Development of technique for decontamination of soil from spilled oil in substations

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Abstract: The presence of organic hydrocarbon contaminants in soil continues to be a cause of concern. The contamination is usually due to oil spillage or leakage from transformers. Although every effort is made to minimise spillage, during handling of insulating oil, but accidents can happen resulting in land and water contamination. The clean up of insulating oil spill or oil contaminated with PCBs is costly to electricity industry and labour intensive. In the other hand there is requirement and legislation to clean contaminated sites from spilled hydrocarbons specially those with high water table. Several decontamination techniques available fulfil this commitment. Chemical treatment offers some advantages over the existing methods. This paper reviews different available techniques for soil clean up. It is also reporting a newly developed chemical technique for decontamination of soil from hydrocarbon and PCBs. It is fast, environmental friendly, economy and can be used on site.

Introduction

Mineral insulating oil is used for insulation and cooling in oil filled electrical equipment. A power transformer may contain up to 120000 lit of this oil. The oil is produced from refining of crude oil and consists of different hydrocarbons mainly paraffinic, naphthenic and aromatics. Paraffinic hydrocarbons are mostly biodegradable. Naphthenic groups are less biodegradable and aromatic, especially if more than three rings are involved (polyaromatic hydrocarbons), are not easily biodegradable. Additionally the oil during its service life may be contaminated by polychlorinated biphenyls (PCBs). The presence of organic hydrocarbon contaminants in soil continues to be a cause of concern. The contamination is usually due to oil spillage or leakage. Although every effort is made to minimise spillage but accidents can happen resulting in land and water contamination.

بازگشت

Chlorinated aromatic compounds, as a class, are some of the most persistent organic pollutants. Therefore, action is required to remove these contaminants from soil to avoid further spread of contamination to surface and ground waters

Oil Spillage

When transformer oil is spilled into the soil environment, volatilisation of compounds may occur. Transformer oil, however, does not generally contain many volatile compounds, so volatilisation is unlikely to be of significance when discussing the fate of the hydrocarbons. Although transformer oil is not considered soluble in water, a small percentage (<1%) of the hydrocarbon molecules in transformer oil may be. These will migrate down through the soil towards the aquifer. Upon reaching the saturated zone, these soluble compounds will migrate as a plume with the groundwater flow. This creates a much larger area of contamination, albeit at a reduced contaminant concentration due to dissipation and dilution.

Insoluble compounds will adsorb to the soil. In the unsaturated zone any compound trapped in the soil through adsorption and capillary action can no longer migrate in their pure form. The more hydrophobic the contaminant is, the more is adsorbed to the soil, particularly the organic matter. If the spill is large, the hydrocarbon contamination can exceed the water solubility threshold and the soil adsorbtion capacity. In this case, droplets of oil will form. These droplets will continue to migrate towards the aquifer as a non-aqueous phase liquid under the effects of gravity and eventually float on groundwater (as light non-aqueous phase lipids) or sink below the groundwater (as dense non-aqueous phase lipids, NAPLs).

N-paraffins may exist in transformer oil as individual molecular entities. The number of carbon atoms they contain will determine their solubility. Most species in transformer oil will be relatively insoluble and therefore behave as NAPLs.

Aromatic species are characterised by their low solubility and high volatility. However, in transformer oil, all aromatic species will have substituted side chains and, hence, greatly decreased volatility. These species will tend to adsorb to the soil particles.

PAHs are insoluble in water, non-volatile and have a high affinity for the soil solid matrix. They will migrate down through the unsaturated zone over time due to gravity. This can result in a range of PAHs existing vertically throughout the soil, with the larger (denser, lower solubility, lower reactivity) molecules having migrated furthest down. Naphthalene, although a PAH, is often absent in PAH contaminated vadose zones. Its relatively high water solubility and low affinity for organic matter results in leaching out of the naphthalene and its appearance as a contaminant in the groundwater.

PCBs are equally insoluble in water. Both PAHs and PCBs may form pockets of contamination in the subsurface. The residual saturation is of particular concern as it acts as a continuing source of contamination. In sites were there is fluctuation in the height of the groundwater, any contamination held in the capillary fringe or in pockets will be re-mobilised and dispersed long after the removal of the bulk contaminants .

The complexity of the hydrocarbon mixture in transformer oil leads to the assumption that most, if not all, of the above processes will occur at a spill site. The scenario is further complicated if the contamination is historical. Aged contamination undergoes ‘weathering’. The physical, chemical and biological processes that occur during weathering combine to dramatically alter the fundamental composition of the contaminant. For example, oxidation of the bulk oil will occur leading to an increase of the oxygen content by formation of ketones, phenols, etc. These in turn are used as substrates for microbial metabolism. Likewise, the ratio of n-alkanes to iso-paraffins will decrease as the straight chain molecules are biotically degraded preferentially. PAHs are known to be degraded by microorganisms in the soil and there is some evidence to suggest PCBs may undergo the same fate. Biodegradation is, however, governed by bioavailability. Adsorption to the soil particles and oil droplet formation can severely limit bioavailability. Abiotically, soil pH, temperature and light can all alter the composition of the oil by reduction/oxidation, volatilisation and photodegradation, respectively.

The components and fate of a transformer oil in the soil must be considered when developing a remediation strategy. It is often more productive to develop the remediation strategy from analysis of the contaminated soil, rather than pristine transformer oil and theoretical prediction of fate

Regulations

There is a rapidly growing framework of relevant UK and EC legislation, which applies in cases of discharges of hydrocarbons to soil and /or water resources. This includes surface and ground waters. A brief summary of the most pressing aspects is given below. More information can be found in the CIRIA handbook.

In the UK the frame work for protection of water resources is more fully developed than that for management of contaminated land, indeed there is currently no single agency with has sole responsibility for contaminated land.

The Environment Agency (the Agency) is the main controlling body in England and Wales for issues relating to contamination of controlled waters, although Unitary Local Authorities are also authorities deemed 'competent' to enforce the EC groundwater directive. The Agency also has responsibility for effluent discharges to controlled waters from processes covered by the Integrated Pollution Prevention and Control legislation in England and Wales.

The Water Resources Act, 1991, sets out the role and responsibilities of the Agency. In general key position of the Act include:

- Creation of an offence of causing or knowingly permitting the discharge of polluting or harmful substances, except in accordance with consents given under specific legal provisions
- Powers to prevent and control pollution through various means including the creation of water protection zones
- Power to remedy or forestall the pollution of controlled waters: the Agency may recover costs from the responsible party.

The Agency has been clear to state that groundwater resources in themselves constitute vulnerable receptors of contamination. As such they will be afforded the full protection of the law. This includes the prohibition of hydrocarbon discharges to groundwater.

In case of long established industrial areas located on an aquifer out crop, the Agency has indicated that where necessary it wishes to work with landowner to evaluate the benefit and feasibility of remediation having due regard for local circumstances and available funding. Thus, the Agency aims to minimise contamination from industrial sites and pursue remedial action if it deems that groundwater is at risk. Additionally, the policy of Agency is to consider prosecution if it can demonstrate that a discharge to soil, which has occurred or is occurring, threatens groundwater resources.

The Agency, Department of Environment, Transport and the Regions (DETR) and local authorities all have certain responsibilities for contaminated land. Since the mid-seventies the DETR has published advice and guidance on contaminated land on behalf of the Interdepartmental Committee on the Redevelopment of Contaminated Land (ICRCL). The guidance addresses a priority list of contaminants, which are of concern when land is being redeveloped. Although the guideline, or trigger value for contaminants do not directly apply to hydrocarbon contaminated sites, polycyclic aromatic hydrocarbons (PAH) and lead, which may be found in petroleum products are covered in the ICRCL guidance. The ICRCL guidance does not cover the water environment.

As further step in improving contaminated land management in the UK, new legislation has been implemented during 2000. This placed a responsibility on local authorities to inspect their area for contaminated land, identify areas considered to be contaminated as “potentially contaminated” sites and draw up an action plan for their monitoring and/or clean-up. The Agency plays a role in the implementation of the legislation as an advisor to local authorities and since certain sites, such as major landfill sites will be deemed “special sites”, the Agency will be responsible for ensuring their clean-up.

The registers of land which has been or is being put to potentially contaminative uses called for by the Environmental Protection Act (1990) will be replaced to some extent by the list of potentially contaminated sites.

The DETR has produced a risk-based approach to the assessment of contaminated land and the evaluation of remedial needs for use by local authorities and landowners. This approach is considered to be optimal because it allows the focusing of attention and financial resources on those sites which indeed pose the greatest environmental and health risks.

Soil Decontamination Techniques

During the past two decades, several methods for removal and disposal of hydrocarbons from soil and varied environmental materials have been proposed and implemented on a commercial scale. These include incineration, UV-vis radiation, chemical extraction/ dehalogenation and disposal in secured landfills. The applicability of these techniques is highly site specific and will depend on factors such as the type of contaminant, it’s concentration and distribution, the soil structure, hydrogeological conditions, required clean up level and available time and cost. The remedial options currently available range from simple excavation and disposal to more sophisticated techniques and can be divided in to two categories:

- Ex-site (requires excavation)
- In-situ (excavation not required)

Due to low penetration of light and the presence of reactive chemicals, degradation of chlorinated or polyaromatic hydrocarbons in soil through direct photolysis or chemical dechlorination has not been successful. As a result, high temperature incineration continues to be the treatment of choice for highly contaminated soils and other solid materials.

High temperature incineration is highly effective for destruction of polychlorinated dibenzo-p-dioxine (PCDDs) and PCBs. The technique has been successfully used at contaminated sites. However, because of its high cost, the application of this technology is primarily limited to destruction of Askarel, mineral oils with high concentration of PCBs and PCDD in soil.

Solvent extraction techniques have been developed and used for extracting hydrocarbons from soil. The technique offers a more convenient and cost effective means of removal of contaminants from solid material. The major drawback of this technique lies in fact that the technique, in itself, just transfers contaminants from one phase to another. The contaminants transferred into the solvent still need be destroyed through a secondary treatment process.

Bioremediation

Biodegradation is the process whereby organic contaminants in soil can be broken down into carbon dioxide and water. Microbes within the soil can adapt to use these contaminants as a food source. This process is continually occurring in nature, however, if the ground conditions are not optimal, the process can be slow. The process of using microbes to breakdown contaminants is called bioremediation.

There are two basic approaches to bioremediation - bioaugmentation and biostimulation. However, there is a third technique, called natural attenuation. This is the biological degradation of contaminants without the addition of organisms or inorganic nutrients. The technique is cost effective for the treatment of contaminated sites involving the prediction and monitoring on a site-specific basic of in situ attenuation processes that may bring about a reduction in the contaminant concentration. It is dependent upon a detailed knowledge of the chemistry and physico-chemical conditions, soil and groundwater conditions, hydrology and biological activity. With detailed site information mathematical prediction of the rate of attenuation can be made. The technique is very slow and hence time consuming and is not applicable to all types of hydrocarbons. It also carries risk of contaminated run off to watercourses.

Bioremediation rates are heavily dependent on chemical and physical conditions, such as pH and temperature, as well as on microbial factors.

Bioaugmentation involves the addition of organisms that are known to be able to degrade the contaminant. This tends to remove the time lag that would be seen in natural biodegradation, where the indigenous microbe population takes time to build up to a level where it can deal with the contaminant effectively.

Biostimulation is the manipulation of abiotic factors to optimise conditions for microbial remediation of a contaminant. This could include the addition of inorganic nutrients such as nitrates, phosphates or electron acceptors (e.g. oxygen).

Incineration

Organic compounds in the soil can be destroyed by incineration, using a high temperature process. The incineration process can be achieved in two stages by process of pyrolysis and volatilisation at temperatures between 600-800°C followed by contaminant destruction at temperature of 1100-1300°C. An alternative technique is a single stage process where destruction can take place within the soil matrix. The advantage of this technique is rapid clean up and destruction of contaminant. It is also can handle large volume of waste. However, the cost of the operation is high and requires subsequent air emission treatment.

Landfill

Contaminated soils can be excavated and transported to licensed landfills for disposal. The excavation must then be back-filled with clean inert material or the site regraded to a lower level. The technique is fast and effective for removing the contamination. It is also cost effective method of cleaning isolated pockets of highly contaminated soils. However, there are some disadvantages: -

- Contamination is not treated and just transferred elsewhere.
- Landfill costs in the UK are high and likely to escalate with decreasing availability of suitable sites and new regulations imposed by the Environmental Protection Act 1990, which controls waste disposal.

Soil Venting

The aim of soil venting is to remove light, volatile hydrocarbons by inducing air movement through the soil. Additionally the enhanced oxygen concentration in the soil increases the rate of biological activity. Venting can either be forced or passive.

Forced venting involves the use of blowers or vacuum pumps to draw air through the soil where as passive venting relies only on changes in barometric pressure and concentration gradients.

The cost of in-situ processing is highly variable and depends mainly on the area and depth of contamination as well as the method of effluent air treatment.

This method is not suitable for low permeable soils and also not suitable for petroleum products with low concentration of volatile hydrocarbons as the vapour may require treatment before it can be discharged.

Chemical Treatment Technique

Chemical treatment offers some advantages over the existing methods. Solvent extraction technologies offer a more convenient and cost effective means for removal of organic hydrocarbons from the soil. In principal a suitable solvent is injected in to the soil, the hydrocarbon contamination dissolves in the solvent, which is then removed from the soil. The contaminant transferred into the solvent must then be extracted from the solvent and destroyed in an appropriate manner, often by incineration.

The choice of solvent is the most important factor in developing successful chemical treatment processes. Type of soil also plays an important role in the application of this technology.

The major draw back of these techniques lies in the fact that contaminants are transferred from one phase to another. The contaminants themselves must still be removed from the solvent and destroyed through secondary treatment.

However, the technology can have significant benefits too. It can be used on the contaminated site, which eliminates the need to transfer contaminated soils from one site to another, it is a fast and relatively simple process.

Chemical treatment techniques are relatively new and research is required before this technique can be applied to decontaminate any sites. A research project is therefore being undertaken to develop a chemical treatment technique for decontamination of soil from hydrocarbons.

Technique Development

Research was conducted to develop a rapid, mobile, efficient and cost effective chemical technique for decontamination of soil. The developed technique is base on washing contaminated soil with mixture of water and environmental friendly chemical to maximise oil extraction from the soil. The system is based on feeding the soil from one end of the equipment and introducing extraction mixture solution, warmed to 60 °C, from opposite side to maximise contact of the soil with extraction mixture. Once soil leaves the equipment it is totally free from oil and hydrocarbons. The extraction solution back to tank for further use and separation of the oil from the solution. The clean soil is transferred back to the previous contaminated area, which was excavated. During this process sample of washed soil was taken and send to laboratory for analysis of hydrocarbons and no trace of hydrocarbon were observed in the decontaminated soil. The extraction mixture returned in second tank, oil is separated from this aqueous based mixture and removed mechanically. This oil if it is contaminated with PCB then should be passed through PCB destruction unit for decontamination and disposal. The extraction mixture is reused again for decontamination of soil and therefor no waste is generated. The equipment was developed as result of joint research project with Sea Marconi, Italy and manufactured by Sea Marconi. The UK Environmental Agency approved the technology and results of soil testing for before and after decontamination are shown in table 1.

PCB Destruction

The extracted oil from extraction mixture was checked for PCB content and if PCB was detected then the oil was decontaminated using CDP technique. Several techniques for destruction of PCBs in the oil have been developed since 1980. In general they are based on stripping chlorine from PCB molecules using an alkaline metal, follow by reclamation of the oil. Of the commercially available techniques the **C**hemical **D**ehalogenation **P**rocess (CDP), developed by Sea Marconi Italy, offers several advantages. The process is safe, reagent is solid and easy to handle, the unit can be used as mobile or stationary, operates at low temperature, destroy super toxic compounds such as PCDD (polychlorinated dibenzo-dioxins) and PCDF (polychlorinated dibenzo-furans) and operates in close loop in continuous mode or single pass. All by-products of dehalogenation are non toxic and immobilised in the solid reagent. The process dehalogenates and reclaimed the oil simultaneously. Depending on the economic situation, the dehalogenated oil can be used as insulating oil or for other purposes.

During the dehalogenation process the PCB content of the processed oil should be monitored regularly. The monitoring should be performed by implementation of a rapid and reliable method. For this reason total chlorine of the oil, before and during the process, can be measured using Dexsil chloride analyser. Once the test indicated undetectable level of PCBs in the oil then the process can be stopped. This measurement also should be used for suitability of the decontamination reagent for further use or change of the reagent. The PCB content of the final products should be measured by method given in standard IEC61619.

Health and Safety

Users should obtain a **m**aterial **s**afety **d**ata **s**heet for the insulating oil in use. Although there is no special risk involved in the normal handling of mineral insulating oil, attention should be focused on the general need for personal hygiene and practice of washing skin and clothing that may have come in contact with insulating oil. Personnel should avoid contact of the fluid with their eyes.

During equipment inspection or service, routine checks should be made of the equipment and surroundings for leakage. Areas to check and repair should include valves, bushings, gauges, tap changers, welds, sample points, manhole covers, pipe fittings, pressure relief valves etc.

Unused mineral insulating oil received from a refiner is very unlikely to contain PCBs. However, many older transformers or oil filled electrical equipment in service may be filled with mineral insulating oil that contains PCBs.

Soil Sample	**Total oil content before treatment, ppm**	**Oil content after treatment, ppm**
7/08	2580	<1
9/08	3147	<1
15/08	1259	<1
16/08	9382	<1
19/08	20327	<1
2/09	124	<1
3/09	2692	<1
5/09	83	<1

Table 1: Results of soil analysis for oil content before and after treatment.