, and positively charged organic compounds move toward the cathode (*FRTR, version 4.0 section 4.5*). Anions such as chloride, cyanide, fluoride, nitrate, and negatively charged organic compounds move toward the anode. The current creates an acid front at the anode and a base front at the cathode. This generation of acidic condition in situ may help to mobilise sorbed metal contaminants for transport to the collection system at the cathode.

This methodology is used for removal of metals, inorganic components from contaminated soil. The performance of this technology drastically varies if the inputs are not homogenous. Effectiveness is sharply reduced for wastes with a moisture content of less than 10 percent. Maximum effectiveness occurs if the moisture content is between 14 and 18 percent.

2.2.1.3. *Soil washing*

The concept of reducing soil contamination through the use of particle size separation is based on the finding that most organic and inorganic contaminants tend to bind, either chemically or physically, to clay, silt, and organic soil particles. The silt and clay, in turn, are attached to sand and gravel particles by physical processes, primarily compaction and adhesion (*FRTR, version4.0 section 3.5*). Gravity separation is effective for removing high or low specific gravity particles such as heavy metal-containing compounds. Attrition scrubbing removes adherent contaminant films from coarser particles. However, attrition washing can increase the fines in soils processed. The clean, larger fraction can be returned to the site for continued use.

The disadvantage for this technology is oil removal from clay based sludge is difficult hence cannot be applied for refinery or interceptor wastes that might contain clay/fine particles. Sludge washing can however be used in order to decrease the viscosity of sludge in order to aid oil/water/solids separation.

2.2.1.4. *Stabilisation/Solidification*

Solidification/stabilisation reduces the mobility of hazardous substances and contaminants in the environment through both physical and chemical means. Unlike other remedial technologies, this technology seeks to trap or immobilise contaminants within their "host" medium (i.e., the soil, sand, and/or building materials that contain them) instead of removing them through chemical or physical treatment (*FRTR, version4.0 section 3.5*). Leachability testing is typically performed to measure the immobilisation of contaminants. This process is generally used to contain inorganic contaminants and is an onsite treatment.

The organics cannot generally be stabilised and hence Stabilisation or Solidification generally is not applied for removal of oil in sludge.

2.2.2. *Chemical treatment technologies*

2.2.2.1. *Solvent extraction*

Chemical extraction does not destroy wastes but is a means of separating hazardous contaminants from soils, sludges, and sediments, thereby reducing the volume of the hazardous waste that must be treated (*FRTR, version4.0 section 3.1*). The technology uses an extracting chemical and differs from soil washing, which generally uses water or water with wash-improving additives. Commercial-scale units are in operation. They vary in regard to the chemical employed, type of equipment used, and mode of operation.

Physical separation steps are often used before chemical extraction to grade the soil into coarse and fine fractions, with the assumption that the fines contain most of the contamination. Physical separation can also enhance the kinetics of extraction by separating out particulate heavy metals, if these are present in the soil.

Solvent extraction is a common form of chemical extraction using organic solvent as the extractant. It is commonly used in combination with other technologies, such as solidification/stabilisation, incineration, or soil washing, depending upon site-specific conditions. Solvent extraction also can be used as a stand alone technology in some instances.

This is a proven concept for removal of hydrocarbons from contaminated solids. However, it has certain drawbacks so that it is not very effective with longer chain hydrocarbons and some soil content and organic matter adversely affect the performance of the system.

2.2.2.2. *Advanced oxidation process*

Reduction/oxidation (Redox) reactions chemically convert hazardous contaminants to nonhazardous or less toxic compounds that are more stable, less mobile, and/or inert (*FRTR, version4.0 section 3.12*). Redox reactions involve the transfer of electrons from one compound to another. Specifically, one reactant is oxidised (loses electrons) and one is reduced (gains electrons). The oxidising agents most commonly used for treatment

of hazardous contaminants are ozone, hydrogen peroxide, hypochlorites, chlorine, and chlorine dioxide. Chemical reduction/oxidation is a short- to medium-term technology.

The advanced oxidation technology is widely used for reduction of hydrocarbons in water treatment. The technology has a limitation for its use in solids waste treatment, as the efficiency of dissipation of light/energy in turbid and solid conditions is very low. Also, the process is not cost-effective for high contaminant concentrations because of the large amounts of oxidizing agent required.

Some unpublished work indicate that AOP can be used for hydrocarbon reduction from soils, the practical ability of which needs to be verified.

2.2.3. Biological treatment technologies

2.2.3.1. Bioremediation

Bioremediation is a process in which indigenous or inoculated micro-organisms (e.g., fungi, bacteria, and other microbes) degrade organic contaminants found in soil and/or ground water, converting them to innocuous end products. Nutrients, oxygen, or other amendments may be used to enhance bioremediation.

Petrolsynth (Geolife product) uses inoculated micro-organisms/enzymes in order to enhance the biodegradation of hydrocarbon-contaminated soils.

Solbrite aids in breaking down long chain hydrocarbons to shorter chain hydrocarbons thereby making it simple for the indigenous micro-organisms to degrade the simple molecules.

2.2.3.2. *Phytoremediation*

Phytoremediation is a process that uses plants to remove, transfer, stabilize, and destroy contaminants in soil and sediment (*FRTR, version4.0 section 3.1*). Contaminants may be either organic or inorganic. This is an onsite treatment process and is mostly used for remediation of heavy metals contaminated soils. Hence it is not suitable for treatment of waste streams identified.

2.2.3.3. *Landfarming*

Landfarming is a full-scale bioremediation technology, which usually incorporates liners and other methods to control leaching of contaminants, which requires excavation and placement of contaminated soils, sediments, or sludges(*FRTR, version4.0*). Contaminated media is applied into lined beds and periodically turned over or tilled to aerate the waste. Soil conditions are often controlled to optimise the rate of contaminant degradation. Conditions normally controlled include:

- Moisture content (usually by irrigation or spraying).
- Aeration (by tilling the soil with a predetermined frequency, the soil is mixed and aerated).
- pH (buffered near neutral pH by adding crushed limestone or agricultural lime).
- Other amendments (e.g., Soil bulking agents, nutrients, etc.).

There are various limitations to treat the waste streams identified such as a large amount of space is required, conditions affecting biological degradation of contaminants (e.g., temperature, rain fall) are largely uncontrolled, which increases the length of time to complete remediation, dust control is an important consideration, especially during tilling and other material handling operations and treatment of longer chain hydrocarbons require more time for bioremediation.

2.2.4. *Thermal treatment technologies*

2.2.4.1. *Thermal desorption*

Thermal desorption is a physical separation process and is not designed to destroy organics (*FRTR, version 4.0 section 3.6*). Wastes are heated to volatilise water and organic contaminants. A carrier gas or vacuum system transports volatilised water and organics to the gas treatment system. The bed temperatures and residence times designed into these systems will volatilise selected contaminants but will typically not oxidise them.

Two common thermal desorption designs are the rotary dryer and thermal screw. Rotary dryers are horizontal cylinders that can be indirect or direct-fired. The dryer is normally inclined and rotated. For the thermal screw units, screw conveyors or hollow augers are used to transport the medium through an enclosed trough. Hot oil or steam circulates through the auger to indirectly heat the medium. All thermal desorption systems require treatment of the off-gas to remove particulates and contaminants. Particulates are removed by conventional particulate removal equipment, such as wet scrubbers or fabric filters. Contaminants are removed through condensation followed by carbon adsorption, or they are destroyed in a secondary combustion chamber or a catalytic oxidiser. Most of these units are transportable.

2.2.4.2. *Incineration*

High temperatures, 870 to 1,200 °C, are used to volatilise and combust (in the presence of oxygen) halogenated and other refractory organics in hazardous wastes (*FRTR, version 4.0 section 3.6*). Often auxiliary fuels are employed to initiate and sustain combustion. The destruction and removal efficiency for properly operated incinerators exceeds the 99.99% requirement for hazardous waste. Off gases and combustion residuals generally require treatment.

Incinerator off-gas requires treatment by an air pollution-control system to remove particulates and neutralize and remove acid gases (NO_x and SO_x). Baghouses, venturi

scrubbers, and wet electrostatic precipitators remove particulates; packed-bed scrubbers and spray driers remove acid gases.

Even though technically incinerators would treat the waste, this mechanism of burning would create pollutant emissions that need to be treated prior to discharge. This makes the system costlier and also recently there have been instances of regulators recommending closure of incineration plants due to social protests.

2.2.4.3. Pyrolysis-Plasma based

Pyrolysis is defined as chemical decomposition induced in organic materials by heat in the absence of oxygen (*FRTR, version 4.0 section 3.6*). In practice, it is not possible to achieve a completely oxygen-free atmosphere; actual pyrolytic systems are operated with less than stoichiometric quantities of oxygen. Because some oxygen will be present in any pyrolytic system, nominal oxidation will occur. If volatile or semi-volatile materials are present in the waste, thermal desorption will also occur.

Pyrolysis transforms hazardous organic materials into gaseous components, small quantities of liquid, and a solid residue (coke) containing fixed carbon and ash. Pyrolysis of organic materials produces combustible gases, including carbon monoxide, hydrogen and methane, and other hydrocarbons.

Plasma arc treatment is a high-energy technology able to treat a range of scheduled wastes. In plasma arc treatment, directing an electric current through a low pressure gas stream creates a thermal plasma field. Plasma arc fields can reach 5000 to 15000°C. The intense high temperature zone can be used to dissociate the waste into its atomic elements. This is done by injecting the waste into the plasma, or by using the plasma arc as a heat source for combustion or pyrolysis.

2.2.4.4. *Radio frequency/ Electromagnetic heating – Microwave heating*

Microwave-assisted soil remediation applies to the remediation of sites contaminated with volatile compounds (e.g. polycyclic aromatic hydrocarbons (PAH)s, polychlorinated biphenols (PCBs), etc.) as well as non-volatiles (e.g. heavy metals). In the latter, decontamination follows the vitrification process where glass and other materials are placed on top of the contaminated soil. The glass and soil melt in an amorphous mass, immobilising the contaminants.

Microwave radiation has also been applied to the removal of volatile and semi-volatile components, however, it is especially effective in the case of polar compounds. In the case of non-polar compounds, addition of magnetic nanoparticles ensures an increase in the microwave absorption characteristics of the contaminant. All vapours (including soil moisture) are removed from the soil after the application. Further work found that microwaves could be used to enhance solvent extraction of the contaminants from the soil but the properties of the soil greatly affected the extent to which the contaminants were removed.

This technology is not commercially available although there are certain suppliers like Rotawave claiming the treatability of hydrocarbon-contaminated soils.

Physical treatment technologies

	Name	Method	Advantages/Disadvantages	Suitability	Suppliers
1	Centrifuging	Uses filtering or decanting methods to separate solids from the liquid.	<ul style="list-style-type: none"> • Comparatively lower operating costs. • Widely spread technology. • Can be used only for solid-liquid separation. • Does not remove hydrocarbons from solids. 	Pre-treatment	1.Alfa-laval 2.Euroby 3.Huber 4.Solids control services
2	Electro kinetic separation	Method of removing metals and other inorganic pollutants from contaminated soils using electrodes.	<ul style="list-style-type: none"> • Can be used on site and ex site. • Can be used only for metal reduction. • Does not remove hydrocarbons from solids. 	Not suitable for hydrocarbon reduction.	Not applicable
3	Soil washing	Contaminants sorbed onto fine soil particles are separated from coarse soil in an aqueous-based system on the basis of particle size.	<ul style="list-style-type: none"> • Separates fine particles most commonly attached to hydrocarbons from coarse particles. • Can be used for volume reduction. • Does not remove hydrocarbons from clay/silts. 	Not suitable	Not applicable
4	Solidification/ Stabilisation	Contaminants are physically bound with a stabilised mass (solidification), or chemical reactions are induced between the stabilising agent and contaminants to reduce their mobility (stabilisation).	<ul style="list-style-type: none"> • Converts hazardous waste to non-hazardous by solidification or stabilisation of waste. • Can be disposed as inert waste. • Organics are not generally stabilised 	Not suitable	Not applicable

Table 2-3 : Physical treatment technologies. Primarily used for volume reduction. In this case shaker and decanter is proposed and hence can be termed as pre-treatment.

Chemical treatment technologies

	Name	Method	Advantages/Disadvantages	Suitability	Suppliers
1	Solvent extraction	Waste contaminated soil and extractant are mixed in an extractor, thereby dissolving the contaminants. The extracted solution is then placed in a separator, where the contaminants and extractant are separated for treatment and further use.	<ul style="list-style-type: none"> • Has been shown to be effective in treating sediments, sludges, and soils containing primarily organic contaminants such as VOCs and petroleum wastes. • Least effective on very high molecular weight organic substances. • Some soil types and moisture content levels will adversely impact process performance. 	Suitable (Based on trials)	Would be a combination of technologies such as mixing, centrifuging and distillation. Each item can be purchased separately.
2	Advanced oxidation process	Advanced Oxidation Processes including ultraviolet (UV) radiation, ozone, and/or hydrogen peroxide are used to destroy organic contaminants.	<ul style="list-style-type: none"> • It is a destruction process, as opposed to solvent extraction, for which contaminants are extracted and concentrated in a separate phase. • UV oxidation processes can be configured in batch or continuous flow modes, depending on the throughput under consideration. • The aqueous stream being treated must provide for good transmission of UV light (high turbidity causes interference). 	Currently not suitable. Current work going on in the labs, which may yield promising results.	Not applicable

Table 2-4 : Chemical treatment technologies. Can treat hazardous components of waste. Solvent extraction theoretically removes hydrocarbons however technology needs to be further explored for its suitability with oily sludges.

Biological treatment technologies

	Name	Method	Advantages/Disadvantages	Suitability	Suppliers
1	Bioremediation	Indigenous or inoculated microorganisms (e.g., fungi, bacteria, and other microbes) degrade organic contaminants found in soil, converting them to harmless end products.	<ul style="list-style-type: none"> • Can treat hydrocarbon contaminated soils. • Comparatively cheaper operating costs. • Large amount of space is required. • Homogenised feed required. 	Suitable. Trials planned.	Geolife. Solbrite.
2	Phytoremediation	Phytoremediation is a process that uses plants to remove, transfer, stabilize, and destroy contaminants in soil.	<ul style="list-style-type: none"> • Can treat hydrocarbon contaminated soils. • Cannot be used for treating wastes such as oily sludge, as this is an onsite treatment. • High concentrations of hazardous materials can be hazardous to plants. 	Not suitable.	Not applicable
3	Landfarming	Contaminated soil, sediment, or sludge is excavated, applied into lined beds, and periodically turned over or tilled to aerate the waste.	<ul style="list-style-type: none"> • Can treat hydrocarbon contaminated soils. • Large amount of space is required. • Large amount of time is required for treatment of longer chain hydrocarbons. • Cannot tolerate shock loads. 	Not suitable.	Not applicable

Table 2-5 : Biological treatment technologies. Phytoremediation and land farming are not suitable for the purpose. Bioremediation with Geolife and Solbrite are claimed by the suppliers and is being verified by the RGU through a Msc project.

Thermal treatment technologies

	Name	Method	Advantages/Disadvantages	Suitability	Suppliers
1	Desorption	Wastes are heated to volatilise water and organic contaminants. A carrier gas or vacuum system transports volatilised water and organics to the gas treatment system.	<ul style="list-style-type: none"> • Can treat hydrocarbon contaminated soils. • Commercial systems incorporate air and water pollution control techniques. • High capital and operating cost. 	Suitable	RLC technologies
2	Incineration	High temperatures, 870-1,200 °C (1,600- 2,200 °F), are used to combust (in the presence of oxygen) organic constituents in hazardous wastes.	<ul style="list-style-type: none"> • Can treat hydrocarbon contaminated soils. • Combustion process produces pollutants. • Recently incineration plants like SITA have been shut down due to legislations. 	Not recommended in short term due to planning difficulties.	
3	Pyrolysis-Plasma based	Chemical decomposition is induced in organic materials by heat in the absence of oxygen. Organic materials are transformed into gaseous components and a solid residue containing fixed carbon and ash.	<ul style="list-style-type: none"> • Can treat hydrocarbon contaminated soils. • It digests the organic waste as against burning hence less pollution related problems. • High capital and operating cost. 	Suitable	Tetronics Solena
4	Radio frequency/ Electromagnetic heating – Microwave heating	Radio frequency heating (RFH) is an in situ process that uses electromagnetic energy to heat soil.	<ul style="list-style-type: none"> • Can treat hydrocarbon contaminated soils. • No data on existing plants that treat hydrocarbon contaminated soil using this technology. 	Suitable (To be verified)	Rotawave

Table 2-6 : Thermal treatment technologies. Thermal desorption and plasma options are suitable for reduction of hydrocarbons to required levels.

3. Experimental Methods

3.1. Oily sludge quality analysis

Oily sludge samples were analysed in The Robert Gordon University laboratories for Water content, oil content, solids content, content analysis with GCMS and heavy metal content.

3.1.1. Total Solids analysis

3.1.1.1. w/v measurements using Retort kit

Water, Oil and Solids content

A known quantity of sample (W) is taken and heated for 15 minutes on an electric hot plate with mixing/stirring. The purpose is to remove the water content. The difference in weight between the initial (W) and final samples (W15) is the quantity of water in the sample and helps determine the water content. The dry samples post water content determination is heated to 660°C in a furnace. The oil and organics get vaporised at these temperatures. The difference in weight between the initial (W15) and final samples (W660) is the quantity of oil in the sample and helps determine the oil content. W660 determined from the oil content experiments is the weight of solids in the sample and is used to determine the solids content of the sample.

3.1.1.2. Organic and Inorganic solids using solvent extraction

- a) Weigh out approximately 10g of sample into beaker and record exact weight (S).
- b) Weigh filter paper (A).
- c) Place filter paper on the filter apparatus and apply vacuum.
- d) Add 25mL of acetone to sample and mix to homogenise sample.
- e) Filter through filter paper, add another 25mL of acetone to beaker and rinse through filter paper again.

- f) Remove vacuum and carefully remove filter paper and place in drying oven for 1 hour.
- g) Remove from oven and when at room temperature weigh on balance (B).
- h) Carefully add to furnace for 30 minutes.
- i) Weigh filter paper on balance (C).

The calculations for measuring inorganic and organic solids are as follows:

Total Solids = B-A

Organic Solids = B-C

% Solids = Total Solids/S*100

% Organic Solids = Organic Solids/S*100

3.1.2. Gas Chromatography- Mass Spectrometry

The Gas chromatograph/ Mass Spectrometry (GC/MS) is used for chemical analysis of basic organic contents in a sample. The GC is a separation method and MS is generally an analytical detection instrument. The GC instrument is effective in separating compounds into their various components. However, the GC instrument cannot be used for reliable identification of specific substances. The MS provides analytical measurement to identify specific analysis but produces uncertain qualitative results.

The GC instrument accepts samples only in liquid or gaseous form for detection of chemical components. In the initial trial, the interceptor waste and tank bottom samples were dissolved in hexane and the supernatant was filtered prior to placing the liquid in the analyser. This did not give any results and hence both the samples were heated in a water bath for 15 minutes and the vapour samples were collected and analysed. The results indicate that the components are diesel-based hydrocarbons and the detailed plots are as attached in Appendix 1.

4. Oily Sludge Treatment- Development of Treatment Chain

Decanter centrifuge can separate the sludge into two phases, solid and liquid. The solid phase produced by the centrifuge (referred to as sludge cake) is classed as hazardous waste and the aim of treatment trials and review is to determine the optimum route for disposal.

4.1. Primary Treatment- Solids Separation

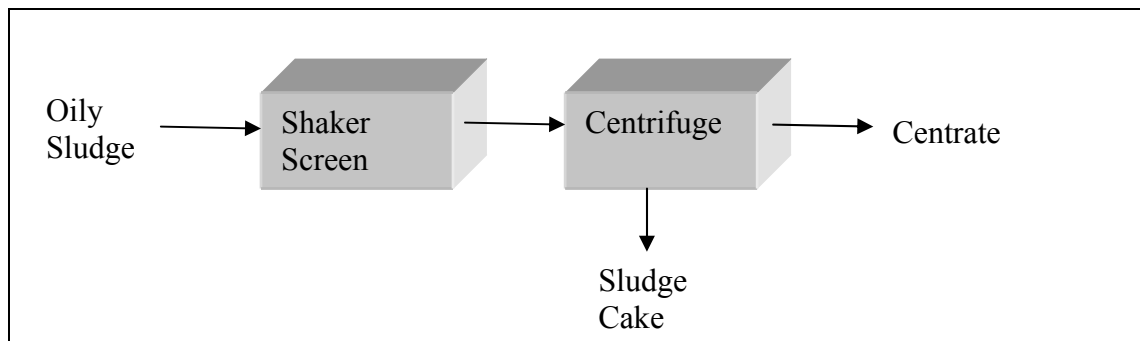


Figure 4-1: Solids Separation flow diagram representing recommended method for dewatering oily sludge for volume reduction

4.1.1. Shaker Screen

The use of shaker screens is an important pretreatment for oily sludge treatment system as it helps remove large sized particles such as gloves, stones etc. that can mechanically damage centrifuges. The treatment philosophy is that of a sieve or a filter wherein a vibrating sieve or wire-cloth screen vibrates while the oily sludge is on top of it. The liquid phase of the oily sludge is smaller than the wire mesh and so can pass through the screen, while larger solids are retained on the screen and eventually fall off the back of the device and are discarded. Obviously, smaller openings in the screen clean more solids from the input sludge; however there is a corresponding decrease in flow rate per unit area.

4.1.2. Centrifuge

Decanter centrifuge is used to for phase separation of oily sludges. This acts as a volume reduction treatment mechanism thereby forming the first in chain of waste treatment hierarchy wherein the volume of waste is reduced by separating the solids from liquids.

Mechanical energy is utilised to increase the gravitational force exerted on solids that are present in the oily sludge. Decanting Centrifuge is able to apply over 3,000 G-forces on the liquid/solids mixture, which separates the heavier solids from the lighter solids. Additionally, high G-forces separate fine solids from liquid.

A variety of parameters such as operating temperature, flocculants, flow rate etc. affect the separation efficiencies of oil-water-solids in a centrifuge. Below table summarises the results from lab centrifuge trials on oily sludge monitored over various operating temperatures:

Temperature	20 degrees C	40 degrees C	60 degrees C	80 degrees C
Oil	10%	12%	15%	25%
Water	70%	55%	45%	38%
Solids	20%	30%	40%	42%

Table 4-1: Impact of temperature on oily sludge separation in centrifuge

As can be seen, the higher the temperature, the greater the solids removal efficiency and phase separation between oil and water layer.

Decanter centrifuges are generally available for around 3000G's centrifugal force. The percentage removal of solids depends on particle size. Generally particle sizes above 100 microns have good separation efficiencies at 3000G. Sludges with a higher ratio of solids particles less than 100 microns will have lower separation in a decanter centrifuge without addition of flocculants or change in centrifuge gravity force.

4.2. Sludge Cake Treatment- Oil concentration reduction

4.2.1. Landfill Disposal Quality

Since tank bottom sludge and refinery arisings are classified as Hazardous Waste (HW), the relevant quality limits that limit disposal to landfill are detailed under the Waste Acceptance Criteria (WAC) (*Technical Guidance; EWC Codes WM2*).

Further discussions with the Regulator has indicated that if the oily sludge is subjected to suitable treatment in a licensed facility, the dewatered sludge cake could potentially be re-classified as a non-hazardous waste if it could be demonstrated that the cake presented no hazardous properties when assessed by the appropriate procedure (WM2).

4.2.1.1. Quality Targets

The quality targets set for the trials are detailed below:

4.2.1.1.1. Conversion to Non Hazardous Waste

Since the sludge contains oil, the main risk phrase associated is “R45 – may cause cancer”, linked to the presence of a Category 1 carcinogen. By removing the oil in the centrifuge, the sludge could cease to be described as oily waste and be re-classified as “... sludges from on-site effluent treatment other than those containing hazardous waste” (e.g. non hazardous waste).

The determination of whether it is non hazardous would depend on it exhibiting no hazardous properties when assessed using the Regulator’s assessment procedure. Since this procedure could be quite arduous, one specific parameter has been identified as an indicator. The determination of “Carcinogenic” has specified concentration limits set out in the Hazardous Waste Regulations, above which a waste would be hazardous. If the oil could be reduced to a concentration below 0.1%, then it is an indicator that the waste could be classified as non hazardous.

The quality target set is the ability of the treatment to reduce the oil content to less than 0.1%

4.2.1.1.2. Conversion to SNRHW

Should the waste be deemed to still be classified as a hazardous waste, the determination on whether it could be classified as SNRHW would rest on its ability to achieve the Waste Acceptance Criteria (WAC). The most sensitive parameters for oily sludge are the absolute Total Organic Carbon (TOC) content and the leachable dissolved organic carbon (DOC).

The quality target set is the ability of the treatment to achieve the WAC for SNRHW, specifically to reduce the TOC content of the sludge below 5%.

4.2.1.1.3. *Reducing solids content in centrate*

Oil recovery from centrate stream forms an important part of centrifuge operations. The quality of recovered oil depends on the quantity of solids and the water content in the centrate stream. Oil can be recovered from the centrate (combination of oil, water and solids) if solids content are low (i.e. in ppm range).

4.2.2. *Sludge Cake Treatment trials and Results*

4.2.2.1. *Experience with Biological treatment*

4.2.2.1.1. *Bioremediation*

Under the aegis of a KTP program a project was carried out in RGU. This included laboratory trials which were carried out under controlled conditions of temperature, moisture and mixing to verify treatment potential of oily sludge (OS) from interceptor waste and tank bottoms (TB) under three conditions that are:

1. No additives
2. Petrolsynth
3. Solbrite

Petrolsynth and Solbrite are two commercially available product mixes. Solbrite is a degreaser and cleaner product and Petrolsynth consists of a combination of nutrients and enzymes.

Sampled on 20/12/05	TPH Conc.(µg/g)	% Reduction	Sampled on 19/01/06	TPH Conc.(µg/g)	% Reduction
Initial Reading	86000			86600	
Dry solid	80200	7	Dry solid	62500	27
S+ Water*	10500	87	S+ Water	10100	88
S+Pet-T	27200	68	SNA	-	-
S+Pet-I	23500	72	S+Pet-I	58800	30

S+Sol-T	138500	NRO*	S+Sol-T	299300	NRO*
S+Sol-I	58000	32	SNA	-	-

Table 4-2: Results from biological treatment of oily sludges. Showing various bioremediated samples reduction in TPH concentration (S =Sample Sludge, Pet = Petrosynth, Sol = Solbrite, T = Tank bottom waste, I = Interceptor waste, NRO = No reduction observed, SNA = Sample was not available)*-water sprinkled. All trials were carried out in duplicate and indicative sample size error is + or – 30%.

As can be seen from the above table, TPH reduction efficiencies of around 88 % in a period of 2 months can be obtained by treating oily sludge with nutrients and providing appropriate conditions in terms of temperature, moisture and mixing. The waste still remains as Hazardous in nature as the oil content is greater than 0.1% however can with respect to waste acceptance in landfills can be disposed to a Stabilised cell in non hazardous landfill thereby reducing the disposal cost from £300 per ton to £70 per ton. This solution can be implemented however capital investments in terms of land requirements, windrow facilities etc. makes the option unviable for large quantities of waste to be treated off site.

4.2.2.2. *Experience with Chemical treatment*

The following successful trials were conducted as a part of KTP project;

Peroxide Treatment

- a) Solid Calcium Peroxide
- b) Solid Calcium Peroxide at reduced pH
- c) Liquid Hydrogen peroxide

Solvent extraction

- d) Hexane
- e) Toluene
- f) Hexane and Toluene (50:50)
- g) Tetrachloroethylene

4.2.2.2.1. Peroxide Treated Samples

Treatment	Quantity (% w/w)	Days of Treatment	TPH Conc. (µg/g)	Reduction (%)
Initial Sample			51400	
CaO ₂	10	42	33000	34
Replicate	10	42	36000	29
CaO ₂	5	42	37000	27
Replicate	5	42	35000	31
CaO ₂ with reduced pH	10	20	3000	90
Replicate	10	20	5000	89
Liquid H ₂ O ₂	10	28	62000	NRO
Replicate	10	28	59000	NRO

Table 4-3: Results from peroxide treatment of oily sludge. All trials were carried out in duplicate and indicative sample size error is + or – 30%.

As can be seen from the above table, TPH reduction efficiencies of 90 % can be obtained by treating oily sludge with Solid peroxide at reduced pH of 4. This corresponds to 0.4% of TPH content in treated solids.

The waste still remains hazardous in nature as the oil content is greater than 0.1% however can be disposed to a Stabilised cell in non hazardous landfill. This solution is however not recommended as the soil will require further treatment in terms of pH correction and there is a possibility of waste by products being generated in the process. At present conditions the economics do not favour such a treatment facility due to high costs of solid peroxides and pH correction facilities.

4.2.2.2.2. *Solvent Extraction:*

Soxhlet Extraction	TPH($\mu\text{g/g}$ of sample)	TPH($\mu\text{g/g}$ of Residue)	Extraction Efficiency (%)
Hexane	56000	14000	80
Hexane Replicate	48000	14000	76
Toluene	18000	14000	55
Toluene Replicate	18000	11000	61
Toluene: Hexane	19000	13000	59
Tol: Hex Replicate	16000	12000	56
Tetrachloroethylene	30000	20000	59
TTE Replicate	24000	29000	45

Table 4-4: Results from solvent extraction treatment of oily sludge. All trials were carried out in duplicate and indicative sample size error is + or – 30%.

Maximum treatment efficiencies of 80% were obtained during treatment trials. The waste still remains hazardous in nature as the oil content is greater than 0.1% however can be disposed to a Stabilised cell in non hazardous landfill. This solution is however not recommended due to high capital and chemical costs which do not justify the treatment efficiency.

4.2.2.3. *Thermal Treatment*

Oil contaminated wastes such as interceptor wastes, oily tank bottoms, oil contaminated soil, oil based drilling mud etc. are classed as hazardous in nature since the oil content greater than 0.1% and are costly to dispose. It is the idea to explore various treatment options in order to select a suitable technology to treat 5T/hour of oil contaminated solids to reduce the oil content to less than 0.1% and render it non-hazardous.

4.2.3. *Plasma Technology (Thermal Treatment)*

4.2.3.1. *Tetronics , Faringdon*

Plasma technology is an identified technology which has the potential to treat such oily solids. Tetronics are plasma technology suppliers and have a research and test facility in Farringdon. Tetronics plasma treatment facilities includes a hopper feed system, plasma reactor and gas cleaning systems. The whole unit is supervisory control and data acquisition (SCADA) controlled and monitors various parameters within the test facility such as temperature, power, gas parameters etc. During our visit to the test facility Tetronics were carrying out trials with Refuse Derived Fuel (RDF) which is a by product of municipal solid waste treatment.

- The largest plant based on capacity supplied by Tetronics is 5500T/year located in Japan.
- The approximate gross electricity consumption for a plasma treatment would be 800 KW/ton.
- Optimum capacity plasma treatment is 25000-30000 Ton/Year plant.
- The space required for a 25000T/Year plasma treatment plant would be 100 m long by 25 m wide 2 storied building.
- Any plasma treatment for asbestos has to be a standalone plant .i.e. no other waste streams can be treated in any such plant.
- Plasma is capable of treating a flexible range of waste streams, however the treatment plant should have separate feed systems and the waste streams cannot be mixed during treatment.
- The barriers to entry of plasma treatment include its high capital cost, and operating cost.
- The treated material is classed as 19 04 01 in the EWC codes. Tetronics is working with Environment agency to class the treated material as inert which would increase the viability of any treatment facility.

4.2.3.2. Pyrogenesis-Montreal

Pyrogenesis is based in Montreal and have supplied plasma systems for treatment of municipal and hazardous waste to US navy and Carnival cruises. On a comparative note

with Tetronics (based in UK), Pyrogenesis has more experience and exposure in supplying commercial systems. Since the capital and operating costs are expensive for such high end waste treatment technologies, Plasma can only be used for specialised applications such as ship based waste treatment or oily solids (in our case) in which case the economics would work out favourably. Pyrogenesis is willing to work with partners in UK on a Build Own Operate basis in which case the partner has to provide a guarantee of waste streams and facilitate location and licensing requirements. One of the outstanding technical advantages of Plasma over other thermal systems is fact that there is no formation of dangerous gases as dioxins and furans which have always been a sore point in approval of incineration/thermal plants.

- Pyrogenesis supplies two types of plasma systems depending on the type of waste
- The Plasma Arc Waste Destruction System (PAWDS) is a combination of Waste shredder, waste silo, waste mill, plasma torch, plasma chamber, quench system, venture cyclone and related control systems.
- US Navy and Carnival cruise lines have PAWDS systems installed in their ships and PyroGenesis have ongoing contracts with US Navy for supply of PAWDS in next generation ships.
- The Plasma Resource Recovery System (PRRS) is designed for land based treatment and is a combination of Feed Pre-treatment System, graphite arc plasma furnace, plasma chamber, synthetic gas cleaning system and energy recovery system.
- The PRRS is recommended for oily sludge applications since it involves a 2 stage process of vitrification and gasification
- All inorganic waste will be vitrified using graphite based furnace in the first stage, in this stage the organics gets converted to gas form.
- The second stage involves introducing this gas through a plasma jet, thereby creating a synthetic gas which is treated using a synthesis gas cleaning system.
- The synthesis gas can be used for recovering energy post treatment.

- Pyrogenesis have carried out more than 50 pilot tests with variety of waste streams ranging from municipal solid waste to tires and other solid and liquid waste.
- Since plasma is a combined ultimate treatment for solid, liquid and gaseous wastes it can be used to treat nay type of solid and liquid waste and flexibility can be designed in the system. More energy is required to treat liquids.
- The footprint of a 25TPD PRRS system is 500m² with additional 200m² for energy recovery systems.
- During treatment of liquid waste additional solids such as silica and other material needs to be added.
- Slag falls out as molten lava from the graphite chamber. This could potentially be a safety issue.
- Daily and weekly maintenance and replacements form an important part of operations. The graphite rods need replacement daily. The plasma chamber needs a cleanup/water wash to remove any settled solids and plasma torch needs to be replaced once a week (150 hours of operation)
- Fully automatic plant can be designed based on Programmable Logic Controller controls as supplied for US navy and Carnival cruises.
- Most of the closed vessels are designed to be flame proof.
- The feed material to plasma is designed such that all materials have a contact time which is maintained automatically
- If more chlorides or sulphides are present in solids then water and air treatment needs to be designed accordingly.
- Pyrogenesis have experience in air and water treatment plants and would supply a comprehensive solution as a package.
- Pyrogenesis have a good R&D base in Montreal with 5TPD PAWDS and 2TPD PRRS plant.
- Pyrogenesis is open for potential tie-ups for special developments particularly targeted towards specific markets.

4.2.3.3. Plasma Treatment-Order of magnitude Cost Benefit Analysis

Plasma Treatment-Cost benefit Analysis				
Capital cost				
Mechanical	£10,000,000			
Civil	£1,000,000			
Total Capex	£11,000,000			
Operating cost				
Power	£20	per ton		
Maintenance and spare parts	£20	per ton		
Chemicals	£5	per ton		
Labour	£11	per ton		
Licence + documentation cost	£1	per ton		
Flue gas treatment	£5	per ton		
			(Based on £11 million Capital costs over 5 years @ 12%)	
Finance costs	£210	per ton		
Total		£272	per ton	
Existing disposal costs	Landfill-Case1		Waste Operators-Case2	
Landfill Gate fee	£78.00	per ton	£300.00	per ton
Landfill tax	£21.00	per ton		
Transportation costs	£35.00	per ton	£35.00	per ton
Labour	£10.00	per ton	£10.00	per ton
TOTAL	£144.00	per ton	£345.00	per ton
Notes:				
<ul style="list-style-type: none"> • Energy recovery included in mechanical price • System operating revenues such as electricity sales and slag/metals sale is not included. This will reduce the operating cost by £100/ton. • The operating cost including revenues generated is £172/ton of treated solids • Capex cost based on offer from Pyrolysis-Canada for 60T/day, i.e. 3T/hour considering 20 average operating hours per day 				

Table 4-5: Plasma Treatment – Cost benefit analysis

4.2.4. Microwave Treatment (Thermal Treatment)

Microwave treatments for 2 applications were discussed. A) Contaminated soil treatment and B) Usage of microwave as alternate heating source for preheating solids/liquids.

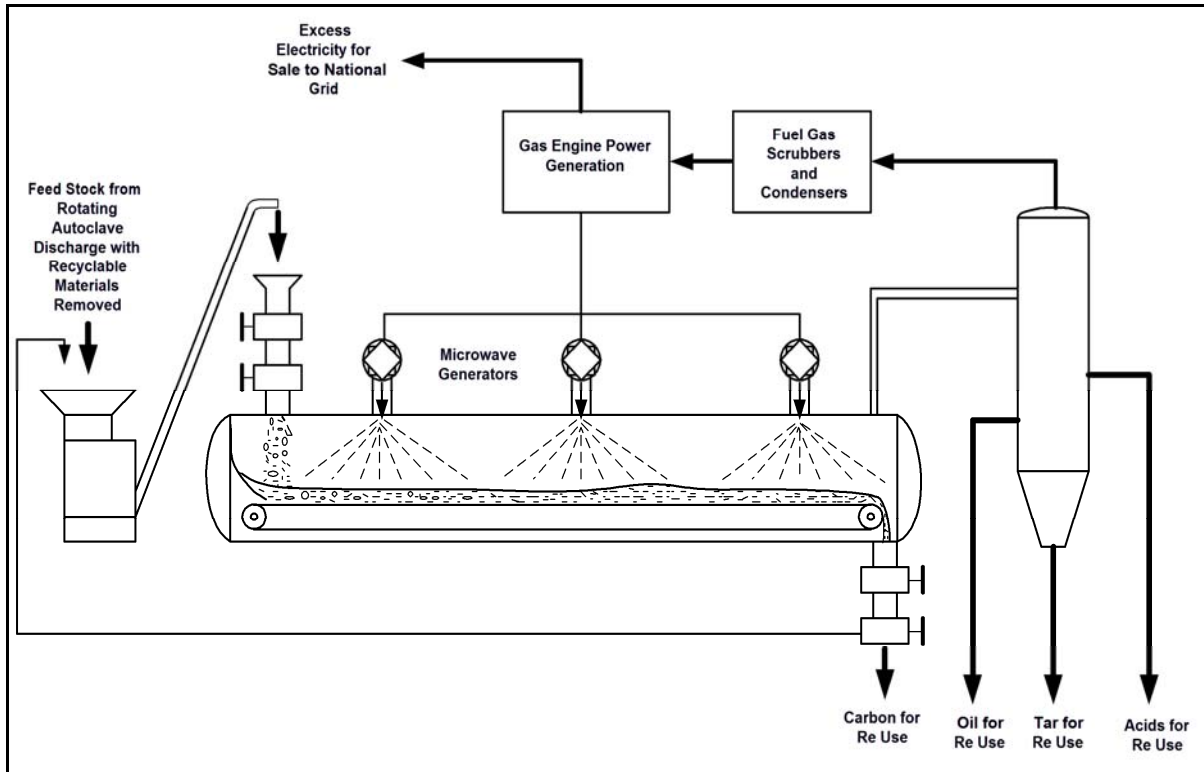


Figure 4-2: Microwave treatment flow diagram (IMSL Website)

4.2.4.1. Microwave for oily solid treatment applications

- The microwave based treatment is a thermal approach to treat oily solid waste and uses microwave energy to remove oil from solids.
- The temperatures can be raised up to 400 deg C in order to achieve this.
- The above flow diagram shows the involved mechanisms. This includes a preheating system, hopper feed system, microwave system, air pollution management systems and energy generators.
- 120KW power is required to treat 1T/hour.
- Dimension wise a 100 KW machine is 2 m long.

- It is recommended to preheat the solids to about 70-80 deg C as pre-treatment to remove water content prior to the microwave treatment. The higher the water content in solids more microwave energy is required to evaporate it.
- The approximate space requirement for a 5T/hr plant would be 10mx10m.
- The risks include microwave exposure, air pollution, high voltages and other mechanical operation risks. However these are taken into consideration and safeguards are provided.
- Time scale to supply a plant would be 9-10 months since supply of magnetrons has long lead times.
- The approximate capital cost for a 1T/hr plant is £200,000 and Operating cost would be as Electricity-£6.25/T and £2/T for magnetron maintenance.
- It is important that data is collected prior to any purchase of equipment in terms of treatment capability and air pollution control requirements.
- PERA (Product Engineering Research Association) based in Melton Mowbray has microwave trial facilities and need to be involved in order to collect more data which would also give information for any further PPC requirements.
- The treated solids will have a temperature of 400-450 deg C and this heat can be utilised by provisions in design to capture the heat.

4.2.4.2. *Microwave for preheating applications (Pipe based without screw mechanism)*

- IMSL pipe based microwave systems can be used to preheat oily sludge to 70 deg C in order to get greater efficiencies from the decanter centrifuge. 5T/hr microwave heating for such application would require 210 KW power.
- Dimensions would be 2mlong x 1m wide x 2m high and could be placed in a container along with the generators. 2X100KW generators would be required.
- Approx Capital cost is £200,000 and operating cost is £3/Ton for electricity and £2/T for magnetron maintenance.
- Assumptions: Specific heat of water, oil and solids as 0.7, 0.4 and 0.3 respectively.

4.2.4.3. Microwave Treatment-Order of magnitude Cost Benefit Analysis

Microwave Treatment-Cost Benefit Analysis			
Capital cost			
Mechanical	£3,000,000		
Civil	£1,000,000		
Total Capex	£4,000,000		
Operating cost			
Power		£10	per ton
Maintenance and spare parts		£5	per ton
Chemicals		£2	per ton
Labour		£5	per ton
Licence + documentation cost		£1	per ton
Flue gas treatment		£10	per ton
Byproducts treatment and disposal		£15	per ton
Finance costs		£46	per ton
			(Based on £4 million Capital costs over 5 years @ 12%)
Research and Development	£500,000	£5	per ton
			(Based on £500,000 Capital costs over 5 years @ 12%)
Total		£99	per ton
Existing disposal costs			
	Landfill-Case1		Waste Operators-Case2
Landfill Gate fee	£78.00	per ton	£300.00 per ton
Landfill tax	£21.00	per ton	
Transportation costs	£35.00	per ton	£35.00 per ton
Labour	£10.00	per ton	£10.00 per ton
TOTAL	£144.00	per ton	£345.00 per ton
Notes:			
Capital cost estimate includes 2 times quoted and additional cost for air pollution control kit			
Energy recovery is not considered and will lead to savings in operating cost			

Table 4-6: Microwave treatment-Cost benefit analysis

4.3. Electrocoagulation for oil/water separation

Powell water systems Inc is based in Centennial, Colorado and supply Electrocoagulation technology for water and wastewater treatment. Powell water systems holds worldwide patent for the electrocoagulation systems (designed in a particular way). This new design concept has given them competitive advantage over other suppliers wherein the electricity consumption drives the operating cost high thereby making the system unviable.

Electrocoagulation is a flexible technology for treatment of wastewater from centrifuges and other new waste streams.

Visits included two electrocoagulation plants,

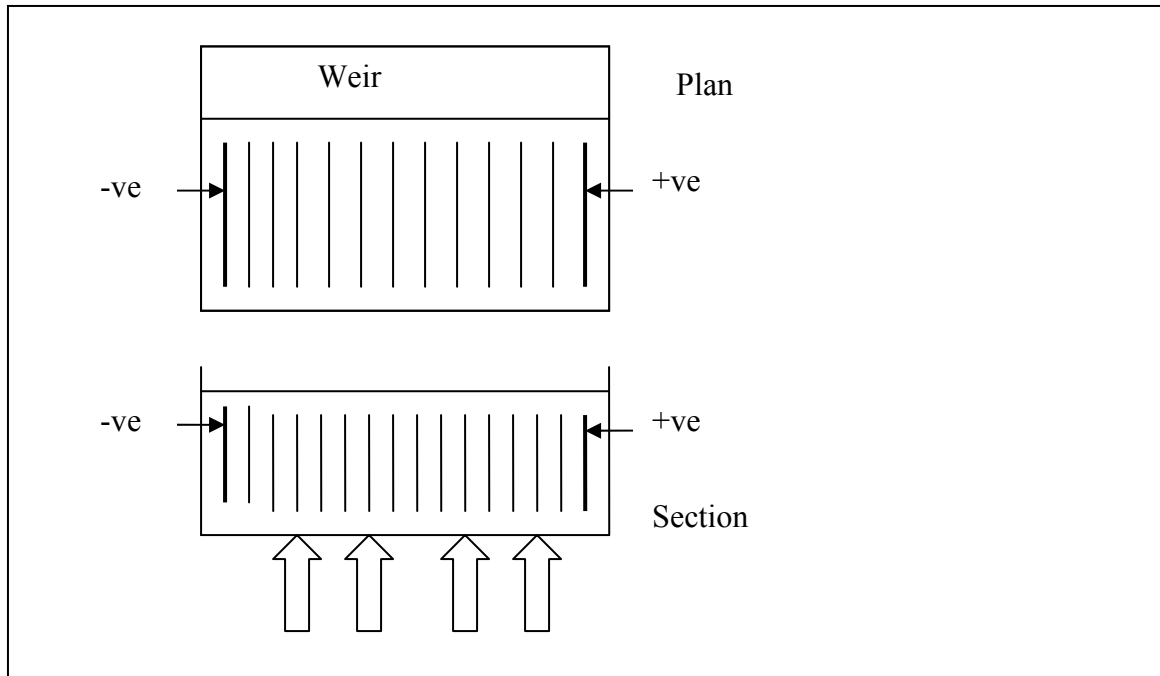
- a) Central waste water treatment plant
- b) US water purification Inc

Central wastewater treatment plant (CWWT) is located in the city of Denver and operates tanker services to empty interceptor and gully waste from gas stations and car wash. Prior to installation of EC unit the central wastewater treatment plant had over ground holding tanks and filter press for sludge separation. This system was not giving the desired results and the plant got closure notices from EPA and local authority. The treatment plant was modified as below:

Shaker→4 Holding tanks→Electrocoagulation→Clarifier→Filter →(Treated Water)

The sludge from all the processes is homogenised and dewater using a filter press.

The treated water has been consistently meeting and exceeding the discharge standards stipulated by EPA and central wastewater now have received a metro award for zero errors in 12 months for discharge of wastewater.



Details of EC system: 217 MS plates with alternating current from the electrodes. Alternating current is timer based.

CWWT operate a 50 GPM plant. Initially aluminium plates were used however due to lack of performance with this particular effluent stream changed it to mild steel plates. Please note a few technical points regarding this plant:

- pH of treated water is neutral
- No chemical addition in the process
- The plant operates from 06:00 am until 13:00 everyday after which a one hour acid cleaning procedure is undertaken.
- EC unit used 480v line with 3 phase current; the EC unit is capable to operate in the range of 200 to 600 v.
- Being in a similar industry CWWT personnel explained the fluctuations in the nature of incoming effluent and how EC system copes with consistent performance.

- The acid wash procedure uses 33% HCL which is stored in a 250 gallon drum. This can be arranged to be on automatic dosing. The acid needs replenishment after about a month.
- The material of construction of skid is Mild Steel powder coated and tank is Polyethylene.
- The system is an up flow treatment with 217 blades each placed at a gap of 3 mm. It is this minimal distance which provides efficiency and patent to Powell water system.
- The whole system including acid wash etc can be automated and the system can be operated from a remote base and data collected.
- The plates need replacement once in 12-16 months.
- The plant in CWWT is located in an elevated platform.
- The plant is mobile, modular and flexible in operations.
- The only drawback I envisage is the lack of proper sludge separation expertise. Various types of effluent can be treated through electrocoagulation however efficient sludge removal is yet to be explored.

4.3.1. EC technology for oily slops treatment

Powell water systems have licensed the EC technology for treatment of Oily slops to Universal Systems Inc based in Baker city. Universal systems Inc is being set up as a service company to cater to the market of oily slops treatment primarily in America. They have supplied their first system to E.A.R.T.H in Trinidad and Tobago (www.earthtt.com) and are expecting order for a \$200 million service contract with American oil major firm.

There are two types of slop oil –"first-stage slop oil" and "second-stage slop oil" or "slop-oil waste". "Slop-oil waste" comes about mainly through failed attempts at breaking the emulsions in first-stage slop oil treatment plus a combination of tank

bottom oils and waste oils from other parts of the refinery. Slop-oil waste consists of oil that is bound up with water, silt, organics heavy metals and a variety of chemical additives. The Universal water System, in coordination with a proprietary chemical, is well suited to handle this waste. Slop-oil waste contain an average of 50% crude oil, however existing market technology cannot separate the value from the slop and it eventually becomes a liability that must be disposed of as a toxic waste. Universal Water Services Company Slop Oil Reclamation System enables to provide value back to the refineries in lieu of their total losses in oil profits and the heavy expenses of toxic waste disposal.

The value returned is in the form of clean, usable crude oil, delivered back to the refineries for close to the same cost that they are currently paying for waste disposal. EC equipment causes oil emulsions to break using electricity. The solids held in the oil are transferred from the oil to the water due to our proprietary chemicals. The treatment combination produces oil for refining continuously. The heavy metal ions in the water are converted to metal oxides, which are non-hazardous.

This can prove to be a new approach in providing solutions to our clients for treatment of Floating Production Storage and Offloading (FPSO), tank bottoms, oily slops and drilling mud waste.

US Water Purification Inc located in Colorado Springs is supplier of water and wastewater treatment plants and specialise in membrane technologies. Our visit was aimed to see EC unit being supplied for a novel application of silica, hardness and heavy metals removal from water prior to reverse osmosis treatment. The EC plant helps the efficiency of water treatment to be 97% which otherwise would have been limited to around 85%.

The EC system was integrated to be a part of larger system and the plant was Programmable Logic Controller controlled and could be remotely operated. Fibre

reinforced plastic (composite plastics) is used instead of steel for skid making the whole unit much lighter and easily transportable.

- The EC system is flexible and variety of wastewater streams can be treated.
- Eliminates the need for chemical addition, chemicals handling and extra sludge production.
- Operating costs are comparable with chemical dosing systems however capital costs are 3-4 times higher.
- Chemical dosing system needs constant monitoring and very tough to control with varying effluent parameters with problems of over chemicals dosing or untreated water, the problems which EC can eliminate.
- BTEX and other organics can be treated effectively using EC system
- Delivery schedule for a kit is 20 weeks from the date of order.
- Considerable time in designing the system for our internal specifications and that of UK industry.

The timescale for the above till delivery of the kit is 24 weeks (maximum of 6 months)

5. Initial assessment of potential solutions to provide sustainable solid waste treatment processing

The aim of this section is to list out the items that need to be considered while initial assessment of any potential project and in particular thermal treatment options as in this case. The list starts by technical assessment and includes risk assessment, deliverability, planning and regulatory, benefits, financial aspects and environmental impacts.

The objective of the project is to render the oil contaminated solids as non hazardous waste. Since oil is greater than 0.1% in the identified waste streams the solids is classed as hazardous waste and needs to be disposed in special landfills in England. The economics of transporting such solids and increasing landfill costs and taxes provide a good justification for investment in treatment plants.

The desired outcome of any treatment plant is to initially reduce the volume of hazardous waste and to render the waste non hazardous and that in this case means to reduce the oil content of solids less than 0.1%. Ideally the treated solids can be reused for some other industrial application such as building aggregates or filtering material. This requirement limits the treatment options available since most of the technologies give only part reduction of oil content and do not meet the required 0.1% criteria. Hence thermal treatment technologies such as Plasma and Microwave are being looked into in much detail.

As an initial and most important step of mixing the waste and reducing the water content a shaker and decanter centrifuge needs to be installed. This helps in reducing the volume and water content of wastes that need to be further treated.

The treatment plant is to be designed for an inlet capacity of 5T/hour and needs to be designed to treat oil contaminated soil, oily tank bottoms and oil based drilling mud.

The heat generated by any thermal treatment can be used locally. The economics of best utilisation of heat generated needs to be worked out depending on the amount of heat generated and additional capital required for any power plants. The possibility of connecting to the local electricity distribution network or large power consumers at a reasonable cost needs to be explored.

5.1. Technology Assessment

1. Materials balance
2. Emissions
 - a. Comparison against WID limits
 - b. Cleaning system requirements
3. Economics
 - a. Capital costs
 - b. Operating costs
 - c. Renewable Obligation Certificates
 - d. Finance costs
4. Visual impact
 - a. Footprint
 - b. Building height
 - c. Stack height
5. Commercial availability
6. Risk Management
7. Effects of scaling up
 - a. On economics
 - b. On land use
 - c. On energy efficiency
 - d. On environmental performance
8. Uses of treated material and byproducts

5.2. The following needs to be addressed while assessing the viability

1. Nature of purchase: Technology purchase or Build Own Operate Transfer
2. Project finance structure
3. Budget and financial constraints
4. Likely planning constraints

5.2.1. Risk Assessment

1. Reliability and efficiency over the project life
2. Comparable reference plants
3. Adequate and relevant track records of suppliers
4. Service agreements with the supplier
5. Treatment plant economics and performance estimates should be realistic.
6. Basis of the estimates
7. Consequences of estimating errors
8. Contract structure, guarantees, and warranties should be adequate
9. Guarantees should reflect the performance objectives and need to be provable
10. The suppliers financial strength and credit capabilities (in case of BOOT plants)
11. Source for disposal/reuse of treated solids
12. Economics depend on sale agreement of heat/power

5.2.2. Deliverability

1. Technical ability
2. Performance ability
3. Finance deliverability (Higher risk as not an outright commercial technology)
4. Capability of the technology supplier to deliver such projects

5.2.3. Planning and regulatory

1. PPC application process
2. Discussions with SEPA and local authorities to confirm their waste strategies for the region.

3. Justification that the chosen technology is BPEO.
4. Project acceptability by locals and environmental pressure groups
5. Project compliance with stringent Waste Incineration Directives
6. Strong environmental case to achieve authorisation under PPC regulation

5.2.4. Benefits

1. Renewable Obligation Certificates; assess the availability and qualification of technology.
2. Materials recovery (quality of materials recovered, recovery rates and cost/revenue for disposal/sale)
3. Energy recovery markets
4. Grants from government

5.2.5. Financial costs

1. Capital cost
2. Operating cost
3. Financing cost

5.2.6. Environmental Impacts

1. Emissions to land, air and water
2. Overall EIA of the project

6. Discussion

Based on my experience of running oily sludge dewatering facilities, the importance of a homogenised feed to the oily sludge treatment facility cannot be understated. Hence installation of a waste reception and mixing facility upfront ensures smooth operation of oily sludge treatment operations.

In terms of oily sludge volume reduction, phase separation using centrifuges proved to be the best solution in comparison with other dewatering technologies such as a filter press due to the ease of operation and maintenance.

The dewatered cake from the centrifuges is still hazardous in nature due to the oil content. Solid calcium peroxide at reduced pH provides 90% reduction in oil content and Solvent extraction with Hexane gave the maximum reduction efficiency of 80%. Solid calcium peroxide treatment and Solvent extraction treatment are not economically viable for the treatment efficiencies it provides.

Bioremediation treatment provides oil content reduction of up to 88%, Biological treatment with oil reduction efficiencies of 88% in 2 months and controlled conditions holds promise and could be implemented however would not be practically feasible given the requirement of large area and varying quality of waste streams.

Thermal treatment methods such as plasma and microwave treatment have proved to reduce the oil content in sludge cake to levels that enable treated cake to be either reused or landfilled in inert waste landfills. Cost benefit analysis provides an analysis of financial feasibility of such investment.

7. Conclusion

This report summarises details of a literature search, laboratory work, experience gathered through technology visits and on site trials carried out in order to develop a sustainable oily sludge treatment process. Oily sludge is usually a very complex mixture of oil-water-solids mixture with other potential additives in the mix and hence designing a waste treatment facility needs to be based on the quality of expected waste arisings. This study and development of treatment chain begins with an appreciation of the importance of homogenising the oily sludge prior to any treatment. While developing the treatment chain, the waste treatment hierarchy of reduce, reuse and recycle has been adopted wherein the first aim of treatment is to reduce the quantity of hazardous waste being handled. In the case of oily sludge this can be achieved by dewatering using centrifuge. Oily sludge is phase segregated to two waste streams that are sludge cake and oily water centrate.

In comparison with sludge cake handling, treatment of oily water centrate is technically proven. Oil and water layer can be phase separated from centrate using a variety of technologies using physical or chemical treatment and hence this is not explored in much detail in the scope of this report. Electrocoagulation is the recommended technology for oil-water separation as this technology has the potential to treat a variety of centrate pollutant parameters such as metals etc. in addition to oil-water separation. The oil recovered can be recycled and wastewater can either be biologically treated on site or discharged through sewer for further treatment.

Due to the inconsistent nature of sludge cake quality, this report concludes by recommending that treatment of oily sludge from hazardous waste to inert waste standards can only be achieved utilising thermal treatment methods. This can either be plasma, microwave or infrared technology based thermal treatment and needs to be decided on a case to case basis. An indicative cost benefit analysis presented provides an indication of capital and operational expenditure for the above technology.

This report also summarises the criteria that need to be adapted for technology assessment and parameters that needs to be studied to verify the viability of an oily sludge treatment facility. The challenges however lie in terms of ensuring the design is based on safe systems of work and includes environmental aspects in terms of air and water pollution.

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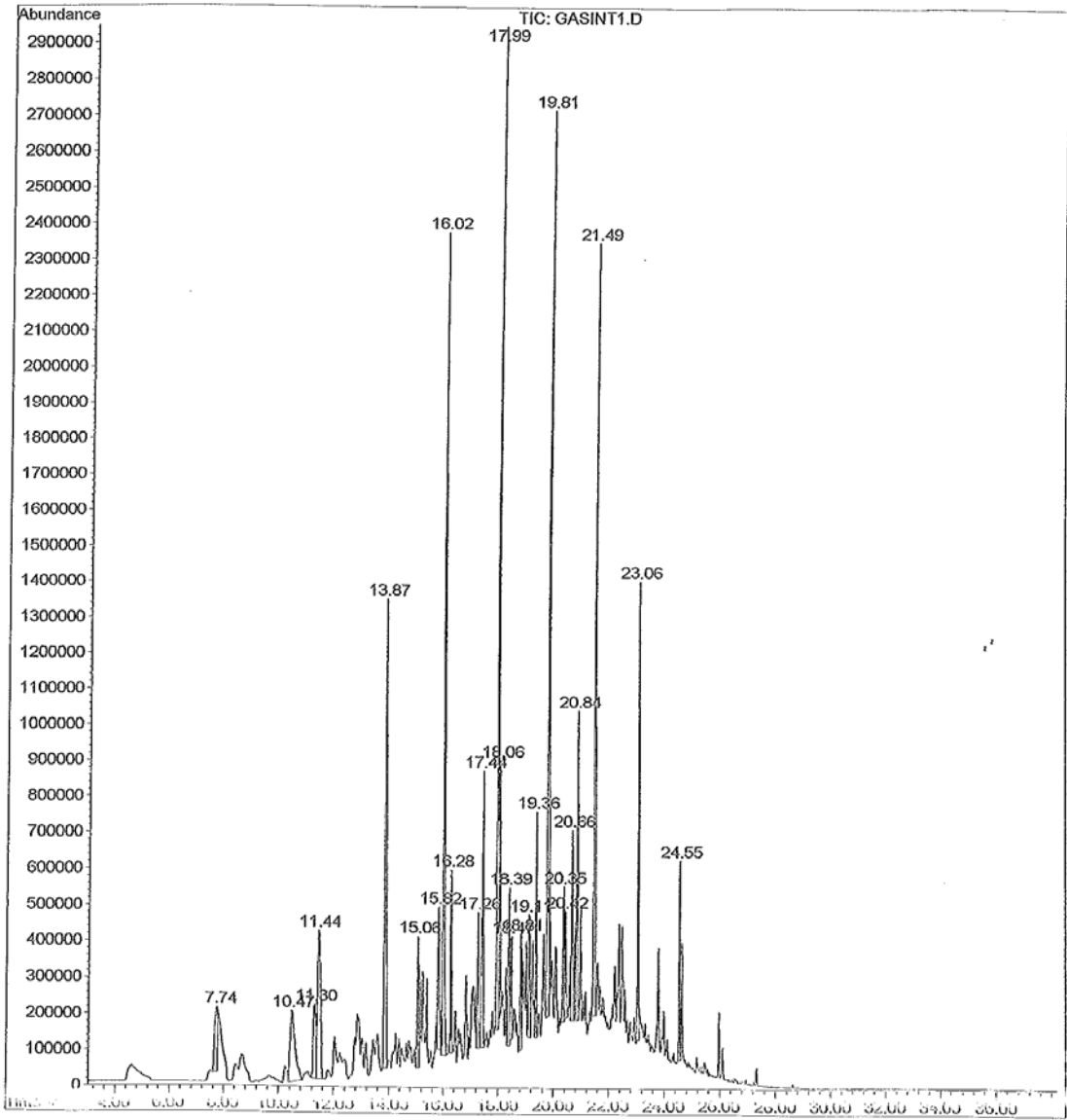
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9. Appendices

Appendix -1 : GCMS Analysis Data

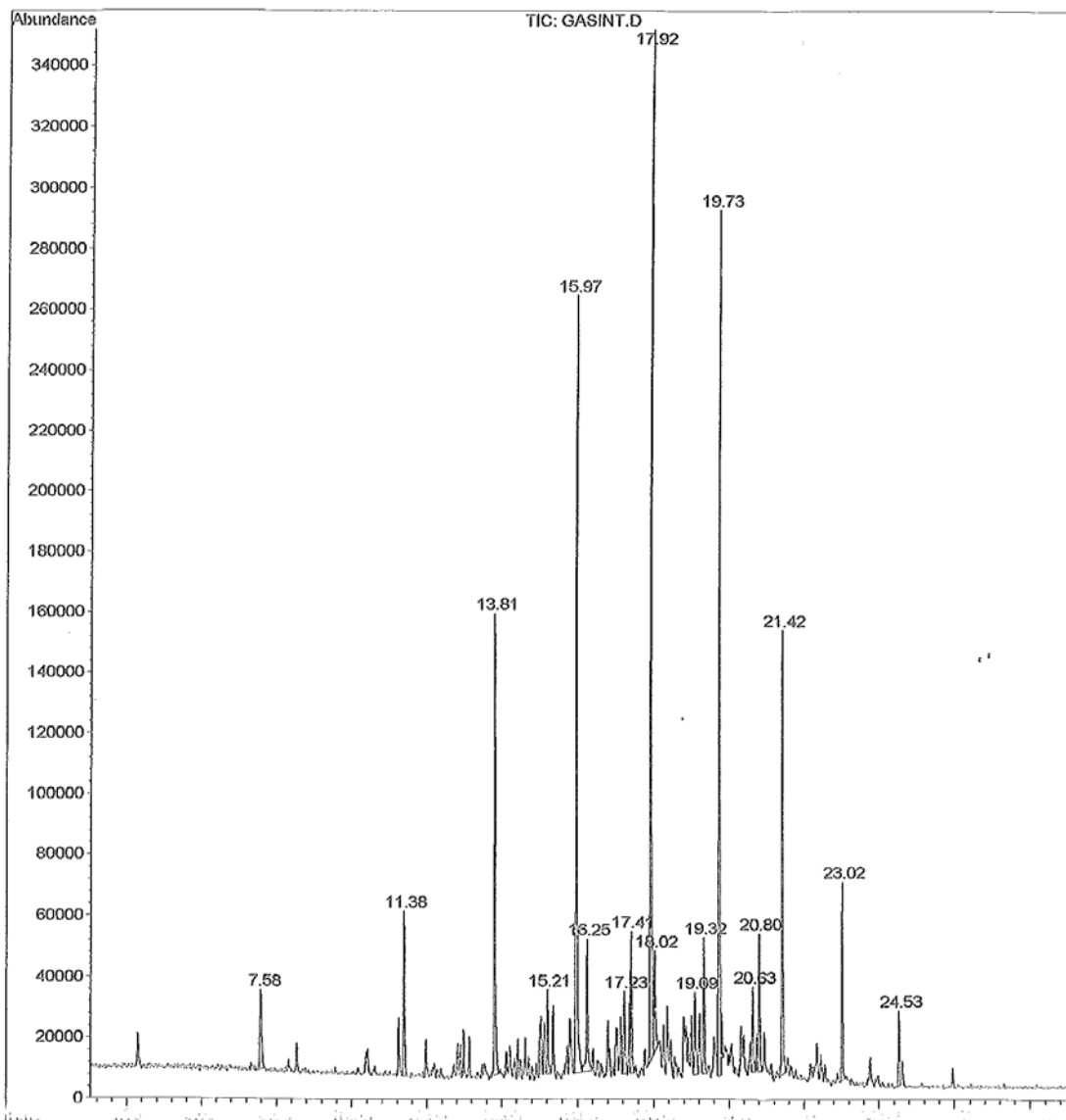
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Acquired : 11 Mar. 05 4:37 PM using A Method PGD
Instrument : GC/MS Ins
Sample Name: SPME interceptor sludge
Misc Info :
Vial Number: 1



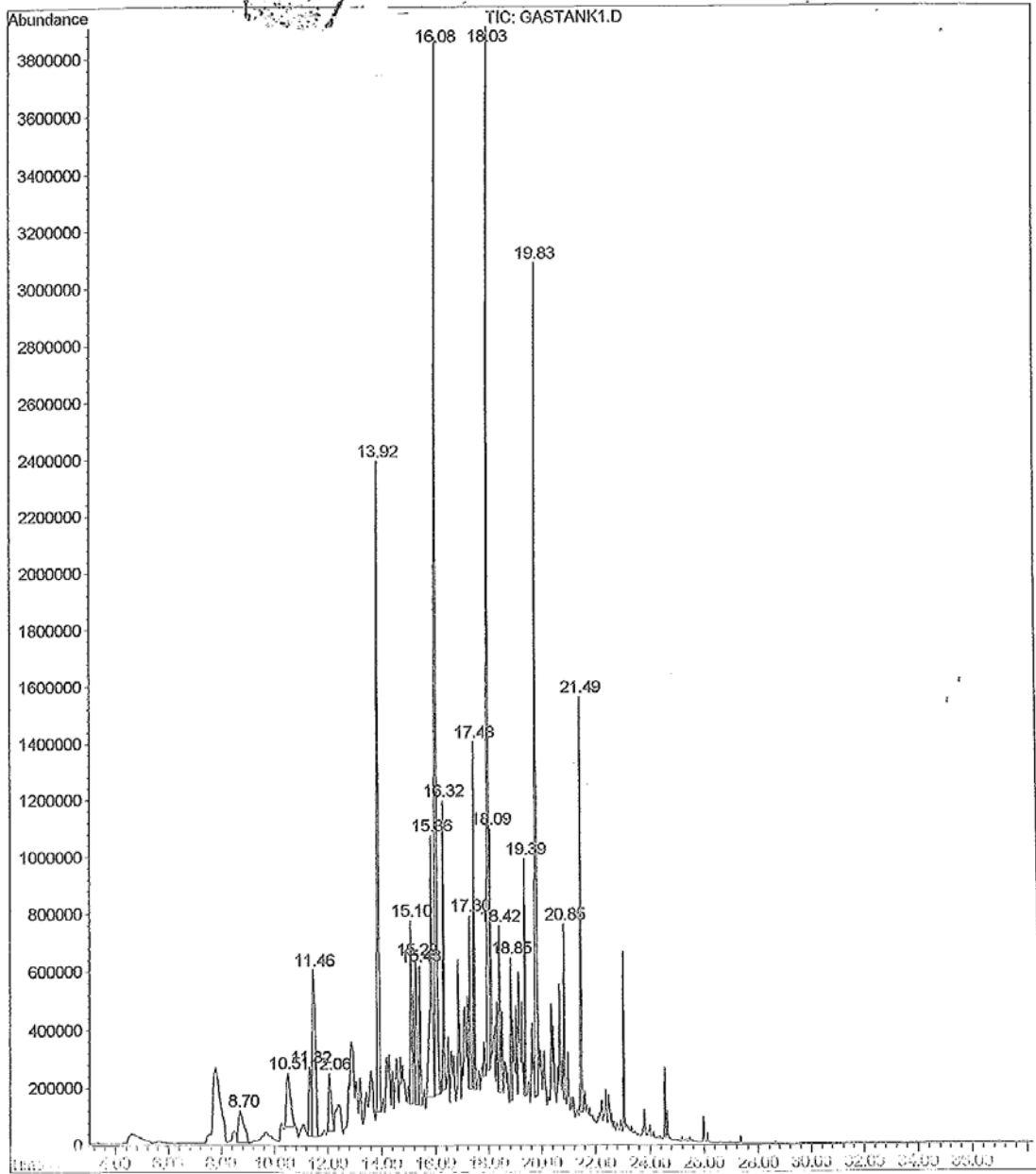
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			Heptadecane, 2,6,10,14-tetramethyl	133325	018344-37-1	72
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Instrument : GC/MS FID
Sample Name: SPME interceptor sludge
Misc Info :
Vial Number: 1



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Operator :
Acquired : 14 Mar 05 ... using AcqMethod PGD
Instrument : GC/MS
Sample Name: SPME tank bottom
Misc Info :
Vial Number: 1



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			Decane, 2-methyl-	124554	006975-98-0	50
14	17.48	3.23	C:\DATABASE\wiley138.L			
			Tridecane, 7-methyl-	34139	026730-14-3	58
			Nonane, 5-propyl-	126026	000998-35-6	53
			Butane, 2,2-dimethyl-	117126	000075-83-2	50
15	18.03	14.52	C:\DATABASE\wiley138.L			
			Tridecane	127252	000629-50-5	96
			Tridecane	27731	000629-50-5	95
			Tridecane	127251	000629-50-5	94
16	18.09	2.69	C:\DATABASE\wiley138.L			
			BENZOCYCLOHEPTATRIENE	10284	000264-09-5	96
			Naphthalene, 1-methyl-	122757	000090-12-0	96
			Naphthalene, 2-methyl-	10279	000091-57-6	95
17	18.42	1.79	C:\DATABASE\wiley138.L			
			BENZOCYCLOHEPTATRIENE	10284	000264-09-5	96
			Naphthalene, 1-methyl-	122757	000090-12-0	96
			Naphthalene, 1-methyl-	10278	000090-12-0	95
18	18.85	1.87	C:\DATABASE\wiley138.L			
			Cyclohexane, (1-methylethyl)-	5458	000696-29-7	64
			Cyclohexane, 1-propenyl-	120440	005364-83-0	64
			Cyclohexane, octyl-	33191	001795-15-9	59
19	19.39	2.03	C:\DATABASE\wiley138.L			
			Heptadecane, 2,6,10,14-tetramethyl	133325	018344-37-1	86
			Dodecane, 2,7,10-trimethyl-	40640	074645-98-0	80
			Dodecane, 2,6,11-trimethyl-	40639	031295-56-4	80
20	19.83	9.83	C:\DATABASE\wiley138.L			
			Tetradecane	128277	000629-59-4	95
			Tetradecane	128275	000629-59-4	94
			Tetradecane	128280	000629-59-4	90
21	20.85	1.71	C:\DATABASE\wiley138.L			
			Heptadecane, 2,6,10,14-tetramethyl	133325	018344-37-1	80
			DECANE, 2,3,5,8-TETRAMETHYL-	34143	000000-00-0	72
			TETRADECANE	128277	000629-59-4	95

PK#	RT	Area%	Library/ID	Ref#	CAS#	Qual
22	21.49	4.16	C:\DATABASE\lley138.L			
			Heptadecane	130827	000629-73-7	91
			Pentacosane	135022	000629-99-2	90
			Pentacosane	135023	000629-99-2	90