

Module 4

CONTAMINATED SITE REMEDIATION

Soil contamination by organic or inorganic pollutants is caused by a number of industries such as chemical, pharmaceuticals, plastics, automobile, nuclear industries, biomedical wastes, mining industries, municipal solid waste. At times it becomes essential to decontaminate soil. Broadly the soil decontamination is done in two ways: (a) pump and treat in which the pollutant is pumped out using external energy source, treated using methods such as incineration, radiation, oxidation etc (b) removal of contaminated soil, treat it and then returning back to its original place. This module is meant to briefly introduce various soil/ water decontamination processes. The scientific basis and the reactions involved in these processes are acid-base chemistry, solubility-precipitation, ion exchange, redox, complexation, sorption, etc. which are discussed in module 2.

4.1 Contaminated site characterization/ assessment

Broadly, site characterization or contaminated site assessment (CSA) is important for:

- a) Determining concentration and spatial distribution of harmful pollutants under consideration.
- b) Determining the extent of site remediation (zonation) based on which the suitable remediation technique is selected.
- c) For assessing environmental and human health risk due to contamination.

More specifically, CSA is required to answer the following questions:

- a) What is the source of contaminants?
- b) What is the type and physical form of contaminants?
- c) Spatial and depth wise extent of contamination
- d) Whether the contaminants are stationery or movable?
- e) If they are movable, then identify the significant pathways.
- f) Identify the potential receptors of contaminants.

4.2 Selection and planning of remediation methods

Fig. 4.1 (USEPA 1991) presents a flowchart on various processes involved in the planning of site remediation.

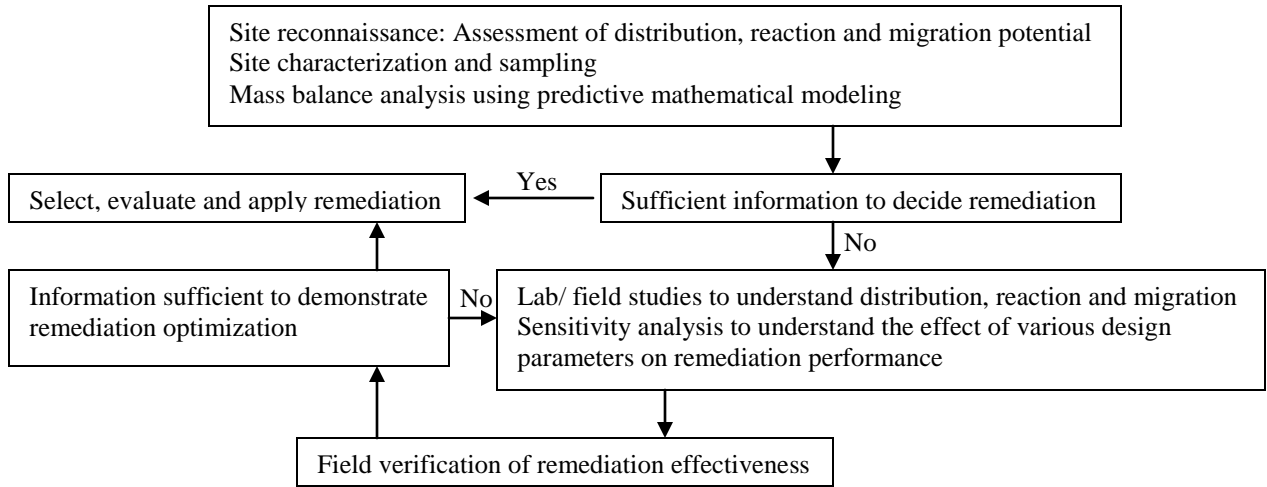


Fig. 4.1 Processes involved in deciding contaminated site remediation

It can be noted from Fig. 4.1 that the most important step for making a decision on site remediation is collection of data. Table 4.1 summarizes the essential data to be collected as part of site reconnaissance and site characterization.

Table 4.1 Summary of data required for planning contaminated site remediation

Data	Details	Method of acquisition
1) Site history and land use pattern	a) Population density within 3 km from the contaminated site b) Proximity to important geographical features like airport, railways, river etc. c) Ownership of the land d) Extent of contamination	Field
2) Geologic and hydrologic	a) Topography b) Soil profile up to bed rock c) Information on aquifer d) Groundwater depth and flow direction	Field
3) Geotechnical	a) Soil sampling and classification b) Permeability of soil c) Chemical characteristics of soil	Field Field Lab

	d) Soil strength	Lab
4) Waste	a) Water quality	Field/ Lab
	b) Identifying the type of contamination	Field/ Lab Lab
	c) Concentration of contaminants	Field/ Lab
	d) Spatial extent of contamination	Field/ Lab
	e) Depth of contamination	Lab
	f) Contaminant retention characteristics	Lab Lab
	g) Contaminant transport characteristics	
	h) Hazard assessment and zonation	

4.3 Risk assessment of contaminated site

Risk assessment or hazard assessment is required to decide the extent of contaminant remediation required for a particular site. The factors influencing risk assessment are:

Toxicity

A material is deemed toxic when it produces detrimental effects on biological tissues or associated process when organisms are exposed to concentration above some prescribed level. Acute toxicity is the effect that occurs immediately after exposure where as chronic toxicity deals with long term effects. It is expressed as mass unit of toxicant dose per unit mass of receiving organism. It must be noted that concentration is an important factor while deciding toxicity. Only when a contaminant crosses a particular concentration, it becomes toxic. If the concentration is within the prescribed limit then no remediation need to be performed. Only those site which have toxic level of contaminant concentration needs remediation. For example, toxic contamination level leading to cancer becomes the basis for some of the site clean-up programs.

Test protocols such as toxicity characteristics leaching procedure (TCLP) (Method 1311, EPA) have been developed for extraction of chemicals from wastes to verify whether the concentration is within the prescribed toxicity limit. TCLP is designed to determine the mobility of both organic and inorganic analytes present in liquid, solid, and multiphase wastes. Several regulatory

agencies such as central pollution control board (CPCB), India, United States Environmental Protection Agency (USEPA) have prescribed toxic concentration levels for various chemicals that get leached from the waste samples by conducting TCLP. In some cases, multiple extractions from the wastes become necessary. For performing TCLP appropriate extraction fluid need to be used. Glacial acetic acid mixed with water is used as the extraction fluid. In some cases sodium hydroxide is also added. For detailed procedure, readers are advised to refer to Method 1311, EPA.

Reactivity

It is the tendency to interact chemically with other substances. These interactions become hazardous when it results in explosive reaction with water and/or other substances and generate toxic gases.

Corrosivity

Corrosive contaminants degrade materials such as cells and tissues and remove matter. It is defined as the ability of contaminant to deteriorate the biological matter. Strong acids, bases, oxidants, dehydrating agents are corrosive. $\text{pH} < 2$ or $\text{pH} > 12.5$ is considered as highly corrosive. Substances that corrode steel at a rate of 6.35 mm/year is also considered hazardous.

Ignitability

It is the ease with which substance can burn. The temperature at which the mixture of chemicals, vapour and air ignite is called the flash point of chemical substances. Contaminants are classified as hazardous if it is easily ignitable or its flash point is low.

Based on the above four factors the risk associated with a particular site is determined by specifying maximum acceptable risk using risk estimation equations (Reddi and Inyang 2000). Risk assessment provides a numerical quantification of the probability of harm from hazardous or toxic contamination. Risk management uses this input of risk assessment in deciding how much regulation and corrective measure need to be taken. The corrective action is mostly the practice of remediation of the contaminated site. The maximum possible concentration that could lead to the maximum acceptable risk is back

calculated. If the level of concentration at a particular site is greater than the maximum possible concentration, then it requires remediation. This approach would clearly indicate the extent of remediation required for the contaminated site. Appropriate remediation scheme is then selected to bring the concentration level much less than the maximum possible concentration. Since risk assessment and risk management is a very broad topic, it is difficult to discuss the mathematical formulation in this course. Interested readers are requested to go through additional literature (USEPA 1989; Asante-Duah 1996; Mohamed and Antia 1998).

4.4 Remediation methods for soil and groundwater

Based on the toxic level of contaminants and the risk it pose to the environment, a suitable remediation method is selected. It must be noted that the remediation does not aim for entire decontamination. The major focus is to bring the contamination level well below the regulatory toxic limit. This is done by removing the toxic contaminants and/or immobilizing the contaminant that prevents its movement through subsurface geoenvironment. The remediation methods are broadly classified as physico-chemical, biological, electrical, thermal and combination of these methods.

4.4.1 Physico-chemical methods

Removal and treatment of contaminated soil

One of the simplest physical methods for remediation is by removing the contaminated soil and replacing it with clean soil. Essentially it is a dig, dump and replace procedure. Such a method is practically possible only if the spatial extent and depth of the contaminated region is small. The dug out contaminated soil can be either disposed off in an engineered landfill or subjected to simple washing as shown in Fig. 4.2.

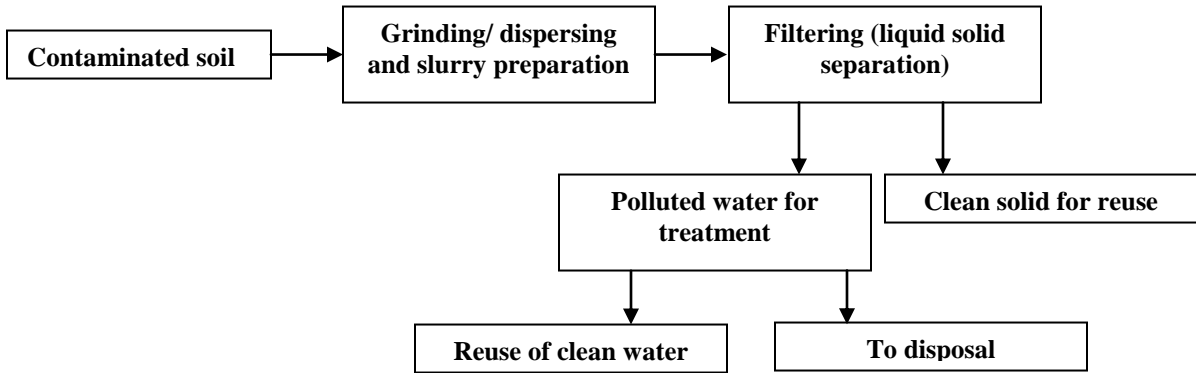


Fig. 4.2 Soil washing for granular soils contaminated with inorganic pollutant

However, washing procedure is mostly suitable for granular soils with less clay content and contaminated with inorganic pollutants. For clay dominated soils, a chemical dispersion agent need to be added to deflocculate and then chemical washing is employed to break the retention of contaminants with the clay surface. Incineration is suggested for soils contaminated with organic pollutants. In case, it is necessary to remove organic pollutants then certain solvents or surfactants are used as washing agents.

The method is directly applied in situ where solvent, surfactant solution or water mixed with additives is used to wash the contaminants from the saturated zone by injection and recovery system. The additives are used to enhance contaminant release and mobility resulting in increased recovery and hence decreased soil contamination.

Vacuum extraction

This method is one of the most widely used in situ treatment technologies. The method is cost-effective but time consuming and ineffective in water saturated soil. The technique, as depicted in Fig. 4.3, is useful for extracting contaminated groundwater and soil vapour from a limited subsurface depth. The contaminated water is then subjected to standard chemical and biological treatment techniques. Vacuum technique is also useful when soil-water is contaminated with volatile organic compound (VOC). The method is then termed

as “air sparging”. Sometimes biodegradation is clubbed with air sparging for enhanced removal of VOC. Such a technique is then termed as biosparging.

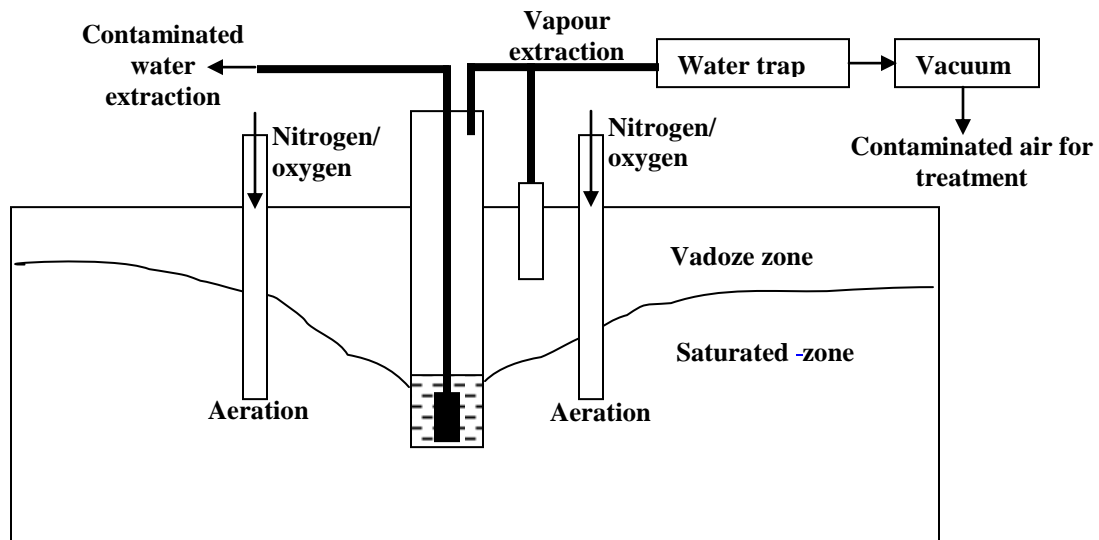


Fig. 4.3 A schematic diagram for vacuum extraction procedure (Reddi and Inyang, 2000)

The vacuum extraction probe is always placed in the vadoze zone. The success of the method depends on the volatilization of VOC from water into air present in voids. An injecting medium is used to extract soil-water and/ or soil-air. When oxygen is used instead of nitrogen as the injecting medium, it enhances aerobic biodegradation.

Soil structure influences a lot on the passage of extracted water and vapour and hence on the success of vacuum extraction technique. It is not only important that the injecting medium is delivered efficiently but also the extracted product reaches the exit with less hindrance. Granular soils provide better passage where as the presence of clay and organic matter impedes the transmission of both fluid and vapour. Organic matter provides high retention leading to less volatilization. High density and water content also minimize transmissivity. Apart from soil, the VOC properties such as solubility, sorption, vapour pressure, concentration etc. also influence the extraction process.

Solidification and stabilization

This is the process of immobilizing toxic contaminants so that it does not have any effect temporally and spatially. Stabilization-solidification (SS) is

performed in single step or in two steps. In single step, the polluted soil is mixed with a special binder so that polluted soil is fixed and rendered insoluble. In two step process, the polluted soil is first made insoluble and non-reactive and in the second step it is solidified. SS process is mostly justified for highly toxic pollutants. In-situ SS process is mostly influenced by the transmissivity characteristics of the soil, viscosity and setting time of the binder. Well compacted soil, high clay and organic content do not favour in-situ SS.

In ex-situ methods, polluted soil is first grinded, dispersed, and then mixed with binder material. The resultant SS material need to be disposed in a well contained landfill. It is essential that the resultant SS product does not undergo leaching. The common binders used in practice include cement, lime, fly ash, clays, zeolites, pozzolonic products etc. Organic binders include bitumen, polyethylene, epoxy and resins. These organic binders are used for soil contaminated with organic pollutants.

Chemical decontamination

This method is mostly applicable for those soils which have high sorbed concentration of inorganic heavy metals (IHM). The first process in this method is to understand the nature of bonding between the pollutant and the soil surface. A suitable extractant need to be selected for selective sequential extraction (SSE) of IHM from the soil mass. The extractants include electrolytes, weak acids, complexing agents, oxidizing and reducing agents, strong acids etc. The use of these extractants in single or in combination will depend upon the concentration of IHM and nature of the soil mass.

In-situ application (as depicted in Fig. 4.4) of extractants would remove IHM from the soil surface and enter into the pore water. The pore water is pumped and treated (pump and treat method) on the ground. While treating the pumped water, both extractants and IHM are removed.

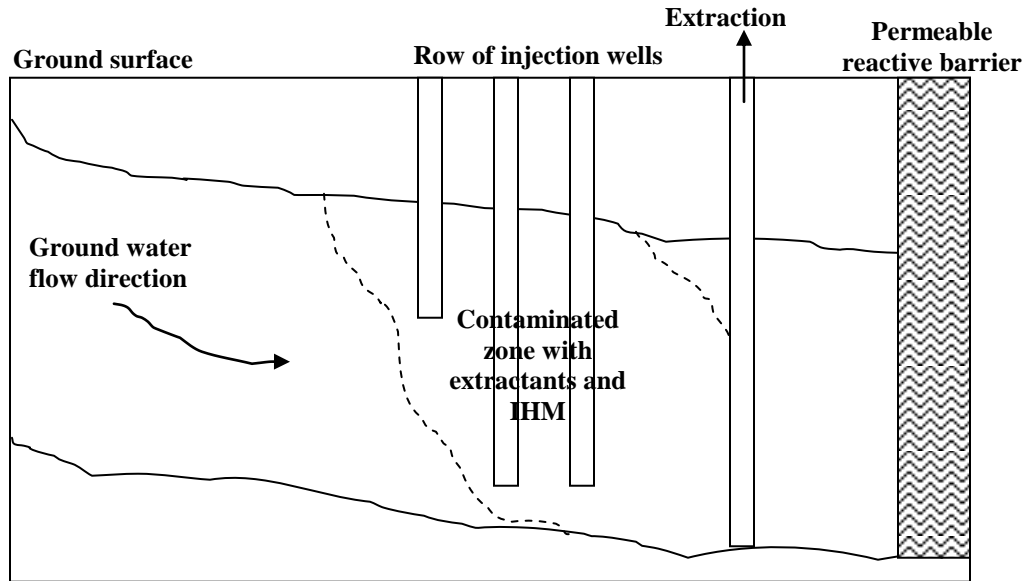


Fig. 4.4 A schematic diagram for in-situ chemical decontamination

Another method is to allow the contaminated pore water to flow through a permeable reactive barrier (PRB). Hence the placement of the barrier is determined by the direction of flow of ground water. The material packed in the barrier will retain IHM by exchange (sorption), complexation or precipitation reaction. The transmission and the reaction time determine the thickness of the reactive barrier to be provided. The material to be provided in the barrier is influenced by the knowledge of IHM to be removed. This is mainly due to the fact that the above mentioned reaction occurs differently when IHM is present as single or as multiple species.

The successful use of PRB or treatment wall (TW) depends upon its location such that majority of the contaminated groundwater flows through it. It is essential to have a good knowledge on the hydrogeological conditions where such barriers need to be placed. In some cases, sheet pile walls are used to confine the flow towards the permeable barrier. Some of the materials used in PRBs are exchange resins, activated carbon, zeolites, various biota, ferric oxides, ferrous hydroxide etc. Hydraulic conductivity of the PRB should be greater than or equal to the surrounding soil for proper permeation to occur. The

knowledge on reaction kinetics and permeability of the barrier would determine the thickness of the wall to be provided such that enough residence time is achieved for the removal reaction to occur.

4.4.2 Biological methods

Remediation by biological treatment is mostly applicable for soil contaminated with organic pollutants and the process is termed as bioremediation. In this method, certain soil microorganisms are used to metabolize organic chemical compounds. In the process these microorganisms degrade the contaminant. If naturally occurring microorganisms such as bacteria, virus or fungi is not capable of producing enzymes required for bioremediation, then genetically engineered microorganisms would be required. At the same time, it should be ensured that such microorganisms do not produce any undesirable effect on the geoenvironment (such as toxins). The process of bioremediation is dependent on reactions such as microbial degradation, hydrolysis, aerobic and anaerobic transformation, redox reaction, volatilization etc. An example of bioremediation is discussed in the next section where in the process is used for the remediation of oil spill land.

4.4.3 Electro-kinetic methods

Electro-kinetic methods are popular field method for decontaminating a particular site by using electrical principles. The procedure is more effective for granular type of soils. Two metal electrodes are inserted into the soil mass which acts as anode and cathode. An electric field is established across these electrodes that produces electronic conduction as well as charge transfer between electrodes and solids in the soil-water system. This is achieved by applying a low intensity direct current across electrode pairs which are positioned on each side of the contaminated soil. The electric current results in electroosmosis and ion migration resulting in the movement of contaminants from one electrode to the other. Contaminants in the soil water or those which are desorbed from the soil surface are transported to the electrodes depending upon

their charges. Contaminants are then collected by a recovery system or deposited at the electrodes. Sometimes, surfactants and complexing agents are used to facilitate the process of contaminant movement. This method is commercially used for the removal of heavy metals such as uranium, mercury etc from the soil.

4.4.4 Thermal methods

Thermal methods include both high temperature ($>500^{\circ}\text{C}$) and low temperature ($<500^{\circ}\text{C}$) methods and are mostly useful for contaminants with high volatilization potential (Evangelou 1998). High temperature processes include incineration, electric pyrolysis, and in-situ vitrification. Low temperature treatments include low temperature incineration, thermal aeration, infrared furnace treatment, thermal stripping. High temperature treatment involves complete destruction of contaminants through oxidation. Low temperature treatment increases the rate of phase transfer of contaminants from liquid to gaseous phase there by causing contaminant separation from the soil. Radio frequency (RF) heating is used for in situ thermal decontamination of soil having volatile and semi-volatile organic contaminants. Steam stripping or thermal stripping is another process useful for soils contaminated with volatile and semi-volatile organic contaminants. It is an in situ process in which hot air, water or steam is injected into the ground resulting in increased volatilization of contaminants. Sometimes vacuum is applied to extract air or steam back to the surface for further treatment. The effectiveness of this method is increased by the use of chemical agents that are capable of increasing the volatility of the contaminants. High cost and its ineffectiveness with some contaminants (with low volatilization potential) make thermal method less attractive. Also, in some cases incineration process produces more toxic gases.

4.5 Some examples of in-situ remediation

Harbottle et al. (2006) have compared the technical and environmental impacts of taking no remedial action with those of two remediation technologies.

The main objective of this study is to verify the sustainability of remediation technologies. The two remediation technologies evaluated in this study are solidification/ stabilization (S/S) and landfilling. In both these methods contaminants are contained rather than destroyed. Therefore, it is extremely important to analyze the long-term effect to avoid any potential problems in future. In this study, sustainable remediation project is defined as the one that satisfies the five criteria listed as follows:

Criterion 1: Future benefits outweigh the cost of remediation.

Criterion 2: Overall environmental impact of the remediation method is less than the impact of leaving the land untreated.

Criterion 3: Environmental impact of remediation process is minimal and measurable.

Criterion 4: The time-scale over which the environmental consequences occur is part of the decision-making process.

Criterion 5: The decision making process

The site selected in this study was an industrial location polluted by BTEX (benzene, toluene, ethylbenzene and xylene) and TPH (total petroleum hydrocarbon). About 4400 m³ of contaminated soil has been remediated. The stabilization mix used was cement:bentonite of 2.5:1 and water:dry grout of 3.8:1. It was found that due to S/S, groundwater pollution reduced by 98 percent and the leachate from S/S sample was well within the limit. S/S process resulted in the increase in strength, reduction in permeability and increase in pH of the soil. The same quantity of contaminated soil has been landfilled at a distance of 96 km from the source. In long term, S/S has been found to perform better than landfill and no action taken for remediation. Other advantages of S/S are low material usage, low off-site waste disposal, potential ground improvement for immediate re-use, and lesser impact on the local community. However, the contaminants remain on the site which increases the level of uncertainty in long term. In the case of landfilling, long term impacts are less due to the fact that contaminated soil is removed from the site. The resources that need to be mobilized for landfill are more than S/S.

Ludwig et al. (2011) have explained the use of permeable reactive barrier (PRB) for the treatment of Cr₆ in groundwater. PRB in the form of trench and fill system, chemical redox curtain or organic carbon based biotic treatment zone induce reduction condition for converting Cr₆ to relatively immobile and non-toxic Cr₃. The most efficient trench and fill application is granular zero valent Iron (ZVI) fillings, which rapidly converts Cr₆ to Cr₃. Alternatively, organic mulch and compost has been used to initiate microbially active Cr₆ reduction. However, the use of organic matter as well as organic carbon does not have the longevity of ZVI. The study quotes an example of ZVI based PRB installed at North Carolina in 1996. This PRB is of 10 m depth, 0.6 m wide and 46 m long. This PRB is found to treat groundwater containing Cr₆ (approximately 15 mg/l concentration) for more than 15 years. This study also quotes the use of chemical reducing agent such as sodium dithionite at US department of energy, Hanford, site for treating large Cr₆ containing groundwater plume.

Asquith and Geary (2011) have compared bioremediation of petroleum contaminated soil by three methods, namely, biostimulation, bioaugmentation and surfactant addition. Bioremediation process depends on microbial activity for biodegrading petroleum hydrocarbons. Since it is a natural process, it is a slow reaction. The above mentioned three methods are used for increasing the rate of bioremediation reaction. Biostimulation enhances the growth and activity of microorganisms by the addition of nutrients and/or additives. Bioaugmentation is the addition of hydrocarbon degrading microbial cultures. Surfactant addition would enhance solubility, emulsify and disperse hydrophobic contaminants to overcome the problem of low contaminant bioavailability. Sandy loam soil with total petroleum hydrocarbon (TPH) > 30000mg/kg has been used to evaluate the three methods. It was noted from this study that biostimulation with nutrients enhanced bioremediation process. Organic amendments provided a better bioremediation than inorganic amendments. Surfactant addition was found to increase bioavailability of hydrocarbon and hence enhance bioremediation.

Ascenco (2009) has discussed about contaminated site characterization and clean up based on two case studies. The first case study pertains to the

excavation and washing of soil in an industrial estate site of 0.12 km². Preliminary investigation of the site revealed contamination upto a depth of 6m with TPH, volatile aromatics such as toluene, ethylbenzene and xylene. Soil was found to be free of heavy metals. A quantitative risk assessment indicated the need for remediation. 40000 tonnes of soil was excavated from the affected site and subjected to soil washing. Washing has been performed in a unit with a capacity of 70 tonnes/ hour. Washed soil has been declared safe after adequate laboratory testing and the clean soil reused in the site. The soil has been first homogenized and sieved. The required surfactant and extracting agents were mixed with water and used for soil washing. The waste water which comes out after washing has been treated and reused. Contaminated sludge and fines after waste water treatment and oversized soil mass rejected during sieving was transferred to landfills.

The second case study is another industrial area of 3 km² near Lisbon. The industrial site comprised mainly of organic and inorganic chemistry industries producing pesticides, acid, copper, lead, zinc, iron pyrites etc. The site consists of 52000 tonnes of hazardous sludge from zinc metallurgy and iron pyrite ashes. The site required investigation and remediation due to the placement of an airport in the vicinity of this site. The groundwater exhibited high levels of arsenic, lead, mercury, cadmium, copper, zinc, cobalt. In some areas the pH was as low as 1, which increased metal mobility. The investigations were mainly focused on developing a conceptual site model and environmental risk analysis for defining remediation options. The efforts are still on for this particular site.

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Model Questions

- 1) What are the important points to be kept in mind for contamination assessment?
- 2) What are the processes involved in the planning of contaminated site remediation?
- 3) What are the important data required for planning contaminated site remediation?
- 4) Discuss the important physico-chemical methods for performing contaminated soil remediation.
- 5) Prepare a scheme for the design of permeable reactive barrier.
- 6) Based on the literature, explain how to plan and design electro-kinetic remediation.
- 7) Discuss case histories related to contaminated site remediation and identify the most popular method.