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REMEDIATION OF SOIL CONTAMINATED WITH HYDROCARBONS – NEW ECOLOGICAL APPROACH IN OIL AND GAS INDUSTRY**

1. INTRODUCTION

Detection of petroleum hydrocarbons in soil can indicate contamination from leaking underground storage tanks (USTs), petroleum refineries, pipelines or other sources. Before the sampling program of the contaminated soil is initiated, site screening techniques such as soil gas and geophysical surveys should be conducted so that soil sampling can be targeted at areas of greatest contamination. Soil characteristics, such as soil type and porosity, should also be determined in order to further define subsurface conditions and to assess chemical movement along various pathways.

2. CONTAMINATED SOIL COLLECTION METHODS

Several different methods which can be used to collect soil samples are available today. Each method is depending upon the depth of the samples to be taken, the soil characteristics of the site and the physical features of the site. The preliminary site assessment and site-screening procedures should be used to determine the appropriate. The individual methods of soil collection methods are listed in the Table 1.

Besides methods listed in the Table 1 two additional methods, which are not related to the depths can be used:

1) Soil Pile – used for determination of contaminant levels in the excavated soil;
2) Tank Pit – used for determination of soil contamination after removal of underground storage tank.

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Table 1

Soil Collection Methods

Collection method	Depth of Collection	Application
Surface sampling	0–15 cm	Recent spills Soil with low migration rates (clay)
Test Pit	0–5 m	Shallow contamination Heterogeneous fill
Borehole	0 m	Deep contamination Dispersed spill Prevents cross-contamination

For test pits, boreholes, and surface sampling, the location and number of samples required are site specific, and will depend on the type of contaminant, its mobility in the environment, and the physical features of the site. The preliminary site assessment and site-screening procedures should be used to determine the appropriate number and location of samples to be taken. An adequate number of sampling locations should be established in order to determine the horizontal and vertical extent of soil contamination. The sampling density should be increased in areas of anomalies. If no information is available for predicting the location of hot spots, a grid pattern can be used to identify sampling locations.

A sufficient number of samples should be collected from each sampling location to analyse for all parameters as well as soil characteristics. The recommended number of samples that are needed is depended on the soil volume and in most cases ranges from 4 to 7 locations. The soil sample should consist of soil particles not greater than 2 mm.

3. REMEDIATION TECHNOLOGIES

Technologies used for the recovery of contaminated soil include wide range of methods and applications. The traditional methods are mechanical and physical-chemical methods. With the advances in biology, new bioremediation methods appeared in soil recovery. These methods minimise the negative side impacts of the recovery and accelerate the whole soil recovery.

Traditional physical-chemical methods are based on contaminated soil cleaning and washing. By using these methods secondary waste is created which include mostly water and sediments. This secondary product of soil remediation has to be later disposed. Physical-chemical methods are also work and time consuming, expensive and their application is limited. Today's trend is to apply bio-remediation methods which use living organisms (bacteria) to decompose the contamination into environmentally harmless elements.

4. BIOREMEDIATION

Bioremediation can be defined as the use of living organisms to reduce or eliminate environmental hazards resulting from accumulations of any toxic chemicals or other hazardous wastes. It is not a new technology. Humankind has practised composting, sewage treatment and fermentation since the beginning of recorded history. All of these processes utilise microbial processes in a degradation process. At present, bioremediation is often the preferred method for remediation of especially petroleum hydrocarbons, because it is cost effective, and it converts the petroleum hydrocarbons into the harmless by-products carbon dioxide and water.

Indigenous and enhanced micro-organisms have been shown to degrade crude oil, industrial solvents, polychlorinated biphenyls, explosives and many different agricultural chemicals, including pesticides. Bioremediation is often the preferred method for remediation of especially petroleum hydrocarbons, because it is cost effective, and it converts the petroleum hydrocarbons into the harmless by-products carbon dioxide and water. Bioremediation can be used to degrade concentrated organic contaminants near their source or as a secondary remediation strategy following specific physical or chemical methods.

Micro-organisms degrade or transform contaminants by a variety of mechanisms. Petroleum hydrocarbons for example are converted to carbon dioxide and water or are used as a primary food source by bacteria, which use the energy to generate new cells. Where the hydrocarbons are chlorinated the degradation takes place as a secondary or co-metabolic process rather than a primary metabolic process. In such a case enzymes, which are produced during aerobic utilisation of carbon sources such as methane, degrade the chlorinated compounds.

Over the past few years, progress has been made in expanding the number and type of contaminants to which bioremediation can be applied and in the number of practical methods for implementing in situ bioremediation. Techniques such as hydrofracturing have been developed for improved delivery of nutrients to micro-organisms in low-permeability geologic media. Methods have been developed for creating passive treatment systems known as bio-filters. Bioremediation is a more cost effective method of remediation as compared to physical and chemical remediation methods, but it has the potential to be one of the most cost effective technologies for dealing with environmental remediation problems.

There are certain restriction of using the biological methods of soil decontamination. Bacteria reproduction (in order to produce enough enzymes, the minimum bacteria concentration is in the range 10^{10} to 10^{12} bacteria in 1 cm^3 [2]) is dependent on volume of pores in soil. In case there is insufficient pore volume, additional chemicals have to be added to soil and they create another source of secondary soil pollution. The other restriction is the size of pores. The bacteria size is in the range from 0.5 to 0.8 micrometers but in the fine grained soil there is over 50% of pores with diameter less than 0.2 micrometers. One of the disadvantages of using bacteria for soil remediation is problem of bacteria removal from soil after soil remediation.

5. EMZYMDEG BIO-REMEDIATION METHOD

Recently new technology has been developed which is used to produce and isolate natural, non-bacterial enzymes of hydrolase type. Special mixture of hydrolase type enzymes can be used to decompose crude, oil and their products as well as polyaromatic hydrocarbons and polychlorinated biphenyls and other contaminants. These non-bacterial enzymatic mixtures do not create secondary soil pollution as bacteria because enzymes are self-destructing.

One of the enzymes application methods is also developed by company GEOPOL Prešov s.r.o. in Slovakia with the name ENZYMDEG [1] shown in Figure 1. In this application the special solution of enzymes in water called ENZYMMIX is applied in the contaminated soil. The solution ENZYMMIX acts in two ways – releases pollution (hydrocarbons) from soil and decomposes it. The ENZYMDEG technology has been successively used both *in situ* and *ex situ*. The final product of hydrocarbon decontamination using ENZYMDEG technology are hydrocarbons C_3 to C_7, CO_2 and water. As enzymes do not include oxidases only hydrolases no glycerine and other environmentally hazardous material are created.

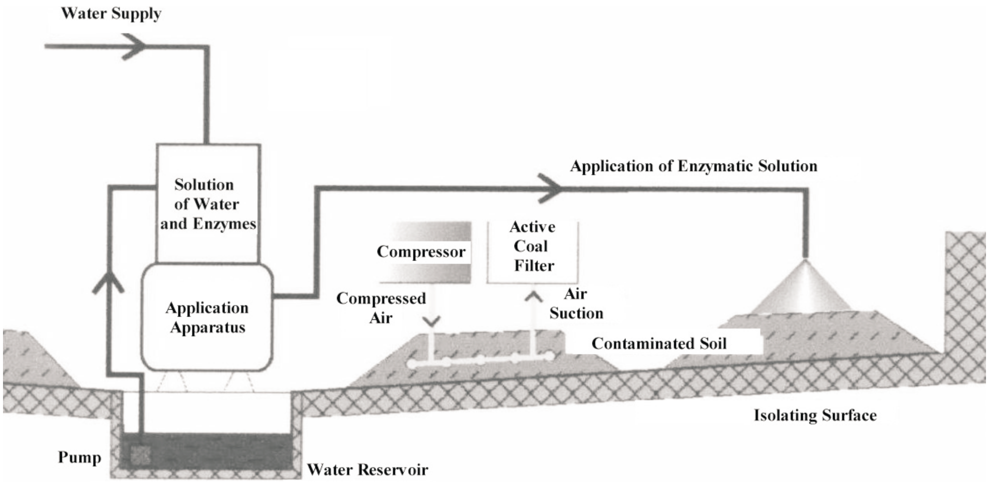

Fig. 1. Schematics of ENZYMDEG application [2]

6. *IN SITU* AND *EX SITU* REMEDIATION

In situ bioremediation is below ground method applied at the site of contamination whereas *ex situ* is above-ground bioremediation, where the sediment or water has been extracted from the subsurface.

The most widespread use of ex situ bioremediation is the cleanup of storage tank leaks and oil spills in pipelines, tank farms and petroleum refineries. The technique is similar to composting, in which soils are physically and chemically manipulated to stimulate breakdown of target organics by resident and exogenous microbes. In soil piles it is necessary to install piping networks to distribute air and allow addition of water and supplemental additives. Application of nutrients, pH regulating chemicals, and microbial strains may be performed by spraying (in a water slurry) or direct application with tillage to distribute the additives into the soil.

The third major category of on site bioremediation is combination of *ex situ* groundwater treatment with *in situ* soil treatment which involves pumping groundwater to the surface for treatment in an above-ground bioreactor. The effluent from the bioreactor, containing oxygen, nutrients and acclimated micro-organisms, is then injected back into the ground to remediate the contaminated soils associated with the groundwater.

In situ bioremediation has following advantages over *ex situ* techniques:

– *In situ* bioremediation can be used to completely degrade and detoxify some organic contaminants, thereby permanently removing liability for the contaminants.
– For some types of contaminants, physical and chemical methods of remediation may not completely remove the contaminants, leaving residual concentrations that are above regulatory guidelines. Bioremediation can be used as a cost-effective secondary treatment scheme to decrease the concentration of contaminants to acceptable levels. In other cases, bioremediation can be the primary treatment method, and followed by physical or chemical methods for final site closure.
– In some cases, natural attenuation (including natural bioremediation) of the contaminant plumes may be the only cost effective solution.
– For complex mixtures of contaminants requiring a combination or sequence of physical and chemical remediation methods, bioremediation techniques that use microbial consortia to concurrently address all contaminants may be faster and more cost-effective.
– It can be applied for very large sites

7. CONCLUSION

The main disadvantage of implementation of bioremediation systems as a destruction technology lies in the longer time required for clean-up. The sites to be addressed are likely to contain a mixture of contaminants. A single micro-organisms system is not likely to degrade all the pollutants components.

The implementation of such a project require training of personnel to enable them to apply all required aspects of the technology. Bioremediation requires a longer term monitoring action to be implemented through which the pollution status must be determined and some compounds may not be prone to microbial degradation and may require an additional chemical degradation step.

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